

APPLICATION OF THE MODIFIED PLASMA ACCELERATOR FOR AMORPHOUS DIAMOND-LIKE FILMS PRODUCTION

A.A. Bizukov, V.N. Borisko, A.E. Kashaba, K.D. Sereda, N.N. Yunakov, D.V. Zinov'ev
Kharkov National University, 61108, 31 Kurchatov Av., Kharkov, Ukraine,
E-mail: [Borisko@pht.univer.kharkov.ua](mailto:borisko@pht.univer.kharkov.ua)

In the paper the problem of diamond-like films production by sputtering of a graphite target in the modified plasma accelerator with closed electrons drift is considered. The diamond-like films with thickness $40 \div 400$ nm with deposition velocity $200 \div 400$ nm/hour were received. For production of hydrogen the metal hydride block of exterior filling was used. As a hydride forming material the intermetallide LaNi_5 was used which ensures necessary hydrogen-capacity and velocity of a sorption - desorption of hydrogen.

The electron-diffraction, electron-microscopic and optical investigations of film properties were carried out. It is shown that the described method allows to get amorphous diamond-like films. It is established that films obtained according to classification of Grigorovici R., concern to a structural sandwich-type. The carbon atoms in a layer have a strong covalent bond and between layers there is a weak double bond such as Van der Waals.

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INTRODUCTION

Much attention has been devoted to chemical vapor deposition of CVD diamond-like carbons films because of their high strength, chemical neutrality and optical transparence [1]. Now there are many methods to obtain the diamond-like films [2].

For the development of the technologies of diamond and diamond-likes coating film production it is necessary to provide the condition of high over saturation of hydrogen isotopes [3]. It's leads to increase of probability of diamond crystal nucleus formation, avoiding of graphite phase and conserving of already formed diamond phase.

In this work the deposition and analysis of a diamond-like films with use as a working gas the pure hydrogen received from metal-hydride supply is carried out.

THE EXPERIMENTAL MODEL OF THE PLASMA-CHEMICAL REACTOR

Diamond-like films were gained by sputtering of a graphite target on ion-beam sputtering system. The model of the plasma-chemical reactor for synthesis of diamond-like coatings was designed and created on the basis of experimental results on investigation of gas discharges in crossed magnetic and electrical fields [4]. Basic elements of the reactor model are ion-beam sputtering system (IBSS), vacuum system, current collector and systems of the power supplies Fig. 1.

The vacuum system of the reactor model 1 was assembled on the basis of serial vacuum installation UVN-71P which provides a pumping speed up to 500 l/s in a range of pressures $p = 10^{-5} \div 10^{-3}$ Torr. The limiting pressure of residual gas did not exceed 6×10^{-6} Torr. A flat metal electrode with holders for samples 3 was used as a current collector 2. The transport area is between the IBSS and current collector. Distance from a sputtered target 6 to the current collector can be changed from 5 to 50 cm.

The IBSS is a gas-discharge system with closed electron drift in crossed magnetic and electrical fields based on a one stage Hall ion source. The basic elements of the IBSS construction are: a modified Hall type ion

source consisting of ring anode 4, cathode block 5 and sputtered graphite target 6 fixed on movable water-cooled substrate holder. The ring anode with average radius of 5 cm is made of non-magnetic stainless steel and insulated from the cathode block. The power supply to the anode and cooling by water is carried out through insulated vacuum lead-ins derived through the bottom of the cathode block. The anode (accelerating) voltage changes in the range of $U_A = 0 \div 4$ kV.

The cathode block of the IBSS serves as the basis of the accelerator, magnetic circuit and cathode of the discharge gap. The magnetic field solenoid 7 and the external working gas inlet system 8 are installed in the cathode block. The solenoid provides creation of radial magnetic field in a ring aperture of the Hall accelerator which value changes within the range of $H = 0 \div 3000$ Oe.

The power supply of the IBSS are carried out from standard supply units BP-94 and BP-100 which allow to change applied voltage within the range of $0 \div 7$ kV and $0 \div 1$ kV accordingly, power of the supply units is about three kilowatts.

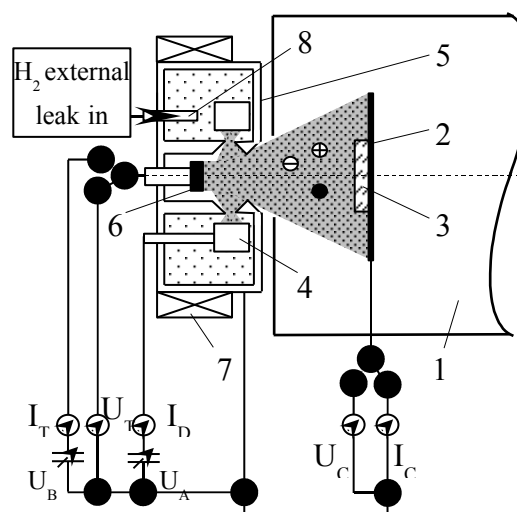


Fig. 1. The scheme of the plasma-chemical reactor for synthesis of diamond-like coats

The working gas pressure is adjusted in a range of $p = 8 \times 10^{-6} \div 10^{-3} \text{ Torr}$. The working gases are hydrogen, argon and their intermixture. For deriving of hydrogen the metalhydride exterior leaking block was used in which the intermetallide LaNi_5 was used as a hydride formative material that ensures necessary hydrogen-capacity and velocity of a sorption-desorption of hydrogen [5]. The inlet of working gas into the discharge gap between the anode and cathode is carried out through the channels in the cathode block.

