Optical Transient Relaxation of an Ag–BaO Composite Thin Film with a Supercontinuum Probe *

WANG Dan-Ling(王丹翎)[1], YANG Hong(杨宏)[1], JIANG Hong-Bing(蒋红兵)[1], GONG Qi-Huang(龚旗煌)[1**], ZHANG Qi-Feng(张琦锋)[2], WU Jin-Lei(吴锦雷)[2]

[1] *Department of Physics and State Key Laboratory for Mesoscopic Physics, Peking University, Beijing 100871*
[2] *Department of Electronics, Peking University, Beijing 100871*

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The optical transient absorption spectra of an Ag–BaO thin film have been detected at a wavelength ranging from 400 nm to 1000 nm using the pump supercontinuum probe technique with a resolution of 130 fs. We have observed the optical ultrafast relaxation, in which the electrons near the Fermi level of Ag nanoparticles were excited to a non-equilibrium state and then returned to an equilibrium state. The decay time was exponentially fitted and varied from 0.67 ps to 4 ps for different components of the supercontinuum probe. The peak of an unoccupied state for silver at level X_4' was estimated to be 1.47 eV above the Fermi level.

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Broadband femtosecond pump–probe spectroscopy has been developed experimentally[1–4] and theoretically[1,5,6] during the last several years. It has been shown to be a powerful tool for studying ultrafast processes both in condensed matter and in gases. In order to monitor the ultrafast evolution, both broad spectral coverage and high time resolution are required. Pump supercontinuum probe spectroscopy (PSCP) has been shown to be efficient for these applications[7,8]. Kovalenko and co-workers have investigated many ultrafast processes in liquid or condensed matter with PSCP[1–4,7,8] and have made great progress in PSCP, e.g. the time correction procedure in PSCP.[1]

Many ultrafast optical processes in quantum confirmed materials[9,10] have been investigated using the PSCP technique. As a new type of photoemissive material,[11] nano silver particles embedded in a BaO semiconductor matrix have been studied regarding its excitation dynamics.[12–17] Qian *et al.*[13] and Nisoli *et al.*[14] have observed coherently excited phonons. Fatti *et al.*[15] have studied the surface plasmon resonant-enhanced nonlinearity in metallic nanoparticles embedded in the semiconductor matrix or glass. Wu *et al.*[16] have recently investigated the optical transient response of silver nanoparticles in the Ag–BaO thin film using the single wavelength femtosecond time-resolved pump–probe technique. Excited by a laser beam at a wavelength of 647 nm and a pulse duration of 150 fs, the optical transient response of the Ag–BaO thin film was probed by another laser pulse of the same wavelength and pulse duration. They found that the decay time of the transmissivity of this thin film was about 1.6 ps. More recently, Bigot *et al.*[17] have studied the electron dynamics in copper and silver nanoparticles embedded in a transparent matrix using the pump–probe technique. However, the wavelength-dependent transient relaxation and the ultrafast dynamics for the composite thin films of metallic nanoparticles embedded into semiconductor matrices have rarely been reported.

In this Letter, the optical transient process of the Ag–BaO composite thin film has been investigated by the pump supercontinuum probe technique with the probe wavelength from 400 nm to 1000 nm. Measuring the absorption changes at different probe wavelengths, we obtained not only the decay time of the film at a certain probe wavelength but also more information about the energy structure of the Ag–BaO thin film. Thus, we have obtained the peak of the unoccupied state of electrons for silver at level X_4' above the Fermi level.[18]

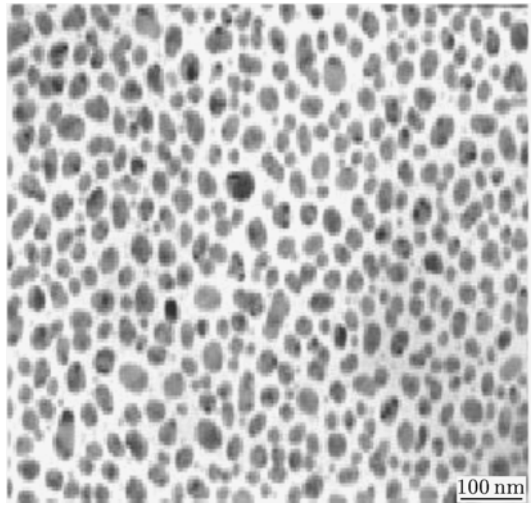


Fig. 1. Transmission electron micrograph of Ag–BaO thin films.

