Monovacancy and Interstitial Migration in Ion-Implanted Silicon

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The migration of monovacancies (V^0) and self-interstitials (I) has been observed in ion-implanted low-doped float-zone silicon by variable-energy positron annihilation spectroscopy. V^0 and I were created by the *in situ* implantation of $\sim$20 keV helium ions below 50 K. Monitoring the time evolution of the vacancy response during isothermal heating enabled the measurement of activation energies for V^0 and I migration of 0.078(7) and 0.46(28) eV, respectively. In highly As-doped Si, partial V annihilation occurs via free I migration, with a second stage of annealing, probably associated with V-As complexes, above room temperature.

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Ion implantation of silicon, widely used in the early stages of device fabrication, creates monovacancy-interstitial (Frenkel) pairs along the ion track. However, both defect types are mobile below room temperature, so that considerable recombination and annealing occurs before implanted silicon is studied. A few percent of the monovacancies survive as divacancies; both these and the excess interstitials can form clusters or complexes on heating [1].

Although it is accepted that neutral monovacancies are mobile at about 220 K, with a migration energy of $\sim$0.5 eV [2–4] considerable uncertainty exists about the behavior of isolated silicon interstitials. In a review in 2004, for example, Lazanu and Lazanu [5] stated that it is thought that monointerstitials are mobile at all temperatures, as stated by Watkins [3], but added that there has been no direct proof of the existence of isolated silicon interstitials and that nothing is known experimentally about the self-interstitial annealing process. Partyka *et al.* [6] concluded that the athermal low-temperature motion of interstitials during electron irradiation occurs via electronic excitation and is much less likely in the case of ion irradiation. Published values for the migration energy of interstitials lie in the broad range 0.1–1.4 eV [6–9]; Voronkov and Falster [10] state that lower values ($\sim$0.2 eV) seem preferable, and a measurement by Hallén *et al.* [11] gives 0.065 ± 0.015 eV. Bech Nielsen and Andersen state that free interstitials are mobile at $\sim$190 K [12], while Partyka *et al.* [6] prefer $\sim$150 K (with di-interstitials moving at temperatures above 300 K). Most of these studies are not of ion-implanted silicon, on which little experimental research on defect evolution at low temperatures has been performed. For example, in order to create the thick (bulk) samples required by electron resonance and positron lifetime spectroscopies, high-energy electron irradiation has often been used, and this creates a somewhat different spatial defect configuration. This last point could also be applied to samples studied by deep level transient spectroscopy, which requires low vacancy concentrations. In the present study, *in situ* variable-energy positron annihilation spectroscopy (VEPAS) has been used to monitor the evolution of defects resulting from helium ion implantation (at <50 K) during isothermal annealing between 100 and 350 K.

The study of the formation and evolution of vacancy-type damage in ion-implanted silicon by VEPAS has been widely pursued over the past two decades [13–15]. There has been considerable success in depth profiling open-volume point defects for a wide variety of ion masses and energies [16] and in identifying vacancy-impurity complexes [17], the interaction of vacancies with hydrogen and helium [18], and agglomeration into voids and cavities [19]. However, almost all of these studies have been performed on samples which have been held at room temperature after ion implantation and before VEPAS interrogation, so that the initial monovacancy damage (modeled, for example, by the widely used simulation code TRIM [20]) recombines and agglomerates so that only a few percent survives, predominantly as divacancies [21].

In order to observe and study monovacancies created by ion implantation—which are predominantly neutral (V^0) for low-doped Si and negatively charged for highly n-doped Si [22]—it is therefore necessary to carry out the implantation at low temperatures and to perform VEPAS without warming the sample. This Letter describes measurements performed at low temperatures in a combined implantation/VEPAS system, which allows *in situ* positron measurements.

