Quantum Confinement in Amorphous Silicon Quantum Dots Embedded in Silicon Nitride

Nae-Man Park, Chel-Jong Choi, Tae-Yeon Seong, and Seong-Ju Park*
Department of Materials Science and Engineering and Center for Optoelectronic Materials Research, Kwangju Institute of Science and Technology, Kwangju, 500-712, Korea

(Received 4 April 2000)

Amorphous silicon quantum dots (*a*-Si QDs) were grown in a silicon nitride film by plasma enhanced chemical vapor deposition. Transmission electron micrographs clearly demonstrated that *a*-Si QDs were formed in the silicon nitride. Photoluminescence and optical absorption energy measurement of *a*-Si QDs with various sizes revealed that tuning of the photoluminescence emission from 2.0 to 2.76 eV is possible by controlling the size of the *a*-Si QD. Analysis also showed that the photoluminescence peak energy E was related to the size of the *a*-Si QD, a (nm) by $E(\mathrm{eV}) = 1.56 + 2.40/a^2$, which is a clear evidence for the quantum confinement effect in *a*-Si QDs.

DOI: 10.1103/PhysRevLett.86.1355 PACS numbers: 78.66.Jg, 61.46.+w, 78.67.-n, 78.40.Pg

Although bulk silicon has the indirect transition property, silicon nanostructures having a quantum confinement effect have provided a breakthrough to optoelectronic applications because the quantum confinement effect enhances the electron-hole radiative recombination rate [1]. Many researches have been mostly related to porous silicon or crystalline nanostructures [2]. In porous Si and nanocrystalline Si structures, a wide range of luminescent wavelengths has been observed from near infrared to ultraviolet. However, the wavelengths shorter than blue have been considered to be related to oxygen-related defects or chemical species. These have been obstacles for the realization of optoelectronic devices including light-emitting diodes [3–6].

Amorphous silicon (*a*-Si) has two important advantages compared with bulk crystalline Si: The luminescence efficiency in bulk *a*-Si is higher than that in crystalline Si due to structural disorder [7]; and the band gap energy of bulk *a*-Si (1.6 eV) is larger than that of bulk crystalline Si (1.1 eV) and *a*-Si is a good candidate for short-wavelength luminescence. It is, therefore, expected that these intrinsic advantages of *a*-Si and quantum confinement effect of *a*-Si quantum dot (*a*-Si QD) lead to the extremely useful optical properties in the short wavelength region compared with porous Si or nanocrystalline Si [8,9]. In addition, the study of the quantum confinement effect in *a*-Si as a function of dimension can yield important information about the physical processes related to the carrier mobility in *a*-Si. In contrast to crystalline Si, little is known about the limiting processes of transport in *a*-Si.

The properties of *a*-Si quantum structures have been studied primarily by theoretical approaches [8,10]. Lu *et al.* [11] and Murayama *et al.* [12] are the only research groups that investigated experimentally the photoluminescence and the optical absorption energy properties in two-dimensional *a*-Si quantum well structures with various well thicknesses. However, zero-dimensional *a*-Si QD structures have not been investigated because *a*-Si has many natural defects that can act as nonradiative centers. Therefore, it is very important to grow high quality *a*-Si nanostructures to experimentally study the origin of light emission and the quantum confinement effect in *a*-Si. In this Letter, we report on the first experimental evidence for the quantum confinement effect in zero-dimensional *a*-Si structure and demonstrate tuning of the optical emission in this structure corresponding to the band gap from 2.0 to 2.76 eV by controlling the quantum dot size. Even though a silicon oxide has been used as a typical matrix material that hosts the Si nanostructures in the film, a silicon nitride matrix was used in this work because electrons and holes can be easily transported to the *a*-Si QDs due to its tunneling barrier which is lower than that of silicon oxide [13–15]. Therefore, silicon nitride film can be used as a good matrix material in the optical device application.

Samples were prepared by plasma enhanced chemical vapor deposition, where nitrogen-diluted 5% SiH_4 and N_2 having a purity of 99.9999% were used as reactant gas sources. *n*-Type (100) crystalline silicon wafers and glass plates were used as sample substrates. Crystalline silicon substrates were employed for photoluminescence and cross-sectional high-resolution transmission electron microscopy studies, and glass plates were used for ultraviolet-visible absorption spectroscopy. The flow rate of SiH_4 was maintained at a constant rate at 10 sccm. The total pressure, the plasma power, and the growth temperature were fixed at 0.5 torr, 6 W, and 300 °C, respectively. The additional N_2 flow rate served to modulate the growth rate of the silicon nitride film containing *a*-Si QDs and, eventually, to control the *a*-Si QD size. The growth rate of silicon nitride film was increased from 1.4 to 3.2 nm/min by increasing the N_2 flow rate from 100 to 800 sccm. Details of the relation between N_2 flow rate and the *a*-Si QD size will be reported elsewhere [16].

