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Time-resolved photoluminescence and capacitance–voltage analysis of the neutral vacancy defect in silicon implanted SiO_2 on silicon substrate

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The nanosecond photoluminescence (PL) dynamics of neutral oxygen vacancy (NOV) defects at 410–460 nm, and less pronounced nanocrystallite Si precursor (E'_δ) defects at 520 nm in multi-energy silicon-ion-implanted SiO_2 ($SiO_2:Si^+$) are investigated. The density of NOV defects in as-implanted $SiO_2:Si^+$ of 8×10^{16} cm^{-3} (or 2.5×10^{16} cm^{-3} calculated from time-resolved PL) is determined by using capacitance-voltage measurement. After annealing at 1100 °C for 3 h, the NOV defects are completely activated with a concentration of 4.8×10^{17} cm^{-3} and a corresponding absorption cross section of 9×10^{-17} cm^2. The time-resolved PL lifetime of NOV defects in $SiO_2:Si^+$ is significantly shortened from 26 to 3.6 ns and these defects are fully activated after annealing for 3 h. Longer annealing time greatly attenuates the blue-green PL intensity and eliminates the NOV defects, whereas the PL intensity and concentration of E'_δ defects with lifetime of 20–50 ns increases by a factor of 2.

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Various defect-related blue-green photoluminescence (PL) from Si-implanted SiO_2 (Ref. 1) materials ($SiO_2:Si^+$) at 410–550 nm has been reported.[2] Identifying these irradiative defects in $SiO_2:Si^+$ film is very important for white-light emitting applications. In principle, Si^+ implantation introduces irradiated defects in SiO_2, such as the neutral oxygen vacancy (NOV) $[O_3\equiv Si—Si\equiv O_3]$ with PL at 410–460 nm,[2] and the E'_δ defect $[Si\uparrow Si—Si]$ with PL at 520–550 nm,[3] etc. The high-temperature annealing of $SiO_2:Si^+$ normally causes the quenching of defect-related PL and the generation of Si nanocrystals (*nc*-Si). Time-resolved PL (TRPL) was applied to determine the lifetime and rate of evolution of the concentrations of irradiative defects. Lopez *et al.* reported a lifetime of 55–70 μs for Si dangling-bond centers in $SiO_2:Si^+$ annealed at 1100 °C for 2 h.[4] Amorphous Si exhibited an absorption cross section of 1×10^{-17} cm^2 and a lifetime of 20 ps, respectively.[5] In particular, Garcia *et al.* characterized the wavelength-dependent TRPL lifetime of SiO_2 with embedded *nc*-Si, which ranges from 20 to 200 μs as the *nc*-Si size increases from 2.5 to 7 nm (associated with absorption cross sections from 1×10^{-16} to 1×10^{-15} cm^2). However, few reports have addressed the emission lifetime and concentration of the irradiative defects or their transient luminescent dynamics in $SiO_2:Si^+$. Only defect-dependent TRPL lifetime from 2.3 to 45 ns in oxygen-implanted SiO_2 has been discussed.[3] This work characterizes the category, the concentration and the lifetime of the main irradiative defect in a multi-recipe $SiO_2:Si^+$ with excess uniformly distributed Si density. The lifetimes and the concentrations of irradiative defects at various annealing periods are calculated from the capacitance-voltage ($C–V$) hysteresis curve and the TRPL plots. The absorption capture cross section of the NOV defects is determined and is compared with the value presented elsewhere.

A 500-nm-thick SiO_2 film was grown on a (100)-oriented *n*-type Si substrate with a resistivity of 4–7 Ω cm, by plasma enhanced chemical vapor deposition with flowing tetraethoxysilane fluence at 10 sccm and flowing O_2 at 200 sccm, under a pressure of 400 mTorr and a forward power of 150 W, respectively. The $SiO_2:Si^+$ samples were prepared by multi-energy implanting the SiO_2 film and almost flat excess Si (up to 1%) profile at a depth of between 100 and 500 nm below the surface of the sample is obtained (Fig. 1). The $SiO_2:Si^+$ samples were annealed in a quartz furnace using N_2 gas at 1100 °C that flowed from 0.5 to 5 h. The room-temperature continuous-wave PL (CWPL) of the $SiO_2:Si^+$ pumped by an He-Cd laser at a wavelength of 325 nm and a mean power intensity of 5 W/cm^2 was analyzed using a photon counting system. In

