Deposition of Diamond-Like Carbon Films by Unbalanced Magnetron Method in Ar/CH_4 Gas Mixture

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Abstract – The diamond-like carbon (DLC) films deposited by unbalanced magnetron sputtering (UBMS) in the Ar/CH_4 gas mixture have been investigated. The combination of hydrocarbon dissociation in unbalanced magnetron glow discharge and graphite target sputtering was used as a carbon source. The sputtering of carbon target was carried out at the pressure of 0.1–0.2 Pa with a discharge power up to 1.2 kW. Si (100), optical glass BK7 and Ge were used as substrates. The films were deposited up to the thickness of 0.2–1.6 μm with the rate of 0.55–1.6 nm(s · kW)$^{-1}$.

A critical thickness of DLC film, under which coating lift-off takes place owing to internal stresses, did not exceed. Doping of CH_4 allowed both an increase in the critical thickness of films from 0.47 μm up to 1.6 μm and a more than two times increase in the deposition rate. Dependencies of refractive index and microhardness on DLC films as a function of process parameters (Ar/CH_4 ratio, deposition rate, ion energy) has been estimated. The deposition of DLC films with hardness within the range of 1300–2100 kgf/cm^2 and $n \geq 2.0$ is possible under bombardment ion energy in the range of 50–90 eV and concentration CH_4 in gas mixture in the range of 5–10%.

DLC films were applied for blooming of IR Ge windows.

1. Introduction

During the last decade using of diamond-like carbon films (DLC) poses great interest, due to their outstanding properties, such as high hardness, thermal conductivity and wear resistance, high transparency in IR range, chemical inertness and biocompatibility. This unique combination of physical, chemical and mechanical properties makes them suitable for use in a wide range of technological and industrial applications, such as microelectronic, optical, biomedical applications, wear-resistant and protective overcoats.

The DLC hard coatings may be produced by many low-pressure methods based on activated chemical vapor deposition (CVD) or physical vapor deposition (PVD). In CVD methods the reaction of hydrocarbon dissociation often is activated by plasma discharge (PECVD) [1]. At that substrate temperature for optimal growth of DLC films to reach up to 900 °C, what limited variety of using substrates. If compared to CVD methods PVD methods allow deposition of DLC films at low temperatures involved in the process, permitting to coat almost any substrate (plastic, glass, e.a.). Its methods as ion beam [2] or magnetron sputtering [3], arc evaporation [4] or laser PVD [5]. Among PVD methods the unbalanced magnetron sputtering (UBMS) method deserves special mentioning, [6], which along with high deposition rate provides low-energy ion bombardment of growing film. The bombardment by ions gives possibility in wide range to control of deposited DLC films properties and has a key role in sp^3-bonded carbon formation. Moreover, in UBM the unbalanced magnetic field to forms a semi-self-maintained discharge in substrate-target field, which was found to be applicable to the PECVD of DLC coating.

Thus, the aim of this work is the investigation of DLC films formation by PVD and PECVD methods when a combination of hydrocarbon dissociation in glow discharge of UBM and sputtering of graphite target were used as carbon sources.

2. Experimental

The scheme of experimental setup for deposition of DLC films by UBMS method is shown in Fig. 1. The vacuum chamber was equipped by UBM, in which change of configuration and intensity of magnetic field in substrate-target space is achieved by the magnetic field created by additional electromagnetic coil, that enables varying the unbalance level of magnetron in a wide range and to achieve UBM discharge characteristics optimization [7, 8]. Field strength at the target surface is 0.065 T.

Before the deposition target clearing by sputtering on the shutter was performed. The time, voltage and discharge current of UBM at clearing made 1 min, 470 V, 1.0 A, accordingly. As a working gas Ar was used at pressure in chamber 0.1 Pa. Clearing of substrate surface was made by the ion flux generated by the Hall ion source (IS). For that Ar was fed in IS up to working pressure of $2.0 \cdot 10^{-2}$ Pa. Time of clearing, ion energy and discharge current in all experiments were constant and were equal to 3 min, 700 eV, 40 mA, accordingly. Depending on the experimental condition simultaneously with clearing either heating up to 300 °C or cooling of substrates was performed.

