

ON THE PHOTOLUMINESCENCE OF Si NANOPARTICLES

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Abstract. Silicon nanoparticles with diameters ranging from 3 to 50 nm were prepared by thermal evaporation. The nanoparticles showed visible light emissions from 5000 Å to 9000 Å, with peak intensity at 8000-8200 Å, when excited with a He-Cd laser. The intensity increased with decreasing particle size. Based on the photoluminescence (PL) characteristics, it is suggested that the PL for particles larger than 9 nm is surface state-induced, while the PL for those smaller than 9 nm is ascribed to quantum confinement effects.

1. INTRODUCTION

There has been considerable effort to develop luminescent materials in the past decades. Crystalline Si has an indirect band gap and it is difficult to excite luminescence. Nevertheless, impurities or defects can be introduced into Si to act as luminescence centers. Previously, PL has been observed in *a*-Si [1], Si films [2], as well as *a*-SiO₂ films [3]. Recently, there have been extensive studies on Si quantum dots (SQD or Si nanoparticles) that have a quasi-direct band gap. Si quantum dots such as porous Si were found to have stronger PL intensity than Si films [4-7]. In this study, SQD with various sizes were prepared and the PL characteristics and mechanisms are discussed.

2. EXPERIMENTAL

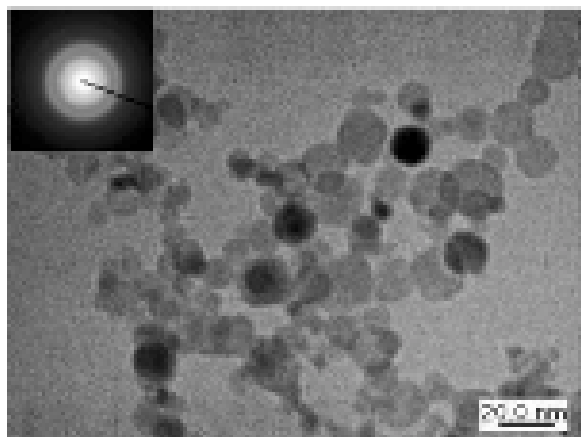
Si nanoparticles were prepared by vapor condensation. Silicon chips were placed in a tantalum boat in a thermal evaporation chamber. A glass slide was placed under the rotating plate which was cooled by liquid nitrogen. Si nanoparticles were grown either on the glass slide or directly on the plate. The chamber was evacuated to $1 \cdot 10^{-3}$ Pa, and Ar at pres-

ures from 7 Pa to 14.6 kPa was charged to the chamber during deposition to control the size of Si nanoparticles. The distance between the Ta boat and the plate was fixed at 10 cm.

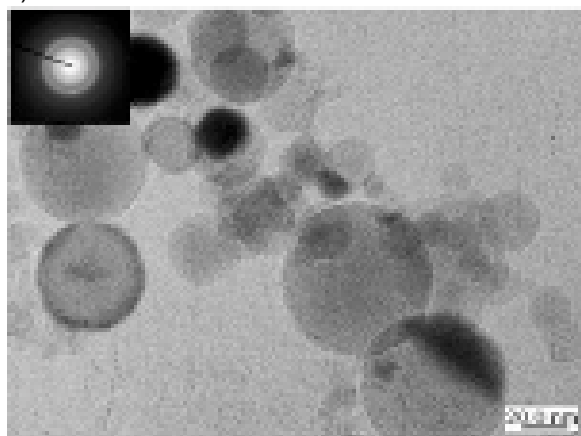
The crystal structure, crystallinity, and average particle size of the silicon nanoparticles were determined by X-ray diffraction (XRD, Regaku) patterns with a Cu K_{α} source. The particle size and morphology were examined by transmission electron microscopy (TEM, JEOL JEM-200 FX II). Fourier transform infrared (FTIR) absorption spectroscopy was used to analyze the surface bonding of the sample. The surface composition was determined by energy spectrum for chemical analysis (ESCA, PHI 1600). A PL system (He-Cd laser, 325 nm, 40 mW) was employed to measure the light emission. In addition, the optical absorption of the nanoparticles was measured by UV-visible light absorption spectroscopy (Hitachi U3410).

