CONDUCTIVITY of a-C:H FILMS MODIFIED WITH Ag NANOCLUSTERS

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Abstract

The conductivity of diamond like carbon films embedded with silver nanoclusters were investigated as a function of silver concentrations in the film. By increasing the concentration of silver in the film from 0 to 20 at% the conductivity varied from10^{-13} to 10^2 ohm^{-1} cm^{-1}. The data have been discussed within the model of a dielectric matrix containing conductive inclusions. The conductivity data analysis using percolation theory has been showed that percolation threshold occurred at Ag percentage in the film x_c=5 at %.

Introduction

The growing interest in the dispersion of metallic particles in dielectric matrix is motivated by the prospect of developing of new materials with technological applications such as high near-infrared reflector [1] and composite layers for laser applications [2]. Such composite systems indeed present significant electrical and optical properties that are a function of the metal volume fraction in the dielectric matrix [3]. Diamond like carbon (DLC) films are promising hard coatings because they exhibit small friction [4] and low wear rates [5].

In the last years, several techniques were used to fabricate amorphous carbon matrix embedded with metal nanoclusters such as sputtering techniques, arc discharge and laser abalation. Depending on the method we can get a heterogeneous mixture carbon structure or various type of amorphous carbon ranging from graphite like carbon sp^2-bonded (a-C) , hydrogenated amorphous carbon (a-C:H) or diamond like carbon with a significant fraction of sp^3 bonded carbon atoms. Like gold and copper, silver is weakly interacted with carbon, therefore the probability of occurring Ag carbon composite very small [6]. This means, we can expect in our case pure metal nanoclusters embedded in dielectric matrix.

In this work, we studied the dependence of the electrical conductivity of diamond like carbon films, embedded with silver nanoclusters, on the percentage of silver in the film. Also we try to apply percolation theory on our data to find out a correlation between the size and shape of metal nanocluster and electrical conductivity of the film.

Experimental details

The diamond like carbon films embedded with silver nanocluster, DLC(Ag), were deposited using direct current magnetron co-sputtering of combined target from graphite and silver. The quartz and KBr were used as substrates. Phillips–sm12 TEM, which operated at 200 KV, was used to see the distribution Ag nanoclusters in the films and calculate their size [7]. The film thickness was measured using ellipsometer method. Aluminum electrodes were evaporated in coplanar configuration. Dark conductivity of the films was measured as a function of silver concentration using electrometer В7Э-42

Results and discussion

The sputtering rate of DLC(Ag) films as a function in silver concentration are represented in figure 1. For concentrations from 1 to 5 at% Ag the sputtering rate increased with big steps. After 5 at% Ag, it increased with low steps. This trend may be attributed to the following reason. As we found from our experimental data for our magnetron, the sputtering rate of silver itself is about 3 times larger than pure diamond like carbon sputtering rate. This led us to say that, by increasing the silver concentration in the target led to increasing the sputtering rate of the film which embedded with silver and led to increasing in the film thickness.

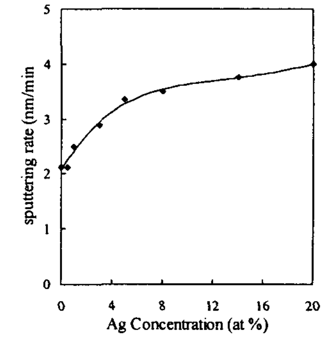

Figure 1 - Variations of the sputtering rate of diamond like carbon films embedded with silver nanoclusters as a function in silver concentration

The electrical conductivity of the DLC(Ag) films (at room temperature) as a function of silver concentrations is shown in figure 3. Figure 3 showed that the conductivity increased gradually to certain Ag concentration (5 at%) which named threshold concentration. Started from Ag concentration 5 at% the conductivity increased drastically and tends to saturate at high Ag concentrations.

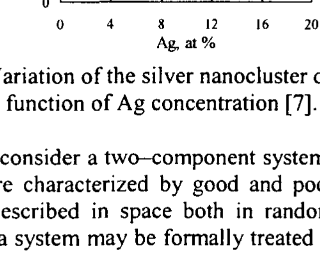

Figure 2 - Variation of the silver nanocluster diameter as a function of Ag concentration [7].