VEPAS response to vacancy-type damage in silicon is usually measured via the Doppler-broadened annihilation line shape parameter S [15], the central fraction of the line between fixed limits, which—because the mean momentum of electrons annihilating positrons trapped in vacancy defects is lower than in bulk silicon—increases as the concentration and/or size of the defects increases. The positron beam system used was a standard magnetic-transport system [23], but the samples were mounted in good thermal contact with a copper cold finger, cooled by closed-cycle refrigeration to 30 K [24]. To perform ion

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implantation, the sample end of the cold finger was electrically isolated from, but thermally attached to, the refrigerator head by a 0.6 mm-thick sapphire disk; the two parts of the cold finger were held together with thin insulating clamps (Fig. 1). The background system pressure was less than 2 μPa, and gas lines and the sample chamber were flushed with He gas prior to implantation. With -20 kV applied to the sample, low-pressure He gas was bled into the sample chamber through a needle valve until a uniform glow discharge was seen around the entire sample. The VEPAS response to the damage was monitored after 2 s intervals until it reached (in stages) the level indicated in Fig. 2. This was typically after plasma discharge for a total of ~6 s, and this procedure was followed for each implantation to ensure similar starting conditions. In this way, it was ensured that the defect concentration was not high enough to lead to a saturated positron response. Although this method strictly results in the implantation of He with a range of energies, the depth of the damage suggested by Fig. 2 is consistent with the mean ion energy being close to 20 keV. TRIM simulations [20] give the range of 20 keV He ions in Si to be 200 nm. The data of Fig. 2 were fitted using the code VEPFIT [25], requiring consistency between the S parameter for the damaged layer and the positron diffusion length in the layer. The average monovacancy concentration over the first 150 nm is estimated to be approximately 2×10^{18} cm^{-3}, corresponding (again approximately) to a total He ion dose of 10^{12} cm^{-2} [16]. The fitted S value characteristic of the monovacancy was found to be 1.027. The temperature of the sample, calibrated against the temperature of the controller thermocouple, was found never to exceed 50 K at any time during implantation.

It has been reported that He can decorate vacancy-type defects in silicon, significantly affecting VEPAS data [19]. However, almost 100 monovacancies are created by each He ion, and so, even if all He ions decorate vacancies (and this is not necessarily true at low temperatures [26]), the effect on the present VEPAS data would be negligible.

Two sets of samples were implanted: low-B-doped float-zone (FZ) Si (111) (resistivity >1500 Ω cm) and highly As-doped Cz Si (resistivity <0.005 Ω cm). Isothermal annealing was carried out after implantation at temperatures from 100 to 350 K; at each temperature, the VEPAS S parameter at a positron implantation energy of 3.5 keV (corresponding to a mean positron implantation depth of 130 nm, to match that of the mean vacancy depth predicted by TRIM [20]) was measured every 600 s for total times of up to four days. After every fifth run, the S value at 24 keV was measured to check that the bulk Si S value was not changing during the run, which would indicate a systematic drift. The data in Fig. 2 illustrate the fact that surface oxide was removed by He ion sputtering (S at incident positron energy $\rightarrow 0 \approx S$ for bulk Si) and no measurable oxide growth occurred during measurements, a conclusion which was independently checked. In this way, any changes observed in S(3.5 keV) could be assigned to physical changes in the structure associated with monovacancy annealing or agglomeration and not to surface or systematic changes. It is also possible to neglect the temperature dependence of the specific trapping rate for positrons in vacancy-type defects, including the influence of shallow trapping, because the annealing measurements are isothermal.

Raw data showing the change in S(3.5 keV) vs time are shown in Figs. 3 and 4 for FZ and n^+-Si for selected temperatures. The data for FZ Si are consistent with a model in which the defect S parameter (normalized to the bulk Si value) and specific trapping rate for the neutral monovacancy (divacancy) in Si are 1.027 (1.04) and 3.4×10^{14} (6.8×10^{14}) s^{-1}, respectively, and that the postanneal samples contain only divacancies formed from 5% of the initial monovacancies. The average monovacancy concen-

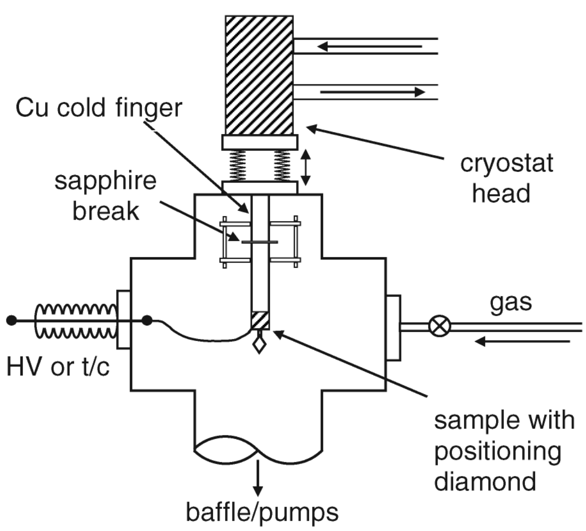

FIG. 1. Schematic diagram of sample chamber.

