Optical properties of a-C:H thin films modified by Ti and Ag

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ABSTRACT

Structure and optical properties of amorphous diamond-like carbon (a-C: H) thin films modified with Ag, Ti and Ag + Ti metal impurities are studied. The films were prepared by ion-plasma magnetron sputtering of combined polycrystalline graphite and metal target in the mixture of Ar and CH_4 gases. AFM, SEM and TEM methods show that a-C:H<Ag+Ti> films are heterogeneous, nanostructured and characterized by the presence of silver nanoclusters on the surface sized ~ 60 nm and both Ti and Ag nanoclusters with a mean size ~ (2 ÷ 3) nm in the bulk of films. It was found that in a-C:H<Ag+Ti> films as well as in a-C:H<Ag> films plasma resonance absorption due to excitation of surface plasmons in silver nanoclusters in the visible region of spectrum takes place. Intensity of the resonance absorption in the a-C:H<Ag+Ti> films increases with increase in concentration of silver. The results are important for produce of nanomaterials with nonlinear optical properties based on the amorphous diamond-like carbon films containing metal nanoclusters.

Keywords: amorphous diamond-like carbon films, ion-plasma sputtering, structure, modification, metal nanoparticles, optical resonance absorption

1. INTRODUCTION

In today material science of nanoscale objects amorphous hydrogenated diamond-like carbon films (a-C:H) modified by metal nanoclusters (a-C:H<M>) cause special interest among researchers. This occurs due to number of unique mechanical and electronic properties of these films. Besides high mechanical strength and reliability, electronic devices which is made with usage of these materials have an extremely high speed and capacity, they are able to operate in a wide temperature range and characterized by high resistance to radiation. [1].

Features of the interaction between metal atoms and the matrix of a-C:H films significantly depends on the possibility of formation stable chemical compounds between metal and carbon. The metals that do not chemically react with the carbon matrix, are Ag, Au, Al, Pt, etc. These metals embeded in the a-C:H films matrix usually form isolated nanoclusters (nanoparticles). Presence of isolated metal nanoclusters in the matrix of a-C:H films leads to resonance absorption of electromagnetic radiation caused by surface electrons in the metal nanoclusters (surface plasmon resonance) [1-3]. The resonance reveals in linear light absorption and stimulates generation of non-linear optical effects in the same spectral range [4].

Such materials are considered be promising for practical applications in picosecond range optical switches and in magnet-optics for information storage. [4]. Modification of a-C:H films matrix by metals which capable under certain conditions form chemical bonds with carbon atoms also leads to a number of new electronic and mechanical properties of the films. Such metals, for example, include Ti, allows significantly increase thermal stability of a-C:H films [5-7]. Thus, diamond-like carbon films modified with metals that have new specific properties represent themselves promising class of nanostructured materials.

Thereby, it is of interest to study the structure and optical properties of a-C:H films simultaneously modified with metal impurities which have fundamentally different nature of interactions with the carbon atoms.

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The goal of the work was to study the structure and optical properties of amorphous diamond-like carbon thin films modified with Ag and Ti impurities.

2. EXPERIMENTAL

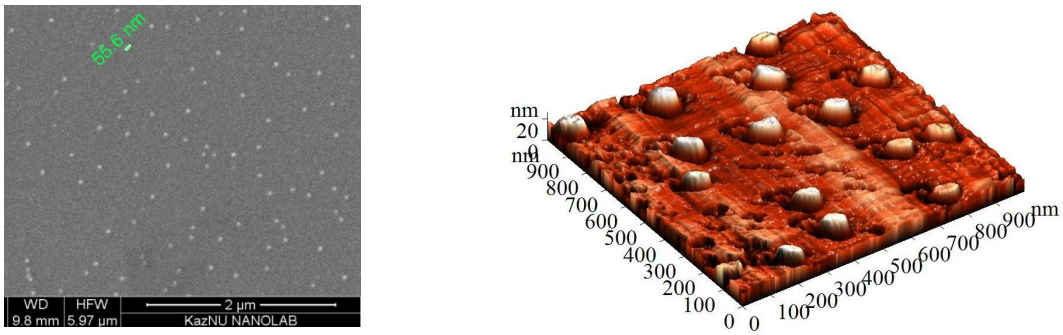
The a-C:H, a-C:H<Ag>, a-C:H<Ti> and a-C:H<Ag+Ti> films were obtained by ion-plasma magnetron sputtering in Ar and CH_4 gas mixture at 0.9 Pa and 50 °C of substrate temperature. Modification of a-C:H films with metal were achieved by sputtering combined target consisting of polycrystalline graphite, silver and titanium. Alteration of metal concentration in the films carried out by changing the area of graphite and metal ratio on the combined target. Thickness of the films was ranged from ~ 80 to ~ 100 nm, and it was determined using scanning electron microscope (SEM) Quanta 3D 200i at electron beam with energy 30 keV by scanning the chip of the c-Si/a-C:H<M> structure.

