Excitation dependence of photoluminescence in silicon quantum dots

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Abstract. We have studied the optical properties of silicon quantum dots (QDs) embedded in a silicon oxide matrix using photoluminescence (PL) and time-resolved PL. A broad luminescence band is observed in the red region, in which the time evolution exhibits a stretched exponential decay. With increasing excitation intensity a significant saturation effect is observed. Direct electron–hole recombination is the dominant effect in the red band. A relatively narrow peak appears around 1.5 eV, which is attributed to the interface states overlapping with transition from the ground state of the silicon QDs. The saturation factor increases slowly with detection photon energy between 1.5 and 1.8 eV, which is attributed to the emission from zero-phonon electron–hole recombination. At higher photon energies the significantly increased saturation factor suggests a different emission mechanism, most likely the defect states from silicon, silicon oxide or silicon rich oxide.
1. Introduction

It is well known that bulk silicon has an indirect band-gap and very low photoluminescence (PL) efficiency and thus is not suitable for an emission device. In recent years it has been shown that, accompanying the size reduction of silicon nanostructures such as in silicon nanocrystals and porous silicon, zero-phonon optical transitions are allowed and oscillator strength of the zero phonon transition is significantly enhanced. This increases the radiative recombination rate via a direct band-to-band recombination process [1]. The discovery of efficient visible PL from silicon nanocrystals and porous silicon has attracted much attention because it can lead to the fabrication of light-emitting devices compatible with silicon-based optoelectronic integrated circuits and result in a new generation of silicon technology from microelectronics to optoelectronics [2, 3]. Extensive studies have been carried out in silicon nanostructures and impressive progress has been made towards understanding the nature of the efficient PL since the initial demonstrations in porous silicon and silicon nanocrystallites [4, 5].

The broad PL band from silicon quantum dots (QDs) has been observed experimentally and studied theoretically, where a quantum confinement model has been proposed. It is now mostly accepted that with reducing the size of silicon QDs the zero-phonon direct band-to-band transition becomes partially allowed and therefore the effective red band originates from two kinds of luminescent mechanisms—direct band-to-band recombination and phonon-assisted indirect recombination in parallel [6]. The size of the QDs is the key factor to determining the ratio of zero-phonon transitions to phonon-assisted transitions. With reducing size of the QDs the quantum confinement effect is enhanced and the ratio increases [7]. More recently, Sychugov et al [8] have found that the luminescence linewidth is less than the thermal broadening for single silicon QDs at low temperature and thus have suggested atomic-like energy states of silicon QDs. However, unlike other direct band-gap semiconductor nanostructures in which most of the optical properties follow the predictions of the quantum confinement model, many of the basic properties of silicon nanocrystals do not follow this model [9]. Thus some different physical mechanisms in addition to the quantum confinement effect involved in the effective room temperature emission in silicon nanostructures have been proposed [10]–[13]. To date there is still controversy concerning the origin and nature of the radiative states that contribute to the PL and the detailed physical processes are still unclear and under debate [14]–[16]. This is most likely due to the variability in sample structure and the many possible states in silicon nanostructures [17, 18].

In this paper, the optical properties of silicon QDs embedded in a silicon oxide matrix are studied using PL and time-resolved PL. A broad luminescence band is observed ranging from 1.4 to 2.0 eV at room temperature. An excitation dependence experiment reveals that different
saturation properties occur for different detection photon energies. The saturation factor exhibits different distributions in the high and low energy regions of the broad band, which suggests that different PL mechanisms are involved in the broad band.

2. Sample and experimental details

The sample used in this experiment consists of silicon QDs embedded in a silicon oxide matrix, similar to the samples used previously [19]. Silicon rich oxide (SRO, SiO$_x$ with $x < 2$) is a substoichiometric oxide with an excess of silicon, which generates silicon precipitations attributed to the diffusion of silicon atoms during high temperature thermal annealing [20]. A deposited SRO film is thermodynamically unstable below 1173 °C and phase separation and diffusion of the silicon atoms in the amorphous SiO$_2$ matrix creates nanoscale silicon QDs [20]–[22]. The size of the silicon dots depends on the thermal budget, film thickness and stoichiometry of the SRO. The silicon QDs sample consists of 15 bi-layers of silicon oxide and SRO with different thicknesses. After the deposition of the multilayer of silicon oxide and SRO, conventional furnace annealing under a nitrogen atmosphere (1100 °C, 1 h) was performed to precipitate silicon and stimulate nanocrystalline silicon growth by the diffusion of silicon in the oxide. As shown in [19] and [20] high definition transmission electron microscopy images show that the sample has an average dot size distribution of 3.5 nm on a sapphire substrate, and the dot density is about 10$^{12}$–10$^{13}$ dots cm$^{-2}$.

