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Citation: Appl. Phys. Lett. **85**, 5355 (2004); doi: 10.1063/1.1814429
View online: http://dx.doi.org/10.1063/1.1814429
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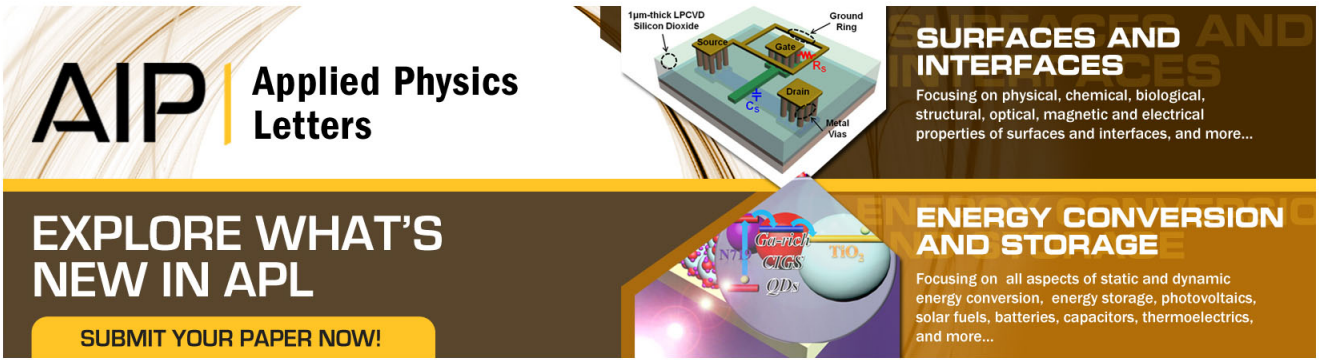

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HTML ABSTRACT + LINKS

Quantum confinement effect of silicon nanocrystals *in situ* grown in silicon nitride films

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(Received 30 April 2004; accepted 2 September 2004)

Silicon nanocrystals were *in situ* grown in a silicon nitride film by plasma-enhanced chemical vapor deposition. The size and structure of silicon nanocrystals were confirmed by high-resolution transmission electron microscopy. Depending on the size, the photoluminescence of silicon nanocrystals can be tuned from the near infrared (1.38 eV) to the ultraviolet (3.02 eV). The fitted photoluminescence peak energy as $E(\mathrm{eV}) = 1.16 + 11.8/d^2$ is evidence for the quantum confinement effect in silicon nanocrystals. The results demonstrate that the band gap of silicon nanocrystals embedded in silicon nitride matrix was more effectively controlled for a wide range of luminescent wavelengths. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1814429]

Because of its indirect band gap of 1.1 eV, silicon is characterized as having a very poor optical radiative efficiency and only produces light outside the visible range. Silicon nanostructures, however, which show a quantum confinement effect have an enhanced rate of electron–hole radiative recombination.[1] In recent years, a great deal of research on silicon nanocrystals embedded in a silicon oxide matrix has been conducted because of their potential for applications in silicon-based optoelectronic devices.[2,3] However, a number of groups have reported that when the crystallite size of silicon nanostructures in a silicon oxide matrix is controlled, the experimental photoluminescence energies in air are not in good agreement with values that are theoretically calculated from quantum confinement effects.[4,5] Wolkin *et al.* proposed that oxygen is related to the trapping of an electron (or even an exciton) by silicon–oxygen double bonds and produces localized levels in the band gap of nanocrystals.[6] Therefore, a quantum confinement effect is not observed in silicon nanostructures, after exposure to air.[7,8] Even when a silicon oxide is used as a typical matrix material that hosts silicon nanostructures, a silicon oxide matrix may not provide an appropriate emission state for a quantum confinement effect in small silicon crystallites. Because of this, the focus of the present study was on an appropriate matrix material for silicon nanocrystals. There appear to be few localized states that correlate with the optical process of carriers at a nanocrystal surface in a silicon nitride matrix, as shown in a previous report related to amorphous silicon quantum dot structures.[9,10] In the present work, we report on silicon nanocrystals that were *in situ* grown in a silicon nitride film by plasma-enhanced chemical vapor deposition. Typically, silicon nanocrystals are obtained by the postannealing of a silicon-rich silicon oxide at 1100 °C for 1 or 2 h.[11] The method described here is desirable in terms of integrating silicon based optoelectronic components. This method permits a good match with the quantum confinement effect in zero-dimensional crystalline silicon by controlling the crystal size, because this provides a good emission state in small silicon nanocrystals, when a silicon nitride matrix is used.