Determination of elemental composition, percentage of component and morphology of the a-C:<M> films was also conducted by Quanta 3D 200i using energy-dispersive analysis. In addition, the morphology of the films was investigated by semi-contact method of atomic force microscope (AFM) Ntegra Therma. For these studies, the films were deposited on the cleaned dioxide surface of single crystal silicon. Concentration of metal impurities in the films varied from 0 to 4.67 at.% in case of Ag and 1.17 at.% for Ti .

Structure of the films was studied by transmission electron microscope (TEM) JEM 2100 JEOL with 200 kV accelerating voltage. The films were deposited on the fresh chips of NaCl. Analysis of the energy-dispersive spectra and morphology of a-C:H<M> films showed that they contain only metal impurities and they are continuous. Optical properties of the films were investigated by Shimadzu UV2000 spectrophotometer in the spectral range from 250 to 1450 nm.

3. RESULTS AHD DISCUSSION

Figure 1 shows SEM and AFM morphology of a-C:H<4.67 at. % Ag+1.17 at.% Ti> film . The figure demonstrates that surface of the film is continuous with isolated inclusions of nanoclusters having the size no greater than ~ 60 nm.

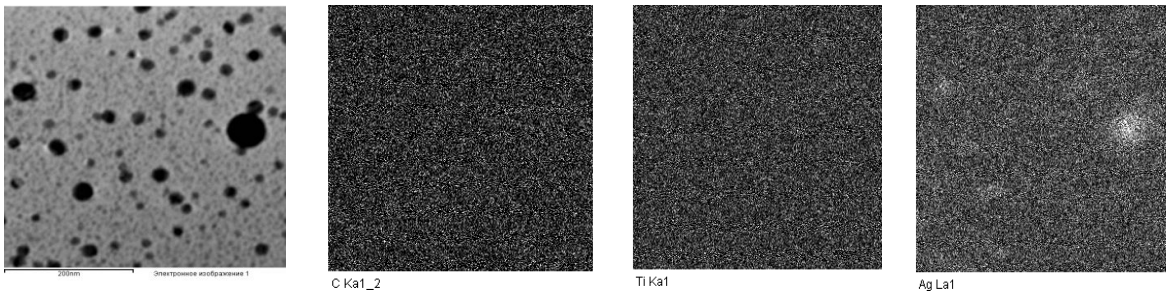


a) b)

Figure 1. SEM (a) and AFM (b) morphology of a-C:H<4,67 at.% Ag+1,17 at.% Ti> film.

Distribution of C, Ti and Ag atoms in a-C:H<Ag+Ti> films was monitored by TEM JEM 2100 JEOL by scanning the surface in bright-field mode. Scanning depth was ~ 2 nm, and scanning area was 500x500 nm (Figure 2). Figure 2 shows TEM image of the scanning area in a dark field mode (Figure 2 (a)) and the distribution of C, Ti and Ag atoms in the a-C:H<Ag+Ti> film (Figures 2 b, c, d, respectively).

