PD Research Report for the 2016 year

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Research Theme　半導体ナノ微粒子系の多励起子素過程の解明と光応答分子システムへの応用
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Semiconductor nanostructures are expected to provide multiexciton generation for photo-switchable systems. In hybrid nanosystems, metal components may influence exciton dynamics by charge separation or electric near-field enhancement. Carrier dynamics in metal and semiconductor nanostructures become basic information to design high efficiency photo-switch systems.

1. Electron and Phonon Dynamics in Hexagonal Pd Nanosheets and Ag/Pd/Ag Sandwich Nanoplates

Pd and its hybrid nanostructures have attracted considerable attention over the last decade, with both catalytic and plasmonic properties. The electron and phonon properties directly govern conversion efficiencies in applications as energy collectors and photocatalysts. We report the dynamic processes of electron–phonon coupling and coherent acoustic phonon vibration in hexagonal Pd nanosheets and Ag/Pd/Ag sandwich nanoplates using transient absorption spectroscopy. As shown in Figure 1a, the electron–phonon coupling constant of Pd nanosheets $G_{\text{Pd-nanosheet}}$ (8.7×10^{17} W/m^3·K) is larger than that of the bulk G_{Pd} (5.0×10^{17} W/m^3·K). The effective coupling constant G_{eff} of Ag/Pd/Ag nanoplates decreases with increasing Ag shell thickness, finally approaching the bulk G_{Ag}. The variation of G_{eff} is explained in terms of reduced density of stats near Fermi level of Pd nanosheets with 1.8 nm ultrathin thickness. In Figure 1b, coherent acoustic phonon vibration in Pd nanosheets is assigned to a fundamental breathing mode, similar to the vibration of benzene. The period increases with increasing Ag shell thickness. For Ag/Pd/Ag nanoplates with 20-nm thick Ag shells, the vibrational mode is ascribed to a quasi-extensional mode. The results show that the modes of the coherent acoustic phonon vibration transform with the geometric variation of Pd nanosheets and Ag/Pd/Ag nanoplates. Our results represent an understanding of quantum-confinement related electron dynamics and bulk-like phonon kinetics in the ultrathin Pd nanosheets and their hybrid nanostructures.

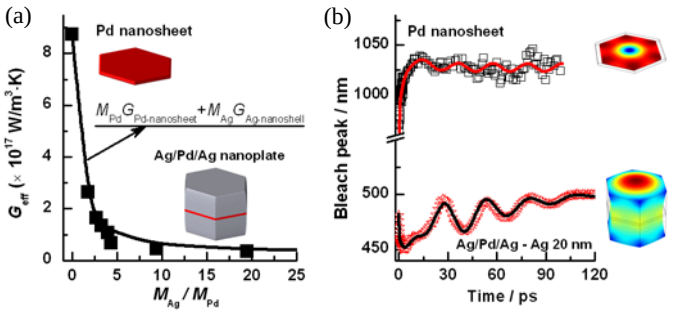

Figure 1. Electron–phonon coupling constants of Pd nanosheet and Ag/Pd/Ag nanoplates (a) and coherent acoustic phonon vibration represented with oscillation of bleach peak wavelength for Pd nanosheet and Ag/Pd/Ag nanoplate with 20 nm Ag shell thickness (b).

2. Charge Transfer Dynamics and Auger Recombination of CdSe/CdS Core/Shell Quantum Dots

Semiconductor nanostructures, with tunable optical and excitonic properties as variations of geometries and sizes, are applied in optical and electronic devices, such as solar cells, LEDs, and

microlasers. To pursue high efficiencies of light collection and energy conversion, hetero-nanostructures are designed. The conduction band offset was reported to be 0~0.3 eV for the hetero-structure of CdSe and CdS while a large valence band offset. A type I energy band-diagram for a CdSe-CdS core-shell hetero-sphere can be expected. Moreover, the energy band-diagrams of CdSe-CdS core-shell QDs were also reported to be quasi-type II and type II structures in terms of CdSe core size, lattice strain induced band shifts, and a reduced overlapping of electron and hole wave functions with increasing the shell thickness. We performed the selective excitation on CdSe core or CdS shell and monitored the electron dynamics by transient absorption spectroscopies.

