Structure and properties of a-C films modified with Ir nanoparticles

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ABSTRACT

In this work, thin amorphous carbon films modified with iridium nanoparticles (a-C <Ir>) synthesized by magnetron ion-plasma co-sputtering in an argon atmosphere are considered.

The morphology and structure of a-C <Ir> films were studied using atomic-force microscopy and Raman spectroscopy. The dispersion of the G peak showed structural changes of a-C with increasing Ir concentration in the films, which is more clearly manifested in the films synthesized on silicon substrates. The optical and electrical properties of a-C <Ir> films were studied. A change in the band gap with increasing Ir concentration additionally showed a structural transition from a diamond-like to a graphite-like matrix. A percolation transition of conductivity at Ir concentration of ~0.2 at.% in a-C <Ir> films was detected and an increase in conductivity by 10^7 when the concentration of iridium was increased by 0.7 at.%.

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1. Introduction

Due to the unique physical-chemical properties, amorphous diamond-like carbon films (DLC) hold a special place in the production of durable and anti-friction coatings for various electronic devices and instruments [1,2]. Metallic nanoparticles synthesized in an amorphous carbon matrix can significantly affect the mechanical and physical properties of DLC films [3–8]. With a decrease in particle size below 100 nm, quantum-size effects may appear, as shown in [7,8]. Embedment of nanoparticles into a dielectric matrix can significantly affect the properties of the matrix and the nanoparticles.

One of the non-carbide-forming metals is iridium. Iridium is a metal of platinum group, belongs to inert substances and reacts with only few chemical elements at temperatures above 600–1000–1200 °C. Iridium acts in the carbon matrix as an independent element of the structure. During the synthesis of a-C <Ir> films, iridium atoms form nanoparticles uniformly distributed over the volume of the film. Iridium nanoparticles in an amorphous carbon film may have properties that do not appear in the bulk state. In addition, the Ir nanoparticles can in a certain way affect the structure and properties of the carbon matrix. Therefore, the study of

such composite material is relevant and of a certain scientific and practical interest.

One of the promising methods to produce carbon films is the method of magnetron ion-plasma co-sputtering. The magnetron method of synthesis, unlike many other applied methods, is a powerful tool for creating nanostructured multicomponent coatings for various purposes. Besides, this method enables to perform structural and chemical modification of films with a disordered structure.

2. Materials and methods

Amorphous carbon films with Ir nanoparticles were synthesized using ion-plasma magnetron co-sputtering of a combined target on quartz and silicon substrates in atmosphere of Ar gas (99.999 at.%). The power of direct current of the ion-plasma discharge was 14 W for all synthesized films. The temperature of the substrate during the synthesis did not exceed 50 °C, and the pressure of the Ar gas was 0.7 Pa. The combined target consists of a graphite (99.999 at.%) disk with segments of iridium (99.9 at.%) wire in the sputtering zone. The diameter of the iridium wire was 0.125 mm. The size and number of iridium nanoparticles per volume unit varied with the number of Ir segments on the carbon target. All investigated a-C <Ir> films were obtained under the same conditions and synthesis time.

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The Ir concentration in a-C films was determined by energy-dispersive X-ray spectroscopy (EDS) using EDAX device (AMETEC Materials Analysis Division, USA) based on a Quanta 200i 3D scanning electron microscope (FEI Company, USA). The Ir concentration – X_{Ir} – varied from 0.0 at.% to 1.58 at.%. In addition, the scanning electron microscope was used to determine the thickness of the films on a freshly cleaved silicon substrate, which varied from 40 to 60 nm. The surface morphology of DLC films was studied using atomic force microscopy (AFM) on Solver Spectrum instrument (NT-MDT, Russia). The local structure of the samples was studied by Raman spectroscopy (RS) on NTegra Spectra instrument (NT-MDT, Russia). The transmission spectra were studied on a Lambda-35 spectrophotometer (PerkinElmer, USA). Also, the conductivity (σ_r) of a-C <Ir> films at a temperature of 300 K was studied.

