Light emission from Si nanoclusters formed at low temperatures

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Photoluminescence (PL) from amorphous Si nanoclusters (Si-ncls) formed by thin-film deposition via electron-cyclotron resonance plasma-enhanced chemical vapor deposition followed by annealing at temperatures $\leqslant$875 °C has been investigated. We find that Si-ncls grow very slowly after their initial nucleation at low temperatures. An increase in the size of Si-ncls, which can be controlled by the annealing temperature, induces a redshift in the Si-ncl PL peak. While the emitted optical power is more than 100 times smaller than that of Si nanocrystals formed in an identically deposited film, it is increased by a factor of up to approximately four times following hydrogen passivation. The incorporation of hydrogen causes a redshift in the PL peak position, suggesting a partial hydrogenation induced bond distortion of the Si-ncls. This redshift decreases with increasing hydrogen ambient annealing temperature. © *2006 American Institute of Physics*.
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Si nanostructures show great promise as the basis for Si-based light-emitting devices with potential for optoelectronic integration.[1,2] Si-rich silicon oxides (SRSO) designated as SiO_x ($x<2$) have been studied extensively as one such system in which nanostructured Si can be produced by conservative thermal treatments.[3–5] It is well known that Si nanocrystals are formed in SRSO films by means of annealing at high temperature (typically 1100 °C). These Si nanocrystals can be both optically and electrically excited and emit light with a peak in the near-infrared region.[6] When the annealing temperature is lower than 1000 °C, the resultant Si nanostructures are Si nanoclusters (Si-ncls); typically amorphous in nature.[7–9] Because of their low processing temperature, Si-ncls are usually smaller than Si nanocrystals. Due to quantum confinement, this causes a blueshift in the light emission peak wavelength, important in terms of general applications of Si-based light-emitting devices. The growth rate of Si-ncls is also expected to be smaller at low temperature, therefore the control of Si-ncl size may be easier than that for Si nanocrystals grown at a temperature in excess of 1000 °C.

Currently, one of the most important applications of Si-ncls is to sensitize Er ions in Er-doped SRSO films, where the low formation temperature aids in the elimination of Er precipitation.[10] Despite the potentially important role of Si-ncls, sparse work has been reported related to their formation and evolution in comparison to Si nanocrystals. This results from a belief that the amorphous structure of Si-ncls intrinsically contains defects and is thus characteristic of low light emission efficiency. However, these defects may be passivated by hydrogen, as demonstrated in hydrogenated amorphous Si.[11] In this work, we study Si-ncls formed at 750–875 °C. The quantum confinement in Si-ncls is compared with that in Si nanocrystals and the effect of hydrogen on the optical properties is determined.

An SRSO film with a Si atomic concentration of 42% was grown on a Si substrate at a substrate temperature of 100 °C by electron-cyclotron resonance plasma-enhanced chemical vapor deposition (PECVD). The deposition system has been described in detail elsewhere.[12] The thickness and refractive index of the film were determined with an ellipsometer to be 1 μm and 1.7, respectively. The film was divided into smaller samples and annealed at a temperature ranging from 750 to 1100 °C in a tube furnace with a flowing argon gas ambient. Four samples, all annealed at 800 °C for 13 h, were further annealed at between 400 and 800 °C for 1 h in the same furnace with a flowing hydrogen gas ambient. The photoluminescence (PL) of all the samples was measured at room temperature. The PL setup comprised a Cd–He laser operating at a wavelength of 325 nm and an Ocean Optics S2000 spectrometer that featured a high-sensitivity linear charge coupled device array. The PL peaks for all the samples were redshifted by more than ~50 nm after correction with respect to the system response. The correction also caused the PL peaks for the samples annealed at temperatures $\leqslant$875 °C to be much less pronounced because of their broadness. Therefore, all PL spectra presented in this work were left *uncorrected* to clearly show the changes in PL peak position. When we calculated the relative power efficiency of light emission, however, corrected PL spectra were used. The effective power density of the laser beam on the surface of samples was ~0.64 W/cm^2.