The longitudinal electric field is created between the anode and cathode of the accelerator when accelerating voltage is supplied to the anode. The concurrent stream of the gas ions generated in the modified Hall source is guided onto the surface of the flat sputtered graphite target at the glancing angle. The angle of incidence of the incoming beam can be adjusted by moving the target and changing the magnetic intensity that in combination with adjustment of the accelerating voltage allows to reach maximum sputtering rate of target material and to optimize a zone of target utilization. The bombardment of the target by the ion beam leads not only to target sputtering, but also to secondary ion-electron emission from the target surface. To increase both the sputtering rate of the graphite target and effective exit of secondary emissive electrons the opportunity of bias-voltage supply to the sputtered target with value of $U_B = -(50 \div 1000) \text{ V}$ is stipulated.

THE INVESTIGATION OF THE OBTAINED FILMS

Depending on operating modes diamond-like films were obtained with width $40 \dots 400 \text{ nm}$ and the deposition velocity $200 \div 400 \text{ nm/hour}$. The width of films was determined by a method of lines equal chromatic order (method Tolanskogo). For electron-diffraction investigations the thin films by width $t \approx 20 \div 30 \text{ nm}$ on substrates NaCl were deposited. For optical measuring the films by width $100 \div 150 \text{ nm}$ deposited on the quartz substrates were made.

The choice of substrate material was determined by its transparence in ultraviolet spectrum. The width of films was selected such that the transmission in ultraviolet spectrum was more than 0,01. The absorption spectrums of thin diamond-like films of carbon were measured on a spectrophotometer CФ-46 at the room temperature in the spectrum range $1,5 \div 6,5 \text{ eV}$.

As a rule at deriving of diamond-like carbon films by the ion-plasma deposition methods are gained of an amorphous film [6,7] representing a fine-dyspersated basis with insertion of larger crystallites of different modifications of carbon. The electron-metric investigations have shown that studied thin diamond-like carbon films are fine-dyspersated with the practically identical sizes of crystallites.

On electron-diffraction of the studied films the wide scoured diffraction rings without any attributes of a texture are observed. Such views of an electron-diffraction are characteristic for amorphous solid bodies. As is known in amorphous bodies a long-range order is absent and the short-range order existing on small number of stationary values of a lattice however is maintained.

Therefore diffraction rings are observed but they are strongly fuzzed and blurred.

Absorption spectrum of a diamond-like carbon film at the temperature $T = 290 \text{ K}$ is given in Fig. 2. Strongly tightened in long-wave area of a spectrum the absorption edge confirms an amorphism of films.

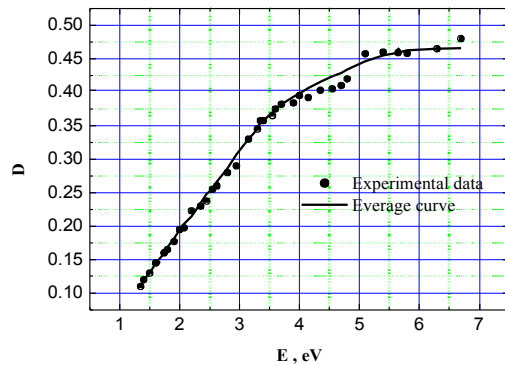


Fig. 2. The absorption spectrum of diamond-like thin carbon film by $T = 290 \text{ K}$ and $t = 120 \text{ nm}$; $D = -\lg 1/\tau$ - optical density, E - energy, τ - transmittance

For straight-zone dielectrics the sharp edge of the intrinsic absorption band well featured by empirical dependence Urbaha is characteristic

$$K = K_0 \exp \left[\gamma' \frac{(h\omega - E_0)}{\kappa T} \right], \quad (1)$$

where γ' - const, E_0 - a forbidden zone.

In amorphous films the absence of the long-range order leads to overlapping allowed bands and as a consequence to occurrence of indirect allowed transitions that gives supplemental absorption in the field of a transparence. The edge of fundamental absorption in the majority of amorphous semiconductors submits to the exponential law (1):

$$\ln K \approx h\omega$$

In the field of energies of above exponential "tail" for absorption constant $K(h\omega)$ in different amorphous compounds the linear, square-law or cubic dependences are observed [5]. In the studied diamond-like carbon films the absorption constant $K(E)$ in the field of energies $1 \div 2 \text{ eV}$ is shown in Fig. 3 by an exponential curve (1) and above the exponential tail $K(E)$ linearly depends on energy

$$K(E) \cdot E = B(E - E_0), \quad (2)$$

where B - const.

