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- Механика наноструктурных материалов (таких как нанокристаллические материалы, нанокомпозиты, нанопористые материалы, нанотрубки, наноструктурные пленки и покрытия, материалы с квантовыми точками и проволоками).
- Физика прочности и пластичности наноструктурных материалов, физика дефектов в наноструктурных материалах.
- Механика процессов деформирования и разрушения в традиционных материалах (твердых телах).
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PREFACE

The Seventeenth International Workshop on Nano-Design, Technology and Computer Simulations (NDTCS-2017) took place on October 25-26, 2017 in Minsk, Belarus. The workshop NDTCS-2013 was organized jointly by Belarusian State University of Informatics and Radioelectronics and the St. Petersburg Academy of Sciences on Strength Problems (Russia). More than 149 participants including scientists, teachers, graduate students and undergraduates from Azerbaijan, Belarus, Germany, Kazakhstan, Lithuania, Poland, Russian Federation and Vietnam prepared and delivered more than 60 reports. The Seventeenth Workshop was focused on nanomaterials, computational methods in the field of micro- and nanoelectronics, and mechanics.

Joint Stock Company 'Integral', leading company in the design and manufacturing integrated circuits, acted as the partner and supporter of Workshop.

Workshop NDTCS-2017 is a continuation of the previous workshops, which were held in:

- Russia, St. Petersburg 1997-2005
- Poland, Olsztyn 2006
- Germany, Bayreuth 2007
- Belarus, Minsk 2008, 2013; Grodno 2015
- Lithuania, Vilnius 2009
- Finland, Espoo 2011

The first nine workshops, which took place in Russia, had the name "Nondestructive Testing and Computer Simulations in Science and Engineering (NDTCS)." In due course, the focus of the meetings gradually moved towards Nanoscience and Computer Aided Design, so the following meetings (2007-2017) had the new name "International Workshop on New Approaches to High-Tech: Nano-Design, Technology and Computer Simulations (NDTCS)" what reflects better their profile.

All the contributions to the Workshops were published in English:

- Modelling and Computer Simulation in Materials Science and Engineering, 6 (4) 1998
- Proceedings of St. Petersburg Academy of Sciences on Strength Problems (SPAS) vols. 2-11, 1998–2007
- Proceedings of the International Society for Optical Engineering (SPIE), vols. 3345, 3687, 4064, 4348, 4627, 5127, 5400, 5831, 6253, 6597, 7377; 1998–2008
- Proceedings of NDTCS, vols. 12-13, 15-17; 2008, 2009, 2013, 2015, 2017
- Reviews on Advanced Materials Science, 20 (1, 2) 2009
- Materials Physics and Mechanics, 9(1-3) 2010; 13(1-2) 2012; 20(1-2) 2014; 34(1) 2017
- St. Petersburg State Polytechnical Journal: Physics and Mathematics, 2 (242), 3 (248), 4 (253) 2016; 10 (1) 2017

This issue of Materials Physics and Mechanics Journal contains the selected papers presented at the Workshop. All the papers have been peer-reviewed prior to publication. The issue will be of interest to researchers and graduate students in the field of nanotechnology, physics, chemistry, and mechanics.

Alexander I. Melker, Viktor R. Stempitsky

REDUCTION OF GRAPHENE FROM GRAPHENE OXIDE IN DIFFERENT MEDIA

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Abstract. Features of the reduction of graphene from graphene oxide in media containing hydrazine hydrate, ethylene glycol, and hydrogen are studied. X-ray energy dispersive spectroscopy, Raman spectroscopy, and scanning electron microscopy data indicate that this process proceeds through the high-temperature annealing of graphene oxide in a hydrogen environment.

Keywords: graphene, graphene oxide, Hummers method, nanostructure, reduction

1. Introdiction

Graphene is a material whose discovery was awarded with the 2010 Nobel Prize in physics. It is historically the first two-dimensional crystalline material whose properties differ appreciably from its three-dimensional structural analog, graphite. This thinnest of crystalline materials has a surprising combination of properties: transparency, mechanical strength, elasticity, exceptionally high mobility of charge carriers (massless Dirac fermions), and high thermal conductivity; it is elastic and impermeable to molecules of other substances. It is also more inert than gold when it comes to the effects of external conditions [1,2].

All of these characteristics, which are apparent in different physicochemical processes, make graphene a highly promising material for practical use in everything from nanoelectronics to composite materials [3]. This explains the enormous interest of physicists and chemists in synthesizing this exotic material, applications of which are impossible without the development of reliable and relatively inexpensive methods of preparation [4–6]. The best way of achieving this today is to use graphene oxide produced in the form of flakes by delaminating graphite with oxidizing reagents. This material can be considered graphite intercalated with oxygen-containing carbon groups that give it the ability to be thoroughly dispersed in water and hydrophilic organic solvents [7,8].

When interacting with chemical reducing reagents, graphene oxide is converted into thin graphene flakes of low structural quality [5-7] due to the substantial degradation of graphite during the synthesis of graphene oxide. Nevertheless, graphene can be prepared from this material [6-10]. These data are, however, difficult to compare, since reagents that differed in their chemical properties were used, and the processes involving them were performed under different thermal conditions. In addition, graphite materials of different structural quality and fineness were used to obtain graphene oxide [6,7,10]. In this work, we studied the effects of reducing agents used in [4,7-10] had on the structure and chemical composition of graphene oxide in order to assess the prospects for using it for obtaining graphene. In all reduction processes, graphene oxide was prepared from graphite with the same chemical composition, structure, and grain size. Such research methods as X-ray energy dispersive spectroscopy (XEDS), Raman spectroscopy, and scanning electron microscopy (SEM) were used to assess the quantitative and qualitative compositions of the initial and final materials, and their structural features.

2. Experimental

Table 1 presents data on quantitative and qualitative compositions of the materials and the corresponding specific surface areas. Analysis of the data of Table 1 indicates that the C/O atomic ratio of graphene oxide differs significantly from that of the original graphite (Table 1, methods 1 and 2) and coincides with the ones presented in [5,8,9]. In addition, the mass distributions of oxygen in the graphene oxide arrays and materials obtained with methods 1 and 2 have considerable heterogeneity (\pm 4.1 wt %). This is probably because of the nonuniform thickness of the graphene oxide flakes that formed and the nonuniform distribution of water molecules, hydroxyl (OH), carboxyl (COOH), carbonyl (CHO), and epoxy (C–O–C) groups in their conglomerates. The above testifies to the different thickness of graphite delamination during the formation of graphene oxide using the Hummers technique and the weak impact reduction methods 1 and 2 had on this factor.

	[C], wt %	[O], wt %	[Fe], wt %	[S], wt %	[P], wt %	[Mn], wt %	C/O	S, m²/g
1	92.8 ± 0.6	1.7 ± 0.3	0.05	0.00	0.00	0.00	66.1±3.9	11
2	57.8 ± 6.2	39.7 ± 4.1	0.00	0.90 ± 0.10	0.2±0.1	1.00 ± 0.00	1.9±0.2	53
3	69.5 ± 6.3	27.8 ± 4.1	0.00	0.50 ± 0.10	0.2±0.1	0.00	3.3±0.1	57
4	67.1 ± 6.1	31.0 ± 4.1	0.00	0.60 ± 0.10	0.1±0.0	0.00	2.8±0.1	54
5	78.4 ± 3.6	18.0 ± 1.6	0.00	0.08 ± 0.05	0.1±0.0	0.00	5.7±0.1	124
6	88.1 ± 0.5	5.5 ± 0.3	0.00	0.08 ± 0.05	0.1±0.0	0.00	21.0±0.4	258

Table 1. Qualitative and quantitative composition of materials and their specific surface areas

(1) Crushed graphite; (2) graphene oxide; (3) after reduction with method 1; (4) after reduction with method 2; (5) after reduction with method 3; and (6) after reduction with method 4. C/O is the atomic ratio and S is the surface area.

A comparison of C/O atomic ratios of graphene oxide and the materials obtained using methods 1–4 indicates that the latter had higher values. The substances obtained with methods 3 and 4 and subjected to annealing in an Ar/H₂ environment have the greatest values. The annealing of graphene oxide at 200 and 1000°C in particular increased the C/O atomic ratio value by factors of \approx 3 and 11, respectively (Table 1, methods 2, 5, and 6). When methods 1 and 2 were used for the reduction of graphene oxide, the greatest change in the C/O atomic ratio in this case grew by a factor of \approx 1.8.

No	Frequency, cm ⁻¹			Relative intensity		
INO	D	G	2D	I_D/I_G	I_{2D}/I_G	I_{2D}/I_D
1	1349	1579	2700	0.24	0.50	2.1
2	1352	1586	2658	1.06	0.03	0.03
3	1350	1583	2685	1.02	0.09	0.08
4	1349	1586	2685	1.09	0.09	0.08
5	1340	1583	2679	1.50	0.08	0.06
6	1344	1580	2675	0.94	0.24	0.26

Table 2. Characteristics of the materials' Raman spectra peaks

The notation is the same as in Table 1.

Reduction of graphene from graphene oxide in different media

The data of Table 1 also indicate that graphene oxide contains small residual amounts of the reactants used in its synthesis. In particular, it contains $\approx 0.3\%$ of phosphorus, 1.0% of sulfur, and 1.0% of manganese. The chemical composition of the materials obtained by methods 1–4 are of high purity, especially in the case of methods 3 and 4. The latter materials contained 0.1% phosphorus, sulfur impurities more than an order of magnitude less than those of graphene oxide, and no manganese compounds (Table 1, methods 2–6). Overall, these data show that graphene oxide and the materials prepared by its reduction by methods 1–4 had almost no inorganic impurities.



Fig. 1. Raman spectra of (a) crushed graphite and graphene oxide, and (b) materials obtained from graphene oxide via reduction in hydrazine hydrate (method 1) and Ar/H₂ at 1000°C (method 4). Arrows show the axis of intensity

The specific surface areas of the initial crushed graphite and that of graphene oxide (Table 1) were 11 and 53 m²/g, respectively. The specific surface areas of the substances obtained by methods 1 and 2 are almost the same as those of graphene oxide (Table 1, methods 1–4). The materials formed by methods 3 and 4, however, had greater specific surface areas and grew by \approx 500% after treatment by method 4 (Table 1, methods 2, 5, and 6). The structure of graphene oxide was probably subjected to additional delamination processes during annealing, especially under high temperature conditions.

It should be noted that the specific surface areas of graphene oxide and the materials obtained with methods 1–4 were considerably smaller than those observed in [4,10,14]. We may assume this was due to the aggregation of flakes upon drying into conglomerates that contained micropores. There could be volumetric filling by the adsorbate (nitrogen) during adsorption measurements [15], or they might be filled with physically adsorbed water, molecules of which inside the cavities of micropores are grouped into strong energy-stable clusters [16]. The first factor leads to larger surface areas of the materials, while the second results in the smaller sizes observed in this work (Table 1, methods 2–6). This indicates that using adsorption and the BET equation to estimate the specific surfaces of the graphene material can produce values that have no physical meaning, as was noted in [10].

The Raman spectra of the investigated materials are presented in Table 2 and Fig.1. They contain the D, G, and 2D bands at 1350, 1580, and 2700 cm⁻¹, respectively that are characteristic of graphene structures. The D band is due to some amorphous phase or cleaved sp² carbon bonds in the carbon rings of graphene structures (cleaved bonds at the edges of

graphene conglomerates and the emergence of sp3 carbon bonds). The G band is due to sp^2 carbon bonds in the dense hexagonal graphene structures. The shape, position, and intensity of the 2D band are sensitive to the quality of carbon rings in the graphene layers and their number when it is 5 [6,7,11].

The frequencies of bands D, G, and 2D of the investigated materials and intensity ratios I_D/I_G , I_{2D}/I_G , and I_{2D}/I_D , a measure of disorder in graphene layers [7,11], are given in Table 2. At the same time, the high I_D/I_G and low I_{2D}/I_G and I_{2D}/I_D values indicate a higher degree of defectiveness for the graphene materials. Analysis of these data shows that graphene oxide had substantially higher I_D/I_G and lower I_{2D}/I_G and I_{2D}/I_D values than the crushed initial graphite. This indicates there were a great many cleaved sp² carbon bonds in its structure [6–8,10,11]. The frequency shift of the G band toward the high-frequency region also indicates considerable defectiveness of the graphene oxide structure (Table 2, methods 1, 2) [7].

The above is also typical of the materials obtained from graphene oxide by the methods 1–3 (see Table 2, methods 1, 3–5), where there was a large number of oxygencontaining groups (Table 1). In addition, the I_D/I_G , I_{2D}/I_G , and I_{2D}/I_D values of graphene oxide formed by the method 3 (i.e., obtained in an Ar/H₂ environment at 200°C) testify to its high structural defectiveness. This is probably because there was additional delamination of graphene oxide flakes under these conditions, but the effect hydrogen reduction had on their structure was slight. The high-temperature annealing of the material in the same medium (method 4), however, not only lowers the number of oxygen-containing groups in its flakes considerably, as can be seen from Table 1; it greatly improves their graphene structure. This is confirmed by the changes in the corresponding I_D/I_G , I_{2D}/I_G , and I_{2D}/I_D values on the Raman spectra of the materials obtained with methods 1–4 (Table 2, methods 2–6). In addition, the 2D band maximum in the Raman spectrum of the substance obtained with method 4 was observed at 2675 cm⁻¹ (Table 2, method 6), which is typical for single-layer graphene [17].

The shapes of the 2D bands in the Raman spectra (Fig. 1) also illustrate a different quality of the structure of graphene layers in materials 1–3 and 6 (Table 2). The 2D band in the Raman spectrum of the initial crushed graphite (Fig. 1a) is intense and narrow, but does not contain a 2D2 curve in the low frequency region. This indicates initial three-dimensional disorder of the graphene layers in this material [7], due probably to its grinding. The 2D band in the Raman spectrum of graphene oxide is not only of low intensity; it broadens due to the high structural defectiveness of carbon rings in flakes of this material [7,9]. As a result, there is a strong superpositioning of bands D and G.

A considerable overlap of bands D and G was also observed in the Raman spectrum of the material obtained by method 1. The corresponding 2D band is not intense, but it is narrower (Figs. 1b), indicating some slight reductive transformation of the graphene oxide structure. If we compare the shapes of 2D bands in the Raman spectra of the materials obtained by the methods 1 and 4, however, the band of the latter material is much narrower and more intense. Nevertheless, if we compare the 2D bands of this material and graphene obtained micro-mechanically [11], the band of the reduced graphene is broader and less intense. This indicates that monolayer graphene flakes formed by treating graphene oxide by method 4, but their structure is more defective than that of graphene obtained using the micromechanical approach. We may assume that the different shapes of the 2D bands in the Raman spectra of these materials are due to the formation of graphene flakes during the high-temperature annealing of graphene oxide in an Ar/H₂ medium with a wide distribution of their areas.



Fig. 2. SEM images of (a) graphene oxide, (b, c) materials obtained from graphene oxide via reduction in hydrazine hydrate (method 1) and Ar/H₂ at 1000°C (method 4), respectively

Figure 2 shows SEM images of graphene oxide and the materials obtained by the methods 1 and 4. They indicate that morphology of conglomerates in graphene oxide has great relief in which flakes are tightly grouped (Fig. 2a). The structure of the resulting

conglomerates in the material processed by the method 1 is almost similar to that of graphene oxide (Fig. 2b), but conglomerates of the material obtained by method 4 are much looser. In contrast to graphene oxide, the flakes in this material are somewhat affected by strong Van der Waals bonds during aggregation, due to the low number of oxygen-containing structural groups.

3. Conclusions

Our study of features of the reduction of graphene oxide from graphene at different temperatures and in various media indicates that this process is proceeds only upon high-temperature annealing in an inert atmosphere containing hydrogen. This results in [18,19] complete removal of physically adsorbed water from the micropores in a graphene oxide and contributes to the destruction of mobile oxygen-containing carbon groups in the structure of flakes, generally enhancing the effect of hydrogen reduction on them. This leads to dramatic changes in the chemical composition and structure of this material, producing single-layer graphene flakes.

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MECHANICAL IMPULSE ENHANCEMENT IN A MICROSYSTEM BASED ON NANOPOROUS SILICON COMBUSTION

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Abstract. Nanostructured porous silicon impregnated by solid state oxidizer has been studied in order to provide the mechanical impulse for jet-propulsion microsystems. The system with jet-propulsion motion on a silicon chip has been tested for impulse measurements. The silicon chip has been fastened on a carrying platform through an elastic spacer. The elastic spacer promotes the combustion and prevents from explosion of porous silicon fast oxidation. It is shown that such a microsystem gains the impulse up to 200-220 mN·s.

Keywords: combustion, explosion, mechanical pulse, microthruster, multichip structure, nanoporous silicon

1. Introduction

Microthrusters have received significant attention during the last few years, though early development in the microelectromechanical systems (MEMS) field began approximately 15 years ago. The principle applications of microthrusters are for primary propulsion and attitude control of microspacecraft and micro-, nano-, picosatellites. These small-scale satellites require efficient propulsion systems that can approach and maneuver around objects in a space orbit. Technological efforts are converging from two directions: the miniaturization of conventional thrusters and the development of new solid energetic materials and device concepts [1]. One of the solutions for the aforementioned problem is to use energetic nanocrystalline porous silicon as an energy source.

Nanoporous silicon is an inert material, usually formed by the anodization of a silicon wafer in the electrochemical etch process [2,3]. Nanoporous silicon becomes an energetic material when its nanopores are infused with an oxidizer [4]. Porous silicon impregnated with solid state oxidizers has demonstrated the combustion and explosion processes [5,6]. It could be used in silicon based MEMS [7,8]

In this paper we present the measurements of thrust generation using nanoporous energetic silicon fastening a carrying platform with an intermediate spacer from elastic material.

2. Experimental and calculation details

Silicon wafers of p-type (B-doped) with resistivity of 10 Ω -cm were used to fabricate porous silicon samples using the anodization technique in the HF/ethanol electrolyte (3 parts of 48% HF to 1 part of ethanol) at the current density of 50 mA/cm². Ethanol helps to wet the hydrophobic surface of silicon and to remove H₂ bubbles. The porous region was etched from the front surface defined by a mechanical O-ring mask with an internal diameter of 12 mm. The etching time was varied to get porous layer thicknesses from 40 µm to 70 µm. The samples were rinsed in ethanol and the residual ethanol in the pores was slowly evaporated at normal laboratory conditions. The porous silicon samples were then impregnated by ethanol

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saturated solution of NaClO₄. The oxidizer is applied (the pores are filled) by dropping oxidizer solution with a pipette directly on the porous silicon. In all cases we fill the pores with two drops of the solution. Then samples dried in an oven at 40°C.

We designed a simple propulsion system by attaching the silicon chip to a carrying platform (circular metal plate) using a glue. The part of silicon chips has been attached to the carrying platform through an elastic spacer made from rubber (Fig. 1). Another part of silicon chips has been fastened directly on the carrying platform surface. Combustion ignition and explosion processes in the porous layers were initiated by putting the samples to a hotplate heated up to 500^{0} C. After the explosion took place, the thrust lifted up the whole system from the ground. A video camera records (30 frames per second) the motion of the propulsion system, and a scale in the background was used to calculate the velocity and height that the device achieved. The impulse was estimated as

$$P = m \left(\Delta l / \Delta t \right)$$

(1)

where m is the mass of the carrying platform, Δl is the distance that the carrying platform passed within the time (Δt) of recording the picture by the camera.



Fig. 1. Schematic view of the propulsion system consisting of the load carrying platform with the silicon chip attaching through the elastic spacer

3. Results and discussions

In our samples, impregnated by ethanol saturated solution of $NaClO_4$, the lateral dimension of the porous layer is a few orders of magnitude larger than the layer depth. As a result, the reactive forces arising from the explosion process push the sample in the direction perpendicular to the surface plane.

Figure 2 shows the fragments of the jet-propulsion test when the carrying platform is horizontally placed on a hotplate and moves in the vertical direction after ignition. The flight track during the first frame reaches 37 cm while the second frame indicates additional 35 cm. Flight tracks can be seen due to deflagration process in porous silicon. Taking into account the mass of the tested samples, we have calculated the mechanical impulse of the jet propulsion system depicted in Fig. 3 for different porous silicon thickness. Our samples could gain the mechanical impulse up to 130 mN s for carrying platform mass of 13 g.



Fig. 2. Fragments of the jet-propulsion test: *a*) ignition and the first frame of testing flight, *b*) the second frame of testing flight (the flight track is marked by the white oval)

Recently we have found that porous silicon with a thickness more than $30 \,\mu\text{m}$ and impregnated by solid state oxidant demonstrated the explosion process with appearance of a shock wave [5]. Fixing the porous silicon chip on the platform, which mass exceeds the chip, changes shock wave propagation conditions. The sound intensity of shock wave decreases with mass increasing because the shock wave decays intensively for systems with larger mass indicating the explosion process energy to be converted into the mechanical impulse rather than to the shock wave.



As known, p-type porous silicon includes nanoparticles with size in the range from 1 to 15 nm [2,3]. If the shock wave intensity is decreased, only small portion of particles with diameters of a few nanometers leads to the explosion (Fig. 2a). Another portion of particles with sizes of about 10 nm provides the deflagration process (fast combustion) with the lifetime of few milliseconds (see Fig. 2a, b).

The deflagration process supplies additional jet propulsion effect during the take-off resulting in the highest mechanical pulse of 130 mN·s for porous silicon with the thickness

of 70 μ m. Testing samples with porous silicon thickness of more than 40 μ m without the carrying platform were completely destroyed after ignition (Fig. 4a) [7]. Testing samples fixed on the carrying platform with the mass more than 3 g and less than 20 g were destroyed partially (Fig. 4b, c) and with mass more than 20 g kept integrity after testing (Fig. 4d).



Fig. 4. Photos of experimental samples after testing: *a*) silicon chip (without carrying platform) destroying during explosion process, *b*) porous silicon chips fastened on carrying platforms with mass 3 g, *c*) with mass 10 g and *d*) with mass 20 g after testing



Fig. 5. Dependence of the pulse intensity versus porous silicon thickness for investigated propulsion systems (for carrying platform mass 10 g)

The enhancement of a mechanical pulse in the propulsion systems under investigation can be provided by increasing the role of the combustion process. However, the generation of a shock wave in our propulsion system should be avoided. The elastic spacers, which connect carrying platforms with silicon chips. provide necessary conditions for combustion in the testing propulsion system. In this case the accompanied sound was like a muffed clap, meantime the accompanied sound in a microsystem without elastic spacers was close to a gunshot. The external view of tested microsystems, which keep integrity, does not indicate the appearance of the shock wave. Moreover the elastic spacer acts as an accumulator for porous silicon combustion energy. At the beginning of porous silicon combustion we have the maximum energy exit. The size of observed flash (Fig. 2) supports this statement.

The part of porous silicon combustion energy converts to the potential energy of the compressed elastic spacer at the first stage as it is schematically shown in Fig. 6a. Then the intensity of porous silicon combustion decreases (Fig. 6b) and potential energy of the compressed elastic spacer releases in a way of moving microsystem (Fig. 6b). After that combustion process finishes and the microsystem moves due to inertia (Fig. 6c).

It is found that an elastic spacer increases pulses the mechanical of designed microsystems up to 30-50% in comparison with one without it (Fig. 5). The developed approach allows us to obtain the mechanical pulses up to 180 mN·s for porous silicon thickness of 70 µm. For increasing the mechanical pulse we have developed a microsystem based on several Si-chips with a porous silicon layer. The Sichips have been attached to a carrying platform through the elastic spacers as it is shown in Fig. 7a.

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Fig. 6. Propulsion microsystem on different stages of testing: *a*) combustion initiation and motion beginning; *b*) motion in the process of burning out the porous silicon; *c*) motion due to inertia

The silicon chips containing porous silicon layers consecutively subjected to fast combustion process (Fig. 7b, 7c, 7d) in the case of elastic spacers with thickness in the range from 0.5 to 1 mm. The thickness of elastic spacers less 0.5 mm resulted in an explosion process for all silicon chips with the fast (microseconds) destruction of silicon chips. This explosion process provided the mechanical pulse less than 100 mN·s. In the case of elastic spacer thickness of more than 1 mm, the ignition of fast oxidation in the porous layer of silicon chips did not result in subsequent ignition process for the other silicon chips of the

microsystem developed. The measurements of mechanical pulse for the developed microsystem with multichip structure have shown that subsequent ignition of porous silicon combustion provides the pulse values up to 220 mN s for a platform mass of 20 g. The accompanying sound of this process (muffled clap) and the duration of light emission (milliseconds) correspond to the fast porous silicon combustion process.



Fig. 7. Schematical view of the propulsion system based on three silicon chips with porous silicon nanoenergetic materials: *a*) general view, *b*) ignition of porous silicon of first, *c*) second, and *d*) third chips respectively

4. Conclusions

The performed investigations allow us to determinate conditions of porous silicon combustion process in microsystems based on silicon chips containing porous silicon layers. For preventing the porous silicon explosion process, we suggest increasing carrying platform mass and using the special elastic spacers between silicon chips and the carrying platform. It resulted in reducing pressure change during fast oxidation of porous silicon and it supplied the controllable combustion process.

We have shown that our system based on porous silicon provides mechanical impulse which increases with accumulation of porous silicon combustion energy. The estimated impulse value is 200-220 mN s that is very promising, as an energetic material, for MEMS. The developed microsystem can be incorporated in silicon integrated circuit using for controlling and driving.

It should be specially noted that nanostructured silicon is an energy carrier alternative to hydrocarbon fuels. In particular, the flint used in ancient times to obtain fire is nothing other than a nanostructured mineral formation composed of quartz (SiO₂) and chalcedony. The chalcedony mineral differs from quartz in that it has a nonstoichiometric composition: specifically, an increased mass content of hydrogen, as high as several percent. That is, this mineral is "underoxidized" as compared with quartz, and it is this circumstance that is responsible for its unusual properties, that allow its particles to catch fire after a mechanical impact. Taking into account that silicon constitutes ~30% of the Earth's crust, various silicon-containing minerals and silicates can be regarded as potential sources of energy, alternative to hydrocarbon fuel. Consequently, a study of the combustion and explosion processes in nanostructured silicon can be of use in solving the energy problem of humankind.

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ELECTRON TUNNELING TO THE SURFACE STATES AT PHOTOCATALYSIS

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Abstract. Simulation of tunneling electrons excited by the sunlight in TiO_2 to surface states is performed for TiO_2/Si nanostructure. The tunneling transmission coefficient of the surface states created by organic compounds was calculated by phase function method. Dependence of the transmission coefficient of tunneling electrons on potential barrier parameters is explained by interference of transmitted and reflected waves.

Keywords: phase function method, TiO₂/Si nanostructure, transmission, tunneling electron

1. Introduction

Composites with titanium dioxide nanoparticles (nanocomposites) have the widest prevalence in heterogeneous photocatalytic processes of organic compound oxidation [1-5]. Titanium oxide possesses substantial photocatalytic activity in UV range; it is characterized by high resistance to photo-corrosion and absence of toxicity. These features allow applying it as a component of self-purifying surfaces as well as to use it for purification of domestic and industrial waters and air [6]. The TiO₂ photocatalytic properties are connected with the fact that under electromagnetic radiation non-equilibrium electrons and holes are generated in the volume of semiconductor [7,8]. After their separation, they participate in the oxidation of organic compounds on titanium dioxide surface [9,10]. The width of TiO₂ band gap is 3-3.2 eV (it depends on a crystal phase). That is why it displays the significant photocatalytic activity in the UV part of spectrum with the wavelength less than 400 nm.

Titanium dioxide has significant density of unsaturated bonds on a surface that promotes the molecule absorption from the environment. When the non-equilibrium electrons are captured at such levels, dissociation is happened. The sunlight generates the electron-hole pairs in the near-surface area of TiO₂. To eliminate their recombination and to ensure electron transition to the surface states, the pair components must be divided. For this purpose the heterojunctions containing titanium oxide together with silicon are used. The energy diagram of p-Si/n-TiO₂ structure taking into account the TiO₂ surface states is displayed in Fig. 1.

