PHYSICAL REVIEW B VOLUME 50, NUMBER 24 15 DECEMBER 1994-II

Quantum confinement in nanometer-sized silicon crystallites

Xinwei Zhao and Olaf Schoenfeld
Frontier Research Program, The Institute of Physical and Chemical Research (RIKEN), 2-1 Hirosawa, Wako, Saitama 351-01, Japan

Shuji Komuro
Faculty of Engineering, Toyo University, Kawagoe, Saitama 350, Japan

Yoshinobu Aoyagi and Takuo Sugano
Frontier Research Program, The Institute of Physical and Chemical Research (RIKEN), 2-1 Hirosawa, Wako, Saitama 351-01, Japan
(Received 29 April 1994; revised manuscript received 7 September 1994)

Picosecond decay and temperature-dependence measurements of violet and blue-light emissions from nanocrystalline-silicon thin films were carried out. The luminescence band exhibits separated peaks at a wavelength region from 350 to 500 nm and shows no intensity degradation. The emission energies of the peaks shift towards the high-energy side at low temperatures by a temperature coefficient similar to single-crystalline silicon. The photoluminescence decays of these emissions can be completely fitted by a double-exponential equation. The two components of the lifetime τ_1 and τ_2 determined from the decay curves are 170 and 600 ps, respectively. All the optical events finish within 5 ns. The short lifetimes are suggested to be caused by an enhancement effect on the oscillator strength of the confined levels in zero-dimensionally confined silicon nanometer-sized crystallites.

Considerable effort has been undertaken to fabricate silicon (Si) crystallites with grain diameters of less than 5 nm because quantum confinement effects are expected from crystallites like these, also called nanocrystallites or quantum dots.[1] The creation of new materials with size-tunable optical and electronic properties by means of these quantum dots is a subject of interest. In the nanometer range the band gap of the crystallites increases with decreasing size, and the electronic states are predicted to become discrete. In order to achieve nanocrystallites in Si-based materials, microcrystalline Si (μc-Si) thin films were fabricated by chemical-vapor deposition or glow-discharge processes, and porous Si was produced by anodization of Si in HF.[2-4] For these procedures H-terminated surface states of Si grains have to be considered. Photoluminescence (PL) spectra from porous Si as well as μc-Si were observed in the visible wavelength region at room temperature.[3,4] The energies of the emissions are in the red region and are explained to be due to the quantum-size effect, although no discrete levels are observed. As reported previously,[5] nanocrystalline silicon (nc-Si) thin films with a grain diameter of 3–5 nm were fabricated. It was demonstrated that these nc-Si samples emit violet and blue light at room temperature.

In this work we investigated the nc-Si samples by transmission electron microscopy (TEM), x-ray-diffraction (XRD) measurements, and time-resolved and temperature-dependent PL measurements.

The nc-Si samples were fabricated by crystallization of amorphous Si (a-Si) thin films on Si substrates by rapid thermal annealing. The a-Si thin films with a thickness of 200 nm were deposited by electron-beam heating onto single-crystalline silicon held at 300 K. No hydrogen was involved in the deposition process.[5] The thermal annealing procedure took place in a quartz tube infrared furnace flushed with nitrogen in a temperature range from 1023 to 1223 K at annealing times from 10 s to 2 h. Structural investigations by XRD and TEM indicate that the achieved average grain diameter is 3–5 nm. Afterwards the samples were examined for PL using the 337-nm line of a N_2 laser and the 325 nm line of a He-Cd laser excitations. For temperature-dependent PL measurements a boxcar detection method was used. The gate width was 100 μs and the temperature range was applied from 24 to 300 K. The time-resolved PL measurements were carried out at room temperature using a picosecond luminescence lifetime measurement system. The pulse width of the N_2 laser used was 270 ps, and the resolution of this system was 5 ps.