The size and microscopic structure of *a*-Si QDs were confirmed by transmission electron microscopy using a JEOL Electron microscopy 2010 instrument operated at 200 kV. Figures 1(a) and 1(b) show transmission electron microscopic images of *a*-Si QDs embedded in silicon nitride and a normal amorphous silicon nitride film which does not contain *a*-Si QD, respectively. The *a*-Si QDs

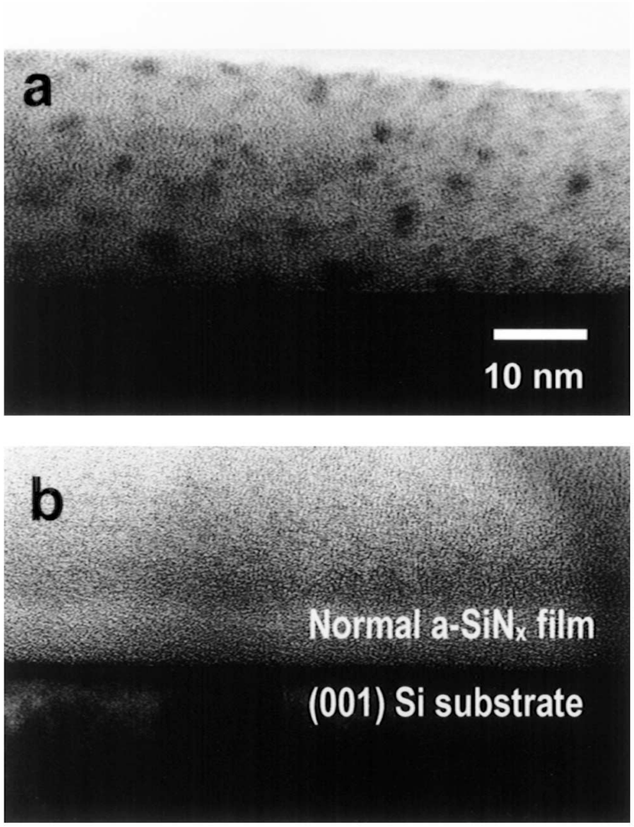

FIG. 1. Cross-sectional high-resolution transmission electron microscopic images of *a*-Si QDs embedded in a silicon nitride film (a) and a normal silicon nitride film (b). Dark spots represent *a*-Si QDs of which the average size is about 1.9 nm and the dot density is about 1.0×10^{19} cm^{-3} in (a), but there is no dark spot in the normal silicon nitride film in (b).

appear as dark spots in the transmission electron microscopic image in Fig. 1(a) because the *a*-Si QD has a higher atomic density than the silicon nitride matrix material. The existence of *a*-Si QDs in silicon nitride was also confirmed by Raman measurement [16]. As shown in Fig. 1(b), however, there is no dark spot in the normal silicon nitride film. The transmission electron microscope image in Fig. 1(a) clearly shows that *a*-Si QDs are well organized in the silicon nitride matrix and the average size of *a*-Si QDs was 1.9 nm. A standard deviation in size distributions was about 0.4 nm. This sample showed a peak of orange-color light (560 nm) in the photoluminescence spectrum as shown in the inset of Fig. 2.

