Identification by photoluminescence and positron annihilation of vacancy and interstitial intrinsic defects in ion-implanted silicon

R. Harding, G. Davies, J. Tan, P. G. Coleman, C. P. Burrows, and J. Wong-Leung

Citation: [Journal of Applied Physics](#) **100**, 073501 (2006); doi: 10.1063/1.2354332

View online: <http://dx.doi.org/10.1063/1.2354332>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jap/100/7?ver=pdfcov>

Published by the [AIP Publishing](#)

Re-register for Table of Content Alerts

Create a profile.

Sign up today!

Identification by photoluminescence and positron annihilation of vacancy and interstitial intrinsic defects in ion-implanted silicon

R. Harding, G. Davies,^{a)} and J. Tan

Department of Physics, King's College London, London WC2R 2LS, United Kingdom

P. G. Coleman and C. P. Burrows

Department of Physics, University of Bath, Bath BA2 7AY, United Kingdom

J. Wong-Leung

Department of Electronic Materials Engineering, The Australian National University, Canberra, Australian Capital Territory 0200, Australia

(Received 15 June 2006; accepted 26 June 2006; published online 2 October 2006)

Defect centers generated in crystalline silicon by MeV Si implants have been investigated by a combination of photoluminescence, variable-energy positron annihilation measurements, depth profiling by etching, annealing studies, and the dependence on impurities. The broad 935 meV photoluminescence band occurs at intrinsic interstitial complexes, the 835 meV band at small vacancy clusters, and the 1062 meV line at a low concentration of vacancy clusters which are possibly formed by aggregation of the 835 meV centers. © 2006 American Institute of Physics.

[DOI: [10.1063/1.2354332](https://doi.org/10.1063/1.2354332)]

I. INTRODUCTION

Despite extensive studies, we do not yet have a full understanding of the evolution of damage in ion-implanted crystalline silicon.¹ We report here on the interstitial/vacancy nature of luminescence centers created when silicon is implanted at room temperature with MeV Si⁺ ions and subsequently annealed. Because zero-phonon lines (zpls) observed by photoluminescence (PL) lines are narrower than 1 meV, even at implantation doses above 10^{14} cm⁻² (see, e.g., Fig. 1), PL can unambiguously monitor each specific defect.² Some PL centers have recently been associated with interstitial clusters,³ on the basis of their stability at 600 °C, well above the annealing temperature of vacancy defects measured by deep level transient spectroscopy (DLTS) on low-dose implanted samples.⁴ However, the annealing temperature of damage clusters depends on size⁴ and consequently may be a function of implantation dose. The behavior of PL centers and vacancies should be compared in similar samples. The damage associated with vacancies and interstitials should be distinguishable by its dependence on the depth profile⁵ and on the carbon content.⁶

In silicon, luminescent defects are typically observable at concentrations $\geq 10^{12}$ cm⁻³, although many defects—for example, the divacancy and other small vacancy aggregates—are not observable by PL because they are nonradiative.⁷ The depth profile of vacancies can be found using variable-energy positron annihilation spectroscopy (VEPAS). In VEPAS, the Doppler broadening of the annihilation gamma photon line around 511 eV is measured and represented by the positron parameter S , the central fraction of the line.⁸ S normally increases above its value in bulk silicon when positrons are trapped in vacancy clusters and

represents an average response over all neutral or negatively charged vacancy defects.⁸ Positron implantation energies are varied to obtain information on the depth distribution of the defects. To improve depth resolution, progressive controlled etching is employed.^{9,10} The program VEPFIT (Ref. 11) fits VEPAS data to obtain S and the positron diffusion length L for a chosen number of sample layers. The *average* number of vacancies N in clusters (V_N defects) and their concentration in these layers are estimated using values for S and L , together with the specific positron trapping rate, assumed

FIG. 1. PL spectra at 4.2 K for 6×10^{13} cm⁻² 4 MeV Si²⁺ implanted *p*-type “Topsil” silicon samples annealed for 30 min at 525 or 600 °C. Spectra displaced vertically for ease of view. Sharp dips between 870 and 920 meV are due to atmospheric water absorption. The relative intensities of the two spectra are not comparable in this figure.