After dividing the holes move to silicon interface, where they recombine, while the electrons move to the surface and participate in tunneling to the surface states. The transfer of generated electrons to the surface states depends on the surface potential relief created by the organic compounds on the TiO_2 surface. A real potential relief has a very complex form and depends on the sunlight intensity. As a result, the photocatalytic activity and oxidation is determined by the sunlight intensity. Therefore, for evaluating and predicting the photocatalytic activity of titanium dioxide surface it is necessary to estimate the spectrum of electrons tunneling to the surface states and its dependence on the sunlight intensity, in particular to determine transmission coefficient of the tunneling electrons.



Fig. 1. Potential diagram of the Si/TiO₂ structure with regard to TiO₂ surface states

For this purpose, we have developed the model based on the phase function method [11]. It lets to calculate tunneling transparency for the potential of a complex form. The model takes into account the barrier parameters, the image force potential, and allows including the potential relief at a surface boundary and in a dielectric volume.

The aim of article is modeling the transmission of electrons excited by the sunlight through the barriers generated by the surface states produced due to absorption of impurities and organic compounds.

2. Model

The tunneling transmission coefficient through a barrier of the width d which is described by the potential U(x) is equal to: [4]

$$D(E) = \exp(\frac{1}{k} \int_0^a U(x) [b(x)\cos(2kx) - a(x)\sin(2kx)] dx),$$
(1)
where $k(E) = (8\pi^2 m^* E/h^2)^{1/2}$ is the tunneling electron wave vector, m^* and E are the effective

where $k(E) = (8\pi^2 m E/h^2)^{1/2}$ is the tunneling electron wave vector, m^2 and E are the effective mass and energy of a tunneling electron, h is the Planck constant, d is the tunneling barrier width. Functions a(x) and b(x) are defined from

$$\frac{da(x)}{dx} = \frac{U(x)}{2k} \left[-\sin(2kx) - 2b + (a^2 - b^2)\sin(2kx) - 2abcos(2kx) \right], \tag{2}$$

$$\frac{db(x)}{dx} = \frac{b(x)}{2k} [\cos(2kx) + 2a + (a^2 - b^2)\cos(2kx) - 2absin(2kx)].$$
(3)

The system of equations (2) and (3) allows model tunneling transport taking into account the charge carrier dispersion and the image forces on the potential relief.

To describe the potential barrier U(x) the following equation is used:

$$U(x) = \frac{8\pi m^*}{h^2} (U_0 - \frac{q}{\varepsilon \varepsilon_0 x} + A_s \exp\left(\frac{(x - p_0)^2}{\sigma}\right) + \frac{\alpha}{\sqrt{\pi}} \exp[\alpha^2 (x - \Delta)^2]), \tag{4}$$

where U_0 is the maximal height of the TiO₂ surface potential barrier, $\varphi(x)$ is the image force potential, q is the electron charge, ε , ε_0 is the relative dielectric TiO₂ permeability and absolute dielectric vacuum permeability, respectively, A_s , p_0 , σ are parameters characterizing imperfection of the potential relief surface. Expression $q/\varepsilon\varepsilon_0 x$ displays counting forces of the mirror images, which smoothed barrier. Expression $\frac{\alpha}{\sqrt{\pi}} \exp[\alpha^2(x-\Delta)^2]$) describes infinitely high peak placed approximately in the middle of the potential well, where α is a parameter, which influences on the peak width. $N = 2m \frac{x_0^2 kT}{(h/2\pi)^2}$ - coefficient, which has influence on the height and form of the potential barrier, in particular on the height and form of the additional barrier.

The above model was implemented for tunneling electron transmission through an absorbed layer on titanium dioxide surface illuminated by the light in neutral gas environment with organic compounds. For the generated electron-hole pairs division TiO_2 nanocomposite is positioned on Si substrate.

3. Results and discussion

Consider the electron tunneling through absorbed layers on the titanium oxide surface; it being a part of Si/TiO_2 heterostructure. The surface is illuminated by the light in neutral gas environment, containing organic pollution. Two potential barriers divided by a potential well represent the potential relief. An additional infinitely high barrier is located between the two barriers in the middle of potential well. This barrier indicates the position of an organic molecule. The results of calculation are presented in Figs. 1–4.



Fig. 1. Dependence of the transmission coefficient on an additional barrier height



Fig. 2. Dependence of the transmission coefficient on a potential dispersion



Fig. 3. Dependence of the transmission coefficient on a potential dispersion



Fig. 4. Dependence of the transmission coefficient on a potential dispersion

The transmission coefficient changes non-monotonically when the additional infinitely high barrier is placed in the potential well middle (Fig. 1). It increases monotonically beginning from E = 0.5 eV. At E = 1-2 eV it decreases drastically from 0.8 up to 0.4, after that it continues increasing. At a certain height of the additional barrier, resonance fluctuations appear. The fluctuations become evident at the higher barrier-growth-correction coefficient α . Duration and frequency of changes rise proportionally to the value of α . The highest fluctuation in the form of two sequential additional peaks on D(E) curve is observed at $p_0 = 0.3$ -0.4 (Fig. 3). When the potential dispersion parameter $p_0 = 0$, the transmission coefficient changes monotonically without peaks and fluctuations. The maximal value of the transmission coefficient is reached at $p_0 = 0.3$, but at further increasing up to $p_0 = 0.4$ -0.52 the peak height decreases and the transmission coefficient change, depending on the dispersion potential parameter, becomes monotonic again (Fig. 4, $p_0 = 0.52$).

4. Conclusion

Calculations of electron tunneling to the surface states, which are created by organic compounds on titanium dioxide surface under the light illumination, are performed. It is found that forming potential barrier on the titanium oxide surface, which contains organic compounds, leads to non-monotonic energy dependence of the transmission electron coefficient at the surface states (N-type). At the maximal transmission coefficient, additional peaks with fluctuations are appeared. Such features of the tunneling electrons transmission coefficient are explained by interference of transmitted and reflected waves.

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LEAKAGE CURRENT IN AIGaN SCHOTTKY DIODE IN TERMS OF THE PHONON-ASSISTED TUNNELING MODEL

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Abstract. The leakage current in the AlGaN Schottky diode under a reverse bias is simulated and compared within the frameworks of the thermionic emission–diffusion and phononassisted tunneling models. It is shown that the phonon-assisted tunneling model is suitable to describe the reverse-bias characteristic of the AlGaN Schottky contact and can also be applied to calculate the gate leakage current in the AlGaN/GaN high electron mobility transistor. **Keywords:** electron tunneling, leakage current, Schottky diode, thermionic emission

1. Introduction

In recent decades, GaN has constantly attracted interest of material researchers and device engineers due to its specific properties afforded by its wide band gap. The AlGaN/GaN high electron mobility transistor (HEMT) has been regarded as a leading candidate for high power microwave applications since its invention in 1993. Nevertheless, in spite of all scientific and technological advances, nitride-based electronics still faces big challenges hindering its commercial viability. One of the critical disadvantages of HEMTs, especially Schottky-barrier transistors, is an abnormal reverse-bias leakage current through the gate, which dramatically degrades device performance and reliability. The common approach to the problem is based on the insertion of dielectric materials with high permittivity into the gate structure [1,2]. Although this technique proves to be very effective in suppressing the leakage current, the issue is yet to be tackled, since the proposed solutions remain complex and expensive.

Until now, investigators have put forward different suggestions about mechanisms of the reverse-bias leakage current in rectifying contacts to GaN and AlGaN. For instance, in Ref. [3], two dominant leakage current mechanisms in the Ni/n-GaN Schottky diode structure grown by molecular-beam epitaxy were identified; one being associated with field emission tunneling and another with an exponential temperature dependence consistent with either trap-assisted tunneling or one-dimensional hopping conduction. In Ref. [4], temperature dependencies of the reverse-bias leakage current in rectifying contacts to both n-GaN and Al_{0.25}Ga_{0.75}N/GaN epitaxial layer structures were obtained; it is revealed that the tunneling current is dominant at temperatures below 150 K, while Frenkel-Poole emission controls the current at temperatures above 250 K. The study of electrical behavior of Au/Ni/GaN Schottky diodes in a temperature range of 300 to 623 K revealed that the current-voltage characteristics are described by a thermionic emission model with a Gaussian distribution of barrier heights at temperatures below 503 K, whereas the leakage current is governed by the generationrecombination process at higher temperatures [5]. It was supposed [6] that Frenkel-Poole emission is responsible for the reverse-bias carrier transport in Schottky diodes fabricated on Al_{0.83}In_{0.17}N/AlN/GaN heterostructures in a temperature range of 250 to 375 K. The authors

of Ref. [7] demonstrated that one of the dominant leakage current mechanisms in the Ni/GaN Schottky sample annealed at 1423 K for 5 minutes was one-dimensional hopping conduction.

A variety of proposed conduction mechanisms employed to estimate the reverse-bias leakage current in GaN Schottky diodes means that fundamental properties of the carrier transport in rectifying contacts to GaN have not yet been completely understood. However, it is claimed in Ref. [8] that the reverse-bias leakage current in the Ni/n-GaN Schottky diode can be interpreted in terms of the phonon-assisted tunneling (PAT) model. Although it is contemplated specially for GaN, the model should remain valid for associated compounds, such as AlGaN [9], thus enabling to accurately describe the transfer characteristic of the AlGaN/GaN Schottky-barrier HEMT.

In this communication, we would like to explain the peculiarities of the reverse-bias leakage current in the AlGaN Schottky diode within the framework of the PAT model, since this device can essentially be treated as an equivalent to the gate junction in the conventional AlGaN/GaN HEMT.

2. Simulation Details

In order to investigate the application of the PAT model to AlGaN, Ni/AlGaN Schottky diode structures were simulated within the framework of the thermionic emission–diffusion (TED) theory [10] and expanded by incorporating the PAT model.

Device structure. The two-dimensional device structure consists of an $Al_{0.3}Ga_{0.7}N$ region occupying the entire simulation domain with a length of 1 µm and a variable width denoted by *w*. Imposed boundary conditions for the primary equations define the electrodes of the Schottky diode. A rectangular mesh consisting of a series of lines along *x*- and *y*-directions is constructed to represent the simulation domain. The distance between the mesh lines perpendicular to the anode and the cathode $\Delta x = 5 \cdot 10^{-5}$ cm, while the lines parallel to the electrodes are located with a spacing $\Delta y = 10^{-8}$ cm. The significantly finer mesh along the *y*-direction is vital, since it allows the space-charge region to be accurately simulated.

Thermionic emission–diffusion model. The electrical behavior of semiconductor devices is operated by a mathematical model consisting of a coupled set of fundamental partial differential equations, which link together the electrostatic potential and the electron concentration. The primary function of general purpose device simulators is to find a self-consistent solution of these equations ensuring the potential profile inside the simulation domain being consistent with its electron concentration profile. The general framework of the model is provided by the Poisson and current continuity equations. The Poisson equation governs the interaction of the electrostatic potential with the space charge density:

$$\nabla^2 \varphi = \frac{q(N_d - n)}{\epsilon \varepsilon_0},\tag{1}$$

where φ is the electrostatic potential, *q* is the elementary electric charge, *N*_d is the donor density, *n* is the electron concentration, ε is the relative permittivity and ε_0 is the electric constant.

In equation (1), the acceptor density and the hole concentration are omitted. From now on, any values associated with the minority carriers are neglected.

The continuity equation describes the way the electron concentration evolves as a result of transport, generation and recombination processes. In a steady state, the generation and recombination rates are equal, the electron concentration is constant, and the continuity equation is given as follows:

$$q\frac{\partial n}{\partial t} = \nabla J = 0, \tag{2}$$

where J denotes the electron current density (for simplicity, referred to hereafter as the current).

Two fundamental theories have been proposed to describe the current transport in the Schottky junction. In the space-charge region of the junction, the electron motion is governed by the usual processes of diffusion and drift. When the electrons are transported from the bulk of the semiconductor to the interface, they can be emitted over the top of the barrier into the metal. These two mechanisms are effectively in series and the current is determined predominantly by whichever causes the larger impediment to the flow of electrons. Within the diffusion theory, the first of these two mechanisms is the limiting factor, whereas in accordance with the thermionic emission theory, the second is more important.

The diffusion theory assumes that the electron concentration in the semiconductor immediately adjacent to the interface is independent of the applied bias and the effective recombination velocity is infinite. Since there is a very high concentration of electrons in the metal, the carrier scattering forces the electrons on the semiconductor side of the junction into thermal equilibrium with those in the metal, which is equivalent to saying that the quasi-Fermi level changes throughout the space-charge region and ultimately coincides at the interface with the Fermi level in the metal. In that case, the driving force for conduction electrons is the quasi-Fermi level gradient and the drift-diffusion current takes the form

$$J_{DD} = g \mu n \nabla \phi_{a}$$

(3)

(5)

where μ is the electron mobility and ϕ_n is the quasi-Fermi level.

By neglecting the gradient of the intrinsic carrier concentration, which takes into account band gap narrowing effects, the current can be decomposed into drift and diffusion ingredients:

$$J_{DD} = q\mu nE + qD\nabla n, \tag{4}$$

where D is the diffusivity and denotes the electric field, which is related to the electrostatic potential through the Gauss law:

$$E = -\nabla \phi$$

It should be noted that the derivation of the diffusion model also assumes the validity of the Einstein relation:

$$D = V_{\rm T} \mu. \tag{6}$$

Here, V_T denotes the thermal voltage:

$$V_{\rm T} = \frac{\kappa I}{q},\tag{7}$$

where κ is the Boltzmann constant and *T* is a temperature.

From the thermionic emission theory, the electrons emitted from the semiconductor over the barrier are not in thermal equilibrium with those in the metal and can be treated as "hot" carriers. The hot electrons gradually lose their energy by carrier scattering as they penetrate the metal. As a consequence, the quasi-Fermi level remains flat throughout the space-charge region and does not have to coincide with the metal Fermi level at the interface. The effect of diffusion and drift in the space-charge region are negligible, which, in turn, implies that the electron concentration in the semiconductor nearest to the interface is altered by an exponential factor when a bias is applied and the effective recombination velocity has a certain finite value. The standard formula for the thermionic emission current is given by

$$J_{TE} = AT^{2} \exp\left(-\frac{\phi_{b}}{V_{T}}\right) \left[\exp\left(-\frac{\phi_{b}}{V_{T}}\right) - 1 \right],$$
(8)

where φ_b is the barrier height.

In equation (8), A represents the effective Richardson constant:

$$A = \frac{4\pi q \kappa^2 m_{\rm eff} m_e}{h^3},\tag{9}$$

where m_{eff} is the electron effective mass, m_e is the electron rest mass and h is the Planck constant.

Several researchers have combined the diffusion and thermionic emission models by considering the two mechanisms to be in series and successfully determining the position of the quasi-Fermi level at the interface equalizing the drift-diffusion and thermionic emission currents. The single TED theory developed in Ref. [10] has long been recognized as an appropriate model for describing the current transport in ideal Schottky barrier diodes; the authors introduced the concept of an effective recombination velocity at the top of the barrier (potential energy maximum) and evaluated the current through the metal-semiconductor barrier as follows:

$$J_{\text{TED}} = q v_{\text{R}} (n_{\text{m}} - n_{\text{eq}}), \tag{10}$$

where v_R is the effective recombination velocity and n_m is the electron concentration at the potential energy maximum when the current is flowing.

In equation (10), n_{eq} is a constant referred to as the "quasi-equilibrium electron concentration" at the potential energy maximum. It means the concentration, which would be obtained if it were possible to reach equilibrium without altering the potential energy maximum. The term with $v_R n_m$ represents the electron flux from the semiconductor to the metal, while the $v_R n_{eq}$ denotes the opposite flux.

The recombination velocity is given by

$$v_{\rm R} = \frac{AT^2}{qN_{\rm e}},\tag{11}$$

where N_c is the effective density of states in the conduction band.

The quasi-equilibrium electron concentration does not depend on the applied bias and is computed in accordance with

$$n_{eq} = N_c \exp\left(-\frac{\phi_b}{V_T}\right).$$
(12)

The actual electron concentration at the top of the barrier is determined by

$$\mathbf{n}_{\mathrm{m}} = \mathbf{n}_{\mathrm{eq}} \left(1 + \frac{\mathbf{v}_{\mathrm{D}}}{\mathbf{v}_{\mathrm{R}} + \mathbf{v}_{\mathrm{D}}} \left[\exp\left(-\frac{\boldsymbol{\varphi}_{\mathrm{b}}}{\mathbf{V}_{\mathrm{T}}}\right) - 1 \right] \right).$$
(13)

Here v_D is the effective diffusion velocity associated with the transport of electrons from the edge of the space-charge region to the potential energy maximum. If the Schottky barrier lowering is comparable to or less than V_T , the effective diffusion velocity is given by $v_D = |\mu E|$. (14)

Inserting equations (12) and (13) into equation (10) yields another formulation of the TED current:

$$J_{TE} = qN_{c} \frac{V_{R}V_{D}}{V_{R} + V_{D}} exp\left(-\frac{\phi_{b}}{V_{T}}\right) \left[exp\left(-\frac{\phi_{b}}{V_{T}}\right) - 1 \right].$$
(15)

If $v_R \gg v_D$, the pre-exponential factor in equation (15) is limited by v_D and the current is governed by the processes of diffusion and drift. If, however, $v_R \ll v_D$, the thermionic emission is dominant. Occasionally, v_R is referred to as the "thermionic emission velocity", which reflects the physical nature of the mechanism [11]. It should be noted that the image-force lowering of the Schottky barrier outlined in Ref. [10] is neglected in equation (15).

Mobility model. For calculating the electron mobility, the low field model [12] is used. It was derived on the basis of fitting a Caughey–Thomas-like model to Monte Carlo

simulation data. The model reflects the influence of temperature and ionized impurity density on the carrier mobility in the binary compounds, InN, GaN and AlN, and their associated ternaries, InGaN, AlGaN and InAlN. When the temperature-dependent factors are omitted, the model is given by

$$\mu = \mu_{\min} + \frac{\mu_{\max} - \mu_{\min}}{1 + \left(\frac{N_t}{N_{ref}}\right)^{\alpha}},$$
(16)

where N_t is the total doping density, μ_{min} , μ_{max} , N_{ref} and α are material-specific parameters, which can be obtained either experimentally or from Monte Carlo simulations.

The default parameters used in equation (16) were extracted for $Al_{0.2}Ga_{0.8}N$ and $Al_{0.5}Ga_{0.5}N$, and are presented for the reference doping density $N_{ref} = 10^{17}$ cm⁻³ in Table 1. The parameters for $Al_{0.3}Ga_{0.7}N$ are calculated by a linear interpolation between the nearest available respective values.

Material	$\mu_{min}, \text{ cm}^2/(\text{V}\cdot\text{s})$	$\mu_{max}, \mathrm{cm}^2/(\mathrm{V}\cdot\mathrm{s})$	α
Al _{0.2} Ga _{0.8} N	132.0	306.1	0.29
Al _{0.5} Ga _{0.5} N	41.7	208.3	0.12

Table 1. Default parameters in (16) for $N_{ref} = 10^{17} \text{ cm}^{-3}$

Phonon-assisted tunneling model. In accordance with the PAT model [8], the current transport through the Schottky barrier is controlled by tunneling from trap centers localized near the metal-semiconductor interface to the conduction band of the semiconductor. Because of continuous charging these centers from the adjacent metal, their occupation density is assumed to be independent of the applied bias. If the electrons emitted from the trap centers dominate the carrier flux through the barrier, the current is evaluated as follows:

$$J_{PAT} = -qWN_s$$

(17)

where W is the rate of PAT of electrons from the trap centers to the conduction band and N_s is the occupied trap center density near the interface.

The rate of PAT as a function of temperature and electric field can be expressed in the form presented in Ref. [13]:

$$W = \frac{\omega}{\beta} \left[(1+\gamma^2)^{\frac{1}{2}} - \gamma \right]^{\frac{1}{2}} (1+\gamma^2)^{-\frac{1}{4}} \exp\left\{ -\frac{2\beta E_s}{3\hbar\omega} \left[(1+\gamma^2)^{\frac{1}{2}} - \gamma \right]^2 \left[(1+\gamma^2)^{\frac{1}{2}} + \frac{\gamma}{2} \right] \right\}.$$
 (18)

Here ω is the frequency of phonon oscillations, E_s is the depth of the occupied trap centers and \hbar is the reduced Planck constant.

In equation (18), β and γ are given by

$$\beta = \frac{2\omega(2m_{\rm eff}m_{\rm e}E_{\rm s})^{\frac{1}{2}}}{q|E|}$$
(19)

and

$$\gamma = \frac{\beta \Gamma^2}{16\hbar\omega E_s}.$$
(20)

Here Γ is the width of the trap center absorption band. When an electron interacts predominantly with the longitudinal optical phonons, the width depends on temperature as follows:

$$\Gamma^{2} = 8\iota \left(\frac{2}{\exp\frac{\hbar\omega}{\kappa T} - 1} + 1\right) \left(\hbar\omega\right)^{2},$$
(21)

where ι is the electron-phonon interaction constant.

Combined model. In case of the TED model expanded by incorporating the PAT model, the total current is determined by

$$\mathbf{J}_{\mathrm{S}} = q \frac{\mathbf{v}_{\mathrm{D}}}{\mathbf{v}_{\mathrm{D}} + \mathbf{v}_{\mathrm{R}}} \left\{ \mathbf{v}_{\mathrm{R}} \mathbf{n}_{\mathrm{eq}} \left[\exp\left(-\frac{\phi_{\mathrm{n}}}{\mathbf{V}_{\mathrm{T}}}\right) - 1 \right] - \mathbf{W} \mathbf{N}_{\mathrm{s}} \right\}.$$
(22)

If WN_s is much less than the minuend in the curly brackets, equation (22) reduces to equation (15) after the quasi-equilibrium concentration of electrons is expressed in accordance with expression (12). In that case, the TED model defines the current and is suitable for describing the forward current-voltage characteristic of the Schottky diode. Otherwise, J_s tends to J_{PAT} from equation (17). Now the current is largely controlled by tunneling from trap centers and the PAT model is suitable for describing the reverse-bias characteristic.

Boundary conditions. After the current density in equation (2) is substituted with the help of equation (22), the system of the Poisson and continuity equations is solved self-consistently to determine the potential and electron concentration profiles. The numerical solution of these coupled non-linear second-order partial differential equations is obtained by the Newton iteration method applied to a linearized version of the complete set of the equations derived by the Scharfetter-Gummel discretization scheme [14].

The self-consistent solutions of the primary equations must simultaneously satisfy the boundary conditions implemented at the diode electrodes.

In case of the rectifying contact, Dirichlet boundary condition is imposed on the Poisson equation, which implies that the surface potential is fixed and defined by

$$\phi_{s} = \frac{E_{g}}{2} + \frac{V_{T}}{2} \ln \frac{N_{c}}{N_{v}} - \phi_{b} - \phi_{n}, \qquad (23)$$

where E_g is the band gap and N_v is the effective density of states in the valence band.

For the continuity equation, the inhomogeneous Neumann condition, when the current through the barrier has to be computed in accordance with the boundary condition (22), is established.

In case of the ohmic contact, Dirichlet boundary conditions are imposed on both semiconductor equations. Assuming charge neutrality and thermal equilibrium along with the validity of Maxwell-Boltzmann statistics, the surface electron concentration can be determined by

$$n_{o} = \frac{N_{d} + \sqrt{N_{d}^{2} + 4n_{i}^{2}}}{2}.$$
(24)

Here n_i is the intrinsic carrier concentration estimated from material-specific parameters as follows:

$$n_{i} = \sqrt{N_{c}N_{v}} \exp\left(-\frac{E_{g}}{2V_{T}}\right).$$
(25)

The surface potential at the ohmic contact is defined by

$$\varphi_{o} = \varphi_{n} + V_{T} \ln \frac{n_{o}}{n_{i}}.$$
(26)

Along the device structure, non-conducting edges, homogeneous Neumann boundary conditions, where the normal component of the electric field becomes zero, are implemented.

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Leakage current in AlGaN Schottky diode in terms of the phonon-assisted tunneling model

Finally, Dirichlet thermal boundary conditions, when the temperature is fixed, are set up around the entire simulation domain, the temperature being constant throughout the whole device structure.

3. Results

The effective density of states in the conduction and valence bands, the electron effective mass and the relative permittivity for $Al_{0.3}Ga_{0.7}N$ are determined through a linear interpolation between the corresponding values for the associated binary materials. The band gap of the ternary compound is calculated as follows:

$$E_{g}(AI_{x}Ga_{1-x}N) = xE_{g}(AIN) + (1-x)E_{g}(GaN) - 1.3x(1-x),$$
(27)

where *x* is the composition fraction.

The electronic band structure and dielectric parameters for $Al_{0.3}Ga_{0.7}N$ are given for convenience in Table 2. The corresponding values for AlN and GaN may be accessed through the references.

Parameter	Value	Unit	References
N _c	3.5.1018	cm ⁻³	[15]
N_{v}	$1.76 \cdot 10^{20}$	cm ⁻³	[15]
E_g	4.019	eV	[16]
m_{eff}	0.238		[17]
3	8.78		[15]

Table 2. Electronic band structure and dielectric parameters for Al_{0.3}Ga_{0.7}N

The Schottky barrier height in the metal/Al_{0.3}Ga_{0.7}N contact is assigned a value of 1.5 eV, which is derived as the difference between the metal work function and the electron affinity of Al_{0.3}Ga_{0.7}N. For the semiconductor layer, a uniform donor density of 10^{17} cm⁻³ is selected. The mobility of electrons computed by equation (16) equals 187.7 cm²/(V·s). The simulation is performed for a temperature of 300 K. The parameters of the PAT model are taken as typical averaged values from Refs. [8,18,19] and are listed in Table 3.

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Parameter	Value	Unit			
N_s	10^{13}	cm ⁻²			
l	1.7				
ω	$1.063 \cdot 10^{14}$	s ⁻¹			
E_s	0.8	eV			

Table 3. Parameters of the PAT model

In Figure 1, two variants of the current-voltage (J/V) characteristic of the Al_{0.3}Ga_{0.7}N Schottky diode under a reverse bias with a width of 0.2 µm are presented on a logarithmic scale, one obtained by the TED model and another by a combination of the TED and PAT models.



Fig. 1. J/V characteristic of the Al_{0.3}Ga_{0.7}N Schottky diode with $w = 0.2 \mu m$ described either by the TED model (line 1) or by the combined model (line 2)

It is obvious that, in accordance with the TED model, the current is not flowing (to be more precise, it is tending to zero), when the diode is at the thermal equilibrium, that is, no bias is applied. At the same time, the combined model predicts a certain non-zero value of the current ($J_s = -5.094 \cdot 10^{-15} \text{ A/}\mu\text{m}$). Moreover, J_{TED} takes a non-zero value immediately after a reverse bias is applied ($J_{TED} = -4.736 \cdot 10^{-28} \text{ A/}\mu\text{m}$ at V = -0.01 V).

In Figures 2 and 3, the same characteristics are drawn separately on a linear scale. It is not difficult to note that J_{TED} exhibits a very weak dependence on the bias, rising only 3.315 times (from -4.763 · 10⁻²⁸ A/µm to -1.579 · 10⁻²⁷ A/µm), when *V* is changed from -0.01 V to -10 V. It can be judged from equation (15) that the reverse-bias leakage current generated by thermionic emission, diffusion and drift depends on *V* primarily through the effective diffusion velocity.







In contrast to J_{TED} , J_s appears to be a strong function of V, increasing $2.3 \cdot 10^5$ times (from -5.094 $\cdot 10^{-15}$ A/µm to -1.461 $\cdot 10^{-9}$ A/µm), when the bias is raised from 0 V to -10 V. Analysis of equation (22) shows that since the density of the occupied trap centers near the metal-semiconductor interface is considered to be independent of the bias, J_s and V are coupled mainly through the electric field or the gradient of the electrostatic potential, which

define the center-to-band tunneling rate. The potential, in its turn, is distributed along the device structure in simultaneous accordance with the bias and the distance between the electrodes. It follows from here that the leakage currents of Schottky diodes with identical parameters but featuring varying widths of the structure are expected to be unequal for the same bias conditions.

