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THEORETICAL DEPENDENCE OF LONG WAVELENGTH PHOTOEMISSION UPON THE SIZE OF Ag NANOPARTICLES EMBEDDED IN BaO SEMICONDUCTOR THIN FILM

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The dependence of long wavelength photoemission upon the size of Ag nanoparticles embedded in a BaO semiconductor is predicted and discussed theoretically. The calculated results show that the increase in the diameter of the Ag nanoparticle, in the range from 1.5 to 37.0nm, leads to the emergence of a roughly Gaussian form of the photoemission spectra and the peaks become markedly narrower. The results also show that the increase in the diameter of the Ag nanoparticle leads to the decrease of the long wavelength threshold. The incident light wavelength corresponding to the peak value of the photoemission gets bigger with the increase of the size of Ag nanoparticles, thus showing a redshift.

Keywords: photoemission, thin film, semiconductors
PACC: 7960, 6855, 7840

I. INTRODUCTION

Dielectric composite thin films, consisting of metal nanoparticles embedded in a dielectric, are third-order nonlinear optical materials having both ultra-fast nonlinear response and large third-order nonlinear coefficient. Some papers on silver, gold and copper nanoparticles embedded in a dielectric show that their nonlinear responses are faster than the laser pulse duration of several picoseconds[1−6] and can be used as nonlinear materials. In the Ag–BaO semiconductor composite thin film, the BaO semiconductor thin film are embedded with Ag metallic nanoparticles. Its response is also faster than the laser pulse duration of several picoseconds.[7] This kind of semiconductor composite thin film is different from dielectric composite thin films. Its potential applications in ultra-fast optical communication and detecting ultrashort laser pulses prompt experimental and theoretical studies of it. To our knowledge, however, the dependence of the long wavelength photoemission upon the sizes of Ag nanoparticles embedded in the BaO semiconductor has not yet been reported. Valuable information on electronic properties of materials can be obtained from the photoemission study.[8−10]

In this paper, based on the theory established by Wu *et al.*,[11] we investigate the dependence of the long wavelength photoemission upon the size of Ag nanoparticles in the BaO semiconductor composite thin film.

II. THE DEPENDENCE OF THE LONG WAVELENGTH PHOTOEMISSION UPON THE SIZE OF Ag NANOPARTICLES EMBEDDED IN BaO SEMICONDUCTOR

Wu *et al.*[11] derived a formula of long wavelength photoemission for the Ag–CsO photocathode, and pointed out that the long wavelength photoemission of Ag–CsO comes from Ag nanoparticles in the CsO semiconductor. Bates and Alexander[12], using the formula derived by Wu, presented and discussed a theoretical calculation of the quantum yield for photons of wavelengths from 300 to 1200nm.

The formula given by Wu reads

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

where $J(h\nu)$ is the photoemission current density, illuminated by incident light of intensity I_0 with pho-

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ton energy $h\nu$. The factor before the integral is the contribution of light absorption. The integral is the photon–electron transport, and $\Delta\omega_{1/2}$ is the full width at half maximum of optical absorption for Ag nanoparticles. Bates and Alexander called the integral term 'Wu's transport function'. Wu *et al.*[7] showed that the theoretical spectral response curves of Eq.(1) closely matched the experimental curves for the Ag–BaO semiconductor composite thin film.

The normal energy band structure of the Ag–BaO semiconductor composite thin film is shown in Fig.1. After vacuum deposition, metal silver is brought into close contact with the BaO semiconductor. The Fermi levels in the two materials must coincide at thermal equilibrium, which form the metal Ag–BaO semiconductor barrier. The behaviour of the metal Ag–BaO semiconductor is similar to that of the p–n junction. In Fig.1, the vacuum level is $E_{\rm v}$, the Fermi level is $E_{\rm F}$, E_- and E_+ are the conduction band bottom level and valence band top level of the BaO semiconductor matrix, respectively, and there is an equivalent barrier E_τ around the Ag nanoparticles. All values of the energy levels presented above are referenced to the conduction band bottom level in the Ag nanoparticles. The photoelectrons coming from the Ag particles will probably enter the BaO semiconductor layer and escape from the surface if their energy is higher than E_τ.

