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Preparation and Investigation of Diamond-Like Carbon Nanostructured Films

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Abstract: A novel equipment of preparation of films by low temperature plasma assisted chemical vapor deposition (CVD) technique is built which allowed controlling the technological process in real-time mode. Diamond-like carbon (DLC) films were synthesized which exposed 99% transparency in wide range of spectrum, $\lambda = 250 – 1100$ nm. Also, technical modes using Ta_2O_5 stimulator were found allowing to obtain low resistivity of DLC as low as 310 – 4 Ohm cm at the optical transparency remaining as high as 85%. The features of the surface of films were studied by atomic force microscopy (AFM) and the layer adjacent to the surface by scanning electron microscopy (SEM). It is shown that stimulating centers on the substrate surface form nanotubes arranged parallel to the surface due to which electrical conductivity of the DLC film grows higher.

Keywords: Technology of Nanostructure, Diamond-Like Carbon Films, Plasma Enhanced CVD Method, Conductive and Transparent Films, AFM, SEM

1. Introduction

DLC films got great demand in the economy and engineering and other fields due their unique mechanical, optical, chemical and electrical properties as well as for low cost, environmentally cleanness and availability of row materials [1 – 3]. These special properties remain to be important for amorphous films containing diamond and other carbon phases and for 2D crystals of grapheme [4, 5].

Plasma assisted CVD method exposes great potential in developing layers of unprecedented electrical properties ranging from insulator to conductor as well as materials of different refractive and extinction indices [5, 6]. The latter parameter allows one to use DLC films in devices of conversion of Solar energy [7, 8]. Here, the difficulties of identification are mentioned, since in the spectrum of plasmonic radiation due to neutral atoms, molecules and their radicals, and due to ionized atoms, the lines overlap [9 – 11]. For this reason the plasma radiation spectra of different materials – toluene, argon or nitrogen and other gases used in the work – were studied which allowed identifying separate radiation lines or line complexes in low temperature plasma used for obtaining nanostructured carbon films [12]. Transparent films of DLC were obtained and their electrical properties were studied, the resistivity of which were decreased to $3 \cdot 10^{-3}$ Ohm · cm [12]. This work aimed to obtain transparent DLC films with resistivity lower by an order by means of developed method of generating nanotubes.

2. Method of DLC Preparation and Deposition Apparatus

The method of preparation of carbon films based on previously developed method of low temperature plasma assisted CVD is described in [5, 7]. For synthesizing nanostructured films, more powerful and different ion sources as well as much more sensitive methods of controlling were needed. To solve the problem, and to enhance the capability of synthesizing method apart from DC magnetron evaporating facility and radial ion source a new linear ion source was mounted at the watching window, which guarantees synthesizing of a film at higher power of 80 to 240 W. The real-time control of technological parameters gets more importance by registration of the spectrum corresponding to the plasma composition and determination of energy of plasma particles as well as their control through the whole process. It is important also to control the rate of growing of the film thickness during the process. To measure it, a

thickness measuring device (Mikron 7) was installed in the vacuum chamber. The view of improved technological apparatus and the scheme of vacuum chamber are given in Figure 1.

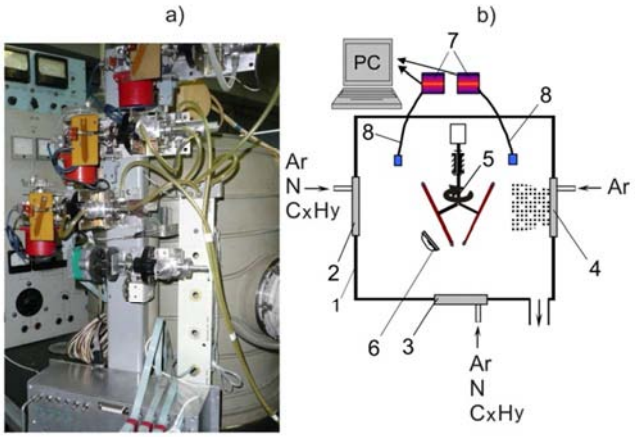

Figure 1. *a) The view of technological equipment and b) the internal layout of vacuum chamber. 1 – vacuum chamber, 2 – radial ion source, 3 – linear ion source, 4 – magnetron evaporation source, 5 – substrate rotating system, 6 – head of the system of measuring the film thickness, 7 – system of the registration of plasma spectrum, and 8 – fiber optics.*

