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Size dependence of the plasmon peak position in electron stimulated photon emission spectra of Ag clusters supported on amorphous carbon film

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Abstract. The plasmon energy of Ag clusters produced on an amorphous carbon substrate by gas-aggregation technique has been measured. It has been determined from the plasmon peak position in the light emission spectrum obtained during bombardment of Ag clusters by low-energy electrons. For Ag cluster films with maximum of the cluster size distribution at 30, 8 and 2.5 nm, the plasmon energy comprised 3.76, 4.13 and 4.28 eV (the wavelength was 330, 300 and 290 nm), respectively. The blue shift of the plasmon energy is probably related to the effect of confounding of collective and single-particle excitations.

PACS. 61.46.+w Nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals – 73.22.Lp Collective excitations

1 Introduction

The emission properties of Ag clusters prepared by the gas-aggregation method have been investigated in [1,2]. A cluster film was deposited on a glass substrate and its resistance per square was $R_{\square} = 0.5 \div 1$ MΩ. The film was excited by the tunnel passage of a current through it. The electron and light emission observed in that case can be used in practice. Besides, a study of light emission is of basic importance because the electron structure influences the obtained spectra. Intraband and interband transitions [3] as well as inelastic tunneling and reflection of electrons [4–7] can contribute to the light emission. In the latter mechanism, the energy dependence of density of electron states plays an essential role [7]. Plasmon excitation followed by its decay also contributes to the light emission. This mechanism is of particular importance for Ag clusters because plasmon of Ag is in the visible spectral range as opposed to the most of other metals for which plasmon lies in the UV range. At the same time, the spectral feature at the plasmon frequency in the light emission spectra obtained for Ag clusters excited by the tunnel passage of a current through them is weakly pronounced [2,8]. It can be explained by the fact that only a few of electrons had sufficient energy to generate plasmon at this excitation mode. But the plasmon peak is more pronounced, if Ag clusters are excited by bombardment with electrons having energy of several hundred of eV [9]. Such an electron-stimulated photon emission by Ag clusters prepared by the gas-aggregation method on a glass substrate covered with an amorphous carbon film was studied in the present work.

The plasmon peak carries information on the cluster film structure because the plasmon frequency depends on the clusters' size, their shape, distance between them and dielectric constant of medium, *i.e.* on the substrate material. The size dependence of plasmon for Ag clusters given in [10] can be used as reference data. Ag clusters studied in this work were also prepared by the gas-aggregation method. The energy of plasmon was determined from the experiments on the light scattering by Ag clusters in a flow of Ar. Within the flow, Ag clusters have no effect on one another because of their low density. As there was no substrate, it did not contribute to the effective dielectric constant of medium. It did not distort the spherical or near-spherical cluster shape as well.

The aim of the present paper is to study the effect of external factors such as substrate on a deformation of plasmon size dependence of Ag clusters in comparison with its well-defined size dependence obtained for the identical, but unsupported clusters [10].

2 Experimental

The gas aggregation method makes it possible to produce the Ag clusters from several atoms up to several

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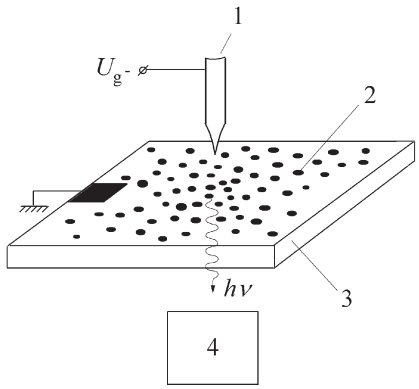

Fig. 1. Schematic drawing of the experimental arrangement: 1 – field emitter, 2 – Ag cluster film, 3 – glass substrate covered with an amorphous carbon film $\sim$ 10 nm thick, 4 – monochromator combined with a CCD chip.

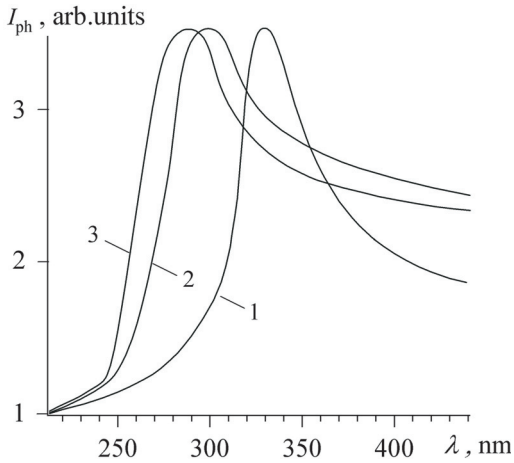

Fig. 2. The intensity normalized spectra of light emission by Ag clusters with the average size of 30 (1), 8 (2) and 2.5 nm (3) excited by electron bombardment.

nanometers in size [11]. The cluster source used as well as the potentialities for varying the cluster size are described in [12]. Ar was used for creating a gas flow in the source. An Ag cluster film was prepared on a glass substrate covered with an amorphous carbon film $\sim$ 10 nm thick. The electrical conductivity of such a carbon film allowed us to avoid charging the substrate during the electron bombardment.