In Figure 4, the profiles of the electric field constructed on several mesh nodes nearest to the metal-semiconductor interface are drawn for the $Al_{0.3}Ga_{0.7}N$ Schottky diode with different distances between the electrodes. A bias voltage of -10 V is applied. It follows from the simulation results that for identical bias conditions the intensity of the electric field at the metal-semiconductor interface is larger for the diode structure with a lesser width. The intensity rises by 5.5 % (from -7.764 $\cdot 10^5$ V/cm to -8.192 $\cdot 10^5$ V/cm) when the structure is narrowed from 0.2 µm to 0.18 µm, and 13.1 % (from -7.764 $\cdot 10^5$ V/cm to -8.778 $\cdot 10^5$ V/cm) in case the width is decreased from 0.2 µm to 0.16 µm.

In Figure 5, three variants of the J_s/V characteristic of the Al_{0.3}Ga_{0.7}N Schottky diode are presented, each obtained for a different width. It is evident that the less the distance between the electrodes the larger the leakage current of the Al_{0.3}Ga_{0.7}N Schottky diode for identical bias conditions, since the electric field defines the probability of electron center-toband tunneling. At V = -10 V, J_s rises 1.9 times (from $-1.461 \cdot 10^{-9}$ A/µm to $-2.844 \cdot 10^{-9}$ A/µm), when the diode structure is narrowed from 0.2 µm to 0.18 µm, and increases 4.6 times (from $-1.461 \cdot 10^{-9}$ A/µm to $-6.681 \cdot 10^{-9}$ A/µm) in case the width is lessened from 0.2 µm to 0.16 µm. Concerning the Schottky-barrier AlGaN/GaN HEMT, it means that if the total thickness of the barrier and buffer layers does not exceed the width of the space charge region, the gate leakage current increases, when the epitaxial layers are made thinner, thus, limiting design flexibility.



Fig. 4. Profiles of the electric field for Al_{0.3}Ga_{0.7}N Schottky diode with $w = 0.2 \ \mu m$ (line 1), 0.18 μm (line 2), 0.16 μm (line 3) at $V = -10 \ V$



Fig. 5. J_s/V characteristic of Al_{0.3}Ga_{0.7}N Schottky diode with $w = 0.2 \ \mu m$ (line 1), 0.18 μm (line 2) and 0.16 μm (line 3)

Overall the combined model employed to estimate the leakage current in the AlGaN Schottky contact shows a good agreement with experimental data. In Figure 6, the J/V characteristic of the Al_{0.3}Ga_{0.7}N Schottky diode ($w = 1.42 \mu$ m) calculated either by the TED model or by the combined model is compared with the input characteristic of the Al_{0.3}Ga_{0.7}N/GaN HEMT (the total thickness of the epitaxial structure equals 1.42 μ m) obtained experimentally in Ref. [20].



Fig. 6. *J*/*V* characteristic of the Al_{0.3}Ga_{0.7}N Schottky diode ($w = 1.42 \mu m$) described by the TED (line 1) and the combined (line 2) models in comparison with the input characteristic of the Al_{0.3}Ga_{0.7}N/GaN HEMT obtained experimentally (line 3)

Analysis of Figure 6 shows that the combined model provides a much more accurate estimation of the leakage current than the TED theory. Thus, the currents in the Schottky contacts of the diode and the HEMT are predicted to be of the same order, when the applied bias is at least -7 V. The discrepancy observed at low biases is thought to be mainly due to the presence of the heterojunction in the transistor structure.

4. Conclusions

The combination of the TED and the PAT models proves to be efficient in describing the reverse-bias characteristic of the AlGaN Schottky contact. It can serve as a base to develop a more sophisticated model, which would predict accurately the gate leakage current in the AlGaN/GaN HEMT.

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STUDY OF THERMIONIC AND TUNNEL COMPONENT CONTRIBUTION IN CONDUCTANCE OF InGaAs/GaAs HETEROSTRUCTURES WITH A SINGLE QUANTUM WELL BY ADMITTANCE METHODS

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Abstract. A study of $In_xGa_{1-x}As/GaAs$ heterostructures with single quantum well (SQW) carried out by admittance methods demonstrates two competing emission mechanisms for carriers: thermionic and tunnel. The dependence of thermionic conductance peaks on the reverse bias has resonance character. We noticed a temperature independent plateau on the conductance-temperature spectra, which is always related to the tunnel nature. We guess the observed effect is the resonant tunneling through the two-barrier potential formed at the QW borders due to doping.

Keywords: admittance, heterostructure, single quantum well, thermionic, tunnel

1. Introduction

Semiconductor heterostructures containing quantum wells (QW) have taken strong positions as materials for creating effective electronic devices: lasers, LEDs, photo-sensor elements, high-speed transistors. Such systems differ in the cardinal reorganization of properties due to size effects. Quantum-dimensional structures, in which free charge carriers are localized in one, two or three directions in the area compared with de Broglie wavelength, are characterized by discrete energy spectrum and in specific conditions may reveal a pure quantum-mechanical tunnel effect. The study of tunneling fundamental principles is perspective for further development of nanoelectronics that creates principally new devices, such as resonant tunnel diodes, quantum-cascade lasers, HEMT transistors, etc.

The admittance method is the most prime and efficient research technique, both for bulk semiconductors and for heterostructures with QW [1-3,5,7]. It is known that in doped heterostructures due to redistribution of charge carriers the bottom of conduction band or the top of valence band is bent, forming additional barriers, close to triangular. In Ref. [4] the detailed theoretical and experimental study of capture and emission of charge carriers in heterostructures with QW is presented. It is shown that in the heterostructures containing QW there are two competing mechanisms of charge carrier escape: thermionic emission and tunneling, which make different contribution to total conductance at different temperatures. In this work the isotype *n*-type heterojunctions $In_xGa_{1-x}As/GaAs$ ($x = 0.065 \dots 0.29$) with elastically strained single quantum well (SQW) grown by MOCVD were investigated [1,2]. The sample structure is presented in Fig. 1. The active layer thickness of the samples was 6.0...9.5 nm. The structure parameters and its quality were controlled by local cathodoluminescence, HRXRD, etc. The measurements were taken in the temperature range 10-375 K, voltage range ± 40 V, and the frequency range of a test signal was 20 Hz – 2 MHz.

It was found that at small indium content in the solid solution, it is impossible to notice in the conductance spectra the features related to the tunnel emission, because of the small band discontinuity giving a response, which cannot be registered even at low temperatures. This fact is illustrated in Fig. 2.



Fig. 1. Structure of samples with SQW InGaAs/GaAs





Earlier we investigated pseudomorphism in similar samples and its influence on electronic characteristics of structure [2]. The experimentally obtained dependence is close to a straight line with little bowing. From fitting the curve to parabola, we had proposed the expression:

$$\Delta E_{a} = 0.814 x - 0.21 x^{2}$$
.

(1)

In this study, we analyze the contribution of tunnel conductance to the total response of the system.

2. Experimental results and discussion

The best qualitative characteristics were obtained for structure x = 0.29 (the end of pseudomorphism growth). The results are presented in Fig. 3. Here the characteristics CV-GV are located in the center, the temperature spectra of conductance in the reference points of the CV-curve are outside; the points just referred to belong to the plateau, to the plateau adjacent regions, and far from it. From the figure it follows that the delay effects begin to play an important role at low temperatures. At temperatures close to RT, the SQW manages to relax on the test signal frequency (the quasi-static measurement mode is implemented). The conductance-voltage (GV) characteristics of the structure demonstrate clearly the complex resonance mechanism of active conductance formation for the structure with SQW. The strong modification is experienced by the conductance temperature spectra depending on the reverse bias. Indeed, we have shown in [7] that the conductance spectra for QW structure is influenced by the applied bias unlike a deep center evenly distributed in the structure.

The peaks are the most clearly expressed at the reverse bias -2.3 V that corresponds to the part of CV characteristic adjoining the plateau from the small biases. This area is responsible for the beginning of intensive thermionic emission of charge carriers from quantization levels with the electric field penetrating into the QW. The temperature shift of

the conductance maximum on frequency confirms the thermally activated nature of the process studied. The observed phenomenon has a resonance character and exists in the narrow voltage range about 0.5 V. Depending on the test signal frequency ω , the maximum burst of charge carriers occurs at temperatures corresponding to the condition of optimum carrier escape from the energy level:

$$w = e_n$$

(2)

At the same time, the thermal emission rate from a level is defined by the expression: $e_n = AT^p \exp(-E_a/kT)$, (3) where *A* is a temperature independent coefficient, E_a is the activation energy of charge carriers from the level, *k* is Boltzmann constant. The value of *p* is defined by the nature of the emitting center and is different for a deep center in the bulk semiconductor (*p* = 2) and

for a quantization level in the quantum well (p = 1/2) [8]. The activation energy of charge carriers from levels was determined by plotting the temperature dependence of emission rate constructed in Arrhenius coordinates (without T^p multiplier) (Fig. 4).



Fig. 3. Generalized results of the admittance measurements for the structure with QW $In_{0.29}Ga_{0.71}As/GaAs$

The activation energy, experimentally obtained for emission of charge carriers from QW, is significantly less than the depth of quantization levels in QW and needs separate justification. The point is that the definition of activation energy from a slope of Arrhenius plot is based only on thermoactivated interpretation of charge carriers' emission. The competing tunnel emission with the temperature independent rate increases the total emission rate [6], especially at low temperatures when the contribution of the tunnel component is raised.

It is illustrated in Fig. 5: defined from the experiment the result dependence of $n(e_n) = f(1/T)$ (shown by dotted line) manifests the deviation from a straight line in the low

temperature area, and its standard processing by least squares method results in the underestimated E_a value.



Fig. 4. Temperature dependence of chargecarrier-emission rate from QW in Arrhenius coordinates



Fig. 5. Calculation of "apparent" activation energy. Curves are calculated using the values: e_{tunn} is the tunnel emission rate, e_{term} is the thermoemission rate, e_{sum} is the total emission rate

Therefore, it is necessary to consider the activation energies, found from conductance spectra by means of drawing Arrhenius curves, only as the "apparent" values; the determination of true values is not possible without special modeling the quantum levels depth in QW. Thus, the net activation energy for charge carrier emission from SQW should be determined by the high-temperature part of Arrhenius curve, minus the tunnel component. Such derived activation energy deviates in the considered case from 36 to 70 meV, depending on the reverse bias.

For the adequate determination of activation energy, we will address to Fig. 3. In the region of thermionic response (at -2.3 V) the activation energy, determined by the Arrhenius curve, reaches the maximum and the experimental points of the Arrhenius curve most exactly keep on a straight line. At other reverse biases, where the thermionic component is expressed poorly against the tunnel background, the experimental points in the Arrhenius plot significantly deviate from the straight line that leads to the considerable decrease of "activation energy". Thus, the variation of activation energy, derived from the experiment, is caused by the different contribution of tunnel and emission components.

3. Conclusions

The study of high-quality heterostructures with SQW by admittance spectroscopy confirms the existence of two competing mechanisms for emission of charge carriers: thermionic and tunnel ones. It is shown that thermionic peaks in the conductance spectra have resonance character, showing the maxima in the narrow region of reverse biases. The "shelves" in the spectra corresponding to tunnel component at reverse biases 0-3.0 V accepted the maximal value at -0.3 V, and then had sharp fall in more than 10 times. Such behavior of tunnel component can be explained on the basis of resonance tunneling. For the case considered, it is necessary to bear in mind that the top part of the band diagram for doped heterostructures with a SQW represents a two-barrier structure in energy region E > 0. It was shown earlier that the structure with identical barriers (the equal width and height) has the greatest probability for carrier tunnel transmission. In this case, the probability for resonance tunneling is maximal. A minor relative change of parameters for one of barriers leads to a strong reducing of transfer coefficient. This qualitative conclusion, based on analytical calculation,

allows explaining the experimental results obtained here. Really, at small reverse biases, the external electric field does not reach yet the QW region, and the QW remains with symmetric barriers, identical in form. At the same time, the "shelves" on temperature conductance spectra get the maximal values. On increasing reverse bias the left-hand edge of space charge region begins "to rise", the symmetry of barriers is broken and the tunnel transfer probability drastically falls. In the experimental results, it is expressed by sharp falling of the "shelf" at U = -1.3 V. Address now to Fig. 6 where the temperature spectra of conductance depending on the reverse bias are presented.



Fig. 6. Conductance temperature spectra. Main mechanisms of carrier charge emission: twobarrier resonant tunneling, thermoactivation, tunneling through a single triangular barrier

Changing the predominating role in the carrier emission goes in the following order. At low reverse biases, it is the resonance tunneling across the two-barrier structure formed at the QW top due to doping. As soon as the edge of SCR approaches the QW, the thermo activation begins to play the dominant role. And finally there is the second turning to tunneling through a triangular barrier. It is worth noting that the maximal response is provided by the resonance tunneling al low reverse biases. Its value exceeds the thermo activated contribution one order. To our opinion, this effect is very perspective for the device applications.

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MODELING FULLERENE GROWTH BY FUSION REACTIONS OF CUPOLA HALF-FULLERENES: Δn=16 SERIES

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Abstract. Fusion reactions of cupola half-fullerenes C_{22} , C_{24} , C_{32} , C_{40} and C_{48} with each other are considered on the basis of Arrhenius's postulate. It means that at first there forms an intermediate compound and only afterwards a usual chemical reaction is going on. The final structure of fullerenes is obtained with the help of geometric modeling and is optimized through the use of Avogadro package. In general, the fullerenes which tend to take the appearance of a perfect spheroid have lesser formation energy. The energy of nanotubes and fullerenes C_{44} , C_{48} , C_{64} , C_{60} and C_{96} obtained is calculated.

Keywords: cluster, cupola, energy, fullerene, fusion, modeling

1. Introduction

Up to now mechanism of fullerene formation is a controversial point (see [1] and references therein). In the majority of cases there suggests that fullerene assemblage originates of separate atoms and C_2 – dimers, and probably of very small clusters. In Ref. [2-4] we have investigated these mechanisms of growing fullerenes. The fullerene growth of separate carbon atoms is conceptually identical with the usual diffusional growth of vacancy clusters in irradiated metals [5]. The growth through the use of dimer embedding into fullerenes was suggested by M. Endo and H.W. Kroto in 1992 [6]. According to it, a carbon dimer embeds into a hexagon of an initial fullerene. This leads to stretching and breaking the covalent bonds which are parallel to arising tensile forces (Fig. 1). As a result, there arises a new atomic configuration and there is mass increase of two carbon atoms.



Fig. 1. Carbon dimer embedding into a hexagon (a) and its consequence (b)

This mechanism resembles in some respects evolution of an interstitial atom embedded into an octahedral hole of a bcc lattice of alpha-iron, the process being modeled with the help of molecular dynamics by J.M. Beeler, Jr. in 1966 [5]. The result is shown in Fig. 2. We exhaustively studied Endo-Kroto mechanism in Ref. [3,7]. On the basis of these investigations we suggested the periodic system for embedded fullerenes. However this mechanism does not allow obtain pentagon-isolated fullerenes.



Fig. 2. Plane complex of the most displaced ten atoms forming a bow tie lying in a (110) plane with wings along <111> directions. Atoms 1 are displaced by 17%, atoms 2 by 7%

Fortunately the above-stated mechanisms of fullerene growth are not unique. One may imagine that fullerenes can grow reacting with each other, similar to bubbles in a soap solution. This possibility was demonstrated by the example of such reactions as $C_{24}+C_4 \rightarrow C_{28}$, $C_{30}+C_6 \rightarrow C_{36}$, and $C_{30}+C_{30} \rightarrow C_{60}$, through the use of a new molecular dynamics that takes into consideration both atomic and electronic degrees of freedom simultaneously, especially the excited electronic states created by electronic transitions [8-10]. Fullerenes and nanotubes are formed at high temperatures and the new molecular dynamics, named charged-bond molecular dynamics, accounts for this factor properly. At first, this molecular dynamic was developed as a rather sophisticated design, but later it obtained a strict theoretical basis [11].

Any molecular dynamics needs input data. For mini-fullerenes (up to C_{20}) the number of possible configurations is not very large, but as one passes to midi ($C_{20} - C_{60}$) and maxifullerenes (> C_{60}) one obtains a monstrous size of isomers. It is clear that there is no big sense in studying all of them, so it is desirable to restrict their number to the most stable which are usually symmetric. In this respect it is very useful using geometric modeling as a first step of a computer simulation for further theoretical analysis [5]. We suppose that the geometric modeling allow us to imagine from the very beginning a possible way of growing carbon clusters and thereby to decrease the number of configurations being worth for studying. Using the geometrical modeling, we have considered the growth of fullerenes through a series of joining reactions of cupola half-fullerenes [12]. We have obtained the most symmetric isomers of fullerenes in the range from C_8 to C_{72} , calculated their energy and constructed their graphs. Moreover, on the basis of these investigations we suggested the periodic system for basic perfect fullerenes [13, and references therein]. For the purpose of enlarging the periodic system discovered, in this contribution we present the structure and energy of the $\Delta n=16$ series fullerenes, C₄₄, C₄₈, C₆₄, C₈₀ and C₉₆, obtained by fusion reactions of cupola half-fullerenes C₂₂, C₂₄, C₃₂, C₄₀, and C₄₈.

2. Reaction between two cupolas C₂₂

In 1889 Svante August Arrhenius postulated that a chemical reaction goes in the following way [14]. At first there forms some intermediate compound and only afterwards a usual chemical reaction is going on. For fullerenes this postulate can be written as $A + B \leftrightarrow (AB) \rightarrow C$.

In Ref. [12] we have developed an algorithm that has proved itself in predicting the growth of perfect fullerenes conserving an initial symmetry, so called the fusion reaction algorithm. Consider now the reaction for fullerenes of the $\Delta n=16$ series.

The atomic configurations corresponding to reaction $C_{22} + C_{22} \rightarrow (C_{22}C_{22}) \rightarrow C_{44}$ between two cupolas C_{22} are shown in Fig. 3. At first two molecules C_{22} are moving towards each other (Fig. 3a). Then the atoms, marked with red, interact with each other producing a compound (Fig. 3b). During this process new covalent bonds (thick red lines) are formed. As a result, a distorted polyhedron is formed that relaxes into a perfect polyhedron (Fig. 3c). It should be emphasized that the symmetry of double bond location about the major axis of cupolas coincides with that of fullerene C_{60} .

To make clear the symmetry of the fullerene obtained one needs to turn to its graph. It is shown in Fig. 4 together with the graph of the initial cupolas. The atomic configuration of initial cupolas consists of six pentagons and three hexagons; due to the fusion there appear six new hexagons and so we have twelve pentagons and twelve hexagons forming a polyhedron.



Fig. 3. Joining two cupolas C₂₂: *a*) separate cupolas C₂₂; *b*) intermediate compound; covalent bonds (blue lines), neutral atoms (blue spheres); reacting atoms (red spheres), new covalent bonds (heavy red lines), *c*) nanotube C₄₄ after relaxation



Fig. 4. Graphs of cupola C₂₂ and nanotube C₄₄; new covalent bonds are heavy red lines

3. Reaction between two cupolas C24

Similar to the previous reasoning one may consider the atomic configurations corresponding to reaction $C_{24} + C_{24} \rightarrow (C_{24}C_{24}) \rightarrow C_{48}$ between two cupolas C_{24} . As before, we have rotation-reflection-symmetry joining (Fig. 5). The graphs of reacting molecules and polyhedron obtained are shown in Figure 6; they enable us to gain a better insight into the symmetry of the process. The atomic configuration of initial cupola consists of one trigon, three pentagons and six hexagons; due to the fusion there appear six new hexagons and so we have two trigons, six pentagons and eighteen deformed hexagons forming a polyhedron.



Fig. 5. Joining two cupolas C₂₄: *a*) separate cupolas C₂₄; *b*) intermediate compound; covalent bonds (blue lines), neutral atoms (blue spheres); reacting atoms (red spheres), new covalent bonds (heavy red lines), *c*) nanotube C₄₈ after relaxation



Fig. 6. Graphs of cupola C₂₄ and nanotube C₄₈; new covalent bonds are heavy red lines

4. Reaction between two cupolas C₃₂

The procedure for visualization of reaction $C_{32} + C_{32} \rightarrow (C_{32}C_{32}) \rightarrow C_{64}$ is the same as before (Figs. 7 and 8). The atomic configuration of initial cupola consists of one square, four pentagons and eight hexagons; due to the fusion there appear eight new hexagons and so we have two squares, eight pentagons and twenty-four hexagons forming a polyhedron.



Fig. 7. Rotation-reflection-symmetry joining of two half-fullerenes C₃₂: a) separate cupolas C₃₂; b) intermediate compound; covalent bonds (blue lines), neutral atoms (blue spheres), reacting atoms (red spheres), new covalent bonds (heavy red lines); c) fullerene C₆₄ after relaxation



Fig. 8. Graphs of cupola C_{32} and fullerene C_{64} ; new covalent bonds are heavy red lines

5. Reaction between two cupolas C₄₀

The procedure for visualization of reaction $C_{40} + C_{40} \rightarrow (C_{40}C_{40}) \rightarrow C_{80}$ is the same as before (Figs. 9 and 10). The atomic configuration of initial cupola consists of six pentagons and ten hexagons; due to the fusion there appear ten new hexagons and so we have twelve pentagons and thirty hexagons forming a polyhedron.



Fig. 9. Rotation-reflection-symmetry joining of two cupolas C_{40} : *a*) separate cupolas C_{40} ; *b*) intermediate compound; covalent bonds (blue lines), neutral atoms (blue spheres), reacting atoms (red spheres), new covalent bonds (heavy red lines); *c*) fullerene C_{80} after relaxation



Fig. 10. Graphs of cupola C_{40} and fullerene C_{80} ; new covalent bonds are heavy red lines

6. Reaction between two cupolas C₄₈

The procedure for visualization of reaction $C_{48} + C_{48} \rightarrow (C_{48}C_{48}) \rightarrow C_{96}$ is similar to the previous cases and is shown in Figs. 11 and 12. The atomic configuration of initial cupola half-fullerene consists of six pentagons and thirteen hexagons; due to the fusion there appear twelve new hexagons and so we have twelve pentagons and thirty-eight hexagons forming a polyhedron.



Fig. 11. Rotation-reflection-symmetry joining of two cupolas C_{48} : *a*) separate cupolas C_{48} ; *b*) intermediate compound; covalent bonds (blue lines), neutral atoms (blue spheres), reacting atoms (red spheres), new covalent bonds (heavy red lines); *c*) fullerene C_{96} after relaxation



Fig. 12. Graphs of cupola C₄₈ and fullerene C₉₆; new covalent bonds are heavy red lines

7. Discussion

Today there are a lot of papers on fullerene properties. Using different computational methods (there are also a lot of programs), the authors calculate the properties of the most popular fullerenes which structure is known. As a result, the numbers obtained contradict to each other and only increase disordered information. The absence of appreciable progress in understanding fullerene nature is determined by the domination of numerical calculations on the known structures. However, any numerical calculations are unable to predict new structures, so the 'numerical progress' results mainly in increasing numerical entropy. It should be emphasized that numerical calculations are not a theory, but a kind of numerical experiment [15].

The theoretical approach to fullerenes is based on the topological and graph treatment. "The fullerene graphs contain all the information we need, and we able to sort through the millions of isomers, finding a few candidates for the most stable, by way of simple, easily computed topological indices for pentagons or hexagons" [16]. At that, the authors define (classical) fullerenes as "cage-like, hollow molecules of pseudospherical symmetry consisting of pentagons and hexagons only, resulting in a trivalent (and in the most ideal case) convex polyhedron with exactly three edges (bonds) joining every vertex occupied by carbon, idealized as sp^2 hybridized atoms".

Modeling fullerene growth by fusion reactions of cupola half-fullerenes: $\Delta n=16$ series

The theoretical approach to fullerenes, based on the topological and graph treatment, is developed only for classical fullerenes consisting of pentagons and hexagons only. Luckily there is another approach to the fullerenes (classical and non-classical), where "the fullerene is defined as any convex shape inscribed into a spherical surface which can be composed of atoms, each atom having three nearest neighbors, as in usual fullerenes, whenever discussing hollow carbon clusters" [2]. It should be emphasized that there is no restriction on the electronic structure and on the polyhedrons; they can be not only pentagons and hexagons, but also triangles, square and heptagons. Such approach allowed obtaining possible forms of mini-fullerenes from C_4 and C_{20} . At that, we have constructed graphs for all the mini-fullerenes [2, 4] and incorporated them into the family of classical fullerenes.

In Ref. [17] we have considered forming fullerenes and nanotubes in the context of a single graph approach. In this study we have obtained the fullerenes which geometrically resemble in some aspects small nanotubes. The question arises where the boundary between fullerenes and nanotubes is. An intuitive idea says: a fullerene is a spheroid; a nanotube with open ends is a cylinder; a nanotube with closed ends is a cylinder with two hemispheres. However the effort to reduce physical phenomena to mathematics can justify hopes only at the early stage of investigation. We need an exact quantitative criterion. Under these circumstances we should look at the electron theory for clues.

Electronic aspects to structure and stability of fullerenes are briefly considered in Ref. [16]. In C_{60} – I_h there are two different types of bonds according to atomic field microscopy (AFM) image. The measured bond lengths are $r_{hh} = 1.38(2)$ Å and $r_{hp} = 1.4654(12)$ Å. This fullerene is considered as an ideal one, having only equal isolated pentagons and forming a perfect sphere. The larger bonds are singular, the lesser bonds are double ones. Therefore in an ideal fullerene each hexagon has three single and three double bonds. In contrast to this, in an ideal nanotube with open ends there are only has hexagons with four single and two double bonds. Each spheroid can be divided into three parts; two hemispheres with hexagons having three single and three double bonds and one cylinder with four single and two double bonds. If the height of cylinder is less than the height of two hemispheres, we assume that it is a fullerene. On the contrary we have a nanotube.

8. Conclusion

The growth of fullerenes through a series of joining reactions of cupola half-fullerenes C_{22} , C_{24} , C_{32} , C_{40} , and C_{48} is considered. We supposed that during the reactions new covalent bonds are formed; the final structure of fullerenes is obtained through the use of geometric modeling. The fullerene symmetry is shown by means of graphs constructed. The geometric modeling is very effective as a first step of a computer simulation. The reason is that any molecular mechanics needs input data. For mini-fullerenes (up to C_{20}) the number of possible configurations is not very large, but as one passes to midi ($C_{20} - C_{60}$) and maxi-fullerenes (> C_{60}) one obtains a monstrous size of isomers. It is clear that there is no big sense in studying all of them, so it is desirable to restrict their number to the most stable. In this respect the geometric modeling allows one to imagine from the very beginning a possible way of growing carbon clusters and thereby to decrease the number of configurations being worth for studying. Using geometrical modeling we obtained fullerenes C_{44} , C_{48} , C_{64} , C_{80} , and C_{96} fullerenes having the form close to an ellipsoid of revolution. All of them, except fullerene C_{44} , have isolated pentagons. The final structure of the fullerenes is optimized through the use of Avogadro package.

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SUMANENE AND FULLERENE C₆₀

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Abstract. In this contribution we have considered fusion reaction of carbon clusters obtained from the natural blocks of sumanene. We obtained four natural isomers of fullerene C_{60} . Together with the fifth natural isomer found elsewhere through the use of the Endo-Kroto mechanism (dimer embedding model), now we have the structure of all the experimentally observed isomers of fullerene C_{60} . One isomer is a perfect, the other are imperfect and differ in the number of pairs of two adjacent pentagons.

Keywords: fullerene, fusion reaction, graph, natural isomer, sumanene

1. Introduction

Since the discovery of fullerenes more than 30 years ago, there has been considerable activity from the experimental and theoretical side [1, and 277 references therein; 2, and 350 references therein] to gain a detailed understanding of fullerene formation. "However, the formation mechanism, and especially high yield of C_{60} – I_h and C_{70} – D_{5h} , remains elusive and somewhat controversial" [2]. In 2002 we have suggested and confirmed, through the use of molecular dynamics calculations, the fusion reaction mechanism of joining two hemispheres C_{30} for obtaining fullerene C_{60} [3]. This approach has succeeded further development only 15 years later [4-6], at last leading to designing the periodic system of basic perfect fullerenes [5]. According to this system, fullerene C_{60} belongs to the $\Delta n=12$ series, the five-fold symmetry column, and has the lower formation energy than any of its nearest neighbors.