In Figure 1, a view of technological chamber with controlling drivers and sensors is shown. The plates on which the nanostructured films were deposited were mounted on the system providing satellite movement (Figure 1b). Initial vacuum of 10^{-6} mm Hg is maintained by Pfeiffe turbo molecular pump, after which Ar and N_2 gases and hydrocarbon composition of C_xH_y with desired ratio are injected into the ion and magnetron sources with 1 – 2% accuracy. On the outer side of vacuum chamber three systems of gas control and of sensors are mounted, which were run by microcontrollers. In this system plasma flow distribution at different points are controlled by the system of sensors of real-time registration of plasma spectrum, using flexible optical fibers. This allows controlling the 3D distribution of plasma from the ion source to the plate. The plasma spectrum was measured by HR2000 + spectrometer of Ocean Optics in the range of 200 – 1100 nm. The measuring period is about 100 s, which allows conducting measurements along with the changes occurring in plasma.

At constant power and for the same composition of gas mixture a bias voltage in the range of –300 to +300 V was applied to the substrate rotating system. The bias voltage applied to the plate, which varies the kinetic energy of the particles causes the change in ratio of diamond-like and graphite phases in the film structure. The change in that ratio causes changes in conductivity and optical transmission. In case of domination of diamond-like phase the resistivity and optical transmission of the film are high.

In Figure 2 the radiation spectrum of mixture of C_7H_8, nitrogen and argon gases injected into ion source at given power 80 W. In the range of 315.21 – 315.02 nm there are the lines of radiation of nitrogen ion, and in ranges of 336.23 – 336.7 nm and 427.13 – 247.59 nm the lines of carbon oxide ions, in 357.2 – 357.24 nm and 390.62 – 391.08 nm lines of nitrogen oxide and nitride and a group of weak lines of hydrogen atoms in 656.05 – 655.98 nm range. With increasing the power of ion source up to 200 W gradually the lines of atomic hydrogen intensify and new plasma radiation lines appear in 400 – 800 nm region, which, due to widening of spectral lines, cause difficulties in identification [12]. Previously, it was shown that the ratio of plasma spectral lines H_λ at 656.2 nm and H_λ at 485.92 nm is determined by comparison of diamond and grapheme phases [11].

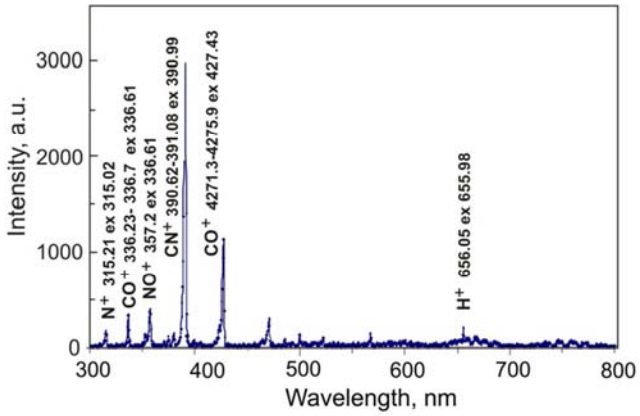

Figure 2. *The radiation spectrum of N_2 : C_7H_8 – 15 : 20% gas mixture for ion source power of 80 W.*

To reach reproducible physical parameters of nanostructures, an automated system of regulation of gas flow as well as of identification and control of plasma composition is installed in vacuum chamber. The volume of gases injected into the chamber was estimated with the help of relative variation in vacuum level in comparison with plasma radiation values. This allowed keeping the injected volume of gases with accuracy up to two percent. The control of composition of plasma flow was carried out by comparing of the spectrum of radiation and results.

