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Influence of external field and particle size upon theoretical photoelectron emission spectral response of silver nano-particles embedded in BaO thin film*

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The dependence of the spectral distribution of photoelectron emission from silver nano-particles embedded in BaO semiconductor thin film on external voltage and the size of silver nano-particles is predicted and investigated theoretically. The photoelectron emission response curves to light of wavelength between 0.2 and 0.8μm are given. The dependence of the wavelength threshold on the size of silver nano-particles and external field strength is also shown. Photoemission in the visible spectrum is explained as due to the optical resonance absorption in the silver particles. This could be of importance in designing field-assisted photocathodes and finding their optimum operation conditions.

Keywords: photoemission, photoelectron spectra, semiconductor films
PACC: 7960, 7360F

1. Introduction

Researchers are paying much attention on dielectric composite thin films for optical switching and computing and detecting ultra-short light pulses,[1−7] in which silver, gold and copper nano-particles are usually dispersed. SiO_2[8] and Al_2O_3[9] are often used as materials for the dielectric thin films. BaO semiconductor thin film can be used as a substitute for the dielectric thin film. When the noble metal silver is embedded in it, forming the Ag–BaO semiconductor thin film, its nonlinear response is faster than the laser pulse duration of several picoseconds.[10] It appears to be useful as a nonlinear material. This new kind of semiconductor composite thin film is different from dielectric composite thin film. Some papers on the plasma resonance absorption spectra of silver, gold and copper embedded in dielectric and semiconductor thin film have been published.[11−15] However, studies on the spectral distribution of the photoelectron emission form Ag–BaO thin film are rarely reported.

The study of photoelectron emission may give more information on the initial and final states involved in optical transitions than that of the absorption spectra of silver in semiconductor and dielectric thin film does. It is known that if the final state lies above the vacuum level of silver nano-particles, only strong peaks of plasma resonance absorption will appear in the photoelectron emission spectra, while weak peaks may also appear in the photoelectron emission spectra if the final state lies below the vacuum level. Because of this property, relatively weak peaks, which cannot be resolved in plasma resonance absorption because of the masking effect of a nearby strong peak, may sometimes be resolved in the photoelectric emission curves. This work is an extension of our early research.[16]

It is the main purpose of this paper to investigate the dependence of the wavelength threshold upon the size of silver nano-particles and external voltage. Our explanation of the observed photoelectron in the visible region is consistent with the experimental data.

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2. Spectral distribution of field assisted emission of photoelectrons of Ag–BaO thin film

In the Ag–BaO thin film, silver nano-particles are brought into contact with BaO semiconductor, as shown in Fig.1. Upon close contact of metallic silver and BaO semiconductor, the electrons in the metal flow into the BaO semiconductor. The Fermi levels in the two materials must be coincident at thermal equilibrium, forming the metal–semiconductor barrier. As a result the metal silver nano-particles and BaO semiconductor behave like a p–n junction. In Fig.2(a), (b), (c), the vacuum level is E_{V}, Fermi level is E_{F}, Fermi level of metal silver is E_{FM}, Fermi level of BaO semiconductor is E_{FS}, conduction band bottom level and valence band top level for BaO semiconductor matrix are E_- and E_+, respectively, and E_τ is an equivalent barrier around silver nano-particles. All values of the energy levels presented above are referenced to the conduction band bottom of silver nano-particles. The photoelectrons coming from silver nano-particles will probably enter the BaO semiconductor layer and escape from the surface if their energy is higher than E_τ.

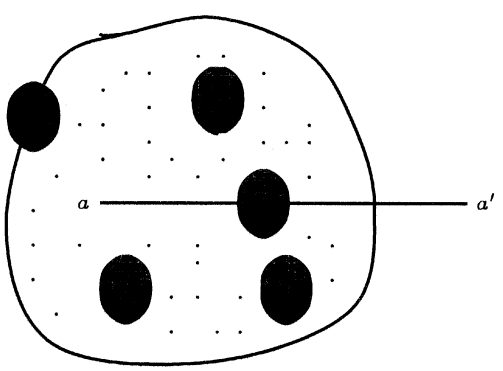


Fig.1. BaO semiconductor thin film embedded with silver nano-particles (shaded areas represent silver nano-particles, dotted areas represent electrons).