It should be emphasized that the structure of hemisphere C_{30} , both in Ref. [3] and in Ref. [5], was postulated. The question arises: Are there in nature similar molecules, from which it is possible to obtain the hemispheres? To our mind corannulene $C_{20}H_{10}$ with $C_{5\nu}$ symmetry and sumanene $C_{21}H_{12}$, which possesses $C_{3\nu}$ symmetry, could be such molecules. We have calculated their optimized structures and energy through the use of Avogadro package [7]; they are shown in Fig. 1. It should be emphasized that we developed a modified geometric color graphics because the package graphics is incomprehensible.

These molecules are usually considered as key fullerene fragments [8,9]. Being π -conjugated compounds, they are bowl-shaped or cupola-shaped species; it depends on a point of view (Fig. 1). The bowl of sumanene (1.15 Å) is anticipated to be deeper than that of corannulene (0.89 Å). According to Ref. 8, deeper π -bowls are more interesting because they may have properties more similar to those of fullerenes. However the mechanism of fullerene assembly from such fragments is not known.

In this contribution we are trying to clarify this problem.



Fig. 1. Sumanene as a bowl and corannulene as a cupola (energy, kJ/mol)

2. Sumanene as an origin of fullerene

Carbon clusters. Suppose that we have removed twelve hydrogen atoms from sumanene and added nine carbon atoms instead. In doing so we obtain bowl-shaped carbon cluster C_{30} with two types of carbon atoms (Fig. 2). The carbon atoms of sumanene remain in the initial electronic state; they are considered, as is customary, being sp^2 hybridized atoms. The new added ones are reactive carbon atoms, which are connected with the initial carbon atoms by single or double bonds, they being ionized to a different degree.

Cluster reactions. Two such clusters, combining with each other, are able to create fullerene C_{60} . The atomic configurations, corresponding to reaction between two clusters C_{30} , $C_{30} + C_{30} \rightarrow (C_{30}C_{30}) \rightarrow C_{60}$, are shown in Fig. 3. At first two molecules C_{30} are moving towards each other. Then the atoms, marked with red-grey, react with each other producing a compound. During this process new covalent bonds (red lines) are formed.





Fig. 2. Carbon cluster obtained from sumanene by replacing hydrogen atoms with carbon ones

It should be emphasized that there are possible four types of the reaction, namely: perfect reaction (Fig. 3a); one-fault reaction (Fig. 3b); two-fault reaction (Fig. 3c); and three-

fault reaction (Fig. 3d). To gain a better understanding of the reaction structures, their main features are given in the form of scheme (Fig. 4).



Fig. 3. Joining two hydrogen-replaced-by-carbon sumanene compounds: a) perfect reaction, b) onefault reaction, c) two-fault reaction, d) three-fault reaction

Fig. 4. Scheme reflecting the main structural changes during the fusion of two compounds

Graph representation of perfect reaction. To make clear the structure of the fullerenes obtained, one needs to turn to their graphs. They are shown in Fig. 5 for the initial bowl and the polyhedron obtained. The atomic configuration of the initial bowl consists of three pentagons, four hexagons and nine excited atoms; due to the fusion there appear six new pentagons and twelve hexagons. Therefore we have twelve pentagons and twenty hexagons forming polyhedrons. It should be emphasized that all pentagons are isolated from each other, creating perfect fullerene C_{60} .



Fig. 5. Graphs of bowl C_{30} and fullerene C_{60} ; new covalent bonds are heavy red lines

Structure of fullerenes obtained. Consider the fusion reactions in detail. As a result of the reactions, at first the distorted polyhedrons are fashioned, and then they relax into a perfect polyhedron (Fig. 6a) or faulted structure polyhedrons (Fig. 6b, c, and d). The perfect fullerene C_{60} is shown in Fig. 6a. It can be imagined as composed of pyracylene units. A pyracylene unit contains two pentagons and two hexagons and a central reactive double bond [10]. One of the units is shaded in Fig. 6a; the atoms of the central bond are marked in green. The faulted fullerene, presented in Fig. 6b, contains the same unit; its boundary atoms are connected by brown lines. It looks, as if its shaded pyracylene unit had undergone the Stone-Wales transformation [11, 12]. The latter corresponds to the rotation of the central bond by 90 degrees, resulting in the creation of two adjacent pentagon-pentagon pairs; their atoms marked in turquoise (Fig. 6b'). In a similar way one can think over other faulted fullerenes. They differ in the number of pairs, namely, four (Fig. 6c) and six ones (Fig. 6d).

Graph representation of fullerene structures. Here again, to make clear the structure of the fullerenes obtained, one needs to turn to their graphs. They are shown in Figs. 7 and 8. In Fig. 7 the boundaries of pyracylene units are brown-colored and the atoms of the rotating central bonds are marked in green. In Fig. 8 the isolated pentagons and adjacent pentagon-pentagon pairs are marked in brown.



Fig. 6. Fullerenes obtained from sumanene-like carbon compounds after relaxation: a) perfect reaction, b) one-fault reaction, c) two-fault reaction, d) three-fault reaction

Sumanene and fullerene C60



Fig. 7. Graphs of fullerenes C₆₀; the boundaries of pyracylene units are brown-colored and the atoms of the rotating central bonds are marked in green: a) perfect reaction, b) one-fault reaction, c) two-fault reaction, d) three-fault reaction



Fig. 8. Graphs of fullerenes C₆₀; the isolated pentagons and adjacent pentagon-pentagon pairs are marked in brown: a) perfect reaction, b) one-fault reaction, c) two-fault reaction, d) three-fault reaction

From the Figs. 6, 7, and 8, it follows that the most drastic changes occur inside the pyracylene units. Here the rotation of the central double bonds by 90 degrees leads to displacement of their four nearest-neighbor atoms; the other parts of fullerenes remaining stable.

3. Discussion and conclusion

Five isomers of fullerene C_{60} were generated in microwave plasma of chloroform [13]. They were stable at room temperature but four of them disintegrated at 250°C. The authors have suggested possible structures and calculated the formation energies of these isomers. However, a thought pattern of final configuration does not guarantee that the postulated configurations coincide with the structures obtained experimentally. It seems more reasonable to study the final configurations obtained by one of well-known mechanism of fullerene formation, which demonstrated its validity in many cases. This raises the question how to choose the best mechanism. To our mind, the best mechanism must satisfy the principle of least action. As a rule, this principle is tightly connected with symmetry and conservation laws.

Consider the analogy with house-building. It is clear that more cheaply and easier to build a house from blocks than from bricks. In the case of fullerenes, the nature gives us the ready blocks in the form of sumanene and corannulene. Replacing hydrogen atoms with carbon ones, we obtain cement for binding together the blocks.

In this contribution we have considered fusion reaction of carbon clusters obtained from the natural blocks of sumanene. Now we have four natural isomers of fullerene C_{60} . For completeness sake it is necessary to add the fifth, probably also natural, isomer. It was obtained earlier [14] by another way, through the use of the Endo-Kroto mechanism (dimer embedding model), i.e. from natural bricks (dimers C_2). The structure and graph of this isomer are shown in Fig. 9. It contains four isolated pentagons and four pairs of two adjacent pentagons, its energy being equal to 5747 kJ/mol. To gain a better understanding of its structure, the isolated pentagons and pentagons pairs are specially marked.



Fig. 9. Single and double bonds of fullerene C₆₀ with four isolated and four pairs of two adjacent pentagons (top); arrangement of two pairs of adjacent pentagons (bottom)

Thus we have the structure of all the experimentally observed isomers of fullerene C_{60} . The isomer (a) is a perfect, the other are imperfect and differ in the number of pairs of two adjacent pentagons. It should be emphasized that the imperfect isomers possess topological symmetry.

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TETRAHEDRAL MINI- AND MIDI-FULLERENES

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Abstract. We have considered possible ways of forming the simplest tetrahedral fullerenes, namely elementary tetrahedron C_4 , truncated tetrahedron C_{12} , half-truncated cube C_{16} , fullerenes C_{28} and C_{36} . By analogy with ionic crystals, we introduced "mathematical" compounds, which form a topological cube of two tetrahedra inserted into each other, and construct graphs for them. Combined with the graph analysis, this approach allows obtain a clear knowledge of the tetrahedral fullerene structure. We extended our model to other tetrahedral fullerenes, in particular, tetrahedral fullerenes C_{64} and C_{76} .

Keywords: energy, fusion reaction, graph representation, growth, mathematical compound, periodic system, tetrahedral fullerene, topological cube

1. Introduction

The periodic system of fullerenes, based on symmetry principles, consists of horizontal series and vertical columns. The horizontal series form the Δn periodicities, where the fullerene structure changes from threefold symmetry to sevenfold through four, five and sixfold ones. The system leaves room for the following series: Δn = 2, 4, 6, 8, 10, 12, 14, 16, 18, 20 and may incorporate into it carbon clusters, nanotubes and fullerenes from C₂ to C₁₄₀. However, it is known that there are fullerenes with tetrahedral structure [1 and references therein]. To complete the system, it is necessary to add these fullerenes to the periodic system.

The question arises how to do it. We only know some separate tetrahedral fullerenes which are not connected with each other. We do not know whether the connection laws, established for the fullerenes incorporated into the periodic system, are valid for such fullerenes. In other words, we know almost nothing. For this reason, we will follow the action plan outlined in Ref. [2], namely, "the next step in our investigation is obtaining the structure and energy of missing fullerenes with the purpose to incorporate the missing known and unknown fullerenes into the periodic system". What kind of missing fullerenes it necessary to design, first of all? To our mind, it is essential to begin with the simplest ones and to develop, similar to Ref. [3], the algorithm of the fullerene growth for the fullerenes conserving the tetrahedral symmetry. Then the fullerenes obtained should be arranged to give a successive growing array. What is wanted is the law which connects the nearest neighbors.

In the periodic system of fullerenes the vertical columns (groups) include the fullerenes of one and the same symmetry, the mass difference Δm for each column being equal to a double degree of symmetry. In this contribution we have tried to construct a similar column for the tetrahedral fullerenes and to define its Δm index.

Tetrahedral mini- and midi-fullerenes

2. The simplest known tetrahedral fullerenes

Folding and growth by adding dimers. We begin with cluster CC_3 as one of the germs of future carbon structures. The possible ways of its formation are considered in Ref. [4]. If the further growth is suppressed, the cluster is compelled to fold creating a tetrahedron, the energy being depended on its electronic structure (Fig. 1). If the growth is possible, there are different ways of growing. In particular, the cluster can transform into a cupola adding carbon dimers (Fig. 2). In a similar manner, one may imagine the growth of cluster C_3 . The process is shown in Fig. 3. Here we have threefold cluster and threefold cupola C_{12} , and tetrahedral fullerene C_{12} .



Fig. 1. Folding CC₃ cluster into tetrahedra; energy in kJ/mol. Dark-red balls are reacting atoms; other color atoms are neutral ones



Fig. 3. Growth of cluster C₃ and formation of a cupola and a fullerene: some triangle atoms showing three-hold and tetrahedral symmetry are marked with green; energy in kJ/mol

Fusion reactions. The structure of tetrahedral fullerene C_{16} was designed elsewhere [5]. It is a half-truncated cube and can be obtained by adding cluster C_4 to cupola C_{12} (Fig. 4).



Fig. 4. Fusion of cluster C₄ with cupola C₁₂: (*a*) Separate species; (*b*) Intermediate compound; (*c*) Fullerene C₁₆ after relaxation. Red and blue balls are reacting and neutral atoms, respectively; blue solid and dashed lines are old covalent bonds; red solid and dashed lines are

new ones; atoms showing tetrahedral symmetry are marked with green; energy in kJ/mol

The next and last known tetrahedral mini-fullerene is C_{28} . Its structure was suggested in Ref. [6]. The possible way of the realization is shown in Fig. 5. It is a fusion reaction of cupola C_{10} and bowl C_{18} , which can be written in the form $C_{10} + C_{18} \rightarrow (C_{10}C_{18}) \rightarrow C_{28}$.



Fig. 5. Fusion of cupola C_{10} with bowl C_{18} and formation of fullerene C_{28} ; all notations are the same as before; energy in kJ/mol

3. A new tetrahedral midi-fullerene

For completeness sake, it is desirable to add to the simplest fullerenes one more fullerene C_{36} . It can be imagined as a truncated fullerene C_{28} . The situation is similar to that of a tetrahedron and a truncated tetrahedron, C_4 and C_{12} . But how the truncated tetrahedral fullerene C_{36} can be obtained naturally?

Let us consider the structure of fullerene C_{28} . It is seen from Fig. 5 that this fullerene consists of two parts: the bottom part, or bowl C_{18} , having six-fold symmetry and the upper part, or cupola C_{10} , with three-fold symmetry. By analogy, it seems reasonable to take bowl C_{24} and truncated cupola C_{12} as constituents for producing the tetrahedral fullerene C_{36} . The corresponding reaction $C_{12} + C_{24} \rightarrow (C_{12}C_{24}) \rightarrow C_{36}$ is illustrated in Fig. 6. To gain a better understanding of the tetrahedral symmetry, the triangle atoms are specially marked with green.

Tetrahedral mini- and midi-fullerenes



Fig. 6. Fusion of cupola C_{12} with bowl C_{24} : separate species (*a*); intermediate compound (*b*); fullerene C_{36} after relaxation (*c*); old covalent bonds to be destroyed are blew dotted lines, other notations are the same as before

4. Graph representation

Consider the graphs which characterize the formation of the tetrahedral mini-fullerenes. We have five fullerenes: C_4 , C_{12} , C_{16} , C_{28} , and C_{36} . Their graphs are shown in Figs. 7 and 8.



Fig. 7. Graphs of mini-fullerenes C_4 , C_{12} and C_{16} : light-turquoise ball are simple vertices (one-atomic); grey circles are big-size vertices (atom clusters); symbols and numbers inside the circles indicate the number of atoms in a cluster as well as the number of single (brown color) and double (blue color) bonds



Fig. 8. Graphs of mini-fullerene C_{28} and midi-fullerene C_{36} : light-turquoise ball are simple vertices (one-atomic); grey and green circles are big-size vertices (atom clusters); other notations are the same as before

Here different presentations of the fullerenes are given. The reason is as follows. It would endeavor natural to illustrate the structure of a graph considered with the help of lesser–size graphs having more simple structure. Hence, for tetrahedron C_4 it is a routine

graph, each vertex (zero-size point) corresponding to one carbon atom. For truncated tetrahedron C_{12} we used the innovation to the graph theory developed in Ref. [4]. Here each vertex (big-size point) agrees to a cluster of three atoms. In this case we obtain a graph, which is identical to the graph of a simple tetrahedron. It is worth noting that such approach allows do some operations with such graph in the same manner as with a usual graph that simplifies an analysis.

It should be emphasized that in Ref. [4], where the innovation was first presented, a distinction is not made between single and double bonds, so all the edges were identical. Here we use two kinds of edges, single and double, so the graphs presented reflect not only geometry (atomic structure), but also electronic one. It allows gain a more penetrating insight into the fullerene structure, and therefore to study them more elaborately.

For truncated cube C_{16} , we utilize both kinds of vertices, one-atomic and atom-cluster, as well as both kinds of edges, single and double bonds. The left-hand graph coincides with a tetrahedral symmetry; it shows that the structure is composed of two tetrahedra inserted into each other. The right-hand graph reflects a cubic symmetry.

In a similar manner, the graphs are designed for fullerenes C_{28} and C_{36} . From the graphs it follows that their structure is also composed of two tetrahedra inserted into each other.

5. Summary and discussion

We have considered possible ways of forming the simplest tetrahedral fullerenes, namely elementary tetrahedron C_4 , truncated tetrahedron C_{12} , half-truncated cube C_{16} , fullerenes C_{28} and C_{36} . We assume that tetrahedron C_4 could be produced by folding cluster CC_3 under high pressure similar to diamond. It has three different electronic isomers, which differ in number of single and double bonds, and therefore in energy.

The growth of truncated tetrahedron C_{12} is a more complex process. It can be envisaged as a successive increase of cluster CC_3 through appearance of intermediate clusters C_6 , C_8 and C_{10} ; and by folding the final cluster C_{12} . Another way is the appearance of cupola C_{12} and folding it. Since the energies of the cluster and cupola are close to each other, both ways seem probable.

The formation of fullerene C_{16} is designed as the fusion of cluster C_4 with cupola C_{12} . From the graph of this fullerene it follows that its structure is composed of two tetrahedra inserted into each other. It is worth noting that in this case two species, entering into the reaction, conserve its own electronic structure. As a result, we obtain the fullerene, in which electronic and atomic configurations do not coincide, and we have so called hidden symmetry. This situation is thoroughly analyzed in Ref. [2].

Fullerene C_{28} was suggested by Nobel Prize winner H.W. Kroto [6] as one of fullerenes having magic number of enhanced stability. He is also thoroughly discussed its possible electronic structure. To his mind, "the stability depends on the ability of spare electrons on the four carbon atoms at the centers of the four ten-atom configurations of adjoined pentagons to stabilize by configuration". These four electrons are the nearest neighbors of an atom marked with green in Fig. 5. We have obtained fullerene C_{28} using the fusion reaction $C_{10} + C_{18} \rightarrow (C_{10}C_{18}) \rightarrow C_{28}$. It has the energy 749 kJ/mol. It is not the only one way of generation. In other study, where we modeled the formation of fullerene C_{28} similar to the growth and folding of cupola C_{12} , the electronic structure of some of such four carbon atoms was changed. As a result, we have obtained 1399 kJ/mol and a less distorted structure, more close to a sphere.

Fullerene C_{36} is a truncated fullerene C_{28} . It was imagined at first by analogy with truncated-tetrahedron fullerene C_{12} and only afterwards a possible fusion reaction was found.

Analogy with ionic crystals. From the geometry standpoint, fullerenes C_4 and C_{12} are simple tetrahedra. Beginning with fullerene C_{16} , they are composed of two tetrahedra inserted

into each other. In nature there are alkali-haloid compounds (ionic crystals A_1B_7), which crystallize in f.c.c. structure, which is called the structure of NaCl type. However, in this structure it is possible to isolate a primitive cube of two tetrahedra inserted into each other, each tetrahedron having the atoms of only one kind (Fig. 9). The plane graph of such cube is shown in Fig. 10.



Fig. 9. Tetrahedra of NaCl type structure



Fig. 10. Plane graph of a primitive cube in the NaCl structure

By analogy, we can imagine "mathematical" compound, which forms a topological cube of two tetrahedra inserted into each other, and construct graphs for it. In this case, instead of atoms one has clusters of two kinds. Strictly speaking, we have already considered this possibility for the simplest fullerene C_{16} , having two tetrahedra (Fig. 7, C_{16} b). For this fullerene two plane graphs, shown in Fig. 7, are isomorphic. In ionic crystals A_1B_7 (alkalihaloid compounds), the inferior index denotes the number of valence electrons, which are able to take part in reactions. By analogy, for our mathematical compound, fullerene C_{16} , we can write the 'chemical' formula in the form A_1B_3 . However, here the inferior index denotes the number of atoms in each tetrahedron interacting with atoms of another tetrahedron. For example, the tetrahedral fullerenes studied in this research, C_{28} and C_{36} ; have the formulas A_1B_6 and A_3B_6 , respectively. Combined with the graph analysis, one can obtain a clear knowledge of the tetrahedral fullerene structure.

We can extend this model to a broad spectrum of tetrahedral fullerenes. Consider, for example, tetrahedral fullerenes C_{64} and C_{76} , their structure being given in Ref. [1]. Fullerene C_{64} contains 12 squares, 10 hexagons and 12 heptagons. Each face of the structure is formed by 3 adjoined heptagons, which are surrounded by 6 squares and 6 hexagons. Fullerene C_{76} contains 24 pentagons, 4 hexagons and 12 heptagons. Each face of the structure is formed by one hexagon, surrounded by 3 pentagons and 3 heptagons. Such description gives detail, but does not allow find correlation between the fullerenes.

We have designed the graphs for these fullerenes by analogy with that of fullerene C_{36} . They are presented in Fig. 11. Since we do know the history of fullerene designing, there is no distinction between chemical single and double bonds. This problem is beyond the scope of geometry. It is necessary to do some elucidation of the symbols used. The correspondence between graph symbols and atomic structure is shown in Fig. 12.



Fig. 11. Graphs of midi-fullerenes $C_{64} \mbox{ and } C_{76}$



Fig. 12. Graph symbols and their relation to atomic structure

From this figure it follows that only outer atoms of atom clusters take part in the interaction with other atom clusters. In other words, the big-size vertices of graphs, characterizing the structure of fullerenes C_{64} and C_{76} , are more complex than those of fullerene C_{36} . To emphasize this fact, we have changed the chemical formulas of these fullerenes, and write them as $A_3(C_1)B_6(C_6)$ and $A_3(C_1)B_9(C_6)$. Here the additional symbol C refers to inner, passive core atoms. It must be also emphasized that double lines in the graph for fullerene C_{76} do not refer to double chemical bonds. As we mentioned above, we do not know the electronic structure of this fullerene. These lines only show that apices 9(6) are connected between themselves by two edges.

Search for periodicity. The aim of our study is to find the mass difference Δm -index for tetrahedral fullerenes with the purpose to incorporate this fullerene group into the periodic system of fullerenes. Now we have the following information:

Fullerenes	Chemical formula	Number of atoms
C_4	A1	4∘1=4
C ₁₂	B_3	4.3=12
C ₁₆	A_1B_3	4°(1+3)=16
C_{28}	A_1B_6	4°(1+6)=28
C ₃₆	A_3B_6	4°(3+6)=36
C_{64}	$A_3(C_1)B_6(C_6)$	4°[(3+1)+(6+6)]=64
C ₇₆	$A_3(C_1)B_9(C_6)$	4°[(3+1)+(9+6)]=76

This allows do some predictions.

The mass difference for these fullerenes can be written as $\Delta m = 8, 4, 12, 8, 28, 12$. It is clear that the gap between fullerenes C_{36} and C_{64} is too large. However it can be decreased by the following way. Let us change in formula A_3B_6 for fullerene C_{36} component A_3 to component $A_3(C_1)$. Then we obtain fullerene C_{40} , in which instead of 12 hexagons there will be 12 heptagons. In a similar way, changing component $A_3(C_1)$ in formula $A_3(C_1)B_6(C_6)$ for fullerene C_{64} with component A_3 creates fullerene C_{60} . As a result, we have now the following data series: $\Delta m = 8, 4, 12, 8, 4, 20, 4, 12$. Although the gap became less, it is nevertheless is again large. Probably it is worth to search after fullerene C_{48} or C_{52} , or both.

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EFFECT OF ANODIC VOLTAGE ON PARAMETERS OF POROUS ALUMINA FORMED IN SULFURIC ACID ELECTROLYTES X. Huang¹, W. Su¹, L. Sun¹, J. Liu¹, D.A. Sasinovich², O.V. Kupreeva², D.A. Tsirkunov², G.G. Rabatuev², S.K. Lazarouk^{2*}

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Abstract. Local porous aluminum anodizing with a photolithography mask has been carried out at anodic voltages varying from 15 to 200 V in sulfuric acid electrolytes. Record anodic voltages at room temperature have been achieved leading to new parameters of porous alumina such as interpore distance up to 320 nm, forming cell factor up to 1.2 nm/V, thickness expansion factor up to 3.5, porosity up to 1%, sulfur concentration up to 7.7 at.%. A central angle of porous alumina cells has been measured in concave points as well as in peak points of porous alumina cells at the border with aluminum. The measurements have shown that central angles can reach 90° at anodic voltages larger than 100 V. The electric field distribution in porous alumina cells has been simulated for different central angles. It is found that the electric field reaches 2.7×10^{10} V/m in the layers with a porosity of 1% in growing alumina.

Keywords: combustion, explosion, mechanical pulse, microthruster, multichip structure, nanoporous silicon

1. Introduction

Porous aluminum anodizing provides formation of hexagonal alumina cells with pores in their centers. Porous alumina attracts much attention because of its self-ordered hexagonal structure with cell sizes depending on anodic voltage [1]. Self-ordering of alumina hexagonal cells during anodizing is considerably improved at high forming voltages [2]. Such an electrochemical process was called the high field anodizing and provided the fabrication of ordered porous alumina with tubular structures [3,4]. Porous alumina structure parameters include interpore distance, pore diameter, film thickness, volume (thickness) expansion factor and the central angle of the barrier layer in alumina hexagonal cells. Unfortunately, only a few papers are devoted to the investigation of the central angle [5,6]. Usually, central angle measurements have been performed between the center and concave point at the cell border. Angle measurements between a center and a point of the aluminum peak have not been made yet.

In this paper, the high voltage aluminum anodizing in sulfuric acid electrolytes is analyzed. The porous alumina parameters obtained at different anodic voltages up to 200 V have been studied. The special attention has been paid to studying the central angle in porous alumina hexagonal cells. The central angle has been measured in concave points as well as in peak points of porous alumina cells formed in a wide range of anodic voltages. The influence of the peak central angle on electric field distribution in porous alumina nanocells is discussed.

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2. Experimental

Aluminum foil (purity 99.9%) with the thickness of 100 μ m and 1.0 μ m thick aluminum films deposited on silicon wafers were used as initial samples. A 0.2 μ m niobium film was deposited on the aluminum surface to form a mask. Then the niobium mask was configurated by standard photolithography operations and plasma-chemical etching in SF₆ gas. Porous aluminum anodizing was carried out in 0.2 M - 6.3 M H₂SO₄ aqueous solutions at room temperature. The anodizing voltage was linearly increased from 0 to 15200 V with a rate of 10 V/s.

The thickness expansion factor of the anodic oxide was calculated from the metal and oxide thickness measurements. The structure parameters of the anodic films were analyzed by a scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The film porosity was estimated by using SEM and TEM measurements of the pore diameters and the interpore distances. Atomic composition of the samples was studied by Energy Dispersive X-Ray (EDX) analysis.

The electric field distribution has been calculated based on porous alumina cell structure parameters and anodic voltage used during anodizing process. The Comsol Multiphysics program complex has been used to solve Poisson's equation for a given configuration [5,7].

3. Results and discussion

Figure 1 shows a schematic view of aluminum porous anodizing with a photolithography mask indicating possible ways for Joule heat to disperse. It is evident that aluminum anodizing with a mask provides additional ways to heat dissipation. The heat sink through aluminum tracks and a niobium mask prevents overheating in the alumina barrier layer. This approach allows reaching the maximum forming voltage of 200 V for sulfuric electrolytes, whereas an ordinary full-area anodizing process can be carried out at the maximum forming voltage of about 70 V [2].



Fig. 1. The schematic view of heat sinks during porous aluminum anodizing with a photolithography fabricated mask

Porous alumina films include close-packed hexagonal alumina cells where each cell consists of a hexagonal prism with a cylindrical pore at the center and a barrier layer at the boundary with metallic surface (Fig. 2 a). The barrier layer is the space between the lower

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base of hexagonal prism and a spherical surface at the border with aluminum. Such configuration provides the presence of peak points and concaves at the aluminum surface (Fig. 2 b, c). The barrier layer structure in porous alumina nanocells is characterized by the following parameters: interpore distance (*L*), pore diameter (*d*) and central angle (θ) (Fig. 2 a). The central angle is an angle which apex (vertex) is the center of a circle and whose legs are radii intersecting the circle in two distinct points. The first point is the center of spherical surface in the alumina cell. The second point can be chosen in metal peak points as well as in concave points (Fig. 2 b, c). Obviously, the peak central angle is larger with respect to concave one for the same hexagonal alumina cell. The simple calculation shows that the difference between peak and concave central angles can reach 50%. Therefore, the central angles for porous alumina cells should be specified as θ_{peak} and as $\theta_{concave}$.



