UDC 669.018; 621.315.392

The percolation mechanism of conductivity in nanocomposite a-C:H<Ag+Ti> films

Ye.S. Mukhametkarimov[1*], S.L. Mikhailova[1], K. Dautkhan[1], A. Bashen[1], Zh.N. Zhumatayev[1], O.V. Rofman[2], S.Ya. Maksimova[1], O.Yu. Prikhodko[1]

[1]*National Nanotechnological Laboratory of Open Type, Al-Farabi Kazakh National University, 71, Al-Farabi Ave., 050040, Almaty, Kazakhstan*

[2]*National University of Science and Technology, MISiS, 4, Lenin Ave., 119049, Moscow, Russia*

e-mail: ye.mukhametkarimov@gmail.com

The presented work is about percolation mechanism of electrical conductivity of composite a-C:H<Ag+Ti> films. The a-C:H<Ag+Ti> thin films were deposited onto quartz substrates by ion-plasma magnetron sputtering method. High purity argon (Ar) and methane (CH_4) gases mixture and combined target of polycrystalline graphite with the purity of 99.99%, silver (99.99%) and titanium (99.99%) were used to produce a-C:H<Ag+Ti> films. Resistance of the produced films has been measured using «two probe» method to obtain concentration dependence of electrical conductivity. Conductivity of a-C:H<Ag+Ti> films was described theoretically in two ways: using the classical theory of percolation and a general effective medium (GEM) theory. Staircase percolation can be seen from the experimental results. The first percolation threshold occurs at the concentration $x_c = 0.015$ and the second one - at $x_c = 0.07$. This could take place due to the fact that a-C:H<Ag+Ti> composite material consist of two different inclusions, silver and titanium dioxide nanoparticles. The percolation mechanism of a-C:H<Ag+Ti> film conductivity could be described by classical percolation theory and by effective medium model as well.

Key word: Amorphous carbon thin films, silver nanoparticles, nanocomposite, percolation, effective medium theory.
PACS:61.00

Introduction

Composite materials based on the dielectric matrix with metal nanoparticles inclusions are of considerable interest in connection with possibility of their wide practical application in various fields of science and technology. A wide variety of functional properties of these composites allows using them, starting from energy sector (in solar cells) to targeted delivery of drugs in medicine [1-5].

Plasmon resonance absorption of electromagnetic radiation in the visible region of the spectrum on free surface electrons of metal nanoparticles takes place in nanocomposite materials based on the dielectric or semiconductor high-resistivity matrix and some metals nanoparticles in it [6]. Role of the matrix in such nanocomposite materials is to isolate the metal nanoparticles and preventing their agglomeration. Parameters of the resonance absorption are determined by dielectric permittivity of the matrix and by physical and chemical nature of the metal [6,8]. This is shown in the studies of composite materials based on semiconductor matrices as SnO_2 [9], ZnO [10] and CdS [11, 12] and polymer matrices [13] with inclusions of silver and gold nanoparticles.

It is significant, that in such composite materials, under certain conditions, great surface amplification of Raman scattering of light (SERS effect) [14] is manifested, which allows to detect even individual molecules, and using silver nanoparticles, significantly enhance the antibacterial properties of coatings as well.

In modern nanomaterials science, amorphous diamond-like hydrogenated carbon films (a-C:H) have a special interest of researchers. This is due to a number of unique mechanical and electronic properties of these films. Taking into account high mechanical strength and reliability of the films, electronic devices made on the basis of these materials have extremely high speed, power, able to operate in a very wide temperature range and have high radiation resistance.

Diamond-like carbon materials containing metal nanoparticles represent a new class of nanostructured materials, called nanocomposites. In connection with this, development of nanomaterials with new properties based on diamond-like carbon media modified by metal impurities that significantly differ in nature by chemical interaction with carbon atoms and study of their structure and electronic properties is one of the most relevant and extremely important areas of research in nanotechnology and nanomaterial science [15].

In addition, to optical effects of the a-C:H<Ag+Ti> film [16], there are unique electrical properties. In the a-C:H<Ag+Ti> films, a double percolation transition with respect to conductivity is realized. Films with concentration of silver nanoparticles near the percolation threshold can be promising for creating highly sensitive small bending sensors [17, 18].

Experiment

Deposition of a-C:H<Ag+Ti> nanocomposite films was carried out in the vacuum chamber using ion-plasma magnetron sputtering of the combined target. Basic technological parameters of a-C:H <Ag+Ti> film production represented in the Table 1.

Table 1 – Basic technological parameters for a-C:H <Ag+Ti> film production

Working gas composition	The pressure in chamber P, Pa	Deposition temperature, ^{o}C	The distance from the target to the substrate, cm	Specific discharge power, W/cm	The magnetic field strength H, mlT
96% Ar + 4% CH_4	0.8-1.0	100	3.5	3-4	~30

High purity argon (Ar) and methane (CH_4) gases mixture and combined target of polycrystalline graphite with the purity of 99.99%, silver (99.99%) and titanium (99.99%) were used to produce a-C:H<Ag+Ti> films. The a-C:H<Ag+Ti> films were deposited on a glass and quartz substrates.

