Time Resolved and Time Integrated Photoluminescence for Study of Optical Properties of Silicon Quantum Dots

Lap Van Dao¹, Xiaoming Wen¹, My Thi Tra Do¹, Peter Hannaford¹, Eun-Chel Cho², Young H. Cho², Yidan Huang², and Martin A. Green².

¹) Centre for Atom Optics and Ultrafast Spectroscopy, Swinburne University of Technology, Melbourne, Australia 3122
²) Centre of Excellence for Advanced Silicon Photovoltaics and Photonics, The University of New South Wales, Sydney, Australia, 2052

Abstract

In this paper we report studies of the optical properties of silicon quantum dot structures. From time-resolved and time-integrated photoluminescence measurements we investigate the state-filling effect and carrier lifetime and discuss the parabolic confinement of quantum dot structures. The photoluminescence intensities for different quantum dot levels decay with a stretched exponential function and the decay times are in the range 2 – 60 μs.

Keywords - Optical properties of low-dimensional structures, Photoluminescence, Laser spectroscopy.

I. INTRODUCTION

The efficient light emission from silicon nanostructures involved in quantum confinement effects has led to current interest in Si as a material for optoelectronic devices[1]. Si is the most technologically important material of this century and the development of light-emitting Si devices could result in a new generation of Si technology from microelectronics to optoelectronics. Light emission from silicon, an indirect band-gap semiconductor, is possible in Si nanocrystals as a result of quantum confinement. Quantum confinement in Si nanocrystals results in an enlargement of the band gap and efficient emission in the visible at room temperature.

In this paper we present the studies of the optical properties of Si quantum dot (QD) structures. From time-resolved and time-integrated photoluminescence studies we investigate the state filling effects and carrier lifetimes and discuss the parabolic confinement of quantum dot structures. The photoluminescence intensities for different dot levels are decayed with a stretched exponential function and decay times are in the range 2 to 60 μs.

II. SAMPLE STRUCTURES

An excess of silicon in sub-stoichiometric oxide, also known as silicon-rich-oxide (SRO), i.e., SiOₓ (x<2), generates Si precipitations which are attributed to the diffusion of Si atoms from the stoichiometric oxide (SiO₂) during high temperature thermal annealing. A deposited SRO film is thermodynamically unstable below 1173°C and phase separation and diffusion of the Si atoms in the amorphous SiO₂ matrix creates nano-scale Si quantum dots [1]. The size of the Si dots depends on the thermal budget, film thickness, and stoichiometry of the SRO. In our experiment Si QD superlattices were fabricated by alternate deposition of silicon oxide and SRO with differing thicknesses. Conventional furnace annealing under a nitrogen atmosphere (1100°C, 1 hour) was performed to precipitate Si and nanocrystalline Si growth by the diffusion of Si in the oxide [1]. Only lateral Si diffusion and Si grain growth occurs in thin SRO films enclosed by amorphous silicon oxide so that the maximum size of the Si quantum dots is determined by the SRO thickness. Two shapes of quantum dots (of about 4 nm diameter), spherical dots and near-spherical dots, with the same vertical thickness, observed in high-resolution transmission electron microscopy (HRTEM) images, are favoured by the surface energy minimisation, which is thermodynamically stable. A typical HRTEM image is shown in Fig. 1. The size of the Si quantum dots was controlled by the deposition time and other sputtering parameters (gas mixing ratio, deposition pressure, and RF power). The spacing or distance between the dots is determined by the amount of silicon in the SRO layer.

Figure 1. HRTEM images of a Si quantum dot superlattice with 8 bilayers of Si dots.
III. EXPERIMENTS

Time-resolved and time-integrated photoluminescence (PL) signals are used to study the optical properties of the samples. The PL signal is dispersed by a 0.27 m grating spectrometer and detected with a photomultiplier (PMT). The sample was mounted in a closed-cycle helium cryostat with a variable temperature ranging from 15-300 K. In the time-integrated PL measurements the spectra were recorded using a lock-in amplifier. For the time-resolved measurements the response time of the PMT is reduced to reach a time resolution of about 5 ns, which is much shorter than the decay time of the signals (in the microsecond range) and the signal is recorded by a 500 MHz (5 Gs/s) digital oscilloscope or a boxcar system. Femtosecond laser pulses with a duration of 100 fs and a repetition rate of 1 kHz are used for the excitation. The femtosecond pulses are generated by the conversion of a 1 mJ amplified pulse (80 fs, 800 nm) in a tunable optical parametric amplifier that covers a wide range of wavelengths (200-2000 nm) with high pulse energy (1-100 μJ/pulse).