Fig. 2. Schematic view of porous alumina nanocells: *a*) cross-sectional view with the specified structure parameters; *b*) general view of porous alumina nanocell with the specified central angle in the peak point, *c*) general view of the spherical aluminum surface with a peak point and a concave point marked

Figure 3 shows SEM cross-section images of porous alumina formed at different anodic voltages in the range from 15 V up to 200 V. Porous alumina formed at 15 V has a "honey comb" structure and its cross section passes through pore centers (Fig. 3 a). The anodic films formed at 30 V and higher have a tubular structure and their cross sections pass through tube borders (Fig. 3 b-d). Further increase of anodic voltage is limited due to appearing local breakdown effects.

It results in microplasma glow visualized by optical microscopy (Fig. 4 a, inset). Microplasma causes inhomogeneity of porous alumina structure (Fig. 3 d). Figure 4 shows structure parameters of porous alumina *vs* anodic voltage. Its growth leads to increasing the distance between pore centers (interpore distance) up to 300 nm in the 6.3 M H₂SO₄ electrolyte (Fig. 4 a). The higher interpore distance for anodic films formed in 6.3 M H₂SO₄ electrolyte can be explained by lower electrolyte resistivity with respect to the 0.2 M H₂SO₄ electrolyte [8]. Formation cell factor (ratio between interpore distance and anodic voltage) decreases from 2.5 nm/V at $U_a = 20$ V to 1.2 nm/V at $U_a = 200$ V for the 0.2 M H₂SO₄ electrolyte. Thickness expansion factor increases up to 3.5 whereas porosity decreases to 1% with the anodic voltage growth.

EDX analysis has shown that the oxygen and aluminum concentration ratio is 1.4 for porous alumina formed at low anodic voltages while the same parameter is 3.5 for anodic films formed at 140 V. Besides the sulfur concentration increases from 1 up to 7.7 at.% with the anodic voltage growth. It means that porous alumina films formed at low anodic voltages consist of stoichiometric Al_2O_3 while anodic films formed at high anodic voltages consist of $Al(OH)_3 + Al_2O_3 + (SO_4)^2$ -anion complexes as it was proposed in Ref. [3]. The thickness expansion factor data validate this assumption because the value of 3.5 corresponds to $Al \rightarrow Al(OH)_3$.


Fig. 3. SEM and TEM cross-section images of porous alumina formed at different anodic voltages: (a) 15, (b) 30, (c) 70, (d) 200 V



Fig. 4. Porous alumina structure parameters *vs* anodic voltage: a) interpore distance in porous alumina formed in different sulfuric acid electrolytes (photo of microplasmas at anodic voltage 200 V is shown in inset); b - thickness expansion factor and porosity

SEM images of porous alumina and aluminum surface are illustrated in Figure 5 a, b. Alumina tubes with a semispherical barrier layer are in the upper part of the photo (Fig. 5 a). Concave central angles were measured in spherical parts of porous alumina cells similar to the method in Refs. [5,6]. Peak central angles were measured on the aluminum surface relief (bottom part of the photo). As can be seen in SEM images (Fig. 5 a, b), peak central angles exceed concave central angles. The aluminum peaks have sharp forms. Their curvature radius is less than a few nanometers.

Figure 5 c exhibits peak central angles and concave central angles *vs* anodic voltage. The difference between the peak and concave angles is small for porous alumina formed at low anodic voltages. The central angles are increased with the anodic voltage growth. 66 X. Huang, W. Su, L. Sun, J. Liu, D.A. Sasinovich, O.V. Kupreeva, D.A. Tsirkunov, G.G. Rabatuev, S.K. Lazarouk

The average peak central angles reached 90 deg whereas the average concave angles attained 60 deg for high anodic voltages.

Figure 6 presents the calculated electric field distribution in the porous alumina nanocells with different central angles. The cells have been formed at $U_a=140$ V. The maximum field strength appears at the pore bottom and near the aluminum peaks. With increasing the center angle, the electric field enhances.



Fig. 5. SEM images of porous alumina and aluminum surface relief formed at different anodic voltages (a) 70, (b) 100 V; central angles *vs* anodic voltage (c)



Fig. 6. Electric field distribution in porous alumina cells with different peak central angles:
 (a) 60, (b) 75 deg. The cells have been formed at U_a=140 V. The lighter areas correspond to the higher electric field strength

The maximum electric field strength surpasses 10^{10} V/m. This value is close to the interatomic electric field of 10^{11} V/m. Such high electric fields can result in impact ionization of aluminum atoms with creation of Al^{3+} - ions near the aluminum peaks. The similar impact ionization of oxygen atoms can occur near the pore bottoms. Thus, we propose that high field nanoplasma regions inside the porous alumina barrier layer are present during the high voltage anodizing process. These nanoplasma regions supply anodizing process with Al^{3+} and O^{2-} ions resulting in appearance of self-organized hexagonal structure and the record anodizing growth rate up to 1 µm/s [4].

Such nanoplasma regions can play the role of self-focusing seeds for pore growth, which ensures the structure self-organization of the growing porous oxide (Fig. 7 a). Note that this phenomenon is analogous to the effect of self-focusing of a light beam in nonlinear optics in an electric field of 10^{10} – 10^{11} V/m.



Fig. 7. SEM images of porous alumina: (a) self-ordered frontal surface formed at $U_a = 70 \text{ V}$, (b) cross section of porous alumina formed by local anodizing at $U_a = 80 \text{ V}$

Another new effect that appears during porous anodizing of aluminum at a high voltage is the anisotropy of anode growth with a masking coating. The anisotropy consists in a noticeable difference between the anodic oxide growth rate in the vertical (V_{vert}) and horizontal (V_{hor}) directions that ensures the minimum lateral shifts during the formation of the pattern specified by a mask (Fig. 7 b). Note that porous anodizing at low voltages is isotropic: the process rate in the horizontal and vertical directions being almost the same [7].

The formation of aluminum interconnections in integrated circuits using porous anodizing of aluminum at a high degree of anisotropy allows using this process for producing VLSI metallization with a submicron element size [9] and opens up new opportunities for the integration of optical and metallic interconnections on silicon chips by planar porous alumina waveguides [10-12]. Another possible application for high field anodizing is to use aluminum surface with high peak central angles for the vertical alignment of liquid crystal materials in display devices [4,13].

Thus, our studies showed that during porous anodizing of aluminum at a high voltage the electric field exceeds 10^{10} V/m in local regions inside oxide that can generate new effects. They include the self-organization of a porous structure, the appearance of nano- and microplasma regions, an anisotropy of porous anodizing. Moreover, other new effects are to be expected during aluminum anodizing under conditions that ensure a high electric field inside the barrier layer of porous oxide.

4. Conclusions

High field porous aluminum anodizing with a photolithographic mask can be carried out in sulfuric acid electrolytes at the highest forming voltage reaching 200 V. It allows obtaining new parameter ranges for the anodic films formed. The central angles of porous alumina can be increased up to 90 deg with the anodic voltage growth. The simulation showed that during anodizing process the electric field strength could exceed 10^{10} V/m in porous alumina nanocells with high central angle values. It allows us to propose the existence of nanoplasma regions near the pore bottom and near aluminum peaks at the border of alumina cells during

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high field porous aluminum anodizing. High field anodizing opens new possibilities for porous alumina nanotechnology applications [14].

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NANOSTRUCTURED COMPOSITE MATERIALS FOR 3D ELEMENTS OF ADVANCED OPTICAL SYSTEMS

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Abstract. Nanocomposite materials electroplating for nano- and micro-fabrication with Si mold and LIGA-like technological process is proposed. UV lithography based on SU-8 photoresist for ultra-thick 3D structures is described. Two-stage process for high aspect ratio vertical metal structures fabrication is considered. Possible applications of the proposed technological approaches for advanced optical systems are described.

Keywords: nanocomposite electroplating, nanostructured material, optical system, photoresist

1. Introduction

Formation of various micro- and nanostructures plays an important role in the modern display and optical devices such as LCD, OLED-, PLED-displays, etc. Functional structures' pattering is achieved through the use of up-to-date technologies, which allow obtaining a light control systems [1]. Modern industry requires using high-end technologies, such as roll-to-roll (R2R) nanoimprint processing, 3D printing; application for optical elements manufacturing being profitable due to its high throughput, 3D shaping and low cost of production [2,3]. Application of nanocomposite materials with good wear resistance, high microhardness and good anti-sticking surface properties could improve lifetime of molds and heads, and reduce imperfection of these modern high accurate technologies. Application of high-grade coating with complex nanoscale geometry can improve electrical, optical characteristics and thus device performance of multiple optical systems.

Micro- and nano-electromechanical systems (MEMS and NEMS) and microoptoelectromechanical systems (MOEMS) are the most promising state-of-the-art devices. Mechanical interaction between nano-, micro-, and macro-world is the limiting factor for such complex systems. Moreover, reliability of the whole systems is determined by the reliability of the mechanical part. The use of nanocomposite materials is the most promising method to solve the reliability issue [4-7].

In the context of the problem, the integration of nanocomposite materials electroplating with deep UV lithography based on SU-8 photoresist is proposed as a method of the solution.

2. UV lithography of SU-8 photoresist

To fabricate micromoulds in LIGA-like technology (Fig. 1), we use photoresists SU-8 2150 and SU-8 3050 on various substrates (glass, ceramic, metal, ITO, etc.). To remove all organic contaminants from the substrates, chemical cleaning and UV treatment were used. Chemical cleaning was carried out in peroxysulphuric acid, which is a mixture of a 25% hydrogen peroxide and 98% sulfuric acid in a one-to-two ratio. The more feasible method is

UV treatment with the use of Photo Surface Processor PL16-110D. The cleansing process consists of three steps. The first is ozone generation from atmospheric oxygen at a wavelength of 184.9 nm. The second step is ozonolysis, when atomic oxygen is generated at a wavelength of 253.7 nm. The final step is decomposition of organic pollutants. Atomic oxygen has a strong oxidative activity which helps it to react with pollutants and to form reaction products. These products, such as water, carbon dioxide, etc., then are simply evaporated. Thin Omnicoat sublayer and thick photoresist layer was spincoated in two-stage mode by VTC-100 Spin Coater (MTI Corporation, USA). The dependence of coating thickness on rotational velocity, time, and temperature were determined.



Fig. 1. LIGA-like technological process

One of the most important processes during the fabrication of thick micromoulds is soft baking. It provides evaporation of the solvent from the photoresist. The soft backing was conducted on a hot plate Wise Stir MSH-D (Labortechnik, Germany). Exposure of the SU-8 photoresist was performed by the contact lithography through a mask in the 365 nm wavelength. UV-LED module Lightningcure LC-L2 (Hamamatsu, Japan) was used as a light source. To expose photoresist layers with the thickness of 100-250 µm, the exposure energy was 250-300 mJ/cm². The post exposure backing (PEB) was carried out right away the exposure. During PEB the radiation absorption by an initiator occurs. It leads to local photochemical reactions that provide polymer crosslinking. The crosslinked regions are insoluble in the subsequent development process and uncured polymer removing.

To avoid spreading the structures because of melting and also to reduce mechanical stresses, the following temperature mode was selected. The substrate was placed on a hotplate preheated to 65°C for 5 min, was heated to 95°C at 15°C/min and then was stood at 95°C for 15 min.

To remove the unpolymerized parts of photoresist, the organic SU-8 Developer (Microchem Corp, USA) was used. After further hard backing at 150°C, the micromoulds become chemically and mechanically resistant. Farther nanocomposite coatings, containing ultra-fine particles, were electroplated into SU-8 or Si molds. Soft magnetic alloys such as Ni, Co, Cu, NiFe, CoP were codeposited. The concentration of ultra-fine particles was varied

This procedure allows getting the micromolds with a thickness from 50 to 250 μ m and minimum feature size of 1 μ m for optical elements processing.

3. Nanofabrication for structures and interconnections of integrated optical devices

A promising way in the development of modern optical systems is the use of electron field emitters to improve their basic characteristics. Thus, the use of such emitters allows produce the displays with a high surface homogeneity and temporal stability; lighting lamps with an enhanced conversion factor of the embedded energy; portable X-ray sources with a high-scale temporal and spatial resolution; amplifiers of microwave radiation for satellite communication systems with reduced mass-dimensions characteristics [8]. High aspect ratio vertical structures with low specific resistivity should be obtained for effective field emission cathodes. This provides electrical conductivity between the conductive substrate and the array of emitting elements.

Metal conductive and catalytic channels were formed in insulating blind holes in 2 μ m thick silicon oxide. The diameter of the holes is 0.35-3.5 μ m, the pitch is 0.5-7 μ m, and the matrix contains 20,000 to 750,000 contacts. The holes were filled with copper and nickel through vacuum technologies, electroplating and integrated processes. Such processes provide catalytic activity and compatibility with the integrated technological process.

High-grade and precise coating of the complex patterns is a serious problem in polarizers, functional optical layers, optical retarders and other optical elements with irregular shape. Addressing this issue metallic materials and alloys based on nickel (Fig. 2), cobalt (Fig. 3) and copper (Fig. 4) were electroplated in trenches.



Fig. 2. Nickel-based coating



Fig. 3. Cobalt based coating with 170 nm wide patterns in Si wafer

Typical defects like voids, seams and reasonably coarse surface were not observed in the deposited coatings. The use of such coatings for optical systems interconnections reduces their return loss.

High aspect ratio vertical metal structures were obtained in two stages. At first, a layer with a high conductivity of 50 Å to 300 Å thicknesses was formed. On the second stage, electrochemical deposition was carried out using two technological regimes: potentiostatic and galvanostatic. The influence of hydrodynamic conditions on the filling of structures was investigated. It was determined that the filling quality is significantly improved by varying

from static to laminar and, further, to turbulent regime. The samples were studied by optical and SEM microscopy. EDX analysis was performed to establish the chemical composition.



Fig. 4. Copper-based coating

4. Nanocomposites for reliable micro-optoelectromechanical components

Composite coatings for MEMS and MOEMS applications based on nickel and cobalt were electroplated with inert nanoparticles of ultradispersed diamond (UDD), alumina, aluminium monohydrate, boron nitride. The size of the dispersed phase varied from 7 to 50 nanometers. The nanoparticles were incorporated into the metal matrix (Fig. 5).



Fig. 5. Cross-section SEM (a) and AFM surface image (b) of nickel nanocomposite coating

The influence of nanoparticles concentration in the electrolyte (0-10 g/l), pH of the electrolyte and current density on the nanocomposite coating were studied. According to the behavior of dispersed phase in the electrolysis, a model for the joint electrolytic deposition of magnetic alloys and dispersed particles in a 3D matrix has been developed. In comparison with homogeneous coatings, nanocomposite coatings showed improved mechanical properties: The microhardness was increased by 20-80 %, the wear resistance was increased in 4 times, the friction coefficient was reduced in 2 times. Nanocomposite materials with such mechanical properties will improve the reliability of moving parts and the whole system of such MEMS and MOEMS as moving micromirrors, optical shutters, MOEMS-actuators, *etc.*

5. Conclusion

There are described positive prospects of nanocomposites and nanostructured electroplating introduced in modern technologies. Application in NEMS, MEMS, SOFC, ULSI, roll-to-roll, nanoimprint and other advanced systems and technologies makes it possible to improve quality and reliability of final products and enables their industrial development.

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MORPHOLOGY INVESTIGATION OF NANOPOROUS ANODIC ALUMINA FILMS WITH IMAGE ANALYSIS

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Abstract. Aluminum films approximately 100 nm thick were deposited on silicon substrates (SiO_2 / Si) by thermal evaporation in a vacuum. Porous anodic alumina films were obtained in a potentiostatic mode at 20 V in 0.3 M aqueous solution of oxalic acid and 1.8 M aqueous solution of sulfuric acid. The main pore diameter was determined using the ImageJ software from SEM images. An algorithm determining the pore diameter in porous anodic alumina films was developed. In the nanoporous alumina films formed in sulfuric acid at 20 V the average pore diameter was 12.3 \pm 0.1 nm. In the case of the oxalic acid electrolyte, the nanoporous alumina films formed at 20 V had an average pore diameter of 14.8 \pm 0.1 nm. The obtained results are in a good agreement with the literature.

Keywords: anodic alumina, pore diameter, SEM image, surface morphology

1. Introduction

Porous anodic aluminum oxide (AOA) is of great interest because of its unique properties, primarily, such as a highly ordered porous structure, nanosized pores, and the ability to control structural parameters at the stage of their formation using aluminum anodizing [1,2]. High mechanical hardness, thermal and chemical resistance allows using anodic alumina for chemical and biochemical separation (filtration), as well as for the synthesis of various nanomaterials, such as nanowires and nanotubes. For expanding the application areas of anodic alumina films and increasing the reproducibility of their properties, it is necessary to know the nanostructure obtained in various modes of aluminum anodizing. It is well known that the basic properties of anodic aluminum oxide depend on the pore diameter, so there is a need for precise regulation of their geometric dimensions during its formation. In this regard, it is important to apply statistical analysis methods to process large arrays of nanosized pores and to develop a methodology and algorithm for studying the surface morphology and nanoporous structure of anodic films [3,4].

2. Experimental

The aluminum films approximately 100 nm thick were deposited on silicon substrates (SiO_2/Si) by thermal evaporation in a vacuum. Then the square samples of 4 cm² were cut out and anodized in a potentiostatic mode at 20 V in an aqueous solution of 0.3 M oxalic acid and 1.8 M aqueous solution of sulfuric acid. The anodizing area of aluminum (about 0.22 cm²) was set with Viton-o-ring. The aluminum anodizing process was carried out in a twoelectrode fluoroplastic cell at a constant temperature of 18°C using the thermostat F 12 (Julabo). As DC power source, PS-2403D (Voltcraft) was used. The cathode was a platinum grid. The electrolyte during anodizing was vigorously stirred using a mechanical stirrer. The main pore diameter was calculated from the SEM images using the ImageJ software.

3. Results and discussion

For processing SEM images of the nanoporous anodic alumina surfaces, the ImageJ software was used. The program includes all the necessary functions for digital image processing: correction of brightness and contrast, selection of image limits, high-frequency and low-frequency filtering, etc. The following algorithm in the ImageJ program (Fig. 1) consists of:

1) Transforming the image into 8 bits to improve the contrast and simplify the subsequent analysis.

2) Filtering the image to eliminate random noise (which forms small porous structures and unnecessary pore bonds).

3) Preliminary segmentation to isolate homogeneous regions.

4) Finding the threshold value for image segmentation (separation into foreground and background). Segmenting the image based on this threshold value that allows fully define the object.

5) Analysis of the selected objects.



Fig.1. Processing SEM images using ImageJ software: a) original SEM image, b) contrast enhanced image, c) threshold image, d) final image

The ImageJ software allows calculate the areas and statistical values of the pixel values of various areas selected manually or by means of threshold functions on the images. It supports standard image processing functions, such as logical and arithmetic operations between images, contrast manipulation, convolution, Fourier analysis, sharpening, smoothing, border detection. The program also allows perform various geometric transformations, scaling, rotation and reflection. The ultimate task of image analysis is statistical processing the data obtained at measuring characteristics of an object having a porous structure, i.e. determining the average value of pore diameters and plotting graphs to visualize the analysis process. The main pore diameter (d_{pore}) was determined from the surface images of porous anodic aluminum oxide obtained by SEM, the pore size distribution curves being approximated with the Gaussian functions. It was assumed, as in Ref. [5], that the initial pore size distribution contained both initial small-diameter pores and major pores of a larger diameter. To obtain correct results, the SEM images were processed at least ten times and a new time was selected each time for comparison. Since only the data on the main pores are of practical importance, and the presence of the initial pores interferes with the analysis, some of the pores with a small diameter were not taken into account at activities of approximating. At this, only one smaller value was left to the maximum on the pore size distribution curve. The maximum on the Gaussian curve corresponds to d_{pore} .

We have found that $d_{pore} = 12.3 \pm 0.1$ nm for porous alumina films obtained in sulfuric acid (Fig. 2b) and $d_{pore} = 14.8 \pm 0.1$ nm for the anodic alumina films obtained in oxalic acid (Fig. 3b). The structure parameters of the porous alumina films obtained coincide with the data reported in Ref. [6].



Fig. 2. Porous alumina films obtained in 1.8 M aqueous solution of sulfuric acid: (a) SEM image of surface; (b) results of processing image with ImageJ software



Fig. 3. Porous alumina films obtained in 0.3 M aqueous solution of oxalic acid: (a) SEM image of surface; (b) results of processing image with the ImageJ software

4. Conclusions

Methods of modern software image processing have a full set of functions necessary to obtain information about the surface morphology of nanoporous films. However, the general picture after processing images contains also side shapes that arise from surface defects and scratches that make analysis difficult. Therefore, for processing images of nanoporous structures, algorithms that take into account the patterns of growth of the nanoporous films are necessary. Using the regularities of anodic oxide film growth at the analysis of histograms showing the distribution of pores over the diameter, it is possible to identify the region that relates to the oxide growth and to determine the pore diameter of nanoporous structures.

Porous alumina films obtained in sulfuric and oxalic acids at 20 V have $d_{pore} = 12.3 \pm 0.1$ nm and $d_{pore} = 14.8 \pm 0.1$ nm respectively.

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PHYSICAL AND INFORMATION PARAMETERS OF NANOSCALE ELECTRONIC ELEMENTS AS A PART OF COMPUTING SYSTEMS WITH NEURAL NETWORK ARCHITECTURE

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Abstract. Problem of ensuring specified reliability indices when designing computation components of the telecommunication systems built via use of a nanoscale electronic element base is considered. Computer models of the computation components with neural network architecture and integrated nanoscale titanium oxide-based memristors and nanoscale graphene-based field-effect transistors are studied. Correlation between the physical and information parameters, integrated into the system of nanoscale electronic elements, as well as an impact of parameter variation on the system reliability, has been investigated. **Keywords:** computing system, graphene, nanoscale, neural network, transistor

1. Introduction

Nowadays conceptually new opportunities for building high-performance computing systems appear at the confluence of nanoscale technologies and neural network technologies [1]. The reason for this is that the system acquires some extra opportunities due to a combination of parallel information processing and nanoscale electronic element base [2,3]. However, as a rule, the application of nanoscale electronic elements reduces system reliability indices which should be established at the design engineering stage and which are not achieved automatically [4]. The reliability indices of such systems are characterized by their operation accuracy. As for the elements of computing systems, they should be studied as uniform physical and information objects. Consequently, the operation accuracy of the systems under study represents the degree of conformity of the real physical and information parameters in question to the theoretical (nominal) parameters of the system electronic elements.

The aim of this study is to define a correlation between the physical and information parameters of the nanoscale electronic elements integrated into a computing system and to define the impact of parameter variation on the system reliability indices.

2. Methods

A computer model of the artificial neural network (ANN), built in the MATLAB environment, has been investigated. The model has been trained to make an approximation of a differential equation with maximum precision. Using nanoscale electronic elements as the research object is an essential part of the experiment. In particular, the research involves models of the nanoscale titanium oxide-based memristors as synaptic connections (synapses) between the layers of neurons and the nanoscale field-effect graphene-based transistors which control signals inside the system [5,6]. The structure of nanoscale titanium oxide-based memristor being modeled is shown in Figure 1.



Fig. 1. Nanoscale titanium oxide-based memristor Simscape/MATLAB model of a memristor

Several models of nanoscale titanium oxide-based memristors have been developed on the basis of the stated-above mathematical model in the Simscape environment, which is used to simulate physical systems integrated into the MATLAB mathematical computation toolkit. An example of such a model is shown in Figure 2.

Figure 3 demonstrates a neuron synapse model based on memristor in Simscape/MATLAB. A synapse is an element that performs a weighed signal transfer (1) from the neuron of one layer to the neuron of the next layer within an ANN. $f(x) = w \cdot x$, (1)

where f(x) is the neuron input, w is the synapse weight, x is the output of a previous neuron.

Besides, the field-effect graphene-based transistor has been selected as one of the nanoscale electronic elements integrated into a computation system. Such field-effect transistors function as the control matrix elements inside a computation system under development. A mathematical model of the nanoscale graphene-based transistor has been formulated on the basis of the theory developed in Refs. [7,8]. The operating principal of such a device is based on the effect of electric field that changes the charge carrier concentration (carrier density) in graphene.



Fig. 2. Simscape/MATLAB model of memristor



Fig. 3. Neuron synapse model based on memristor in Simscape/MATLAB

Using the gate voltage, one can control the graphene conductivity which is approximately proportional to the concentration. The structure of graphene-based nanoscale transistor being modeled is shown in Fig. 4. Such a transistor consists of a semiconducting channel separated from the metal gate by a graphene layer. The areas designated in Fig. 4 by "Source" and "Drain" are contact pads that have high conductivity. The channel resistance determines current I flowing from the source to the drain when voltage V_{Drain} is applied between them. Gate voltage V_{Gate} is used for controlling the electron density in the channel and consequently its conductivity. Typically, earthed source schemes are used, therefore $V_{Source}=0$.

Several models of nanoscale graphene-based transistors have been developed on the basis of the mathematical model [9] in the Simscape environment, which is used to simulate physical systems and which is part of the MATLAB mathematical computation toolkit. An example of such a model is shown in Fig. 5.



Fig. 4. View of field-effect graphene-based nanoscale transistor



Fig. 5. Control element model based on field-effect transistor in Simscape/MATLAB

The desired values of the major parameters of the modeled nanoscale elements have matched the values obtained in the developed models. Therefore, it can be concluded that the models have been built correctly. A two-phase methodology has been used within the scope of the experimental research into the physical parameters of memristors. In the first phase it is intended to formulate and apply some possible mechanisms for impacting various properties of the nanoscale objects under study, capable of triggering the system reaction in the form of parameter variation. The second phase is needed to define qualitative and quantitative dependences between the variation of the system-element parameters and its element properties predetermining such variation.

Analyzing the memristor physical parameters, based on the proposed approach, come down to a few procedures:

- Synthesizing computer models of the memristors meeting the specified requirements.
- Developing a computation system in the form of ANN to define the indices of information conversion accuracy when the information state of the system elements has been varied.
- Modeling various impacts on the geometrical parameters of the memristors functioning as synaptic connections in the ANN.
- Measuring the system technical indices and forming statistical data on the element parameter variations at different levels of the factor impacting the memristor geometrical parameters.
- Analytical estimation and defining the target dependence of the system operation variation and element-parameter variation caused by the impact on their properties.

A few geometrical parameters of the memristor have been brought out: top contact surface, lower contact surface and a dielectric-layer thickness. The memristors have been exposed to factor variation at different levels. Each time the memristor properties varied, the variations of information parameters were registered. What is more, the ANN operation with the information parameter variations of the synapses was emulated. The overall research results are demonstrated in Tables 1 and 2 [10]. These dependences make it possible to obtain the tolerance limits of element parameter variation and to help define the mechanisms influencing the element physical properties with the purpose of optimizing the system technical indices. The methodology aimed to study the information parameters of memristors replicates the one used before [10, Table 3].

3. Conclusions

We investigated a correlation between the physical and information parameters integrated into a computation system of nanoscale electronic elements; the effect of parameter variation on the system reliability being defined. The results obtained demonstrate that the physical processes in the nanoscale elements, which carry information in a neural network computation system, define the reliability index of this system, since geometrical parameters impact information parameters and so define the system operation accuracy.

The undertaken study serves as a practical basis for solving the problem of tolerance limits for physical and information parameters of nanoscale electronic elements. It ensures the operation accuracy of designed neural network computation components of telecommunication systems.

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USE OF X-RAY ANALYSIS FOR CONDUCTING INPUT AND PROCESS CONTROL OF ELECTRONICS MATERIALS

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Abstract. The paper presents examples of using X-ray diffraction and X-ray phase analysis for monitoring and researching materials for electronic equipment.