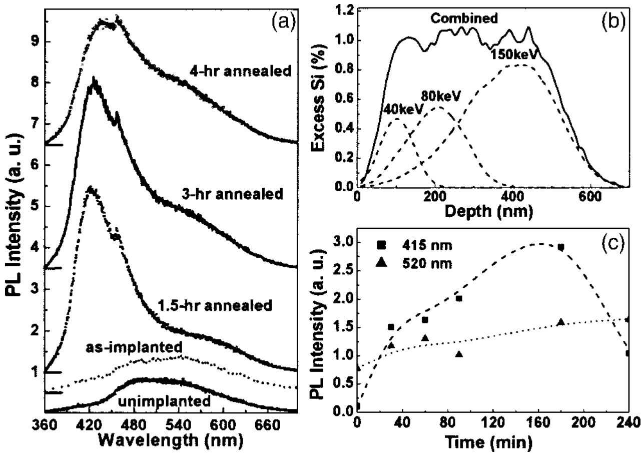

FIG. 1. (a) PL spectra of pure Si substrate, as-implanted $SiO_2:Si^+$, and $SiO_2:Si^+$ annealed at 1100 °C for 1.5, 3, and 4 h, respectively. (b) Excess Si-atom density as a function of implanting depth with dosages of 5×10^{15} ions/cm^2 at 40 keV, 1×10^{16} ions/cm^2 at 80 keV, and 2.5×10^{16} ions/cm^2 at 150 keV, and their combining effect. (c) Annealing-time dependent PL intensities at different wavelengths of 415 and 520 nm.

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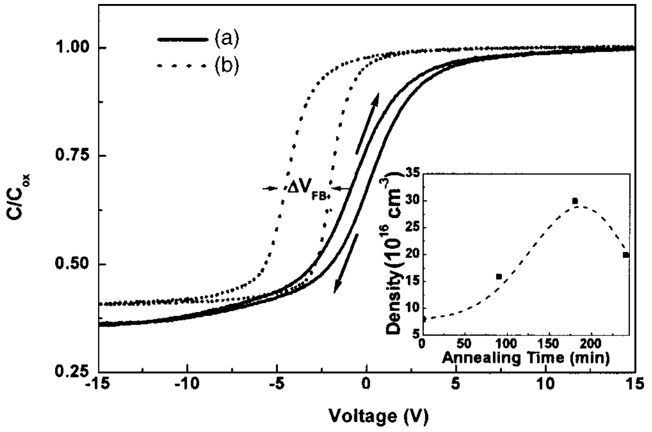

FIG. 2. *C-V* hysteresis measurement of MOS diode made on (a) as-implanted $SiO_2:Si^+$ and (b) $SiO_2:Si^+$ annealed at 1100 °C for 3 h. The inset figure shows the NOV defect concentration as a function of annealing time obtained from *C-V* analysis.

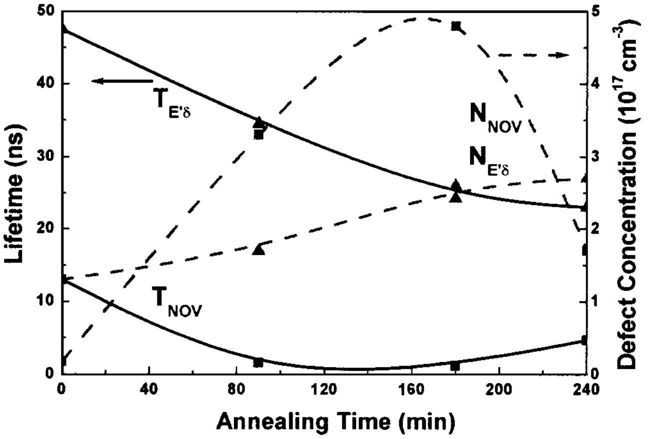

FIG. 4. TRPL lifetime and concentrations of NOV and E'_δ defects in $SiO_2:Si^+$ at different annealing times.

the TRPL experiment, the $SiO_2:Si^+$ sample was pumped using a subnanosecond flash lamp at a wavelength of 325 nm and a repetition rate of 40 kHz. It was analyzed using a time-correlated single-photon counting system (Edinburgh Instruments, Model FL920) at a wavelength of 410 nm. The lifetime (τ_n) and concentration (N_n) of defects could be determined from the deconvoluted TRPL plot. The $C-V$ analysis of an $Al/SiO_2:Si^+/n$-Si/Al metal-oxide-semiconductor (MOS) diode with an electrode area of about 1.26×10^{-3} cm^2 was conducted using a $C-V$ meter (Hewlett-Packard, 4280A) at a modulation frequency of 1 MHz to verify the concentration of defects in $SiO_2:Si^+$. The hysteresis $C-V$ curve is measured between +15 and −15 V at a stepping rate of 0.05 V/s. The density of hole-trapped defects in $SiO_2:Si^+$ (N_{NOV}) is determined using the equation $N_{\mathrm{NOV}} = -\Delta V_{\mathrm{FB}} C_{\mathrm{OX}}/e$, where C_{ox} is the capacitance of $SiO_2:Si^+$ in the accumulation regime, and ΔV_{FB} is the shift in flatband voltage obtained from the hysteresis $C-V$ curve of the $SiO_2:Si^+$ MOS diode.