In this work the PL spectra of the QDs taken at an excitation wavelength of 400 nm, which is well above the band gap of the Si QDs, and the excited carriers are generated in the SRO layer or very high excited states of the QDs. The energy of the excitation laser pulse varies from 0.05 to 2 μJ with a photon density of about 10^{12} to 10^{15} photons/cm^2. Under these conditions at high excitation energy we estimate that more than 10 electrons/dot can be generated.

IV. RESULTS AND DISCUSSION

Figures 2 show PL spectra of the samples at room temperature taken at different excitation intensities. A very broad band (~350 meV) PL signal around 750 nm with no clear structure [8] is observed. The emission involves electron-hole recombination between distinct QD states in the conduction band (CB) and the valence band (VB).

When the excitation intensity is increased the PL intensity of the low energy part of the spectrum (800 nm, 850 nm) increases more slowly than that of the high energy part and a small shift of the maximum of the PL spectrum is observed (780 nm for 0.05 μJ excitation and 750 nm for 2 μJ). Because the spectrum is very broad and the peaks due to recombination of carriers in different energy levels cannot be clearly resolved we evaluate the PL intensity for different levels by recording the spectrally integrated signal with a spectral window of 2 nm in 50 nm steps across the spectrum (600 – 850 nm). The results are shown in Fig.3 for three different wavelengths 650 nm, 750 nm, and 850 nm. The dependence of the PL intensity on excitation intensity and saturation of the PL intensity is different for different detection wavelengths. According to the state-filling effect [2,3], lower energy levels with a low density of states will become saturated at low intensity as the higher energy levels will be still populated as the excitation intensity increases.

The time-integrated luminescence intensity I_{PL} at a given wavelength for recombination of electrons or holes from level i can be written

\[ I_{PL} \sim \eta_i D_i (1 + \alpha_i D_i / I) , \]

where \( \eta_i \) is the quantum efficiency, \( \alpha_i D_i \) is the saturation factor which depends on the optical properties of level i, I is the laser intensity, \( D_i \) is the dots density.

The QD energy levels can be described by a harmonic oscillator model for parabolic quantum confinement [4]. The potential function can be written by \( V_j = \frac{m^* \omega_j^2 r^2}{2} \), where \( j \) represents an electron or a hole, \( \omega_j \) is the frequency, \( m^* \) is the effective mass, and \( r \) is the radial coordinate of the dot. The
The eigenenergies for a single electron or hole are $E_{lm} = \hbar \omega (2l - |m| + 1)$, where $l$ is the radial quantum number, $m$ is the angular momentum quantum number, and $\hbar$ is Planck’s constant. We can set $i = 2l - |m|$, in which case the eigenenergy is of the form $E_i = \hbar \omega (i + 1)$. If we take the spin degeneracy into account the degeneracy of each state is $g_i = 2(i + 1)$, with $i = 0, 1, 2, \ldots$.

Equation 1 provides a good fit for the intensity dependence of the PL at different wavelengths, as shown by the solid line in Fig. 3. The saturation factor $(\alpha_{0}D_0)$ increases with increase of detection photon energy and is proportional to the degeneracy of the energy level. We deduce the degeneracy of the energy level in the quantum dot from the saturation parameter $(\alpha_{0}D_0 / \alpha_{i}D_i \sim g_i / 2)$ where $\alpha_{0}D_0$ is the saturation parameter of the ground level $(i=0)$. The results calculated from fitting of saturation parameter are shown in the inset of Fig. 3 and are represented by the symbol $(\bullet)$, when the ground level luminescence is observed at 850 nm.

Figure 4 shows a non-exponential PL decay taken at different detection wavelengths. In order to analyse the temporal evolution of the PL we have fitted the decay signals to a stretched-exponential function [5], which is frequently used to describe dispersive processes in disordered systems having a distribution of relaxation times, and is given by

$$I(t) = I_0 \exp[-(t/\tau)^\beta],$$

(2)

where $\tau$ is the PL lifetime and $0 \leq \beta \leq 1$ is the dispersion exponent. For different detection wavelengths the lifetimes are vary from 10 to 60 $\mu$s with increasing detection wavelength. The dispersion factor is $\beta = 0.6$. The stretched function is related to a distribution of relaxation times or a time-dependent relaxation rate which reflects the inter-level relaxation processes in the QD.

In conclusion, time-resolved and time-integrated PL measurements have been used to study the optical properties of Si QDs. The state-filling effect and the intensity dependence of the measurements give more information about the energy structures of QDs and provide strong evidence for the origin of the observed PL. From the discussion of the degeneracy of energy levels of the QDs we conclude that the confinement of the QDs can be described by a parabolic model.