^{a)}Author to whom correspondence should be addressed; electronic mail: gordon.davies@kcl.ac.uk

FIG. 2. PL and VEPAS response vs dose of 4 MeV Si^{2+} ions implanted in p -type "Topsil" silicon annealed for 30 min at 600 °C. The PL data are measured at 4.2 K in arbitrary units: triangles are integrated intensity in 970–1070 meV; circles are area of 997 meV zpl; squares are area of 1062 meV zpl. Filled diamonds show the VEPAS response, $[V_{3.5}]$ per atom, in 2.2–3.6 μm . The lines are fits to the data for VEPAS and for smaller PL doses.

here to be $5 \times 10^{14} \text{ N s}^{-1}$ for V_N . The limits on the concentration of neutral V_N traps for quantitative VEPAS measurements are $\sim 4 \times 10^{14} / \text{N cm}^{-3}$ to $7.5 \times 10^{18} / \text{N cm}^{-3}$,¹¹ the lower sensitivity limit is thus roughly two orders of magnitude greater than that of PL to luminescent defects.

II. EXPERIMENTAL PROCEDURE

Samples of Topsil p -type (001) silicon wafers were implanted with 4 MeV Si^{2+} ions at room temperature to doses of 10^{12} – 10^{14} cm^{-2} . In addition, edge-defined film-fed growth p -type silicon with carbon and oxygen concentrations of 2×10^{18} and $< 1 \times 10^{16} \text{ cm}^{-3}$, respectively, was implanted with 5.6 MeV Si^{3+} to a dose of 10^{14} cm^{-2} at room temperature. The samples were tilted by 7° off axis to avoid channeling of the implant ions. The projected ranges (R_p) for 4 and 5.6 MeV Si are ~ 2.7 and 3.3 μm , respectively.¹² Sample annealing was carried out for 30 min periods in a tubular oven under constant argon flow. Selected samples were etched in stages to remove from 0.5 to 3.6 μm of the sample surface, using the "CP-8" wet etch to produce a highly polished surface. The hydrogen concentration introduced during this type of etching is estimated¹³ to be $\leq 10^{14} \text{ cm}^{-3}$. Etch depths were measured by Talistep profilometry. PL was performed using Bomem DA8 Fourier transform and Spex dispersion spectrometers. Samples were immersed in liquid helium for measurements at 4.2 K and excited by a 400 mW, 514 nm argon laser.

PL spectra for samples implanted with 4 MeV Si ions to a dose of $6 \times 10^{13} \text{ cm}^{-2}$ after single-shot anneals at either 525 or 600 °C are shown in Fig. 1. All the spectral features below 1075 meV are related to ion-implantation damage. Figure 2 shows the PL intensity integrated between 970 and 1070 meV, the intensity of some individual PL centers, and the concentration of vacancy-type defects deduced from VEPAS, as a function of ion dose, for samples annealed at 600 °C for 30 min. The PL intensities are slightly superlinear (power ~ 1.3) in dose until saturation of the intensity starts to occur at the highest dose. VEPAS suggests that the vacancy clusters contain three to four vacancies on average at depths of 2–3 μm , whose concentration increases as (dose)^{2.6}.

FIG. 3. PL spectra at 4.2 K for $6 \times 10^{13} \text{ cm}^{-2}$ 4 MeV Si^{2+} implanted p -type "Topsil" silicon sample annealed for 30 min at 525 °C and successively etched by 2.2, 3.2, and 3.6 μm . Spectra displaced vertically for ease of view.

III. RESULTS

A. Lines at 997.5, 981.9, 972.1, and 965.3 meV

We consider first the four zpls at 997.5, 981.9, 972.1, and 965.3 meV. Their intensities increase monotonically with dose to at least 10^{14} cm^{-2} in the carbon-free samples (e.g., the 997.5 meV data, Fig. 2), demonstrating their intrinsic character. They are suppressed in samples with high carbon content, when self-interstitials are strongly trapped by carbon, confirming their interstitial nature.³ Significant PL intensities remain after removing $3.6 \pm 0.5 \mu\text{m}$ from the surface, Fig. 3, in contrast to the loss of the VEPAS vacancy signal, Fig. 4, a result also observed for smaller-dose samples. These PL lines have constant intensity when annealed for another 30 min at 600 °C, while the VEPAS signal almost disappears. In samples implanted with 10^{14} cm^{-2} 4 MeV Si ions and then annealed for 30 min at 50 °C steps between 100 and 700 °C, the VEPAS response disappeared