Sputtering of a graphite target (99.95%) ∅ 80 mm realized by UBM using as working gases Ar/CH_4

(99.98%) at commong pressure in chamber 0.1–0.2 Pa. In case using of CH_4 UBM plasma discharge executed both the ion generation, which sputtered the target material, and hydrocarbon dissociation and ionization. That enabled the depositing the DLC films both with an ion graphite sputtering and by a combination of CH_4 dissociation the in UBM discharge and ion sputtering. To maintain the given gas flow are electronic mass-flow controllers were used. Si(100), optical glass BK7 and Ge were used as substrates. Substrates were situated at the distance 8.5 cm from the UBM target surface.

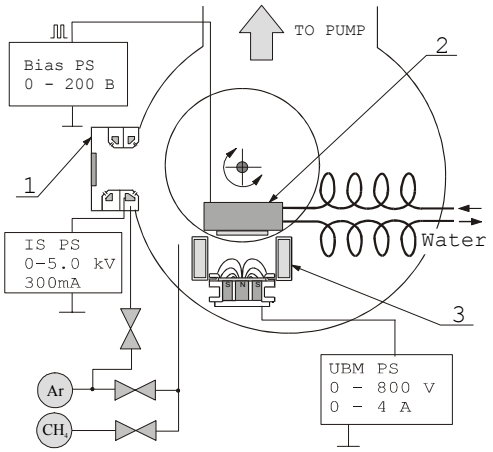

Fig. 1. Scheme of experimental setup for deposition DLC films by UBMS method: 1 – ion source; 2 – cooling substrate holder; 3 – UBM

The UBM supply the power supply source featuring the output power of 1.5 kW and a capability to operate in the current or power stabilization mode was used. UBM discharge current to vary at 0.2 to 3.0 A. The UBM unbalance degree, and hence ion/atom ratio on the substrate was varied by altering additional coil current [7, 8]. For control bombarding ion energy the impulse substrate bias (100 kHz frequency at impulses amplitude up to 200 V) was used.

The films were deposited up to the thickness of 0.1–1.5 μм. Transmission of films was evaluated by the IR spectroscopy method in the range of 400–4000 cm^{-1} by IR spectrophotometer *UR-20*. Refractive index and extinction coefficient in visible range was determined by indirect method by the reflection spectrum of DLC in the range of 400–1200 nm. Reflective specters by spectrophotometer *Hitachi U-3501* were obtained. The physical thickness of the coating was determined by microinterferometer *MII-4*. DLC films surface resistance was measured by the method of four probes using a *IUS-3* device. Relative hardness of DLC was evaluated by scratching off by corundum at loading in the range of 0–400 g. In the course of this the film break critical loading was determined. Absolute value of DLC films microhardness *f* by digital of microhardness tester *HXD-1000* at an indenter loading 25 g were obtained. The loading storage time is 15 s.

3. Results and Discussion

The investigation of DLC films deposited by UBMS of graphite target in Ar gas has been made. The deposition rate practically linearly depends on the UBM discharge power and was 0.55–0.65 nm/(c·kW). Deposited films were transparent in visible range and has taupe colour. The thickest films were been deposited on the Si substrates. At that the critical thickness of DLC amount to 0.47 μm. Excess in the critical thickness resulted in partial peeling of films after their interacting with air.

It was determined that dramatic effect to DLC films surface resistance is made by the substrate temperature. The surface resistance of DLC films thickness by 200 nm as a function of substrate temperature is shown in the Fig. 2. In the course of that all the remaining parameters of deposition were constant (P_t = 500 W, p = 0.1 Pa, unbalanced coefficient K = 2.9 [8]). As the substrate temperature sharply increases, a decrease in film resistance and microhardness was observed, that is evidently related to intensive graphitization processes under the influence of temperature. Moreover, the films deposited under increased substrate temperature, are characterized by enhanced extinction coefficient in visible range of spectrum. However, by increasing the temperature it was possible to rise critical thickness of the coating up to 0.8 μm due to decreasing of internal stresses in films at graphitization.