THE DISCUSSION OF RESULTS

Calculated on (2) values E_0 for our samples are varied from $1,41$ up to $1,81 \text{ eV}$ and $B \approx 5 \cdot 10^4 \div 10^5 \text{ cm}^{-1} \text{ eV}^{-1}$. In order of magnitude the values E_0 and B are typical for amorphous semiconductors [8]. The small values E_0 testify to a considerable impurity of a graphite phase. However it is impossible to approve with confidence that E_0 is actual forbidden zone, as we have not the additional information about dependence of a density of states from energy and matrix element.

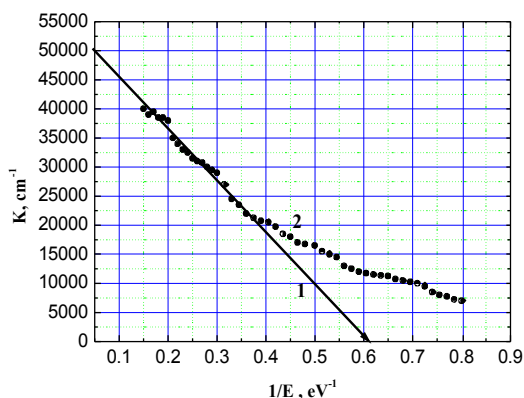


Fig. 2. Handling of dependence $K(E)$:

1 - calculation on eq. (2)

2 - the experimental diversion from straight line are described by eq.(1)

In the intrinsic absorption band of studied diamond-like carbon films down to energies $6,5 \text{ eV}$ any features are not shown. Strongly displaced in red area of a spectrum an absorption edge and major absorption at the energy $E < 4,6 \text{ eV}$ according to examinations [9] testifies to a considerable impurity of a graphite phase. At the same time the good optical quality of samples (optical homogeneity, high reflectivity) and also high transparency of films are characteristic for diamond-like carbon films. Apparently the additional examinations the electrical and

optical constants are necessary for the final deductions on a composition of studied films.

Thus the described method of the film deposition allows to obtain amorphous diamond-like coatings distinguished high durability and optical properties.

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ЗАСТОСУВАННЯ МОДИФІКОВАНОГО ПЛАЗМОВОГО ПРИСКОРЮВАЧА ДЛЯ ОТРИМАННЯ АМОРФНИХ АЛМАЗОПОДІБНИХ ПЛІВОК

А.А. Бізюков, В.Н. Бориско, Д.В. Зинов'єв, А.Е. Кашаба, К.Д. Серєда, Н.Н. Юнаков

У роботі розглянута можливість отримання алмазоподібних плівок шляхом розпилення графітової мішені в модифікованому плазмовому прискорювачі з замкнутим дрейфом електронів. Для отримання водню використовувався металогідридний блок зовнішнього напуску, у якому в якості гідридоутворюючого матеріалу використовувався інтерметалід LaNi_5 , що забезпечує необхідну водневу ємність і швидкість сорбції-десорбції водню.

Були отримані алмазоподібні плівки товщиною $40 \dots 400 \text{ nm}$ зі швидкістю осадження $200 \dots 400 \text{ nm/g}$ для різних режимів роботи прискорювача. Показано, що даний спосіб дозволяє отримувати аморфні алмазоподібні плівки. Проведені електронографічні, електрономікроскопічні та оптичні дослідження властивостей плівок. Виявлено, що отримані плівки, відповідно до класифікації Grigovicic R., відносяться до шаруватого структурного типу. Атоми вуглецю в шарі мають сильний ковалентний зв'язок, а між шарами існує слабкий зв'язок типу Ван-дер-Вальса.

ПРИМЕНЕНИЕ МОДИФИЦИРОВАННОГО ПЛАЗМЕННОГО УСКОРИТЕЛЯ ДЛЯ ПОЛУЧЕНИЯ АМОРФНЫХ АЛМАЗОПОДОБНЫХ ПЛЕНОК

А.А. Бизюков, В.Н. Бориско, Д.В. Зиновьев, А.Е. Кашаба, К.Д. Серєда, Н.Н. Юнаков

В работе рассмотрен вопрос получения алмазоподобных пленок путем распыления графитовой мишени в модифицированном плазменном ускорителе с замкнутым дрейфом электронов. Для получения водорода использовался металлогидридный блок внешнего напуска, в котором в качестве гидридообразующего материала использовался интерметаллид LaNi_5 , который обеспечивает необходимую водородоемкость и скорость сорбции-десорбции водорода.

В зависимости от режимов работы были получены алмазоподобные пленки толщиной $40 \dots 400 \text{ nm}$ со скоростью осаднения $200 \dots 400 \text{ nm/g}$. Проведены электронографические, электрономикроскопические и оптические исследования свойств пленок. Показано, что описываемый способ позволяет получать аморфные алмазоподобные пленки. Установлено, что полученные пленки, согласно классификации Grigovicic R.,

относятся к слоистому структурному типу. Атомы углерода в слое имеют сильную ковалентную связь, а между слоями существует слабая связь типа Ван-дер-Вальса.