Resistance of the produced films has been measured using «two probe» method to determine concentration dependence of electrical conductivity which represented on Figure 2. Note that conductivity of a-C:H<Ag+Ti> films at the maximum of Ag concentration remains much lower with respect to conductivity of polycrystalline graphite. This means that in these films there is no through-conduction channel over the regions of graphite-like carbon with sp^2-hybridized bonds presented in diamond-like matrix with sp^3-hybridized bonds.

Simulation of the percolation conductivity processes in a-C:H<Ag+Ti> nanocomposite films

Conductivity of nanocomposite material can be described in two ways: using the classical theory of percolation (flow) and the model of a general effective medium.

Let us consider the main conclusions of percolation theory for conductivity analysis of the disordered structure, which is a set of conducting elements with concentration x and conductivity σ_M randomly distributed in a dielectric matrix with conductivity σ_D ($\sigma_D << \sigma_M$). According to percolation theory, conducting structure is a set of percolation clusters. For small values σ_M of x, all clusters are small. However, as we reach the percolation threshold, individual clusters merge, and their average size increases. At a certain concentration of x_c, the percolation cluster becomes infinite, i.e. there appears a path connecting remote to arbitrarily large distances the conducting regions inside the dielectric matrix and wholly passing through the conducting phase.

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 by [19]

$$\sigma_c = \sigma_D (x_{cr} - x)^{-q}, \text{ for } x < x_c, \qquad (1)$$

where σ_D is conductivity of the matrix.

To the right of the percolation threshold, the concentration dependence of conductivity varies according to the law

$$\sigma_c = \sigma_M (x - x_{cr})^t, \text{ for } x > x_c, \qquad (2)$$

where σ_M is the conductivity of the conducting phase.

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

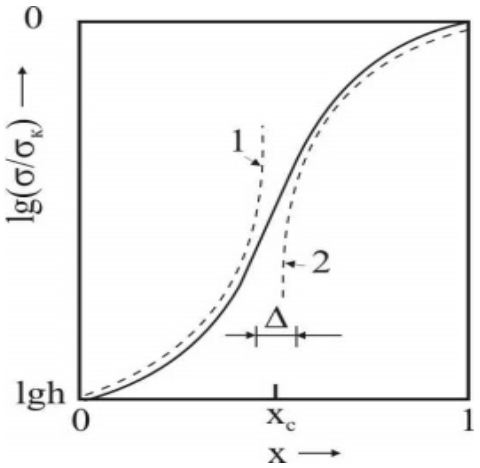
$$\sigma(x_c) = \sigma_M \left(\frac{\sigma_D}{\sigma_M} \right)^s, \; x = x_c, \; s > 0. \qquad (3)$$

The quantities q, t and s in (1-3) are called the critical indices of the conducting cluster.

The curve of theoretical dependence $\sigma(x)$ describing $\sigma(x)$ before and after the percolation threshold is shown in Figure 1. The transition curve (1) to (2) takes place in a small interval Δ in the vicinity of the x_c point. Relation (1) is satisfied if $\sigma(x) << \sigma(x_c)$ or $x_c - x >> \Delta$, and relation (2) holds for $\sigma(x_c) << \sigma(x) << \sigma(x_M)$ or $x - x_c >> \Delta$. The conducting cluster is also characterized by a correlation radius or a characteristic size l

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

where ν is critical index, also called the critical index of the correlation radius, l_o is the lattice period.



1 - $\sigma(x)$ at $x < x_c$, 2 - $\sigma(x)$ at $x > x_c$.

Figure 1– The theoretical dependence σ(x) (solid line) [19]

Quantity l for $x < x_c$ is in the order of cluster size itself, and for $x > x_c$ in the order of nonconducting pores size in it.

The critical indices of the percolation theory q, t, s and ν are related to each other by the relations

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

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

where d is dimension of space. For a three-dimensional composite the classical values are: t = (1.6 ÷ 2.0), q≈1, s≈0.62.

We note that index t plays a very important role, since, unlike the percolation threshold x_c, it does not depend on the type of the problem, but depends only on the dimensionality of the space. Therefore, in real systems, this index is primarily compared with the theory. On the other hand, the universality of critical indices of percolation theory just allows us to involve it for the analysis of heterogeneous disordered structures conductivity.

