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Plasmon Resonance in a-C : H Films Modified with Platinum Nanoclusters

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Optical density spectra of amorphous diamond-like films of hydrogenated carbon modified with platinum impurity (a-C : H<Pt>) have been investigated. a-C : H<Pt> films were prepared by the method of ion plasma magnetron co-sputtering of graphite and platinum in argon-hydrogen atmosphere. Platinum content in the films was varied from 0 to 9 at. %. In the optical spectra of a-C : H<Pt> films with different Pt content the peaks of resonance absorption in the range from 496 to 501 nm were found, whilst in the spectrum of a-C : H films the absorption peak is absent. The appearance of these absorption peaks in a-C : H<Pt> films is explained by resonance plasmon vibrations of free electrons in platinum nanoclusters. The average diameter of the Pt nanoclusters was estimated using electromagnetic theory of Mie, and it is ~ 5 nm.

Keywords: Amorphous diamond-like films of hydrogenated carbon (a-C : H) modified with platinum, Optical density, Nanoclusters, Plasmon resonance, Extinction section.

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1. INTRODUCTION

It is known that impurity of the metals weakly interacted with carbon atoms can form the metal nanoclusters in the matrix of a-C : H films at certain conditions [1]. Those heterophase systems reveal nonlinear optical properties and, as a rule, plasmon resonance absorption takes place [2, 3]. Among the metals chemically non-interacting with the a-C : H matrix Pt is of particular interest, since the structures with platinum nanoclusters can be applicable in an air-hydrogen fuel cells [4].

The goal of this work was to study the optical properties of amorphous diamond-like carbon films modified with platinum nanoclusters (a-C : H<Pt>).

2. TECHNIQUE

The a-C : H<Pt> films were produced by the ion plasma magnetron sputtering of the combined polycrystalline graphite-platinum target in the atmosphere of argon-hydrogen gases mixture at deposition temperature 200 °C.

The composition and morphology of the films were determined by scanning electron microscope Quanta 3D 200i with energy-dispersive analysis. The results show that there are no unintentional impurities and the micron sized defects in studied films, and a-C : H<Pt> films, as well as a-C : H films, are continuous [5]. The concentration of Pt in a-C : H matrix reached 9 at. %. Optical properties of the films were studied using Spectrophotometer CF 2000 and Shimadzu UV2000.

3. RESULTS AND DISCUSSION

Figure 1 represents the optical density spectra $D(\lambda)$ of a-C : H<Pt> films with different Pt content. It follows from fig. 1 that the presence of platinum impurity leads to significant increase of a-C : H the films optical density. Moreover, in $D(\lambda)$ spectra of a-C : H<Pt> films there are the distinct absorption peaks in the region from 496 to 501 nm, whilst in the spectrum of a-C : H films such absorption peak is absent. The intensity of the absorption peaks increases with platinum concentration in the films. The detected absorption peaks can be explained by photons absorption of surface free electrons of platinum clusters, i.e. resonance plasmon vibrations excitation. It should be noted that the same phenomenon was observed in materials containing isolated nanoclusters of metals [6-8].

The average diameter d of Pt nanoclusters in a-C : H<Pt> films can be estimated from electromagnetic theory of Mie [6, 7] using the half-width of resonance optical absorption peak $\Delta\lambda$ and characteristic wavelength of plasmon resonance λ_p

$$d = \frac{v_f \lambda_p^2}{\pi c \Delta\lambda}, \qquad (1)$$

where v_f is the electron velocity corresponding to the Fermi energy of the metal, c – is the velocity of light.

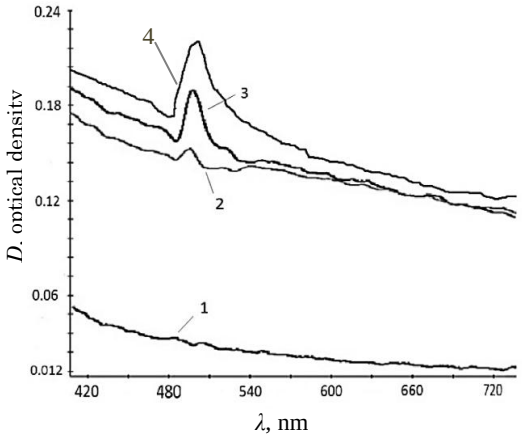

Fig.1 – Optical density spectra of a-C : H<Pt> films with Pt content (at. %): 1 – 0; 2 – 4.6; 3 – 7.1; 4 – 9.0

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For the films with Pt content 4.6, 7.1 and 9.0 at. % λ_p is equal to 496, 498 and 501 nm, respectively. The spectral position of the resonance peak and his half-width can be determined from $D(\lambda)$ spectra since the absorption coefficient a is proportional to optical density

$$D = -\lg T = a\lg(e), \tag{2}$$

where T is the optical transmission. According to the calculation, the average diameter of Pt nanoclusters in a-C : H<Pt> films with 4.6, 7.1 and 9.0 at. % of platinum is~ 5 nm.

