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Effect of total pressure on the formation and size evolution of silicon quantum dots in silicon nitride films

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The size of silicon quantum dots (Si QDs) embedded in silicon nitride (SiN_x) has been controlled by varying the total pressure in the plasma-enhanced chemical vapor deposition (PECVD) reactor. This is evidenced by transmission electron microscopy and results in a shift in the light emission peak of the quantum dots. We show that the luminescence in our structures is attributed to the quantum confinement effect. These findings give a strong indication that the quality (density and size distribution) of Si QDs can be improved by optimizing the deposition parameters which opens a route to the fabrication of an all-Si tandem solar cell. © *2010 American Institute of Physics*. [doi:10.1063/1.3427386]

During the past decade, a great deal of research activity has been focused on optical properties of silicon nanostructured materials such as porous silicon or Si nanoparticles. The previous interest was in the light emission from Si QDs embedded in a silicon oxide matrix.[1,2] However, in SiO_2 an extremely high potential barriers decrease drastically the injection efficiency of carriers. In silicon nitride dielectric matrix carriers are expected to be easily transported between Si QDs due to the lower tunneling barriers for electrons and holes.[3] These properties make $Si-SiN_x$ composite structure a promising candidate for different application fields such as optoelectronics, photonics,[4] and third generation photovoltaics.[5,6]

It has been reported that the synthesis of silicon quantum dots can be achieved by high-temperature annealing of Si-rich silicon oxide films via the phase separation reaction.[7,8] However, several groups have succeeded in showing the *in situ* formation of silicon quantum dots in Si-rich silicon nitride matrix without any postdeposition annealing.[9–11] The question that can be asked in this case concerns the formation mechanisms of these nano-objects. Some authors suggested that Si clusters can be grown in the gas phase into a plasma-enhanced chemical vapor deposition (PECVD) reactor even at room-temperature and depending on plasma conditions.[12] However, the control of the size and the density of Si QDs using this technique remains a challenge. We have recently focused on the study of plasma conditions that promote the formation of Si QDs with the desired properties required for an all-silicon tandem solar cell application.

In this work, low-frequency-PECVD technique was employed to prepare hydrogenated amorphous silicon nitride ($a\text{-}SiN_x{:}H$) layers on n-type (100) silicon substrate. A mixture of silane (SiH_4) and ammonia (NH_3) were used as precursor gases. The plasma power, substrate temperature, and gas flow ratio (NH_3/SiH_4) were fixed at 1000 W, 370 °C, and 4, respectively, while the total pressure was varied from 1000 to 4000 mTorr. The square wave modulation of the power amplitude applied to the plasma which consists of alternating periods of plasma duration time (t_{on}) followed by plasma extinction time (t_{off}), was used allowing the *in situ* formation of Si QDs. The deposition time was adjusted to obtain a film thickness of approximately 40 nm. No postannealing process was required after growing the silicon nitride film. In order to experimentally verify the density and the size evolution of Si QDs *in situ* grown into SiN_x films, a clear correlation between structural and optical properties has been unambiguously demonstrated. In this way, high resolution transmission electron microscopy (HRTEM) and photoluminescence (PL) spectroscopy have been used. The PL measurements were performed at room temperature using an Ar^+ 458 nm laser as the excitation source and a Jobin-Yvon type HR-640 spectrometer grating coupled to a Hamamatsu H5701–50 GaAs cathode photomultiplier for light detection. The structural characterization was accomplished by a JEOL-2010 F transmission electron microscopy. Samples specimens have been prepared in "plan view" in order to achieve electron transparency. The size and the concentration of the observed silicon quantum dots have been estimated from a statistical analysis of the HRTEM images.

Five samples (P1, P2, P3, P4, and P5) were grown corresponding to a total pressure of 1000 mTorr, 1500 mTorr, 2000 mTorr, 3000 mTorr, and 4000 mTorr, respectively. A verification of the size and density variation in Si QDs was provided by the PL analysis. The change in PL peak energies and intensities with the pressure is shown in Fig. 1(a). As the total pressure was increased from 1000 mTorr (P1) to 4000 mTorr (P5), the PL peak energy shifted from 1.98 to 1.63 eV. This redshift in our structures is believed to result from the quantum confinement effect (QCE) and may be attributed to the increase in the size of the Si QDs. This result is in a good agreement with the previous reports on the effect of the chamber pressure on the light emission from crystalline silicon quantum dots embedded in SiN_x films.[12] It is known that the increase in the total gas pressure promotes the reactions between different species in the plasma (radicals, positive