The PL spectra demonstrate that the intensities of the near-infrared PL peaks associated with *nc*-Si at 820–850 nm are much lower than those from the irradiative defects under all processing conditions. The displacement of oxygen from a normal SiO_2 site generates neutral oxygen vacancies instead of dense Si interstitials, which remain in SiO_2 following Si implantation,[6,7] and the oxygen interstitials (the precursors for the weak oxygen bond defects) are generated concurrently. This reaction can be described as $O_3{\equiv}Si{-}O{-}Si{\equiv}O_3 \rightarrow O_3{\equiv}Si{-}Si{\equiv}O_3 + O_{\mathrm{interstitial}}$. Therefore, annealing for 1.5–3 h greatly increases the CWPL of $SiO_2:Si^+$ at 410–460 nm. This enhancement is not observed for the pure Si substrate and is relatively weak in as-implanted $SiO_2:Si^+$ (see Fig. 1). Such a strong blue-green emission is caused mainly by the activation of dense irradiative NOV defects in $SiO_2:Si^+$, which is generated by physically bombarding the SiO_2 using such as the ion-implanting process. The luminescence in this band is thus attributed to the transition between the ground state (singlet) and the elevated state (triplet) of the NOV defect.[2,6] The PL intensity is increased by more than one order of magnitude, because of the full activation of the NOV defects during 3 h annealing. The strongest PL peaks at 410–460 nm with a linewidth of 35–50 nm are very similar to those obtained by Nishikawa, Nakamura, and Stathis.[3] Similar results were also obtained from the Si-implanted SiO_2 grown by thermal oxidation ($2-3 \times 10^{17}$ cm^{-2}, 80–190 keV),[1] Ge-implanted SiO_2 (5×10^{15} cm^{-2}, 80 keV)[2] and Ir^{2+}-implanted silica glass ($0.6-7 \times 10^{16}$ cm^{-2}, 2 MeV).[8] However, these PL peaks were rarely obtained from other Si-rich SiO_2 samples prepared without applying ion-implantation methods.

After annealing for 1 h, the density of NOV defects greatly exceeds that in as-implanted samples. However, the rate of increase in the NOV defect is reduced. A notable stabilization of the defects thermally activated after 2 h annealing is observed (Fig. 1). However, a longer annealing process (>4 h) only results in the abrupt decay of both the CWPL intensities and the NOV defect density. As the annealing time is increased to 4 h, the decay of NOV defects is greater than that of other defects—the E'_δ centers with a PL of 520 nm formatted after annealing. The E'_δ center is a small Si cluster that is regarded as a precursor of *nc*-Si in SiO_2; its PL intensity grows slowly and linearly even following a 4 h annealing. These results reveal that the promotion in defect-related CWPL is related to the complete activation of NOV defects in the multi-recipe $SiO_2:Si^+$ annealed for up to 3 h, while the optimal annealing temperature and anneal-

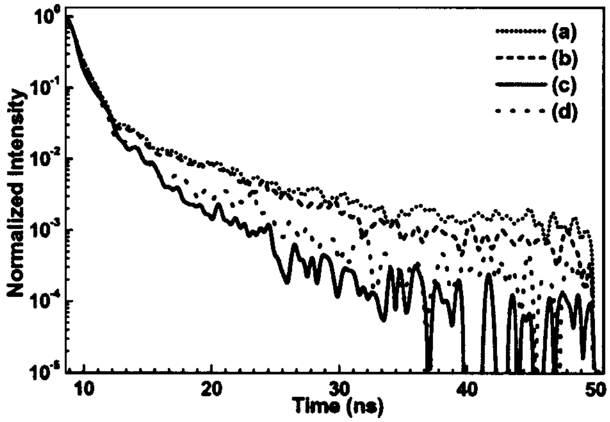

FIG. 3. Normalized TRPL spectra of $SiO_2:Si^+$ samples at (a) as-implanted condition, or annealed at 1100 °C for (b) 1.5 h, (c) 3 h and (d) 4 h.

TABLE I. Lifetime, cross section and concentration of NOV defects in $SiO_2:Si^+$ before (as implanted) and after annealing for 1.5, 3, and 4 h.

		As implanted	1.5 h	3 h	4 h
τ_{NOV}	(ns)	25.9	4.1	3.6	5.1
σ_{NOV}	(cm^2)	1.5×10^{-16}	5.2×10^{-17}	8.0×10^{-17}	1.5×10^{-17}
N_{NOV}	(cm^{-3})	2.5×10^{16}	3.3×10^{17}	4.8×10^{17}	1.7×10^{17}

ing time of 1350 °C and 8 h for activating the same defects in $Si:O^+$ are somewhat higher.[3] The observations herein also reveal that defect-related CWPL is initiated much more quickly than *nc*-Si dependent PL in $SiO_2:Si^+$. The CWPL intensity ratio among as-implanted, 1.5 h annealed, 3 h annealed and 4 h annealed $SiO_2:Si^+$ samples, $P_{\text{as-imp}}:P_{1.5\text{ h}}:P_{3\text{ h}}:P_{4\text{ h}}$, is 1:20:28:10, respectively. In contrast, the E'_δ-related PL intensity only doubles after 4 h annealing.