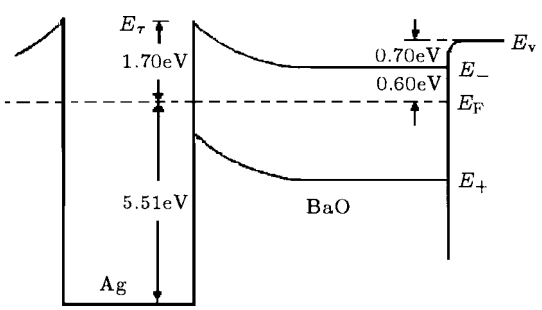


Fig.1. Energy band positon diagram in the neighbourhood of the Ag–BaO surface.

In Eq.(1) the photoemission threshold (work function) is determined by $(E_\tau - E_{\rm F})$=1.7eV, and the thermionic emission threshold is determined by $(E_{\rm v} - E_{\rm F})$=1.3eV; here $E_{\rm F}$=5.51eV. The electron affinity is $E_A = E_{\rm v} - E_-$=0.7eV. So we obtain $E_\tau - E_{\rm v}$=0.4eV, $E_- - E_{\rm F}$=0.6eV, $E_{\rm v}$=6.81eV. Wu *et al.*[7] put $h\nu$=2.43eV ($\lambda_{\rm p}$=510nm), $E_{\rm m}=h\nu-1.3$eV, $\Delta\omega_{1/2}$=0.6eV and T=300K, and obtained the theoretical spectral response curves which closely match the experimental curves for the Ag–BaO semiconductor thin film.[7]

It is well known in solid-state physics that the static conductivity σ_0 of metal nanoparticles is given by

$$\sigma_0 = \frac{q^2 N_{\rm e} L}{m V_{\rm F}}, \tag{2}$$

where $N_{\rm e}$ is the number of valence electrons per unit volume, L is the mean free path of electron, $V_{\rm F}$ is the velocity of electrons at the Fermi level, and m is the mass of the electron. From the theory of Mie[13] and Doyle,[14,15] the full width at half maximum of the optical absorption curve for nanoparticles is given by

$$\Delta\omega_{1/2} = \frac{q^2 N_{\rm e}}{m\sigma_0}, \tag{3}$$

From Eqs.(2) and (3), we obtain

$$\Delta\omega_{1/2} = \frac{V_{\rm F}}{L}. \tag{4}$$

For silver, $V_{\rm F}=1.4\times10^8$cm·s^{-1} (at 273K). From Eq.(4), we get L=1.54nm. This value is much less than the electron mean free path, which is 57nm for bulk silver at 273K. This result is due to the fact that the dimension of the nanoparticle limits the free electrons. It can be shown that in such cases L should be equal to the diameter of the particle. Therefore, the equivalent diameter of the nanoparticle will be L.

III. DISCUSSION OF THE RESULTS

Here we take a series of L values, 1.5, 2.8, 3.7, 4.0, 6.2, 9.2, 18.5 and 37.0nm, for the diameter of the Ag nanoparticles embedded in the BaO semiconductor and calculate, using Eqs.(1) and (4), the theoretical spectral distributions of photoemission for the corresponding composite thin films at room temperature. The results are shown in Figs.2(a)–(h).

The curves of Figs.2(a)–(h) show clearly three striking features, as follows.

Firstly, the increase in the diameter of the Ag nanoparticle leads to the emergence of a roughly Gaussian form of the spectral peaks, and the peaks markedly narrow and the peak intensity increases. When the diameter of the Ag nanoparticle is 37nm, the curve shape becomes exactly Gaussian.

Secondly, the increase in the diameter of the Ag nanoparticle makes the long wavelength threshold decrease. When the diameter of the Ag nanoparticle is 1.5nm, the threshold is 0.725μm. When the diameter increases to 37.0nm, the threshold is 0.56μm.