Cross-sectional TEM observations indicate that the nanocrystalline phase achieved in nc-Si samples consists of a random grain size distribution from 3 to 5 nm at its surface. The PL spectra also change in different areas at the surface. XRD measurements show a distribution of small crystallites having different crystal growth directions. More than 90% of the crystallites have $\langle 111 \rangle$ and $\langle 220 \rangle$ crystal growth directions. The grain sizes achieved depend on the crystallization conditions. TEM investigations show a more detailed picture. At the interface between the nc-Si layer and the substrate sharp needlelike Si crystallites with lengths ranging from 10 to 50 nm are observed.[6] In the regions near the surface of the nc-Si samples, rectangularly shaped crystallites with sharp grain boundaries occur. The length of these crystallites varies from 3 to 5 nm in the $\langle 111 \rangle$ direction. The width was estimated to vary from 1 to 3 nm. Strain-related crystallization processes in the original a-Si layer might lead to such small sizes and sharp boundaries of the nanocrystallites. The periodic spacing of the lattice of the nanocrystallites is 0.31 nm, corresponding to that of the $\{111\}$ planes of the Si substrate.

0163-1829/94/50(24)/18654(4)/$06.00 ©1994 The American Physical Society

Figure 1 shows the PL spectra of a nc-Si thin film at room temperature under He-Cd cw-laser excitation. The intensities and emission energies are different in several areas on the nc-Si surface, as shown in Fig. 1. Points 1 and 2 were measured at two parts of the sample using the same PL system. The PL spectra show a violet and blue luminescence band including separated peaks at a wavelength region from 350 to 500 nm, as well as a defectlike luminescence band at longer wavelengths. Numbers and positions of the peaks depend on preparation conditions. TEM data indicate a distribution of crystallite sizes from 3 to 5 nm. Thus the difference in the PL spectra is assumed to be due to the difference in the crystallite sizes. In addition, the surrounding of the crystallites should also vary between the measurement points. The emissions are intense and show no intensity degradation during laser illumination at a temperature range from 4.2 to 373 K. This fact is very different from the degradation behavior of the PL from porous Si.[4] For PL measurements using N_2 pulsed laser excitation with a pulse width of 270 ps, only the violet and blue emissions can be observed even for a gate width as long as 100 μs. The emissions at longer wavelengths might be caused by some defect levels such as dangling bonds and the surrounding *a*-Si phase at the surface of the nanocrystallites which could have very long relaxation time constants or show different excitation behavior. These defect states might be different in different crystallized regions, as mentioned above. The spectrum of point 1 in Fig. 1 shows more intense blue-light emissions than that of point 2, and its emissions at wavelengths from 600 to 700 nm are reduced.

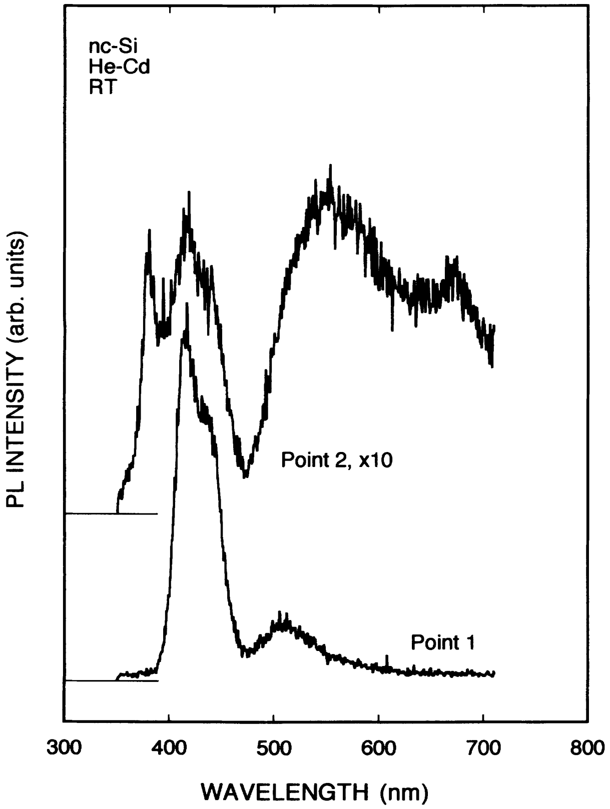

FIG. 1. Photoluminescence spectra from a nanocrystalline silicon thin film at room temperature. Points 1 and 2 are measured from different areas on the surface of the sample.

