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Electrical properties of a-C:H films modified by Pt

Abstract. There have been investigated the conductivity of a-C:H and a-C:H<Pt> films, obtained by ion-plasma magnetron sputtering with different substrate temperatures. It is found that the conductivity of a-C:H films substantially dependent on deposition temperature and by changing it from 50 to 200°C conductivity reduced from about 10^{-15} to about 10^{-2} (ohm • cm)$^{-1}$. This is due to increase of sp^3-hybridized bonds and decrease in concentration of sp^2-hybridized bonds characteristic for graphite (t_s = 50°C) and diamond-like (t_s = 200°C) a-C:H films structure. Imposition of platinum impurities into the amorphous diamond-like C:H film that were deposited at a temperature of 200°C, resulted in substantially, by 13 orders of magnitude, increase in their conductivity. Effect of platinum impurities on the conductivity of a-C:H<Pt> film deposited at temperatures of 120 and 50°C are not significant. Analysis of the results for the conductivity of the films using percolation theory shows that the percolation transition occurs at concentration of platinum films $x_c \approx 5$ at.%.
Key words: amorphous diamond-like carbon films, ion-plasma magnetron sputtering, electrical properties, platinum nanoclusters.

Introduction

A-C:H amorphous hydrogenated carbon films are promising material due to combining such physical properties as high strength, high transparency in a wide spectral range, chemical inertness and high radiation resistance. It is a significant fact that a-C:H films are nanostructured material. It is established that as nanoscale objects in a-C:H protrude graphite nanoclusters size of 0.5 to 2 nm with sp^2-configuration of valence bond embedded in a matrix with a diamond-like sp^3-configuration bonds. Ratio in such a films of diamond and graphite component (percentage of sp^2 and sp^3 bonds) determine physical and chemical properties of a-C:H films In particular the electrical conductivity and optical characteristics. One of the effective methods of modification of the electronic properties of thin films is the introduction of impurities of different metals, for instance gold, silver, platinum copper and aluminum. An important feature of these metals is a fact that they don't form a chemical compounds with carbon. Moreover, platinum, in particular, don't become an admixture substitution, it modifies amorphous carbon matrix creating metal nanoclusters.

In this connection, development of nano-materials with new properties on the basis of diamond-like carbon media with varying concentrations of metal nanoclusters and study their impact on the electrical properties is currently one of the most urgent and extremely important area of research in the field of nanomaterials and nanotechnologies.

Techniques of producing

Thin films were prepared by ion-plasma magnetron sputtering with a combined target: polycrystalline graphite – platinum. a-C:H<Pt> films were deposited on quartz and silicon substrates. The process was conducted in a gaseous mixture of hydrogen and argon. The substrate temperature varied between 50 and 200°C during the experiment. Gas pressure in the chamber was maintained at 1 Pa. The impurity content of platinum in the films varied by changing the proportion of platinum in the combined target and was determined by energy-dispersive analysis using a scanning electron

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microscope Quanta 3D 200i. The concentration of platinum in the films varied from 0 to 10 at. %.

Results and discussion

Like it was established earlier by research of films structure, changing the deposition temperature t_s accompanied by significant changes in the matrix of the a-C:H films in ratio of sp^3/ sp^2 configuration connections. In a a-C:H film structure by increasing t_s of 50 to 200°C there is a marked increase in concentration and decrease in concentration of sp^3/sp^2-hybridized bonds typical fom diamond (t_s = 200°C) and the graphite (t_s = 50°C) structure.

This change in the structure of the films leads to a change in conductivity that varies from 10^{-15} till 10^{-2} (ohm • cm)$^{-1}$. Thus, the ratio change of sp^3/sp^2 bonds in the configuration of a-C:H films by changing the temperature deposition of the films, i.e., a modification of the structure of a-C-H films, leads to the effective modification of their electronic properties. Changing the deposition temperature we can within a wide range smoothly alter the electronic properties of films of pure a-C:H films from diamond-like properties to graphite-like properties.

The dependence of the electrical conductivity (σ_k at T = 300K) films of a-C: H <Pt>, obtained at different deposition temperatures, the impurity concentration of platinum is shown in Figure 1. The most detailed investigated of a-C: H <Pt>thin films were carried out with deposition of them at 200°C.