On completing the emission measurements, the Ag cluster film on the amorphous carbon film was separated from the glass substrate and transferred to a copper grid for determination of size of the clusters with a transmission electron microscope (TEM) Philips CM 200 FEG (the accelerating voltage of 200 kV, the ultimate resolution of 0.14 nm). Sometimes an Ag cluster film was simultaneously deposited on a glass substrate with an amorphous carbon film and on an amorphous carbon film on a copper grid placed alongside the glass substrate.

Ag clusters were excited by the bombardment with low-energy electrons. Their energy fell within the range 200 to 600 eV. To do this, a W tip was installed at the distance of 1–2 mm from the cluster film (Fig. 1). It served as a field emitter. Vacuum during the emission measurements comprised 10^{-7} mbar. Parts of the vacuum chamber surrounding W tip and the Ag cluster film were cooled by liquid helium. The current from the tip was of the order of several μA.

The light emission spectra, obtained during bombarding of the Ag cluster film by low-energy electrons, were measured *via* a quartz window by a monochromator combined with a CCD chip [1,2,8,13]. The spectra were measured in the range of 200–1050 nm (6.2–1.18 eV), *i.e.* it included the plasmon peak in the light emission spectra for Ag clusters.

3 Results and discussion

Figure 2 (curves 1–3) shows the light emission spectra measured during the electron bombardment of Ag clusters 30, 8 and 2.5 nm in size, respectively. These spectral curves are normalized by intensity. In these measurements, the bombarding electrons' energy was 450 eV and the current changed from 1 up to 5 μA. The following facts should be taken into account. First, low-energy electrons have short path length in a metal. Second, the possibility of the volume plasmon excitation in clusters decreases sharply because it is proportional to the cube of the cluster size [14]. One can conclude, on these grounds, that an intensive maximum observed at 3.76 eV (wavelength 330 nm) in the light emission spectrum for Ag clusters of 30 nm in size (Fig. 2, curve 1) can be caused by the radiative decay of dipole surface plasmon [15]. When the particles' sizes decrease, this maximum shifts towards higher energies, and the spectral band of the plasmon resonance becomes wider (Fig. 2, curves 2 and 3).

A spreading of plasmon line with reducing particle size was predicted in all theoretical works. However, the widening observed in experiments can be attributed to increasing the size dispersion. The observed shift of plasmon frequency is contradictory to the conclusions drawn by using the hydrodynamic approximation [16] as well as to those based on assumption on an essential role of damping [17,18] and capture of free electrons on the surface levels [19]. The experimental widening is also in conflict with an assumption which takes into account the spatial dispersion of the dielectric constant caused by the fact that the electron density at the cluster geometric boundary is lowered because it does not terminate in a step-like way, but it is characterized by a stepless profile [18,20–22]. There is a qualitative correspondence with predictions of theories taking into consideration an effect of quantization of single-particle states on the spectrum of plasmon oscillations [6] and an important role of screening [23]. However, curve 2 in Figure 2, presenting a plasmon frequency shift, corresponds to a film consisting of clusters 8 nm in size which are too large for quantization of the electron spectrum in them.

The observed shift of plasmon resonance is probably caused by the influence of confounding of collective and single-particle electron states. This conclusion was also made on the basis of optical measurements of Ag cluster films prepared on quartz substrate [24]. The effect of confounding of collective and single-particle electron excitations depends on the strength of oscillators of the corresponding transitions. It is also important how peculiarities are far apart from one another by frequency. In its turn, the strength of oscillators of the interband transitions increases with decreasing cluster size due to the less strict rules of selection for the optical transitions close to the surface. Thus, the plasmon peak can shift towards either low energies, or high energies depending on whether a peculiarity caused by an intensive (with great strength of oscillator) interband transition is on the low-energy side or on the high-energy one relative to the plasmon peak. In the present case, the plasmon peak shifts towards higher energies with the decrease of Ag cluster sizes.

It should be noted that the intensive plasmon band could be observed even in the light emission spectrum measured for a film consisting of 2.5 nm clusters. The coefficient of substrate coating by Ag clusters comprised only several percent for such a film. At least, in this case it is possible to guarantee that the observed effect is not caused by the influence of clusters one another. So low cluster concentration on a substrate testifies that there was no coalescence. Ag clusters are decahedrons and icosahedrons, *i.e.* they have near-spherical shape due to the weak bonding with the carbon substrate.

Measurements shown in Figure 2, curves 1–3 are integral, because they were performed for a big number of clusters. However, the histogram of cluster size distribution within a cluster film has rather narrow maximum [11]. Measurements carried out in a scanning tunneling microscope (STM) for individual Ag clusters also show the plasmon energy shift towards the blue side of spectrum as the clusters diminish in size [25,26]. However, it was difficult to determine the sizes of three-dimensional clusters being apart from one another on the distance of the order of their size which is far less than the radius of curvature of the STM tip.