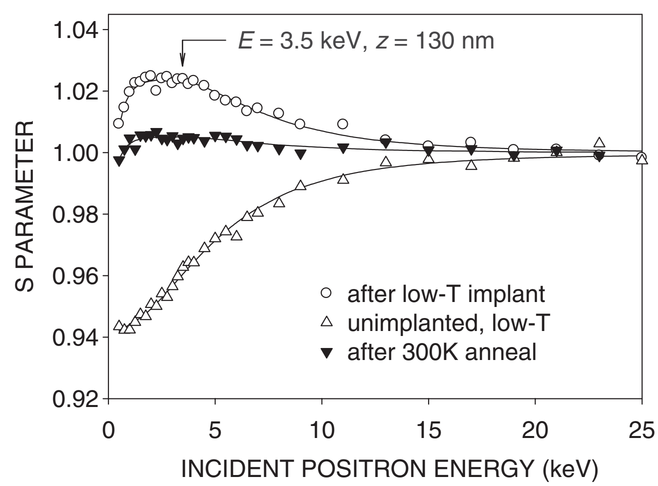

FIG. 2. S parameter vs incident positron energy for FZ Si at 25 K, before and after irradiation with ~20 keV He ions, and after annealing at 300 K. The solid lines are fits to the data.

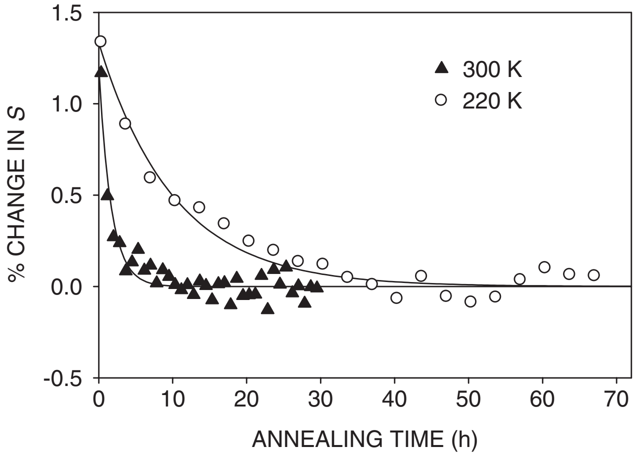

FIG. 3. Percentage difference between the S parameter for implanted FZ Si (measured at an incident positron energy of 3.5 keV) and its asymptotic value at times $>3d$ as a function of time at 220 and 300 K.

tration over the first 150 nm is estimated to be approximately 2×10^{18} cm^{-3}, corresponding (again approximately) to a total He ion dose of 10^{12} cm^{-2}. [16] At the start of a typical measurement run, about 80% of implanted positrons are trapped in monovacancies, and at the end about 25% are trapped in divacancies; as a consequence, the measured S value in the defected region decreases with time.

If the monovacancy concentration decreases exponentially with a time constant λ, it can be shown, by using expressions for the fractions of positrons trapped in mono- and divacancies such as those in Ref. [16], that the S parameter decreases here as

$$S(t) \approx [1.01 + 2.32 \exp(-\lambda t)]/[1 + 2.25 \exp(-\lambda t)]. \tag{1}$$

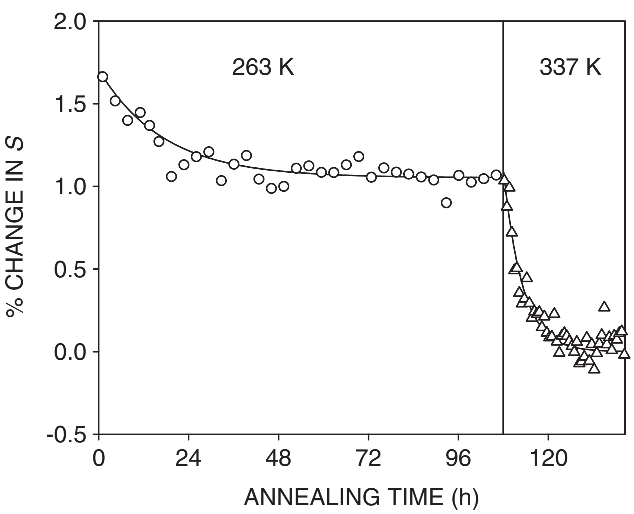

FIG. 4. As for Fig. 3, for n^+Si at 263 and 337 K.

