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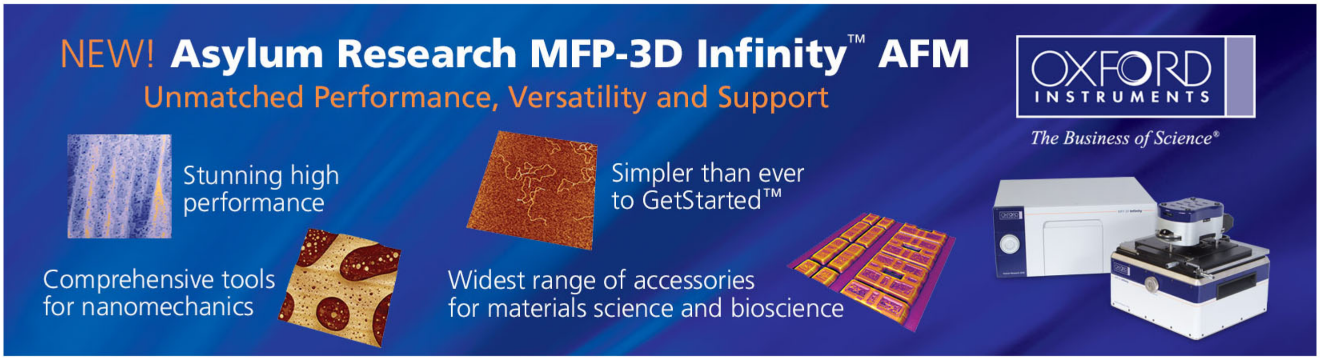

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Pumping intensity dependent surface charge accumulation and redshifted microphotoluminescence of silicon-implanted quartz

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The pumping-intensity dependency of nanocrystallite silicon (nc-Si) related microphotoluminescence (μ-PL) from multirecipe Si-implanted quartz is characterized. After annealing at 1100 °C for 3 h, theμ-PL at 724 nm contributed by nc-Si with a diameter of about 4 nm is maximized. By increasing the pumping intensity from 10 $\mathrm{kW/cm^2}$ to 300 $\mathrm{kW/cm^2}$, the μ-PLs of 1 and 3-h-annealed Si-implanted quartz samples are redshifted by <1.2 and 11 nm, respectively. The μ-PL of 3-h-annealed sample further redshifts by 2.5 nm after pumping at 300 $\mathrm{kW/cm^2}$ for h. Such a redshift in PL is attributed to the anomalous quantum Stark effect under strong illumination, which photoionizes the buried nc-Si and initiates an electric field beneath the surface of Si-implanted quartz. The measurement of accumulating charges and voltage drop during illumination primarily elucidate the correlation between redshift in PL and the photoionized nc-Si induced surface electric field. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1777818]

Si ion implantation has recently emerged as an alternative method of synthesizing Si nanocrystals (nc-Si) in SiO_2 matrix. Various photoluminescence (PL) bands from Si-implanted SiO_2 materials ($SiO_2:Si^+$) have been identified to originate from principle defects such as the neutral oxygen vacancy (NOV), denoted as $O_3\equiv Si-Si\equiv O_3$ with PL at 410–460 nm,[1] and the precursor of nc-Si (E'_δ, denoted as $Si\uparrow Si-Si$) with PL at 520–550 nm,[2] among others. The high-temperature annealing of $SiO_2:Si^+$ usually quenches defects and formats nc-Si, providing a more pronounced near-infrared PL (700–900 nm). The nc-Si related PL wavelength depends strongly on the size of nc-Si. The Si-rich $SiO_2:Si^+$ material with self-assembled Si quantum dots (QDs) has attracted considerable interest for their potential use in fabricating light-emitting or charge-storage devices. Recently, the electric-field dependency of the luminescence of QD-embedded materials under changing charge distribution beneath or inside the QDs has been reported and attributed to the quantum-confined Stark effect of the QDs.[3,4] The sign of the Stark shift was found to depend strongly on the change in external electric field and the built-in dipole momentum of the QD.[5,6] Sheng *et al.*[7] observed an anomalous Stark shift of the stacked InAs/GaAs self-assembled QD structure, in which a three-dimensional field drastically modified the hole state. The micro-PL (μ-PL) of QDs further indicates some extraordinary phenomena, such as the intermittent fluorescence and a long coherent time, among others.[8,9] Unlike the size-dependent PL redshift of nc-Si,[10,11] the correlation between pumping intensity and wavelength shift in PL of $SiO_2:Si^+$ materials has not yet been satisfactorily explained. This work investigates the pumping-intensity dependent μ-PL of the Si-implanted quartz prepared by multirecipe implantation. Long-term annealed Si-implanted quartz exhibits buried nc-Si, which corresponds a redshift in μ-PL as the pumping intensity is increased. The shifts in wavelength at various pumping intensities and durations are evaluated. The accumulating rate of surface charges and the corresponding change in the space charge field strength of the Si-implanted quartz under illumination are measured, which corroborates the effect of the electric field induced by accumulation of surface charges is more pronounced than other mechanisms.