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** Author to whom any correspondence should be addressed.

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To prepare the Ag–BaO thin films, pure barium metal was deposited on to a transparent glass substrate using the vacuum thermal evaporation method. The film thickness controlled at the monitor light transmissivity was 80% of the initial one. Oxygen was then introduced into the vacuum system under the pressure of 10 Pa to oxidate Ba into BaO when the transmissivity became the initial one. Then the thin film was annealed for 20 min at a temperature of 280°C in the vacuum. The silver was then deposited until the transmissivity. The thickness of the sample film was approximately 50 nm. The morphography of the Ag–BaO thin films was studied with transmission electron microscopy (TEM) and is shown in Fig. 1. It is noted that Ag nanoparticles with an average radius of 20 nm dispersed randomly in the BaO semiconductor matrix.

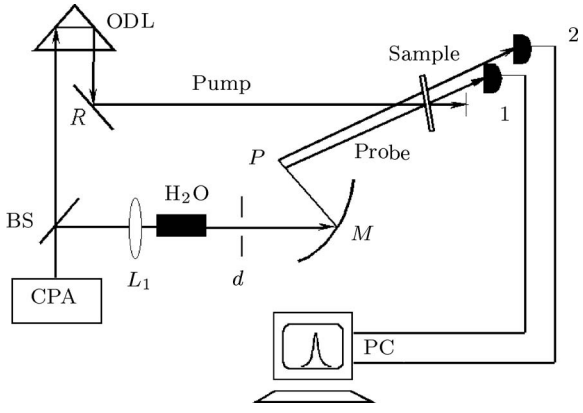


Fig. 2. Experimental set-up of time-resolved pump supercontinuum probe: CPA, chirped-pulse amplifier; ODL, optical delay line.

The experimental set-up for white-light continuum generation has already been described in detail.[19] As shown in Fig. 2, the femtosecond laser pulse was split into two parts by a beamsplitter (BS). The transmitted part, after passing a variable optical delay line (ODL) controlled by a computer, was used for optical pumping. The pump beam had a diameter of 2 mm on the sample with a pulse energy of 0.1 mJ. The reflected part with an energy of about 1.0 mJ was focused with a 6.5 cm lens ($L1$) into distilled water to generate the supercontinuum probe pulse. The supercontinuum with a total energy of about 1.0 μJ was converged by a dispersion-free concave mirror with metal coating and reflected by a fused silica plate (P). The probe reflected from the rear surface, noted as probe 2, was used as a reference to monitor the fluctuation of the generated supercontinuum. The reflected probe from the front surface, called probe 1, was imaged on to the sample film to intersect with the pump beam for detecting the dynamic absorption changes induced by the pump beam. The transmitted probe signal after the sample film was collected by a fibre spectrometer system (PC2000, Ocean Optics, USA) and the spectra were recorded and displayed by a computer. The transient behaviour of the absorption spectroscopy was detected by changing the optical delay of the pump beam with respect to the probe beam.

In Refs. [20] and [21], absorption peaks around 400 nm were observed in the thin film of metallic nanoparticles embedded in the BaO semiconductor or glass matrix. This was considered to be the surface plasmon resonance absorption of the metallic nanoparticles. Furthermore, the energy level of silver nanoparticles above the Fermi energy level is quasi-continuum and the bandgap of Ag is about 4 eV, which leads to neglect of absorption at 807 nm. When the thin film was excited with the near-infrared pump pulse at 807 nm, the absorption in Ag nanoparticles generated non-equilibrium electrons from the initial occupied states to the unoccupied states by two-photon absorption. The non-equilibrium electrons with a temperature higher than that of the lattice temperature would lose their energy by scattering within the lattice (electron–phonon coupling) and interface, and finally cool to the lattice temperature. Therefore, under the excitation of an ultrafast laser pulse, the energy was firstly absorbed by free electrons near the Fermi level in metallic nanoparticles and transferred to other electrons via electron–electron scattering. As a result, the electrons were thermalized. The lattice can subsequently obtain energy through electron–lattice scattering. In other words, the electron temperature was changed by the incident laser pulses, which can result in a change of the electron state densities in the vicinity of the Fermi level, and then in changes of the dielectric constant and the absorption coefficient of the sample. This would lead to the change of the absorption behaviour of the Ag–BaO thin film, which was proven directly in the experiment as shown in Fig. 3.