Keywords: crystal lattice parameter, diffraction line, materials for electronic equipment, phase composition, technological control, X-ray phase analysis

1. Introduction

X-ray structural and X-ray phase analysis allows determining the phase composition and crystallographic modification of analyzed material with the sensitivity of at least 5% of the mass. Analysis of results is based on the use of the ASTM X-ray data base. The phase composition of a sample is defined from the analysis of the diffraction pattern taken in a wide range of angles. To obtain information about the crystallographic structure (composition of the solid solution, the degree of formation of the crystal lattice), a survey is carried out in the region of large diffraction angles, which makes it possible to determine the lattice parameter and the broadening of diffraction lines with the required accuracy. In complex cases, additional information about the chemical composition of the sample is involved [1].

Based on this approach, we have developed a number of techniques for conducting input and current process control of materials for electronic equipment [2].

2. Experimental

Input control. Silver-palladium alloys. Ag-Pd alloys are used as materials for internal electrodes of multilayer ceramic capacitors and varistors [3]. In the process of work, it turned out that for the production technology of the above-mentioned products, information not being stipulated by the alloy specification may be significant. The technique developed allows determining a more wide range of phases that can be present in the alloy, including X-ray amorphous phase, by recording the X-ray pattern of the sample in a wide range of diffraction angles; for example, Ag₂O, PdO, Ag₂S phases. It includes also the determination of crystal lattice parameter that is necessary for defining alloy composition. Silver and palladium form a continuous series of solid solutions [4] for which Vegard's law is fulfilled. This enables the composition to be found from the dependence of crystal lattice parameter of a solid solution on component concentration (Fig. 1),

In addition to the phase composition and the lattice parameter, the half-width of the diffraction lines is fixed that indicates the size of coherent scattering domain of and, thus, the degree of structure formation.

Consider also an alloy with the addition of cladding elements. To determine the concentration of incoming components, a diffraction line is taken in the region of large diffraction angles. Recording and decoding the radiogram (Fig. 2) shows that, in addition to the alloy, there is a cladding element $BaTiO_3$. Since the crystal lattice of the alloy is cubic, it

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is enough to record only one diffraction line. We use diffraction line (422), since no other diffraction lines are superimposed on it. The structure formation is estimated by the separation degree of doublet $\alpha_1 \bowtie \alpha_2$ (Fig. 3): if the structure is well formed, the doublet is separated (Fig. 3, at the right).



Fig. 1. Vegard's law for system Pd-Ag



Fig.2. X-ray pattern of the alloy Ag-Pd with the addition of cladding elements



Fig. 3. Diffraction line (422)

Technological control of the preliminary synthesis of NLBS material. NLBS is ferroelectric material with the structure of potassium-tungsten bronze based metaniobate lead:(Pb, Ba, Sr) Nb₂O₆ that is used in capacitor manufacturing [3, 5]. The synthesis of this ceramics takes place in two stages: preliminary synthesis and final one during high-temperature sintering. We have found correlation between the crystallographic structure of the material formed during the primary synthesis and the electrophysical properties of the subsequent high-temperature firing of ceramics. We have deciphered the phase composition

of the material obtained by the preliminary synthesis. There are two phases in its foundation: tetragonal structure $Pb_{0.3}Ba_{0.7}Nb_2O_6$ and orthorhombic structure $Pb_{0.7}Ba_{0.3}Nb_2O_6$. The crystal lattice parameters of these phases are changing depending on the introduced additives, their quantity and synthesis conditions. Under normal conditions of synthesis, a material with a quantitative advantage of the tetragonal phase should be obtained. The complexity of decoding and evaluating the phase ratio is connected with the fact that the diffraction lines of these phases superimpose on each other. However, having a "good" reference sample, which was preliminarily synthesized in a tunnel kiln, we were able to isolate diffraction lines of each of the indicated phases (not overlapping on each other) and to determine the ratio of their intensities and diffraction angles (Fig. 4).



Fig. 4. Radiogram of a reference sample

These lines are (002), (620) for the tetragonal phase, and (732) for the orthorhombic phase. The diffraction lines under consideration are located in the region of diffraction angles $2\theta = 44^{\circ}-48^{\circ}$. The recording of these lines and the determination of their intensity ratio and diffraction angles allow us to compare them with the standard and make conclusion about the quality of synthesis.

3. Conclusion

The developed technique of input control of the phase composition and crystallographic parameters of the silver-palladium alloy allows controlling the presence of foreign phases, the composition of solid solution and the formation degree of crystal lattice of the alloy.

The proposed method of controlling the phase composition of NSBS material after preliminary synthesis allows predicting the quality of ceramics after high-temperature firing.

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EFFECT OF COOLING RATE ON THE CRYSTALLIZATION OF ALUMINUM ALLOYS UNDER PRESSURE

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Abstract. The influence of pressure on the compressibility of liquid metal and the release of latent crystallization heat is studied. It is found that the pressure application combined with the cooling rate creates metastable structures. It can be used for improvement the properties of metals and alloys.

Keywords: aluminum alloy, cooling, crystallization, microstructure, pressure

1. Introduction

One of the most important problems influencing the efficiency of metal products is the structure and properties formation of metals and alloys during their transition from melt (liquid) to solid [1]. Unlike the conventional approach, which tends to use cooling rate as a defining parameter of crystallization, the paper dwells on the pressure influence, which combined with cooling rate can be used for target changing alloy properties. We tried to elucidate how the pressure of up to 100 MPa/s, with the temperature of 150 - 200 K higher the crystallization temperature, influences on crystallization and structure of AK7 aluminum alloy. It is known that alloy amorphization is achieved under ultrafast cooling from liquid state. It reduces the possible range of amorphized alloys products to thin foils, bands, fiber less than 0.1...0.2 mm thick [12-17>2-7].

We have studied the amorphization of aluminum-based alloys, which can be reached in 70 mm ingots \emptyset 80 mm through programmed high pressure application on the liquid metal with the heat removal at approximately 3..5 K/sec.

2. Research technique and results

The aluminum alloy was produced in a graphite crucible under a flux layer in an electric resistance furnace. The form was filled from a 2 dm³ cup by way of popping the stopper. The cup's room was vacuumed; the residual pressure was 0.01 MPa. The temperature was measured by platinum-rhodium-platinum thermocouples with the electrodes 0.5 mm in diameter and 500 mm operating length. The temperature patterns were measured in two modes: 1 – crystallization under 500 MPa pressure; 2 – crystallization without pressure. Working fluid pressure in the hydraulic pressure was measured with the help of a strain gauge. The pressure is applied on the mold from two sides along the centre line of the blank by two injection plungers moving towards each other. All motions of the plungers during the mold casting were recorded by induction sensors with the precision ± 0.1 mm and stroke length up to 150 mm. Pressure was applied till the end of crystallization. A compute information-control system was used to gather and process the experimental data [18>8].

Figure 1 shows the thermocouple data in real-time mode. Curves 2-1 and 1-1 give the data from the thermocouples installed into the metal; curves 2-2 and 1-2 correspond to the thermocouples installed at an 8 mm distance from the form walls. It follows from the cooling http://dx.doi.org/10.18720/MPM.4112019 14

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curve analysis that the crystallization under pressure performs in different way. The value of pressure directly influences the release time of the latent crystallization heat. Such effect is equivalent to a fast cooling of a metal in water or any other medium. The pressure application reduces the time from ~ 30 to ~ 8 sec.



Fig. 1. Cooling curves of aluminum alloy AK7: curves 1-1 and 1-2 without pressure application; curves 2-2 and 2-2 with 500 MPa pressure application

The positive influence of accelerated cooling during crystallization onto the structure and mechanical properties of metals and alloys is well known [19, 20>9, 10]. Cooling rates of 10^4 - $10^{6\circ}$ C/sec allow boost properties of different alloys. The degree of dispersion of the cast structure increases with the growth of cooling rate. The sample shown in Figure 2a was obtained by ultra fast application of high pressure; it represents the second-phase precipitates of 0.5 – 2.5 µm. The sizes of such precipitates in the melt produced samples without pressure application (Fig. 2b) are significantly larger (5-30 µm).



Fig. 2. AK7 alloy microstructure crystallized under pressure of 500 MPa (a) and without pressure (b) (x10000)

From the results it follows that pressure application and cooling can be treated as a working technology for metal transition from liquid to crystalline or amorphous state with the property change that such transition entails. The presented technological cycle of the alloy casting production can be commercialized in order to produce alloy castings equal in their strength properties to foreign leading aluminum alloys of medium and high-strength.

3. Conclusion

The pressure applied onto the liquid aluminum alloy before and during crystallization affects the latent crystallization heat release. The applied pressure decreases significant (80 to 100 times) the grain medium diameter (0.5-2.0 μ m). Alongside the grain disintegration metastable phases appear. The use of ultra fast high pressure application technology and further casting under optimum conditions boosts the creation of metal products with the targeted metastability level, 40-60% enhancement of strength characteristics of aluminum alloys while preserving the paste-forming properties on a relatively high level.

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EVOLUTION OF STEAM AND GAS PLUME GENERATION ON LASER TREATING OF METALS IN LIQUID

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Abstract.Evolution of steam and gas plume generation on the surface of an irradiated metal was investigated experimentally. It is shown that on using GOR-100M operating in a free oscillating regime the form of a crater developed in an irradiated target beingin water and air differs drastically. It is found that the substantial difference in the forms of crater surfaces developed is determined by different character of plasma, steam and gas mixture flow. **Keywords:** fast holographic filming, laser radiation, steam and gas mixture flow

1. Introduction

The main opinions about the destruction mechanisms of solids surrounded with gas during their treatment by laser beams with the radiation flux density varied from 10^5 to 10^6 W/sm²are considered. The work aim is the investigation of processes running near a metal target mounted in water.

2. Experimental equipment and experimental results

The scheme of the experimental setup used in the study is presented in Fig. 1. The radiation of the GOR-100M ruby laser (1) ($\lambda = 0.694 \mu$ m) operating in the free oscillation regime (pulse duration ~1.2 mc) passed through the focusing system (2) and was directed onto the sample (3) that was mounted in water. The radiation spot diameter on the sample with sharp edges was varied in the course of the experiments from 1 to 2 mm.



Fig. 1. Schematic diagram of the experimental setup

http://dx.doi.org/10.18720/MPM.4112019_15 © 2019, Peter the Great St. Petersburg Polytechnic University © 2019, Institute of Problems of Mechanical Engineering RAS From the front face of the glass wedge (5) a part (4 %) of laser radiation was directed into the IMO-2N energy meter (6), which entrance window was located in the focal plane of the lens (7). The laser pulse energy was varied from 5 to 60 J. The FEK-14 coaxial photodetector (8), the signal from which was coupled to the S8-13 oscilloscope, was used to record the temporal shape of the laser pulse. To study the spatial and temporal evolution of the laser plasma torch in the course of laser radiation action on a sample, we used the method of high-speed holographic motion-picture recording [1]. The sample (3) was placed in one of the arms of Mach–Zehnder interferometer (9), which was illuminated with the radiation of the ruby laser (10) ($l = 0.694 \mu m$) operating in the free oscillation regime. The pulse duration of the radiation amounted to 400 ms. The transverse mode selection in the probing laser was accomplished using the aperture placed in the cavity, and the longitudinal mode selection was provided by the Fabry–Perot cavity standard used as the output mirror.

The probing radiation after the collimator (11) was a parallel light beam with the diameter up to 3 cm, which allowed observation of the steam-plasma cloud development. The interferometer was attached to the SFR-1M high-speed recording camera (12), in which the film plane was conjugate with the meridian section of the laser beam, acting on the sample, by means of the objective (13).

The high-speed camera operated in a time magnifier regime. The setup described allowed recording the time-resolved holograms of the focused image of a laser plasma torch. Separate holographic frames provided temporal resolution no worse than 0.8 μ c (the single frame exposure time) and the spatial resolution in the object field ~ 50 μ m. The diffraction efficiency of the holograms allowed one to reconstruct and record interference and shadow pictures of the studied process under the stationary conditions.

The experimental results have shown that the crater topography obtained on laser treating of a lead sample in water (Fig. 2) differs considerably from that of obtained on laser treating of the same sample in air under normal conditions (pressure $\sim 10^5$ Pa, Fig. 3).



b). c). **Fig. 2.**Craters obtained in water after treating a lead sample by laser pulses with energy 10 J (a), 20 J (b), 40 J (c)

To study the shape of crater that appears on the plate, we used the fringe projection method [2], which in the present case appeared to be more efficient than holographic methods of surface relief imaging and the stereo-photogrammetric method, since, already at the stage of fringe projecting, it allowed obtaining a picture with controllable measurement sensitivity and sufficiently good visibility of a relative fringe displacement. The first was set by changing the projected fringeperiod; the good visibility was provided by changing the illumination angle to the studied surface till removing the light flares from the crater surface. The present method is thoroughly described and successfully used in Ref. [3]. The crater surface obtained in water after treating of the lead sample by laser pulses is foamed; the macroscopic alveolus is practically absent (Fig. 2). The crater obtained in air after treating of lead sample by laser

pulse has an alveolus with a plane surface (Fig. 3a). The crater topography (Fig. 3b) is determined by distribution of light energy density over the transverse cross-section of the laser beam [4]. The shadow pictures obtained at different time are represented in Fig. 4. Near the surface of irradiated sample, there appear steam and gas bubbles. At the first stage its form is spherical. A bubble rapidly grows (especially during the early stages).



Fig. 3.Crater obtained in air after treating of a lead sample by laser pulse with energy 40 J (a) and its topography (b)





b).

c).



Fig.4.Shadow pictures of steam and plasma bubble obtained at 10 (a), 50 (b), 500 (c), 1200 (d), 2000 (e), 3000 (f) μc after the start of laser treating a lead sample

Figure 5 represents, defined from the shadow pictures, temporal dependences of the bubble radius and growth velocity.

Approximately in 500 μ s after beginning the laser treating of the lead sample, the bubble form begins to change (Fig. 4c, d). After the cessation of laser irradiation (~ 1.2 ms) the bubble dimension stabilizes and only in ~ 1.5 ms starts its slow decay. It is important that the bubble form at this stage changes accidentally and it don't repeat oneself from one experiment to the other.

It should be mentioned that the metal drops, illuminated by laser radiation, were seen in the bubble and out of it at all the stages of laser treating. Both spectral analysis and X-ray analysis provided using devise ElvaX showed that a small amount of lead appears in the water after laser treating the lead sample because of nanoparticle gel formation.



Fig. 5. Temporal dependences of the bubble radius (*) and its growth velocity (◊)

3.Discussion

During the treating of metal sample mounted in air by laser radiation with the parameters corresponding to our experiment [3] under normal condition (pressure $\sim 10^5$ Pa) dimension of generated plasma plume reached several centimeters. In the water shining zone of plasma plume has dimension ~ 1 mm; temperature on the plume board reaches ~ 7000 K [5]. The difference is explained by intensive heating and evaporation of water that leads to steam and gas bubble formation. There are two components inside the bubble: products of the irradiated sample erosion (lead steam) and water steam. The motion equations of these components are:

• Euler equations for each component

$$\begin{split} \rho_1 \frac{\partial V}{\partial t} + \rho_1 \left(\vec{V} \cdot \nabla \right) \vec{V} &= -\nabla p \ , \\ \rho_2 \frac{\partial \vec{U}}{\partial t} + \rho_2 \left(\vec{U} \cdot \nabla \right) \vec{U} &= -\nabla p \ , \end{split}$$

Continuity equations for each component

$$\frac{\partial \rho_1}{\partial t} + div \left(\rho_1 \vec{V} \right) = A(t) \delta(r - r_0), \quad \frac{\partial \rho_2}{\partial t} + div \left(\rho_2 \vec{U} \right) = B(t) \delta(r - r_b),$$

• State equations for each component

$$p = p_1 + p_2, \ p_1 = \rho_1 \frac{R_u T}{\mu_1}, \ p_2 = \rho_2 \frac{R_u T}{\mu_2},$$

Heat and mass transfer equation

$$\left(\rho_{1}c_{p1}+\rho_{2}c_{p2}\right)\frac{\partial T}{\partial t}+\left(\rho_{1}c_{p1}\vec{V}+\rho_{2}c_{p2}\vec{U}\right)\cdot\nabla T=div\left((\alpha_{1}+\alpha_{2})\nabla T\right).$$

Here ρ_1 is the ablation products gas density, ρ_2 is the water steam density, \vec{V} is the ablation products gas velocity, \vec{U} is the water steam velocity, A(t) is the power density of the ablation products source (its temporal form repeats the temporal form of the laser pulse shown in Figure 6), $r = r_0$ is the equation of the plasma plume board, B(t) is the power density of a water steam source, p_1 is the ablation products partial pressure, p_2 is the water steam partial pressure, T is the system temperature, μ_1 is the ablation products molar mass, μ_2 is the water steam molar mass, R_{μ} is the universal gas constant, c_{n1} is the ablation products specific heat capacity under constant pressure, c_{p2} is the water steam specific heat capacity under constant pressure, α_1 is the ablation products heat conductivity, α_2 , is the water steam heat conductivity, h is the specific heat of water evaporation, D is a coefficient, p_a is the atmospheric pressure, M is the mass of the water in the cuvette, S_{i} is the bubble surface area, a is the bubble surface acceleration.

$$B(t) = D \frac{(\alpha_1 + \alpha_2) |\nabla T|}{h} |r = r_b.$$



products (*) and water steam (\diamond) velocities at the distance $r = \Delta r / 2$ from the bubble surface

The solution of the equation system with the boundary conditions

 $T|r = r_0 = 7000 K$, $T|r = r_b = 373 K$, $V_n|z=0 = U_n|z=0 = 0$, $(p - p_a)r = r_b = a \cdot M / S_b$ gives the following results. A small plasma plume emits a stream of hot ablation products in the opposite direction with respect to the laser beam. At the first stage ($t \le 10 \ \mu c$) because of the high density and temperature ($T|r = r_0 = 7000 K$) of erosion products, plasma motion is similar to that of observed in air. Here r_0 is plasma plume near a treated surface radius. The motion of erosion products is supersonic and practically one-dimensional (radial). The erosion products cool evaporating water. The velocity of bubble board motion is also supersonic. An intensive flow of the lead drops from the erosion zone is typical for this stage.

At the second stage $(10 \ \mu c \le t \le 50 \ \mu c)$ the erosion products motion is also supersonic, but at this stage the water steam mass is considerably greater than the mass of erosion products in the bubble. The velocity of bubble board \vec{U}_b is under-sonic, the velocity of water steam motion \vec{U} is also under-sonic and considerably less \vec{U}_b , but $|\vec{U}|$ increases. The motion of two-component (lead and water steam) system is radial. A part of evaporated products of erosion leave the bubble and form the water and lead nanoparticle gel.

At the third stage ($50 \ \mu c \le t \le 500 \ \mu c$) the velocities of all bubble components become under-sonic. The system of bubble motion equations for the components can be transformed into a linear one, being solved analytically. For instance, temperature in the bubble

$$T(r,t) = \frac{4T_0 \,\Delta r}{\pi^3} \sum_{n=1}^{\infty} \frac{(1-(-1)^n)}{n^3} \exp\left(-\left(\frac{\pi n}{\Delta r}\right) A t\right) \frac{\sin\left(\frac{\pi n}{\Delta r}r\right)}{r}.$$

Here $T_0 = T \left| r = r_0, \ \Delta r = r_b - r_0, \ A = \frac{\alpha_1 + \alpha_2}{\rho_{01} \,c_{p1} + \rho_{20} \,c_{p2}}, \ A = \frac{\alpha_1 + \alpha_2}{\rho_{01} \,c_{p1} + \rho_{20} \,c_{p2}},$
$$\rho_{01} = \frac{\mu_1 \, p \left| r = r_b}{R_u \, T \left| r = r_b}, \ \rho_{02} = \frac{\mu_2 \, p \left| r = r_b}{R_u \, T \left| r = r_b}.$$

Figure 6 represents the temporal dependences of ablation products and water steam velocities at the distance $r = \Delta r/2$ from the bubble surface. It is considerable that at the end of this stage of process a stream of water steam becomes supersonic.

At the forth stage ($t \ge 500 \ \mu c$) the water steam motion becomes not one-dimensional (radial). Reaching a bubble board the water steam stream moves transversal to the bubble board of a sample, reaches it, moves along the sample to its centrum, reaches a plume, heats and moves opposite to a laser beam together with erosion products. So the stream of water steam moving along the sample to its centrum, don't avoid the melted metal flow out of the crater and froths it. In the contact zone of "direct" and "reverse" streams there appear vortexes. The vortexes exist among all bubble. This is the reason of incidental decay of the steam and gas bubble.

4. Conclusion

The investigations have showed that substantial difference in the forms of crater surfaces developed as a result of processing the identical targets, being in water or air, by laser pulses with the identical parameters are determined by principally different character of plasma and steam and gas mixture flow in the mentioned cases.

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INFLUENCE OF AN EXTERNAL ELECTRIC FIELD ON PARTICLE GENERATION DURING LASER-PLASMA TREATING OF METALS

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Abstract. Evolution of plasma torch at the surface of some metals (Cu, Al, Sn, Pb) induced by varying external electric field of different polarity from 0 to 10^6 V/m^{-1} in the course of laser processing with the mean radiation flux density ~ 10^6 W/cm^{-2} is studied. A size of the target material droplets, carried out from the irradiated zone, becomes several times less, as the field strength amplitude grows, independently of the field polarity.

Keywords: fast holographic filming, laser radiation, strip projection method

1. Introduction

Technological applications of lasers generate new problems, which solution requires investigation of processes taking place under the action of light fluxes on the surface of solids. Such studies are of particular importance for choosing the most efficient regimes of laser processing of materials, including laser pattern cutting, perforation, welding of materials, modifying their surface properties, and laser film deposition, as well as for developing new control methods for laser technological processes. In addition, such studies are of separate scientific interest. It is urgent to study the surface relief of a solid in the course of exposing it to pulsed laser radiation under different external conditions, particularly, in the presence of external electric fields. The processes that occur in a steam-plasma cloud arising near the surface of irradiated material are also of great interest since they affect the material processing. The aim of the present paper is to study the surface of different metals (copper, aluminum, tin, lead). The formation mechanism of the surface relief is also the subject of investigation.

2. Experimental equipment

The radiation of GOR-100M ruby laser ($\lambda = 0.694$ mm) operating in the free oscillation regime, pulse duration ~1.2 mc, passed through the focusing system and was directed through the hole in the first electrode onto a sample that served as the second electrode and was mounted in air at pressure of 10⁵ Pa. The radiation spot diameter on the sample with sharp edges was varied in the course of the experiments from 1 to 2 mm. From the front face of the glass wedge a part (4 %) of laser radiation was directed into the IMO-2N energy meter, whose entrance window was located in the focal plane of the lens. The energy of the laser pulses varied from 5 to 60 J. FEK-14 coaxial photo-detector, which signal was coupled to the S8-13 oscilloscope, was used to record the temporal shape of the laser pulse. The voltage was applied to the electrodes from the source, built on the basis of the UN 9/27-13 voltage

multiplier of the TVS-110 unit. The source allowed the voltage variation within 25 kV and its stabilization in the course of the experiment.

To study the spatial and temporal evolution of the laser plasma torch in the course of laser radiation action on the sample, we used the method of high-speed holographic motionpicture recording [1]. The sample was placed in one of the arms of Mach–Zehnder interferometer, which was illuminated with the radiation of the ruby laser ($l = 0.694 \mu m$) operating in the free oscillation regime. The pulse duration of the radiation amounted to 400 mc. The transverse mode selection in the probing laser was accomplished using the aperture, placed in the cavity, and the longitudinal mode selection was provided by the Fabry–Perot cavity standard used as the output mirror. The probing radiation after the collimator was a parallel light beam with the diameter up to 3 cm, which allowed observation of the steam-plasma cloud development. The interferometer was attached to the SFR-1M high-speed recording camera, in which the film plane was conjugate with the meridian section of the laser beam, acting on the sample, by means of the objective.



Fig. 1. Radiation pulse oscillogram produced by GOR-100M laser. The scanning rate is 200 m/s div^{-1}

The high-speed camera operated in the time magnifier regime. The described setup allowed recording time-resolved holograms of the laser plasma torch. Separate holographic frames provided temporal resolution no worse than 0.8 mc (the single frame exposure time) and the spatial resolution in the object field ~ 50 mm. The diffraction efficiency of the holograms allowed one to reconstruct and record interference and shadow pictures of the studied process under the stationary conditions.

3. Results and discussion

The interferograms reconstructed from the holograms recorded at different instants in the course of high-speed holographic motion-picture shooting clearly illustrates both the initial stage of the laser plume development and the plasma flow around the electrode at different directions of the external electric field strength vector. The data on the distribution of concentration of free electrons in the plasma of an evaporated metal at different instants, obtained by processing the interferograms [2], show that although the energy distribution over the laser radiation focusing spot is not uniform, the lines of equal concentration are practically smooth, which is an evidence of relatively uniform ionization of the eroded substance steams. It is essential that, despite a substantial increase in the plasma formation over time, the mean electron concentration in the plume remains practically unchanged and even slightly grows, which may be associated both with a constant increase in the mass of emitted substance and with secondary ionization of plasma by the laser radiation. Note, that the presence of an external electric field weakly affects the concentration of electrons in the laser plasma plume.

When either positive or negative potential is applied to the sample, many small droplets appear on its surface after the laser action (Fig. 2). In particular, at the laser pulse energy 20 J, the focusing spot diameter 2 mm, and the electric field strength 10^6 V/cm, we observed ejection of droplets having the mean characteristic size less than 0.1 mm to the distance up to 2 cm from the crater centrum. The maximal characteristic size of drops was ~ 0.4 mm. In the absence of the external electric field the mean size of the droplets was ~ 0.4 mm. The droplets were seen at the distance up to ~ 1 cm from the crater centrum.



Fig. 2. Photograph of the microscopic surface relief of the crater outer zone

In accordance with the results presented above, the process dynamics on the surface of a sample, placed in an external electric field with the strength from 0 to 10^6 V/m and subject to the action of the pulsed laser radiation with the parameters mentioned above, is thought to be as follows. The primary plasma formation and the initial stage of the laser plume development, in principle, do not differ from those observed in the absence of the external electric field. The metal is melted and evaporated. As a result of local formation of steam and

plasma, the erosion plume begins to form with the fine-dispersed liquid-drop phase. Note, that the bulk evaporation is promoted by the gases, diluted in the metal, and by the spatiotemporal non-uniformity of the laser radiation. At a radiation flux density $10^6 - 10^7$ W/cm² the bulk evaporation is typical of all metals used in the experiments [3]. Obviously, the presence of the external electric field affects (increases or decreases depending on the direction of the field strength vector) the motion velocity of the plasma front and causes some distortion of the plasma cloud shape. It is essential that the mentioned differences (at the considered parameters of laser radiation) are observed only at the initial stage of the laser plume development, because after the steam-plasma cloud reaches the electrode an electric breakdown (short-circuit) occurs, and the external field in the interelectrode gap disappears.

Consider now the motion of the molten metal droplets in the steam-plasma cloud. In our opinion, the significant difference in the droplet sizes observed on the surface of the irradiated sample in the presence of the external electric field (independent of the direction of the field strength vector) and in the absence of the field, is a manifestation of the following mechanism of droplet formation. It is known that at the surface of a liquid (including a liquid metal) the formation of gravity-capillary waves [4] is possible under the action of various perturbations. Undoubtedly, the examples of such perturbations are the spatially non-uniform evaporation of the target material due to non-uniform heating caused by non-uniform energy distribution over the focusing spot, the non-uniform primary plasma formation [5] caused by roughness of the irradiated sample surface, and, in the first place, the slop of the molten metal initiated by each spike of laser radiation, acting on the exposed sample [6].

Using the method presented in [4], one can show that at insignificant thickness of the molten metal layer (confirmed by the view of the 'outer' (directed) zone of the crater, particularly, the absence of fillets of significant height at the crater edge) the dispersion equation for the gravity-capillary waves takes the form

$$\omega^{2} = \frac{\alpha k^{3}}{\rho} + g k - \frac{k E_{0} E}{4 \pi \rho \xi^{*}} \Big|_{z=0} , \qquad (1)$$

where α is the surface tension coefficient of the molten metal; ρ is the metal density; g is the free fall acceleration; k is the magnitude of the wave vector of the gravity-capillary wave; E_0 is the electric field strength at the surface z = 0 of the molten metal (the z axis is perpendicular to the surface of the irradiated sample, directed towards the laser radiation source and parallel to the vector \vec{E}_0); $\vec{E} = -\partial \varphi' / \partial z$ is the perturbation of the electric field in the space surrounding the molten metal; ξ' is the small displacement of the liquid surface in the z axis direction in the gravity-capillary wave.

