Photoluminescence response of ion-implanted silicon

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The photoluminescence intensity from ion-implanted silicon can be quenched by the radiation damage implicit in the implantation. Annealing is then required before the intensity of the luminescence from a defect center is approximately proportional to the concentration of that center. Data from positron annihilation and photoluminescence experiments establish that severe quenching of the luminescence occurs when the mean separation of the small vacancy clusters is less than ~30 atomic spacings, and the authors map out where, in the annealing and implantation phase space, the luminescence intensity is expected to be approximately proportional to the concentration of the optical centers. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2378402]

The increasing interest in defect engineering for silicon devices[1,2] emphasizes the need to understand the evolution of the radiation damage produced by ion implantation. In Si, the oscillator strengths of optical transitions are typically very low, for example, with radiative decay times of over 120 μs for the *X* line used later in this work.[3] Combined with the small thickness of the implanted zone (a few micrometers here), the defect-induced optical absorption is usually too weak to measure in the samples. Photoluminescence (PL) is another way of investigating damage defects. Very high spectral resolution is possible with PL from ion-implanted crystalline silicon,[4] and the resolution is only slightly degraded by the MeV Si implants used in this work.[5] Consequently, PL spectra are highly characteristic of the species of defects produced by the implant. It would be very convenient if the intensity of each band was proportional to the concentration of the corresponding defect, so that, for example, the production and destruction statistics of particular defects could be measured. Unfortunately, the intensity of the PL is reduced by nonradiative processes as the level of damage, produced by the implant, increases with the dose. Conversely, the intensity is increased by annealing out the nonradiative damage centers. As an example of the problem, Fig. 2 of Ref. 6 shows that the *W* luminescence *increases* as crystal's surface is etched for high Si-implant doses of 10^{14} and 10^{15} cm^{-2}, but *decreases* on etching samples with a lower dose of 10^{13} cm^{-2}. The results do not immediately give the distributions of the *W* centers without considering the nonradiative processes.

Here we map out the conditions when the PL intensity is expected to be approximately proportional to the concentration of the center producing it. We consider implantation by Si ions, so that no impurities are introduced. The key assumption made in this work is that the intensity of the PL from an intrinsic center is proportional to the concentration of that center in the dose range where there is a monotonic increase in the intensity with increasing implant dose. (The concentration of an *extrinsic* damage center would be expected to be proportional to the intensity of its PL in the same range.) PL has previously been used to measure the concentrations of centers using a variety of methods: low excitation power,[7] or high power to saturate the PL,[8] and using the measured intensity of the PL (Ref. 9) or the intensity relative to an intrinsic signal.[10] Usually excitation has been by above-band-gap excitation,[11] but bulk excitation has also been used for homogeneous samples.[12] We have excited the samples with 514 nm light from an Ar^+ laser, which is absorbed with a $1/e$ depth of 1 μm, less than the ion implantation depth of 2–3 μm for Si^+-implant energies of 3–4 MeV used here. The laser power was in the range in which the PL intensity increased monotonically with the power. In this case, some (unknown) fraction of the PL centers is activated. The PL intensity is proportional to the concentration in a set of samples if the same fraction of centers luminescences in all the samples. This criterion may be checked by seeing if the PL intensity from a dopant (e.g., boron) in implanted samples is the same as in an undamaged reference sample. Another check is to see if the PL of an implantation center, such as the *X* center, increases in a series of samples with the same dependence on dose as the known concentration of the center ($[X] \propto \text{dose}^{0.7}$, Ref. 13). We note that the concentrations of carbon-related centers have been successfully measured by using the intensity of PL for fixed experimental conditions when there have been larger mismatches than here of the defect and excitation depth profiles.[9] The implant depth is accessible by positron annihilation measurements, which probe vacancy clusters and allow us to establish a very simple empirical criterion to determine when the nonradiative processes become dominant.

For this study, float-zone *p*-type (001) silicon wafers, doped with 2×10^{15} cm^{-3} boron, were implanted with 3 or 4 MeV Si^{2+} ions at room temperature, with the samples tilted by 7° off axis to avoid channeling of the implant ions. Doses in the range of $\sim10^{8}$–10^{14} cm^{-2} have been used. For PL measurements, samples were mounted in a drip-feed liquid helium cryostat and excited in a 2 mm diameter spot by a

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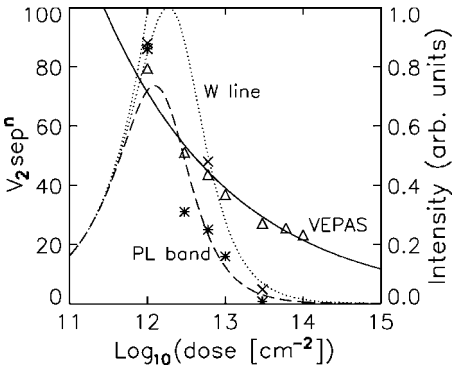

FIG. 1. Triangles show the mean separation $\bar{d}$ in atomic bond lengths of the equivalent divacancies, measured in the first 2 μm of the sample by VEPAS, as a function of 4 MeV implant dose, in the as-implanted state. The full line shows $\bar{d}$ in bond lengths (left scale) corresponding to fractional concentrations of $[V_2]=10^{-15}\phi^{0.79}$. The measured intensities of the *W* line (crosses, dotted line) and of the integrated luminescence between 800 and 1100 meV (stars, broken line) are in arbitrary units, scaled to convenient sizes for plotting. The uncertainty in each point is about ±25%. The lines are calculated with the energy-transfer model. With no energy transfer the *W* intensity would increase as shown by the rising dotted curve to a limit determined by the excitation power.

