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Receiving and research of thin films of graphite and oxide of aluminium as bases for high capacitance capacitors

Receiving nano-carbon, in particular, graphitic films of nanometer thickness and research of their properties is one of current problems of the modern science. Structural characteristics of such materials lead to origin of a row of unique features in their physical properties which can be used for creation of new types of electronic and optic instruments and devices. One of perspective forms of application of thin graphitic films can read use them as capacitors plate. Now the main type of the rechargeable batteries which are widely used in different areas, electrochemical sources are. At the same time row of their shortcomings, somehow: complicates their application, for example, in electric vehicles and different robotic devices. One of possible solutions of the matter, use of energy «collected» condensers is. At the same time it is possible to have the almost instantaneous charging and an opportunity of monitoring and control behind time and power of discharge. However application as similar power supplies of condensers of «traditional» construction does not allow receiving rather high capacity. Use as plates of the condenser of materials with minimum possible size of particles can be one of possible candidate solutions of the matter. As those the electrodes consisting of the thin carrying-out films on the basis of the particles of graphite applied on the transparent substrates can be used, for example. However in order that graphitized electrodes could be used in practice, they shall meet certain requirements. First of all to have high conductance, to be the transparent in optical band that is necessary for monitoring of thickness and in general structure of films by spectral methods. And, at last, they shall be steady against mechanical influences. Proceeding from the above, the real operation is devoted to receiving and a research of thin films of graphite and aluminum oxide as perspective materials for creation of high capacitance capacitors.

Keywords: graphite films, capacitor, aluminum oxide, spectral characteristics, element composition.

I Introduction

To carbon and its form as graphite, is paid much attention now. This interest is caused by recent opening of quasi-one-dimensional form and quasinolymer form of graphite (nanotubes and fullerenes). The science shows new opportunities of their application today. However before there were practically no data on a two-dimensional or quasit-two-dimensional form of graphite. On the available publications [1-2] it is possible to draw a conclusion that the closest to a 2D case was extraction from a crystal of hundreds of layers of graphite. It is natural that such gap in graphite studying (material with surprises) attracts keen interest of researchers [1-5].

In [1] films by thickness only several monolayers of graphite (ultrathin films) have been for the first time received. The conducted researches have proved that on the properties the received material is semimetal with small overlapping of a conduction band and a valence band. Authors [1-3] observed effect of the field, also noticeable by size, and ambipolar Hall Effect. Thus, in the received material becomes possible to change conduction of material and to change the main type of charge carrier by means of external electric field.

Existence of field effect and metallic conduction of the received material gives the grounds to assume that the two-dimensional form of graphite can be of the considerable interest to microelectronics and Nano electronics. The modern microelectronics is in continuous development. The main aspiration of this science to microminiaturization stimulates the scientific and technological research connected to it. As the materials and technologies existing at the moment approach a limit of the opportunities, the active search of new materials and the principles of operation of devices are carried.

The semiconductor materials used in the modern microelectronics have a row of basic restrictions. One of the mains is restriction of concentration and mobility of charge carriers. At the same time use of metal as the main material of microelectronics, perhaps, positively would affect high-speed performance and other important characteristics of microelectronic devices. However in case of implementation of this idea there are considerable hindrances, namely: it is impossible to control conduction of «thick» metal films as the field is almost completely screened already at a depth less nanometer.And films of such thickness can't almost be used for the specified purposes as they are extremely unstable. At the same time decanter researches graphene (graphite monolayer) and fine graphite and also ultra-thin graphite (several atomic layers) have shown that these materials are surprisingly stable. Samples, even contained in usual conditions, showed the reproduced results throughout rather long time. As conductivity of thin and ultra-thin graphite, as well as a decanter, it is possible to operate by means of the external field, a conclusion arises that these materials are of undoubted interest to microelectronics.

Along with it graphite films in combination with thin and ultra-thin conductor layers can be considered as a perspective object for creation of miniature condensers with high capacity. Now in the modern technical devices as power supplies electrochemical rechargeable batteries are, as a rule, used (SLO, NiCd, NiMH идр.). But all of them possess a number of essential shortcomings: they have big duration of receiving a charge, too small ratio «capacity weight», high cost, need of use of various types of chargers and so forth [4].

The specified shortcomings of electrochemical rechargeable batteries are of particular importance in case of their use in electric vehicles and different robotic devices. This circumstance constrains their application.

