Evidence for small interstitial clusters as the origin of photoluminescence *W* band in ion-implanted silicon

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We have investigated the origin of the photoluminescence (PL) *W* band in ion-implanted Si by studying the temperature evolution and depth profile of the related defects. Evolution of the PL spectra induced by postimplant annealing is correlated to a transition of small interstitial clusters to extended {311} defects in self-ion-implanted Si. Growth of *W* band intensity after step-by-step removal of the damaged layer rules out the involvement of vacancy-related defects in the formation of the *W* center and establishes that migrated and clustered interstitials give rise to an intense *W* band. The annealing behavior and the thermally activated growth of the *W* center suggest the involvement of small interstitial clusters, larger than di-interstitial. In accordance with recent results based on simulational studies, we argue that the *W* center consists of tri-interstitial clusters of silicon. [DOI: 10.1063/1.1339253]

Ion implantation or irradiation of silicon with high energetic particles produces an intense and sharp photoluminescence *W* band or I_1 band with a zero-phonon line at 1018 meV.[1] The origin of the *W* band has been believed to be related to either self-interstitials or to vacancies created by the collision of the incident particles, while the exact microscopic structure of the defect is still under debate.[2,3] Several proposals have been suggested as to the structure of this center, which involves pentavacancy or tetravacancy cluster,[1] ⟨111⟩ silicon split-interstitials,[4] and divacancies.[2] It is known that slightly modified luminescence bands are introduced in Si by bombardment with inert gas ions and, from an *ab initio* calculation, the *W* band was argued to originate from neutral divacancies.[2] However, Davies *et al.* carried out a comprehensive study on the uniaxial stress and magnetic perturbation of this luminescence band and showed that the center possesses a trigonal symmetry and it incorporates silicon self-interstitials.[4] Subsequently, various other experiments have supported the interstitial nature of the *W* center.[5] However, more direct evidence about the exact structure of the *W* center has yet to emerge.

In contrast to the wealth of information available on the growth of extended defects, very little is known about the first stages of the aggregation process of self-interstitials and their subsequent evolution to various rod-like and chain-like defects through intermediate defect configurations (IDCs). In recent work, Coffa *et al.*[6] investigated the transition of small interstitial clusters to extended {311} defects in self-ion-implanted silicon. The annealing characteristic of the *W* center shows that the defect is stable up to ~535 K,[5] and several studies indicate that the center does not involve a large cluster. Hence, a study on the growth and evolution of the *W* center with postimplant annealing up to the temperature where extended defects are formed is expected to shed light on the structure of this center.

In this letter, with a view to understanding the origin of the photoluminescence *W* band, we have studied the growth and evolution of the *W* band in silicon with implantation at elevated temperatures and postimplantation annealing. By careful monitoring of the intensity of the PL signal after step-by-step removal of damaged Si layers, we show that the *W* band related defects are located in regions rich in self-interstitials atoms. It is shown that the formation of the *W* center is thermally activated, and we argue that the *W* center is a tri-interstitial cluster of silicon.

Epitaxially grown *n*-type Si wafers were implanted with 80 keV ions of Si^+, Al^+, B^+, and P^+. To study the depth profile of the *W* center, one set of samples was implanted at 265 °C (the temperature at which the *W* band intensity is known to achieve a maximum) with various fluences in the range of 1×10^{13}–$1\times10^{15}\,cm^{-2}$. The implanted surface of these samples was removed up to a depth of 1 μm by sputter etching in several steps. Another set of samples was implanted with low-fluence ($5\times10^{12}\,cm^{-2}$) Si^+ ions at various elevated temperatures to study the growth kinetics of the *W* band. Some samples were implanted with 1.2 MeV Si^+ ions with fluence of $5\times10^{13}\,cm^{-2}$ and postimplant annealed at 600, 680, or 750 °C to study the evolution of the PL spectra. Some of the keV-implanted samples were postannealed under flowing N_2 at various temperatures in the range of 150–750 °C. PL measurements were performed at 17 K using the 488 nm line of an argon laser.

