

MODIFICATION OF THE ELECTRONIC PROPERTIES OF DIAMOND LIKE CARBON FILMS USING THE SUBSTRATE TEMPERATURE EFFECT

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Highly insulated and highly transparent hydrogenated amorphous carbon films (a-C:H), that named diamond like carbon films, were deposited by magnetron sputtering at 200 C. By changing the substrate temperature from 200 C to 50 C, we can modify the properties of this film where the optical band gap of the films changed from about 2 eV to about 0.3 eV, the activation energy varied from 0.9 eV to 0.16 eV and the films conductivity varied from 10^{-13} to 10^{-2} ohm⁻¹ cm⁻¹. These results were explained on the background that the films consist of mixed phases of tetrahedrally bonded (sp³) and trigonally bonded (sp²) carbon atoms and the relative amounts of these two phases are dependent on the deposition conditions.

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1. Introduction

During the last decade studies on amorphous hydrogenated carbon films (a-C: H) attracted much attention due to their high potential in technological applications. In general, the films consist of a mixed phase of tetrahedrally bonded (sp³) and trigonally bonded (sp²) carbon atoms and the relative amounts of these two phases are depending on the deposition conditions. The optical and electrical properties of the films are determined by π states of sp² sites which form the conduction and valence band edges and lie close to the Fermi level. These sp² sites form clusters consisting of several atoms and are embedded in the σ bonded sp³ matrix. The relative amounts of sp³ and sp² bonded carbon atoms determine the film properties [1-2].

By controlling the deposition conditions both sp³ (σ) and sp² (π) bondings in the films could be controlled and the properties of the films could be tailored for different applications. Increase of sp² cluster in the film reduces the diamond like properties. Films rich in sp³ carbon were suitable for hard coating applications whereas sp²-rich films were useful for tribological application. It was found that hydrogen in the atomic state helps to stabilize the sp³ character. So, many workers added hydrogen for the formation and stabilization of the sp³ bonds [1-2].

In this paper we report upon the modification of diamond like carbon films, deposited by direct current magnetron sputtering, by changing of the substrate temperature in a wide range from 200 to 50 °C. Within this range, the dominant character of the bonding varies from diamond like carbon to graphite like carbon.

2. Experimental details

The carbon films were depositing using direct current magnetron sputtering. The source of the carbon was a target of graphite of 10 cm diameter, which mounted directly on the magnet. The

distance between the target and the substrate holder is stabilized at 5 cm for all samples. The substrate could be heated to the desired temperature by passing current through a heater embedded inside the substrate holder. The temperature was ranged from 200 to 50 °C. The temperature is monitored by copper constantan thermocouple attached to the substrate holder. A temperature controlling circuit is connected to avoid the sudden drop of the substrate holder temperature. The temperature controlling circuit consists of ULTRA-THERM type C-300-420 temperature controller, to adjust the temperature at the required value. The target was sputtered in gas mixture from argon 80% and hydrogen 20% with constant flow rate. Gas pressure was kept at 1 Pa. The quartz which is suitable for optical and electrical measurements was used as substrate. The sputtering was performed at 500 V with 24 mA current. The deposition time was constant for all samples about 40 minutes. The films were annealed in the experimental chamber for about one hour directly after preparation.

The film thickness was measured using Gaertener Scientific Corp LC117C ellipsometer, which operated with He-Ne laser with wavelength 632.8 nm

The transmittance measurements were performed with spectrophotometer lambda 900 Perkin Elmer in UV-visible ranges. The transmittance measurements are recorded at normal incidence. During the transmittance measurements, one beam passing through the uncoated substrate as a reference and the other passes through the sample. The ratio of the sample to the reference transmittance was made to give the film transmittance and this enabled us to correct any light absorption in the substrate itself. The absorption coefficient (α) was calculated from the transmittance (T) according to

$$T = \frac{(1 - R)^2 e^{-\alpha d}}{1 - R^2 e^{-2\alpha d}} \quad (1)$$

when R is very low or the film is highly absorbing, $R^2 e^{-2\alpha d}$ is nearly zero.

$$\alpha = 1/d [2 \ln (1-R) - \ln T] \quad (2)$$

where d is the film thickness.