A 1-mm-thick quartz substrate was preannealed for 1 h and concurrently implanted with Si ions at 5×10^{15} $\mathrm{ions/cm^2}$ at 40 keV, 1×10^{16} $\mathrm{ions/cm^2}$ at 80 keV, and 2.5×10^{16} $\mathrm{ions/cm^2}$ at 150 keV. The secondary-ion mass spectroscopy (SIMS) of Si-implanted quartz reveals that the Si atoms with a maximum excess density of 0.8% are uniformly distributed at depths between 40 and 300 nm below the surface, this result agrees quite well with that obtained using TRIM simulation. The Si-implanted quartz samples were subsequently annealed at 1100 °C in quartz furnace with flowing N_2 gas for 1–3 h. Afterwards, a continuous-wave μ-PL measurement was performed using a 325-nm-He–Cd laser with a focused spot size of 2.5 μm. The pumping intensity changes from 10 to 300 $\mathrm{kW/cm^2}$. The μ-PL was detected using a fluorescence spectrophotometer (Jobin Yvon, TRIAX-320 with wavelength resolution of 0.06 nm) and a photomultiplier (Jobin Yvon, Model 1424M). A high-resistance electrometer (Keithley, 6517A) and a probe station (Karr Suss, Munchen-Garching) were employed to measure the charges accumulated on the surface of Si-implanted quartz, with the spacing between microprobes fixed at 100 μm.

Three μ-PL peaks from the pure quartz sample were observed at 410, 520, and 754 nm (inset of Fig. 1), which correspond, respectively, to weak oxygen-bond defects with PL at 410 nm;[12] self-trapped exciton centers (irradiation-induced transient oxygen Frenkel pairs composed of an oxygen vacancy and a peroxy linkage) with PL at 515–560 nm;[13,14] and Al-hole centers with PL at 729–755 nm.[15] The Al-hole centers greatly strengthen the μ-PL since the density of residual Al in quartz is as high as 14 ppm. These defect-related peaks can be completely eliminated after annealing for 1 h or longer, which excludes the

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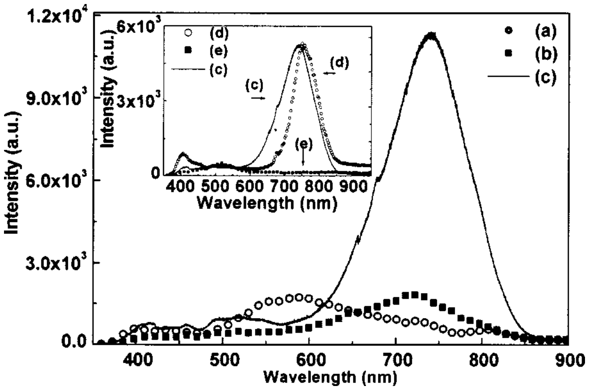

FIG. 1. μ-PL spectra of Si-implanted quartz samples at (a) as-implanted condition, or annealed at 1100 °C for (b) 1 h and (c) 3 h. The inset figure shows the pure quartz samples (d) before and (e) after annealing at 1100 °C for 1 h.

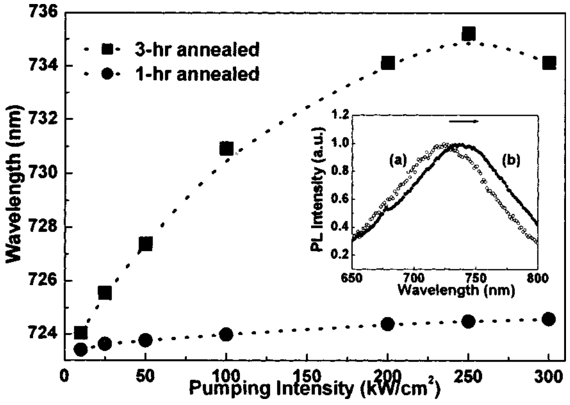

FIG. 3. Wavelength shift of μ-PL for 1- and 3-h annealed Si-implanted quartz samples at different pumping intensity. The inset shows the redshifted μ-PL spectra for the 3-h-annealed sample at pumping intensities of (a) 10 and (b) 300 kW/cm^2.