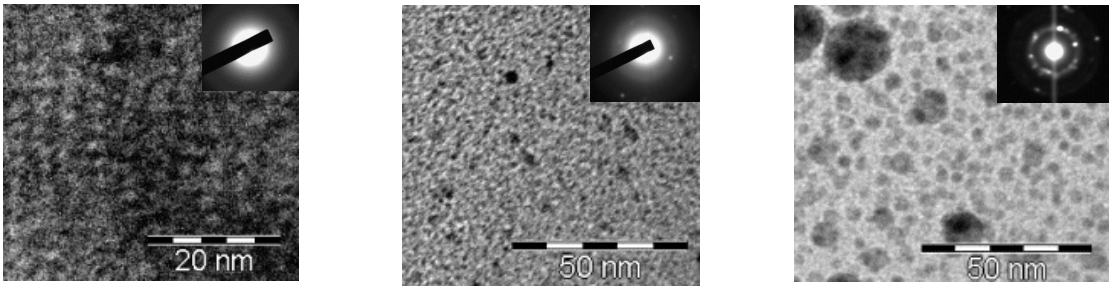
From Figure 2 one can conclude that a-C:H<Ag+Ti> film has complex structure with inclusions of the different size nanoclusters, and both C and Ti atoms are distributed evenly. Distribution of Ag on the film is uneven. There are areas with more higher concentrations of Ag (bright areas in Figure 2 (d), in bright field mode). Hence, nanoclusters on the surface of a-C:H<Ag+Ti> films detected by SEM and AFM (see Figure 1) are silver clusters.



a) b) c) d)

Figure 2. SEM-image scan area (a) and distribution of C (b), Ti (c) and Ag (d) in a-C:H<4.67 at.% Ag+1.17 at.% Ti> film.

It follows from Figure 3 (a) that a-C:H film has an amorphous structure. In a-C:H<Ti> films on the background of electron diffraction (Figure 3 (b)) one can see diffuse halo with some point reflections. This suggests that the matrix of these films is amorphous, and it contains a fraction of isolated titanium nanocrystallites. In the TEM-image of a-C:H<Ti>films (Figure 3 (b)) on the background of homogeneous matrix one can see the small nanoclusters.



a) a-C:H b) a-C:H<1.09 at.% Ti> c) a-C:H<3.30 at.% Ag>

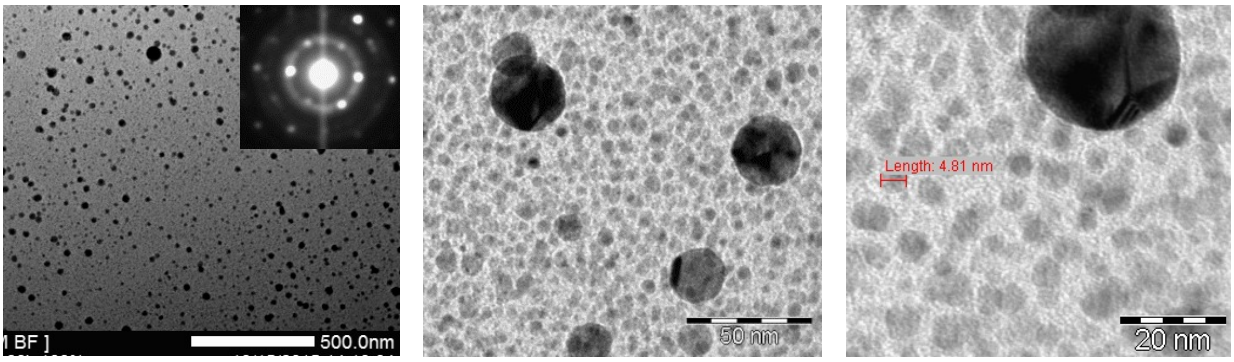
Figure 3. Electron diffraction pattern and TEM-image of a-C:H (a), a-C:H<Ti> and a-C:H<Ag> films.

The electron diffraction pattern of a-C:H<Ag> films (Figure 3 (c)) was received from the region containing large silver nanocluster. Therefore, it describes mostly Ag nanoclusters structure and small area around it. It follows from electron diffraction pattern evidence, that the cluster has a single crystal structure, and it is in the amorphous matrix. From TEM-image of a-C:H<Ag> films in Figure 3 (c) one can see that in the amorphous a-C:H matrix appears large number of isolated silver nanoclusters with different sizes, and concentration of big-sized nanoclusters is minor. Figure 4 shows electron diffraction pattern and TEM-image of a-C:H<Ag+Ti> films.

The electron diffraction pattern of a-C:H<Ti+Ag> films as well as that of the film mentioned above were obtained from the region with big-sized nanocluster and describes its monocrystalline structure. TEM-image of a-C:H<Ti+Ag> films (Figure 4 (b, c)) testifies to complex heterophase structure of the films.