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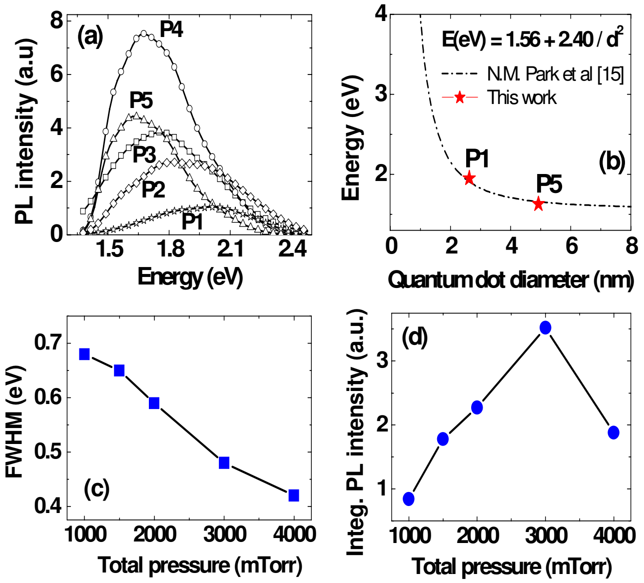

FIG. 1. (Color online) (a) Room temperature PL spectra of SiN_x composite layers deposited at different pressure ranging between 1000 (P1) and 4000 mTorr (P5). (b) Fitted PL energy obtained from the effective mass theory for three-dimensionally confined Si QDs (solid line) and measured PL energy of Si QDs in SiN_x (filled stars) as a function of quantum dot size. (c) Variation in the FWHM of the PL peak with the total pressure in the PECVD reactor. (d) Integrated PL intensity vs total pressure.

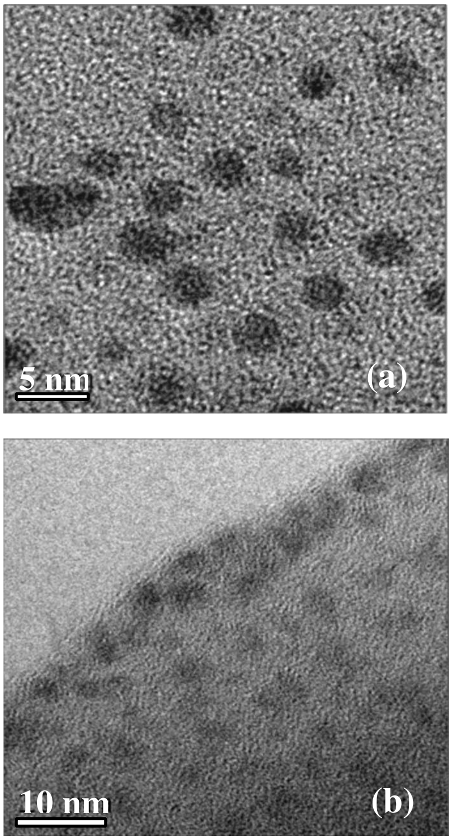

FIG. 2. HRTEM images of amorphous Si QDs embedded in silicon nitride films grown at (a) 1000 mTorr and (b) 4000 mTorr.

and negative ions, and electrons)[13] which results in an efficient dissociation of SiH_4 and NH_3 and thus the formation of silicon clusters. Further increase in pressure leads to the agglomeration of already existing silicon clusters to form larger quantum dots. Vach *et al.*[14] reported that the plasma can be described by 12 species interacting through a set of 38 chemical reactions and resulting in a growth of nanometric silicon clusters. However, they do not give detailed information on such reactions. Figure 1(c) shows the trends of the full width at half maximum (FWHM) of the emission band versus the total gas pressure. The FWHM decreases from 0.68 to 0.42 eV with increasing the pressure. This feature could be related to the evolution of the size distribution of Si QDs. Figure 1(d) shows the plot of the integrated PL intensity for different total pressure. As the total pressure increases, there is further formation of silicon quantum dots accompanied by an agglomeration of the small ones. Therefore, the PL intensity increases and reaches a maximum at P4 (3000 mTorr). Above this value, the number of Si QDs decreases due to the coalescence between adjacent dots. In addition, the electron-hole radiative recombination rate caused by the quantum confinement effect decreases for large Si QDs. This could be a possible reason for the decrease in the intensity of PL signal for higher pressure (P5 sample).