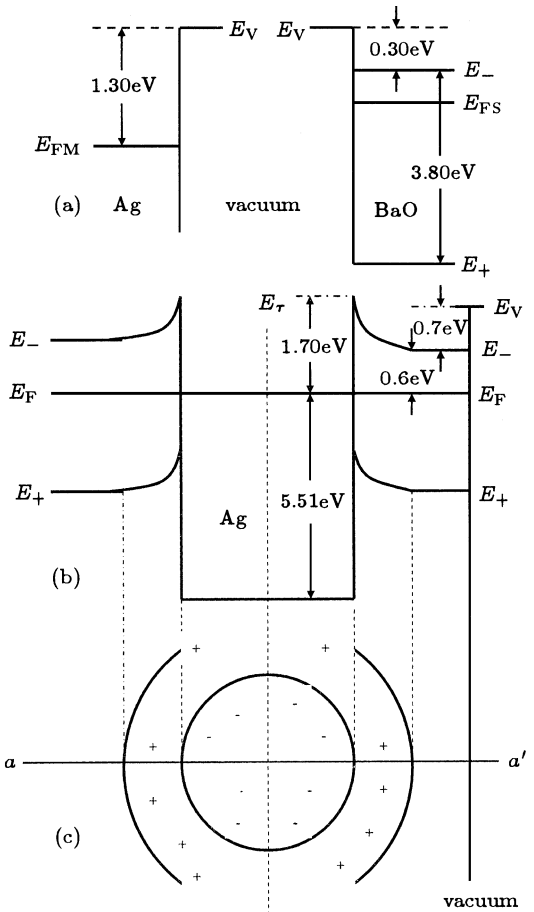


Fig.2. (a) Energy level diagram of silver and BaO semiconductor before the contact; (b) Energy band position diagram in the neighbourhood of Ag–BaO surface; (c) Charge distribution.

When an external voltage is applied, image force induces lowering of the potential barrier for the emission of photoelectron so that the low-energy electrons can escape into the vacuum. The barrier lowering between silver and BaO semiconductor is $\Delta\varphi$. Owing to the Schottky effect, the barrier lowering is given by[17]

$$\Delta\varphi = \sqrt{\frac{qE}{4\pi\varepsilon\varepsilon_0}} = \sqrt{\frac{q}{4\pi\varepsilon\varepsilon_0}} \cdot \sqrt{E} = \sqrt{\frac{q}{4\pi\varepsilon\varepsilon_0}} \cdot \sqrt{\frac{V}{d}}, \tag{1}$$

where ε is the dielectric constant of BaO thin film, ε_0 is the permittivity of vacuum. E and V are the externally applied field and applied voltage, respectively. d is the distance between the positive and negative electrodes. In our early research,[16] the following formula is used to calculate photoelectron current from Ag–BaO thin film,

$$J(h\nu)/I_0 = \frac{h\nu}{[(h\nu_r)^2-(h\nu)^2]^2+(\hbar\triangle\omega_{1/2})^2(h\nu)^2} \times \int_{E_\tau-E_v}^{\infty} \frac{[E+(E_v-h\nu)]^{1/2}}{[E+(E_v-E_-)]^{1/2}} \times \frac{E}{[\exp(E-E_{\rm m})/kT]+1}\mathrm{d}E. \quad (2)$$

The factor before the integral is due to resonance absorption of radiation by silver nano-particles suspended in BaO. The integral is the photon-electron transport.