FIG. 4. Raw VEPAS profiles for $6 \times 10^{13} \text{ cm}^{-2}$ 4 MeV Si^{2+} implanted p -type "Topsil" silicon sample annealed for 30 min at 525 °C and successively etched by 0.55, 2.2, 3.2, and 3.5 μm . Inset: (fitted) average V_n concentration vs depth.

between 500 and 600 °C, while the four zpls decreased only slightly in area and only disappeared between 650 and 700 °C. For the many different samples used, these self-interstitial related PL centers consistently survive when the VEPAS signal indicates the removal of the vacancies. All the data are consistent with the lines occurring at interstitial centers.

B. 935 meV band

The 935 meV band is seen only at high doses in the carbon-lean material, again establishing its interstitial nature. The decrease in the integrated intensity of this broad band after the removal of $3.6 \pm 0.5 \mu\text{m}$, Fig. 3, implies that these interstitial-related clusters lie on average close to R_p , deeper than the $V_{3,5}$ defects suggested by VEPAS, Fig. 4. Both the 935 meV intensity and the $V_{3,5}$ concentration drop by $\sim 50\%$ after annealing at 600 °C, Fig. 1, but the correlation fails after a further 30 min annealing at 600 °C, again distinguishing the 935 meV centers from the vacancies.

C. 835 meV band

The 835 meV band is broad, indicating a disordered region. It is independent of carbon content, implying a *vacancy* nature. In samples annealed at 525 °C, Fig. 4, the buried layer of $V_{3,5}$ clusters has an average concentration of $(7 \pm 3) \times 10^{17} \text{cm}^{-3}$. There is a similar concentration of smaller defect clusters between the surface and $2.2 \mu\text{m}$ [which are not isolated divacancies, as these are not stable at 525 °C (Ref. 14)]. Annealing at 600 °C destroys the smaller, near-surface clusters, but the larger, deeper clusters survive. The relative magnitude of the 835 meV band decreases significantly as the sample is etched, Fig. 3, and disappears on annealing at 600 °C, Fig. 1. Both observations are consistent with the 835 meV band occurring at the *small* (undefined) vacancy clusters in the near-surface region, and also in the $2\text{--}3 \mu\text{m}$ region, at a sufficiently *low* concentration to not measurably affect the VEPAS response.

D. 1062.3 meV line

The 1062.3 meV line also occurs at an intrinsic defect, Fig. 2. In samples annealed at 600 °C the zpl decreases in intensity by $\sim 85\%$ between 30 and 60 min anneals (not shown), while other PL features show no significant change, but the equivalent VEPAS response (to $V_{3,5}$ at $2\text{--}3 \mu\text{m}$) also decreases by about 85%. The 1062 meV line also correlates with the VEPAS vacancy response following a variety of annealing and etching, in both high- and low-dose implants, although the depth profile suggested by the more sensitive PL technique may be more widely spread. This evidence suggests that the line is vacancy related. This intrinsic center has very shallow electrical level(s), suggesting that it does not contain broken bonds. V_6 has the requisite structure;¹⁵ stable V_4 and V_6 clusters have been predicted theoretically^{16–18} and observed after different implantation and annealing regimes.¹⁰ V_6 could be formed by the agglomeration of the smaller clusters of low concentration associated with the 835 meV band, which disappears as the 1062 meV line appears at 600 °C, Fig. 1. Remembering the

higher sensitivity of PL, V_6 could exist at a concentration up to two orders of magnitude lower than that of the $V_{3,5}$ defects which dominate the VEPAS response. However, there is a significant difference in the dose dependences of V_6 (the intensity of the 1062 meV line) and $V_{3,5}$ (from VEPAS) in Fig. 2. The difference may occur because the $V_{3,5}$ are formed at the damage peak at the time of implantation with a significantly superlinear dependence on ion dose ϕ (i.e., $\phi^{2.6}$), and simply survive annealing at 600 °C, whereas the V_6 are formed only *after* annealing at 600 °C via agglomeration of the very small clusters created initially by the implant, and whose concentrations before annealing are found by VEPAS to have an approximately linear dose dependence.