We have performed HRTEM analysis on samples P1 and P5 [Figs. 2(a) and 2(b)] in order to confirm the existence and evolution of Si QDs in silicon nitride films and to verify the emission mechanism of our composite structures. It was found that silicon nanodots which appear as dark spots are in the amorphous state with a density of $\sim 4 \times 10^{11}$ cm^{-2} for the sample grown at 1000 mTorr. As the total pressure increases, the concentration of silicon dots increase and reaches a value of $\sim 8 \times 10^{11}$ cm^{-2} for 4000 mTorr. The changes in the diameter and the size distribution of Si quantum dots have been also deduced from the statistical analysis. Dots from the silicon nitride film deposited at 1000 mTorr have a wide size distribution and its histogram in Fig. 3(a) indicates that Si QDs have two average sizes of 2.63 and 4.59 nm. This provides a good explanation of the PL band broadening with a FWHM of 0.68 eV. In this case, the light emission mechanism seems to be dominated by the radiative transitions in the smaller quantum dots. The average dot size of 2.63 nm is in good agreement with the size of ~2.61 nm which corresponds to the maximum of the global PL peak intensity according to the QCE model for amorphous silicon quantum dots.[15] For sample P5, the sizes of Si QDs are more homogeneous than those observed in the P1 sample and the average size is about 4.93 nm which is compatible with the dot size of 4.9 nm estimated from the QCE model [Fig. 3(b)]. The good correlation between the quantum dot sizes determined by HRTEM and those obtained from the empirical equation $E(eV) = 1.56 + 2.40/d^2$, where d is the dot size in nanometer, as shown in Fig. 1(b) clearly shows that the light emission of our structures is dominated by the QCE in amorphous Si QDs. Moreover, an optimized value of the pressure which allows the preparation of a high Si QDs quality in term of density and size has been obtained based on the PL analysis. As can be seen from Fig. 1(a), sample P4 grown at 3000 mTorr shows an intense PL signal as well as a relatively weak FWHM of the emission peak corresponding to a high density and small size distribution of silicon quantum dots, respectively. Considering the founding in this work, there is a possibility of successful control of the size and the density of Si quantum dots in silicon nitride matrix indicating that these nanostructures can be a good candidate for an all-silicon tandem solar cell application.

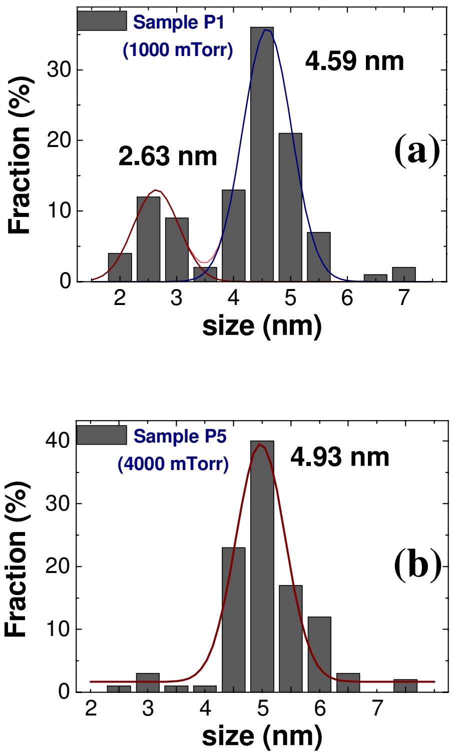

FIG. 3. (Color online) Fraction histograms of the Si QDs sizes distribution for sample grown at (a) 1000 mTorr and (b) 4000 mTorr. Solid curves represent the fitting of the crystallite sizes with a Gaussian distribution.

In summary, PL and transmission electron microscopy were used to analyze the total gas pressure effect on the light emission of Si QDs embedded in SiN_x films. The correlation between structural and optical properties of our samples provided convincing evidence of a quantum confinement effect in silicon quantum dots. We have shown that the band gap of silicon quantum dots can be tuned from 1.98 to 1.63 eV by varying the gas pressure in the PECVD reactor from 1000 to 4000 mTorr. It was also found that the increase in the total pressure leads to the formation of Si QDs with a monodisperse size distribution. In addition, PL results suggest that the pressure of 3000 mTorr gives the highest density of silicon quantum dots. Further work is underway to study the effect of other deposition parameters on the optical and electrical properties of our composite layers in order to use them as a top cell in the Si-based tandem solar cell.

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