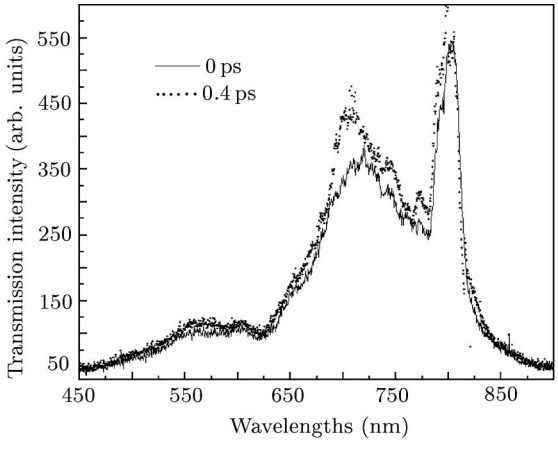


Fig. 3. Transient spectra at 0 and 0.4 ps from 450 nm to 900 nm.

The time-resolved transient transmissivity spectra of supercontinuum probe beams can reveal the decay

dynamical process of non-equilibrium electrons at different probe wavelengths. Figure 4 shows the typical result at 700 nm probe wavelength. The different exponential decay time τ at various probe wavelengths, ranging from 4 ps to 0.67 ps, was also obtained and is exhibited in Fig. 5. The decay time decreased when the probe wavelength changed from 450 to 800 nm. The result is in reasonable agreement with the prediction of 1.6 ps decay time at wavelength 647 nm measured by Wu *et al.*[16] using the single wavelength pump–probe technique and the theoretical prediction[22] of the time constant for non-equilibrium electrons returned to the Fermi level, $T_b = [1/(f_s+f_p)]\cdot(\Delta E/\delta E)$. Here, f_s is the average scattering frequency between the electrons and the interface which is related to the size of the Ag nanoparticles; f_p is the frequency of the electron–phonon scattering in the metallic nanoparticles; δE is the energy loss of every electron interface scattering; and ΔE is the energy of the non-equilibrium electron. Meanwhile, the transmission difference at zero delay caused by the pump was also

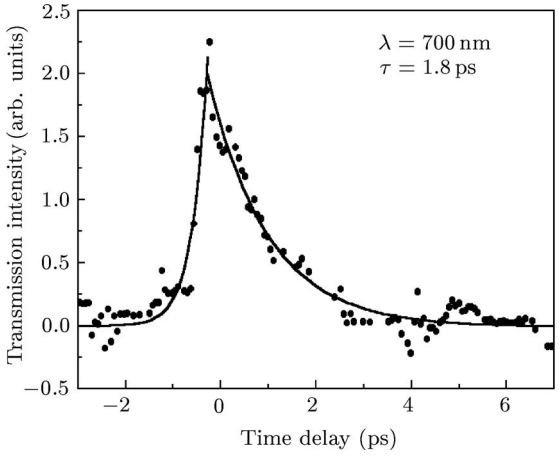


Fig. 4. Optical transient signals of the Ag–BaO thin film at a probe wavelength of 700 nm.

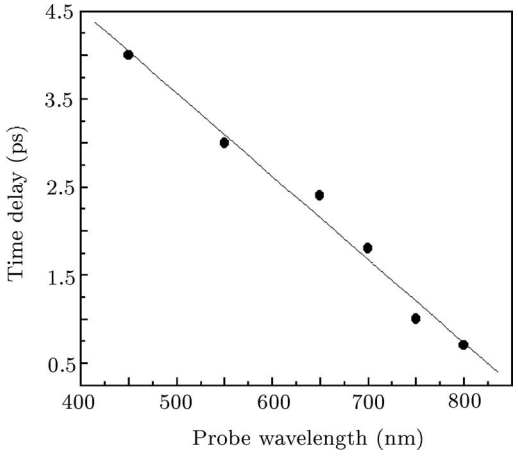


Fig. 5. Time decay at different compositions of probe wavelengths under 807 nm wavelength pump.