Temperature-dependent PL measurements were carried out from 24 to 300 K for point 1 in Fig. 1 using N_2 pulsed laser excitation. Four peaks at wavelengths of 390 and 415 nm (violet emissions) and 437 and 466 nm (blue emissions) were observed at 300 K. The peaks shift towards the high-energy side as temperature decreases as shown in Fig. 2. The temperature coefficient of the peaks is determined to be $\sim 3\times 10^{-4}$ eV/K which is near to the correspondent value of the band gap of single-crystalline Si (4×10^{-4} eV/K). This result suggests that the violet and blue emissions arise from Si nanocrystallites but are not due to defect levels. It should be pointed out that the four peaks in the spectra have the same temperature coefficient and do not change their energy separations at different temperatures. The intensities and linewidths of the emissions also remain constant. In addition, the intensities of the four peaks depend linearly on the excitation power density. These facts suggest that the observed violet and blue emissions are due to direct transitions in confined Si crystallites which are not affected by phonons. The transition probability of the emissions is almost constant at the measured temperature range. This is different from the indirectlike transitions observed in oxide-capped Si small crystals.[1] Theoretical descriptions of the quantum confinement effect in Si quantum dots indicate an indirect-to-direct conversion of the optical transitions.[7,8] A large blueshift of about 1.9 eV of the exciton energy is calculated for a dot diameter of 2.6 nm.[7] Although only experimental results achieved from porous Si are referred to, the direct transitions in Si quantum dots with sizes like these reported here can be considered in the same way. In addition, due to the strain effect on the surface atoms of the Si crystallites, the effective confinement length sould be smaller than that achieved by the structural investigations.[6] The summation of the structural influences by size distribution, crystallite shape and strain effects at the surface suggests stronger confinement effects in the Si crystallites in any case. Taking into account the electron-hole Coulomb interaction, the size reductions of the Si nanocrystallites should lead to a geometrical restriction of excitons or electron-hole pairs which dramatically enhances the oscillator strength of the direct optical transitions.

In order to investigate the transition dynamics in Si nanocrystallites picosecond PL decay measurements were carried out at room temperature. Curve *a* in Fig. 3 shows an integrated intensity decay curve of the emissions in a wavelength interval from 380 to 530 nm for the 300-K spectrum in the inset of Fig. 2. Curve *b* in Fig. 3 is the intensity decay of the N_2 laser. The pulse width used here is 270 ps. At the delay time axis 0 ns is the starting point of the measurement. For drawing in logarithmic scaling the intensities were added by means of 10. The noise level during the measurements was about ten counts. The inset of Fig. 3 shows the decay curves drawn on a linear scale. The decay curves of all nc-Si samples can be completely fitted by a double exponential equation. The two components of the determined lifetimes τ_1

and τ_2 in Fig. 3 are 170 and 600 ps, respectively. The rising time of the violet and blue emissions is some picoseconds. All the optical events finish within 5 ns. This fact is very different from the luminescence decay behavior of porous Si materials and capped Si clusters, in which nonexponential decay curves with lifetimes from nanoseconds to milliseconds were observed.[1,8] The PL decay measurements were also carried out for each wavelength of the same spectrum. The measured decay curves correspond to the integrated ones. In contrast, the luminescence from porous Si shows different lifetimes at different wavelengths.[8]

As described by TEM investigations the obtained grain size at the surface of the nc-Si thin films ranges from 2 to 5 nm. It is expected that quantum confinement effects occur in small crystallites like these. The geometrical restriction of electron-hole pairs should lead to a strong enhancement effect of the oscillator strength of the confined levels resulting in direct transitions in zero-dimensional systems. It is described from the theory[7,9,10] that the recombination rate of transitions with an energy of about 3 eV ranges from milliseconds to microseconds, but is not predicted to be in the picosecond-to-nanosecond region. It has to be pointed out that all proposed models for quantum confinement effects in Si quantum dots overestimate the indirect nature of the transitions. The continuous phonon modes were used as in bulk Si to calculate the radiative transition rate and the confinement effect of phonons, which means that discrete phonon distribution in k space, is neglected. No valid models are proposed for treating the direct transitions in Si quantum dots. Even there exist several reports about the picosecond and nanosecond PL decays observed in Ge crystallites and oxide-capped Si crystallites.[11,12] To consider the formation of quantum states in k space for a Si dot, all the zero-phonon transitions give energies of about 3 eV. A 2.72-nm Si spherical dot, for instance, forms ten discrete states ($k = k1 - k10$) from Γ to X in the k space. The nature of electrons relaxed from $k = k1$ to $k = k2$ should be different from that in the bulk due to the confinement of phonons which leads to an enhancement effect on the probability of the direct optical transitions in such confined systems. Thus the decay times of the PL reported here are concluded to be caused by direct transitions in Si quantum dots. Subnanosecond PL decays were also observed in Ge nanocrystallites, and were concluded to be evidence of direct transitions.[11] Indeed, we have observed a 3 eV quantum state by Zeeman splitting investigations in the nc-Si samples,[13] which supports the PL picosecond decay results. The predicted indirect transitions in Si quantum dots of the present models seem to be supported by the red PL and the millisecond decay behavior of porous Si (Ref. 8) and oxide capped nanocrystals.[12] However, it is determined that the red PL from capped Si crystallites is surface state in-