The possible solution of the matter is use for functioning of the specified devices of the energy which is saved up by capacitors [5-6]. Advantages of use of condensers as power supplies are obvious: almost instant battery charging, possibility of control and management of time and power of the category. However the capacitors of the condensers manufactured on technologies known now, as a rule, is rather small. In our opinion, use as high-capacity facings of the condenser of materials with minimum possible size of particles, for example, of films of thin and ultra-thin graphite can be one of possible versions of the solution of the matter. But in order that graphite films could be used in practice, they have to meet certain requirements. First of all they have to have high conductivity and to be stable to mechanical influences. Besides, films have to be transparent in the optical range as it gives the chance to exercise control of thickness and in general structure of films by spectral methods.

Various methods of receiving graphite films are known: magnetron dispersion of graphite [6], dispersion by his ionic bunch [7], laser ablation of a target [8] etc. However all these methods demand the difficult and expensive equipment and creation of special conditions for the realization.

In the real work researches on receiving films of ultrathin graphite and a research of their microstructural and electric characteristics for the purpose of assessment of a possibility of their application in quality as capacitor plate high capacitance. These researches of properties of the aluminium oxide films received by us which can be considered as the dielectric placed between condenser facings, and at the same time as a substrate for graphite films are also presented.

II. Experimental technique

As it was already mentioned, for receiving films of thin and ultra-thin graphite it is necessary to use particles with the smallest sizes (within several nanometers).

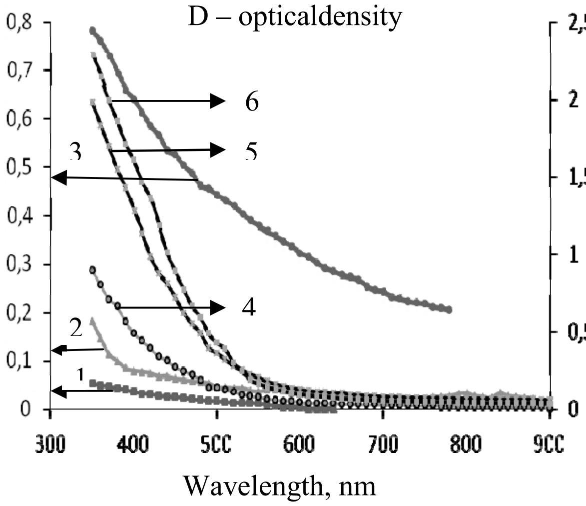
In general the problem of receiving nanoparticles now, despite abundance of the publications devoted to this problem is far from the decision. Especially it concerns receiving nanoparticles commercially. All methods used today, both physical, and chemical, are rather expensive and demand existence of the high-vacuum equipment. In the real work for this purpose the method offered by us [9], consisting in mechanical crushing of graphite, dissolution of the received powder during which there is a natural division of particles according to the sizes, and sampling for filling of films from various depths of solution was used. For receiving initial powder of graphite single-crystal graphite was used, powder of oxide of aluminium has been received from natural clay with his high content. For dissolution of powder of graphite toluene (chemically pure brands) was used, powder of oxide of aluminium was dissolved in the distilled water. Films received by method of putting solution on substrates.

As a substrate glass and quartz substrates, FTO substrates, substrates from stainless steel were used. For substrate solvent evaporation acceleration with the applied solution got warm at a temperature about 40 °C within a day. For the specified time solvent completely evaporated and on a surface of a substrate there was a thin film of graphite or oxide of aluminium. The holder designed by us a ditch with windows at the height of 1,2,5 and 3,5 cm from the upper edge standard ditches was applied to measurement of ranges of absorption at various depths of solutions. In one series of experiments of a particle of graphite were entered into a polymeric matrix of polyvinyl alcohol (PVA).

The research of spectral characteristics of films was conducted on the spectrophotometer Federation Council-46. The microstructure of the received films and their element structure were studied by means of an electronic raster microscope of MIRA3 LMU (TESCAN, the Czech Republic) [9]. Electric characteristics of films were measured by a digital multimeter of UNI-T.

III. Results and discussion

The absorption spectrum of solutions of clay received during the experiment in water and graphite in toluene are given in the Figure 1.



Curves 1-3 – water solution of oxide of aluminium; curves 4-6 – graphite solution in toluene

Figure 1. Ranges of absorption of solution of oxide of aluminium and graphite [9]

Absorption spectrum of the film samples of graphite received by selection of particles from different depths of solution (Fig. 2) have shown that the optical plane of the films received from the particles which are selected from solution depth in 1 cm (a curve h=1 cm), is much less than similar indicators for the films received by sampling from deeper layers (curves h=2 cm and h=3 cm).