Comparison of the plasmon energy measured in the present study (Fig. 2, curves 1–3) with the data given in Figure 6a in [10] shows clearly that there is the significant influence of the substrate on the value of plasmon energy. The influence is the greater, the smaller is the cluster size. If an Ag cluster on an amorphous carbon substrate is 2.5 nm in size, the plasmon energy increases by 0.5 eV that comprises 15%. The influence of substrate is in distortion a spherical or near-spherical clusters shape, changing of the dielectric constant of medium in which clusters are situated, etc. [27,28]. This effect occurs for an insulating substrate as well as for a conducting one. Besides, free electrons containing in a reservoir, located close to the clusters, dramatically affect the frequency of the collective electron excitations in clusters [29]. In our case, a conducting carbon film was such a reservoir.

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References

1. S.A. Nepijko, W. Schulze, I. Rabin, L.V. Viduta, Ann. Phys. **7**, 101 (1998)
2. S.A. Nepijko, D.N. Ievlev, W. Schulze, Physica B **304**, 45 (2001)
3. M.P. Klyap, V.A. Kritskii, Yu.A. Kulyupin, Yu.N. Kucherenko, K.N. Pilipchak, S.S. Pop, Sov. Phys. JETP **59**, 653 (1984)
4. R. Berndt, J.K. Gimzewski, P. Johansson, Phys. Rev. Lett. **67**, 3796 (1991)
5. P.M. Tomchuk, in *Discontinuous metal films* (Institute of Physics, Academy of Sciences of the Ukr.SSR, Kiev, 1972), Electroluminescence in discontinuous metal films, p. 238
6. P.G. Borziak, V.M. Kolomiets, Yu.A. Kulyupin, E.A. Pashitskij, K.N. Pilipchak, P.M. Tomchuk. *Nature of light emission from discontinuous metal films. 2. Theoretical notions of light emission from discontinuous metal films*, preprint of Institute of Physics, Academy of Sciences of the Ukr.SSR, No. 5, Kiev, 1973 (in Russian)
7. P.M. Tomchuk, Ukr. Fiz. Zhurnal **24**, 182 (1979)
8. S.A. Nepijko, R.D. Fedorovich, L.V. Viduta, D.N. Ievlev, W. Schulze, Ann. Phys. **9**, 125 (2000)
9. I.A. Konovalov, K.N. Pilipchak, P.M. Tomchuk, Opt. Spectrosc. (USA) **50**, 348 (1981)
10. K.-P. Charlé, L. König, S. Nepijko, I. Rabin, W. Schulze, Cryst. Res. Technol. **33**, 1085 (1998)
11. F. Frank, W. Schulze, B. Tesche, J. Urban, B. Winter, Surf. Sci. **156**, 90 (1985)
12. H. Abe, W. Schulze, B. Tesche, Chem. Phys. **47**, 95 (1980)
13. M. Adelt, S. Nepijko, W. Drachsel, H.-J. Freund, Chem. Phys. Lett. **291**, 425 (1998)
14. A.A. Lushnikov, A.J. Simonov, Z. Phys. **270**, 17 (1974)
15. P.G. Borziak, Yu.A. Kulyupin, *Electron processes in island metal films* (Naukova dumka, Kiev, 1980) (in Russian)
16. F. Fujimoto, K. Komaki, J. Phys. Sci. Jap. **25**, 1679 (1968)
17. L. Genzel, T.P. Martin, U. Kreibig, Z. Phys. B **21**, 339 (1975)
18. P. Apell, Å. Ljungbert, Phys. Scripta **26**, 113 (1982)
19. I.N. Shklyarevskii, T.N. Korneeva, K.N. Zozulya, Opt. Spectrosc. (USA) **27**, 174 (1969)
20. B.B. Dasgupta, R. Fuchs, Phys. Rev. B **24**, 554 (1981)
21. P. Apell, Å. Ljungbert, Solid State Commun. **44**, 1367 (1982)
22. G. Mikhopadhyay, S. Lundqvist, Solid State Commun. **44**, 1379 (1982)
23. L.P. Gor'kov, G.M. Eliashberg, Sov. Phys. JETP **21**, 940 (1965)
24. E.A. Bondar', Yu.A. Kulyupin, N.N. Popovich, *Optical properties of island metal films*, preprint of Institute of Physics, Academy of Sciences of the Ukr.SSR, No. 20, Kiev, 1978 (in Russian)
25. N. Nilius, N. Ernst, H.-J. Freund, Phys. Rev. Lett. **84**, 3994 (2000)
26. N. Nilius, N. Ernst, H.-J. Freund, Chem. Phys. Lett. **349**, 351 (2001)
27. G. Mie, Ann. Phys. **25**, 377 (1908)
28. U. Kreibig, M. Vollmer, *Optical properties of metal clusters*, Springer series in materials science (Springer-Verlag, Berlin, Heidelberg, New-York, 1995), Vol. 25
29. A.O. Govorov, S.A. Studenikin, W.R. Frank, Phys. Solid State **40**, 499 (1998)