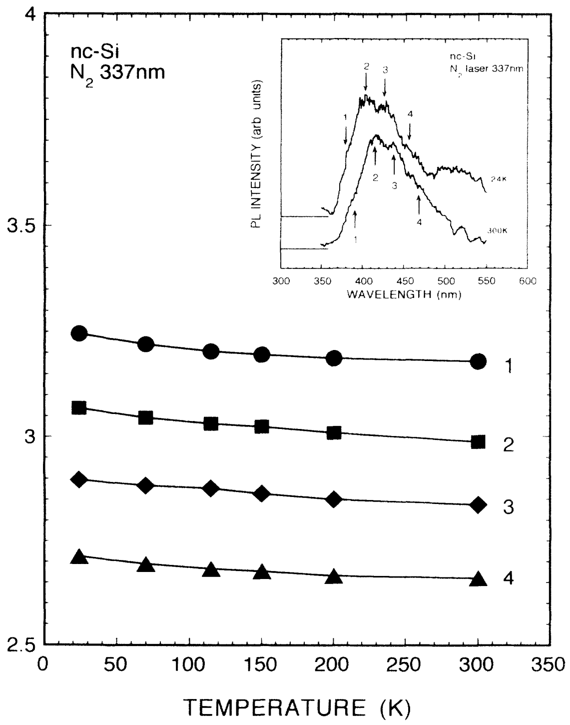

FIG. 2. Temperature dependence of the peak energies of the photoluminescence from a nanocrystalline silicon thin film. The inset shows the photoluminescence spectra measured at 24 and 300 K.

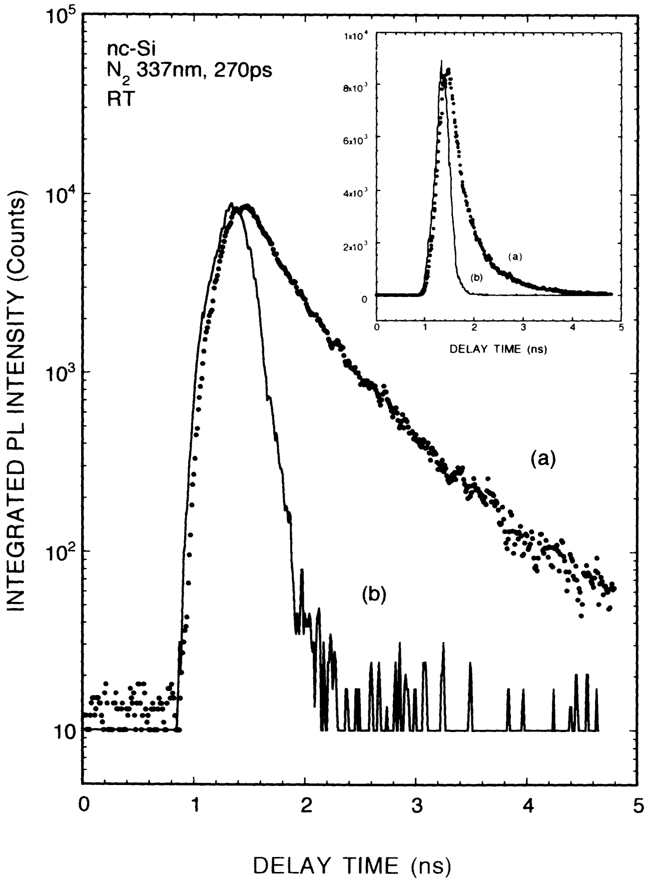

FIG. 3. Integrated photoluminescence intensity decay of a nanocrystalline silicon thin film (curve a). Curve b is the intensity decay of the excitation N_2 laser. The inset shows the linear decay curves.

duced.[12] The red PL from porous Si is also strongly affected by the surface.[8] Therefore the origin of these PL's differs from the predicted indirect transitions in Si quantum dots. This fact is neglected by the present models.