3. RESULTS AND DISCUSSION

Transmission electron micrographs revealed that the size of the Si nanoparticles varied from 3 to 80 nm, as illustrated in Fig. 1. The distribution of particle



a)



b)

Fig. 1. TEM micrographs of Si nanoparticles prepared under different pressures. (a) 0.67 kPa, (b) 12 kPa.

size was in a narrower range at lower Ar pressures. The average particle size analyzed by XRD ranged from 3 to 50 nm, and reduced as the pressure decreased. Table 1 summarizes the particle size ranges observed by the TEM images and the average particle sizes analyzed by XRD.

The surface bonding of Si nanoparticles examined by FTIR spectrum is displayed in Fig. 2. The broad absorption between 1050 cm⁻¹ and 1200 cm⁻¹ is assigned to the Si-O vibration. Absorption peaks due to the Si-H and Si-N vibrations were also observed. As the particle size increased, the peak intensities of Si-O, Si-N and Si-H decreased. In addition, ESCA also indicated that the intensity of Si 2p (silicon oxide) increased as the particle size decreased.

Fig. 3 displays the PL spectra of Si nanoparticles in vacuum with various size distributions. For the sample with the particle size range of 30-80nm, the average size calculated from XRD was 50nm. Par-

Table 1. Particle size range (from TEM) and average size (from XRD) of the Si nanoparticles.

Working Pressure (kPa)	Particle Size Range (nm)	Average Size (nm)
0.007	2-5	3
0.013	3-8	5
0.067	6-12	9
0.13	8-14	11
0.67	10-18	14
2.0	15-20	17
4.0	20-25	24
6.7	25-40	35
9.3	30-50	40
12.0	30-70	42
14.6	30-80	48

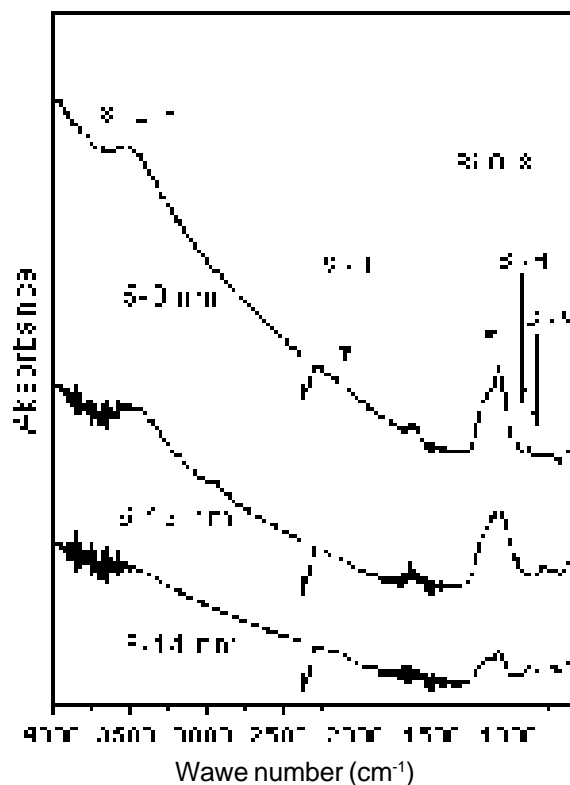


Fig. 2. FTIR spectra of Si nanoparticles of different sizes.

ticles larger than this range did not show PL. The wavelength of the peak intensity occurred at about 8000-8200 Å, with a broad range from 5000 Å to 9000 Å. The PL intensity increased as the particle size decreased, but no peak shift was observed. Atomic absorption spectra showed that they all had the same absorption edge at ~4750 Å. However, for