Based on the previous experimental and theoretical results, three bands labeled with black letters in Figure 2a are assigned to 1S(e)-1$S_{3/2}$(h), 1S(e)-2$S_{1/2}$(h), and the overlap of 1S(e)-2$S_{1/2}$(h) and 1P(e)-1$P_{3/2}$(h) transitions, and the other two bands 445 and 501 nm are assigned to 1S(e)-1$S_{3/2}$(h) transition of CdS shell and a transition from 1$S_{3/2}$(h) state in the valence band of CdSe core to 1S(e) state in the conduction band of CdS shell. Hence, 0.32 and 0.3 eV band offsets of conduction and valence bands are declared for the CdSe/CdS core/shell QDs (3.0 nm CdSe core and ~2 monolayer CdS shell). With 400 nm excitation, CdS shell was mainly excited owing to the large oscillation strength. A sub-ps rising process of 1S excitonic state in CdSe/CdS core/shell QDs was due to the electron and hole transfers from the shell to the core as shown in Figure 2b. In Figure 3a, a 118 ns Auger recombination lifetime was estimated form the excitation intensity dependence of the dynamics at 1S excitonic state, which is owing to the reduced overlapping of electron and hole wave functions in CdSe/CdS core/shell QDs. The analysis of electron transfer process in CdSe/CdS core/shell QDs is still in progressing.

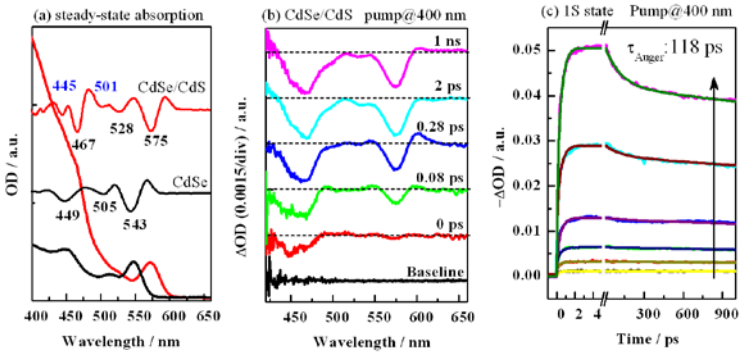

Figure 2. Steady-state absorption spectra and the second derivatives of CdSe core and CdSe/CdS core/shell QDs (a), transient absorption spectra with low shell excitation intensity (b) and Auger recombination lifetime determined from excitation intensity dependence of the decay profiles at the band edge of CdSe/CdS core/shell QDs (c).

Conferences:

1) L. Wang, T. Sagaguchi, T. Okuhata, M. Tsuboi, and N. Tamai, “Electron and Phonon Dynamics in Hexagonal Pd Nanosheets and Ag/Pd/Ag Sandwich Nanoplates”, NFO-14, We10B4
2) L. Wang, T. Sagaguchi, T. Okuhata, M. Tsuboi, and N. Tamai, “Electron and Phonon Dynamics in Hexagonal Pd Nanosheets and Ag/Pd/Ag Sandwich Nanoplates”, 第 10 回分子科学討論会 2016 神戸, 2E15

Publications:

1) L. Wang, T. Sagaguchi, T. Okuhata, M. Tsuboi, and N. Tamai, “Electron and Phonon Dynamics in Hexagonal Pd Nanosheets and Ag/Pd/Ag Sandwich Nanoplates”, ACS Nano, (2016) doi: 10.1021/acsnano.6b07082

2) K. Nonaka, L. Wang, T. Okuhata, and N. Tamai, “Charge Transfer Dynamics and Auger Recombination of CdSe/CdS Core/Shell Quantum Dots”, (In draft)