The short lifetime of 170 ps observed here is similar to that of confined excitons in GaAs quantum wells.[14] Thus the fast decay of the violet and blue emissions is concluded to be caused by quantum confinement. The fact that no luminescence was observed at delay times longer than 5 ns indicates that the system might be almost completely confined, and that there are no killer centers which affect the original fast luminescence decay. In addition, the nc-Si samples which show more intense luminescence indicate shorter lifetimes, and vice versa. It is suggested from this and from the result of the same decay behavior at different wavelengths that the transition rate of the confined levels is affected only by the confined energies and the sizes of the Si nanocrystallites. Furthermore, the PL spectra of the violet and blue emissions measured at different delay time intervals show no energy shift. The relative intensities between the emission peaks remain constant. Similar observations were reported for $CdSSe_{1-x}$ quantum dots.[15] Thus the observed violet and blue luminescence is concluded to be caused by the quantum confinement effect in Si nanocrystallites.

In conclusion, we investigated the violet and blue luminescence of Si nanocrystallites with grain diameters of 3–5 nm. The summary of the results reported here supports the explanation of the light emissions from confined levels in Si nanocrystallites. These results give an interesting view of the zero-dimensionally confined electrons in Si-based materials.

The authors would like to thank Dr. J. Kusano, Dr. S. Nomura, and Dr. H. Issiki of RIKEN, and Professor J. Christen of Magdeburg University "Otto von Guericke" for stimulating discussions. One of the authors would like to thank the German Peoples Foundation for its support.

---

[1] L. Brus, Adv. Mater. **5**, 286 (1993).

[2] S. Komuro, Y. Aoyagi, Y. Segawa, and S. Namba, J. Appl. Phys. **58**, 943 (1985).

[3] H. Takagi, H. Ogawa, Y. Yamazaki, A. Ishizaki, and T. Hakagiri, Appl. Phys. Lett. **56**, 2379 (1990).

[4] L. T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).

[5] X. Zhao, O. Schoenfeld, J. Kusano, Y. Aoyagi, and T. Sugano, Jpn. J. Appl. Phys. Lett. **33**, L649 (1994).

[6] X. Zhao, O. Schoenfeld, Y. Aoyagi, and T. Sugano, J. Phys. D **27**, 1575 (1994).

[7] T. Takagahara, and K. Takeda, Phys. Rev. B **46**, 15 578 (1992).

[8] T. Matsumoto, M. Daimon, T. Futagi, and H. Mimura, Jpn. J. Appl. Phys. Lett. **31**, L617 (1992).

[9] M. S. Hybertsen, Phys. Rev. Lett. **72**, 1514 (1994).

[10] J. P. Proot, C. Delerue, and G. Allan, Appl. Phys. Lett. **61**, 1948 (1992).

[11] Y. Masumoto, in *Microcrystalline Semiconductors: Materials Science and Devices*, edited by P. M. Fauchet, C. C. Tsai, L. T. Canham, I. Shimizu, and Y. Aoyagi, MRS Symposia Proceedings No. 283 (Materials Research Society, Pittsburgh, 1993), p. 15.

[12] Y. Kanemitsu, Phys. Rev. B **49**, 16 845 (1994).

[13] S. Nomura, X. Zhao, O. Schoenfeld, Y. Aoyagi, and T. Sugano, Solid State Commun. **92**, 665 (1994).

[14] A. Vinattieri, J. Shah, T. Damen, K. Goossen, L. Pfeiffer, M. Maialle, and L. Sham, Appl. Phys. Lett. **63**, 3164 (1993).

[15] A. Bugayev, H. Kalt, J. Kuhl, and M. Rinker, Appl. Phys. A **53**, 75 (1991).