existence of nc-Si (contribute to PL at 700–800 nm) in quartz. In contrast, the μ-PL of Si-implanted quartz includes a new peak at 550–600 nm and a weak one at 720–725 nm (shorter than that contributed by the Al-hole centers). The former PL peak attributed to the E'_δ defect in SiO_2 matrix diminishes during 1 h annealing, whereas the intensity of the μ-PL at 720–725 nm is enhanced. As the annealing time lengthens, most of the E'_δ defects are transformed into larger nc-Si in Si-implanted quartz. The correlation between the PL wavelength and the nc-Si size has been theoretically calculated and confirmed by TEM analysis. For example, Delerue *et al.*[16] determined that the nc-Si size-dependent PL wavelength is $\lambda \cong 1.24/(E_0+3.73/d^{1.39})$, where E_0 is the band-gap energy of the bulk silicon and d is the diameter of nc-Si buried in Si-implanted quartz. Mutti *et al.*[17] observed that the Si-rich SiO_2 annealed at 1000–1250 °C can efficiently precipitate nc-Si with a diameter of about 3–4 nm in the SiO_2 matrix. In our case, the enhancement of μ-PL at 724 nm from Si-implanted quartz is contributed by the buried nc-Si with a diameter of about 4 nm.

The μ-PL wavelength of Si-implanted quartz annealed for 3 h is redshifted from 724 to 735 nm as the pumping intensity increases from 10 to 300 kW/cm^2 (see Fig. 2). In contrast, the redshift of the μ-PL of the Si-implanted quartz annealed for 1 h is only 1.2 nm, as shown in Fig. 3. This phenomenon cannot be attributed to the bandfilling effect of excited states in nc-Si since the bandfilling only causes a blueshift. Furthermore, the required temperature change of nc-Si for such a redshift is calculated as >100 K according to $\Delta E(T)=\alpha T^2/(T+\beta)$,[18] where $\Delta E(T)$ is the change in band-gap energy as a function of substrate temperature (T), and α and β are 7.021×10^{-4} and 1108, respectively, for Si. The absorption of SiO_2 at 325 nm is negligible ($\alpha \ll 10^{-2}$ cm^{-2}), which causes a temperature change of the Si-implanted quartz of 0.3 °C during illumination, corresponding to a redshift of only 0.02 nm without linewidth broadening. This observation excludes the correlation between the substrate heating effect and the redshift of μ-PL from Si-implanted quartz. Previously, Ma *et al.*[19] have observed similar redshift of the PL phenomenon in InAs/AlAs quantum well structure that consists of coupled QDs. As the pumping intensity is increased, the carriers captured in the coupled QDs preferentially tunnel from smaller QD to larger QD with lower energy state.[20] Two significant and neighboring PL peaks were observed as a further evidence of the occurrence of such a coupled-QD-induced PL redshift. The carrier redistribution occurs especially when carriers are in excited states of the coupled QDs because of ground-state filling effect, which eventually results in a redshifted and narrower PL peak. However, the Si-implanted quartz exhibits no adjacent μ-PL peaks, and coupled Si QDs can barely generated at such a low excess density of Si.

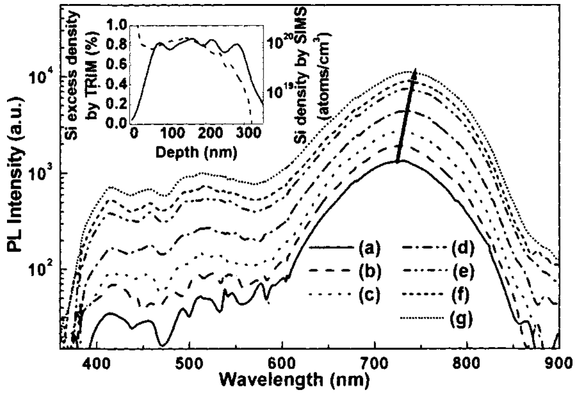

FIG. 2. Power dependent μ-PL spectra of the 3-h-annealed Si-implanted quartz at pumping intensity of (a) 10, (b) 25, (c) 50, (d) 100, (e) 200, (f) 250, and (g) 300 kW/cm^2. The inset plots the TRIM-simulated and SIMS-measured Si excess density as a function of depth.