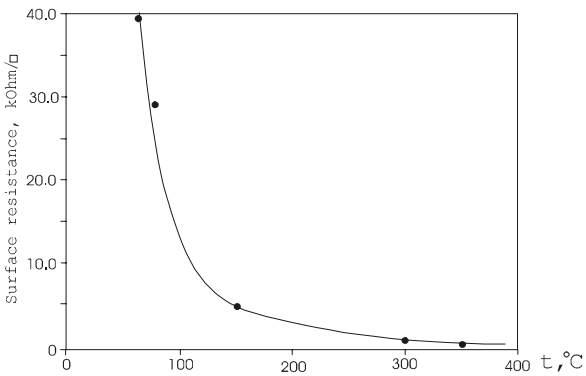

Fig. 2. Surface resistance DLC films deposited by UBMS method as a function of substrate temperature

In Fig. 3 shown dependence of DLC films surface resistance from thickness for various deposition conditions. Without heating the deposition rate exerted significant influence on film resistance. Increasing UBM discharge current resulted in a decrease in DLC surface resistance (curves a, b, c), what may be accounted for a rise in the substrate temperature under growing deposition rate. The substrate cooling considerably enhanced the DLC surface resistance at constant thickness (curve d). Moreover, an increase in the surface resistance was reached at the substrate self-bias (U_s = –35 V) due to low energy ion bombardment (curve d).

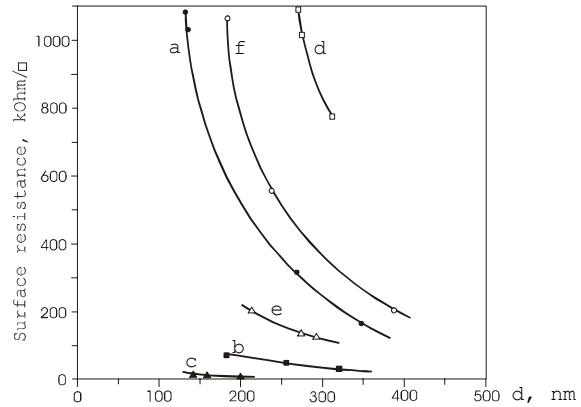

Fig. 3. DLC films surface resistance as a function of thickness for various deposition condition: (a) $I_t = 0.5$ A, $U_s = 0$ V; (b) $I_t = 1.0$ A, $U_s = 0$ V; (c) $I_t = 2.0$ A, $U_s = 0$ V; (d) $I_t = 0.5$ A, $U_s = -35$ V; (e) $I_t = 1.5$ A, $U_s = -35$ V; (f) $I_t = 1.0$ A, $U_s = -35$ V, substrate cooling

In Fig. 4 shown dependence of the DLC films critical loading with thickness 300 nm on Si substrate on the UBM discharge power. As it can be seen the relative hardness of DLC was decreased at increasing of UBM discharge power. Refractive index n_2 of DLC films deposited by PVD, was found in the range 2.0–2.2. Refractive index to decrease at increasing of deposition rate and substrate temperature.