The *W* band PL signal was detected in all the samples implanted at room temperature with different ions at a flu-

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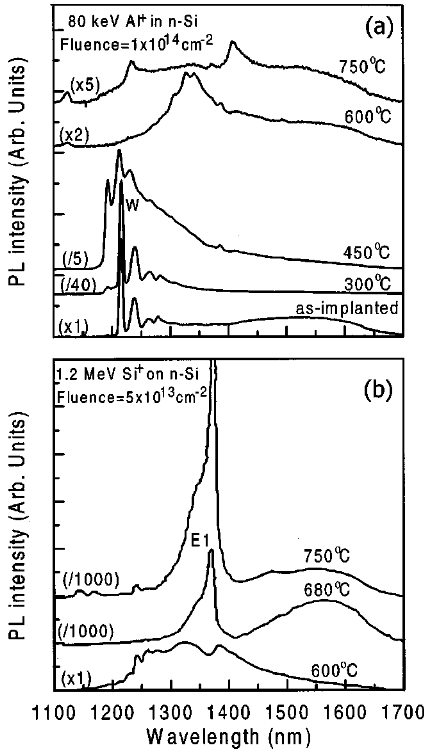

FIG. 1. (a) PL spectra recorded at 17 K on n-Si implanted with 80 keV Al^{+} ions followed by postimplantation annealing at various temperatures up to 750 °C. The spectra are scaled appropriately and shifted upward vertically for clarity. (b) PL spectra for n-type Si implanted with 1.2 MeV Si^{+} ions at a fluence $5\times10^{13}\,cm^{-2}$ and subsequently annealed at 600, 680, and 750 °C.

ence of $1\times10^{14}\,cm^{-2}$, indicating that the defect does not incorporate any impurity and is related to intrinsic defects. Figure 1 shows a set of PL spectra measured at 17 K on 80 keV Al^{+} implanted n-type Si subjected to postimplantation annealing at various temperatures. The respective scaling factor used for plotting is mentioned on the left side of each curve and it illustrates the large change in PL intensity with annealing. The sharp peak at 1220 nm corresponds to the well-known W band and an associated band at ~1244 nm appears to be a phonon replica of the W band, since it is present in a fixed proportion to the W band intensity for differently treated samples. From Fig. 1(a) it is seen that the W line intensity attains a maximum for 300 °C annealed samples and for samples annealed at 450 °C a dramatic change is seen in the PL spectra, it consists of a broad peak with small features at 1205 and 1218 nm. Upon annealing the samples at higher temperatures (600 and 750 °C), a broad featureless spectrum with very low intensity is obtained and it may be related to defect-impurity complexes formed as a result of irradiation.[1]

The increase in intensity of the W band with annealing is indicative of thermally activated growth of the center.[5] Figure 1(b) shows the PL spectra for postimplantation annealed (600, 680, and 750 °C) samples implanted with 1.2 MeV Si^{+} ions. The as-implanted Si shows the characteristic W band in the PL spectra (not shown). Annealing at 600 °C for 30 min results in a broad peak related to small clusters of defects, whereas a distinct and sharp PL peak ($E1$) appears after annealing at 680 °C for 75 min. The broad feature of the spectra in the 600 °C annealed samples is common to both Al- and Si-implanted Si, as seen in Figs. 1(a) and 1(b). However, in case of self-ion implantation and subsequent annealing at 680 or 750 °C, it results in a PL band with a distinct peak at 1376 nm corresponding to {311} defects.[6] This implies that in contrast to self-ion implantation, Al^{+} implantation does not produce a sufficient number of self interstitials for the formation of large agglomerates and for their eventual growth to extended {311} defects. Thus, the present results strongly suggest that small interstitial clusters are involved in the formation of the W center and that they evolve into bigger clusters or an extended (110) chain of interstitials when aided by supersaturation of interstitials.