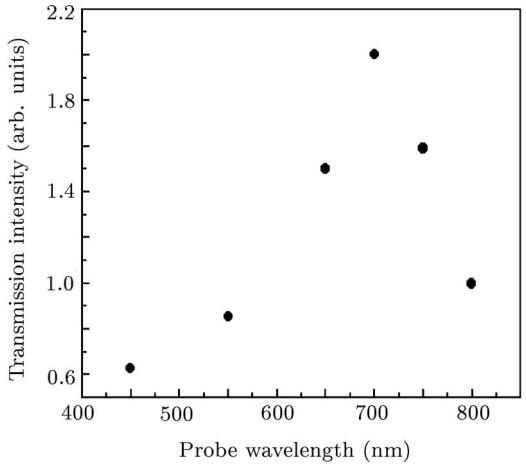


Fig. 6. Transmission change of the transient signals at different probe wavelengths.

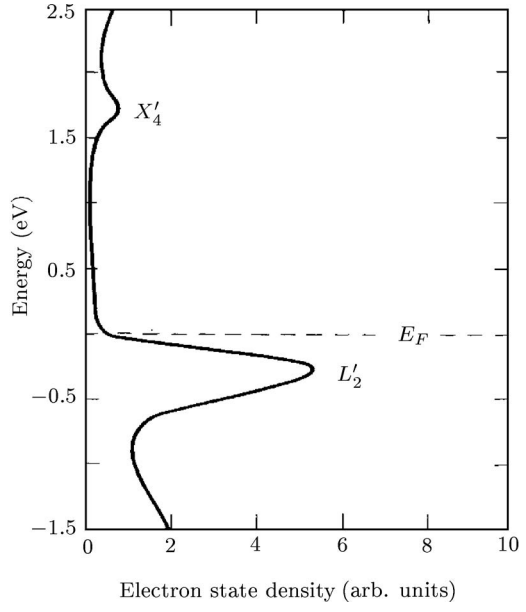


Fig. 7. Electron state density distribution near the Fermi energy level E_F in Ag nanoparticles.

measured and is exhibited in Fig. 6. The maximal one is found at a 700 nm wavelength.

The energy of the pump photon is 1.55 eV, corresponding to the light wavelength of 807 nm. As the bandgap energy of BaO is above 3.5 eV, the optical absorption of the semiconductor BaO can be neglected. However, the BaO semiconductor hastened the dissipation of the non-equilibrium electronic energy and played an important role in the ultrafast optical response of the Ag–BaO composite thin film.[23] Therefore, the non-equilibrium relaxation in the Ag–BaO composite thin film is more complex than the dynamics in the pure Ag thin film.[24] On the other hand, as the size of metal nanoparticles was around 20 nm in our sample film, it was convenient to describe the photo-dynamics in nanoparticles using a small solid

approach,[25−27] where the band structure is not modified by the quantum confinement.[28] According to the calculation of Segall[29] on the energy state structure of silver, the maximal probability for electron transition should be the state gap energy between the occupied state density peak L_2' below the Fermi level and the unoccupied state density peak X_4' above the Fermi level, which is shown in Fig. 7. Thus, the maximal transmissivity difference at 700 nm in Fig. 6 should represent this transition and the estimated state gap energy between L_2' and X_4' is 1.77 eV. This is in good agreement with the result of Berglund *et al.*,[18] i.e. the energy gap between X_4' and L_2' is about 1.6 eV–2.0 eV. Moreover, using the conclusion that L_2' was at 0.3 eV below the Fermi level,[18] the exact unoccupied state density peak X_4' was estimated to be 1.47 eV above the Fermi level in silver.

In summary, under the two-photon absorption of femtosecond laser pulses at wavelength 807 nm, the transient absorption spectra of an Ag–BaO thin film have been measured using the time-resolved pump supercontinuum probe technique. The exponential decay time constant of the optical transient process, representing the non-equilibrium electrons scattering with the lattice and the interface between silver nanoparticles and BaO matrix, was measured to range from 4 ps to 0.67 ps at a probe wavelength from 400 nm to 800 nm. Meanwhile, the maximal bleaching occurring at the 700 nm probe wavelength has predicted that the peak of the unoccupied state X_4' is 1.47 eV above the Fermi level.

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