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Getting high-efficiency photoluminescence from Si nanocrystals in SiO₂ matrix

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Silicon nanocrystals in SiO₂ matrix are fabricated by plasma enhanced chemical vapor deposition followed by thermal annealing. The structure and photoluminescence (PL) of the resulting films is investigated as a function of deposition temperature. Drastic improvement of PL efficiency up to 12% is achieved when the deposition temperature is reduced from 250 °C to room temperature. Low-temperature deposition is found to result in a high quality final structure of the films in which the silicon nanocrystals are nearly strain-free, and the Si/SiO₂ interface sharp. The demonstration of the superior structural and optical properties of the films represents an important step towards the development of silicon-based light emitters. © 2002 American Institute of Physics. [DOI: 10.1063/1.1525395]

In the last decade the optical properties of Si nanocrystals have attracted great interest for the potential application in optoelectronics. $^{1-4}$ Of all the forms of the material, the most attention has been paid to porous silicon, mostly because of its high external quantum efficiency (1%-10%) of photoluminescence (PL).⁵ Unfortunately, many problems with porous silicon, including instability of PL efficiency in ambient condition, inhomogeneous structural, and fragile mechanical properties, prevent its use in practical applications. On the other hand, embedding Si in SiO₂-matrix has a number of advantages, such as high stability, the selforganized quantum well structure, and the compatibility with microelectronic technology.⁶⁻⁸ However, the reported PL external quantum efficiency of Si in SiO2 matrix was only 0.1%-0.3%.⁹⁻¹¹ In the present letter, we report that stable external quantum efficiency as high as more than 12% can be realized by optimizing the conditions in producing the material from plasma enhanced chemical vapor deposition (PECVD). The key trick in reaching the superior properties is actually simple yet very effective. That is, we deposit the films on RT substrates instead of heating them to above 200 °C as usually accepted in PECVD.

Silicon oxide films of about 1.6 μ m thick were deposited onto both polished and roughened quartz as well as crystal Si (100) wafers in a conventional capacitance-coupled PECVD system using a gas mixture of SiH₄, N₂O, and H₂. During deposition, the deposition temperature (T_d) was varied from 250 °C to RT, while the flow ratio of SiH₄:N₂O:H₂, the rf power density and the reaction gas pressure was held at 1:3:10, 50 mW/cm² and 160 Pa, respectively. The films were then annealed at 1100 °C in N_2 ambient for 30 min in order to form silicon nanocrystals in silicon oxide matrix. The formation of silicon nanocrystals in annealed films was identified by micro-Raman scattering, using a Renishaw system 1000 Raman imaging microscope. The mean grain size of the silicon nanocrystals was evaluated by x-ray diffraction, using a Philips diffractometer. The local atomic environments and bonding configurations of silicon oxide matrix in films were characterized by measurements of infrared absorption, using a Perkin Elmer 2000 Fourier-transform IR (FTIR) system. For excitation of steady-state PL, an Ar⁺ laser operating at wavelength of 514.5 nm was used with a low power density of 0.2 mW/mm². Detection was achieved with a chargecoupled detector within the wavelength range from 520 to 900 nm. All PL spectra were taken at RT and corrected for wavelength-depended sensitivity of the detection.

The influence of the substrate temperature on the PL intensity is well demonstrated in Fig. 1. Drastic increase of PL intensity and slight shifts of the peak position of the PL spectra are observed with the decrease of T_d , while the mean grain size of the silicon nanocrystals for different films is found to change a little, from 3.4 to 3.8 nm. Thus, the size changes might be responsible for the shifts of the PL peak wavelength, but not enough for the improvement of the PL efficiency. To get a quantitative estimation, the PL efficiency of our samples was calibrated with a standard lightly doped ruby $(0.05\overline{\%} \text{ Cr}^{3+})$ sample under the same conditions of ex-



FIG. 1. Room temperature PL spectra of the annealed Si-in-SiO₂ films fabricated by PECVD with different T_d from RT to 250 °C.

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FIG. 2. PL spectra of one of our Si-in-SiO₂ samples deposited at RT and a standard pink ruby (0.05% Cr^{3+}) sample. For comparison the PL spectrum of an independently well-characterized porous silicon sample with an external quantum efficiency of 4% is also included.

citation and detection. Using the well-determined quantum efficiency of the ruby^{12,13} and after integration of the emitted photons over the full emission band, the quantum efficiency of the samples can be deduced.¹⁴ The PL external quantum efficiency of our samples deposited at RT is found to be about 12%, far higher than the level ever reached in previous reports with Si-in-SiO₂ films. Figure 2 shows the PL spectra of one of the Si-in-SiO₂ samples deposited at RT and the standard ruby sample. For comparison the PL spectrum of an independently well-characterized porous silicon sample with an external quantum efficiency of 4% is also included. It can be seen that the PL intensity of the Si-in-SiO₂ sample is three times higher than that of the porous silicon.