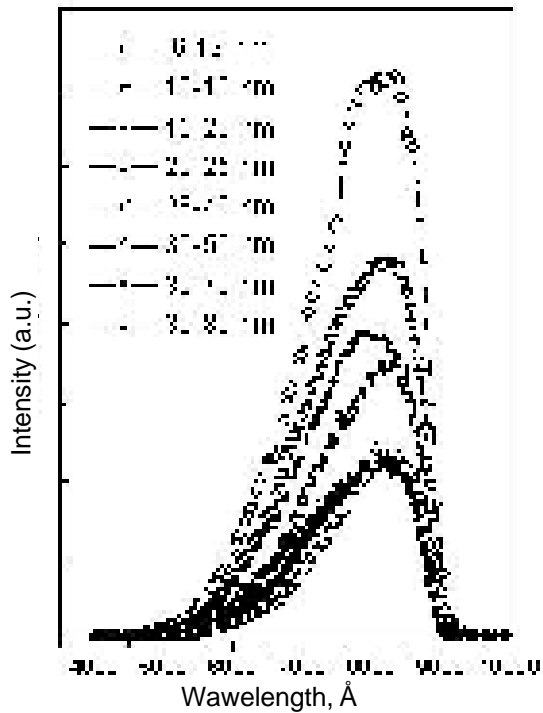


Fig. 3. PL spectra of Si nanoparticles of different sizes.

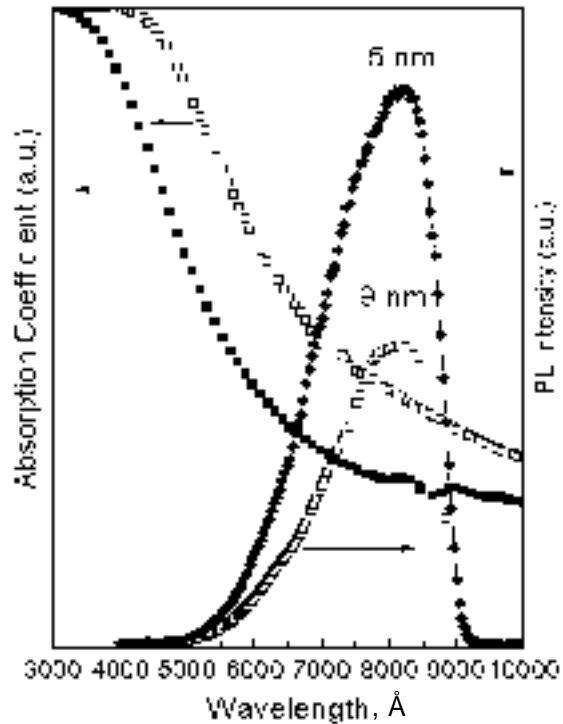


Fig. 4. PL and absorption spectra for Si nanoparticles with the average size smaller than 9nm.

the particles with an average size of 5 nm, it had the same PL but the absorption edge shifted to 3500 Å, as shown in Fig. 4. It was also noted that the PL intensity increased as the Si nanoparticles were aged. For particles larger than 9 nm, the peak remained unchanged, Fig. 5. For particles of 5 nm, however, a blue shift of the peak to 7500 Å occurred, Fig. 6. An even larger blue shift to 6100 Å was observed for particles of 3 nm.

Some reports have proposed that the quantum confinement effect (QCE) is a possible mechanism of the photoluminescence of Si nanoparticles when the particle size is smaller than 5 nm [4,6,8]. The emitted photons generally have energies in the wavelength range from 6500 Å to 7700 Å. In this study, the smaller particles (5nm) after aging showed peak shift in this range, presumably because the size was further reduced to exhibit the QCE due to oxidation during the aging. However, the PL of Si nanoparticles was observed even when the particles were as large as 50 nm in this study. According to the FTIR spectra and ESCA, the Si nanoparticles were covered with oxygen (oxide), and the amount of oxygen (oxide) depended on the particle size. From the PL spectra, there is a fixed peak position,

