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Photoactivation of silicon quantum dots

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ABSTRACT

We show that free-standing silicon quantum dots (QDs) can be photoactivated by blue or UV optical irradiation. The luminescence intensity increases by an order of magnitude for irradiation times of several minutes under moderate optical power. The cut-off energy for photoactivation is between 2.1 and 2.4 eV, not very different from the activation energy for hydrogen dissociation from bulk silicon surfaces. We propose the mechanism for this effect is associated with silicon-hydride bond breaking and the subsequent oxidation of dangling bonds. This phenomenon could be used to "write" luminescent quantum dots into pre-determined arrays.

1. Introduction

Semiconductor quantum dots (QDs) have surface areas exceeding 1200 m^2 per cubic centimeter of material, and the interface can therefore have a profound influence on their physical and optoelectronic properties. Fluorescent QDs, in particular, are finding new applications in areas ranging from biomedical imaging [1,2] to microphotonics [3,4]; however, even low abundances of surface defects or the presence of charge trapping species can modify or quench the luminescence. This is one reason commercially available QDs are generally protected with an epitaxial shell consisting of a second, larger-bandgap semiconductor [5]. This structure ensures a high-crystal-quality interface, maintains strong confinement in the core, and prevents unwanted interactions between the dot surfaces and the surroundings.

Silicon QDs (Si-QDs) are attractive because of their low toxicity, compatibility with microelectronic fabrication methods, high quantum efficiency [6], and ease of fabrication. Unfortunately, epitaxial core-shell structures similar in quality to those achievable in the II–VI compound QDs are not yet known; therefore, the Si-QD interface can have a substantial influence on the luminescent properties [7–10]. In particular, the nature of the Si/SiO$_2$ interface is thought to play an important role in producing the typical red luminescence demonstrated by oxide-embedded Si-QD nanocomposites [5,7,11].

For oxide-embedded Si-QDs, the following surface structures are thought to influence the luminescence spectrum and intensity: (i) the Si=O bond [10,12], (ii) the silicon dangling bond, or neutral P_b center [13], (iii) the silicon-hydride bond [14], and (iv) the Si–O–H surface termination [15–17]. Structures (i) and (iv) are thought to produce sub-gap radiative states associated with the typical red luminescence of oxide-embedded Si-QDs [10,12,17]. Structure (ii) produces a fast non-radiative trap that can be passivated by hydrogen, leading to structure (iii). Hydride (as well as oxygen) passivation effectively removes non-radiative trapping processes associated with unsatisfied silicon bonds, thereby increasing the luminescence efficiency [14].

There is evidence that interface defects in Si-QDs can evolve upon exposure to UV irradiation. For example, irradiation of hydride-passivated, oxide-embedded Si-QDs causes a red-shift of the photoluminescence (PL) spectrum, along with a temporary increase in the PL intensity [14]. This behavior was attributed to the introduction of oxide-related interface states during irradiation in air. Continued irradiation resulted in a subsequent decrease in the PL intensity, an effect hypothesized to arise from a re-introduction of P_b centers. In another work, UV irradiation also caused a minor increase in PL intensity that was attributed to the oxidation of P_b centers on the surface of Si-QDs.[18].

The majority of previous investigations have focused on silicon QDs embedded in an oxide matrix. Unfortunately, these materials provide fairly limited physical access to the interface structures, which, e.g., can be controlled to a limited degree by thermal processing at elevated temperatures (by hydride or deuterium passivation and cycling [19]) and by UV irradiation. The irradiation-induced changes in the luminescence intensity were also

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quite small, on the order of 10%. In the present work, we used samples in which Si-QDs embedded in a silica matrix were liberated using HF etching to yield free-standing hydride terminated nanocrystals. These particles were initially suspended in solution, in order to enable a more direct manipulation and control of surface chemistry, and to ensure minimally-oxidized structures were used [9,20,21].

2. Materials and methods

2.1. Preparation of free-standing Si-QDs

Silicon QDs were prepared using hydrogen silsesquioxane (HSQ: chemical formula $H_{12}Si_8O_{12}$) dissolved in methyl isobutyl ketone (MIBK). HSQ was heated to 1100 °C under a 95% Ar+5% H_2 atmosphere to produce nanocrystal QDs embedded in a silica matrix. Full details of the present QD synthesis and characterization may be found in Ref. [21]. The process provides gram quantities of Si-QDs embedded in a silica matrix.

The Si-QDs were liberated by HF etching of the matrix using a 1:1:1 mixture of ethanol, water, and hydrofluoric acid (49% HF) (by volume) for 50 min while stirring under ambient conditions. This process removes the SiO_2 matrix and yields hydride terminated Si-QDs. The suspended QDs were then extracted into toluene [22], and subsequently dropped onto silicon wafers. To prevent excessive agglomeration, the toluene solution was evaporated drop-by-drop by gently blowing dry $N_{2(g)}$ over the surface of the wafer in a circular motion until the solvent was evaporated. This method yielded a discontinuous coating of free-standing Si-QDs on the surface of the wafer.