Figure 1 shows the PL results for the samples annealed at 875 °C for up to 13 h in an argon ambient. The as-grown film is also included for comparison. Every PL spectrum in the present work is very well fitted with a Gaussian curve, as demonstrated in Fig. 1 for the sample annealed at 875 °C for 13 h. For the sake of clarity, all the spectra presented are thus the fitting results, unless otherwise stated. There exists a PL signal with an apparent peak at 649 nm for the as-grown film. Nonbridging oxygen hole centers are generally regarded as the origin of the luminescence around 650 nm in a silicon oxide compound.[13] However, they should not be re-

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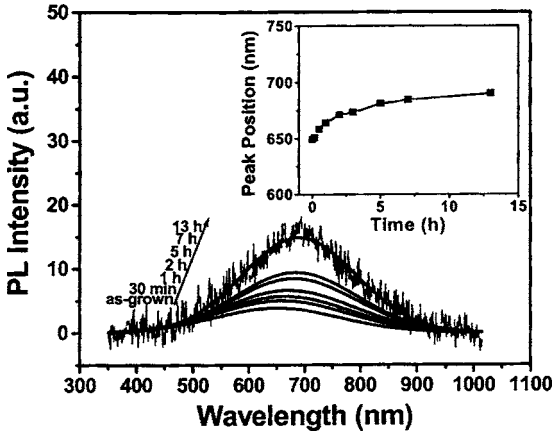

FIG. 1. The PL results for a SiO_x ($x<2$) film with a Si atomic concentration of 42% annealed in an argon ambient at 875 °C for up to 13 h. The as-grown film is also included for comparison. For clarity, Gaussian curves fitted to the spectra are shown rather than the raw spectra, except for the sample annealed for 13 h. The change in PL peak position with time is illustrated in the inset. In the PL measurements the excitation wavelength and power density are 325 nm and 0.64 W/cm^2, respectively.

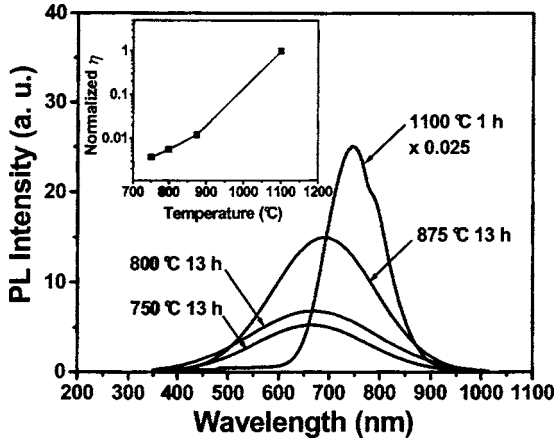

FIG. 2. The PL results for the samples annealed in an argon ambient for 13 h at 750, 800, and 875 °C. The measured PL spectrum from the sample annealed at 1100 °C for 1 h in an argon ambient is included for comparison. The power efficiency η of the samples annealed at low temperatures has been normalized with respect to that of the sample annealed at 1100 °C, as shown in the inset. In the PL measurements, the excitation wavelength and power density are 325 nm and 0.64 W/cm^2, respectively.

sponsible for the light emission from the as-grown film given the fact that the peak at 649 nm is significantly redshifted after correction with respect to the system response. It is known that oxygen-deficient centers, such as divalent cations and neutral oxygen vacancies, usually give rise to luminescence in a SRSO structure. The light emission from them is in the range from ultraviolet to blue.[14–17] Clearly, oxygen-deficient centers cannot be used to explain the red emission in the as-grown film, either. Park *et al.*[18] have recently demonstrated *in situ* formed Si-ncls by PECVD. Thus, we believe that in the present work, there exist *in situ* formed Si-ncls, which lead to the light emission in the as-grown film. Upon annealing at 875 °C, the PL peak redshifts to 690 nm with increasing annealing time (Fig. 1). It is clear that the rate of change in the PL peak position slows as the annealing time increases (inset of Fig. 1). In terms of classical nucleation theory[19,20] it is expected that following initial nucleation of the Si-ncls, they reach a certain temperature-dependent critical size. There then follows a very slow subsequent growth, mainly as a consequence of the annealing temperature being much lower than the melting point of Si. This is consistent with the change in the PL peak position shown in the inset in Fig. 1, which appears to confirm that quantum confinement effects indeed take place in Si-ncls: i.e., the band gap (PL peak energy, which is inversely proportional to PL peak wavelength) of Si-ncls decreases with the increase of Si-ncl size.[21]

A direct comparison of the results for annealing at 875 °C, and those for 800 and 750 °C (not shown) reveals similar trends for all three sample sets although both nucleation rate and growth rate for Si-ncls decrease with a decrease of temperature, as suggested by the thermodynamics of nucleation and growth. The PL intensity for the samples annealed at 875 °C is observed to increase with an increase of annealing time.