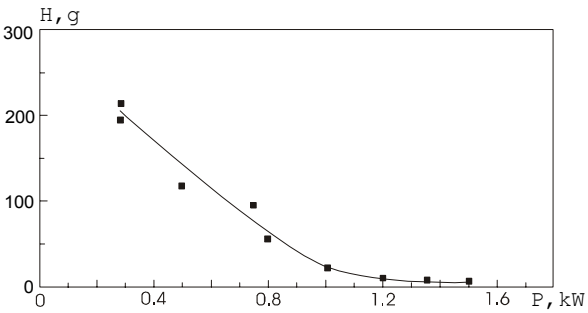

Fig. 4. Critical loading of DLC films as a function of UBM discharge power

To eliminate disadvantages of DLC deposition by PVD method, it was suggested as an additional carbon source to use dissociation reaction of CH_4 in UBM glow discharge (PECVD method). The mixture Ar/CH_4 was used as the working gas. In the course of that the condensing flux on the substrate material resulted from the combination of CH_4 dissociation and graphite sputtering (PVD+PECVD). Doping of CH_4 allowed a more than two times increase in the deposition rate, if compared to PVD and reached 1.6 nm/(c·kW) at a distance of 8.5 cm (Fig. 5). The profile of the DLC film deposition rate distribution at PVD+PECVD, значительно отличалось from profile of deposition rate distribution at PVD (Fig. 6).

Surface resistance of DLC films deposited by PVD+PECVD reached several tens of MOhm, exceeding more then by two orders the surface resistance of films deposited by PVD. Moreover, doping of CH_4 enabled to increase the critical thickness of films up to 1.6 μm on different substrates. However, it is possible to rise CH_4 concentration up to the limit of 35%. Excess of this level results in instability of UBM discharge combustion, that is obviously related to "poisoning" of the target by hydrogen, taking place in the process of CH_4 dissociation.

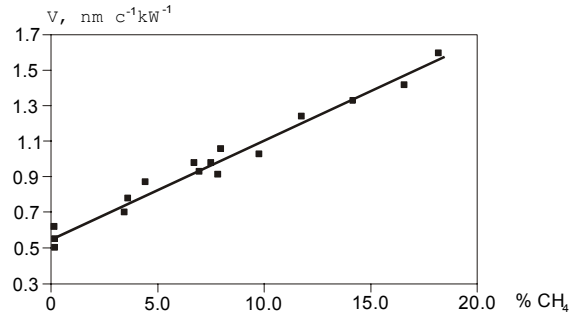

Fig. 5. DLC films deposition rate as a function of methane concentration in Ar/CH_4 gas mixture

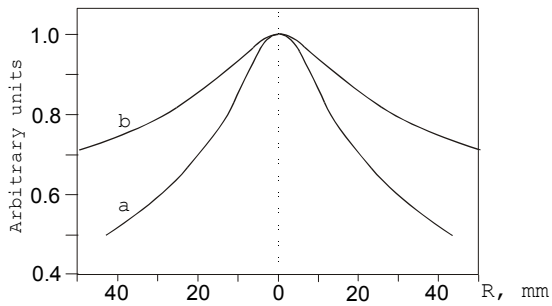

Fig. 6. Normalized profiles of deposition rate distri bution of DLC films at PVD (a) and PVD+PECVD (b)

Refractive index of DLC films depends on working gases Ar/CH_4 ratio, deposition rate and ion energy. Dependence of n_2 from CH_4 concentration in gas mixture for various UBM discharge current are shown in Fig. 7. Thus, in films deposited at discharge current $I_t = 0.6$ A (curve a), n_2 was increased at growing of methane concentration with maximum at CH_4 concentration about of 4.0%. Further increasing of CH_4 concentration brought about a fall in n_2. At $I_t = 1.5$ A (curve b) n_2 decreased with CH_4 concentration increasing and was considerably lower than n_2 of films deposited at $I_t = 0.5$ A. It was supposed, that increasing of CH_4 concentration results in increasing of hydrogen concentration in deposited film owing to incomplete CH_4 dissociation in UBM discharge. A rise in hydrogen concentration increased a probability of polymeric chain formation with $n_2 \leq 1.6$ and, as a consequence, n_2 decrease [9]. It is worth mentioning, that the dependencies presented in Fig. 7 were obtained at pulse substrate bias with amplitude of 70 V ($E_i \approx 60$ eV). Refractive index of films deposited at more high U_s of substrate (more than 110 V), and hence and more high ion energy, did not exceed 1.84.