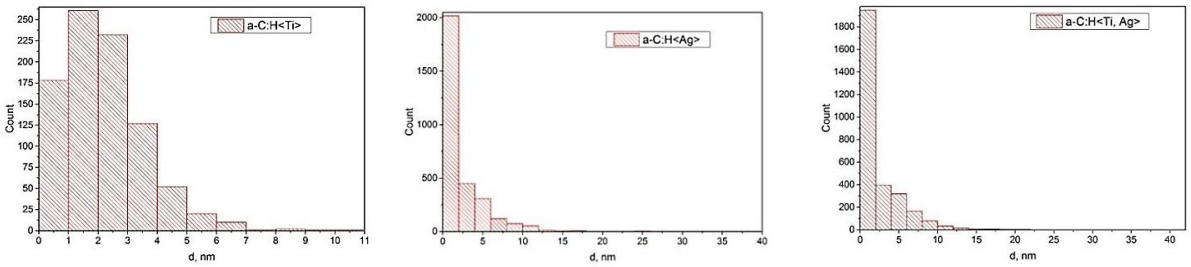
The size distribution of nanoclusters in a-C:H <Ti> (Figure 3 b), a-C:H<Ag> (Figure 3 c), and a-C:H<Ti+Ag> (Figure 4) films was determined from the data of TEM images processing using ImageJ program (Figure 5).

It follows from the analysis of the data presented in Figure 5 that an average size of metal nanoclusters in a-C:H<Ti>, a-C:H<Ag> and a-C:H<Ag+Ti> films is ~ (2 ÷ 3) nm.



a) b) c)

Figure 4. Electron diffraction pattern and TEM-image of a-C:H<3.49 at.% Ag+0.99 at. % Ti> film.



a) a-C:H <1.09 ат.% Ti> b) a-C:H <3.30ат.% Ag> c) a-C:H<3.49 ат.% Ag + 0.99 ат.% Ti>

Figure 5. Size distribution of nanoclusters in a-C:H<M> films.

Optical density spectra of $D(\lambda)$ a-C:H and a-C: H <M> films were studied. Figure 6 shows the $D(\lambda)$ spectra of a-C:H and a-C:H<Ag> films with different content of silver.

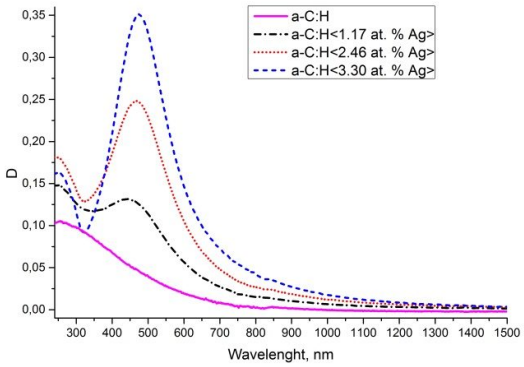


Figure 6. Influence of the Ag concentration on the optical density of a-C:H<Ag> films.

It can be seen that a-C:H film has a low optical density (high transparency) within the studied optical spectrum range from 250 to 1450 nm. Modification of a-C:H films with Ag leads to a resonance absorption in the visible region of the spectrum (plasma absorption). Growth of Ag concentration in the films leads to significant increase in absorption intensity and to slight displacement of the peak maximum from 450 to 474 nm. The observed resonance absorption in a-C:H<Ag> films occurs due to the absorption of electromagnetic radiation by free electrons in silver nanoclusters [4].

Figure 7 shows a-C:H, a-C: H<Ti>, a-C:H<Ag> and a-C:H<Ag+Ti> films $D(\lambda)$ spectra. One can see that modification of a-C:H films with Ti leads to a significant shift of the fundamental absorption edge towards longer wavelengths, i. e. it reduces optical band gap. Besides it leads to slight increase in optical density in transmission region in comparison with that in a-C:H films. In contrast, resonant absorption peak is observed in the visible region of the $D(\lambda)$ spectrum of a-C:H films modified simultaneously with Ag and Ti impurities. This peak in the spectrum is associated with presence of silver nanoclusters in the structure of the a-C:H<Ti +Ag> films.