Figure 2 illustrates the PL results for the samples annealed for 13 h at 750, 800 and 875 °C, peaking at 664, 668, and 690 nm, respectively. The peak wave increases with an increase of temperature, indicating an increase in Si-ncl size with increasing annealing temperature. The increase in PL intensity corresponds to a relative reduction in nonradiative defects such as dangling bonds for larger Si-ncls. We have calculated the relative power efficiency η of the Si-ncls (inset of Fig. 2). It is clear that η of Si-ncls increases with the increase of temperature. Although η of Si-ncls is increased by a factor of four times from 750 to 875 °C owing to the reduced concentration of defects, it is more than 100 times smaller than that of Si nanocrystals formed in an identically deposited film by means of annealing at 1100 °C for 1 h. The PL peak position of 750 nm for the Si nanocrystals indicates that they are larger than Si-ncls. The larger number of constituent Si atoms and the crystalline nature of the nanostructure lead to the significantly reduced concentration of defects and thus the relatively high value of η.

It is well known that defects in amorphous Si can be passivated by hydrogen. We expect that this also applies in the study of Si-ncls.[22] Figure 3 shows the PL results for samples annealed at 800 °C for 13 h in an argon ambient and then at 400–800 °C for 1 h in a hydrogen ambient. η of

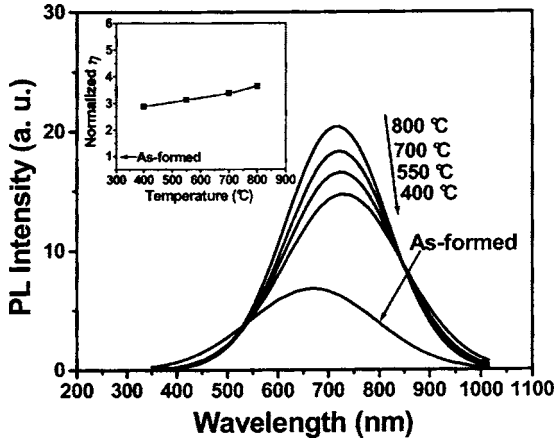

FIG. 3. The PL results for the samples annealed in a hydrogen ambient for 1 h at 400, 550, 700, and 800 °C. These samples have been previously annealed at 800 °C for 13 h in an argon ambient to form Si-ncls. The power efficiency η of the hydrogenated samples is normalized with respect to that of a sample with as-formed Si-ncls, as shown in the inset. In the PL measurements the excitation wavelength and power density are 325 nm and 0.64 W/cm^2, respectively.

Si-ncls is increased by more than three times after annealing in a hydrogen ambient (inset of Fig. 3). This is attributed to the passivation of nonradiative defects in the Si-ncls by hydrogen. Since the solubility of hydrogen increases with the increase of temperature in Si structures,[11] a larger concentration of hydrogen is incorporated in the Si-ncls at a higher temperature, inducing more complete passivation of defects. Thus, the largest enhancement with a factor of approximately four times for η is achieved at 800 °C.

After annealing in a hydrogen ambient the PL peak exhibits a redshift, the value of which decreases with the increase of temperature (Fig. 3). As described above, the growth of Si-ncls following initial precipitation is very small at temperatures <900 °C. The enhanced growth of Si-ncls in the presence of hydrogen is dismissed. Otherwise, Si-ncls should have grown faster and thus demonstrated a larger redshift of PL peak in a hydrogen ambient at 800 °C compared to that for 400 °C. Therefore, the redshift of the PL peak is not due to the growth of Si-ncls after annealing in a hydrogen ambient. Yu *et al.* have theoretically studied fully and partially hydrogenated Si nanocrystals and nanoclusters.[23] They indicate that the incorporation of hydrogen in Si-ncls causes a structure expansion, which is in the order of 10^{-4} to 10^{-3}. Such a small structure expansion would not then explain the redshift of PL peak after annealing in a hydrogen ambient.