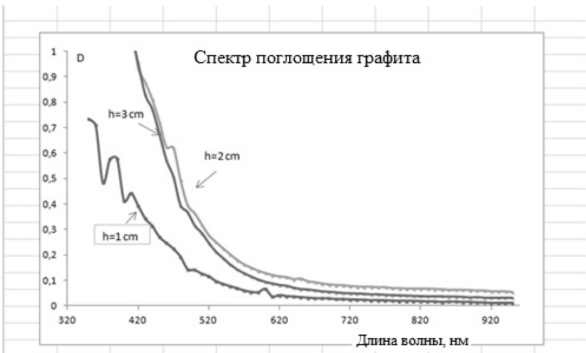
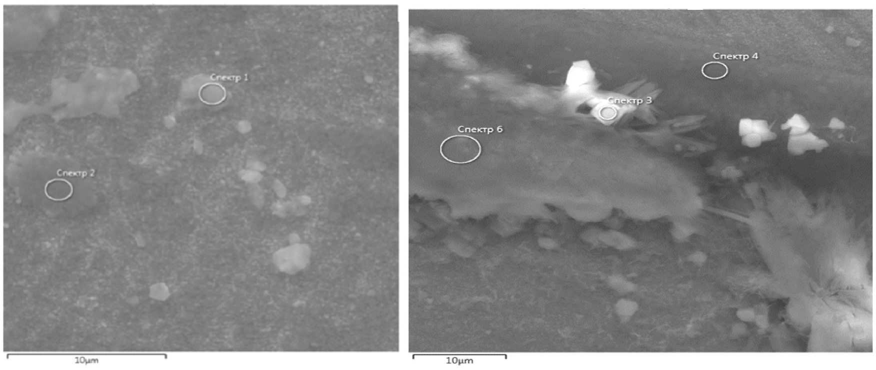


Figure 2. Absorption spectrum of films of graphite,
received by sampling from different depths of solution [9]

For aluminum oxide films ranges of absorption of water solutions and film samples practically coincide. The analysis of the received dependences shows that optical density of both solutions, and films grows with increase in depth of sampling that can be considered as an indirect demonstration of that fact that particles of the dissolved substances (oxide of aluminium and graphite) settle down in volume of solution unevenly: in the top layers the smallest particles accumulate, then – particles of the average sizes, and, at last, in the lower layers – the heaviest. The general course of curves of absorption demonstrates existence of the centers of absorption in short-wave area, in a visible part of a range and near infrared area absorption is practically absent.

The dimension of the received particles and structure of the formed films of aluminium oxide have been investigated by methods of electronic microscopy. In the Figure 3 the photo of the electronic image of a film of aluminium oxideon the scale of 10 microns is submitted.



a) b)

Figure 3. Micro photos of aluminium oxide

In photos the zones («a spectrum 1» and «a spectrum 2» in Fig. 3, a, and «a spectrum 3», «a spectrum 4», «a spectrum 5» and «a spectrum 6» in Fig. 3, b) containing the increased concentration of particles of oxide of aluminium are accurately visible.

Results of a research of element structure of the films consisting of particles of aluminium oxide of different dimension in the designated zones («spectra» 1,2,3,4) are presented in Figures 4-6. As appears from the submitted data, on the sites of a film designated as «a spectrum 1» and «a spectrum 2» is observed the increased maintenance of such elements as Sn tin, Na sodium, oxygen O, Cl chlorine, Ca calcium, Si silicon. High content of tin in films can be connected with the fact that as the carrying-out covering in substrates of FTO the tin oxide film alloyed by fluorine is used. And a significant amount of atoms of sodium is probably caused by composition of natural clay which was used as an aluminium oxide source.

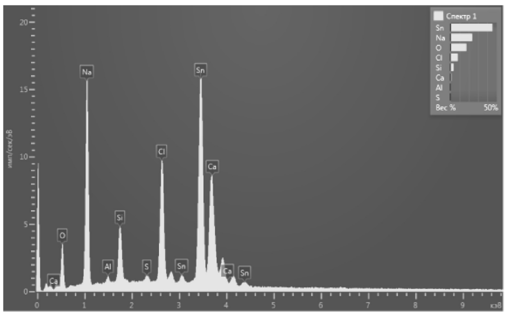


Figure 4. Element structure of a film with aluminium oxide (zone «spectrum 1»)