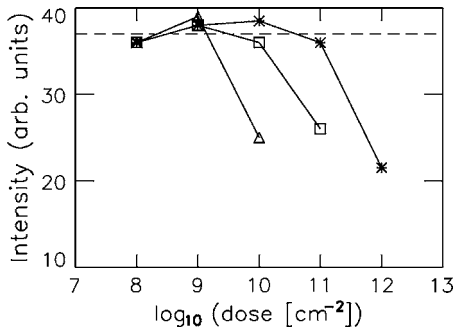

FIG. 2. Integrated intensities (linear scale) of the boron PL, from 1080 to 1100 meV, as functions of 3 MeV implant dose. Samples have been annealed for 30 min at 300 °C (triangles), 400 °C (squares), and 500 °C (stars). The solid lines are guides for the eyes. With no effect from the implantation, the intensities would all lie on the broken line. The uncertainty is ~10%.

400 mW, 514 nm argon laser. PL was detected by a Bomen DA8 Fourier transform spectrometer fitted with a germanium detector. A fixed experimental setup and the same sample temperature were used for each set of measurements. Spectra were further corrected to standard optical conditions by the use of a standard sample. Variable-energy positron annihilation spectroscopy (VEPAS) data, taken as in Ref. 2, have been analyzed by the VEPFIT program[14] to give the concentration of vacancies.

First, we consider as-implanted material, in which the well-known *W* luminescence line is readily observable. The *W* optical center is a trigonal complex[13] created in the small damage clusters produced by the implantation.[15] It has been ascribed to a self-interstitial cluster[16] that also produces the *B*5 paramagnetic resonance signal.[17] At sufficiently small doses, the PL intensity is expected to be proportional to the dose, and for doses $\sim 10^8$ to $\sim 10^{10}$ cm^{-2}, the integrated PL intensity of the *W* zero-phonon line at 1018 meV increased in proportion to the dose. However, at doses larger than $\sim 10^{12}$ cm^{-2}, the *W* intensity decreases with implantation dose, as does the total luminescence integrated between 800 and 1100 meV, Fig. 1. Even before annealing, we expect vacancies to have aggregated into divacancies or very small vacancy clusters. All small vacancy aggregates, with the possible exception of some fully bonded configurations,[18,19] are believed to be nonradiative. The concentration of vacancy defects in the first 2 μm of the sample, where most of the PL originates in these samples, has been determined by VEPAS, assuming that they are divacancies. The concentration $[V_2]$ of the equivalent divacancies, expressed as a fraction of the Si atomic sites, increases in this higher ion dose range as $[V_2]=10^{-15}\phi^{0.79}$, where the dose ϕ is in cm^{-2}. Figure 1 shows that the PL intensity decreases when the mean separation, $\bar{d}=[V_2]^{-1/3}$, of the equivalent divacancies becomes less than ~80 atomic spacings, and that essentially complete quenching occurs for $\bar{d} \leqslant 30$ atomic spacings. The data *do not* determine the quenching mechanism. The lines in Fig. 1 are calculated for illustration only, and assume that quenching occurs by energy transfer from the luminescent centers to the vacancy aggregates. Since there is no spectral overlap of the luminescence and the divacancy absorption band, the dipole-quadrupole coupling mechanism is a possible energy transfer mechanism, with a transfer probability that is inversely proportional to the eighth power of the separation *r* between the luminescent center and the nonradiative trap.[20] The luminescence from a center is quenched by a factor $\tau_n/(\tau_n+\tau_r)$, where τ_r and τ_n are the radiative and nonradiative lifetimes for the center. For simplicity we assume that an isolated center is 100% luminescent, so that all the nonluminescence processes are caused by energy transfer with $\tau_n \propto (\bar{d})^8$. The concentration of the luminescence centers is assumed to be proportional to $\phi^{0.79}$ as for $[V_2]$. The intensity is then $a\phi^{0.79}\tau_n/(\tau_n+\tau_r)$, with $\tau_r/\tau_n=b(\bar{d})^{-8}$. The curves in Fig. 1 are calculated with $b\sim 10^{14}$ for $\bar{d}$ in bond lengths. If there was no energy transfer, the *W* intensity would increase (to the limit allowed by the excitation density) as shown by the rising dotted line: quenching is predicted to be negligible below $\phi=10^{11}$ cm^{-2}, as observed experimentally above. In reality the problem is complicated by the variations with depth of the species and concentrations of the defects, and the possible multiple causes for loss of luminescence. However, the experimental data show that, as implanted, the luminescence is severely quenched when the nonradiative centers (small vacancy clusters) are closer than about 30 atomic spacings.