In the time-resolved and time-integrated PL experiment, the PL signal is dispersed by a 0.27 m grating spectrometer and detected with a photomultiplier (PMT). For the time-integrated PL experiments 100 fs laser pulses from a Ti : sapphire mode-locked laser with a repetition of 82 MHz was used for excitation and the beam diameter was about 4 mm. The spectra were recorded using a lock-in amplifier. The laser wavelength was tuned to 400 nm, which is well above the band gap of the silicon QDs and thus the excited carriers are generated in the SRO layer or in very high-excited states of the QDs. For the time-resolved measurements laser pulses with 1 kHz repetition rate and 100 fs duration from a regenerative amplifier were used. The response time of the PMT is reduced to about 5 ns, which is much shorter than the decay time of the signals, which is in the microsecond range, and a 500 MHz bandwidth digital oscilloscope was used for recording the signals.

3. Experimental results and discussion

Figure 1 shows the PL spectra excited by laser pulses with a repetition rate of 82 MHz at room temperature and at various intensities in an atmosphere of air (solid lines). In this case, the laser creates a continuum excitation because the pulse separation is much shorter than the decay time of the silicon QDs at an excitation power of 2.2 mW. A broad red band is observed ranging from 1.4 to 2.0 eV, which has been attributed mainly to electron–hole recombination between QD states in the conduction band (CB) and the valence band (VB) and phonon-assisted emission plays only a minor role [23]. In a previous investigation a temperature dependence experiment shows that the PL intensities at 20 K are almost the same as those at room temperature and the lifetimes do not show a significant decrease. This indicates that the direct transition from silicon QDs makes the dominant contribution [23]. On the other hand, strong inhomogeneous broadening due to the distribution of dot sizes leads to overlapping between the transitions from the ground state and excited states, which conceals the details of the spectral structures.
With decreasing excitation intensity the PL intensity on the high-energy side decreases significantly and the maximum of the peak intensity shifts to the red. At the low excitation of 50 µW a narrow band can be identified peaked at around 1.5 eV with a significantly smaller bandwidth. A similar PL spectrum has been reported for a silicon nanocrystal embedded in a silicon oxide matrix and the peak has been ascribed to interface states [24], which are related to the composition and dot size. At very low excitation, 5 µW, the band is significantly narrower than at the high excitations. At this very low excitation the peak from the interface states may overlap partially with the peak for transitions from the ground state of the silicon QDs. A weak high-energy tail is also observed, which can be attributed to transitions from the excited states of the QDs.

The PL spectrum excited by 1 kHz ultrashort pulses from the regenerative amplifier with power 2 mW is compared in figure 1 (dashed line, normalized), which corresponds to extremely high-peak intensity excitation. Significantly higher intensity at high photon energy is observed compared to the spectrum excited by the 82 MHz pulses. This significant saturation effect also suggests that phonon-assisted transitions are not the main resource of the emission.

An enhanced Auger effect may result in a shift of the band maximum [25]. If two excitons accumulate in a silicon QD simultaneously, one of them can recombine nonradiatively by giving kinetic energy to an electron or hole of the other exciton, resulting in a saturation of the PL intensity. The effect is more significant in a large dot than that in a small dot due to the longer lifetime. With increasing excitation the PL on the lower energy side saturates faster and thus the maximum of the band shifts toward the high-energy side. However, in this model the PL band originates as a combination of the outputs from individual QDs—larger dots for the low-energy side and small dots for the high-energy side. Thus the spectrum should depend on the inhomogeneous broadening due to the distribution of dot size. For quite low excitation there is

Figure 1. PL spectra of silicon QDs excited by a 400 nm 82 MHz laser at various intensities (solid lines). The PL intensity on the high-energy side decreases significantly with decreasing excitation intensity. The PL spectrum excited by high-peak intensity (2 mW of 1 kHz repetition rate laser) is included (dashed line), which shows a significantly higher intensity on the high-energy side.