2.2. Optical characterization and irradiation

Si-QD luminescence was obtained by pumping the sample with 325 nm light from a HeCd laser operated at a continuous wave power of 13.8 mW. The PL spectra were collected using a fiber optic spectrometer that was calibrated with a standard blackbody source (for intensity) and an HgAr lamp (for wavelength). The luminescence emitted by the Si-QDs was passed through a long-pass filter to minimize the amount of scattered laser light when collecting PL spectra.

A series of PL experiments were performed. These included:

(i) The effect of irradiation wavelength was investigated using a single-line ArKr ion laser operated at 457, 514, 568, or 647 nm with a continuous-wave power of 50 mW. Irradiations were also performed using the 325 nm line from the HeCd laser.

(ii) Time-resolved PL experiments were performed by "chopping" the ArKr laser beam with an acousto-optic modulator (using a wavelength of 476 nm and power of 22 mW). The resulting PL dynamics were measured with a single-photon-counting photomultiplier system with a multiscaler set to 200 ns time bins.

(iii) Si-QD films were heated in ambient atmosphere to temperatures up to 300 °C, before and after which PL spectroscopy and laser irradiation were performed.

(iv) The PL spectrum was measured on samples irradiated in vacuum ($\sim 10^{-6}$ Torr) and the results compared to those from air-irradiated samples. For consistency, all PL spectra were collected using the 325 nm excitation source. When irradiating the samples with other wavelengths, precautions were taken to minimize the influence of the 325 nm laser needed to excite the PL. This was achieved by using a programmable servo to switch between the 325 nm excitation source and the irradiation source. The 325 nm source excited the sample for PL data collection at intervals of 4 s every minute, while for the remaining 56 s the sample was exposed only to the ArKr laser. Control samples were only exposed to the 4 s data-collection intervals.

2.3. TEM characterization

Samples were prepared for transmission electron microscopy (TEM) by dropping a small fraction of the toluene solution containing the Si-QDs onto a 400 mesh copper grid with a 16 nm-thick carbon film. Bright field imaging and electron diffraction were performed on a JEOL 2010 TEM with a LaB_6 filament. High-resolution imaging and energy-filtered scanning transmission electron microscopy (EFSTEM) employed a JEOL field emission 2200FS TEM equipped with an Ω-filter. EFSTEM imaging was accomplished by centering an energy-filtering slit at an energy loss of 99 eV, corresponding to the L_{23} absorption line of silicon. The slit width corresponded to a 10 eV energy window. Using these values, silicon QDs will appear bright against a darker background.

2.4. FTIR characterization

Samples were prepared for Fourier transform infrared spectroscopy (FTIR) analysis by casting the solution containing the Si-QDs onto a potassium bromide plate and allowing the toluene to evaporate. For each experiment, two samples were prepared; a control sample that was not irradiated, and one that was irradiated in air for 1 h using the 325 nm HeCd laser. An additional pair of samples was prepared to examine the effect of temperature; one was heated but not irradiated, and the other was heated and subsequently irradiated with the HeCd laser for 1 h. Spectra were acquired using a Thermo Nicolet Nic-Plan FTIR microscope attached to a Magna 750 main bench with a wavelength resolution of 4 cm^{-1} and a spectral range of 4000–650 cm^{-1}. Thirty-two scans were taken per spectrum and averaged in order to reduce noise.

3. Results

3.1. Microstructure

Low magnification bright-field TEM imaging (Fig. 1a) revealed the presence of Si-QDs, as confirmed by electron diffraction (Fig. 1b) and HRTEM (Fig. 1c). Most QDs were aggregated into small clusters clearly observable in Fig. 1a. Fig. 1d shows an EFTEM image of a small cluster of nanoparticles that indicates the presence of Si in this imaging region. The size distribution obtained from the bright field imaging was fit with a lognormal function, resulting in a mean QD diameter of 3.1 nm and a geometric standard deviation of 0.55 nm.

3.2. Irradiation in air

Initially, the dropcoated hydride terminated Si-QDs showed a weak luminescence centered at approximately 800 nm. Following exposure to 325 nm laser irradiation (13.8 mW, beam diameter ~2 mm; flux $\sim 2.2 \times 10^{16}\ m^{-2}\ s^{-1}$), the integrated PL intensity initially decreased and blue-shifted to 675 nm. Upon extended exposure (i.e., 60 min), the PL emission intensity increased markedly, and red-shifted slightly (Fig. 2). The PL intensity and shift in peak wavelength approached, but did not reach saturation after a 60 min irradiation. We refer herein to the observed increase in