Let us consider a two–component system, whose single components are characterized by good and poor conductivity and may be described in space both in random and ordered manner. Such a system may be formally treated as the entity of metal and dielectric medium. Let us denote the conductivity of the first medium by σ_d (dielectric medium), whereas that of the second, by σ_m (metal); ($\sigma_d \ll \sigma_m$). Let us also consider the regularities of the change in the conductivity of the entire system as a function of the concentration of the metal x. At very small concentrations of the metal very small points from metal are first formed in the system [9]. Then, by increasing of the concentration of the metal, the metal single clusters begin to form. At some metal concentration x_c, referred to as the percolation threshold, clusters network occurred. Thus, we can assume that the originally isolated clusteres are combined into infinite conducting cluster (IC) which named percolation cluster. At these conditions the nonconducting system is transformed into a conducting state [9].

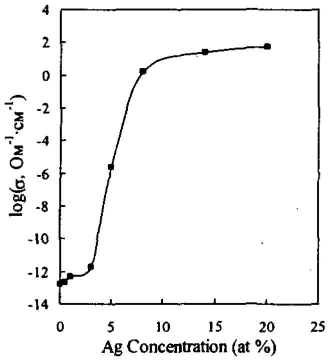

Figure 3 - Dependence of electrical conductivity of DLC (Ag) films on the concentration of Ag.

By applying the percolation theory [10-11] in our system we can derive the parameters of the percolation system (percolation indices) from the conductivity data. According to percolation theory, the conductivity of such composites at low metal content is given by [10]

$$\sigma = \sigma_d \left(\frac{x_c - x}{x_c} \right)^{-q} , \quad x < x_c , \qquad (1)$$

where q is the critical index related to the conducting clusters, x_c is the percolation threshold, σ_d conductivity of pure diamond like carbon film. By plotting relation between $\log\{(x_c-x)/x_c\}$ and $\log(\sigma/\sigma_d)$ (figure 4), the value of q can be derived. As we see in table 1 the value of q is 2.16 which is closed to the expected value from the theoretical studies of percolation systems.

Conductivity σ grows with x and at $x = x_c$, percolation appears. This means that the network between the silver clusters start to occur in the diamond like carbon matrix.

Conductivity at $x = x_c$ is given by

$$\sigma(x_c) = \sigma_d \left(\frac{\sigma_m}{\sigma_d} \right)^{s} , \qquad (2)$$

where s is the index of critical conductivity, σ_m is the conductivity of silver.

By knowing the values of $\sigma(x_c)$, σ_d, σ_m we derived the value of $s = 0.65$ from equation 2.

For $x > x_c$, the conductivity of the material increased and described by

$$\sigma = \sigma_m \left(\frac{x - x_c}{1 - x_c} \right)^{t} , \qquad (3)$$

where, t is the critical index of conductivity,

The three indices are correlated by the equation

$$q = \frac{t}{s} - t \; . \qquad (4)$$

From equation 4 , the value of t could be derived , and t is equal to 4.0

Table 1 show the percolation system parameters. We see that the value of q,s,t are very closed to the value of most 3D percolation networks given in [10-11] which means that our system consists of dense silver objects (near–spherical drops). In other words, the values of the percolation parameters (q,s,t) for our system is closed to the values derived for conducting points which have spherical shape embedded in dielectric matrix.

Table 1. Percolation-system parameters

x_c (at %)	σ_d (ohm cm)$^{-1}$	$\sigma(x_c)$ (ohm cm)$^{-1}$	q	s	t
5	$1.6\cdot10^{-13}$	$2.3\cdot10^{-6}$	2.16	0.65	4.01

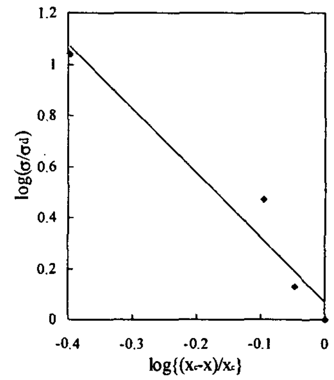

Figure 4.Variation of log (σ/σ_d) of DLC (Ag) films as a function of log $[(x_c-x)/x_c]$

Conclusion

The conductivity of diamond like carbon films embedded with silver nanoclusters, increased gradually at low silver concentrations and sharply when concentration arrived to ≥ 5 at%, which named percolation threshold and this may due to the increasing in the size of the silver nanoclusters in the film. The conductivity of the films was described well using the percolation theory and the percolation parameters were obtained. The calculated values of the percolation parameters (q,s,t) for our system is closed to the values derived from theory which described the conductivity of dielectric matrix which embedded with conducting spherical nanoclusters.

References

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