The quantum confinement effect increases the band gap of material as the size of quantum structure decreases, which results in a blueshift in optical luminescence and absorption energy. To demonstrate this effect, we measured photoluminescence and optical absorption energy of *a*-Si QD samples with various dot sizes. For photoluminescence measurements, a He-Cd 325-nm laser was used as an excitation source, and a photon-counting technique with a photomultiplier tube was employed at room temperature. The optical absorption energy was determined by ultraviolet-visible absorption spectroscopy using a Perkin-Elmer Lambda 12 instrument. When the dot size was decreased from 2.4 to 1.4 nm, the photoluminescence peak shifted toward higher energy from 620 (2.0 eV) to 450 nm (2.76 eV). The change in the photoluminescence peak energies with the quantum dot sizes that were determined by the transmission electron microscopy is shown in Fig. 2. This figure clearly shows the blueshift of photoluminescence peak with decreasing the dot size. The inset shows the room-temperature photoluminescence spectrum obtained from *a*-Si QDs with a diameter of 1.9 nm. Assuming an infinite potential barrier, the energy gap E for three-dimensionally confined *a*-Si QD can be expressed as $E(\mathrm{eV}) = E_{\mathrm{bulk}} + C/a^2$ according to effective mass theory, where E_{bulk} is the bulk *a*-Si band gap, a is the dot size, and C is the confinement parameter. The data in Fig. 2 are best fitted by the equation of $E(\mathrm{eV}) = 1.56 + 2.40/a^2$. The fitted bulk band gap of 1.56 is very close to the literature values of bulk *a*-Si (1.5–1.6 eV) that was grown by molecular beam epitaxy [17]. This is a low value for hydrogenated *a*-Si grown by the plasma enhanced chemical vapor deposition method. However, the Fourier-transform infrared and Raman analyses of these samples showed that *a*-Si QDs contain very little hydrogenated silicon, presumably due to the use of both high N_2 dilution and low plasma power [16]. Lu *et al.* [11,18,19] reported on the quantum confinement effect and light emission in the *a*-Si/SiO$_2$ quantum well. In their work, the photoluminescence peak energy E was expressed as $E(\mathrm{eV}) = 1.6 + 0.72/d^2$ where d is the well width in nm. The confinement parameter of 2.40 eV $\cdot$ nm^2 obtained for *a*-Si QD in this work is about 3× larger than 0.72 for *a*-Si quantum well. The increment of confinement parameter by a factor of 3 is very reasonable for *a*-Si QD because the confinement parameter behaves as $1/\mathrm{m}^*$ (m^* is the reduced mass, $1/\mathrm{m}^* = 1/\mathrm{m}_e^* + 1/\mathrm{m}_h^*$ where m_e^* and m_h^* are the electron and the hole effective masses,

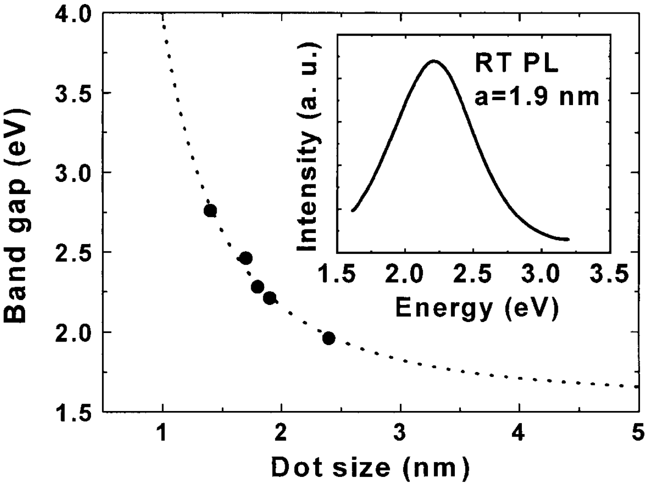

FIG. 2. Photoluminescence peak energy of *a*-Si QDs as a function of the dot size. The dashed line was obtained from the effective mass theory for three-dimensionally confined Si dots. The inset shows a room-temperature photoluminescence spectrum from *a*-Si QDs with $a = 1.9$ nm.

respectively), and the effective masses are assumed to be isotropic for three directions in amorphous materials. Therefore, the confinement parameter for a-Si QD can be 3× larger than that for a-Si quantum well. In addition to transmission electron microscopic measurements, these photoluminescence results support the quantum confinement effect in a-Si QDs and a direct recombination process for optical emission from a-Si QDs.

However, the photoluminescence peak does not always reflect the actual band gap because the creation of electron-hole pairs can be strongly influenced by dot/barrier interface states during the excitation process. To confirm the actual absorption band gap, optical absorption energies were measured for the same series of samples. The optical absorption energy shift was about 630 meV when the quantum dot size was decreased from 2.4 to 1.4 nm, as shown in Fig. 3. The optical absorption energy shift is well represented by a dependence of $E(\mathrm{eV}) = 2.2/a^2$, which is also in good agreement with the photoluminescence result of $E(\mathrm{eV}) = 2.40/a^2$. These photoluminescence and optical absorption measurements of a-Si QD band gap clearly show that the carriers are quantum confined in the a-Si QDs and the origin of the photoluminescence is the quantum confinement effect in the a-Si QDs. The average Stokes shift, the difference between luminescence energy and absorption energy is about 300 meV for a-Si QDs. This value is very small compared to the nanocrystalline Si in which a large Stokes shift (about 1 eV for a crystalline Si having a diameter ~1.5 nm) has been reported [19,20]. This result shows that the surface of a-Si QDs are well passivated compared to that of nanocrystalline Si and the density of deep luminescence centers such as the surface states related to a large Stokes shift [21], is much smaller in a-Si QDs embedded in a silicon nitride than in nanocrystalline Si.