Thus with the external voltage applied, the barrier height is considerably lowered, and becomes $(E_{\rm i}-E_{\rm V}-\Delta\varphi)$. From equation (2), the expression of emission of photoelectron from Ag–BaO thin film with external voltage is given by the following formula:

$$J_{\rm field}(h\nu)/I_0 = \frac{h\nu}{[(h\nu_r)^2-(h\nu)^2]^2+(\hbar\triangle\omega_{1/2})^2(h\nu)^2} \times \int_{E_\tau-E_v-\triangle\varphi}^{\infty} \frac{[E+(E_v-h\nu)]^{1\ 2}}{[E+(E_v-E_-)]^{1\ 2}} \times \frac{E}{[\exp(E-E_{\rm m})/kT]+1}\mathrm{d}E. \quad (3)$$

In Eq.(3), physical parameters are as follows:[18] $(E_\tau - E_{\rm F})$=1.7(eV), $(E_{\rm V} - E_{\rm F})$=1.3(eV), where $E_{\rm F}$=5.51(eV). The electron affinity is $E_A = E_{\rm V} - E_-$, so we obtain $(E_\tau - E_{\rm V})$=0.4(eV), $(E_- - E_{\rm F})$=0.6(eV), $E_{\rm V}$=6.81(eV). We let $h\nu$ = 2.43(eV)(λ_P=519 nm), $E_{\rm m} = (h\nu - 1.3)$(eV), $\hbar\triangle\omega_{1/2}$=0.6(eV) (the full width of half maximum of plasma resonance absorption of silver nano-particles) and T=300 K. $V_{\rm F}$ is the velocity of electrons at the Fermi level, L is the mean free path. There is the following relation between L and $V_{\rm F}$:

$$L = \frac{V_{\rm F}}{\triangle\omega_{1/2}}. \quad (4)$$

For silver, $V_{\rm F} = 1.4\times10^8 \mathrm{cm\cdot s^{-1}}$ (at 273K). From Eq.(4), L=1.54 nm is obtained, which is much smaller than the mean free path (57nm for bulk silver at 273K). The silver nano-particle surface is regarded as a scatterer of conduction electrons. Assuming this scattering process to be diffusion and the silver nano-particles to have uniform size and spherical shape, the mean free path $L_{\rm sphere}$ of electrons, disregarding its coupling to the Fermi liquid, can easily be calculated for spherical particles:

$$L_{\rm sphere} = \frac{\int L(\theta)\mathrm{d}W}{\int \mathrm{d}W}, \quad (5)$$

where $L(\theta)$ is the free path of an electron leaving an infinitesimal surface element $\mathrm{d}f$ at an angle θ to its normal, after a scattering event. Provided that all scattering mechanisms of the conduction electrons in a spherical particle are independent of one another, and the number of scattering events per unit time is

$$\mathrm{d}W = \text{constant} \times \mathrm{d}f\mathrm{d}\phi, \quad (6)$$

where $\mathrm{d}\phi$ is the solid angle, we get:

$$L_{\rm sphere} = R. \quad (7)$$

This result means that the dimension of silver nano-particles limits the free electrons. Therefore, the equivalent diameter of silver nano-particles will be L. Here we let $(\hbar\Delta\omega_{1/2})$=1.0267, 0.6000, 0.3197, 0.2310, 0.1500, and 0.1000 (eV), the equivalent diameter of silver nano-particles will be 0.90, 1.54, 2.89, 4.00, 6.16, and 9.24 (nm), respectively.

3. Discussion

Under three different forward bias voltages three theoretical photoelectron spectral distributions for silver nano-particles embedded in BaO thin film are calculated at room temperature, as shown in Fig.3(a)–(f). The forward bias voltage ranges from 0 to +26V, which corresponds to 0 to 900 kV/cm. The dependence of the wavelength threshold on the size of silver nano-particles embedded in BaO thin film and the external field voltages is also shown in Fig.4.