3. Results and discussion

Structure of a-C <Ir> films

Fig. 1 shows the result of phase contrast imaging obtained in the AFM tapping mode for three different X_{Ir} concentrations. The changes in the phase of the oscillating probe tip with respect to the drive signal due to the variation in the potential of the interaction between the probe tip and the surface of the film reveals a difference in the phase composition of the film. As can be seen from Fig. 1(a), the surface is almost uniform and has no pronounced colour (phase) changes. At the same time, in Fig. 1b and c, in a-C films with Ir, dark areas with clear boundaries appear on the general homogeneous background. Such areas associated with phase inhomogeneity indicate changes in the composition of the film. Thus, it can be concluded that the iridium atoms are not distributed homogeneously throughout the film volume, but coagulate and form nanoparticles in the carbon matrix. It can be seen from the images that the iridium nanoparticles in the carbon matrix form a spherical shape and have a maximum size of ~80 nm.

Raman spectra were obtained using 473 nm and 633 nm lasers. As it is known [9,10], the Raman of carbon structures are characterized by two main bands in 1500–1600 cm^{-1} and 1350–1400 cm^{-1} frequency ranges, which are denoted by G (graphite) and D (disordered) peaks, respectively. Fig. 2 shows the Raman spectra of a-C <Ir> films on a silicon substrates. It can be seen that all spectra are characterized by the main G peak and a D shoulder in the low-frequency region. With an increase in Ir concentration (Fig. 2, a), the G peak is observed at a frequency of 1550 cm^{-1} for all films. Such a position of the G peak corresponds to a diamond-like structure [9] and the percentage of sp^3 hybridized

bonds may be about 55–70%. In Fig. 2b, when excited at a wavelength of 633 nm, the G peak shifts to the high-frequency region with increasing Ir content, i.e. we observe a transition to a graphite-like phase. This, apparently, can be explained by the influence of the silicon (1 0 0) substrate on the formation of the a-C structure and the effect of Ir nanoparticles on the formation of certain sp^2 carbon structures. It is worth noting that in a-C <Ir> films synthesized on a quartz substrate, similar behaviour of the G peak is not observed for two different laser wavelengths. Thus, the carbon matrix of films with iridium nanoparticles grown on a quartz substrate differs from that grown on a silicon substrate. However, it is difficult to say how much this difference is significant. So far, we can only accept this as a real experimental fact.

Fig. 3 shows the change in the position of the G peak in a-C <Ir> films on quartz Fig. 3(a) and silicon Fig. 3(b) substrates. As can be seen from Fig. 3 (a), the position of the G peak does not change for both 473 and 633 nm excitation wavelengths. For a-C <Ir> films on a silicon substrate a change in the G peak position is observed only at 633 nm excitation (Fig. 3(b)). The position of G peak determines the structure of the film matrix and is a function of the structure and exciting wavelength. Therefore, it is important to consider the dependence of G peak position on the excitation wavelength in a-C <Ir> films with different Ir concentrations. Thus, the determination of the dispersion of the G peak will make it possible to reveal the degree of disorder and, accordingly, the nature of the structure change.

As shown in [11], the dispersion of the G peak (G_{disp}) can be determined by the formula

$$G_{disp} = \frac{G_{pos}(473nm) - G_{pos}(633nm)}{(633 - 473)nm}$$

A change in the G peak dispersion indicates a change in the structure of a-C films or a change in the ratio of sp^2/sp^3 sites. The increase of the G peak dispersion indicates the increase of structural disorder; and vice versa, the decrease of G_{disp} value is due to the rise of a crystalline phase.

From Fig. 4, it can be seen that the G peak dispersion in a-C <Ir> films on quartz substrates does not change significantly and its value is ~0.32 cm^{-1}/nm. On silicon substrates, we observe a decrease in G_{disp} from ~0.3 to 0.23 cm^{-1}/nm. Thus, it can be concluded that the crystal surface of the silicon (1 0 0) substrate affects the formation of the carbon matrix structure and this effect increases with increasing Ir concentration. Thus, we observe graphitization of the amorphous structure. Iridium nanoparticles contribute to the formation of sp^2 sites and additionally enhance