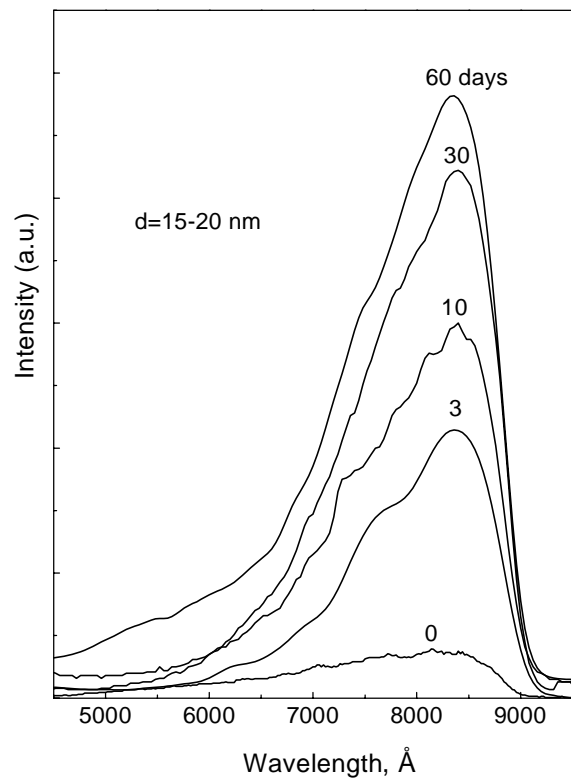


Fig. 5. PL spectra of Si nanoparticles ($d = 15-20$ nm). As-prepared and after aging.

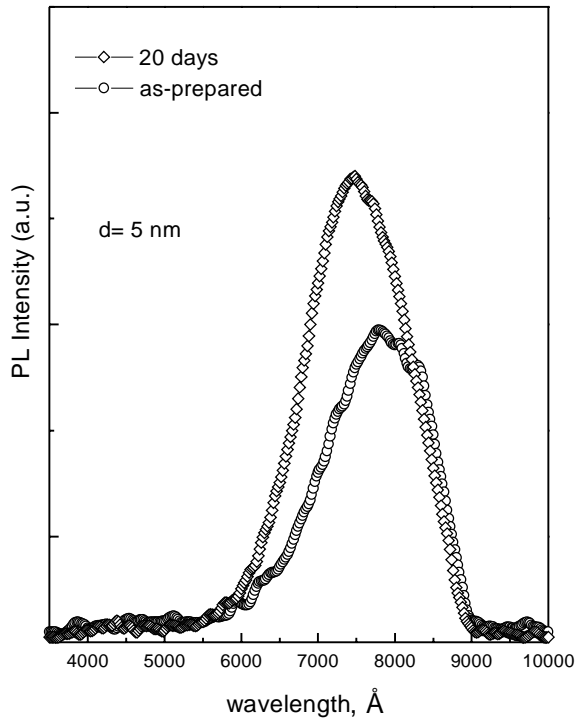


Fig. 6. PL spectra of Si nanoparticles (average size 5 nm). As-prepared and after aging.

and the intensity increased as the particle size decreased and as the aging time increased, i.e., the PL intensity increased as the amount of oxygen (oxide) increased. It implies that the surface layer played a key role in the visible light emission for the larger nanoparticles.

The size-dependent peak energies and the strength of the dominant factors for the PL process can be shown in Fig. 7. The PL for large particles (> 9 nm) can be attributed to the surface states effect in the near-surface region or the oxidized layer. Experimental evidence of the existence of these deep-level states has been documented by electron spin-resonance (ESR) [9,10]. These states have a direct energy gap and yield visible luminescence [11]. With the highly irregular arrangement of Si and O atoms on the surface, it is expected that there are numerous strained bonds as a result of the lattice distortion. The existence of the dangling bonds on the surface results in various surface states deep in the energy gap. As the electron-hole pairs are generated by the laser, light emission will be observed after the recombination of electrons and holes on the surface states. The wavelengths of the emission light observed in this study were consistent with the magnitude of the energy gap (~1.55 eV).