Because for the uniform field E_0 , the potential is $\varphi = -E_0 \cdot z$ (the potential at the metal surface is considered to be zero), the displacement of the mentioned surface by the small quantity ξ' leads to a small distortion of the potential:

$$\varphi'\Big|_{z=0} = E_0 \cdot \xi'. \tag{2}$$

In our case the maximal concentration of electrons in the plasma formation does not exceed $\sim 10^{18} \text{ cm}^{-3}$, which corresponds to the change in the dielectric constant of the medium ε by approximately 10^{-5} . Therefore, near the metal surface $\varepsilon \cong 1$ and with the boundary condition (2) taken into account

$$\varphi' = E_0 \, \xi' \, e^{-k \, z} \, .$$

In this case, the dispersion equation for gravity-capillary waves takes the form

$$\omega^{2} = \frac{\alpha k^{3}}{\rho} + g k - \frac{k^{2} E_{0}^{2}}{4 \pi \rho} .$$
Influence of an external electric field on particle generation during laser-plasma treating of metals

Since the frequency of the gravity-capillary waves ω is determined by the temporal characteristics of the abovementioned perturbations and, therefore, does not depend on the electric field strength E_0 , the growth of the magnitude E_0 (independent of the direction of

the vector \vec{E}_0) should cause the increase in the magnitude of the wave vector $k = \frac{2\pi}{\Lambda}$ and the

decrease in the wavelength Λ of the gravity-capillary wave. If we assume that the droplets are 'torn away' by the plasma flow from the 'tops' of the gravity-capillary wave and, therefore, their characteristic size is proportional to Λ , then it becomes clear why in the presence of the external electric field (of any direction) the observed mean size of the droplets becomes essentially reduced.

The escaped droplets possess the charge of the same sign as the sample. That is why the droplets begin to move with acceleration towards the second electrode. However, since the maximal initial velocity of the outgoing droplets under the analogous conditions [7] is ~ 45 m/s, i.e., an order of magnitude smaller than the velocity of steam-plasma cloud spreading, the droplets do not reach the electrode before the breakdown in the interelectrode gap. In what follows (in the absence of the external electric field) the droplets move under the action of the same forces as in Ref. [7] and, therefore, in the way, described in Ref. [7]. In this case, having acquired at the stage of accelerated motion in the electric field the velocity, exceeding the initial one, the droplets may fly to a greater distance along the surface of the experiment. Moreover, having moved to a greater distance from the sample surface and, therefore, being affected by the plasma for longer time before returning to the surface, the droplets can be split into finer parts than in the absence of the external field.

It should be noted that the droplets in the erosion plume may appear not only due to the molten pool surface instability, but also due to the condensation of the steams of the erosion products. Moreover, since the droplets produced in the course of condensation of steams may be charged, they, similar to those carried out from the molten pool, in the electric field may be removed from the crater to a greater distance than in the absence of the electric filed. However, this mechanism of plasma formation is dominating under somewhat different conditions of laser radiation acting on the material, namely, at significantly greater mean radiation flux density $(10^8 - 10^9 \text{ W/cm}^2)$ and smaller exposure duration (single pulses of laser radiation were used with the duration 100 - 200 ns and with less smooth temporary shape). In the case of such a regime of laser metal processing, one observes the screening of the irradiated sample by the plasma cloud, which is possible only at the concentration of the ablated material steam essentially exceeding 10^{18} cm⁻³. In this case, one observes intense formation of droplets with the dimension ~ 200 nm and smaller, and this process is most active at the late stages of laser radiation action on the material (at decreasing intensity of laser action) and even after its termination. At smaller radiation flux density, characteristic of the experiment considered in the present paper ($\sim 10^{18}$ cm⁻³), the condensation of droplets from the steam of ablation products is expected to be less intense. Therefore, the essential contribution of the condensation mechanism to the formation of drops (having the size 0.1 - 0.4 mm, see Figs. 1 and 2), especially at early stages of the process, i.e., before filling the entire interelectrode gap by the plasma cloud, seems to be hardly probable.

4. Conclusion

Under the action of laser radiation with the mean radiation flux density $\sim 10^{6}$ W/cm⁻² at the surface of some metals (Cu, Al, Sn, Pb) in the external electric field with different polarity and the strength up to 10^{6} V/m, the characteristic size of the target substance droplets, carried out of the irradiated zone, decreases by several times with increasing external electric field strength. Probably, this is due to a change in the wavelength of the gravity-capillary wave,

excited on the molten metal surface. The observed effect offers the possibility to control the size of the metallic droplets in the course of laser deposition of thin films.

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SKEW BROWNIAN MOTION WITH DRY FRICTION: PUGACHEV-SVESHNIKOV APPROACH

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Abstract. The Caughey–Dieness process, also known as the Brownian motion with two valued drift, is used in theoretical physics as an advanced model of the Brownian particle velocity if the resistant force is assumed to be dry friction. This process also appears in many other fields such as applied physics, mechanics, astrophysics, and pure mathematics. In the present paper we are concerned with a more general process, skew Brownian motion with dry friction. The probability distribution of the process itself and of its occupation time on the positive half line are studied. The approach based on the Pugachev–Sveshnikov equation is used.

Keywords: Skew Brownian motion, Pugachev-Sveshnikov equation, dry friction, local time

1 Introduction

Brownian motion plays an important role in statistical physics and other applied areas of science. The classical physical theory of Brownian motion was developed by Einstein and Smoluchowski [1] in the beginning of 20th century. In this theory, a weightless Brownian particle is driven by a random force resulting from the collision with molecules. The friction between the particle and the molecules, in other words the resistant force due to collision, is assumed to be viscous, that is, proportional to the particle's velocity. Mathematically, these assumptions lead to the Wiener process. The major drawback of this model is that almost all the trajectories of the particle are continuous but nowhere differentiable, so the velocity cannot be defined properly. Later on, this problem was solved by Ornstein and Uhlenbeck [2], who developed a refined physical theory that accounts for the particle's inertia.

A more evolved model of Brownian motion uses the assumption that along with viscous, dry friction is present, being independent of the particle's velocity, but depending on the motion direction. Such a model in its simplest form, when the viscous friction is absent, is called Brownian motion with dry friction and was first studied by Caughey and Dienes [3] in 1960s. The authors considered a process similar to the Ornstein–Uhlenbeck's one, but the linear term was replaced by the sign function. This process turned out to be useful in analysis of different phenomena in control theory [4], seismic mechanics [5], communication systems theory [6], radio physics [7], nonlinear stochastic dynamics [8], and also in pure mathematics [9–11]. In 2000s, other applications of the Caughey–Dienes process emerged. The major interest was in nanofrictional systems [12], particles separation [13], ratchets [14,15], granular motors [16], dynamics of granular media [17,18], and in dynamics of droplets on moving surfaces [19–22]. Some additional publications on the subject can be found in author's work [23].

The present paper deals with the model of skew Brownian motion with dry friction, or

more precisely with the so-called skew Caughey–Dienes process, which can be understood as the velocity V(t) of a particle in this model. In what follows, for simplicity, we limit ourselves to studying skewing at zero only.

In order to understand how skewing works, we consider an excursion of the process V(t); an excursion is the part of the process's trajectory, located between two time points at which V(t) vanishes, namely, between two consequent stops of a particle. An excursion of the Caughey–Dienes process without skewing is known to be a sufficiently good approximation of the real Brownian particle behavior. However, we note that for such a process, due to symmetry, positive and negative excursions appear with the same probability 0.5, which is not always the case. Generally speaking, in reality the probability α to have a positive excursion is different from 0.5, thus, in effect some skewing takes place. In this way we arrive at the model of the skew Caughey–Dieness process, where the probability α is an additional parameter of the model, which has to be estimated from the experimental data.

Skew processes are tightly connected with diffusion in discontinuous media and have numerous applications in several fields of physics [24]. For example, they describe shock acceleration of charged particles in a magnetic field [25] and diffusion in geophysical problems associated with the study of inhomogeneous porous media [26]. It should also be noted that such processes arise in some special randomly perturbed Hamiltonian systems [27]. Besides, the skewing procedure has been studied from a mathematical standpoint for a number of typical stochastic processes. However, we point out that the most detailed results are available for the skew Brownian motion process [24], skew Ornstein–Uhlenbeck process [28], and skew Cox–Ingersoll–Ross process [29]. Unfortunately, the skew Caughey–Dienes process is not well known, and this, in particular, motivates our study.

Generally, calculating the probabilistic characteristics of a skew diffusion is considered to be a difficult mathematical problem [10]. The standard tools to solve it are the Fokker–Planck–Kolmogorov equation, Feynman–Kac equation, or the random walk approximation. We propose an alternative way, based on the Pugachev–Sveshnikov equation, which was used in authors' previous works [23,30]. From our perspective, this approach allows one to get to the result faster, and in a more algorithmic way.

2 Skew Caughey–Dienes process

Skewing is intimately connected with the notion of local time. It is possible to prove [24] that the skew Caughey–Dienes process, described in the introduction, is a unique strong solution of the following stochastic differential equation

$$dX(t) = -2\mu \operatorname{sign}(X(t))dt + (2\alpha - 1)dL_X^0(t) + \sqrt{2} \, dW(t), \ t > 0, \quad X(0) = 0, \tag{1}$$

where $\alpha \in (0,1)$ is a skewing parameter, the probability of an excursion to be positive. By W(t) we denote the standard Wiener process starting at zero, and $L_x^0(t)$ is the symmetric local time of X(t) at the level zero:

$$L_X^0(t) = \lim_{\varepsilon \to +0} \frac{1}{2\varepsilon} \int_0^t \mathbb{1}_{\{-\varepsilon, +\varepsilon\}}(X(s)) d[X]_s,$$
⁽²⁾

where $[X]_s = 2s$ is the so-called quadratic variation of X(s). Further, we will be interested in the positive-half-line occupation time of X(t):

$$\mathcal{I}(t) = \int_0^t 1_{(0,+\infty)}(X(s)) \, ds. \tag{3}$$

One can think of X(t) and $\mathcal{I}(t)$ as of the components of the vector diffusion process $(X(t), \mathcal{I}(t))$ governed by the system of SDEs

Skew Brownian motion with dry friction: Pugachev-Sveshnikov approach

$$\begin{cases} dX(t) = -2\mu \operatorname{sign}(X(t))dt + (2\alpha - 1)dL_X^0(t) + \sqrt{2} \, dW(t), \\ d\mathcal{I}(t) = 1_{(0,+\infty)}(X(s))\, ds, \quad X(0) = \mathcal{I}(0) = 0. \end{cases}$$
(4)

In what follows, we derive explicit formulas for the probability density function of (4), following ideas from [30].

It can be shown [30] that the characteristic function $E(z_1, z_2; t) = \mathbb{E}e^{i(z_1X(t)+z_2\mathcal{I}(t))}$ of the process $(X(t), \mathcal{I}(t))$ satisfies the equation

$$\frac{\partial E}{\partial t} + (z_1^2 - iz_2/2)E + (2\mu z_1 - z_2/2)\hat{E} - 2i(2\alpha - 1)z_1\Psi_0 = 0, \quad E(z_1, z_2; 0) = 1,$$
(5)

where we adopted the short notation $E(z_1, z_2; t)$ and $\Psi_0(z_2, t)$ for the following Cauchy principal value integrals:

$$\hat{E} = \frac{1}{\pi} \text{v.p.} \int_{-\infty}^{+\infty} \frac{E|_{z_1 = s}}{s - z_1} ds, \quad \Psi_0 = \frac{1}{2\pi} \text{v.p.} \int_{-\infty}^{+\infty} E|_{z_1 = s} ds.$$
(6)

For Im $\zeta \neq 0$ let us introduce the Cauchy-type integral $\Phi(\zeta, z_2; t)$ and its limit values $\Phi^{\pm}(z, z_2; t)$ on the real axis from upper and lower half planes (with respect to the first argument):

$$\Phi(\zeta, z_2; t) = \frac{1}{2\pi i} \int_{-\infty}^{+\infty} \frac{E|_{z_1=s}}{s-\zeta} ds,$$

$$(z, z_2; t) = \lim_{z \to \infty} \Phi(\zeta, z_2; t), \text{ Im } z = 0.$$
(7)

 $\Phi^{\pm}(z, z_2; t) = \lim_{\zeta \to z \pm i0} \Phi(\zeta, z_2; t), \text{ Im } z = 0.$

It is well known that $\Phi(\cdot, z_2; t)$ is analytic when Im $\zeta \neq 0$, and that Φ^{\pm} satisfy the Sokhotski–Plemelj formulas when Im z = 0:

$$\Phi^{+} - \Phi^{-} = E, \ \Phi^{+} + \Phi^{-} = -i\hat{E}.$$
(8)

Clearly, one can rewrite (5) in terms of Φ^{\pm} , which gives the condition of the Riemann boundary value problem. Applying the Laplace transform with respect to *t* to this condition, and denoting its argument by *p*, we obtain the following formula:

$$(z_1^2 + 2\mu i z_1 + p - i z_2)\tilde{\Phi}^+ - i(2\alpha - 1)z_1\tilde{\Psi}_0 - \frac{1}{2} = (z_1^2 - 2\mu i z_1 + p)\tilde{\Phi}^- + i(2\alpha - 1)z_1\tilde{\Psi}_0 + \frac{1}{2}.$$
(9)

The Laplace transforms are labeled with tildes above the functions. Now, the Riemann boundary value problem is to recover analytic functions $\tilde{\Phi}^{\pm}$ from condition (9), which is specified on the real line Im $z_1 = 0$.

Note that the left-hand side of (9) can be analytically continued for all $z_1 \in \mathbb{C}$ such that Im $z_1 > 0$, also the right-hand side can be analytically continued for all $z_1 \in \mathbb{C}$ such that Im $z_1 < 0$. Since they match when Im $z_1 = 0$, they turn out to be the elements of the same entire function of argument $z_1 \in \mathbb{C}$. Assuming that $\Phi^{\pm}(z, z_2; t) = O(1/|z|)$ when $z \to \infty$ for Im $z \ge 0$, by generalized Liouville theorem one can realize that this entire function is actually linear: $G_0(z_2, t) + z_1G_1(z_2, t)$. This leads to the equality

$$\tilde{\Phi}^{\pm} = \frac{G_0 + z_1 G_1 \pm i(2\alpha - 1)z_1 \tilde{\Psi}_0 \pm 1/2}{z_1^2 \pm 2i\mu z_1 + p - (1\pm 1)iz_2/2}.$$
(10)

Note that the denominator in (10) has zeros $iv^{\pm} = i(-\mu \pm \sqrt{\mu^2 + p - iz_2})$ and $iz^{\pm} = i(\mu \pm \sqrt{\mu^2 + p})$ such that $\operatorname{Im}(iv^{\pm}) \ge 0$ and $\operatorname{Im}(iz^{\pm}) \ge 0$. At the same time, $\tilde{\Phi}^{\pm}$ should

be analytic in upper and lower half planes, therefore, the singularities at iv^+ and iz^- have to be removable. This gives a system of linear equations to determine G_0 and G_1 . Taking into account the definition of Ψ_0 in (6) and performing integration in (10), one finds that $\tilde{\Psi}_0 = -iG_1$. After that, the system of linear equations for G_0 and G_1 can be written in the following form

 $G_0 + 2iv^+ \alpha G_1 + 1/2 = 0, \quad G_0 + 2i\varkappa^- (1-\alpha) G_1 - 1/2 = 0.$ (11)

Finally, substituting G_0 and G_1 from (11) into (10), one can get to the final expression for \tilde{E} , using the first of Sokhotski-Plemelj formulas (8). Particularly, after necessary simplifications one can arrive at the Laplace transform of the characteristic function of X(t)and of $\mathcal{I}(t)$:

$$\tilde{E}_{\chi}(z_{1},p) = \tilde{E}(z_{1},0;p) = \frac{1}{i\varkappa^{-}} \left(\frac{\alpha}{z_{1} + i\varkappa^{+}} - \frac{1 - \alpha}{z_{1} - i\varkappa^{+}} \right),$$

$$\tilde{E}_{\chi}(z_{2},p) = \tilde{E}(0,z_{2};p) = \frac{\alpha\varkappa^{+} - (1 - \alpha)\nu^{-}}{\nu^{-}\varkappa^{+}((1 - \alpha)\varkappa^{-} - \alpha\nu^{+})}.$$
(12)

Straightforward computation using the table of Laplace and Fourier transforms for the first expression in (12) gives us the probability density function of X(t):

$$f_{X}(x,t) = \left(\frac{1}{\sqrt{\pi t}}e^{\frac{-(|x|+2\mu)^{2}}{4t}} + \mu e^{-2\mu|x|} \operatorname{Erfc}\frac{|x|-2\mu t}{2\sqrt{t}}\right) \cdot \begin{cases} \alpha, & x > 0, \\ 1-\alpha, & x < 0. \end{cases}$$
(13)

Letting t tend to $+\infty$, one can also obtain the steady-state probability density function

$$f_{X}^{\infty}(x) = f_{X}(x, +\infty) = 2\mu e^{-2\mu|x|} \cdot \begin{cases} \alpha, & x > 0, \\ 1 - \alpha, & x < 0. \end{cases}$$
(14)

The plot of the probability density function of X(t) for different α is presented in Fig. 1. Note that for $\alpha \neq 0.5$ the curve has a jump at zero, so that the probability that X(t) > 0 is equal to α .



Fig. 1. Probability density function $f_x(x,t)$ for different α ($\mu = 1, t = 1$)

Handling the second line in (12) takes somewhat more effort. First, we introduce the function:

$$S(w_1, w_2) = \frac{\alpha(w_2 + \mu) + (1 - \alpha)(w_1 + \mu)}{(w_1 + \mu)(w_2 + \mu)(\alpha(w_1 - \mu) + (1 - \alpha)(w_2 - \mu))},$$
(15)

then the expression for $E_{\mathcal{I}}(z_2, p)$ can be written as

Skew Brownian motion with dry friction: Pugachev-Sveshnikov approach

$$\tilde{E}_{\mathcal{I}}(z_2, p) = S(\sqrt{\mu^2 + p - iz_2}, \sqrt{\mu^2 + p}).$$
(16)

After that, we note that since $\mathcal{I}(t)$ is non-negative, instead of using the inverse Fourier transform with respect to z_2 , one can use the inverse Laplace transform with respect to $q = -iz_2$:

$$f_{\mathcal{I}}(y,t) = \mathcal{L}_{p,t}^{-1} \left[\mathcal{L}_{q,y}^{-1} \left[S(\sqrt{\mu^2 + p + q}, \sqrt{\mu^2 + p}) \right] \right], \tag{17}$$

where $\mathfrak{L}_{p,t}^{-1}[\cdot]$ is the inverse Laplace transform with respect to parameter p, and the argument of the original is t.

Now, we write the following chain of equalities:

$$f_{\mathcal{I}}(y,t) = \mathcal{L}_{p,t}^{-1} \left[\mathcal{L}_{q,y}^{-1} \left[S(\sqrt{\mu^2 + p + q}, \sqrt{\mu^2 + p}) \right] \right] = e^{-\mu^2 t} \mathcal{L}_{p,t}^{-1} \left[\mathcal{L}_{q,y}^{-1} \left[S(\sqrt{p + q}, \sqrt{p}) \right] \right]$$
(18)

$$= e^{-\mu^{2}t} \mathfrak{L}_{p,t}^{-1} \left[e^{-py} \mathfrak{L}_{q,y}^{-1} \left[S(\sqrt{q}, \sqrt{p}) \right] \right] = \chi(t-y) e^{-\mu^{2}t} \mathfrak{L}_{p,t-y}^{-1} \left[\mathfrak{L}_{q,y}^{-1} \left[S(\sqrt{q}, \sqrt{p}) \right] \right]$$
(19)

$$=\frac{\chi(t-y)e^{-\mu^{2}t}}{4\pi(y(t-y))^{3/2}}\int_{0}^{t}\int_{0}^{t+\infty+\infty}\mathcal{L}_{q,s_{1}}^{-1}\left[\mathcal{L}_{q,s_{1}}^{-1}\left[S(q,p)\right]\right]s_{1}s_{2}\ e^{-\frac{s_{1}}{4y}-\frac{s_{2}}{4(t-y)}}\ ds_{1}ds_{2}$$
(20)

$$=\frac{4\chi(t-y)e^{-\mu^{2}t}}{\pi\sqrt{y(t-y)}}\int_{0}^{+\infty+\infty}\int_{0}^{\infty}\mathcal{L}_{p,2-ys_{2}}^{-1}\left[\mathcal{L}_{q,2s_{1}}^{-1}\left[S(q,p)\right]\right]s_{1}s_{2}\ e^{-s_{1}^{2}-s_{2}^{2}}\ ds_{1}ds_{2}.$$
(21)

In the first and second lines we used some well-known properties of the Laplace transform, in the line three we applied Efros's theorem [31], and in the last line we made a change of variables in the double integral.

As the function *S* in (15) is rational, it is easy to calculate its inverse Laplace transforms $\mathcal{L}_{p,2-ys_1}^{-1}\left[\mathcal{L}_{q,2s_2}^{-1}[S(p,q)]\right]$. Skipping cumbersom but trivial in nature computations and takeing into account (21), we get to the final formula for the probability density function of the occupation time $\mathcal{I}(t)$:

$$f_{\mathcal{I}}(y,t) = \frac{4e^{-\mu^2 t}}{\pi \sqrt{y(t-y)}} \int_{0}^{+\infty} \int_{0}^{+\infty} \chi(2\sqrt{y}s_1, 2\sqrt{t-y}s_2) s_1 s_2 e^{-s_1^2 - s_2^2} ds_1 ds_2, \quad 0 < y < t,$$
(22)

where $\operatorname{Erfc}(\cdot)$ is the complementary error function, and

$$\chi(s_1, s_2) = \frac{1-\alpha}{\alpha} e^{-\mu \left(s_1 - \frac{2-\alpha}{\alpha}s_2\right)} \chi^+(s_1, s_2) + \frac{\alpha}{1-\alpha} e^{\mu \left(\frac{1+\alpha}{1-\alpha}s_1 - s_2\right)} \chi^-(s_1, s_2),$$

$$\chi^+(s_1, s_2) = 1_{(0, +\infty)} (\alpha s_1 - (1-\alpha)s_2), \quad \chi^-(s_1, s_2) = 1-\chi^+(s_1, s_2).$$
(23)

Not performing any other simplifications of this formula, we illustrate the generic shape of the scaled occupation time T(t) = I(t)/t density in Fig. 2. The probability density function of T(t) is given by $f_T(y,t) = t f_T(ty,t)$. It is worth noticing that unlike the well-known arcsine law, the distribution in Fig. 2 is unimodal; the mode can be controlled by the parameter α . This completely agrees with the physical interpretation of the skew Caughey–Dienes process given in the introduction.

At the end of the section, we formulate our result as the following theorem.

Theorem 1. The PDF of X(t), the steady-state PDF of X(t), and the PDF of the positive half-line occupation time $\mathcal{I}(t)$ are given by:

$$f_{X}(x,t) = \left(\frac{1}{\sqrt{\pi t}}e^{\frac{-(|x|+2\mu)^{2}}{4t}} + \mu e^{-2\mu|x|} \operatorname{Erfc}\frac{|x|-2\mu t}{2\sqrt{t}}\right) \cdot \begin{cases} \alpha, & x > 0, \\ 1-\alpha, & x < 0. \end{cases}$$
(24)

$$f_{X}^{\infty}(x) = f_{X}(x, +\infty) = 2\mu e^{-2\mu|x|} \cdot \begin{cases} \alpha, & x > 0, \\ 1 - \alpha, & x < 0. \end{cases}$$
(25)

$$f_{\mathcal{I}}(y,t) = \frac{4e^{-\mu^2 t}}{\pi\sqrt{y(t-y)}} \int_{0}^{+\infty} \int_{0}^{+\infty} \chi(2\sqrt{y}s_1, 2\sqrt{t-y}s_2) s_1 s_2 e^{-s_1^2 - s_2^2} ds_1 ds_2, \quad 0 < y < t,$$
(26)

where Erfc (·) is the complementary error function, and $\chi(s_1, s_2)$, $\chi^+(s_1, s_2)$, and $\chi^-(s_1, s_2)$ are given by (23).



Fig. 2. Scaled occupation time density function $f_{\tau}(y,t)$ for different α ($\mu = 1, t = 2$)

3 Conclusions

We derived explicit formulas for the probability density function of the skew Caughey–Dienes process and its occupation time on the positive half line, which generalizes the known results for the regular Caughey–Dienes process. In fact, a stronger result was obtained, which is the Laplace transform of the joined characteristic function. Essentially, our approach is based on the reduction to the Riemann boundary value problem, and clearly it can be used to find the characteristics of more general SDEs with piecewise linear coefficients and the local time.

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INFLUENCE OF LCV BEARING STIFFNESS ON ITS STATIC AND DYNAMIC CHARACTERISTICS OF STABILITY AND STEERABILITY

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Abstract. Study of the frame stiffness influence on vehicle dynamics and stability of light commercial vehicle is done. The simulations were conducted by using ADAMS/CAR software package. The model approbation was carried by comparing the results of simulation and real tests. The objects of the studies were four different models of a vehicle having different parameters of the frame rigidity. For the needs of the research where conducted such tests as: "going into corner", "line change" and "tilt test". The results showed that a car with a rigid frame has better handling properties.

Keywords: frame stiffness, handling, stability, roll over, vehicle dynamics

I. Introduction

In order to improve drivability of a designed vehicle, manufacturers often try to increase torsional stiffness of a bearing system. Lately it has become to evolve a class of light commercial vehicles which have good handling qualities like light cars and have loading capacity comparable to trucks. While simulating the light car behavior for the purposes of stability control, the stiffness of their supporting systems is usually not accounted. This parameter can be ignored because of high stiffness together with low center of gravity and light weight. But a usual light commercial vehicle has a low stiffness of the bearing system, high center of gravity and it is heavier. Stiffness of the bearing system of a light car has an influence on the normal forces appearing in the wheels and on their dynamic reallocation while moving along an arc. Reallocation of the normal forces has an effect on vehicle handling and stability.

The study deals with the problem of calculation and experimental research of the influence of torsional stiffness of chassis frame, cab and the cargo platform on LCV dynamics in conditions of static rollover and dynamic curvilinear motion: going into corner and line changing. The objects of the research are LCVs with cargo beds (the vehicles loading capacity is up to 3.5 tons) that have a wide range of wheel base dimensions and, as a result, different torsional stiffness of the chassis frame. Thanks to the development of the simulation software, the authors had an opportunity to create a model for studying the car handling and stability properties, taking into account the stiffness of bearing systems. We assume that the study can help to determine the required stiffness of the supporting system, in order to meet the regulatory requirements on vehicle handling and stability at the design stages.

2. Object of research

The object of research is a light commercial vehicle. The object of the study was selected according to the contract Key parameters. A GAZelle NEXT LCV was chosen, having 3500 kg total weight and a distribution between the front and rear axle of 37.4% to 62.5% respectively. The vehicle has a frame structure. The wheelbase of the model is 3145mm, track width 1750mm for a front axle and 1560mm for a rear axle. The front axle suspension has a double wishbone structure with an antiroll bar. Suspension of the rear axle has a dependent structure based on semielliptical leaf springs with additional leaf springs and antiroll bar. The torque from the engine is transferred to the rear axle. The steering system of the car has a rack and a pinion. The tires used on the vehicle have a road tread and the following dimensions: 185 / 75R16.

3. Model

Handling and stability studies were carried out, the method contained in GOST 52302-2004 being used [1]. The critical velocity of the vehicle is the main indicator of passing the tests «Skid Pad» and «Lane change». The critical angle of inclination of the supporting area is the main indicator for the static stability of the vehicle. Car model and tests were carried out using the software package ADAMS/Car. The graphic image of the model is shown in Fig. 1. The vehicle model takes into account the sprung and unsprung mass with inertia moment. The elastic model has a sprung mass distributed in total between 7 parts.

