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Description	

Photoinduced fluorescence enhancement in CdSe/ZnS quantum dot monolayers: Influence of substrate

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Photoinduced fluorescence enhancement (PFE) of CdSe/ZnS core/shell quantum dot (QD) films on SiO_x substrates was investigated. The fluorescence intensity of the QD film on SiO_{1.9} was greatly enhanced by continuous irradiation in vacuum, while the same QD film on SiO_{0.6} showed a small enhancement of the fluorescence intensity. After irradiation, the rate of fluorescence decay of the QD film on SiO_{0.6} was smaller than that of the QD film on SiO_{1.9}. Our results suggest that the origin of PFE derives from the photoejection of electrons into the substrate, and that the oxygen-excess-related defects work as trap sites for the electrons. © 2006 American Institute of Physics. [DOI: 10.1063/1.2227053]

Colloidal semiconductor quantum dots (QDs) have been intensively investigated on account of their fascinating size-dependent photophysical and optical properties.¹⁻⁶ One of the most interesting properties of these CdSe QD ensembles is the reversible photoinduced fluorescence enhancement (PFE), which has been investigated under differing conditions.⁷⁻¹⁶ However, the PFE mechanism has yet to be clarified, because the optical property of the QD film is very sensitive to the surrounding atmosphere,⁷⁻¹⁰ capping ligands,¹¹ irradiation intensity,^{12,16} and morphology of the QD film.¹³⁻¹⁶ We recently reported that a CdSe QD monolayer shows large PFE, yet the corresponding QD multilayer (ten-layer) showed barely any.¹⁶ This result suggests that the photoionized electrons ejected from some QDs into the deep traps existing in the substrate suppress the ionization probability of the remaining neutral QDs. However, the dependence of the substrate on PFE was unclear. In this letter, we report on the PFE and the following fluorescence decay behaviors in monolayers of CdSe/ZnS core/shell QDs on different stoichiometric SiO_x substrates, to investigate the effect of trap sites existing within the substrate.

SiO_x thin films of 50 nm thickness were deposited onto *n*-Si(100) substrates (Shin-Etsu Chemical) in an Ar atmosphere (0.268 Pa) using a helicon sputtering system (ULVAC, MB00-1018) with Si and SiO₂ targets. Four kinds of SiO_x substrates were prepared by changing the applied voltage of the Si target (V_{Si}), as shown in Table I, while maintaining the applied voltage for the SiO₂ target constant (200 W). The stoichiometry of SiO_x calculated from the Si and SiO₂ (x_{calc}) deposition rates is shown in Table I. X-ray photoelectron spectroscopy (XPS) spectra of the SiO_x substrates were recorded on a Rigaku model XPS-7000 apparatus at a base pressure of 10⁻⁷ Pa. The x-ray source, voltage, and current were Mg K α , 10 kV, and 20 mA, respectively. Binding energies were referred to the C 1s line ($E_B=284.8$ eV).

Tri-*n*-octylphosphine oxide capped CdSe/ZnS core/shell QDs were synthesized by a known colloidal chemical method^{17,18} as previously reported¹⁶ (diameter: 4.2 nm, shell thickness: two monolayers, absorption peak: 550 nm, fluorescence peak: 565 nm). A chloroform dispersion of QDs of

0.1 wt % solid content was spin coated onto SiO_x substrates (15 × 15 mm²) at 3000 rpm for 60 s. The formation of QD monolayers on SiO_x was confirmed for all samples using atomic force microscopy (AFM).

The sample was set in a handmade acrylic vacuum chamber (60 × 25 × 85 mm³) and evacuated with an oil pump (ULVAC, GHD-030). The resulting vacuum was measured using a Pirani gauge (ULVAC, GP-1S). The chamber was positioned within the sample compartment of a fluorescence spectrophotometer (Jasco, FP-6500), and the fluorescence spectra and evolution of the peak intensity were obtained in vacuum at room temperature. The pressure in the chamber was kept below 60 Pa during all measurements. The wavelength and power of the excitation light were 420 nm and 5 mW/cm², respectively. The fluorescence spectrum of the QD film was obtained by subtracting the base line from the recorded spectrum of the sample. The base line was obtained by the irradiation of SiO_x in the vacuum chamber under the same conditions.