3. Increasing of Conductivity of Nanostructured DLC Films

In case of increased power the probability of formation of more defragmented nanostructures with comparatively higher kinetic energy increases. Embedded into the carbon matrix they cause decrease in the resistivity of the film without any significant changes in optical properties. The improved technological equipment allowed obtaining stimulating centers of metal oxides on the plate surface during the same technological process. These centers later act as stimulating centers for formation conductive nanostructures in the carbon matrix. These isle-like Ta_2O_5 centers were grown from a metallic target by reactive magnetic evaporation. On the basis of these isles conductive nanostructures are formed from the condensation of plasma flow, which being embedded in carbon matrix change the physical properties of the whole

structure. Physical properties of embedded nanostructures mainly depend on the power of ion source and the composition of gas mixture. Adding more powerful linear ion source in vacuum chamber allowed us to change the composition of ionized particles in plasma flow in a wider range of power (80 – 240 W), particle kinetic energy and as a result obtain higher conductive films.

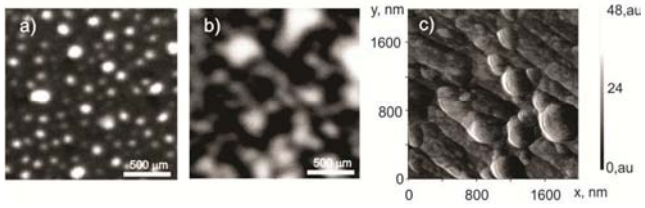

Figure 3. *SEM images of DLC films with × 10^5 magnification: a) high resistive films, 2 · 10^{-3} Ohm · cm, b) films with lower resistivity of 3 · 10^{-4} Ohm · cm, and c) an AFM image of a middling resistive film of 10^{-3} Ohm · cm.*

By improved technique, 150 nm thick carbon films with 80% of optical transparency in the visible range and with 10^{-4} Ohm · cm resistivity were synthesized on n-Si substrates. With improved equipment a method was developed with the use of Ta_2O_5 metal oxide stimulating centers to synthesize conductive DLC on n-Si single crystal plate.

In Figure 3 secondary electron SEM images of DLC films with different resistivity are shown. The bright points in Figure 3a are the clusters of carbon atoms on the dark background of amorphous carbon. Changes in technological parameters stem the formation of conductive channels by combination of carbon clusters (Figure 3b). Similar results were obtained by AFM when investigating surface clusters [12].

4. Characteristic Features of Nanostructured Carbon Films

Depending on the conditions of growing these layers exhibit diverse electrical and optical properties ranging from an insulator to superconductor and as it was shown they can also be semiconducting with different resistivity. A characteristic feature of 50 nm thick insulating DLC film on sapphire is that the optical transmittance remains nearly constant and as high as about 99% in a wide range of light wavelength (250 to 1100 nm) (Figure 4a, Curve 1).

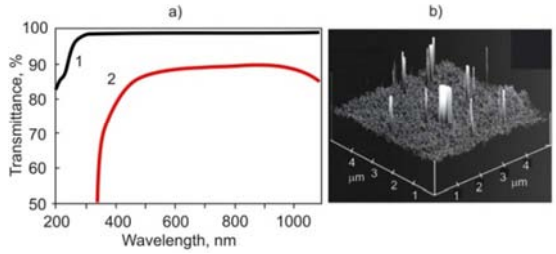

Figure 4. *a) Transmittance spectrum of dielectric DLC obtained with improved technological equipment on sapphire (1) and conducting DLC on glass substrate (2), b) AFM image of nanotubes grown perpendicular to the surface of Si substrate for dielectric DLC.*

Nanotubes grown perpendicular to the surface of these films have work function the least of known values. Conductive 150 nm thick DLC deposited on glass substrate exhibit optical transmittance of about 85% (Figure 4a, Curve 2).

