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INFLUENCE OF SUBSTRATE AND FILM THICKNESS ON THE MORPHOLOGY AND DIAMOND BOND FORMATION DURING THE GROWTH OF AMORPHOUS DIAMOND-LIKE CARBON (DLC) FILMS

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The influence of substrate type and of film roughness during deposition of amorphous diamond-like films was investigated. The film morphology was characterized by atomic force microscopy (AFM) and the diamond bond concentration was determined by Raman and Fourier Transform Infrared (FTIR) spectroscopy. The relation between thickness and diamond bond formation was revealed. During film growth the surface roughness vanishes. The effect can have practical applications: smoothing of substrates without polishing.

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1. Introduction

In the last decade, deposition methods and the transport (current/voltage characteristics), optical (absorption, scattering, photoconduction), mechanical (microhardness) and other properties of amorphous diamond-like carbon (a:DLC) of the hydrogen-free, amorphous carbon (a-C) films [1-3], were studied. These films are used in industry, due to the similarity of their properties to those of diamond (e.g., chemical stability, high hardness, high thermal conductivity and low optical absorption in a large spectral interval). A particular advantage of a:DLC is the possibility to deposit uniform amorphous films on various substrates and on large surfaces [4-5].

Several applications, such as protection of soft materials and devices (e.g. germanium infrared detectors or solar cells for space utilization [6-8]), were developed. One of the important problems studied in these papers is the finding of the optimum deposition conditions for the maximization of the diamond bond concentration, Φ, which is defined as the ratio $N_3\,sp^3/(N_3\,sp^3 + N_2\,sp^2 + N_1\,sp^1)$, where N_1, N_2 and N_3 are the concentrations of sp^1, sp^2 and sp^3 bonds of linear (acetylenic), trigonal (graphite) and tetrahedral (diamond) type, respectively. Studies of the evolution of the morphology from the initial stages of deposition (thickness d~1 nm) up to about d~100 nm [9-11], were performed using atomic force microscopy (AFM).

In a previous paper [12], we have reported measurements of the diamond bond concentration using FTIR and Raman spectroscopy and microhardness methods, as a function of deposition parameters (radio frequency power, CH_4, CH_4+N_2 and Ar gas pressure, type of substrate and film thickness). The experimental data offered informations on the optimal deposition conditions for getting an uniform film and a maximum value of Φ on large surfaces. Doping with various elements by adding gases (nitrogen and iodine) to the CH_4 [13-17] and by diffusion of copper changed the microhardness and optical energy gap.

Although the diamond bond concentration (Φ) is an important parameter in the characterization of a:DLC films, the dependence of Φ on morphology, substrate type and film thickness has not been yet investigated.

The main purpose of this paper is to investigate the influence of surface morphology and type of substrate on the formation of sp^3 bonds in the deposited films during the growth of the film thickness.

2. Experimental method

a:DLC films were deposited using plasma R.F. (13.56 MHz) glow discharge in methane gas (CH_4) [18-19]. Deposition was carried out after the evacuation of the air in the chamber down to the pressure $p \leq 1.33 \times 10^{-4}$ Pa. The vacuum chamber had 50 cm diameter and 80 cm in height. The electrode diameter was 20 cm and the distance between anode and cathode was 8-10 cm. The optimum value of RF power to obtain a:DLC with maximum Φ was found at 200 W and growth rate (10 nm/min). The substrate was held at room temperature and the purity of the admitted gases in the chamber was better than 99.99%. For etching out poorly adhered molecules from the surface, a mixture of CH_4/Ar (30 % Ar) was used.

The film and substrate morphology and the average film roughness were studied by using an atomic force microscope (AFM) and the film thickness was measured by a step profilometer. Ratio Φ was determined by using FTIR and Raman spectroscopy. a:DLC films on silicon of orientation (100) and (110), on germanium, sapphire and GaAs were investigated. During this experiment, all the process parameters were kept constant, excepting the time of deposition and type of substrate.

3. Results and discussion

As can be seen in Fig. 1 the average roughness (σ) of a silicon substrate and of the deposited a:DLC decreases from the initial σ_i=20 nm for the substrate, to the final value $\sigma_f \cong 0.8$ nm, after deposition of 0.6 μm thick a:DLC film.

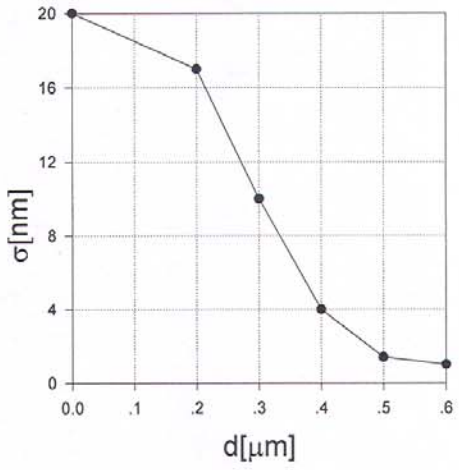

Fig. 1 The variation of the roughness of the a:DLC film deposited on silicon substrate as a function of the film thickness.