Figure 1 shows the XPS spectra of Si_{2p} core levels of four kinds of SiO_x substrates. The peak appearing at a binding energy of around 99.5 eV corresponded to the Si-Si bonds. A second related peak, observed in a slightly higher energy region (~103 eV), is ascribed to Si-O bonds. Detailed data of the resulting binding energies and peak area ratios of both peaks are presented in Table I. By linear approximation between the binding energies of SiO₂ (103.4 eV) and Si (99.5 eV), the stoichiometry of the Si-O domain was estimated. The averaged stoichiometry of the SiO_x substrate (x_{expt}) was determined according to the peak area ratio of Si-O to Si-Si (Table I). Although some deviation was observed due to charging effects, x_{expt} still agreed well with x_{calc} . Thus, x_{calc} was used as the value of SiO_x hereafter.

Figure 2 shows the fluorescence spectra of QD monolayers on SiO_x substrates after long-term continuous irradiation. In all cases, the fluorescence intensity of the QD film (I) increased with irradiation time without any peak shift from 568 nm. The result indicates that the evacuation procedure was enough to prevent photo-oxidation of the QDs, because photo-oxidation of the QDs would cause a blueshift in the fluorescence peak.^{6,7} The initial fluorescence intensity (I_0) and the increasing rate of I (ΔI) both increased with increas-

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TABLE I. Sputtering conditions and results of XPS analysis of SiO_x films.

Sample No.	V_{Si} (V)	x_{calc}	Binding energy of Si_{2p} level (eV)		Percentage ratio of peak integral area (%)		x_{expt}
			Si–O	Si–Si	Si–O	Si–Si	
1	200	0.6	102.0	99.34	56.5	43.5	0.7
2	100	1.0	102.7	100.0	73.9	26.1	1.2
3	55	1.5	103.0	98.69	93.1	6.9	1.7
4	0	1.9	103.8	...	100	...	2.1

ing x for the SiO_x substrate. An observed decrease in I_0 with decreasing x is possibly due to fluorescence resonant energy transfer,¹⁹ dipole-surface interaction,²⁰ and/or interference of excitation light at the SiO_x substrate.²¹ Ozasa *et al.* reported that the fluorescence intensity of QDs on an insulator film depends on excitation wavelength, insulator thickness, and refractive index of the insulator film.²¹ The results imply that the incident excitation light interferes with the light reflected at the insulator surface and at the insulator/semiconductor interface, resulting in enhanced/decreased excitation intensity for the QDs. Since they reported that the interference of excitation light is mainly responsible for the fluorescence intensity of CdSe/ZnS QDs on a thick insulator film of 40 nm thickness or more, the change of I_0 might be attributed to the difference of the refractive indices of SiO_x substrates. In order to focus on the PFE phenomenon, the evolution curves of the peak intensity were normalized by I_0 , as shown in Fig. 3, where the dependence of ΔI on x is more clearly depicted. Note that this tendency was reproducible, except for the order of cases of $\text{SiO}_{1.5}$ and $\text{SiO}_{1.9}$. This result suggests that there is no significant difference when $x \geq 1.5$.

The proposed PFE mechanism can be interpreted as follows. Electrons ejected into the trap sites in a substrate,¹⁶ such as nonbinding oxygen hole centers (NBOHCs) ($=\text{SiO}\cdot$),^{15,22} are achieved through the ionization of certain QDs, to produce an electrostatic potential. This potential suppresses the further ionization of adjacent QDs, such that the total emission efficiency of the QD film increases.^{12–16} This suggestion was supported by the results in Fig. 3, where an increase in the fraction of O atoms in SiO_x should lead to an