E. 991 meV line

Finally, Nakamura and Murakami³ suggested that the 991 meV luminescence is created by a self-interstitial cluster. However, the line is strongly sample dependent, it decreases in intensity at high doses, consistent with an impurity being involved, and its observation in samples with a high carbon content is inconsistent with a self-interstitial cluster.

IV. SUMMARY AND CONCLUSION

In summary, the broad band centered on 935 meV is shown to occur at interstitial complexes, as do the PL lines at 997.5, 981.9, 972.2, and 965.3 meV. The 835 meV band occurs at a low concentration of small vacancy clusters in the “near-surface” region, which appear to agglomerate under annealing into the larger (possibly V_6) vacancy clusters that produce the 1062.3 meV band. Despite their very different sensitivities to defect concentrations, the combination of PL and VEPAS measurements provides a way of unraveling some complexities in ion-implantation damage.

ACKNOWLEDGMENTS

This work was supported by EPSRC Grant No. GR/R10820/01 and by the EU Coordination Action program CADRES. One of the authors (J.W.L.) thanks the Australian Research Council for a fellowship.

¹See, e. g., *Properties of Crystalline Silicon*, edited by R. Hull (INSPEC, London, 1999), pp. 731–774.

²D. C. Schmidt, B. G. Svensson, M. Seibt, C. Jagadish, and G. Davies, J. Appl. Phys. **88**, 2317 (2000).

³M. Nakamura and S. Murakami, J. Appl. Phys. **94**, 3075 (2003).

⁴J. L. Benton, K. Halliburton, S. Libertino, D. J. Eaglesham, and S. Coffa, J. Appl. Phys. **84**, 4749 (1998).

⁵N. Abelgader and J. H. Evans-Freeman, J. Appl. Phys. **93**, 5118 (2003).

⁶G. Davies and R. C. Newman, in *Handbook on Semiconductors*, edited by T. S. Moss and S. Mahajan (Elsevier Science B. V., Amsterdam, 1994), Vol. 3, p. 1557.

⁷G. Davies, Phys. Rep. **176**, 83 (1989).

⁸R. Krause-Rehberg and H. S. Leipner, *Positron Annihilation in Semiconductors* (Springer, Berlin, 1999).

⁹P. G. Coleman, R. E. Mason, M. van Dyken, and A. P. Knights, J. Phys.: Condens. Matter **17**, S2323 (2005).

¹⁰M. Fujinami, T. Miyagoe, and T. Sawada, J. Appl. Phys. **94**, 4382 (2003).

¹¹A. van Veen, H. Schut, M. Clement, J. M. M. Denijs, A. Kruseman, and M. R. Ijpma, Appl. Surf. Sci. **85**, 216 (1995).

¹²J. F. Ziegler, J. P. Biersack, and U. Littmark, *The Stopping and Range of Ions in Solids* (Pergamon, New York, 1985) (<http://www.srim.org>).

¹³J. Weber, S. Knack, O. V. Feklisova, N. A. Yarykin, and E. B. Yakimov,

- Microelectron. Eng. **66**, 320 (2003).
- ¹⁴R. Poirier, V. Avalos, S. Dannefaer, F. Schiettekatte, and S. Roorda, Nucl. Instrum. Methods Phys. Res. B **206**, 85 (2003).
- ¹⁵B. Hourahine, R. Jones, A. N. Safonov, S. Öberg, P. R. Briddon, and S. K. Estreicher, Phys. Rev. B **61**, 12594 (2000).
- ¹⁶V. Makhov and L. J. Lewis, Phys. Rev. Lett. **92**, 255504 (2004).
- ¹⁷S. K. Estreicher, J. L. Hastings, and P. Fedders, Appl. Phys. Lett. **70**, 432 (1997).
- ¹⁸T. E. M. Staab, M. Haugk, A. Sieck, T. Frauenheim, and H. S. Leipner, Physica B **273–274**, 501 (1999).