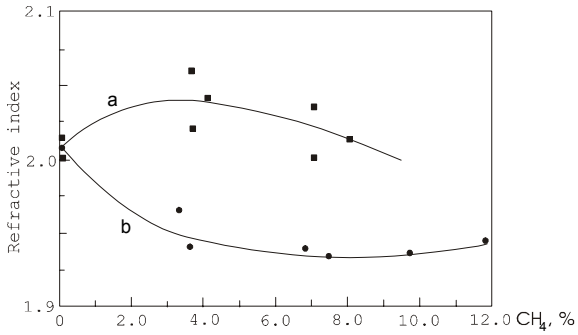

Fig. 7. DLC films refractive index as a function of CH_4 concentration in gas mixture for various UBM discharge current: (a) I_t = 0.6 A, (b) I_t = 1.5 A

Dependences of critical loading from substrate bias voltage and CH_4 concentration in gas mixture are shown in Figs. 8, 9. Increasing of U_s from 0 to 70 V led to a rise in film hardness. Further increasing of bias voltage brought about decreasing in film hardness. Absolute value of DLC microhardness on Si substrate, measured at indenter loading of 25 g, has been within the range of 1300–2100 kgf/cm^2. The optimum of CH_4 concentration in gas mixture, from the point of maximal film hardness, lies in the range of 5–20%. It has to be mentioned, that optimum of CH_4 percent concentration, from the maximum refractive index point of view (2–8% CH_4) and DLC hardness are different.

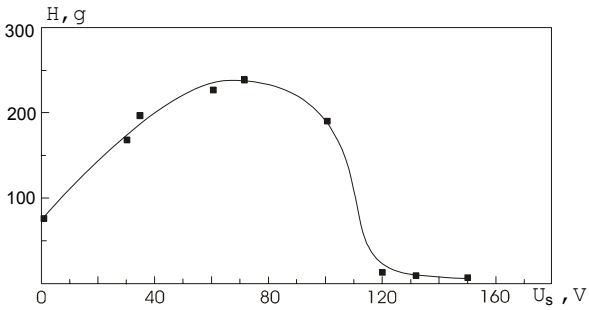

Fig. 8. DLC films critical loading as a function of voltage amplitude of impulse substrate bias

IR transmission and reflection specters of DLC on the Ge substrate were obtained. Films deposited at следующих conditions: U_t = 510 V, I_t = 0.6 A, CH_4 concentration 4.0%, K = 2.9, U_s = 80 V. Application of DLC permitted to increase the Ge window transmission under one-sided deposition of DLC coating from 40 to 62% with the wave-length 10 μm, being 2% lower of theoretical limit for one-sided blooming (64%). Two-sided deposition of DLC films allowed an increase in transmission of Ge window up to 92% with the wavelength of 10.5 μm.

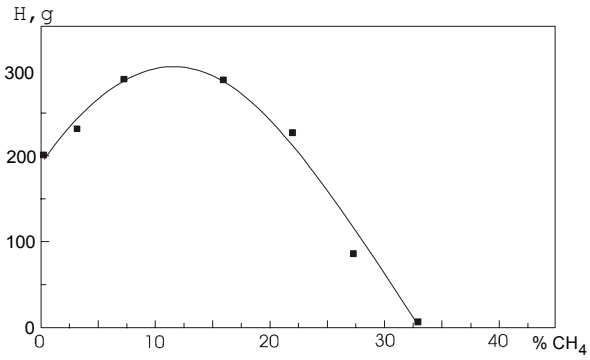

Fig. 9. Critical loading of DLC films as a function of methane concentration in Ar/CH_4 gas mixture

4. Conclusion

DLC films were deposited by UBMS by combination of PVD and PECVD methods with hydrocarbon dissociation in UBM glow discharge and graphite sputtering used as a carbon source. It was established that deposition of DLC films with hardness within the range of 1300–2100 kgf/cm^2 and $n \geq 2.0$ is possible under bombardment ion energy in the range of 50–90 eV and concentration CH_4 in gases mixture in the range of 5–10%.

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