a) X_{Ir}= 0.0 at. %   b) X_{Ir}= 0.65 at. %   c) X_{Ir}= 1.58 at. %
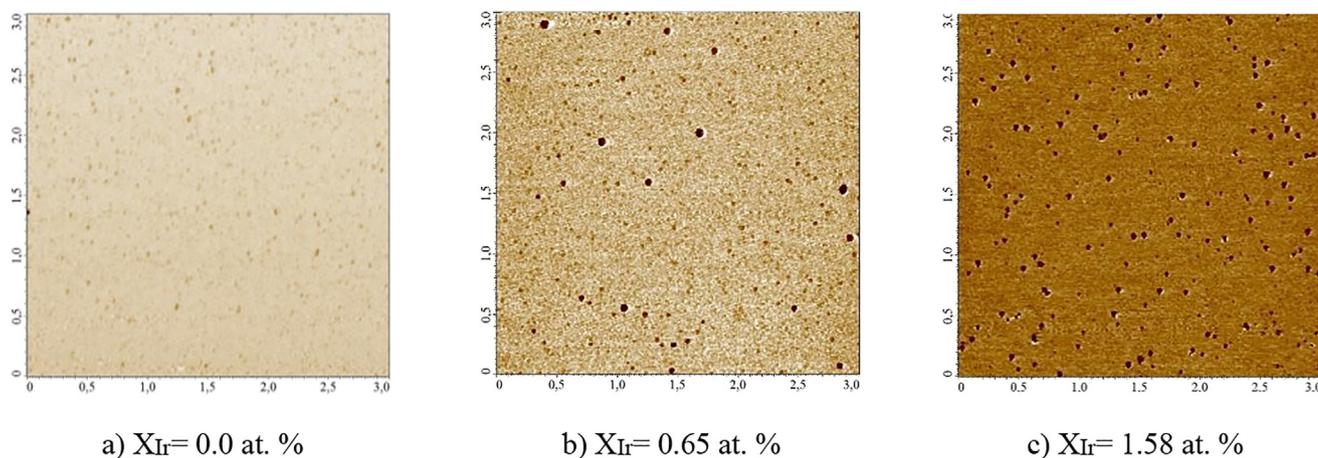
Fig. 1. Phase contrast AFM imaging of the surface of a-C <Ir_x> films.
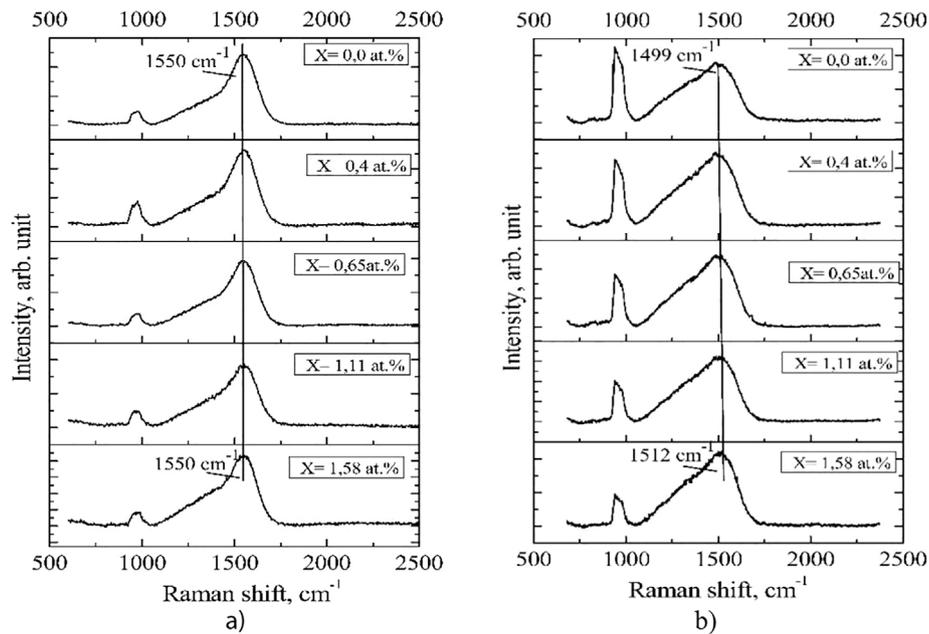
Fig. 2. Raman spectra a-C <Ir> films synthesized on a silicon substratesat excitation wavelength (a) 473 nm, (b) 633 nm.

