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Annealing influence on the structure and plasmon resonance in amorphous diamond-like carbon films modified by titanium and silver

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The spectrum of the amorphous diamond like carbon films containing silver and titanium nanoparticles (a-C:H<Ag, Ti>) has a plasmon resonance in the visible region spectrum. The resonance is due to the absorption of electromagnetic waves by free electrons in the silver nanoparticles. However, thermal stability of these films almost hasn't been studied.

We present the study results of the annealing effect on the structure and optical properties of a-C:H<Ag, Ti> films. The films were obtained by ion-plasma DC magnetron sputtering of the silver and graphite combined target in the gas mixture atmosphere (96% Ar + 4% CH₄) at a pressure ~ 1 Pa and deposition temperature 100° C. The annealing of the films was carried out at 350 ° C during 30 minutes in argon atmosphere. Films thickness was ranged from 50 to 100 nm. Both silver and titanium concentration in films was ~ 1 at. %. Composition and surface morphology of the films was monitored by SEM Quanta 3D 200i with energy-dispersive analysis. Films structure was investigated by means of TEM JEOL JEM 2100 and Raman spectrophotometer Ntegra Therma with $\lambda = 473$ nm laser radiation. Optical properties were studied using a spectrophotometer Shimadzu UV 2000.

It is found that a-C:H<Ag, Ti> films contain only carbon, silver and titanium elements. The films are continuous and don't contain micron-size defects. The TEM-image shows presence of different size particles in the films matrix. The annealing doesn't lead to both change of the films thickness and size of the particles.

According to calculation by the Mie theory average size of the silver particles is about 2.7 nm. Histogram of nanoparticles size distribution in a-C:H<Ag, Ti> films were processed by analysis of TEM-image using ImageJ program. An average size of nanoparticles is \sim 2 nm that is in a good agreement with the calculations of the Mie theory.

The Raman spectra of a-C:H<Ag, Ti> films before annealing are similar to those of diamond-like carbon films. The annealing leads to a slight shift of *G* peak to lower energies without change in its intensity. *D* peak intensity increases, it is slightly shifted in the high-energy region of spectra. Such transformation of the Raman spectra indicates on the increase in the proportion of sp^2 hybridized bonds in a-C:H<Ag, Ti> films structure, i.e. the graphitization of the films structure occurs. Study of the absorption spectra shows that the as-prepared films have a pronounced plasmon resonance peak in the 480 nm region. After the films annealing, the peak shifts to the 520 nm region, and its half-width slightly increases. It should be noted that in the annealed a-C:H films modified only by silver impurity one can see significant intensity decrease and great increase in half-width of resonance absorption peak unlike in the as-prepared films. Thus, the plasmon resonance in a-C:H<Ag, Ti> films is more stable compared to a-C:H<Ag> films.

The obtained a-C:H<Ag, Ti> films are perspective for use in a wide application area, from the optical switches to anti-bacterial coatings.

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