Aluminum electrodes were evaporated in coplanar configuration. Dark conductivity of the films was measured as a function of temperature using (Electrometer V7A-42 (Russia)).

3. Results and discussion

The thickness behavior of films that deposited at constant sputtering time, as a function of substrate temperature is shown in figure 1. As observed from this figure, the film thickness decreased with increasing of the substrate temperature. This may be attributed to the increasing in the compactness of the film by increasing the substrate temperature where by increasing the substrate temperature the percentage of diamond like carbon phase increased in the film [3].

Fig. 2 showed the transmittance $T(\lambda)$ versus wavelength (λ) curves of representative films deposited on quartz at different substrate temperature (200 to 50 °C). One can see from $T(\lambda)$ behavior of the prepared films, the films exhibit high transparency in visible range and $T(\lambda)$ decreased when λ decreased to be the lower value at absorption edge of the material. It is observed in figure 2, $T(\lambda)$ increased with increasing the substrate temperature. We did not attribute this result for the decreasing in the film thickness by increasing the substrate temperature where from figure 1 we can see that the thickness decreased by about 1/3 when the substrate temperature increased from 50 to 200 °C. But, as clearly seen in figure 2, the $T(\lambda)$ increased by about 5 times by increasing substrate temperature from 50 to 200. This led us to assume that the change in the $T(\lambda)$ as a function of substrate temperature due to the change in the structure and not due to the change in the thickness. In other words, this changing in $T(\lambda)$ may be due to increasing in sp^3/sp^2 ratio with increasing the substrate temperature [4].

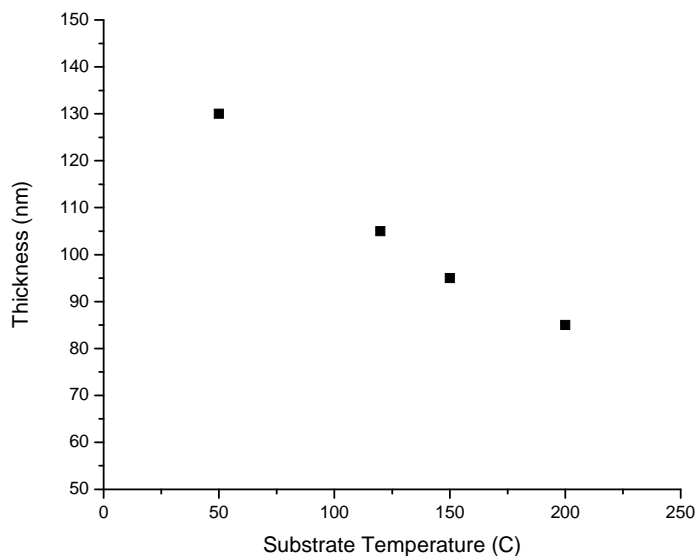


Fig. 1. Variation of a-C:H films thickness as a function of substrate temperature