Based on Mie theory the spectrum of resonance absorption in studied films can be calculated. Platinum nanoclusters are supposed to be embedded in amorphous diamond-like matrix. Let us estimate the extinction sectionQ_{ext} of surface plasmon resonance under the assumption of spherical shape of metal nanoclusters. In general, according to[9] $Q_{ext}$is determined from equation

$$Q_{ext} = \frac{2\pi}{|k|^2}\sum_{L=1}^{\infty}(2L+1)\,\mathrm{Re}(a_L + b_L), \tag{3}$$

where L – is the order of multipole excitation in nanoparticle, k – wave vector, a_L and b_L are expressed through Riccati-Bessels cylindrical functions ψ_L and η_L and are called Mie coefficients [9]. In calculations L was assumed to be equal 1, which corresponds to dipole.

$$a_L = \frac{m\psi_L(mx)\psi'_L(x) - \psi'_L(mx)\psi_L(x)}{m\psi_L(mx)\eta'_L(x) - \psi'_L(mx)\eta_L(x)},$$
$$b_L = \frac{\psi_L(mx)\psi'_L(x) - m\psi'_L(mx)\psi_L(x)}{\psi_L(mx)\eta'_L(x) - m\psi'_L(mx)\eta_L(x)}. \tag{4}$$

Argument (mx) of functions in equation (4) is determined from relation of optical constants of Pt metal particles and a-C : H matrix: $mx = \varepsilon_{\mathrm{Pt}} / \varepsilon_{\mathrm{a\text{-}C:H}}$. Second argument $x = |k|R$, where R is the particle radius measured in nm.

Usually a dielectric constant of metals is determined from Drude theory using known plasmon resonance absorption energy $\hbar\omega_p$ and electron collisions frequency γ. For platinum $\hbar\omega_p = 8{,}13$ eV and $\gamma = 1{,}05 \cdot 10^{13}\,\mathrm{s}^{-1}$.

In its turn the optical extinction is linearly related to absorption coefficient α: $\alpha = \rho Q_{ext}$, where ρ is a density of the particles in the film. Taking into account relation (2) we obtain

$$D = \rho\lg(e)Q_{ext}, \tag{5}$$

The last relation gives the opportunity to compare optical density of the films with extinction section. Figure 2 shows the results of extinction section calculation as a function of quantum energy.

Good agreement the results of calculation with the position of the resonance absorption peak for a-C : H<Pt> films at $\lambda = 498$ nm (2.5 eV) (fig. 1) is obtained when the dielectric constant of a-C : H films is equal to 4.8.

Using the equations 3 and 4 one can obtain a-C : H<Pt> films extinction section (optical density) dependence on photons energy and average metal nanoclusters radius (figure 3).

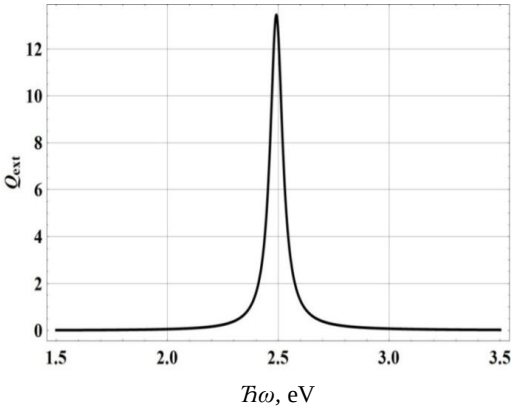

Fig. 2 – Spectral dependency of extinction section for a-C : H<Pt> films

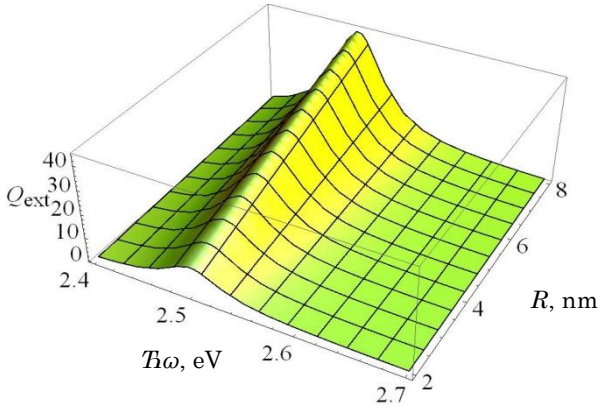

Fig. 3 – Thee xtinction sectionversus photons energy and average metal nanoclusters radius in a-C : H<Pt> films

It follows from fig. 3 that average metal nanoclusters radius increasing leads to an increase in the plasmon resonance intensity and a slight shift of the resonance absorption maximum to higher wavelengths.

4. CONCLUSION

In a-C : H<Pt> films prepared by the ion plasma magnetron sputtering of the combined polycrystalline graphite-platinum target the optical absorption due to the excitation of surface plasmons in platinum nanoclusters was found in the region from 496 to 501 nm. The a-C : H<Pt> films with platinum nanoclusters may be promising for a variety of applications).

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