Figure 2 shows concentric dependence of conductivity of a-C:H <Ag+1.0 at.% Ti> films. In this figure, silver concentration x is represented as the volume fraction in the matrix of the films. The curves describing behavior of concentration dependence of conductivity up to (curves 1 and 2) and after (percolation curves 1 'and 2') are represented using expressions (1) and (2). It follows from this approach that concentration dependence experimental data of a-C:H<Ag+1.0 at.% Ti> films conductivity can be described by two percolation transitions (the so-called staicase percolation).

Note that there are inclusions of both Ag and TiO_2 nanoparticles in the matrix of the studied a-C:H<Ag+Ti> films, and several percolation transitions can occur in such nanocomposites.

Let us consider the concentration dependence of the a-C:H<Ag+Ti> films conductivity using the effective-medium model (General Effective Medium, GEM), which is used to describe concentration dependences of conductivity of composite materials [20]. The expression to determine the conductivity σ in the theory of general effective medium is written as follows [20]

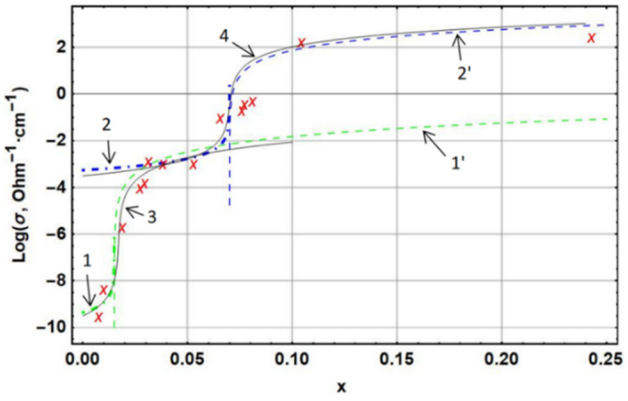
$$\frac{x(\sigma_D^{\frac{1}{t}} - \sigma(x)^{\frac{1}{t}})}{\sigma_D^{\frac{1}{t}} + A\sigma(x)^{\frac{1}{t}}} = \frac{(1-x)(\sigma_M^{\frac{1}{t}} - \sigma(x)^{\frac{1}{t}})}{\sigma_M^{\frac{1}{t}} + A\sigma(x)^{\frac{1}{t}}} = 0, \qquad (7)$$

$$A = \frac{1 - x_c}{x_c}, \qquad (8)$$

where the exponent is defined as $t = (1 - x_c)/(1 - l)$.

The results of a comparison of theoretical description of the percolation process according to the classical theory and general effective medium model with experimental values of concentration

dependence of conductivity of a-C:H<Ag+1.0 at.% Ti> films are shown in Figure 2, curve 3.



X: are the experimental values
1: $x_c = 0.015$, $t = 1.7$; 1': $x_c = 0.07$, $t = 1.4$;
2: $x_c = 0.015$, $q = 0.9$; 2': $x_c = 0.07$, $q = 0.9$;
3 и 4 - effective environment model with parameters $x_c = 0.018$, $t = 1$, $\sigma_D \approx 3 \cdot 10^{-10}\ Ohm^{-1} \cdot cm^{-1}$, $\sigma_M \approx 0.5\ Ohm^{-1} \cdot cm^{-1}$, $l = 0.4$.

Figure 2 – Theoretical (1 and 1 ', 2 and 2', 3 and 3 ') and experimental (x) dependence of conductivity of a-C:H<Ag+1.0 at.% Ti> nanocomposite films on Ag volume fraction

From the figure 2 it follows that classical theory of percolation and approach based on the general effective medium model make it possible to describe the region of percolation transition before and after the percolation threshold in a-C:H<Ag+1.0 at.% Ti> nanocomposite films.

Conclusions

Conductivity of a-C:H<Ag+Ti> films at the maximum of Ag concentration remains much lower compared to conductivity of polycrystalline graphite. This means that in these films there is no through-conduction channel over the regions of graphite-like carbon with sp^2-hybridized bonds presented in diamond-like matrix with sp^3-hybridized bonds. From concentration dependence of conductivity we conclude that two percolation transition occur in the obtained a-C:H<Ag+Ti> composite material. These percolation mechanisms of film conductivity could be adequately described by the classical percolation and general effective medium theories.

Acknowledgments

This research was supported by grant 4608/GF4 of the Committee of Science of the Ministry of Education and Science of the Republic of Kazakhstan.

Reference

1. H. Wenbo, P. Pavaskar, L. Zuwei, J. Theiss, M. Aykol, B. Stephen. Plasmon resonance enhancement of dye sensitized solar cells // Energy Environ. Sci. –2011. – Vol.4. –P.4650–4655.

2. H.A. Atwater, A. Polman. Plasmonics for improved photovoltaic devices // Nature Materials. – 2010. – Vol.9. – P. 205-213.

3. N. Jeffrey, W. Anker, P. Hall, O. Lyandres, N. C. Shah, Jing Zhao, R. P. Van Duyne. Biosensing with plasmonic nanosensors // Nature Materials. 2008.–Vol. 7. – P. 442-453.