Thus, the dominant mechanism of redshifted μ-PL in Si-implanted quartz with buried nc-Si is considered to involve the first-order quantum Stark effect induced by external electric field.[21–24] However, no external field was applied to the Si-implanted quartz instead of a strong illumination during μ-PL analysis. Hence, the only possible mechanism which initiates the quantum Stark effect is attributed to the capture of carriers in nc-Si, generating an internal electric field during high-intensity pumping. This results in the accumulation of charges beneath the surface of long-term annealed Si-implanted quartz during strong illumination. As evidence, the measurement of accumulated surface charges on Si-implanted quartz before and after illumination is illustrated in Fig. 4. A decline in the residual charges is observed on the surface of Si-implanted quartz without illumination. Illumination at 300 kW/cm^2 increases the surface charge from 5 nC to 1 μC within 12 h, corresponding to a surface electric field of up to 2.47×10^4 V/cm, which is due to the

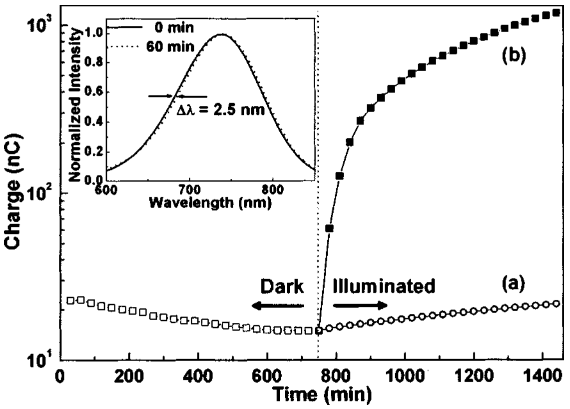

FIG. 4. Accumulated surface charges of (a) 1- and (b) 3-h-annealed samples measured before and after illuminating for 12 h. The inset illustrates the redshifted μ-PL from 3-h-annealed Si-implanted quartz illuminated at 300 kW/cm^2 for 1 h.

extremely low density of nc-Si. In comparison, the surface charges accumulated on the 1-h-annealed sample is only 2×10^{-8} C after illumination for 12 h, which is due to a lower density of nc-Si precipitated in the Si-implanted quartz during 1 h annealing. Since the nc-Si/quartz interface states recombine the photoexcited electrons from the nc-Si, the remaining holes positively charge the nc-Si, which simultaneously buildup an internal electric field from the nc-Si layer to the quartz surface. Elliman *et al.*[25] claimed that the charging effect can occur only in the oxide beneath the nc-Si/quartz interface with highest electron-hole recombination rate. As the pumping intensity is increased, the concentration of photoexcited holes captured in nc-Si and the surface electric field strength become higher, inevitably leading to the redshift of μ-PL from Si-implanted quartz. Longer annealing duration increases the concentration and diameter of nc-Si precipitated in quartz, enlarging the redshift of μ-PL (Fig. 3). Moreover, the μ-PL wavelength can also be redshifted by extending the illumination duration at same pumping intensity. The inset in Fig. 4 indicates a μ-PL wavelength shift of 2.5 nm after illuminating at 300 kW/cm^2 for 1 h. Note that the redshift does not occur under low-intensity condition. These results primarily explain the buildup of internal electric field due to the accumulation of surface and captured charges in Si-implanted quartz with buried nc-Si. The Stark effect induced by strong photoexcitation in thermally annealed, Si-implanted quartz that contains nc-Si is thus elucidated.

In conclusion, the pumping-intensity-dependent μ-PL from multirecipe Si-implanted quartz with 0.8% excess Si density has been characterized. After annealing for 1 h, the weak oxygen-bond and E'_δ defects at 410 and 550 nm are eliminated, while the nc-Si with a diameter of 4 nm contributes to a strong μ-PL at central wavelength of 724 nm. The nc-Si-related μ-PL reaches a maximum after annealing at 1100 °C for 3 h. As the pumping density is increased from 10 to 300 kW/cm^2, the μ-PL of the irradiative defects are associated with blueshift phenomena governed by bandfilling effect. In contrast, the μ-PL wavelength of Si-implanted quartz annealed for 3 h is significantly redshifted from 724 to 735 nm. This phenomenon cannot be well explained by either the substrate heating or the quantum-well coupling reported previously. The dominant mechanism is the anomalous quantum Stark effect induced by the built-in electric field from the buried nc-Si to the surface of Si-implanted quartz under high-intensity or long-term optical pumping. Such a redshift in μ-PL is strongly correlated with the positively charged nc-Si, which has been corroborated by the observations of gradually accumulated charges and enlarged electric field on the surface of Si-implanted quartz during high-power illumination.