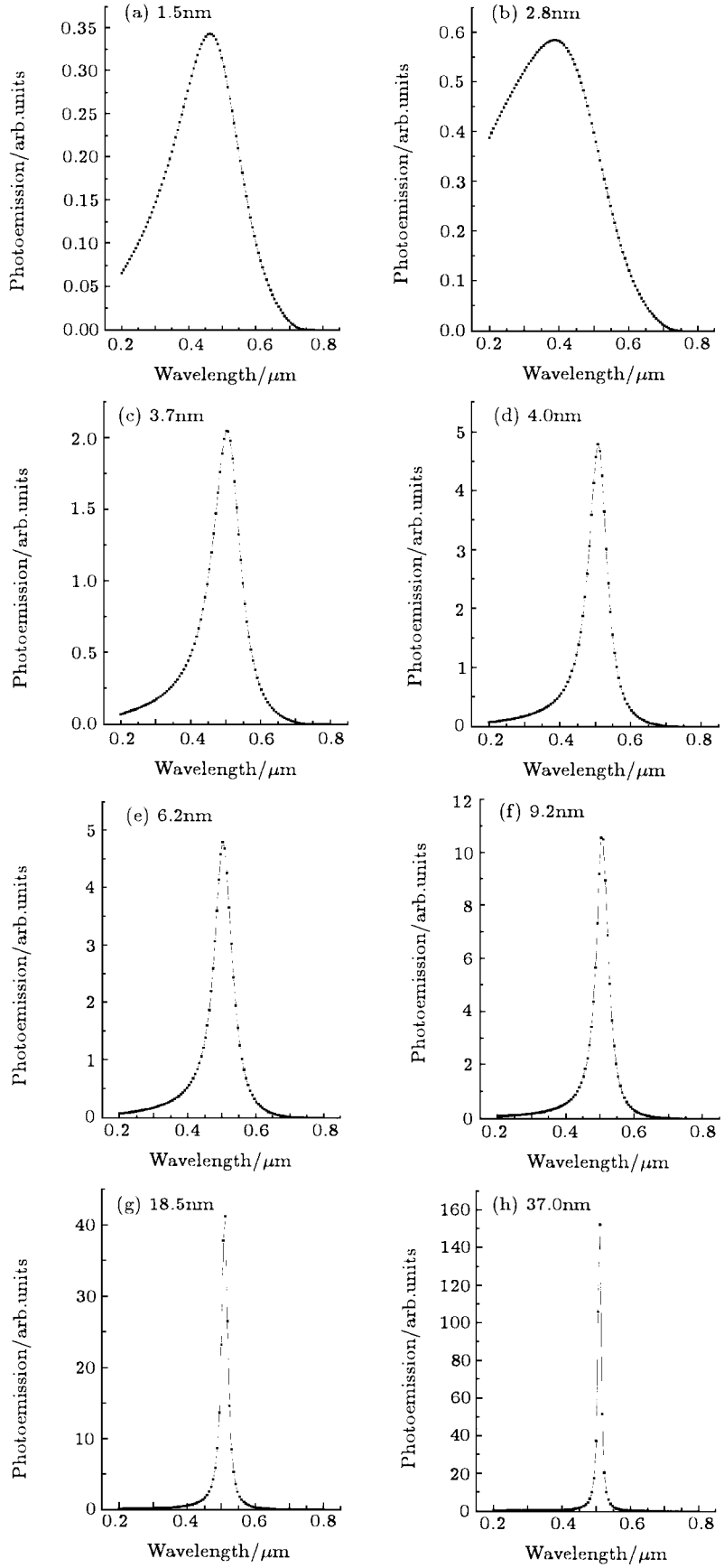


Fig.2. The theoretical dependence of photoemission upon the different sizes of Ag nanoparticles embedded on the BaO semiconductor: (a) 1.5nm; (b) 2.8nm; (c) 3.7nm; (d) 4.0nm; (e) 6.2nm; (f) 9.2nm; (g) 18.5nm; (h) 37.0nm.

Thirdly, with the increase in the diameter of the Ag nanoparticle, the photoemission corresponding to the incident light wavelength range of 0.2 to 0.35μm becomes zero. The incident light wavelength corresponding to the peak value of the photoemission gets bigger with the increase of Ag particle size, resulting in a redshift of the peak.

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