In conclusion, well-organized and well-surface passivated a-Si QDs were grown in a silicon nitride film by plasma enhanced chemical vapor deposition. The photoluminescence and optical absorption measurements showed convincing evidence of the quantum confinement effect in a-Si QDs for the first time, and this quantum confinement effect was believed to be the origin of strong luminescence in a-Si QDs. It was also found that the band gap of a-Si QDs could be controlled from 2.0 to 2.76 eV by decreasing the dot size, demonstrating the viable potential for the fabrication of highly efficient Si-based light-emitting diodes in the blue or shorter wavelength region.

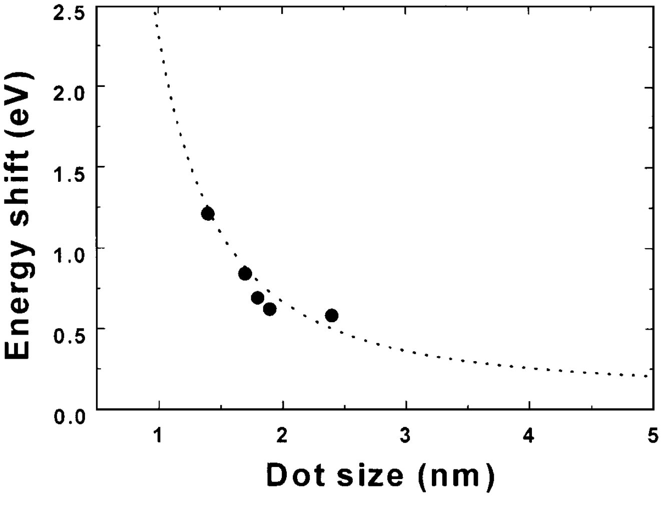

FIG. 3. Optical absorption energy shift as a function of the dot size. The dashed line was obtained from the effective mass theory.

This work was partially supported by the Brain Korea 21 Program in Korea.

---

*Corresponding author: sjpark@kjist.ac.kr

[1] *Light Emission in Silicon: From Physics to Devices,* edited by D. J. Lockwood (Academic Press, San Diego, 1998), Chap. 1.

[2] *Advances in Microcrystalline and Nanocrystalline Semiconductors,* edited by R. W. Collins, P. M. Fauchet, I. Shimizu, J.-C. Vial, T. Shimada, and A. P. Alivisatos, (Materials Research Society, Pittsburgh, 1997).

[3] *Light Emission in Silicon: From Physics to Devices,* edited by D. J. Lockwood (Academic Press, San Diego, 1998), Chap. 6.

[4] H. Tamura, M. Ruckschloss, T. Wirschem, and S. Veprek, Appl. Phys. Lett. **65**, 1537 (1994).

[5] L.-S. Liao, X.-M. Bao, X.-Q. Zheng, N.-S. Li, and N.-B. Min, Appl. Phys. Lett. **68**, 850 (1996).

[6] G. G. Siu, X. L. Wu, Y. Gu, and X. M. Bao, Appl. Phys. Lett. **74**, 1812 (1999).

[7] R. A. Street, Adv. Phys. **30**, 593 (1981).

[8] G. Allan, C. Delerue, and M. Lannoo, Phys. Rev. Lett. **78**, 3161 (1997).

[9] M. J. Estes and G. Moddel, Appl. Phys. Lett. **68**, 1814 (1996).

[10] B. Delley and E. F. Steigmeier, Appl. Phys. Lett. **67**, 2370 (1995).

[11] Z. H. Lu, D. J. Lockwood, and J.-M. Baribeau, Nature (London) **378**, 258 (1995).

[12] K. Murayama, T. Toyama, S. Miyazaki, and M. Hirose, Solid State Commun. **104**, 119 (1997).

[13] K. Chen, X. Huang, J. Xu, and D. Feng, Appl. Phys. Lett. **61**, 2069 (1992).

[14] X. Huang, Z. Li, and Z. Liu, J. Non-Cryst. Solids **198–200**, 821 (1996).

[15] M. Wang, X. Huang, J. Xu, W. Li, Z. Liu, and K. Chen, Appl. Phys. Lett. **72**, 722 (1998).

[16] N.-M. Park, C.-J. Choi, T.-Y. Seong, and S. J. Park (to be published).

[17] D. J. Lockwood, Solid State Commun. **92**, 101 (1994).

[18] Z. H. Lu, D. J. Lockwood, and J.-M. Baribeau, Solid State Electron. **40**, 197 (1996).

[19] D. J. Lockwood, Z. H. Lu, and J.-M. Baribeau, Phys. Rev. Lett. **76**, 539 (1996).

[20] G. Allan, C. Delerue, and M. Lannoo, Phys. Rev. Lett. **76**, 2961 (1996).

[21] F. Koch, V. Petrova-Koch, and T. Muschik, J. Lumin. **57**, 271 (1993).