Figure 1 shows that the modification of a-C:H films by platinum nanoclusters leads to increase their conductivity. The degree of influence of impurities on the conductivity of Pt films are substantially independent of deposition temperature. Modification of platinum of amorphous diamond-like a-C:H films at deposition temperature of 200°C results in substantially by 13 orders of magnitude increase in conductivity. The most significant increase in the conductivity of a-C:H<Pt> films occurs in the range of impurity increase of the concentration of Pt 3 to 7 at.%. It is essential that the concentration dependence of conductivity in this case is typical for percolation systems [1, 2].

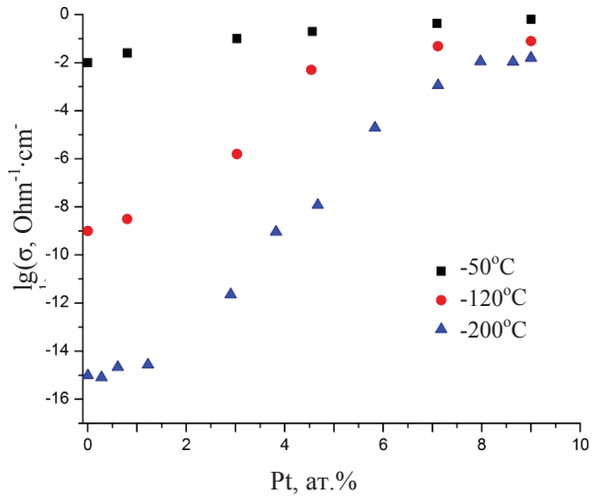


Figure 1 – The dependence of the electrical conductivity of a-C: H <Pt> films obtained at different substrate temperatures versus platinum concentration.

Influence of platinum impurities on the conductivity of films deposited at a temperature of 50°C is insignificant.

Analysis of the results about the influence of Pt impurities on the conductivity of films σ, deposited at a temperature of 200°C, can be carried out from the perspective of the theory of percolation, which is widely used in the physics of disordered structures [2, 3]. The main provisions and conclusions of the theory are applicable to a specific range of issues of charge transport in a heterogeneous environment.

Consider the main conclusions of percolation theory to analyze the conductivity of an ordered structure, which is a plurality of conductive elements with a concentration x and conductivity

σ_M, randomly distributed in a dielectric matrix with a conductivity σ_D ($\sigma_D << \sigma_M$). According to percolation theory, conducting structure is a set of percolation clusters. For small values of x all clusters are small. However, as we approach the percolation threshold, the individual clusters are merged, and their average size increases. At a certain concentration x_c percolation cluster becomes infinite, ie, there is a path connecting the remote at arbitrarily large distances conducting regions within the dielectric matrix and completely passing through the conducting phase. Isolated clusters are placed in the "pores" of the infinite cluster.

To the left of the percolation threshold x_c, at a sufficiently large distance from it, the total conductivity of the medium can be represented as [3]

$$\sigma(x) = \sigma_D \left(\frac{x_c - x}{x_c} \right)^{-q}, \quad x < x_c, \quad q > 0 . \qquad (1)$$

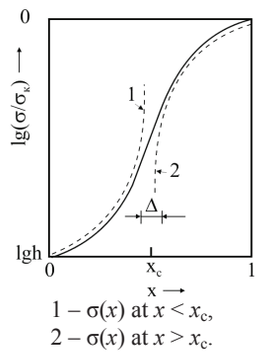
To the right of the percolation threshold concentration dependence of conductivity varies as

$$\sigma(\mathrm{x}) = \sigma_M \left(\frac{\mathrm{x} - \mathrm{x}_c}{1 - \mathrm{x}_c} \right)^{-t}, \ \mathrm{x} > \mathrm{x}_c, \ t > 0 . \qquad (2)$$

Conductivity at the appearance of an infinite percolation cluster is described by

$$\sigma(x_c) = \sigma_M \left(\frac{\sigma_D}{\sigma_M} \right)^{s}, \quad x = x_c, \quad s > 0 . \qquad (3)$$

The values of q, t and s, contained in (1 – 3), called the the critical indices of conducting cluster. View of the theoretical dependence σ(x) describing σ(x) before and after the percolation threshold is shown in Figure 2.