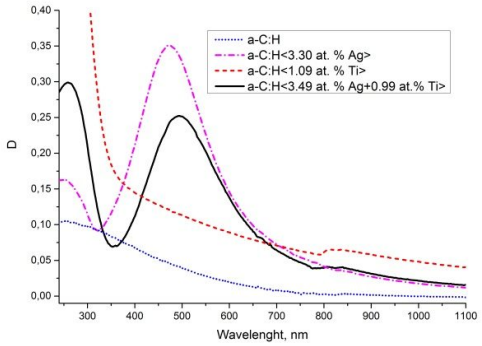


Figure 7. The optical density spectra of a-C:H , a-C:H<Ti>, a-C:H<Ag> and a-C:H< Ag+Ti> films.

It should be noted that simultaneous increase in Ti and Ag concentration in a-C:H<Ag+Ti> films leads to a significant increase of resonance absorption peak and its maximum displacement to 532 nm (Figure 8).

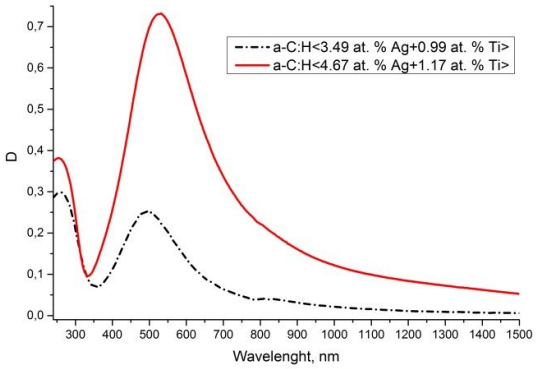


Figure 8. Influence of Ti and Ag impurities concentration on the optical density of a-C:H<Ag+Ti> films.

It is essential that preliminary studies demonstrated higher thermal stability of the resonance absorption in a-C:H<Ti+Ag> films in comparison to a-C:H<Ag> films.

The presence of a resonance absorption band in the optical spectra of a-C:H<Ag> and a-C:H<Ag+Ti> films makes it possible to estimate the average size of silver nanoclusters within their matrix, using the scattering theory of Mie [4]. Spectral dependence of the absorption coefficient of the system with metal nanoclusters sized less than $\lambda/20$, is described by the relation

$$\alpha = \frac{18\pi n^3}{\lambda} \cdot \frac{V\varepsilon_2}{\left(\varepsilon_1 + 2n^2\right)^2 + \varepsilon_2^2}, \qquad (1)$$

where λ - wavelength of incident radiation, $\varepsilon(\lambda) = \varepsilon_1 + i\varepsilon_2$ and V - dielectric constant and the volume fraction of metal nanoclusters, respectively, n - refractive index of the dielectric matrix. Resonant absorption is observed upon condition $\varepsilon_1 + 2n^2 = 0$.

Average diameter d of nanocluster is calculated from the half width of resonant optical absorption peak $\Delta\lambda$ and the characteristic wavelength λ_p at which plasmon resonance occurs

$$d = \frac{v_f \lambda_p^2}{\pi c \Delta\lambda}, \quad (2)$$

where v_f - electrons velocity at the Fermi level in the metal, c - speed of light.

Since the absorption coefficient α is proportional to the optical density D, spectral position of the resonance peak and its half-width for calculation of the average diameter d of nanoclusters can be determined from the absorption spectra. According to calculation the average diameter d of silver nanoclusters in a-C:H<Ag+Ti> films is about 2 nm for the Ag concentration equal to 3.49 and 4.67 at %. This is in good agreement with the estimation results of average size of nanoclusters using the TEM-images.

4. CONCLUSIONS

Thus, a-C:H<Ag+Ti> thin films, obtained by ion-plasma sputtering, are heterogeneous, nanostructured and characterized by presence on the surface of the films ~ 60 nm sized Ag nanoclusters and both Ti and Ag nanoclusters with average size ~ (2 ÷ 3) nm in the bulk of films.

There are plasma resonance absorption due to the excitation of surface plasmons in silver nanoclusters in a-C:H<Ag+Ti> films as well as that in a-C:H<Ag> films in the visible region of the spectrum. Intensity of the resonance absorption increases with silver concentration rise in matrix of a-C:H<Ag+Ti> films. The results of study are important for development of nanomaterials based on the amorphous diamond-like carbon films containing metal nanoclusters, with nonlinear optical properties.

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