increase in the number of NBOHCs. The probability of the photoionization suppression of neutral QDs in the QD film is expected to increase with increasing numbers of electron traps, i.e., NBOHCs. As such, an increasing rate of the QD film emission efficiency would be largely enhanced with increasing x . At the same time, however, an existence of abundant O atoms in SiO_x leads to the formation of a SiO_2 network. Hence, the number of NBOHC sites is thought likely to decrease when $x \approx 2$. This could explain the similar PFE behaviors observed in QD monolayers on both $\text{SiO}_{1.5}$ and $\text{SiO}_{1.9}$ substrates. Although the number density and the type of defects in SiO_x strongly depend on the preparation conditions, we are probably safe in thinking that the number density of NBOHC sites increases monotonically with increasing x when $x < 1.5$, (having a maximum at $1.5 < x < 1.9$), based on the fact that the number density of NBOHC in SiO_x has a maximum at intermediate x in the Si– SiO_x system.²³ When the number of O atoms in SiO_x decreases, the number of oxygen-deficiency-related defects, such as E' centers, is also expected to increase.²⁴ However, these defects are known to work as hole traps, and thus might not influence PFE. In previous reports,¹⁶ we assumed that an electron ejected from a single QD would suppress the ionization rate of the surrounding four QDs based on the calculation of the electrostatic potential¹⁴ and the experimental fitting.¹⁵ Assuming that the electron ejected from a QD was trapped within 5 nm depth from the surface and the QDs 4.2 nm in diameter had hexagonal close-packed structure, the density of the trapped electron was estimated as

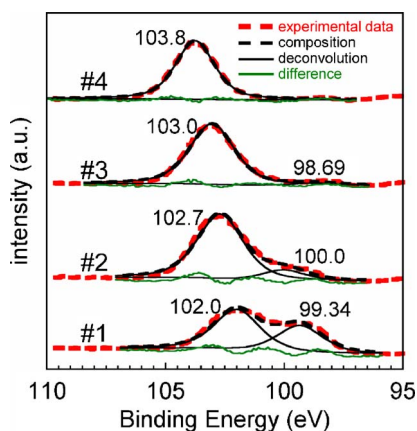


FIG. 1. (Color online) XPS spectra of the Si_{2p} core level of four kinds of SiO_x substrates. The red and black dashed lines represent the experimental data and the Gaussian compositions of the peaks, respectively. The black and green solid lines correspond to the deconvoluted Gaussian curves and the difference between the experimental data and the deconvolution, respectively. Values represent the peak energies (eV).

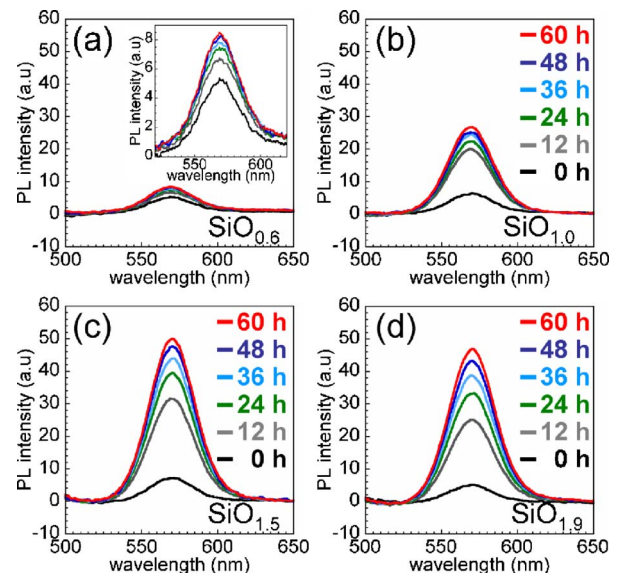


FIG. 2. (Color online) The fluorescence spectra of the QD films deposited on four kinds of SiO_x substrates after 0, 12, 24, 36, 48, and 60 h irradiation.