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a neglectable saturation effect for both large and small dots and thus the spectrum essentially shows the inhomogeneous broadening due to the dot size. The experiment shows that the PL quenches on the high-energy side at low excitation and significantly increases at high excitation (e.g. high excitation with 1 kHz), which is not consistent with the model.

This phenomenon can also be interpreted in terms of the state filling effect [26]. In principle both the state filling effect and the phonon bottleneck [27] can lead to such a broad spectrum originating from transitions from the ground state and the excited states in a three-dimensional confinement QD system. However, in the case of the phonon bottleneck the transitions from the ground state and the excited states can be observed at high and low excitation and the ratio of their amplitudes should not change significantly with decreasing excitation intensity due to the fact that the inter-sublevel relaxation is comparable to the recombination rate of interlevel transitions. The excitation dependence experiment shows that the spectral shape changes significantly with decreasing excitation intensity. Inter-sublevel relaxation in QDs can be fast due to the involvement of other relaxation mechanisms, such as Auger, electron–hole scattering and multiphonon scattering.

With increasing excitation intensity the availability of the low-energy levels of silicon QDs decreases due to the state filling effect, which leads to a significantly slower increase of carriers; i.e. a saturation effect appears in the lower states of the silicon QDs, and thus a different saturation appears at the various detection energies, as observed in many other QD systems [26, 28]. However, even at quite low excitation we do not observe a single Gaussian peak for the transition from the ground state like in other QD systems [26]. This is reasonable because the state filling effect is closely linked to the recombination rate. A small recombination rate leads to a long lifetime and thus significant state filling. The radiative lifetime of electron–hole pairs localized in a silicon nanocrystal is very long, on the order of microseconds. Therefore there is a large probability of exciting a second electron–hole pair before the first one has recombined. The extremely long lifetime may result in a very strong state filling effect in which the low levels are not available until the carriers recombine with an extremely long lifetime. Also the strong inhomogeneous broadening can result in strong overlapping of the transitions from the ground state and excited states. Thermal broadening does not seem to play an important role because the PL spectra at low temperatures are very similar to those at room temperature [23]. Another reason includes the possibility that the PL from the interface states roughly overlaps with the emission of the silicon QDs.

We performed a time-resolved PL experiment at room temperature. The rise time is very short, on the order of femtoseconds or picoseconds [29], which is much shorter than the time resolution of the measurement system. As for the decay, each PL evolution consists of a fast component and a slow component. The fast component cannot be resolved due to the low temporal resolution of the system. The slow component can be fitted with a stretched exponential function used to describe dispersive processes in a disordered system having a distribution of relaxation times, and given by [30]

$$I(t) = I_0 \exp\left(-\frac{t}{\tau}\right)^{\beta},$$

(1)

where $\tau$ is the PL lifetime and $0 \leq \beta \leq 1$ is the dispersion factor. Figure 2 shows the slow component of the PL evolution at various detection energies (points) and the corresponding stretched exponential function fit (solid lines). The deduced lifetimes are listed in table 1 for the various detection energies: each lifetime is on the order of microseconds and a larger detection energy results in a significantly shorter lifetime. The dispersion factor, $\beta = 0.55$, is
Figure 2. Evolution of the PL from silicon QDs and fits with a stretched exponential function at various detection photon energies. A significantly shorter lifetime is observed on the high-energy side.

Table 1. Lifetimes for various detection energies deduced from the fit with a stretched exponential function.

| Detection λ (nm) | 600 | 650 | 700 | 750 | 800 | 850 |
|------------------|-----|-----|-----|-----|-----|-----|
| S107 (µs)        | 3.0 ± 0.5 | 5 ± 1 | 11 ± 2 | 19 ± 2 | 31 ± 3 | 39 ± 5 |

essentially independent of the detection energy, which suggests that this parameter is related to the macroscopic character of the medium, particularly its disorder characteristics, rather than to the microscopic properties which depend on the size of the QDs [9]. Other groups have also observed experimentally or investigated theoretically the stretched exponential decay in silicon nanostructures and various models have been proposed to explain the stretched exponential decay; for instance, a hopping mechanism [31], and the migration of excitons in an interconnected disordered network of crystals [30, 32]. This stretched exponential function is related to a distribution of relaxation times or a time-dependent relaxation rate [9]. In time-resolved PL measurements, the lifetimes of the high-energy levels are significantly shorter than those of the low energy levels, similar to other observations [9, 33].