4. K. Prashant, Jain. Xiaohua Huang, H. Ivan, H. El-Sayed, M. A. El-Sayed. Noble Metals on the Nanoscale: Optical and Photothermal Properties and Some Applications in Imaging. Sensing. Biology and Medicine // Accounts Of Chemical Research. – 2008. –Vol. 41. – P.1578-1586.

5. Jiongxin Lu, C. P. Wong. Recent Advances in High-k Nanocomposite Materials for Embedded Capacitor Applications // IEEE Transactions on Dielectrics and Electrical Insulation. – 2008. – Vol. 15. – P. 1322.

6. M. Quinten. Optical Properties of Nanoparticle Systems // Wiley-VCH. Verlag GmbH & Co. KGaA, Weinheim. Germany – 2011. – P. 502.

7. A. M. Mahmoud, Maysamreza Chamanzar, Ali Adibi, Mostafa A. El-Sayed. Effect of the Dielectric Constant of the Surrounding Medium and the Substrate on the Surface Plasmon Resonance Spectrum and Sensitivity Factors of Highly Symmetric Systems: Silver Nanocubes // J. Am. Chem. Soc. 2012. – Vol. 134. – P.6434–6442.

8. E. Hutter, J. H. Fendler. Exploitation of Localaized Surface Plasmon Resonance // Adv. Mater. – 2004. – Vol. 16. –P.1685.

9. W. Wu, L. Liao, S.F. Zhang, J. Zhou, X.H. Xiao, F. Ren, L.L. Sun, Z.G. Dai, C.Z. Jiang. Non-centrosymmetric Au/SnO_2 Hybrid Nanostructures with Strong Localization of Plasmonic for Enhanced Photocatalysis Application // Nanoscale. – 2013. – Vol.5. – P.5628.

10. Y.K. Mishra, V.S.K. Chakravadhanula, V. Hrkac, S. Jebril, D.C. Agarwal, S. Mohapatra, D.K. Avasthi, L. Kienle, R. Adelung. Crystal growth behaviour in Au-ZnO nanocomposite under different annealing environments and photoswitchability // J. Appl. Phys. – 2012. – Vol. 112. – P.064308.

11. H. DuanaYimin Xuan. Synthesis and optical absorption of Ag/CdS core/shell plasmonic nanostructure // Solar Energy Materials and Solar Cells. -2014. – Vol.121. –P. 8-13.

12. D. Ziemannn, V. May. Exciton Formation and Quenching in a Au/CdS Core/Shell Nanostructure // J. Phys. Chem. Lett. – 2015. – Vol.6. – P.4054–4060.

13. Long-De Wang, Tong Zhang, Xiao-Yang Zhang, Yuan-Jun Song, Ruo-Zhou Li, Sheng-Qing Zhu. Optical properties of Ag nanoparticle-polymer composite film based on two-dimensional Au nanoparticle array film // Nanoscale Res. Lett. –2014. Vol.9. – P. 155.

14. B. Sharma, R. F. Renee, A-I Henry, E Ringe, P.Richard, Van Duyne. SERS: Materials. applications. and the future // Materials Today. – 2012. – Vol.15. – P. 16-25.

15. O.Yu. Prikhodko, S.L. Mikhailova, E.C. Muhametkarimov, S. Ya. Maksimova, N. K. Manabaev, K. Dauthan. Optical properties of a-C:H thin films modified by Ti and Ag /Proc. of SPIE. Nanostructed Thin Films IX. San-Diego. California. USA. – 2016. – Vol. 9929. – P. 99291G-1 – 9929G-6.

16. O.Yu. Prikhodko, Ye.S. Mukhametkarimov, S.L. Mikhailova, K. Dauthan, S.Ya. Maksimova. Structure and Phase Composition of Thin a-C:H Films Modified by Ag and Ti // Optics and Spectroscopy. –2017. – Vol. 123. – P.353–358.

17. M. O. Mendoza, M. Edna, A. Valenzuela, E. Prokhorov, G. Luna-Barcenas, S. Kumar-Krishnan. Percolation phenomena in polymer nanocomposites // Adv. Mater. Lett. – 2016. – Vol. 7. –P. 353-359.

18. M. Segev-Bar, H. Haick. Flexible Sensors Based on Nanoparticles // ASC Nano. – 2013. –Vol. 7. – P. 8366-8378.

19. A.L. Efros, B.I. Shklovskii. Critical Behavior of Conductivity and Dielectric Constant near the Metal-Non Metal Transition Threshold// Phys. Stat. Sol. B. – 1976. – Vol. 76. – P. 475-485.

20. I. Balberg. The percolation staircase model and its manifestation in composite materials // The European Physical Journal B. – 2013. – Vol. 86. – P. 1-17.