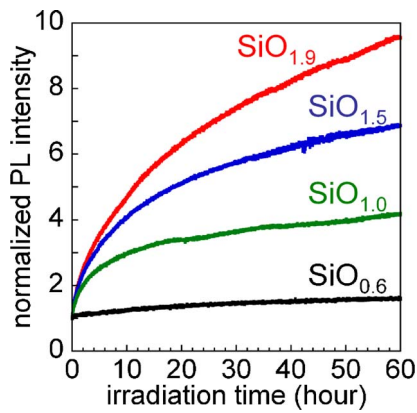


FIG. 3. (Color online) The evolution curves of the fluorescence peak intensity of the QD films on four kinds of SiO_x substrates normalized by I_0 of each sample.

$3 \times 10^{18} \text{ cm}^{-3}$. Although the defect density in SiO_x strongly depends on the deposition condition, the defect density in SiO_x was reported to be of the order of 10^{19} cm^{-3} (Ref. 22) and it is roughly consistent with the estimated carrier density.

Finally, the fluorescence spectra of QD films on $\text{SiO}_{0.6}$ and $\text{SiO}_{1.9}$ in the dark were intermittently measured after 60 h continuous irradiation, and the fluorescence peak intensity was plotted in Fig. 4. In order to consider the difference in the initial and enhanced fluorescence intensities between both samples, I was normalized as $(I - I_0)/(I_{60} - I_0)$, where I_{60} represents the fluorescence intensity after 60 h irradiation. In both samples, the fluorescence intensity gradually decayed with residence time in the dark (t_d). This decay is explained by the electrons escaping from the NBOHC sites in SiO_x and moving towards the charged QDs [i.e., neutralization of QDs (Ref. 5)]. In fact, decayed I was enhanced again by reirradiation after 300 h in the dark, as observed in previous reports.^{12,15,16} As shown in Fig. 4, the decay curves were fitted according to the stretched exponential: $(I_d - I_0)/(I_{60} - I_0) = \exp[-(t_d/\tau)^\beta]$. The time constant of decay ($\tau = 367.5$) and the value of the stretching exponent ($\beta = 0.44$) can be obtained for the QD film on $\text{SiO}_{1.9}$. However, for the QD film on $\text{SiO}_{0.6}$, it is difficult to accurately analyze the data due to the intensity having a poor signal to noise ratio, although the decay curve can be fitted with $\beta = 0.36$ and $\tau \approx 1420$. The smaller value of β (≈ 0.4) in both films was interpreted as a broader distribution of distance from the QD film and/or the trapped level of NBOHC sites in SiO_x . The shorter τ of the QD film on $\text{SiO}_{1.9}$ indicates that the escape rate of the electrons is large. It could be due to the smaller permittivity of $\text{SiO}_{1.9}$ than that of $\text{SiO}_{0.6}$. Alternatively, the larger amount of the trapped electrons in $\text{SiO}_{1.9}$ than that in $\text{SiO}_{0.6}$ might increase the repulsive interaction between the charges, and thus could induce an increase in the escape rate of the electrons.

In conclusion, we have shown that the PFE phenomenon of CdSe/ZnS QD films on SiO_x substrates is dependent on the stoichiometry of the SiO_x substrates. Our results suggest that PFE is attributed to the photoejection of electrons into the NBOHC sites in SiO_x . The slow decay after the irradiation can be explained by the neutralization of the QDs, and the neutralization rate is found to also depend on the substrates.

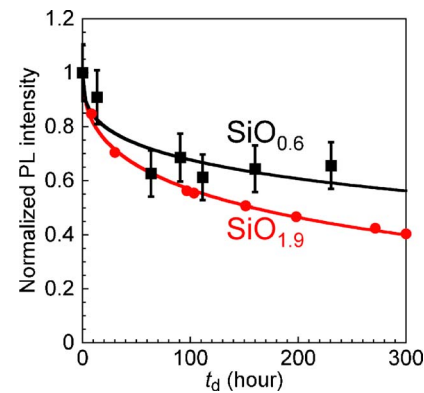


FIG. 4. (Color online) Normalized fluorescence decay curves for the QD films on $\text{SiO}_{1.9}$ (red circles) and $\text{SiO}_{0.6}$ (black squares) after 60 h irradiation. The error bars represent the noise level of the instruments. The solid lines represent the fitting results with stretched exponential.

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