The silicon nanocrystals were prepared by plasma-enhanced chemical vapor deposition, in which argon-diluted 10% silane and nitrogen gas at a purity in excess of 99.9999% were used as the reactant gas sources. (100) crystalline silicon wafers were employed as sample substrates. The total pressure, plasma power, and growth temperature were fixed at 0.5 Torr, 5 W, and 250 °C, respectively. The flow rate of silane and nitrogen was used to modulate the rate of growth of the silicon nitride film and, eventually, to control the size of the silicon nanocrystals. The flow rate of silane and nitrogen was in the range from 4 to 12 sccm and from 500 to 1800 sccm, respectively. No postannealing process was required after growing the silicon nitride film. The size and microscopic structure of the silicon nanocrystals were confirmed by high-resolution transmission electron microscopy using a JEOL Electron Microscopy 2010 instrument operated at 200 kV. To demonstrate the quantum confinement effect, the photoluminescence of silicon nanocrystals with various dot sizes were measured. A charge coupled device detector was used for the photoluminescence measurements at room temperature, with a He–Cd 325 nm laser as the excitation source.

Figure 1 shows high-resolution transmission electron microscopy (HRTEM) images of silicon nanocrystals embedded in a silicon nitride film. The silicon nanocrystals appear as dark spots and the silicon substrate appears as a dark region. The average size and dot density of silicon nanocrystals was 4.6 nm and $6.0 \times 10^{11}/\mathrm{cm}^2$, respectively. The standard deviation for the size distribution was about 0.28 nm. This sample showed a peak for red-colored light (700 nm) in the photoluminescence spectrum. The single dot image in the

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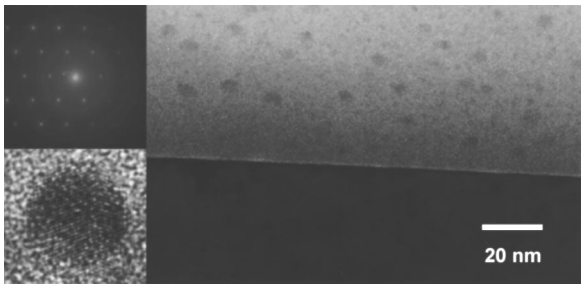

FIG. 1. Cross-sectional high-resolution transmission electron microscopic (HRTEM) images of silicon nanocrystals embedded in a silicon nitride film. The average size and the dot density of silicon nanocrystals was 4.6 nm and $6.0\times10^{11}/\mathrm{cm}^2$, respectively. The insets are the crystal image and the transmission electron diffraction pattern, showing the silicon dot is crystalline.

inset clearly shows that the dark spots are crystallites of silicon nanocrystals separated by an amorphous silicon nitride matrix, and the sharp transmission electron diffraction ring pattern also confirms the crystal structure of silicon nanocrystals. Diffraction pattern was acquired by the image plate technology, and the bright spots are originated from silicon substrate.

As the size of a quantum structure decreases, the band gap of the material increases from the quantum confinement effect. A blueshift in optical luminescence is the result of this effect. To demonstrate the quantum confinement effect, we measured the photoluminescence of silicon nanocrystals with various dot sizes. The change in the photoluminescence peak energies with the nanocrystal sizes, as determined by HRTEM is shown in Fig. 2. When the crystal size was decreased from 6.1 to 2.6 nm, the photoluminescence peak energy shifted toward higher wavelengths from 1.46 eV (850 nm) to 3.02 eV (410 nm). This figure clearly shows that the photoluminescence peak is blueshifted with decreasing nanocrystal size. Assuming an infinite potential barrier, the energy gap, E, for three-dimensionally confined silicon nanocrystals can be expressed as $E(\mathrm{eV})=E_{\mathrm{bulk}}+C/d^2$ according to effective mass theory, where E_{bulk} is the bulk crystal silicon band gap, d the dot size, and C the confinement parameter. The best fit for the data shown in Fig. 2 is to the equation $E(\mathrm{eV})=1.16+11.8/d^2$. Fitted bulk band gap of 1.16 is in good agreement with reported literature values for bulk crystal silicon (1.1–1.2 eV), and there exists a great difference