1 – σ(*x*) at $x < x_c$,
2 – σ(*x*) at $x > x_c$.

Figure 2 – The theoretical dependence σ (x) (solid line) [3].

The transition from dependence (1) to (2) is carried out in a small interval Δ in the neighborhood of xc. Equation (1) holds if $\sigma(x) << \sigma(x_c)$ and $x_c - x >> \Delta$, and the relation (2) holds for $\sigma(x_c) << \sigma(x) << \sigma(x_m)$ or $x - x_c >> \Delta$. Conductive cluster is also characterized by the correlation radius or characteristic size L

$$L = L_o \left| \frac{x - x_c}{x_c} \right|^{-\nu}, \qquad (4)$$

where ν – the critical index, also called the the critical index of the correlation length, L_o – the lattice constant. The value of L for $x < x_c$ order of the size of the cluster, and for $x > x_c$ – about the size of a non-conductive pores in it.

Critical exponents of percolation theory q, t, s and ν are related by

$$q = \frac{t}{s} - t , \qquad (5)$$

$$t = 1 + \nu(d - 2), \qquad (6)$$

where d – the dimension of space.

Numerous studies the problem of nodes and links in the task of percolation theory, conducted on various types of arrays using numerical methods, computer simulation using the Monte Carlo method, and using model experiments possible to determine the critical exponents and the limits of their changes depending on the dimension of the space. For three – dimensional space d = 3.

Note that the index t is very important because, unlike the percolation threshold x_c, it does not depend on the type of task and depends only on the dimension of the space. Therefore, in a real system in the first place, the index is compared with theory. On the other hand, the universality of the critical exponents of percolation theory just to bring you its analysis of heterogeneous conductivity of disordered structures.

Analyzing the type of concentration dependence of conductivity of a-C: H <Pt> films, deposited at a temperature of 200°C, from the standpoint of percolation theory, we can estimate the value of the percolation threshold x_c and percolation index heterogeneous system a-C:H-Pt. For these films a-C:H<Pt>, $x_c \approx 5$ ат.%, σ_D – conductivity diamond a-C:H, σ_M – conductivity of platinum. index is determined from the relationship

$lg(\sigma/\sigma_D) = f(lg[(x_c-x)/x_c])$. The values of percolation parameter q, s and t constitute 1.43; 0.55 and 3.18, respectively, and they are close to the percolation parameter values obtained points of the conductive spherical embedded in a dielectric matrix [4]. Based on the consideration of the submission, the rapid increase in the conductivity of the films of a-C:H<Pt> with increasing concentration of platinum can be explained by the conductivity of graphite sp^2-clusters, the conductivity of which is close to the metal. In the amorphous a-C:H <Pt> film matrix formed irregular metal net consisting of Pt clusters and sp^2-graphite clusters. As shown earlier, the introduction of impurities followed by platinum diamond graphitization matrix of a-C:H films, which coincides with the findings of work on the modification of films of a-C: H doped metals [4, 5].

Conclusion

It was studied the electrical properties of thin films of amorphous hydrogenated carbon a-C:H films and a-C:H films modified by platinum nanoclusters (a-C:H<Pt>). It was found that the electrical properties of the a-C:H films substantially dependent of deposition temperature t_s. Changing t_s of 50 to 200°C the conductivity of the films decreases from 10^{-2} to 10^{-15} (ohm • cm)$^{-1}$. This is due to an increase in concentration of sp^3 and a decrease in the concentration of sp^2-hybridized bonds, characterized for graphite (t_s = 50°C) and a diamond (t_s = 200°C) a-C:H structure.

Modification of diamond-like films a-C:H doped by platinum deposited at a temperature of 200°C results in substantially by 13 orders of magnitude increase in conductivity. It is essential that the films a-C:H <Pt> are characterized by percolation conduction mechanism.

The obtained results are important for the production and application of nanomaterials with new non-linear properties of diamond-like carbon-based media containing nanoclusters metals.

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