This result may be applied to substrates, which are difficult to polish, in order to reduce scattering (e.g. germanium, which is a soft material used for infrared detectors). In Table 1, several substrates and the corresponding values of the initial substrate roughness σ_i and of the film roughness, σ_f, are shown for a deposition time of one hour and film thickness of 0.6 μm.

Table 1
Initial substrate roughness (σ_i) and final roughness (σ_f) after depositing 0.6 μm a:DLC film.

Substrate	σ_i (nm)	σ_f (nm)
Sapphire	30	1.0
Silicon	20	0.8
GaAs	17	0.7
Glass	40	0.5
Germanium	20	0.7

The investigation of the relation σ(d) for substrates with various σ_i, lead us to the conclusion that for the values of σ_i>1 nm, the roughness of the film surface becomes negligible (σ~1 nm) for film thickness higher than 0.6 μm.

Fig. 2, shows the Φ function extracted from FTIR measurements characteristic of the films deposited on silicon, sapphire, germanium and GaAs substrates, as a function of films thickness (d).

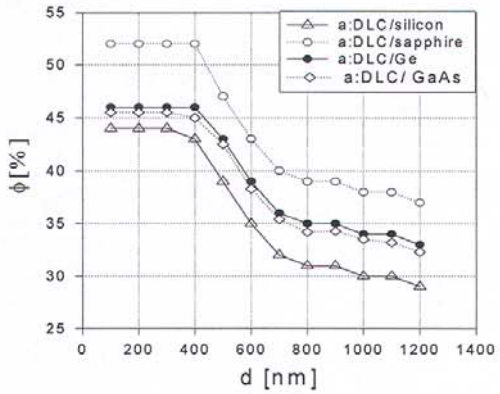

Fig. 2 The variaton of the diamond bond concentration (Φ) as a function of film thickness for four a:DCL films deposited on four different substrates.

Using deconvolution of FTIR data, the variation of bond concentration was analyzed separately for sp^3, sp^2, and sp^1 as a function of thickness was shown in Fig. 2. For small d, Φ was constant (e.g., for sapphire Φ=0.52, up to $d=d_c\cong400$ nm). For $d>d_c$ up to d~1000 nm, Φ decreased. The thickness d_c for which Φ begins to decrease with increasing d is practically the same for all substrates.

The FTIR data indicated that all three types of bonding are constant for all substrates, for $d<d_c$. For $d>d_c$ where Φ decreased, the concentration of sp^1 bonds increased and sp^2 and sp^3 remained constant as resulted from FTIR data. This is an interesting result which may indicate that for thin a:DLC films (d<400 nm), the four types of substrates determine a similar evolution which maintains the diamond bond concentration constant when d increases up to $d=d_c$. The optimum deposition parameters for the substrates shown in Fig. 2 were the same, although the resulting values of Φ for the three substrates were different. The decrease of Φ with increasing d, for $d>d_c$, can be explained assuming that at $d=d_c$, the influence of these substrates on film formation is already negligible. For the new situation created by influence of substrate, the change of the parameters of deposition is necessary in order to find the new optimum conditions of deposition to reach the maximum value of Φ. Another important result which was obtained from FTIR measurements is the dependence of Φ on σ. The IR absorption spectrum for films thickness 0.6 μm on two sapphire substrates of different initial roughness (σ_I = 300 nm and 1.1 nm) are shown in Fig. 3. It may be seen that the absorption is nearly identical in the wavenumber range: 2850 - 3100 cm^{-1}. This proves that σ_i has a negligible influence on Φ in the a-DLC films deposited on sapphire.

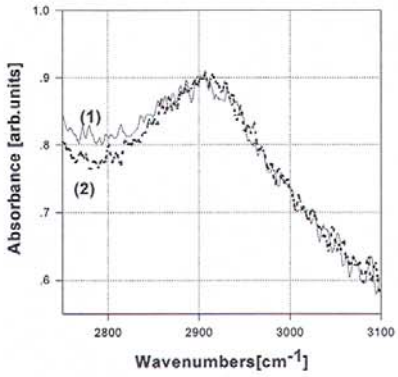

Fig. 3 FTIR spectra of 0.6 μm a:DLC film on sapphire for different roughness: (1) σ_i =300 nm and (2) σ_i =1.1 nm.

4. Conclusions

There was shown that, for the optimum conditions of deposition, the diamond bond concentration in a-DLC films remains constant up to a given thickness $d=d_c$ and then decreases. For several substrates the influence of roughness (σ) on the diamond bond concentration is negligible. The roughness of the a:DLC films can be reduced down to negligible values ($\sigma \leq 1$ nm) when the film thickness overcomes a certain value (in our cases 400 nm). It is suggested to use this effect to smooth substrates that are rather difficult to polish.

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