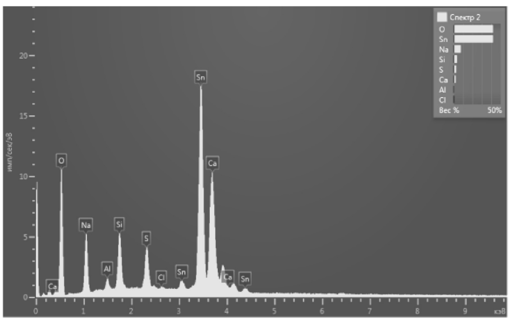


Figure 5. Element structure of a film with aluminium oxide (zone «spectrum 2»)

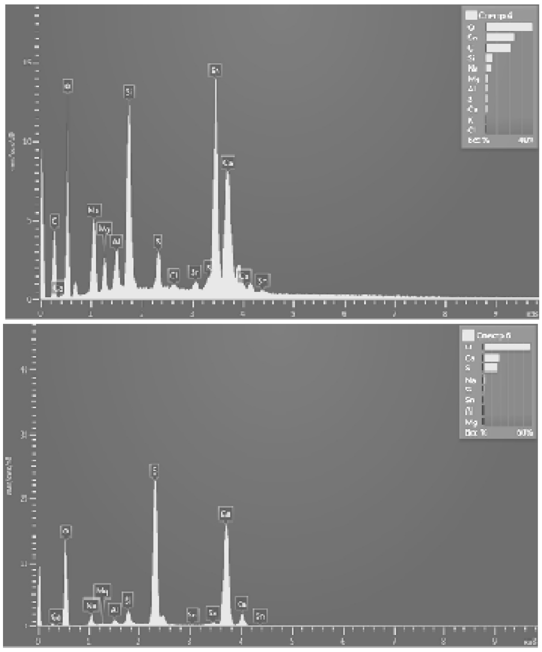
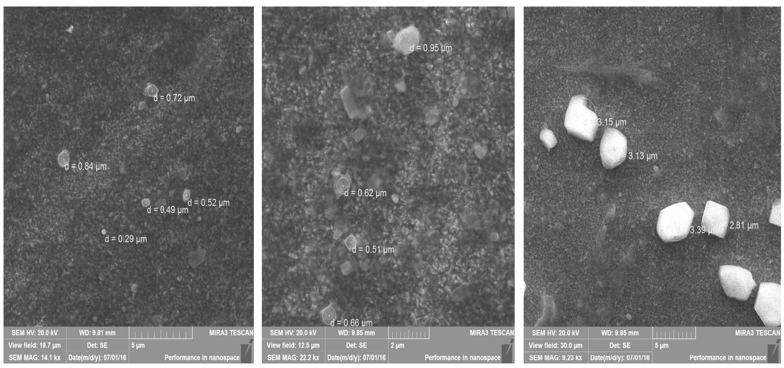


Figure 6. Element structure of a film with aluminium oxide
(the zones «spectrum 3» – top figure and «spectrum 4» - the lower drawing)

The analysis of the submitted data on a research of element structure of films shows that distribution of atoms of aluminium in films is non-uniform and, respectively, aluminium oxide is distributed on a surface of films unevenly. The highest concentration of aluminium oxide is observed in a zone of the film designated as «spectrum 4» (Fig. 6).

The given the element analysis which is carried out by us and received micro photos of films have allowed to carry out more exact assessment of the sizes of particles of aluminium oxide (Fig. 7, a,b,c).



a b c

Figure 7. The results of the study of the microstructure of the oxide films of aluminium

The submitted data unambiguously demonstrate that in process of increase in depth of an intake of solution for production of films the sizes of particles increase. The films created from solution depth in 1 cm (the Fig. 7, a), consist of small particles (from 0,29 microns). From the center of solution the films containing particles which sizes are from 0,51 to 0,66 microns are received. The films received from the lower layers of solution contain the largest particles (the sizes exceed 100 microns). Thus, using the method offered by us, it is possible to receive the films consisting of particles of in advance set dimension.

Test graphitic films have been received from toluene solution by watering on glass and quartz substrates and had rather non-uniform structure. The considerable values of electric resistance of these films (from 200 to 400 Ohm, Ω) received by us are probably connected with this fact. Besides, they were mechanically fragile and difficult separated from substrates (stuck), especially films with the high content of graphite. Similar properties also the films received from graphite solution in polyvinyl alcohol (PVA), created on glass and aluminum surfaces had. When using plastic capacitor plate of sticking effect it wasn't found, films easily separated from substrates, were elastic and mechanically rather strong. The received films can be used as condenser facings. Particles of graphite are packed in a polymeric matrix which is flexible material. Having respectively increased length of a polymeric film, and then having wrapped her in several layers, it is possible to receive facings of capacitor plate of higher capacitance, without increasing at the same time the geometrical sizes of the condenser.