With annealing, the concentration of defects is reduced. Divacancies are expected to anneal and/or agglomerate,[21] depending on the annealing history. To illustrate the effect on the PL, we use the emission from the original boron dopant. The effect on the boron of the implantation damage and annealing depends on the concentration of boron[22] and the details are uncertain.[23] However, when the implantation and annealing have produced little change in the PL of the substitutional boron, and have created neither competitive traps for the excitation nor quenching defects, the PL will have the same intensity in all the samples, shown by the broken line in Fig. 2. Deviations from this value start at doses of 10^{10} cm^{-2} after annealing for 30 min at 300 °C, to 10^{12} cm^{-2} for 500 °C, defining lower limits for the safe doses for proportionality of the PL.

Data gathered from a variety of PL centers for samples implanted with doses of $\sim 10^8$–10^{14} cm^{-2} and annealed for 30 min from room temperature to 800 °C are gathered in

TABLE I. Samples where the low-temperature PL intensity is believed to be proportional to the concentration of the optical centers are shown by ⋆, those where there is not expected to be a correlation by ×, and borderline cases by +. Samples where the PL signal is below the noise level of our system are shown by −. Samples implanted at 4 MeV and annealed for 30 min at each temperature.

Anneal temp. (°C)	Implant dose (cm^{-2})						
	10^8	10^9	10^{10}	10^{11}	10^{12}	10^{13}	10^{14}
800	−	−	−	−	−	⋆	⋆
700	−	−	−	−	⋆	⋆	⋆
600	−	−	−	−	⋆	⋆	+
500	−	⋆	⋆	⋆	+	×	×
400	−	⋆	⋆	+	×	×	×
300	⋆	⋆	+	×	×	×	×
200	⋆	⋆	+	×	×	×	×
100	⋆	⋆	+	×	×	×	×
As imp.	⋆	⋆	+	×	×	×	×

Table I. Here we map out the implantation and annealing conditions in which the implantation-damage centers give luminescence proportional to their expected concentrations. We confirm the table by referring to the data in the literature. First, Fig. 2 of Ref. 24 shows data for other transitions in the same material as used for Fig. 2 above. From VEPAS, after annealing at 600 °C, the vacancy concentration in the depth of 0–2 μm is negligible, and between 2 and 3 μm the vacancies have survived as slightly larger clusters of, on average, three to four vacancies,[24] with a concentration that increases with the dose ϕ as $[V_{3.5}]=c\phi^{2.6}$ over the range $\phi=10^{13}-10^{14}$ cm^{-2}, where $c\sim 2.5\times 10^{-41}$ when ϕ is in cm^{-2} and $[V_{3.5}]$ is per atom. We consider three PL systems: the 1062 meV zero-phonon line, believed to occur at a vacancy cluster in the remaining damaged region, the 997 meV zero-phonon line, believed to occur at a self-interstitial cluster and again with a spatially deep profile, and the broad band of PL between 850 and 1100 meV, much of which remains when the surface of 2 μm of the sample is removed.[24] In each case, the PL increases monotonically to $\phi\sim 6\times 10^{13}$ cm^{-2}, and then begins to be quenched. At this dose the $V_{3.5}$ clusters have a mean separation of $\bar{d}\sim 40$ atoms, close to the condition for quenching in the as-implanted state. Again, published data[25] for weakly *n*-type silicon that had been implanted with 5.6 MeV Si^+ show that the *X* line, an interstitial cluster,[16] is also quenched for doses greater than $\sim 10^{13}$ cm^{-2} after annealing to 525 °C, in agreement with the table. Implanting over 10^{13} cm^{-2} Si ions at 265 °C is, from the table, not in the proportional range, explaining the results of Giri *et al.*[6] quoted earlier.

In summary, we have estimated when the photoluminescence yield is expected to be approximately proportional to the concentration of the optical centers. Following room-temperature implantation, the luminescence is severely quenched when the equivalent divacancies have mean separations of $\bar{d}<30$ atomic spacings. The dose at which that value occurs may be calculated for many ions and energies by using the approximate universal expression of Ref. 26, that $\bar{d}\sim 1.2\times 10^4/(f\phi)^{0.21}$, where $f\phi$ is the actual dose multiplied by a factor f that is closely given by the vacancies per ion per angström predicted by TRIM at half the ion range.[27] For example, $f=0.1$ for 4 MeV Si^+ ions, and $\bar{d}=30$ would occur at $\phi=3\times 10^{13}$ cm^{-2}, as observed in Fig. 1. Partial annealing out of the damage is required before the luminescence intensity is approximately proportional to the concentration of the center, but at 600 °C, when divacancies have aggregated to very small clusters, quenching starts at a similar value of $\bar{d}$ for the separation of the clusters. The data of Table I are for MeV Si implants, with single anneals of 30 min at each annealing temperature, and excitation by visible radiation. Variations on these conditions must be expected to change the data. Among the simplifications we have used is the mean defect separation, which masks events occurring as a result of the proximity of defects within one damage trail. Nevertheless, the table provides an initial guide to when the PL intensity is proportional to the concentrations of the centers.

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