(a) SiO$_2$ substrate (b) Si substrate
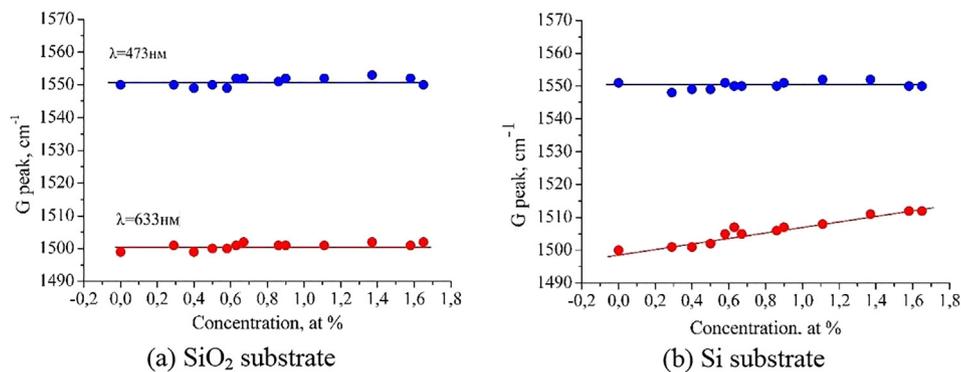
Fig. 3. The dependence of the G peak position on the Ir concentration in a-C films.
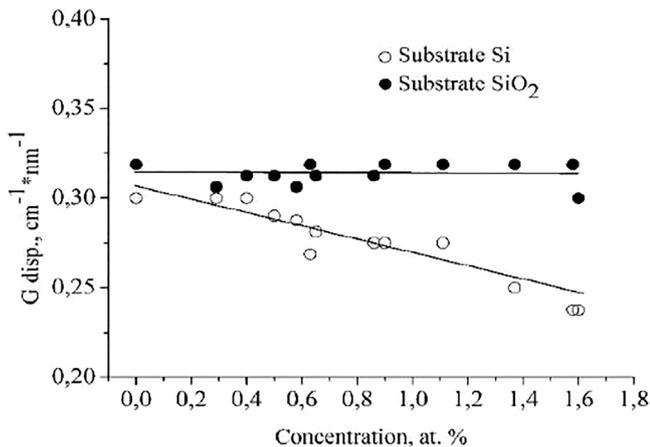
Fig. 4. Dispersion of G peak versus Ir concentration in a-C films.

the effect of the silicon (1 0 0) substrate on the formation of graphite clusters.

Optical and electrical properties of a-C <Ir> films

Optical transmission and reflection spectra were studied in the range from 190 nm to 1100 nm. The absorption coefficient α was calculated by the formula $\alpha = \frac{1}{d} \cdot ln \frac{(1-R)^2}{T}$. For amorphous films $\alpha (h\nu - E_g)^2$, therefore, the value of band gap was determined from the $\sqrt{\alpha h\nu}(h\nu)$ dependence graph [12]. Fig. 5 shows a nonlinear change of E_g from 1.97 eV to 0.8 eV with increasing Ir concentration up to 1.6 at.%. As it is known [12], π electrons of sp^2 sites are responsible for the formation of the edges of the top valence band and the bottom of the conduction band. Therefore, the change in the band gap observed is associated with a change in the number of sp^2 sites. At the same time, the density of states inside the band gap and the edge of the valence band of the carbon matrix are affected by the energy spectrum of electrons of iridium nanoparticles. It should be noted that films with band gap of less than 1 eV belong to graphite-like films. However, according to Fig. 4, in case of films with Ir concentration above 0.9 at.% grown on quartz substrates, carbon matrix has a diamond-like structure. Thus, we can conclude that the formation of the edges of the bandgap is significantly affected by the density of electronic states of iridium nanoparticles.