This feature can formulate DLC to substitute ITO films since DLC is more resistive toward mechanical, chemical and radiation effects and do not contain rare and expensive materials [7].

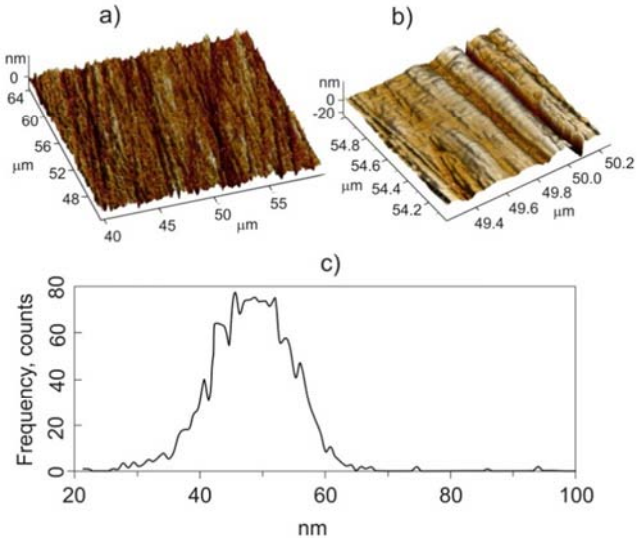

Figure 5. *Images of morphologies of nanotubes formed at different parts of the sample. a) nanotubes mostly with diameter of 50 nm and b) nanotubes with 65 nm diameter, and c) histogram of nanotube diameter counts.*

With the equipment described in this work, on the surface of a substrate, for example semiconducting Si, and in case of a specific distribution of Ta_2O_5 metal oxide stimulating centers nanotubes are formed parallel to the substrate surface which increase the conductivityofabout150 nm thick carbon films.

In Figure 5a and 5b the 2D images of morphologies of nanotubes are shown. In the area shown in Figure 5a nanotubes with diameter of about 50 nm are more of ten, while nanotubes with diameter of 65 nm are much more rare, as it can be seen from histogram in Figure 5c. AFM enables to picture only the surface of clusters and nanotubes, the histogram of which shows how frequent nanotubes with a given diameter are formed (Figure 5b). The resistivity of these samples decreases to 10^{-4} Ohm cm. By means of optimizing the distribution of stimulating centers, the surface potential as well as film growing conditions, tubes with much smaller diameters and uniformly distributed, in comparably high conductivity is possible to obtain.

5. Discussion

Depending on technological methods carbon films can have rather a sophisticated structure when there is a single cluster. Carbon atoms with a definite electronic configuration or when these clusters are rich of hybridized carbon atoms. They can be 1D, 2D or 3D. The physical properties of films are due to the distribution of atoms in clusters. We proposed the

following model of explaining the structural features of clusters. It is supposed that optical electrons are hybridized in atoms with two different energetic states, due to which electrons are exchanged between the atoms at a definite frequency. According to quantum presentation, electrons being in potential wells are shared between the atoms. The transparency of DLC films grows up to 98 – 99% in the region of 250 to 1100 nm, which is characteristic to films rich with that form of structures (Figure 4). The Ta_2O_5 centers foster the formation of nanotubes of different diameters, which in its turn brings to higher conductivity by an order.

6. Conclusions

1. A method of preparing of nanostructured DLC films is developed. The latter, with decreasing the production costs, can replace ITO films.

2. Cluster structures of DLC which foster the increase in film conductivity and optical transmittance of DLC films are studied.

3. The role of stimulating centers in increasing of conductivity of nanotubes arranged parallel to the substrate surface is revealed.

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