The changing position and intensity of the hydrogen annealed sample spectra indicate incomplete hydrogenation after annealing at these temperatures. In these partially hydrogenated Si-ncls, there exists bond distortion, which introduces energy levels extending into the band gap of Si-ncls.[24] As a result, radiative transitions with energies lower than the band gap occur, leading to the redshift of the PL peaks compared with the as-formed Si-ncls, which presumably have either a clean band gap or a band gap with energy levels shallower than those introduced by partial hydrogenation induced bond distortion. When the concentration of incorporated hydrogen is smaller at lower temperature, the bond distortion is larger.[23] Since the energy levels induced by a larger bond distortion extend more deeply into the band gap of Si-ncls, the PL peak redshifts from 716 to 729 nm as the temperature is changed from 800 to 400 °C (Fig. 3).

In summary, we find that Si-ncls grow very slowly after their nucleation at low temperatures. The increase of Si-ncl size with annealing temperature induces the redshift of PL peak of Si-ncls, consistent with a quantum confinement mechanism. η of Si-ncls is more than 100 times smaller than that of Si nanocrystals. However, it is increased by a factor of up to ~ 4 times with hydrogen passivation. There exists bond distortion in partially hydrogenated Si-ncls. When a smaller concentration of hydrogen is incorporated at a lower temperature, bond distortion-induced energy levels extend more deeply into the band gap of Si-ncls, resulting in a PL peak at a longer wavelength.

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[1] G. Reed and A. P. Knights, *Silicon Photonics: An Introduction* (Wiley, New York, 2004).
[2] S. Ossicini, L. Pavesi, and F. Priolo, *Light Emitting Silicon for Microphotonics* (Springer, New York, 2003).
[3] A. J. Kenyon, P. F. Trwoga, C. W. Pitt, and G. Rehm, J. Appl. Phys. **79**, 9291 (1996).
[4] T. Inokuma, Y. Wakayama, T. Muramoto, R. Aoki, Y. Kurata, and S. Hasegawa, J. Appl. Phys. **83**, 2228 (1998).
[5] F. Iacona, G. Franzò, and C. Spinella, J. Appl. Phys. **87**, 1295 (2000).
[6] G. Franzò, A. Irrera, E. C. Moreira, M. Miritello, F. Iacona, D. Sanfilippo, G. D. Stefano, P. Fallica, and F. Priolo, Appl. Phys. A: Mater. Sci. Process. **74**, 1 (2002).
[7] L. X. Yi, J. Heitmann, R. Scholz, and M. Zacharias, Appl. Phys. Lett. **81**, 4248 (2002).
[8] M. Molinari, H. Rinnert, and M. Vergnat, Europhys. Lett. **66**, 674 (2004).
[9] F. Iacona, C. Bongiorno, and C. Spinella, J. Appl. Phys. **95**, 3723 (2004).
[10] G. Franzò, S. Boninelli, D. Pacifici, F. Priolo, F. Iacona, and C. Bongiorno, Appl. Phys. Lett. **82**, 3871 (2003).
[11] W. Beyer, Semicond. Semimetals **61**, 165 (1999).
[12] M. Boudreau, M. Boumerzoug, P. Mascher, and P. E. Jessop, Appl. Phys. Lett. **63**, 3014 (1993).
[13] L. N. Skuja, J. Non-Cryst. Solids **179**, 51 (1994).
[14] K. Raghavachari and G. Pacchioni, J. Chem. Phys. **114**, 4657 (2001).
[15] L. N. Skuja, A. N. Trukhin, and A. E. Plaudis, Phys. Status Solidi A **84**, K153 (1984).
[16] V. B. Sulimov and V. O. Sokolov, J. Non-Cryst. Solids **191**, 260 (1995).
[17] F. Meinardi and A. Paleari, Phys. Rev. B **58**, 3511 (1998).
[18] N. M. Park, C. J. Choi, T. Y. Seong, and S. J. Park, Phys. Rev. Lett. **86**, 1355 (2001).
[19] M. Volmer and A. Weber, Z. Phys. Chem. (Munich) **119**, 227 (1926).
[20] R. Becher and W. Doring, Ann. Phys. **24**, 719 (1935).
[21] G. Allan, C. Delerue, and M. Lannoo, Phys. Rev. Lett. **78**, 3161 (1997).
[22] D. Comedi, O. H. Y. Zalloum, E. A. Irving, J. Wojcik, and P. Mascher, Phys. Technol. (to be published).
[23] D. K. Yu, R. Q. Zhang, and S. T. Lee, J. Appl. Phys. **92**, 7453 (2002).
[24] L. Liu, C. S. Jayanthi, and S. Y. Wu, J. Appl. Phys. **90**, 4143 (2001).