In order to understand quantitatively the main microscopic processes involved in the observed PL transition, we use a simplified rate equation model to describe the transitions involved in the silicon QDs [19]. The electron density $N_i$ in level $i$ of the CB can be written as

$$\frac{dN_i(t)}{dt} = -\frac{N_i(t)}{\tau_{el}^i} + \frac{\eta \sigma I_{ex} N_0}{\tau_{cap}^i} \frac{D_i - N_i(t)}{D_i}.$$ (2)
Figure 3. Excitation dependence of PL intensity at various photon energies for silicon QDs. The solid lines represent fits using the expression $I_{PL}(\lambda) = A(1 + B)/I_{ex}$ with A and B constants.

where $\tau^{\text{el}}_i$ and $\tau^{\text{cap}}_i$ are the effective lifetime and capture time of the $i$th level, $\sigma$ is the absorption cross-section, $I_{ex}$ is the laser excitation intensity, $N_0$ is the total state density in the wetting layer, $\eta$ is the capture efficiency and $D_i$ is the state density. The factor $[D_i - N_i(t)]/D_i$ is a state-filling factor, which takes account of the fact that the electron can only relax to a lower-lying unoccupied dot level (Pauli blocking).

The case of 82 MHz laser excitation can be regarded as continuum excitation because the pulse separation of 12 ns is much shorter than the lifetime of the band which is in the microsecond range. Therefore, the equilibrium condition $dN/dt = 0$ can be applied. The electron density in level $i$ corresponding to an excitation intensity $I_{ex}$ is given by

$$N_i(I_{ex}) \propto D_i/(1 + \alpha_i D_i/I_{ex}),$$

(3)

where $\alpha_i D_i$ is a saturation factor which depends on the level of the silicon QDs, and $\alpha_i = \tau^{\text{cap}}_i/(\sigma N_0 \tau^{\text{el}}_i)$. The corresponding time-integrated intensity of luminescence can be expressed as

$$I^i(I_{ex}) \propto \eta_i N_i \propto \eta_i D_i/(1 + \alpha_i D_i/I_{ex}),$$

(4)

where $\eta_i$ is the quantum efficiency. Equation (4) provides a good fit for the intensity dependence of the PL at various detection energies, as shown in figure 3, in which the points are the experimental data and the solid curves are the best fits. We deduce the saturation factors as a function of detection energy, as shown in figure 4. The PL spectrum at an excitation power of 2.2 mW is also plotted as a reference. Considering the ratio $\tau^{\text{cap}}_i/\tau^{\text{eff}}_i$ (capture time/effective lifetime), which is independent of or weakly dependent on the dot levels, we deduce a degeneracy of the energy level in the QD from the saturation factor $\alpha_i D_i/\alpha_0 D_0 \sim g_i/2 = (i + 1)$ with $i = 0$ for the ground level. With increasing detection photon energy the saturation factor will increase.
We deduce the saturation factor as a function of photon energy, as shown in figure 4. It is interesting to note that the saturation factor increases exponentially over the all range of photon energies. The saturation factor varies only slightly between 1.4 and 1.5 eV, which is attributed to the ground state transition and also the overlapped emission from the interface states. The saturation factor increases slowly with detection photon energy from 1.5 to 1.8 eV, which is consistent with the prediction of the rate equations and thus we attribute the emission in this region mainly to the transition of electron–hole recombination in the silicon QDs. On the high-energy side (>1.8 eV) the saturation factor increases significantly faster, which suggests a different emission mechanism, e.g. defect states in the silicon, silicon oxide or SRO in the high energy region [4]. However further investigation is required to fully understand the detailed emission mechanisms.

4. Conclusions

We have investigated the optical properties in silicon QDs embedded in a silicon oxide matrix. A broad luminescence band is observed in the region 1.4–2.0 eV. Excitation dependence experiments reveal that the saturation factor varies exponentially over the full range of photon energies. In the low photon energy region 1.4–1.5 eV the saturation factor varies only slightly due to the overlapped emission of the ground state of the QDs and the interface states. Between 1.5 and 1.8 eV the saturation factor increases slowly due to transitions of direct electron–hole recombination of the silicon QDs, which is consistent with the prediction of rate equations. With increasing photon energy the defect states from silicon, silicon oxide or SRO are responsible for the emission and thus the saturation factor increases steeply.
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