It is found that if $S(t)$ is fitted to an exponential with a time constant of λ', then $\lambda'/\lambda \approx 2.1$ over a wide range of values of λ; therefore, λ' can be used in the Arrhenius plot of $\ln\lambda'$ vs T^{-1} to obtain activation energies. Such plots are presented in Fig. 5.

The plots in Fig. 5 for FZ Si point to two separable processes leading to V^0 annihilation (denoted I and II here) with activation energies $E_A = 0.078(7)$ and 0.46(28) eV, respectively. The different temperature ranges over which these two processes occur are interpreted as indicating that the first process involves a higher number of steps than the second. While the uncertainty on the activation energy for process II is very large, its value suggests that it is linked with neutral monovacancy migration; that for process I is consistent with that measured for silicon interstitial migration by Hallén *et al.* [11].

A major difference between the results for high-quality FZ and n^+-Si was observed. In the latter case, $S(t)$ decreased slightly to an intermediate value before decreasing again at higher temperatures (Fig. 4); this observation, not seen in FZ Si, is consistent with the partial annihilation of a small fraction of the negatively charged vacancies by migrating interstitials at lower temperatures and eventual annihilation of the remainder above room temperature, probably after the formation of V-As complexes, which form because of the high As concentration ($>10^{19}$ cm^{-3}) [27–31]. In FZ Si, in contrast, pinning in complexes is negligible (the dopant concentration being ~3 orders of magnitude smaller than that for V^0, whereas it was comparable in the n^+-Si sample), and both processes I and II can lead to total annihilation of vacancies. Because of the small changes generally seen in the S parameter in the first stage of annealing in n^+-Si (the data set in Fig. 4 being an exception), the uncertainty in the activation energy for migration was large, and the data are not shown in Fig. 5. However, it was clearly somewhat lower than 0.1 eV, sug-

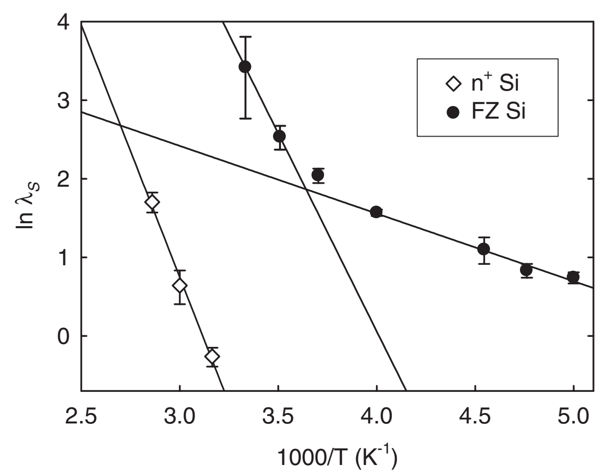

FIG. 5. Arrhenius plots of $\ln\lambda_S$ vs $1000/T$, where λ_S is the decay constant resulting from exponential fits of data such as those in Figs. 3 and 4, and T is the absolute temperature in K.

gesting the migration of a minority I in the free state. The second process in n^+-Si, at just above room temperature, has $E_A \sim 0.59(6)$ eV, again assuming that the change in S can be used in the Arrhenius plot, only slightly higher than the value for free neutral V^0 measured for FZ Si. This may be because the V^- or V^{2-} have to break from the As interstitials, although this is not expected to happen until ~450 K [26]; the differences in E_A and annealing temperature between the present and past results may be associated with the relative spatial distributions of the defects and/or their proximity to the surface.

Zangenberg, Goubet, and Larsen [32] reported that all vacancies formed complexes with dopant boron atoms, which disappeared at about room temperature; however, the concentrations of both V and B were comparable at about 10^{15} cm^{-3}, very different to the situation in the present samples.

The fact that both processes I and II occur at somewhat higher temperatures than reported elsewhere (~200 and 250 K for I and V^0, respectively, compared to figures of <200 and ~220 K in the literature) is again an indication that the effective number of steps required for vacancies to find interstitials or vice versa is higher than in samples used earlier, possibly for the reasons given above.