The formation of both paramagnetic E' centers ($O_3\equiv Si\cdot{}^+Si\equiv O_3$) and diamagnetic NOV defects has also been observed in most ion-implanted or radiation-damaged SiO_2. The oxygen vacancy is the precursor to the formation of the E' center,[9] while a hole trapped at the site of the oxygen vacancy forms the E' center (a positively charged oxygen vacancy).[10,11] That is, $O_3\equiv Si—Si\equiv O_3+h^+\rightarrow O_3\equiv Si\cdot{}^+Si\equiv O_3$, where h^+ denotes the trapped hole state. Hole trapping yields a positively charged NOV defect ($O_3\equiv Si\cdot{}^+Si\equiv O_3$), or the E' center in $SiO_2:Si^+$ can induce a space charge effect, which inevitably leads to the clear hysteresis in the *C-V* response of a MOS diode made on $SiO_2:Si^+$ (see Fig. 2). For example, the as-implanted $SiO_2:Si^+$ exhibits a flatband voltage shift (ΔV_{FB}) of −0.89 V corresponding to a NOV defect concentration of 8×10^{16} cm^{-3}. Fitting the TRPL plots shown in Fig. 3 demonstrates that the lifetime of the NOV defects is shortened from 25.9 to 3.6 ns as the annealing time is increased to 3 h. As the annealing time is increased further to 4 h, the TRPL lifetime is slightly lengthened to 5.1 ns. The TRPL lifetime of the E'_δ centers decreases (from 47.5 to 23 ns) more slowly with annealing time. This result is consistent with the slow formation of E'_δ centers (the *nc*-Si precursor) in $SiO_2:Si^+$. The slowly varied lifetime and concentration of E'_δ defects also indicate that the excess density of Si does not suffice for the efficient precipitation of dense *nc*-Si in the SiO_2 matrix.

Figure 4 plots the carrier lifetimes and corresponding concentrations of NOV and E'_δ defects as a function of annealing time. The lifetime ratio of the NOV (τ_{NOV}) in as-implanted, 1.5 h implanted, 3 h annealed and 4 h annealed $SiO_2:Si^+$ samples, $\tau_{\text{as-imp}}:\tau_{1.5\text{-h}}:\tau_{3\text{-h}}:\tau_{4\text{-h}}$, is about 1:0.16:0.14:0.2. According to the absorption cross section of the NOV defects of $\sigma_{NOV}=8\times10^{-17}$ cm^2 estimated by Nishikawa *et al.*,[10] the NOV defect concentration of $SiO_2:Si^+$ annealed for 3 h has increased from 2.5×10^{16} to 4.8×10^{17} cm^{-3} (Table I). The difference between the calculated NOV defect concentrations obtained by *C-V* and TRPL analyses is less than one order of magnitude. The absorption cross section ($\sim1\times10^{-17}$ cm^{-2}) extrapolated from the experimental data presented by Garcia *et al.*[12] reveals that the E'_δ defect concentration increases from 1.3×10^{17} to 2.6×10^{17} cm^{-3} (as determined by TRPL analysis). The calculated lifetimes of the E'_δ defect of size <0.8 nm, ranging from 23 to 47.5 ns, are much smaller than all those reported for large-scale *nc*-Si (>2.5 nm). Four hours of annealing reduced the density of NOV defects to 1.7×10^{17} cm^{-3}, but left the concentrations of the E'_δ defects at 2.7×10^{17} cm^{-3}.

In conclusion, the categories, concentrations and lifetimes of the two principle defects in multi-energy silicon-ion-implanted $SiO_2:Si^+$ before and after annealing at 1100 °C were characterized. PL at 410-460 and 520 nm is associated with the neutral oxygen vacancies (NOV) and the *nc*-Si precursors (E'_δ), respectively. A longer annealing eliminates a significant number of NOV defects, but the slow increase in the density of the E'_δ defects persists. The NOV defect concentration is found to rise from 2.5×10^{16} to 4.8×10^{17} cm^{-3} during 3 h annealing; the data obtained from the *C-V* analysis agree quite well with those obtained by TRPL analysis. This result is consistent with the CWPL results, which reveal that 3 h annealing increases the intensity by one order of magnitude. In contrast, the decrease in the lifetime of the E'_δ-defect-dependent TRPL is moderate (from 47.5 to 23 ns).

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