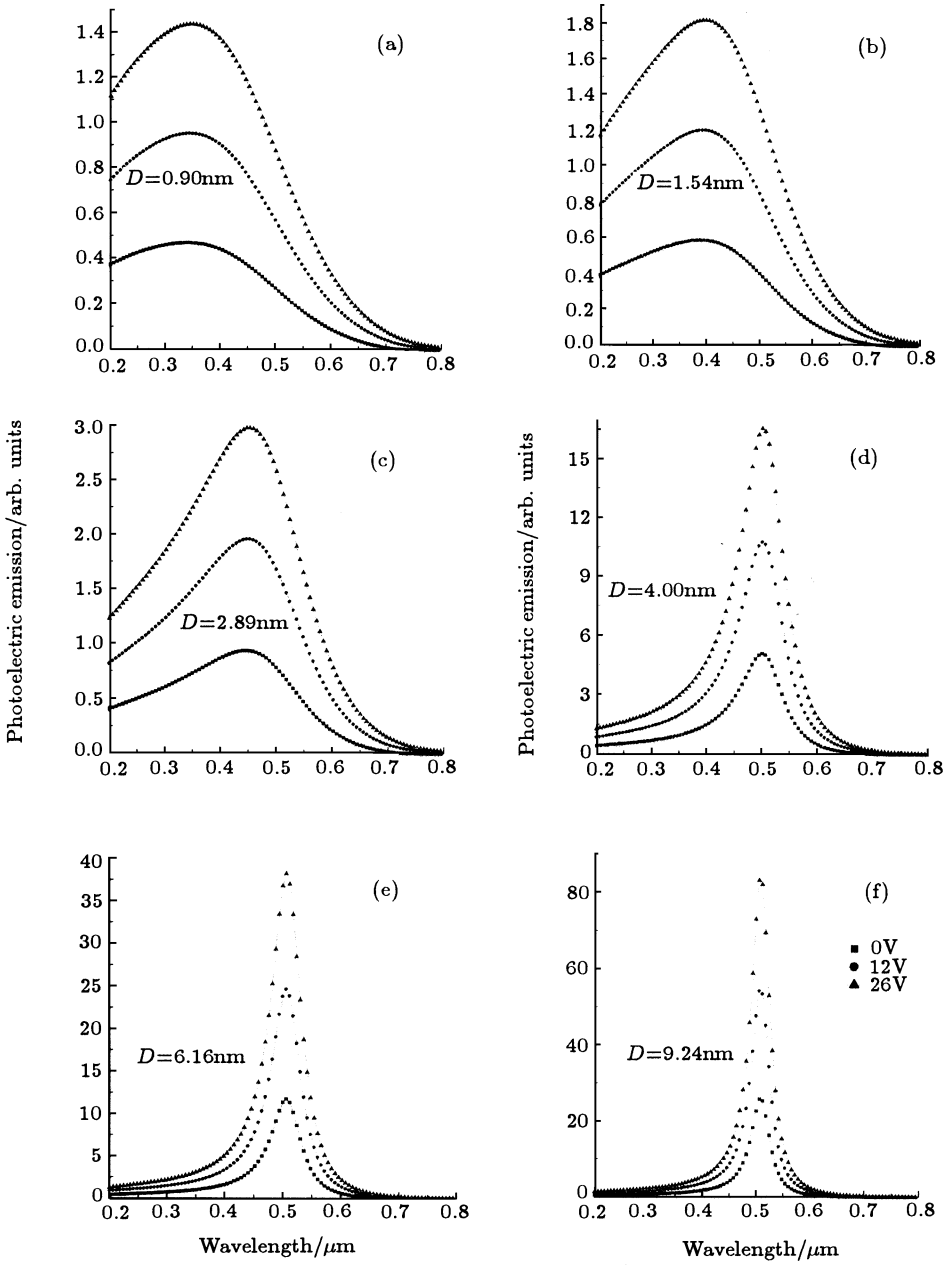


Fig.3. Spectral distributions (a), (b), (c), (d), (e), (f) of the long wavelength emission of photoelectron for Ag–BaO thin film with and without forward bias voltages (0, 12, 26V).

In Fig.3, the greater the external voltages applied, the higher the theoretical peaks that are obtained. External voltage causes an increase in the intensity of peaks in common, due to an increase of the number of the emitted electrons when the external field voltage reduces the barrier between silver nano-particles and BaO semiconductor. The application of external field causes the energy band bending. Band bending distorts the energy distribution of the emitted electrons, and causes the number of emitted electrons to increase and to get the maximum in theoretical photoelectric emission spectra distribution. However, distortion will be reduced if the distance over which band bending takes place is made small compared to the depth of emission, which is actually the case in the optical spectra of silver nano-particles embedded in BaO semiconductor. Then the decrease of the number of the emitted electrons causes the theoretical distribution from silver nano-particles larger than 2.89 nm to drop abruptly. Without the external field (see in Fig.3) the theoretical spectra distributions are in good agreement with the experimental results of Wu.[10,18]

