2P029

シリコン量子ドットの励起子ダイナミクス
–近赤外過渡吸収分光と時間分解発光分光–

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Exciton Dynamics of Silicon Quantum Dots –Near-IR Transient Absorption and Time-resolved Luminescence Spectroscopy–

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【Introduction】 Silicon is one of the most important non-toxic semiconductor materials that are widely applied in electronic and photovoltaic industries. With the study on quantum confinement effect developing recently, Si quantum dots (QDs) attract a great deal of attention due to the significant character of carrier multiplication (CM), which is originated from the carrier-carrier Coulomb interactions [1]. With CM, multiple excitons could be generated by absorption of a single photon. The great potential of Si QDs for application in photovoltaic devices was report before [2]. However, the ultrafast decays caused by Auger recombination (AR) that can be regarded as a resonant energy transfer from the recombination of an exciton to a neighboring excited electron or hole [3] and carrier trapping are important factors to reduce the lifetime of multiple excitons. Normally, the competition between the carrier trapping and AR is a dominant process for free carriers during their non-radiaive decays. In the present study, we prepared two types of Si QDs with ethoxy and 1-octadecene terminations by using a ball milling method and a chemical etching method, respectively. Exciton population dynamics for Si QDs were examined by time-resolved luminescence and transient absorption spectroscopy.

【Experimental Section】 Si QDs with ethoxy and 1-octadecene terminations were prepared with a ball milling and a chemical etching method. They were dissolved in ethanol and toluene, respectively. The exciton dynamics were examined by femtosecond transient absorption (TA) spectroscopy with a pump beam of second harmonic of an amplified Ti:Sapphire laser (Spectra-Physics, 60 fs at 800 nm, 1 kHz). The probe beam was a white-light continuum generated with a sapphire plate or D_2O. The time-resolved luminescence dynamics were examined by a picosecond single-photon timing spectroscopic system and a streak camera system.

【Results and Discussion】 The luminescence of the ethoxy-terminated Si QDs shows very weak spectrum near 480 nm comparable with the Raman oscillation of ethanol. On the contrary, the luminescence of the 1-octadecene-terminated Si QDs appears near 700 nm with a quantum yield of 1.7% and is independent on excitation wavelengths. Its average lifetime was estimated to be 1.6 μs by a streak camera at room temperature. The exciton population dynamics of the ethoxy-terminated Si QDs examined in near-IR region are shown in Figure 1 as a function of excitation intensities. A three-exponential decay function was used for the global fitting of decay profiles. The lifetimes were

estimated to be 0.8 and 40 ps within the low excitation intensities (5 to 20 μJ/cm^2) and an additional fast time constant was estimated to be 0.15 ps at higher excitation intensities (40 to 100 μJ/cm^2). The fast decay (≤ 1 ps) is often attributed to exciton trapping and the slower one is probably due to the non-radiative recombination process. The amplitudes of respective lifetimes against the excitation intensities are illustrated in the inset of Figure 1, where the amplitude of fast decay (0.8 ps) kept increasing as the pump intensity was elevated to 20 μJ/cm^2. When the intensity increased over that, a new amplitude of faster decay (0.15 ps) emerged and kept increasing while the amplitude of 0.8 ps started to decrease. As the 1S states were fully occupied by the multiple excitations caused by higher photon flux, the electrons at 1P or higher excited states would transfer to the trapping sites directly with a time constant of 0.15 ps.

Figure 2 shows the transient absorption spectra of the 1-octadecene-terminated Si QDs between 500 and 1250 nm. The excitation intensity was 100 μJ/cm^2. Within the initial 200 ps, the spectra of near-IR range gradually became flat from $1/\omega^2$ dependence of a free-carrier model [4] in contrast with the two obvious peaks near 560 and 660 nm. In the exciton dynamics of 1100 nm, the slow decay lifetime was estimated to be 1.5 ns and a fast decay of 4 ps emerged at higher excitation intensities by the global fitting, which is in contrast with the dynamics of ethoxy-terminated Si QDs. The fast decay component of 4 ps was probably due to Auger recombination caused by the higher photon flux. The population dynamics of the two spectra in visible regions (560 and 660 nm) were independent on the excitation intensities, indicating that the two spectra were probably originated from the trapping sites.

【References】

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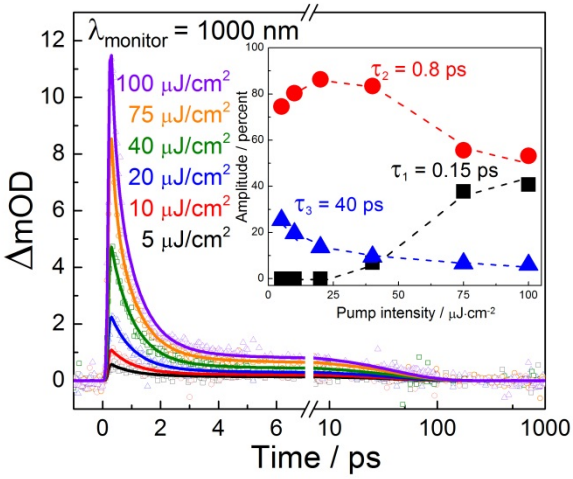

Fig. 1. Pump intensity dynamics of ethoxy-terminated Si QDs. A three-exponential function was used for global fitting to the decay processes (Inset is the amplitudes of three decay components).

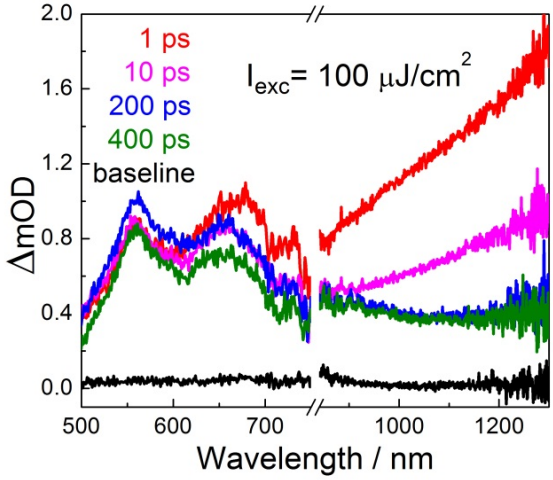

Fig. 2. Transient absorption spectra of 1-octadecene-terminated Si QDs in visible regions as well as near-IR range (the excitation intensity: 100 μJ/cm^2).