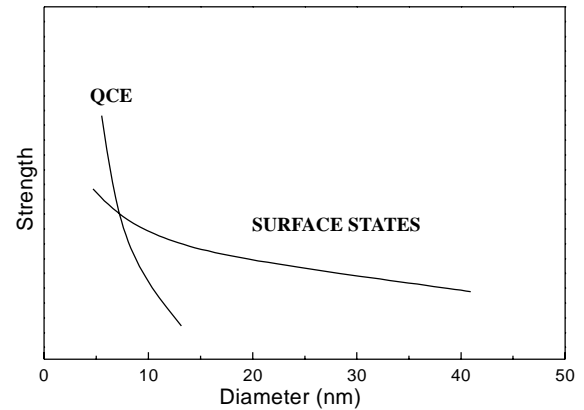


Fig. 7. Schematic strength of the dominant factors in the PL process.

In the transition from the surface-dominated to QCE-dominated region, i.e., with particle size around 9 nm, the PL could be operated by a combination of these two effects. Kanemitsu *et al.* have presented a possible luminescence model to explain the constant peak energy of the PL [12-14]. The model recommends a two-stage luminescence process where the carriers are first photogenerated from the valence band to the conduction band in the nanocrystalline Si core based on the QCE, while they radiatively recombine in the near-surface region. As a result, a constant wavelength of the PL peak is expected.

4. CONCLUSIONS

1. A series of Si nanoparticles ranging from 3 to 50 nm have been fabricated by a vapor condensation method. The particle size reduced as the working pressure decreased, and the distribution of size became more uniform at lower pressure.
2. For particles larger than 9 nm, the PL appeared in the range of 5000-9000 Å, with the peak intensity fixed at 8000-8200 Å. The intensity increased as the particle size decreased and when the particles were aged. Based on the characteristics of PL and the analyses of FTIR, ESCA, and absorption spectra, the cause of PL can be attributed to the surface state effect.
3. For particles smaller than 9 nm, aging induced a blue shift of the peak position. The quantum confinement effect was demonstrated from both theoretical calculation and the absorption spectra.

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REFERENCES

- [1] D. Engemann, R. Fis, E. Drews, R. L. Emerald and M. Slade // *Phys. Rev. Lett.* **26** (1971) 1564.
- [2] J. I. Pankove and D. E. Carlson // *Appl. Phys. Lett.* **29** (1976) 620.
- [3] C. M. Gee and M. Kastner // *Phys. Rev. Lett.* **42** (1979) 1765.
- [4] H. Takagi, H. Ogawa, Y. Yamazaki, A. Ishizaki and T. Nakagiri // *Appl. Phys. Lett.* **56** (1990) 2379.
- [5] L. T. Canham // *Appl. Phys. Lett.* **57** (1990) 1046.
- [6] H. Morisaki, F. W. Ping, H. Ono and K. Yazawa // *J. Appl. Phys.* **70** (1991) 1869.
- [7] H. Morisaki, H. Hashimoto, F. W. Ping, H. Nozawa and H. Ono // *J. Appl. Phys.* **74** (1993) 2977.
- [8] H. Morisaki // *Nanotechnol.* **3** (1992) 196.
- [9] S. M. Prokes, W. E. Carlos and V. M. Bermudez // *Appl. Phys. Lett.* **61** (1992) 1447.
- [10] V. Petrova-Koch, T. Muschik, A. Kux, B. K. Meyer, F. Koch and V. Lehmann // *Appl. Phys. Lett.* **64** (1992) 943.
- [11] F. Koch, V. Petrova-Koch and T. Muschik // *J. Lumin.* **57** (1993) 271.
- [12] Y. Kanemitsu // *Phys. Rev. B* **49** (1994) 16 845.
- [13] Y. Kanemitsu, H. Uto, Y. Masumoto, T. Matsumoto, T. Futagi and H. Mimura // *Phys. Rev. B* **48** (1993) 2827.
- [14] Y. Kanemitsu // *Phys. Rep.* **263** (1995) 1.