In Fig.4 the dependence of wavelength threshold on size of silver particles embedded in BaO and on external voltage is exhibited. External field can cause wavelength threshold to decrease. The External fields cause wavelength threshold of small-sized silver nano-particles lower easily, but have difficulty in decreasing that of large-sized nano-particles (larger than 9.24 nm). It is obvious that the symbols indicating the three different voltages overlap in Fig.4. It leads to the conclusion that external voltages does not change the wavelength threshold for silver nano-particles larger than 9.24 nm. This is caused by that the contribution of the plasma resonance absorption of radiation by silver nano-particles larger than 9.24 nm to photoelectron is more important than that of photon-electron transport.

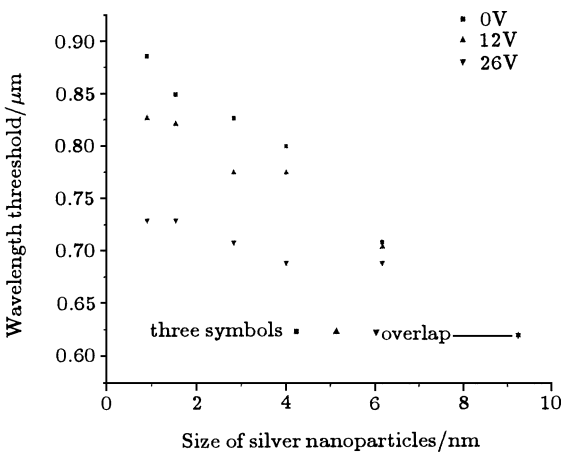


Fig.4. Dependence of wavelength threshold Ag–BaO thin film on size of silver particles embedded in BaO and on external field voltages.

It has been known for many years that the resonance absorption of radiation by small metal particles embedded in a dielectric thin film was derived from a theory developed by Maxwell-Garnet for metal particles dispersed in a dielectric, or in the limit of small isolated spheres from Mie scattering theory. If metal particles and their separations are much smaller than the wavelength of the incident light, the resonance or Mie absorption corresponds to the collective absorption of metal particles much like plasma resonance. The resonance wavelength λ_{R} is strongly dependent on the density of the metal clusters, the ambient dielectric constant, and the presence of nearby inter-band transitions as indicated by the following equation given by Moskovits:[19]

$$\lambda_{\mathrm{R}} = \lambda_P \left[1 + \varepsilon + \frac{2+q}{1-q}\varepsilon_0\right]^{1/2}. \qquad (8)$$

In the above formula λ_{P} is the plasma wavelength for the metal, ε_{b} the inter-band contribution to the complex dielectric constant of the metal (ε_{b} is large due to d–s transitions), and q is the volume fraction of the metal within a dielectric of dielectric constant ε_0.

The peak position of the maximum emission of photoelectron in the visible λ_{R} has been found to vary. We have found this peak to vary from 0.4 to 0.8μm depending upon the method of preparation. For silver, ε_{b} is approximately a constant in the visible region of the spectrum and equals to 4 and λ_{R} is 0.136μm. If one assumes a value of $\varepsilon_0 = 1.0$ for BaO and 0.75 for q, λ_{R} is 0.55μm. When q=0.42, λ_{P} is 0.41μm. For small values of q, λ_{P} occurs in purple region, λ_{R} is in the red region. Thus λ_{R} is a function of the specific particle size distribution and their volume content in the BaO thin film. These numbers are given to show that reasonable values for the parameters involved in the determination of λ_{R} give the experimentally observed λ_{R}.

4. Conclusion

We have presented an explanation of the photoelectron emission for Ag–BaO which is consistent with the observed experimental data for the first time. The peak in the emission of photoelectron in the visible region is due to the resonance absorption of silver nanoparticles and also due to the size of silver particles being smaller than the electron scattering length which cause the escape probability of photoelectrons from small particles to be high. The resonance absorption appears to be the dominant enhancement mechanism.

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