The tire model takes into account vertical, lateral and longitudinal stiffness and adequately simulates the sideslip as consequence of lateral forces appearance. The model takes into account the kinematics of the suspension as it affects on the cross angle of the wheel, tire model takes this phenomenon into account also. The model takes into account force of air resistance because of the possible test speed can be up to 80 km/hr when the power of the air resistance becomes important.



Fig. 1. View of the model with flex elements of the support system

The object of the research is a LCV with cargo platform that presented as a multi-body model with three flexible (deformable finite element models) parts: cab, frame and cargo platform. The simulation is done in MSC.ADAMS/CAR and MSC.NASTRAN software, which allows imitating the LCV dynamics with considering flexibility of chassis frame. The initial stage of this study is presented in Refs. [2,3], where the combination of experimental and simulation methods were described for estimating LCV active safety characteristics such as cornering stability. The experimental method of estimation of cornering stability is based on the regulations of the Russian Standard GOST R 52302-2004 that presuppose static and dynamic vehicle testing. The multi-body simulation method is based on MSC.ADAMS/CAR software capabilities. The approval of developed LCV multi-body model is done on a basis of good correlation between simulation results and experimental data.

Ref. [2] presents the simulation results that were obtained using the multi-body LCV model, which have a frame, a cabin and a cargo platform presented by rigid bodies. Only one modification of LCV was studied (basic modification with wheelbase 3145 mm). This study is a continuation of the research presented in Ref. [2] and pays key attention to:

- Estimation of the influence of wheel base on torsional stiffness of a chassis frame;
- · Analysis of the deformation mode of a chassis frame in dependence of a type of frame

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extender construction and fixation (for different wheel base magnitude);

• Estimation of the influence of subframe construction on the total torsional stiffness of chassis frame with extended wheel base;

• Estimation of the influence of torsional stiffness of a chassis frame on LCV static rollover characteristics (Fig. 2) and dynamics ones: critical speed of a curvilinear maneuver, wheels vertical reaction, roll of a vehicle (Fig. 3).



Fig. 2. Simulation of the static rollover test

Fig. 3. Simulation of "going into corner" test

Four models having different stiffness of the supporting system were studied. The different rigidity was obtained by varying the thickness of the longitudinal and transverse frames. All models and their distinctive characteristics are described in Table 1. Every model has participated in three tests (two dynamic and one static). The torsional stiffness was measured for all of the vehicle elements: frame, cabin and loading platform. The torsional stiffness can be calculated as a ratio of the rotation torque to the radial angle appearing in the supporting system as the result of this torque.

Model	Wheel base, m	Type of carrier	Torsional stiffness of the bearing system, Nm / deg
1	3.1	Rigid	-
2	3.1	Flex standard thickness	1780
3	3.1	Longitudinal longerons thickened by 2 mm and lateral by 1 mm	2138
4	3.1	Longitudinal longerons thinned by 2 mm and lateral by1 mm	826

Table 1. Models and their distinctive properties

4. Input control

During the dynamic tests, the vehicle has to move within a given corridor without run over a cone. To keep moving between the cones, it is necessary to turn a steering wheel. This action was provided using a steering controller. The controller compares the position of the vehicle, relative to a desired path, and turns the steering wheel to provide the motion as near as possible to the path. Fig. 4 shows the trajectory that was used in simulation tests of the «going into corner». The trajectory was obtained by the method of iterative changes for achievement a maximum speed of the vehicle. All the changes for the trajectory should be done manually by a modeling engineer.

Fig. 4 shows that the trajectory does not match the midline; it is connected with changes of the vehicle speed. At the beginning of the test, the vehicle moves at a constant speed. Because of the forces of air resistance and tire rolling resistance, its speed is not constant. That's why throttle control should be done by the speed controller, which compares the actual vehicle speed with a fixed value and changes the throttle, in order to provide constancy of the speed.



Fig. 4. Trajectory of the test «going into corner»

5. Results

The results of research allowed setting the dependence of dynamic curvilinear motion and static rollover stability on torsional stiffness of a chassis frame. The red dotted line (Fig. 5) shows the results of a study "going into corner" obtained for the vehicle rigid model. The model has a better handling and its critical speed is 63.2 km/hr. Thanks to this test, critical speeds for different car models with rigid carrier systems were established. A relationship between the rigidity of the supporting system and the critical speed was found as follows: in order to increase the critical speed by 1%, it is necessary to increase the torsional rigidity by 20%. In its turn, increasing the torsional stiffness of the frame leads to increasing the mass by 34%. Thus the increasing of the torsional rigidity is not efficient for improving the vehicle handling.

Analogous results were obtained for the study "lane change" (Fig. 6). In this case the rigid model had a better handling and its critical speed was 72.5 km/hr.





Fig. 5. Dependence of the maximum speed on the torsional stiffness for the test "going into corner": flex frame - rigid frame

Fig. 6. Dependence of the maximum speed on the torsional stiffness for the test "lane change:" flex frame - rigid frame

Figure 7 shows the results of the study "tilt", i.e. the dependence of the critical angle of the rotary platform on the chassis frame torsional stiffness. Here, in order to increase the critical angle by 1%, it is necessary to increase the torsional rigidity by 20%. As before, increasing the torsional rigidity is not efficient for improving the vehicle static stability. The red dotted line shows the results for the rigid model, which had a better static stability and showed the critical angle of 37.2 deg.

From the study it follows that the indicators of handling and static stability have a direct

connection with the torsional stiffness of the chassis frame. Even small improvements in handling and stability require significant increase of the torsional stiffness.



Fig. 7. Dependence of the critical angle of the supporting rotary platform on the torsional stiffness of LCV frame: flex frame - rigid frame

6. Conclusion

The study showed that the torsional stiffness of the supporting system affects the handling and stability indicators of a light commercial vehicle. Between the torsional rigidity and handling and stability properties there is a positive relation. Dynamic indicators have a negative exponential dependence on the torsional rigidity. Disregarding the stiffness of the supporting system, during the modeling of a light commercial vehicle motion, leads to an overestimation of the dynamic properties by about 5% and of the static stability by about 1%.

This study could be useful for determining the stiffness of a chassis frame for a light commercial vehicle at the design stage. Based on the test results, it is possible to make decision on optimal choice between the torsional stiffness and the weight of a bearing system.

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ADDED MASS STUDY OF PLANE STRUCTURES AT THEIR VARIOUS MOTIONS

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Abstract. Using FE analysis, this work fully devoted to added masses determination of the plate in infinite liquid in the case of different movements. Various forms and sizes of the plate are considered. The problem consists of two parts: first is studying of the plate motion in liquid as rigid; second is studying of the plate vibrations in its own modes, fixed with a hard screen and contacting with liquid by one side. The condition observance of liquid environment continuity leads to the Laplace equation, which is solved by using numerical approach. Finite element analysis of steady state problem is performed for added masses determination using thermal analogy. A compact analytical solution of the two considered problems is presented. The results of finite element analysis and corresponding analytical results of the problems are compared for the case of infinite liquid environment.

Keywords: added mass, finite element analysis, vibration mode, Laplace equation, thermal analogy, velocity potential

1. Introduction

The knowledge of the added masses of bodies contacting with liquid is necessary for solving various applied problems of hydromechanics, such as steady and transient motion of rigid bodies, vibration of bodies in liquid, local vibration of constructions in a fluid environment.

In all equations determining the parameters of ship motion, their general vibrations and hull shell vibration, the inertial properties of liquid are expressed by the added masses. For the last 50 years, a lot of journal articles [1] and sections in monographs [2-4] on theoretical and applied hydromechanics have been devoted to the added mass determination. The studies of the ships dynamics and their particular components lead to the need of solving these problems.

The method of thermal analogy, which is used in this work, is widely known in scientific community [1]. This method is very convenient for solving the Laplace equation, which is used for calculating the added masses of liquid. The motion of any structures as rigid, immersed in liquid, are widely represented in the articles and books, but there are not a lot of publications describing the movements with vibrations and deformations. Thus, for the complete added masses representation for the various structures movements in liquid both types of movements are studied in the work: vibrations and motion as rigid body.

The purposes of the work are the added masses determination of the plate immersed in liquid by numerical method and analyzing the influence on result structure dimensions and liquid environment.

Added mass study of plane structures at their various motions

2. Added masses of bodies

Rigid motion of a body. We will calculate the added masses in the case of translational motions of a circular disk of radius r_d , immersed in infinite liquid. There is analytical solution of the problem [4]. We suppose that a rigid body of volume *V* has an external surface *S*. This body starts to move from initial position in infinite ideal homogeneous liquid without vortexes. Then the flow caused by the body motion will be potential during the motion. We need to introduce some hypotheses to solve this problem [5]:

- We consider only small oscillations of a plate in liquid, which are described by linearized equations. There are small displacements of the plate, and liquid is moving along with the plate in perfect contact;
- We assume that the liquid is incompressible;
- We suppose that shape modes of the plate in liquid environment and empty space are identical.

Thus, the liquid influence on the plate oscillations will be inertial and the mass of the plate is increasing, therefore its own frequencies are decreasing.

We will use coordinate system z, associated with the body. There are no vortexes, so that there is a potential function $\Phi(x, y, z, t)$, which is characterizing velocities of flow, which is arising in the case of structure vibrations in liquid. The components of liquid velocity are determined by the following relations:

$$\nu_x = \frac{\partial \phi}{\partial x}; \nu_y = \frac{\partial \phi}{\partial y}; \nu_z = \frac{\partial \phi}{\partial z}.$$
 (1)

In this case the condition of observance of liquid environment continuity leads to Laplace equation:

 $\Delta \Phi = 0.$

The boundary condition for equation (2) is:

1. There is no leak on the external surface S:

$$\frac{\partial \Phi}{\partial n} | = v_n$$

(3)

(2)

i.e. the projection of the liquid particle velocity on the external normal n to the surface is equal to the projection of the body point velocity on the same normal;

2. The absence of liquid particles motion at an infinite distance from the body:

$$\lim_{r \to \infty} \frac{\partial \Phi}{\partial x} = \lim_{r \to \infty} \frac{\partial \Phi}{\partial y} = \lim_{r \to \infty} \frac{\partial \Phi}{\partial x} = 0, \tag{4}$$

where $r^2 = x^2 + y^2 + z^2$ is – the distance from the origin to an arbitrary point of liquid;

3. The existence of a free surface S_1 on which the body moves (additional condition [3]): $\Phi|_{S_1} 0.$ (5)

Potential Φ can be represented in the following form

$$\Phi = \nu_{0x}\varphi_1 + \nu_{0y}\varphi_2 + \nu_{0z}\varphi_3 + \omega_x\varphi_4 + \omega_y\varphi_5 + \omega_z\varphi_6.$$
(6)

Formula (6) shows that φ_i (i = 1, ..., 6) are the potentials of liquid flows in the cases of the body motion along the x, y, z – axes or rotation about these axes i = 4, 5, 6 with the unit linear (or angular) velocities. Thus, the problem of the body movements in infinite ideal liquid consists of solving six problems. These problems are formulated in the following way: we need to solve the Laplace equation $\Delta \varphi_i = 0$ with the boundary conditions:

$$\begin{split} &\frac{\partial \varphi_1}{\partial n} |_S = \alpha \;, \\ &\frac{\partial \varphi_2}{\partial n} |_S = \beta \;, \\ &\frac{\partial \varphi_3}{\partial n} |_S = \gamma \;, \\ &\frac{\partial \varphi_4}{\partial n} |_S = (y\gamma - z\beta), \end{split}$$

 $\begin{aligned} &\frac{\partial \varphi_5}{\partial n}|_S = (z\alpha - x\gamma),\\ &\frac{\partial \varphi_6}{\partial n}|_S = (x\beta - y\alpha),\\ &\lim_{r \to \infty} \frac{\partial \varphi_i}{\partial x} = \lim_{r \to \infty} \frac{\partial \varphi_i}{\partial y} = \lim_{r \to \infty} \frac{\partial \varphi_i}{\partial z} = 0,\\ &\text{where } r^2 = x^2 + y^2 + z^2. \end{aligned}$

In the work we are studying translational motion along z –axis and rotation about x and y – axes. Thus, we need to solve three problems $\Delta \varphi_{3,4,5} = 0$ with the following boundary conditions:



Fig. 1. Translational motion along *z* – axis



Fig. 3. Rotation about y - axis

 $Lim_{r\to\infty}\frac{\partial\varphi_{3,4,5}}{\partial x} = Lim_{r\to\infty}\frac{\partial\varphi_{3,4,5}}{\partial y} = Lim_{r\to\infty}\frac{\partial\varphi_{3,4,5}}{\partial z} = 0,$

where $r^2 = x^2 + y^2 + z^2$ – the distance from the origin to an arbitrary point of liquid.

In the case, when the plate is moving on the surface of liquid as was noted earlier the additional condition of free surface existence is introduced

$$\varphi_{3,4,5}|_{S_1} = 0.$$

The kinetic energy of liquid enclosed between the surface of a moving body S and a stationary spherical surface Σ of radius a surrounding the body and the volume of liquid V adjacent to it, is defined as

$$T = -\frac{1}{2}\rho \iint_{S} \Phi \frac{d\Phi}{dn} dS, \tag{7}$$

where ρ is the liquid density.

Using the expression for the velocity potential (6), and denoting $v_{0x} = v_1$; $v_{0y} = v_2$; $v_{0z} = v_3$; $\omega_x = v_4$; $\omega_y = v_5$; $\omega_z = v_6$, we have

$$T = \frac{1}{2} \sum_{k=1}^{6} \lambda_{ik} v_i v_k.$$
(8)

The added masses of liquid adjoining to the surface of the moving body can be determined by the following formulas

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$$\lambda_{i} = \rho \iiint_{V} \left[\left(\frac{d\varphi_{i}}{dx} \right)^{2} + \left(\frac{d\varphi_{i}}{dy} \right)^{2} + \left(\frac{d\varphi_{i}}{dz} \right)^{2} \right] dx dy dz, \tag{9}$$

$$\lambda_{ik} = -\rho \iint_{S} \varphi_{k} \cdot \frac{\omega_{k}}{dn} dS . \tag{10}$$

For the numerical computation in the ANSYS software in the cases of translational motion along z – axis and rotation about x and y – axes we can use the thermal analogy of steady state problem [1], i.e. $\Delta \varphi_i = 0 \ll \Delta T = 0$.

The condition of the function assignment $\frac{d\varphi_i}{dn}|_S$ on the surface *S* is equal to the condition of the heat flux existence $-k\frac{dT}{dn}|_S$ on the same surface of the body, i.e.

 $\frac{d\varphi_i}{dn}|_S = -k\frac{dT}{dn}|_S = q_n|_S,$

where k – a thermal conductivity coefficient. When k = 1,

$$q_n|_S = \frac{d\varphi_i}{dn}|_S,$$

where functions $\frac{d\varphi_i}{dn}|_S$ depend on the body motion types.

Additional condition (4), having the form

$$Lim_{r\to\infty}\frac{\partial\varphi_i}{\partial x} = \lim_{r\to\infty}\frac{\partial\varphi_i}{\partial y} = \lim_{r\to\infty}\frac{\partial\varphi_i}{\partial z} = 0,$$

is equivalent to the condition that the temperature gradient is zero at the infinity from the moving body, i.e.

 $\nabla T|_{r\to\infty} = 0 \Longrightarrow q|_{r\to\infty} = 0.$

Additional condition (5) of the free surface existence is equivalent to the condition that the temperature is zero on the liquid free surface, i.e.

 $T|_{S_1}=0.$

Tables 1 and 2 show the results of added masses. These results have calculated by two different ways such as integration over the outer surface (S), which is external surface of considered domain, and volume integration (V). The convergence of added masses on the size of liquid environment is presented in Figs. 4, 5.

Formulation		Added mass, kg			
Analytical estimation					
A.I. Korotkin, 1986 [4]		21 333.33			
Numerical results ($r_d = 2 m$)					
$q_n _S = 1$	R, m	S	V		
$ q_n _{r=R} = 0$	10	20 626.16	20 311.90		
T = 0 on the cut surface	20	20 566.76	20 250.92		
	30	20 560.40	20 239.33		

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Table 2. Added masses in the case of rotation about x or y .	– axes
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Formulation	Added mass, kg				
Analytical estimation					
A.I. Korotkin, 1986 [4]	orotkin, 1986 [4] 11 377.78				
Numerical results ($r_d = 2 m$)					
$q_n _S = -x$	R, m	S	V		
$ q_n _{r=R}=0$	10	10 662.49	10 391.97		
T = 0 on the cut surface	20	10 662.06	10 390.99		
	30	10 661.97	10 390.14		









Vibrations of a fixed rectangular plate. In the second part of the work we are solving more difficult problem of the rectangular plate vibrations in an infinite liquid. The plate dimensions are $a \times b$. Here, as the motion of the plate, we will consider its vibrations by 1st mode shape. In the first part of the work we introduced the hypothesis that the liquid is incompressible. The influence of the liquid compressibility on vibrations is determined by dimensionless parameter, which is called the Strouhal number:

 $S_t = \omega l/c_0$,

(11)

where c_0 is the sound speed in water; l is the characteristic size, i.e. is the distance between the nodes of a vibration mode; ω is the vibrations frequency.

We need to use previous formulas (9) and (10) for determining the added masses in the case of the plate vibrations in an infinite liquid. We are solving the problem in the case, when a part of the volume boundary, adjoining to the plate, is represented by rigid screens S_1 , for which

$$\frac{d\Phi}{dn} = 0.$$

In connection with the new problem formulation, the boundary conditions will change.

We suppose that the displacements of the plate wetted surface along the normal *n* are characterized by the vector of generalized coordinates a(t) and by the vector of coordinate functions f(x, y, z), so that the displacement $w_n(x, y, z, t)$ can be found as the scalar product $w_n(x, y, z, t) = a(t)^T \cdot f(x, y, z)$.

The motion velocity $v_n(x, y, z, t)$ can be found as the scalar product $v_n(x, y, z, t) = \dot{a}(t)^T \cdot f(x, y, z)$,

where x, y, z – the coordinates of points on the surface S.

Using boundary condition (3), the velocity potential Φ can be found similarly as the scalar product

$$\begin{aligned} \phi &= \boldsymbol{\tau}(t)^T \cdot \boldsymbol{\varphi}(x, y, z). \\ \text{We insert (12) into (3)} \\ \frac{\partial \phi}{\partial n} |_S &= v_n \Rightarrow \\ \boldsymbol{\tau}(t)^T \cdot \frac{\partial \phi}{\partial n} |_S &= \dot{\boldsymbol{a}}(t)^T \cdot \boldsymbol{f}(x, y, z) \Rightarrow \\ \boldsymbol{\tau}(t) &= \dot{\boldsymbol{a}}(t), \\ \frac{\partial \phi}{\partial n} |_S &= \boldsymbol{f}(x, y, z). \end{aligned}$$
(12)

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Thus, the velocity potential can be presented in the following form

 $\boldsymbol{\Phi} = \dot{\boldsymbol{a}}(t)^T \cdot \boldsymbol{\varphi}(x, y, z).$

The each function φ_i , i = 1..N, as was noted earlier, is the velocity potential in the case of the wetted surface motion with a unit generalized velocity. So, the vector φ_i is the vector of the unit potentials. There are the boundary conditions for series of N problems, N is the number of modes, which are describing the complex body motion.

Using equation (2) and boundary conditions (3) and (4), we can obtain the equation and the boundary conditions for the functions $\varphi(x, y, z)$ sought. We insert (13) into (2): $\Delta \Phi = 0$,

$$\Phi = \dot{\boldsymbol{a}}(t)^{T} \cdot \boldsymbol{\varphi}(x, y, z) =>, \, \dot{\boldsymbol{a}}(t)^{T} \cdot \Delta \boldsymbol{\varphi}(x, y, z) =>, \, \Delta \boldsymbol{\varphi}(x, y, z) = 0,$$
(14)
on condition that $\dot{\boldsymbol{a}}(t) \neq 0;$
$$\frac{\partial \Phi}{\partial x}|_{S} = v_{n} = \dot{\boldsymbol{a}}(t)^{T} \cdot \frac{\partial \varphi}{\partial x}|_{S} = \dot{\boldsymbol{a}}(t)^{T} \cdot \boldsymbol{f}(x, y, z) =>$$

$$\int_{\partial n}^{\partial n} |_{S} = f(x, y, z); \tag{15}$$

$$(4) \Leftrightarrow \lim_{r \to \infty} \frac{\partial \varphi}{\partial x} = \lim_{r \to \infty} \frac{\partial \varphi}{\partial y} = \lim_{r \to \infty} \frac{\partial \varphi}{\partial z} = 0, \tag{16}$$

where $r^2 = x^2 + y^2 + z^2$ – the distance from the origin to an arbitrary point of liquid. The condition of rigid screen existence is presented in following form

$$\dot{\boldsymbol{a}}(t)^T \cdot \frac{\partial \varphi}{\partial n}|_{S_1} = 0 \Longrightarrow \frac{\partial \varphi}{\partial n}|_{S_1} = 0.$$
(17)

We can obtain the kinetic energy of liquid from formula (7)

$$T = -\frac{1}{2}\rho \iint_{S} \dot{\boldsymbol{a}}^{T} \cdot \boldsymbol{\varphi} \frac{d\varphi}{dn} \cdot \dot{\boldsymbol{a}} dS ,$$

or
$$T = \frac{1}{2} \dot{\boldsymbol{a}}^{T} \cdot [\lambda] \cdot \dot{\boldsymbol{a}},$$

where $[\lambda]$ – the matrix of added masses
$$[\lambda] = -\rho \iint_{S} \boldsymbol{\varphi} \frac{d\varphi^{T}}{dn} \cdot dS .$$
(18)

The problem consists in determining the added masses for two-mode vibrations of the plate:

• $f_Z(x, y) = \sin\left(\pi \frac{(x-\frac{a}{2})}{a}\right) \cdot \sin\left(\pi \frac{(y-\frac{b}{2})}{b}\right) - \text{simple-supported plate};$ • $f_Z(x, y) = \frac{1}{4} \left[1 - \cos\left(\pi \frac{(x-\frac{a}{2})}{\frac{a}{2}}\right)\right] \cdot \left[1 - \cos\left(\pi \frac{(y-\frac{b}{2})}{\frac{b}{2}}\right)\right] - \text{clamped-edge plate}.$

For confirmation of incompressible liquid hypothesis we have solved an additional problem of searching the first natural frequency for these plates (Table 3).

Table 3. First natural vibration frequency of the square plate (a = b = 4 m)

Analytical estimation, Rad/s	Numerical results, Rad/s				
freely-supported plate					
1.937	1.937				
clamped-edge plate					
3.652	3.531				

Knowing these frequencies, we can use formula (11) for determining the Strouhal number. Here parameter l = 4 m corresponds to the first mode shape, the sound speed in water is $c_0 = 1500 m/s$. Then we obtained Strouhal numbers for two types of the plate modes which are much less than one. Our hypothesis is confirmed.

(13)

For the numerical computation in the ANSYS software for the plate modes, simplesupported and clamped-edge plate, we can use the thermal analogy, i.e. $\Delta \varphi = 0 \ll \Delta T = 0.$

Condition (15) of the function assignment $\frac{\partial \varphi}{\partial n}|_{S}$ on the surface S is equivalent to the condition of the heat flux existence $-k\frac{dT}{dn}|_{S}$ on the same surface of the body, i.e.

 $-k\frac{dT}{dn}|_{S} = q_{n}|_{s} = \boldsymbol{f}(x, y, z),$

where k – the thermal conductivity coefficient. When k = 1: $q_n|_s = f(x, y, z)$,

where functions f(x, y, z) depend on the body vibration types.

Condition (16)

 $\lim_{r\to\infty} \frac{\partial \varphi_i}{\partial x} = \lim_{r\to\infty} \frac{\partial \varphi_i}{\partial y} = \lim_{r\to\infty} \frac{\partial \varphi_i}{\partial z} = 0$ is equivalent to the condition that the temperature gradient is zero at infinity, i.e.

$$\nabla T|_{r\to\infty} = 0 \Longrightarrow q|_{r\to\infty} = 0.$$

The condition of rigid-screen existence (17) is equivalent to the condition that the temperature gradient is zero on the rigid-screen surfaces, i.e.

 $\nabla T|_{S_1} = 0 \Longrightarrow q|_{S_1} = 0.$

For the numerical solution, we need to change the boundary conditions, in order to avoid the Neumann boundary condition, i.e. to assume that the velocity potential is zero at infinity

 $\varphi|_{r\to\infty} = 0 \Longrightarrow T|_{r\to\infty} = 0.$

Tables 4 and 5 show the comparison of the analytical and numerical results; the latter are obtained for different sizes of liquid environment R. The convergence of the added masses for the freely-supported plate on the size of liquid environment is presented in Figs. 6, 7.

Table 4. Added masses for a freely-supported plate

Formulation		Added mass, kg		
Analytical estima	tion			
V.V. Davydov, N.V. Mattes, 1974 [9]	6 560			
Yu.A. Shimanskiy, 1963 [2]	6 720			
V.A. Postnov, 1983 [3]		6 880		
Numerical results ($a = 4 m, b = 4 m$)				
$q_n _S = \sin\left(\pi \frac{\left(x - \frac{a}{2}\right)}{a}\right) \cdot \sin\left(\pi \frac{\left(y - \frac{b}{2}\right)}{b}\right)$ $T _{x=0} = 0$		S	V	
		5 867.96	6 477.48	
		6 020.83	6 082.67	
		6 109.81	6 037.70	
$a_n = 0$ on the cut surface	200	6 141.15	6 011.49	
	250	6 147.41	6 008.96	

Added mass study of plane structures at their various motions

Formulation Added mass, kg			, kg		
Analytical estimation					
V.V. Davydov, N.V. Mattes, 1974 [9]	2 970				
Yu.A. Shimanskiy, 1963 [2]		2 970			
V.A. Postnov, 1983 [3]	2 970				
Numerical results ($a = 4 m, b = 4 m$)					
$q_{n s} = \frac{1}{4} \left[1 - \cos\left(\pi \frac{(x-2)}{2}\right) \right] \cdot \left[1 - \cos\left(\pi \frac{(y-2)}{2}\right) \right]$	R, m	S	V		
	10	2 769.97	3 008.26		
$ T _{r-P} = 0$		2 855.67	2 842.77		
$q_n = 0$ on the cut surface	100	2 892.87	2 819.87		
***	200	2 905.50	2 811.47		
	250	2 908.03	2 807.11		









Fig. 7. Convergence of the added masses on the size of liquid environment, the calculations being done by integration over an outer surface and by volume integration

3. Conclusions

Rigid motion of a body.

- 1. The differences between the results of numerical solution and analytical result are less than 5%.
- 2. Increasing the size of liquid environment leads to computational complicating. For the circular plate motion, there is a convergence of the added masses in the case of increasing the liquid environment size R. There is the ultimate size of liquid environment R = 10a, where a is the radius of a plate.
- 3. For determining added masses on the plate translational motion, we used two methods of integration: integration over an outer surface of the plate and integration through the liquid volume. Both methods are acceptable for solving the problem; one can use any of them. However, it should be emphasize that the finite element model for volume integration requires a regular finite element mesh through the overall volume.

Vibrations of a fixed rectangular plate.

- 1. There is a convergence of the added masses for vibrations of a rectangular plate in the case of increasing the liquid environment size R.
- 2. One can select a reasonable limit for the liquid-environment size, above which there is no need to increase it. The difference of added masses for the liquid-environment sizes R = 200 m and R = 250 m is in the range 0.05 0.1%. Therefore the most suitable size is R = 50a, where a is the biggest side of a plate. Further increasing the size leads to computational complications without improving the results.
- 3. For vibrations of the rectangular plate in an infinite liquid, the differences between the numerical solution results and analytical one are no more than 6 %.
- 4. For solving this problem, as in the previous section, we used two methods of integration for determining added masses. As before, both methods are acceptable, but the finite element model requires again a regular finite element mesh through the overall volume.

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