Ultrafast electron relaxation via breathing vibration of gold nanocrystals embedded in a dielectric medium

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We have investigated size- and matrix-dependent relaxation behaviors of hot electrons in gold nanocrystals embedded in various dielectric materials[1,2]. Gold nanocrystal-dielectric composites have been prepared by magnetron sputtering method. We used three different materials, SiO_2 glass, TiO_2 and Al_2O_3 with thermal conductivities of 1.38, 8.4 and 36 $Wm^{-1}K^{-1}$, as a matrix. Average diameters of gold nanocrystals were varied between 3.0 and 17.5 nm. Femtosecond pump and probe measurements have been carried out with 150 fs laser pulses from an amplified Ti:sapphire laser. The photon energy of the pump pulse was set to 3.1 eV corresponding to the band-to-band transition associated with 5*d* electrons of gold nanocrystals.

Figure 1 shows time evolutions of differential absorption detected at the surface plasmon resonance energy for gold nanocrystals embedded in SiO_2 glass (Au/SiO_2) and Al_2O_3 (Au/Al_2O_3). Pump intensity was adjusted so that the absorbed pump energy by unit volume of nanocrystals was kept constant for all the measurements. The observed decay kinetics clearly

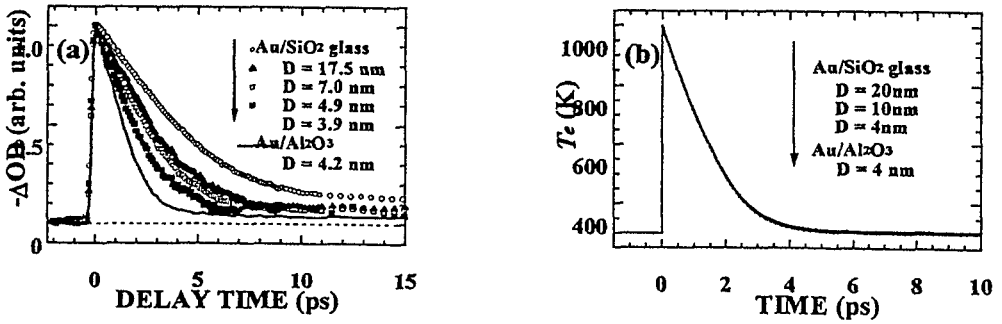

Fig. 1. (a) Time evolutions of differential absorption for Au/SiO_2 (3.9, 4.9, 7.0 and 17.5 nm) and Au/Al_2O_3 (4.2 nm). (b) Calculated time evolutions of electron temperature, T_e, for Au/SiO_2 (solid curves) and Au/Al_2O_3 (dashed curve). Diameters of gold nanocrystals are 4, 10 and 20 nm.

indicates size dependent behaviors. The relaxation times τ_1 obtained by fitting the data to an exponential function are plotted as a function of diameter in Fig. 2. The relaxation becomes fast with decreasing nanocrystal diameter. The decay curve for Au/Al_2O_3 with a diameter of 4.2 nm is also shown in Fig. 1. The decay is faster than for Au/SiO_2, and τ_1 is as short as 1.5 ps. These results suggest that the thermal conductivity is one of the parameters governing the

relaxation dynamics, because the thermal conductivity is about 26 times larger in Al_2O_3 than in SiO_2 glass.

In order to discuss size- and matrix-dependent decay behaviors, we calculated energy relaxation rates by using an extended two-temperature model which takes into account both the hot electron relaxation to the lattice via electron-phonon interaction and the thermal diffusion from nanocrystals to the matrix. Since the relaxation behavior depends on the matrix as well as the size, the size-dependence does not originate from the electron-bulk phonon interaction in gold nanocrystals. Therefore, we assume that the electron-phonon coupling strength is constant in the two-temperature model. We have numerically calculated an electron-temperature T_e from simultaneous differential equations for electron, lattice and matrix temperatures. Time evolutions of T_e for gold nanocrystals with different diameters embedded in SiO_2 glass and Al_2O_3 are shown in Fig. 1 (b). Electrons which are initially in equilibrium with the lattice at 300K are heated up to 1000 K by photo-excitations, and then cooled down to 300 K. The calculated dependence of T_e on size and matrix is much smaller than the observed one. This result suggests that there exists another relaxation pathway giving rise to the size- and matrix-dependence. Here, we consider the relaxation of nonequilibrium electrons via breathing vibration of nanocrystals as an additional pathway. For Au/SiO_2 with a diameter of 17.5 nm, we observed the oscillatory behavior of differential absorption due to excitation and damping of a breathing mode by the pump pulse with relatively weak intensity. The total relaxation rate is calculated from a sum of the relaxation rate via bulk modes and that via breathing modes coherently excited by the optical pulse. The calculated results reproduce well the observed dependence for Au/SiO_2 (solid curve in Fig. 2), Au/Al_2O_3 and Au/TiO_2. Therefore, we have found that the relaxation due to the breathing mode damping gives rise to the size-and matrix-dependence of the relaxation time.

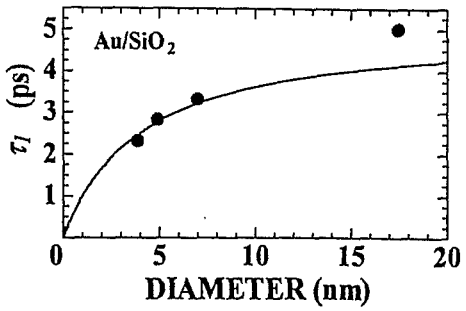

Fig. 2. Diameter dependence of relaxation times for Au/SiO_2. Closed circles and a solid curve indicate experimental results and calculated one, respectively

References

[1]Y. Hamanaka et al.: Proceedings of International Conference on Ultrafast Phenomena, 2000.

[2]Y. Hamanaka et al.: submitted to Phys. Rev. Rapid Communications