Additionally, studies of conductivity (σ_r) at 300 K were conducted. The dependence of σ_r on the Ir concentration in a-C <Ir> films revealed a sharp change by 10^7 for Ir concentration varied from 0.2 to 0.9 at.% (Fig. 6).
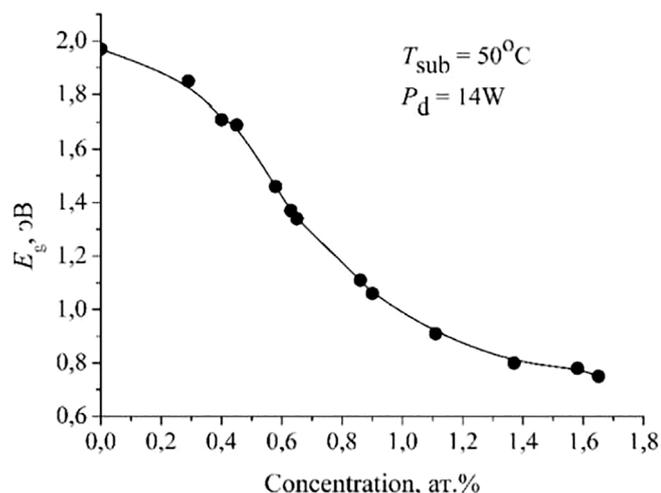
Fig. 5. Dependence of the optical band gap on the concentration of Ir.
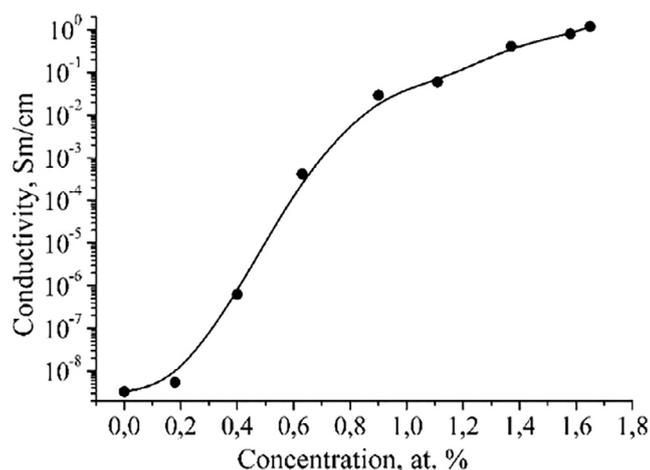
Fig. 6. The dependence of the conductivity on the Ir contentin a-C <Ir> films at 300 K.

A further increase in the concentration of Ir to ~1.6 at.% leads to a smooth linear change in conductivity by 10^2. A sharp change in conductivity by 10^7 in a narrow concentration range is defined as percolation conductivity [13–15]. The concentration of the conducting regions, i.e. iridium nanoparticles, at which we observe an increase in the conductivity, is called the percolation threshold (or percolation transition). However, in the amorphous carbon matrix, there are regions with sp^2 bonds, which are also conductive elements of the structure. As shown above, the concentration of sp^2 sites depends on the number of iridium nanoparticles. Therefore, the flow of charge will be carried out through both the iridium nanoparticles and the sp^2 carbon matrix sites.

4. Conclusion

Amorphous diamond-like carbon films modified with iridium nanoparticles were synthesized by magnetron ion-plasma co-sputtering of a combined target using direct current. Atomic force microscopy showed that Ir atoms coagulate into nanoparticles with a size of no more than 80 nm, with an Ir concentration of 1.58 at.%. Using Raman spectroscopy, the effect of iridium nanoparticles on the formation of a-C film structure is shown. By the changes in the G peak dispersion, it was revealed that with increasing Ir concentration the content of sp^2 carbon sites also increases and this occurs more intensively in the films grown on silicon substrates. The decrease in the optical band gap is associated not only with an increase in the density of π electrons of the sp^2 sites but also with the influence of the density of electronic states of iridium nanoparticles on the formation of the edges of the bandgap. The study of electrical properties showed that at low concentrations, a significant increase, 10^7 times, in the specific conductivity is possible. Such a sharp change in the electrical conductivity is due to a percolation effect with a percolation threshold at Ir concentration of ~0.2 at.%. Thus, the effective control of the electronic properties of amorphous diamond-like carbon films modified with iridium nanoparticles is shown.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

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