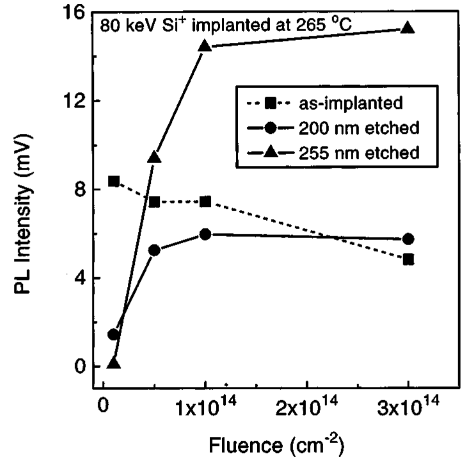

FIG. 2. Intensity of W-band PL as a function of Si^{+} ion fluence in as-implanted (at 265 °C) silicon, after removal of 200 and 255 nm by sputter etching.

Figure 2 shows the intensity of the PL spectra as a function of fluence for samples implanted at elevated temperature (265 °C). In the as-implanted samples, the W-band intensity monotonically decreases with fluence. In contrast, after removal of 200 nm of the top surface layer, the PL intensity increases with fluence initially and then saturates. The signal further increases steeply with fluence upon removal of an additional 55 nm from the surface, as shown in Fig. 2. These measurements were performed under identical experimental conditions. Note that no W band could be detected in sputtered unimplanted Si samples. A Monte Carlo calculation of the damage profile for 80 keV Si^{+} ions predicts that the vacancy profile and the implanted ions do not extend beyond a depth of 200 nm from the surface. An increase in the PL intensity with the successive removal of the damaged layer clearly indicates that the region directly modified by the ion beam does not contribute significantly to the W-band intensity. On the other hand, removal of the fully damaged region systematically enhances the W-band intensity with fluence, confirming that the W band arises from defects which have migrated deeper beyond the ion range profile. Monte Carlo calculations on damage profile and several experimental reports suggest that, due to ion implantation, the near-surface region is vacancy rich and the end-of-the-range region is interstitial rich,[7] especially for self-ion implantation. Rutherford backscattering channeling (RBS-C) analysis on this set of samples. This indicates that the peak region of the damage profile was completely removed by the sputter etching of 200 nm at the first step. Hence, it is quite clear that the migrated interstitial clusters are directly responsible for the W-band

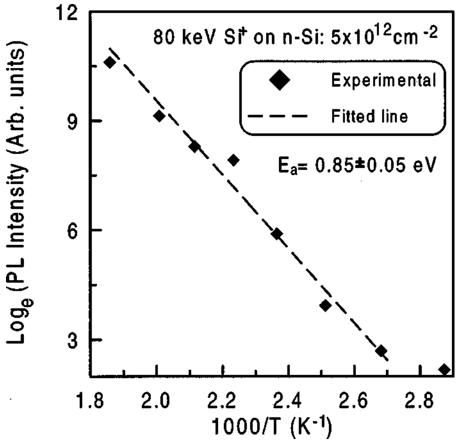

FIG. 3. *W*-band PL intensity as a function of the temperature of implantation for 80 keV Si^+ implanted Si at a fluence $5\times10^{12}\,cm^{-2}$, showing an Arrhenius relationship.

PL in implanted silicon. No *W*-band signal could be detected beyond a depth of $\sim$1 μm from the surface.

Figure 3 shows the PL intensity of the *W*-band zero-phonon line as a function of irradiation temperature. An exponential increase in intensity with temperature in the range of 100–265 °C is evident from the linearity of the plot and we derive an activation energy of 0.85 ± 0.05 eV for this temperature range. Our value is in excellent agreement with the work of Schultz *et al.*[5] This activation energy refers to agglomeration of the point defects and formation of the related defect clusters through a nucleation barrier. However, at the temperature of interest the V_2 defects are relatively unstable. Moreover, no increase in the concentration of the V_2 center with implantation temperature has been found in ion-irradiated Si,[8] in contrast to the marked increase in the *W*-band intensity. Hence, the possibility of V_2 being involved in the formation of the *W* center can be completely ruled out. Involvement of higher order vacancy aggregates is very unlikely, and this has been argued on the basis of the stress response of the *W* band.[4]