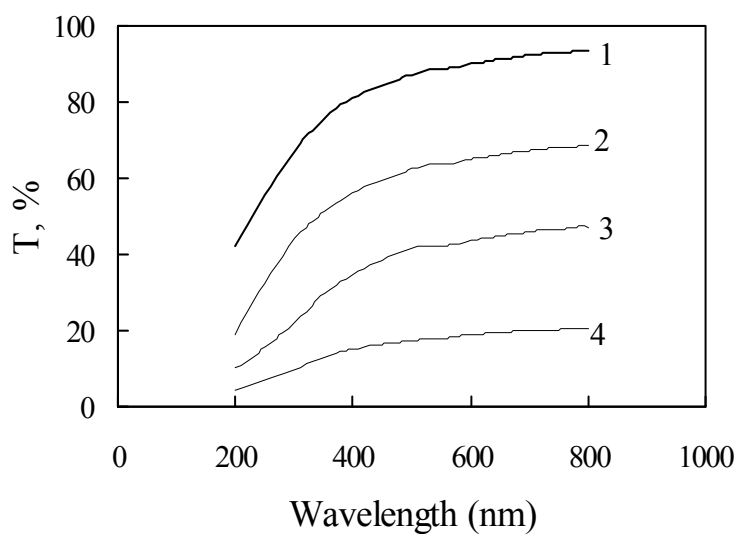


Fig. 2. Transmittance spectral dependence of a-C:H films deposited at different substrate temperatures 1-200 °C, 2- 150 °C, 3- 120 °C, 4- 50 °C

The absorption coefficient (α) was calculated from experimental data by using equation (2). By apply Tauc's relation (equation (3)),

$$(\alpha \cdot hv)^{1/2} = G (hv - E_g) \quad (3)$$

where hv is the photon energy, E_g the optical energy gap, α the absorption coefficient and the slope G is a constant of the relation which proportional to the joint density of states. We can get the values for E_g

It can be seen from figure 3 that the slope G is almost the same for all films. This indicates that sp^2 are clustered in graphite-like islands of various sizes [5]. From Figure 3 we can extract table 1 which give the values of E_g as a function of substrate temperatures. From table 1 one can

see that E_g decreased with decreasing the substrate temperature. Since the E_g value is an indication of the average size of sp^2 clusters [5], this seems to indicate that by decreasing the substrate temperature the average size of sp^2 increased which led to decreasing in sp^3/sp^2 ratio in the film.

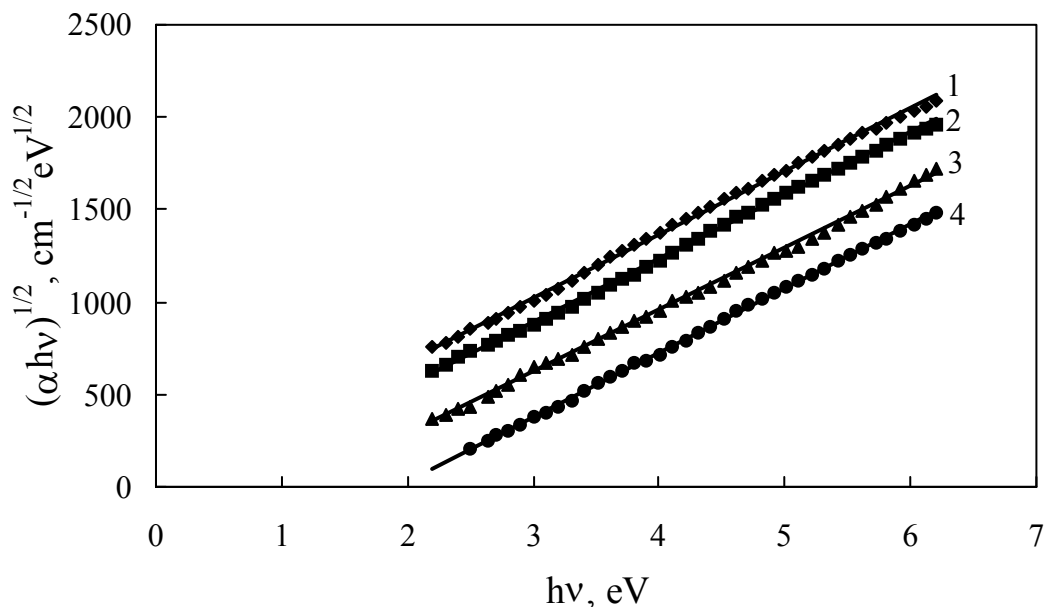


Fig. 3, Spectral dependence of $(\alpha hv)^{1/2}$ for the films deposited at different substrate temperature 1-50 °C, 2- 120 °C, 3- 150 °C, 4- 200 °C

Table 1- Variation of the some physical parameters of the a-C:H films as a function of substrate temperature

Substrate temperature (C)	50	120	150	200
Film band gap (eV)	0.3	0.57	1.2	2
Conductivity $\text{ohm}^{-1} \text{cm}^{-1}$	1.04×10^{-2}	1.2×10^{-5}	1.5×10^{-12}	1.6×10^{-13}
Activation energy (eV)	0.16	0.21	0.62	0.91

Table 1 shows the dependence of the dark conductivity (at room temperature) of the prepared films as a function of substrate deposition temperature. We see that the conductivity increased with decreasing the substrate temperature which may be due to the increasing in sp^2 cluster size in the film, i.e. increasing of the graphite-like carbon in the film [6].