IV. Conclusion

Thus, the conducted researches allow drawing a conclusion that the technology offered by us allows to receive the thin-film carrying-out films on the basis of the particles of graphite packed into a polymeric matrix. Such technology doesn't demand use of the high vacuum technology and the cooling systems. Results of spectral measurements and a research of microstructural characteristics of films have shown that films at which production the tests which were selected from various depths of initial solution were used have various dimensions. The graphitic films which are built in polymeric matrixes of polyvinyl alcohol possess the best mechanical and electric characteristics. Electric resistance of the received films is from 200 to 400 Ohm, Ω.

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Сыйымдылығы жоғары конденсаторлар негізі ретінде жұқа графитті қабыршақтары мен алюминий тотығын алу және оларды зерттеу

Қалыңдығы наноөлшемді графит қабыршақтарын алып, олардың электрфизикалық қасиеттерін зерттеу қазіргі заманғы ғылыми маңызды бағыттардың бірі болып табылады. Көміртегі қабыршақтары қасиеттерінің ерекшеліктері негізінде әртүрлі электрондық, оптоэлектрондық сезгіш тетіктер, құрылғылар жасауға болады. Мысалы, графит наноқабыршақтары негізінде сыйымдылығы жоғары конденсаторлар құрастыруға мүмкіндік бар. Қазіргі кезде негізінен электрхимиялық энергия көздері көп қолданылады. Алайда олардың кейбір сипаттамалары оларды электрмобильдерде, робототехникада кең қолдануға мүмкіндік бермейді. Бұл мәселенің оң шешілу жолдарының бірі — конденсаторда жиналған энергияны пайдалану. Алайда қолданыстағы конденсаторлар арқылы мол энергия жинау мүмкін емес. Бұл мәселені түбегейлі шешудің жолы — конденсатордың астарын нанобөлшектерден құрастыру. Мысалы, конденсатордың астарларын мөлдір төсенішке «жабыстырылған» графит нанобөлшектерінің қабыршағын пайдалану. Графит нанобөлшектерінен жасалған қабыршақтың электрөткізгіштігі жоғары, оптикалық аралықта мөлдір, механикалық әсерге төзімді болуы керек. Мақалада алюминий тотығы тілігі бетінде графиттің жұқа қабыршағын алу әдістері және оның физика-химиялық қасиеттерін зерттеу барысында алынған деректер келтірілген.

Кілт сөздер: графит қабыршағы, конденсатор, алюминий тотығы, спектралдық сипаттама, элементтік құрам.

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Получение и исследование тонких пленок графита и оксида алюминия как основы для высокоемкостных конденсаторов

Получение нано-углеродных, в частности графитных, пленок нанометровой толщины и исследование их свойств являются одними из актуальных направлений современной науки. Структурные характеристики таких материалов приводят к возникновению ряда уникальных особенностей в их физических свойствах, которые могут быть использованы для создания новых типов электронных и оптических приборов и устройств. Одним из перспективных форм применения тонких графитных пленок можно считать использование их в качестве обкладок конденсаторов. В настоящее время основным типом широко используемых в разных областях аккумуляторных батарей являются электрохимические источники. Среди недостатков — затруднено их применение, например, в электромобилях и различных робототехнических устройствах. Одним из возможных путей решения данного вопроса является использование энергии, «собранной» конденсаторами, при этом можно получить практически мгновенную зарядку и возможность контроля и управления за временем и мощностью разряда. Однако применение в качестве подобных источников питания конденсаторов «традиционной» конструкции не позволяет получить достаточно большой емкости. Одним из возможных вариантов решения данного вопроса может быть использование в качестве обкладок конденсатора материалов с минимально возможным размером частиц. В качестве таковых могут быть использованы, например, электроды, состоящие из тонких проводящих пленок на основе частиц графита, нанесенных на прозрачные подложки. Однако для того чтобы графитовые электроды можно было использовать на практике, они должны отвечать определенным требованиям, в первую очередь — обладать высокой электропроводностью, быть прозрачными в оптическом диапазоне, что необходимо для контроля толщины и в целом структуры пленок спектральными методами. И наконец, они должны быть устойчивы к механическим воздействиям. Работа посвящена получению и исследованию тонких пленок графита и оксида алюминия как перспективных материалов для создания высокоемкостных конденсаторов.

Ключевые слова: графитовые пленки, конденсатор, оксид алюминия, спектральные характеристики, элементный состав

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