Before describing what has happened to our samples, we need to briefly review how the light-emission process correlates with the material microstructure. It is generally accepted that the physical mechanism underlying the visible and near infrared light emission in this kind of silicon materials is essentially that of the quantum confinement of carriers in a nanometer-scale crystalline structure, and the Si/SiO₂ interface is also thought to play an active role in both the formation of radiative states and the passivation of nonradiative states.^{15–17} Therefore, a stoichiometric SiO₂ matrix and perfect Si-SiO₂ interfaces are of essential importance. Unfortunately, in films deposited on substrates at elevated temperatures the oxide matrix is not completely stoichiometric, at least in the vicinity of Si crystals, and the latter are actually surrounded by some substoichiometric SiO_x (x<2) transition layers with, possibly, changing x^{18} The existence of such transition layers degrades the PL efficiency in two aspects: It frustrates to a certain extent the quantum confinement and causes many carriers to recombine via the nonradiative rather than radiative centers.¹⁹ Besides, some lattice imperfections such as deposition-induced tensile strain inside silicon clusters are always found in the resulting films, which cannot be completely released by the high-temperature post-annealing.²⁰ The lattice strain, especially its inhomogeneous component, may degrade the mechanical as well as the transport and optical properties of the material.

The present work reveals that when the deposition temperature is reduced the situation can be greatly improved.



FIG. 3. Micro-Raman spectra of the annealed Si-in-SiO₂ films with different T_d from RT to 250 °C.

This is confirmed by the measurements of micro-Raman scattering and infrared absorption. Figure 3 shows the Raman spectra of the annealed films with different T_d . The relative redshift of the first-order Raman scattering of silicon nanocrystals with respect to that of crystalline silicon decreases from 4.2 to 0.6 cm⁻¹ with reducing T_d from 250 °C to RT, while the line shape of Raman peak remains essentially the same. Thus, it is most possible that the redshift is due to the elastic strain rather than to the phonon confinement. Then the lattice strain (ε) can be calculated approximated by²¹

$$\frac{\omega_c - \omega_n}{\omega_c} = -\left(\frac{P + 2Q}{2\omega_c^2}\right)\varepsilon,\tag{1}$$

where ω_c is the phonon frequency of crystalline silicon (521 cm⁻¹), ω_n is the measured phonon frequency of silicon nanocrystals, $P = -1.43 \ \omega_c^2$ and $Q = -1.89 \ \omega_c^2$, the phonon deformation potentials of silicon. The deduced ε upon the redshift of $\omega_c - \omega_n$ decreases from 0.31% to 0.04% when T_d reduces from 250 °C to RT. These data demonstrate that decreasing the deposition temperature T_d indeed renders the resulting silicon crystals with smaller residual strain.

Figure 4 gives the infrared absorption spectra of the annealed films with different T_d . The absence of the absorption feature related to Si–H vibration indicates the annealed films



FIG. 4. FTIR spectra of the annealed Si-in-SiO₂ films with different T_4 from to P RT to 250 °C.

contain no hydrogen. The principal absorption feature in the spectra can be assigned to the stretching vibration mode of Si–O–Si bonds. The frequency of the Si–O–Si stretching vibration shifts to higher wave numbers with decreasing T_d from 250 to RT, in a direction that would be expected from increasing x in SiO_x. This indicates that the chemical composition of oxide matrix becomes more and more close to the stoichiometric SiO₂. The broad shoulder at the low frequency side of the main feature, most probably identified as the substoichiometric SiO_x (x<2), is found to gradually shrink with lowering T_d from 250 °C to RT. All these features promise a marked decrease of the substoichiometric SiO_x phase with low T_d . The quality of the interface region between Si nanocrystals and SiO₂ matrix is thereby expected to be greatly improved.

The earlier facts show that the deposition temperaturedepended "pristine state" of the films is of key importance for a high quality final structure. The result can be understood in the following way. Because films deposited at elevated temperatures are basically substoichiometric SiO_x, the precipitation of silicon from SiO_x is inevitable for nucleation and growth of silicon nanocrystals during annealing process. When such a chemical reaction is involved, it is only natural to expect there are regions where the reaction is incomplete. Low temperature deposition has two advantages. First, the Si and its oxide phase could be well-separated in the pristine films and the composition of the oxide matrix could be very close to stoichiometric SiO₂.²² In this case, mainly thermal crystallization of the Si nanoclusters is involved in the postannealing process and perfect Si-SiO₂ interfaces are expected. Second, a large amount of hydrogen is contained in as-deposited films of low T_d , which is very helpful in releasing the strains of the Si crystals. Therefore, low T_d should greatly improve the abruptness of Si-SiO₂ interfaces, and release the strains in the structure. These structural improvements result in the remarkable increase of PL efficiency, as demonstrated in Figs. 1 and 2. The PL efficiency can be further improved by increasing the compositional ratio of hydrogen (H dilution) in PECVD, while the PL peak energy can be controlled through adjusting the compositional ratio of oxygen in PECVD. With increasing compositional ratio of oxygen, the PL peak wavelength blueshifts due to the size reduction of nanocrystals. These points will be elaborated elsewhere.

In summary, we reported the important advancement in

PL properties of Si-in-SiO₂ films fabricated by PECVD. Due to the structural quality improvement of inner silicon nanocrystals and Si/SiO₂ interfaces, high external quantum efficiency up to 12% has been achieved by reducing the deposition temperature from 250 °C to RT. The much more stable structure and higher PL efficiency than that of porous silicon explore the great possibility of the Si-in-SiO₂ films in fabricating efficient silicon-based light-emitting devices.

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