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[1] H. S. Bae, T. G. Kim, C. N. Whang, S. Im, J. S. Yun, and J. H. Song, J. Appl. Phys. **91**, 4078 (2002).
[2] H. Nishikawa, R. Nakamura, and J. H. Stathis, Phys. Rev. B **60** 15910 (1999).
[3] P. W. Fry, I. E. Itskevich, D. J. Mowbray, M. S. Skolnick, J. J. Finley, J. A. Barker, E. P. O'Reilly, L. R. Wilson, I. A. Larkin, P. A. Maksym, M. Hopkinson, M. Al-Khafaji, J. P. R. David, A. G. Cullis, G. Hill, and J. C. Clark, Phys. Rev. Lett. **84**, 733 (2000).
[4] A. Patane, A. Levin, A. Polimeni, F. Schindler, P. C. Main, L. Eaves, and M. Henini, Appl. Phys. Lett. **77**, 2979 (2000).
[5] J. A. Barker and E. P. O'Reilly, Phys. Rev. B **61**, 13840 (2000).
[6] W. Sheng and J. P. Leburton, Phys. Rev. B **63**, 161301 (2001).
[7] W. Sheng and J. P. Leburton, Phys. Rev. Lett. **88**, 167401 (2002).
[8] M. Nirmal, B. O. Dabbousi, M. G. Bawendi, J. J. Macklin, J. K. Trautman, T. D. Harris, and L. E. Brus, Nature (London) **383**, 802 (1996).
[9] N. H. Bonadeo, J. Erland, D. Gammon, D. Park, D. S. Katzer, and D. G. Steel, Science **282**, 1473 (1996).
[10] S. Takeoka, M. Fujii, and S. Hayashi, Phys. Rev. B **62**, 16820 (2000).
[11] C. G. Ahn, T. S. Jang, K. H. Kim, Y. K. Kwon, and B. Kang, Jpn. J. Appl. Phys., Part 1 **42**, 2382 (2003).
[12] J. C. Cheang-Wong, A. Oliver, J. Roiz, J. M. Hernanaez, L. Rodriguez-Fernandez, J. G. Morales, and A. Crespo-Sosa, Nucl. Instrum. Methods Phys. Res. B **175-177**, 490 (2001).
[13] C. Itoh, T. Suzuki, and N. Itoh, Phys. Rev. B **41**, 3794 (1990).
[14] C. Itoh, K. Tanimura, N. Itoh, and M. Itoh, Phys. Rev. B **39**, 11183 (1989).
[15] G. Pacchioni, F. Frigoli, D. Ricci, and J. A. Weil, Phys. Rev. B **63**, 054102 (2000).
[16] C. Delerue, G. Allan, and M. Lannoo, Phys. Rev. B **48**, 11024 (1993).
[17] P. Mutti, G. Ghislotti, S. Bertoni, G. F. Cerofolini, L. Meda, E. Grilli, and M. Guzzi, Appl. Phys. Lett. **66**, 851 (1995).
[18] Y. P. Varshni, Physica (Amsterdam) **34**, 149 (1967).
[19] Z. Ma and K. Pierz, Surf. Sci. **511**, 57 (2002).
[20] M. Koch, R. Hellmann, G. Bastian, J. Feldmann, E. O. Gobel, and P. Dawson, Phys. Rev. B **51**, 13887 (1995).
[21] D. A. B. Miller, D. S. Chemla, T. C. Damen, A. C. Gossard, W. Wiegmann, T. H. Wood, and C. A. Burrus, Phys. Rev. Lett. **53**, 2173 (1984).
[22] I. Bar-Joseph, C. Kingshirn, D. A. B. Miller, D. S. Chemla, U. Koren, and B. I. Miller, Appl. Phys. Lett. **50**, 1010 (1987).
[23] K. Wakita, Y. Kawamura, Y. Yoshikuni, H. Asahi, and S. Uehara, IEEE J. Quantum Electron. **QE-22**, 1831 (1986).
[24] Y. Shi, J. H. Zhao, J. Sarathy, G. Olsen, and H. Lee, Electron. Lett. **33**, 248 (1997).
[25] S. H. Choi and R. G. Elliman, Appl. Phys. Lett. **74**, 3987 (1999).