In conclusion, activation energies for two distinct processes leading to neutral monovacancy annihilation in FZ silicon implanted with 20 keV He ions have been measured to be 0.078(7) and 0.46(28) eV. The former is associated with silicon interstitial migration, consistent with the result of Hallén *et al.* [11], and the latter monovacancy migration. Both processes occur at higher temperatures than reported for electron-irradiated or implanted with ions at low doses, implying that a greater effective number of steps are involved in the migration. In n^+-Si, a fraction of the negatively charged monovacancies form complexes with dopant (As) atoms before finding an interstitial; this is not seen in FZ Si.

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[1] E. Rimini *et al.*, Defect Diffus. Forum **153**, 137 (1998).
[2] M. Ramamoorthy and S. T. Pantelides, Phys. Rev. Lett. **76**, 4753 (1996).
[3] G. D. Watkins, Mater. Sci. Semicond. Process. **3**, 227 (2000).
[4] L. Shao, J. Liu, Q. Y. Chen, and W. K. Chu, Mater. Sci. Eng., R **42**, 65 (2003).
[5] S. Lazanu and I. Lazanu, Phys. Scr. **69**, 376 (2004).
[6] P. Partyka *et al.*, Phys. Rev. B **64**, 235207 (2001).
[7] L. Shao, J. Liu, Q. Y. Chen, and W. K. Chu, Mater. Sci. Eng., R **42**, 65 (2003).
[8] B. Sahli and W. Fichtner, Phys. Rev. B **72**, 245210 (2005).
[9] K. Nishihira and T. Motooka, Phys. Rev. B **66**, 233310 (2002).
[10] V. V. Voronkov and R. Falster, in *Future Fab International* (Montgomery Research, San Francisco, 2003), Vol. 15, Chapter 6.
[11] A. Hallén *et al.*, J. Appl. Phys. **86**, 214 (1999).
[12] B. Bech Nielsen and J. U. Andersen, Phys. Rev. B **35**, 2732 (1987).
[13] P. Asoka-Kumar, K. G. Lynn, and D. O. Welch, J. Appl. Phys. **76**, 4935 (1994).
[14] A. P. Knights and P. G. Coleman, Defect Diffus. Forum **183-185**, 41 (2000).
[15] R. Krause-Rehberg and H. S. Leipner, *Positron Annihilation in Semiconductors: Solid-State Sciences* (Springer, Berlin, 1999), Vol. 127.
[16] P. G. Coleman, C. P. Burrows, and A. P. Knights, Appl. Phys. Lett. **80**, 947 (2002).
[17] X. D. Pi, C. P. Burrows, and P. G. Coleman, Phys. Rev. Lett. **90**, 155901 (2003); P. J. Simpson *et al.*, Appl. Phys. Lett. **85**, 1538 (2004).
[18] C. Macchi *et al.*, Phys. Rev. B **74**, 174120 (2006).
[19] R. S. Brusa *et al.*, Phys. Rev. B **61**, 10 154 (2000).
[20] J. Ziegler, www.srim.org, 2005.
[21] P. G. Coleman, A. P. Knights, and R. M. Gwilliam, J. Appl. Phys. **86**, 5988 (1999).
[22] S. Szpala and P. J. Simpson, J. Appl. Phys. **89**, 5991 (2001).
[23] N. B. Chilton and P. G. Coleman, Meas. Sci. Technol. **6**, 53 (1995).
[24] R. E. Mason and P. G. Coleman, Appl. Surf. Sci. **252**, 3228 (2006).
[25] A. van Veen *et al.*, in *Proceedings of the Technical Workshop on Monte Carlo Methods, Ontario, Canada, 1990*, edited by P. J. Schultz, AIP Conf. Proc. No. 218 (AIP, New York, 1990), p. 171.
[26] F. Corni *et al.*, J. Appl. Phys. **85**, 1401 (1999).
[27] A. Polity *et al.*, Phys. Rev. B **58**, 10 363 (1998).
[28] K. Saarinen *et al.*, Phys. Rev. Lett. **82**, 1883 (1999).
[29] V. Ranki, J. Nissilä, and K. Saarinen, Phys. Rev. Lett. **88**, 105506 (2002).
[30] V. Ranki, A. Pelli, and K. Saarinen, Phys. Rev. B **69**, 115205 (2004).
[31] M. Ramamoorthy and S. T. Pantelides, Phys. Rev. Lett. **76**, 4753 (1996).
[32] N. Zangenberg, J. J. Goubet, and A. N. Larsen, Nucl. Instrum. Methods Phys. Res., Sect. B **186**, 71 (2002).