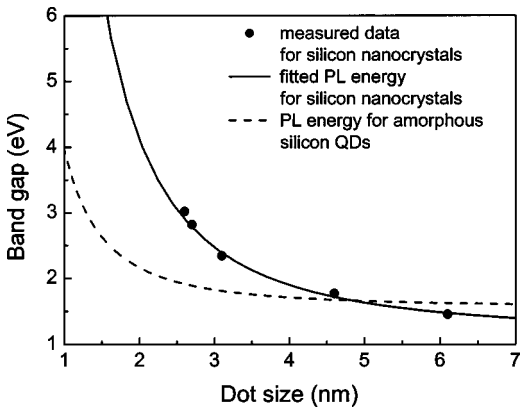

FIG. 2. Photoluminescence peak energy of silicon nanocrystals as a function of crystal size. The solid line was obtained from the effective mass theory for three-dimensionally confined silicon nanocrystals. The dashed line was obtained from the effective mass theory for amorphous silicon quantum dot structure in Ref. 9.

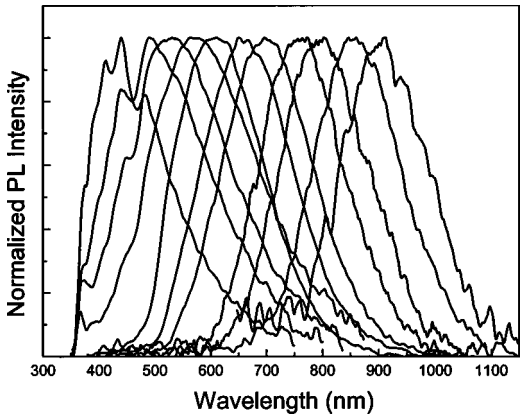

FIG. 3. Room-temperature photoluminescence spectra of silicon nanocrystals. The peak position can be controlled by appropriate adjustment of the nanocrystal size.

between bulk band gap of amorphous silicon (1.5–1.6 eV).[9] This result further verifies that silicon nanoclusters have a crystal structure, as shown in the HRTEM of Fig. 1. The fitted confinement parameter of 11.8 is also very large compared with that of an amorphous silicon quantum dot of 2.4.[9,12–14] In previous studies, it has been shown that the confinement parameter by a theoretical calculation can be changed depending on the calculation method and is about 7 to 14.[12,15–18] Our fitted parameters are consistent with the effective mass approximation. Therefore, the HRTEM measurements and the accompanying photoluminescence results verify the quantum confinement effect in silicon nanocrystals.

Figure 3 shows a room-temperature photoluminescence spectrum obtained from various sized silicon nanocrystals, where the tuning of the photoluminescence emission from 410 to 900 nm is possible by controlling the size of the silicon nanocrystal and, as a result, the emission color can be changed by controlling the size of the nanocrystal. For example, nanocrystal sizes corresponding to red, green, and blue emission are 4.6, 3.1, 2.7 nm, respectively. The formation of silicon nanoparticles was also reported in the case where highly diluted gas plasma conditions were employed.[19,20] An increase in nitrogen gas flow rate or the decrease in silane gas flow rate is thought to result in an increase in dangling bonds of silicon atoms and such an increase would facilitate the creation of nucleation sites. Therefore, the size of the silicon clusters is decreased when the number of silicon cluster nucleation sites is increased due to a large increase in the total number of silicon dangling bonds. The formed silicon nanoclusters are transformed to nanocrystalline silicon by hydrogen radical diffusion through the hydrogenated amorphous silicon nanocluster at a substrate temperature of 250 °C, if the growth rate is sufficiently low to permit the amorphous to crystalline transition.[20,21] In this case, the growth rate is very low ($<$1.7 nm/min) compared to that for amorphous silicon quantum dots ($>$2.3 nm/min). Therefore, a crystalline transition can occur due to the diffusion of hydrogen after the formation of amorphous silicon quantum dots. A theoretical study has shown that the amorphous to crystalline transition can be controlled through appropriate control of deposition parameters, such as lattice expansion and crystallite size.[22]

In conclusion, well-organized silicon nanocrystals were grown in a silicon nitride film by plasma-enhanced chemical

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vapor deposition without a postannealing process. HRTEM measurements and photoluminescence results provided convincing evidence of a quantum confinement effect in the silicon nanocrystals, and a silicon nitride matrix was found to provide a good emission state in small silicon nanocrystals. The band gap of the silicon nanocrystals could be controlled from 1.38 to 3.02 eV by decreasing the nanocrystal size, demonstrating the viable potential for the fabrication of effective silicon-based light-emitting diodes in a wide range of luminescent wavelengths.

This work was supported by the Ministry of Information and Communication in Korea.

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