The Temperature dependence of the films conductivities are shown in figures 4. As we observed for the film deposited at 200 C, the conductivity was much lower (about $10^{-13} \text{ ohm}^{-1} \text{ cm}^{-1}$ at room temperature) and decreased with decreasing the temperature. This behavior was also observed for all films but with different range for conductivity as shown in figure 4. From this figure, we extracted the values of the activation energies of the films on the basis of the equation (4)

$$\sigma = \sigma_0 \exp(-E_\sigma/kT) \quad (4)$$

σ is the conductivity, E_σ is the activation energy, k is the Boltzmann constant and T is the temperature.

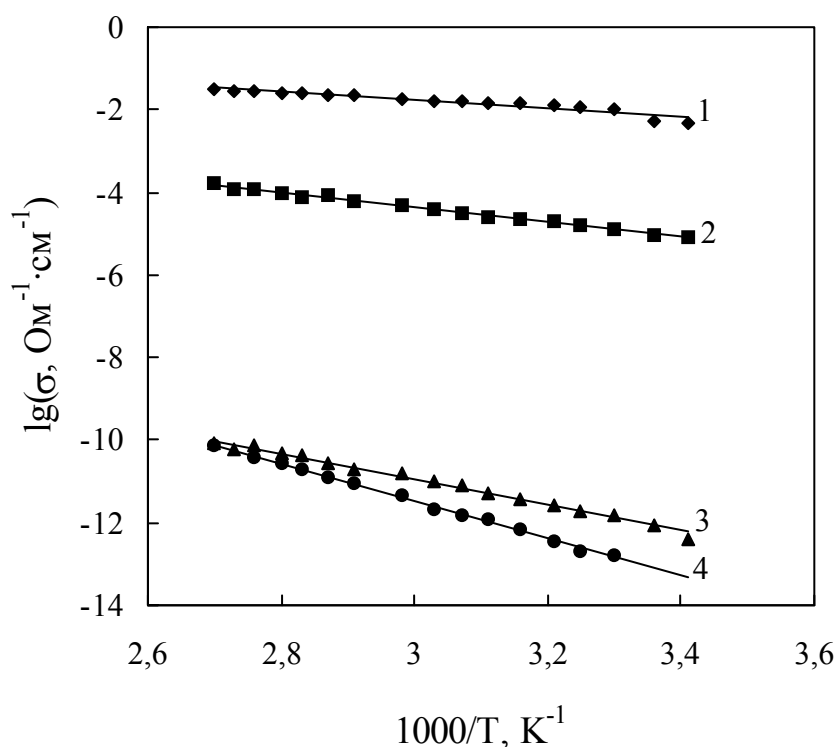


Fig. 4. The temperature dependence of the dark conductivities of a-C:H films deposited at different substrate temperatures 1- 50 °C, 2- 120 °C, 3- 150 °C, 4- 200 °C

From table 1, we can see that E_{σ} decreased with decreasing the substrate temperature which may be attributed to the increasing in graphite like carbon in the films. Also we observed that values are much closed to the values obtained from the optical studies where $E_{\sigma} = E_g / 2$.

4. Conclusions

Highly insulated and highly transperance diamond like carbon films were obtained by magnetron sputtering technique at 200 °C. By changing the substrate temperature, we modified both the optical and electrical properties of the film from diamond like carbon to graphite like carbon. We attributed this change in the properties of the films to the change in sp^3 / sp^2 ratio in the film.

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