LA-UR-02-7479

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Title: ULTRAFAST ELECTRON DYNAMICS IN SILVER NANOPARTICLE ARRAYS

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Submitted to: CLEO/QELS 2003
BALTIMORE, MD
JUNE 2-6, 2003

Los Alamos
NATIONAL LABORATORY

Ultrafast Electron Dynamics in Silver Nanoparticle Arrays

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Abstract: We present the results of ultrafast optical experiments on silver quantum dot superlattices. Dramatic changes in the electron dynamics occur as a function of interparticle spacing due to enhanced dipolar coupling and, most importantly, electron delocalization.

OCIS codes: (320.7130) Ultrafast Processes in Condensed Matter (160.3900) Metals

The metal-insulator (MI) transition remains the most enigmatic problem in condensed matter physics and is deeply connected to unsolved problems in many materials [1]. Metallic quantum dot (QD) superlattices serve as a model system to investigate the MI transition since, to a large extent, the two competing effects that drive a metallic system insulating can be independently controlled. These effects are electron correlation and disorder. The nature of this quantum phase transition in QD arrays has been investigated in detail [2]. Using femtosecond optical spectroscopy, we have observed dramatic changes in the electron dynamics as a function of interparticle spacing due to enhanced dipolar coupling and, for arrays with the least disorder, electron delocalization.

The Ag nanoparticles (nominal diameter 2R = 7.5 nm) were synthesized in chloroform using an inverse micelle technique. The hexagonally close-packed arrays were formed on a Langmuir trough. Films were prepared by transfer to an MgO substrate. To prevent degradation, the samples were kept under vacuum. The photoinduced change in reflectivity ($\Delta R/R$) was measured using a Ti:Al_2O_3 oscillator producing 20-fs pulses at 1.5 eV with an 80 MHz repetition rate. To minimize photodegradation, fluences below 3μJ/cm^2 were used.

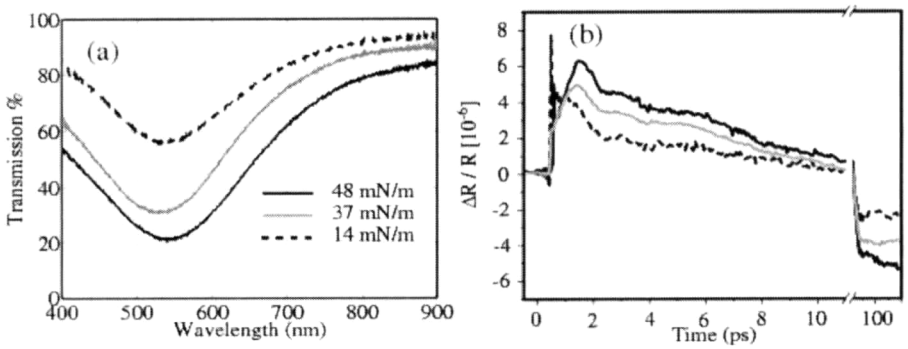

Fig 1: (a) Spectrum for arrays consisting of 7.5 nm diameter heptanethiol coated nanoparticles. (b) Photoinduced changes in reflectivity for the arrays in (a). In going from 14 mN/m to 48 mN/m $D_0/2R$ decreases from ~1.16 to ~1.10 where D_0 is the average interparticle spacing.

Figure 1(a) shows the transmission as a function of wavelength for a series of QD arrays at different compressions. The plasmon resonance is shifted from 400 nm (i.e. the plasmon resonance for isolated nanoparticles) to ~520 nm due to dipolar coupling. With compression there is a strong increase in the absorption, primarily due to an increased polarizability of the QD arrays. Figure 1(b) shows the $\Delta R/R$ dynamics for the same arrays. With compression, the magnitude of $\Delta R/R$ increases, and there is an enhancement of the ~ 2ps oscillation that is related to surface oscillations of the individual nanoparticles [3]. In spite of the strong coupling in the most compressed films, the

changes in the electron dynamics are minimal – we ascribe this to disorder in the QD arrays due to the large size distribution of the nanoparticles.

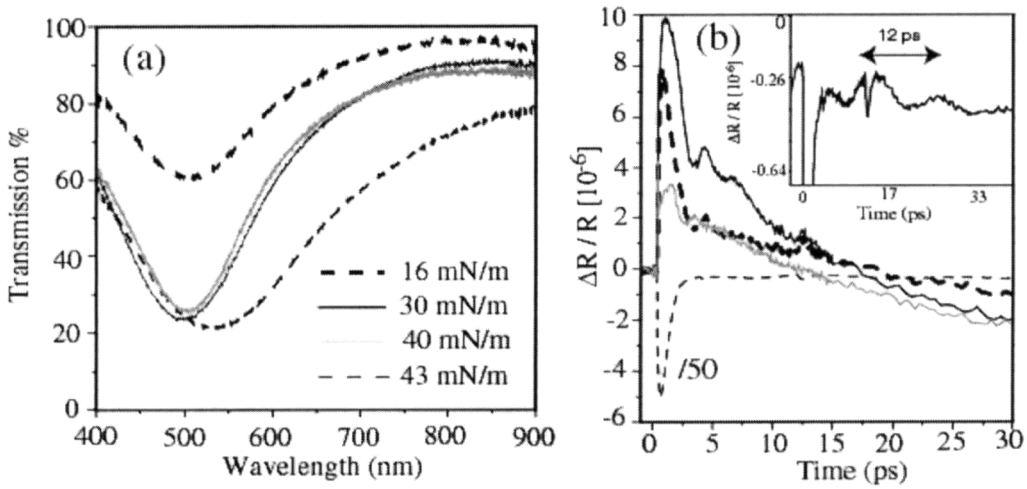

Fig 2: (a) Spectrum for arrays consisting of 7.5 nm diameter dodecanethiol coated nanoparticles. (b) Photoinduced changes in reflectivity for the arrays in (a). In going from 16 mN/m to 43 mN/m $D_o/2R$ decreases from ~1.4 to ~1.2.

Figure 2(a) shows the transmission for a series of QD arrays with a narrower size distribution. For the most compressed film a large increase in the absorption on the low energy side of the resonance is observed. Figure 2(b) shows the corresponding dynamics. Initially, with compression there is an increase in $\Delta R/R$ for the QD arrays as in Fig. 1. However, a decrease in the magnitude of $\Delta R/R$ occurs from 30 to 40 mN/m. In addition, there is a π phase shift in the 2 ps oscillations. With a further compression to 43 mN/m there is a dramatic change in the $\Delta R/R$ dynamics – the signal is negative and increases in magnitude due to electron delocalization in the arrays. Finally, as shown in the inset, an oscillation with a period of 12 ps is observed. This is likely due to the coherent oscillation of a phonon mode of the QD array.

[1] P. P. Edwards, et al., Solid State Phys. **52**, 229 (1999).
[2] K. C. Beverly, et al., Proc. Nat. Acad. Sci. **99**, 6456 (2002) and references therein.
[3] C. Voisin, et al., J. Phys. Chem. B **105**, 2264 (2001).