The *W* center is known to anneal above $\sim$265 °C, indicating that a relatively small cluster is involved in the structure. Various configurations of the small interstitial clusters (I_n) such as I_2, I_3, I_4, I_5, etc. have been proposed in the literature for silicon.[9] Recent studies using *ab initio* tight-binding molecular dynamics simulations show that the first magic number for stable aggregates is I_3,[9] and other configurations having nearest low binding energies were found for I_2 and I_4. I_2 anneals at $\sim$150 °C,[10] which is in contrast to the annealing behavior of the *W* center. Therefore, the possibility of I_2 as the source of the *W* band can be ruled out. On the other hand, higher order clusters are expected to have much higher annealing temperatures. For example, Benton *et al.*[11] reported the presence of electrically active interstitial clusters which were found in 600 °C annealed silicon. The typical dissociation energy of these clusters was higher than the dissociation energy reported for the *W* band,[5] and this value is much lower than the dissociation energy for extended {311} defects. Having ruled out the possibility of I_2 and large clusters as the source of the *W* center, the most probable source of the *W* center remains the I_3 cluster, considering it to be a stable cluster.[12] Our conclusion is strongly supported by recent results based on simulational studies. Coomer *et al.*[12] systematically argued that a tri-interstitial (I_3) defect may account for many of the fundamental properties of the *W* center reported in the literature. The lowest energy I_3 investigated by them possessed C_{3v} symmetry, in agreement with the symmetry of the *W* center.[4] The I_3 structure was closely related to the {311} defect structure proposed by Takeda.[13] Perturbation of the *W* band due to various noble gas ions observed experimentally was also accounted for by this model of I_3. Hence, these pieces of supporting evidence from the literature convince us to believe that I_3 clusters are, indeed, the origin of the photoluminescence *W* band.

In conclusion, from PL studies we have shown that small interstitial clusters are evolved to extended {311} defects when supersaturation of interstitials is present and the origin of the *W* band can be traced to small clusters of self-interstitials. The annealing behavior and the thermally activated growth of the *W* center also suggest the involvement of small interstitial clusters, ones larger than I_2 but smaller than IDCs directly responsible for the growth of {311} defects. Recent results from simulational studies strongly support our view that the *W* center consists of I_3 clusters of silicon.

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[1] See, for example, G. Davies, Phys. Rep. **176**, 83 (1989) and references therein.
[2] S. K. Estreicher, J. Weber, A. Derecski-Kovacs, and D. S. Marynick, Phys. Rev. B **55**, 5037 (1997).
[3] M. Nakamura, S. Nagai, Y. Aoki, and H. Naramoto, Appl. Phys. Lett. **72**, 1347 (1998).
[4] G. Davies, E. C. Lightowlers, and Z. E. Ciechanowsta, J. Phys. C **20**, 191 (1987).
[5] P. J. Schultz, T. D. Thompson, and R. G. Elliman, Appl. Phys. Lett. **60**, 59 (1992).
[6] S. Coffa, S. Libertino, and C. Spinella, Appl. Phys. Lett. **76**, 321 (2000).
[7] R. Kogler, A. Peeva, W. Anwand, G. Brauer, W. Skorupa, P. Werner, and U. Gösele, Appl. Phys. Lett. **75**, 1279 (1999).
[8] B. G. Svensson, C. Jagadish, A. Hallen, and J. Lalita, Phys. Rev. B **55**, 10498 (1997).
[9] M. Gharaibeh, S. K. Estreicher, and P. A. Fedders, Physica B **273–274**, 532 (1999).
[10] G. D. Watkins, in *Materials Science and Technology*, edited by W. Schroter (VCH, New York, 1991), Vol. 4, p. 107.
[11] J. L. Benton, S. Libertino, P. Kringoi, D. J. Eaglesham, J. M. Poate, and S. Coffa, J. Appl. Phys. **82**, 120 (1997).
[12] B. J. Coomer, J. P. Goss, R. Jones, S. Oberg, and P. R. Briddon, Physica B **273–274**, 505 (1999).
[13] S. Takeda, Jpn. J. Appl. Phys., Part 2 **30**, L639 (1991).