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Room-temperature vacancy migration in crystalline Si from an ion-implanted surface layer

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Migration of vacancies in crystalline, *n*-type silicon at room temperature from Ge^+-implanted (150 keV, $5\times10^9-1\times10^{11}\,cm^{-2}$) surface layers was studied by tracing the presence of P–V pairs (*E* centers) in the underlying layer using deep level transient spectroscopy (DLTS). Under the conditions we have examined, the vacancies migrate to a maximum depth of about 1 μm and at least one vacancy per implanted Ge ion migrates into the silicon crystal. The annealing of the *E* centers is accompanied, in an almost one-to-one fashion, by the appearance of a new DLTS line corresponding to a level at $E_C-E_t\approx0.15\,eV$ that has donor character. It is argued that the center associated with this line is most probably the P_2–V complex; it anneals at about 550 K. A lower limit of the RT-diffusion coefficient of the doubly charged, negative vacancy is estimated to be $4\times10^{-11}\,cm^2/s$. © *1999 American Institute of Physics.* [S0021-8979(99)05421-3]

I. INTRODUCTION

Ion implantation into the outermost surface layer of a silicon single crystal held at room temperature (RT) has recently been demonstrated to give rise to migration of point defects into the silicon crystal from the ion implanted layers.[1–3] Both vacancies and interstitials have been demonstrated to migrate, by appearance of phosphorus-vacancy pairs (P–V pairs or *E* centers) in deeper lying layers[1] and by reduction of already existing vacancy-type defects,[3] respectively. Thus, these experiments demonstrate that both vacancies and self interstitials are mobile at room temperature. Estimates of the RT-diffusion coefficients of the point defects were obtained from the experiments: from phosphorus-deactivation profiles measured by spreading resistance of *n*-type Si, a lower limit of $\sim4\times10^{-11}\,cm^2/s$ (Ref. 2) was estimated for the diffusion coefficient of self-interstitials, and from *in situ* measurements of leakage-current reduction values of 1.5×10^{-15} and $3.0\times10^{-13}\,cm^2/s$ for interstitials and vacancies, respectively, were determined.[3]

The observation that the point defects are mobile at room temperature is in agreement with extrapolations to room temperature of results from low temperature irradiation experiments;[4] for the neutral vacancy, a RT value of $\sim5\times10^{-10}\,cm^2/s$ (Refs. 5 and 6) was estimated in this way. Extra polation to RT of point-defect diffusion coefficients estimated at high temperature from diffusion experiments leads to very uncertain values as the high temperature point-defect diffusion coefficients are already uncertain; in general these extrapolations give rather small RT-diffusion coefficients which could not give rise to any measurable diffusion at room temperature.[6] Recent molecular-dynamics simulations of point-defect diffusion in Si[4,7] have given RT-diffusion coefficients which for the neutral vacancy agrees well with the above estimates ($D_v\approx2\times10^{-11}\,cm^2/s$) but which for the neutral self-interstitial is somewhat smaller ($D_I\approx4\times10^{-18}\,cm^2/s$). It should be noted, however, that the point defects can be differently charged depending on the position of the Fermi level; this is known to have a strong influence on the temperature at which they become mobile after low-temperature irradiations.[8]

It has recently been argued by Privitera and co-workers[2,4] that the observed electrical deactivation to large depths of phosphorus dopants in *n*-type Si after shallow RT ion implantations, was due to an interaction with Si self-interstitials and not with vacancies; the above quoted lower limit of the self-interstitial diffusion coefficient of $\sim4\times10^{-11}\,cm^2/s$ (Ref. 2) was estimated under this assumption. A major argument behind this conclusion was the observation that the electrical deactivation was stable above 200 °C which is a temperature where the P–V pairs have annealed[8] (the P–V pair is expected to be the complex responsible for a vacancy-assisted deactivation of the electrical activity). In the present report, however, we will demonstrate that the observed dopant deactivation is in agreement with the formation of P–V pairs. The observed stability of the deactivation above 200 °C, when the P–V pairs anneal, is explained as being due to the formation of a new donor center in an almost one-to-one ratio with the disappearence of the P–V pairs. Our estimate of the lower limit of the RT vacancy-diffusion coefficient from the in-growth of the P–V pairs after ion implantation is $4\times10^{-11}\,cm^2/s$, a value which is similar to the above estimate of the lower limit of the self-interstitial diffusion coefficient at room temperature from the observed deactivation of phosphorus.

II. EXPERIMENTAL PROCEDURE

The presence of the P–V pairs in *n*-type Si after ion implantation was, in the present investigation, monitored by

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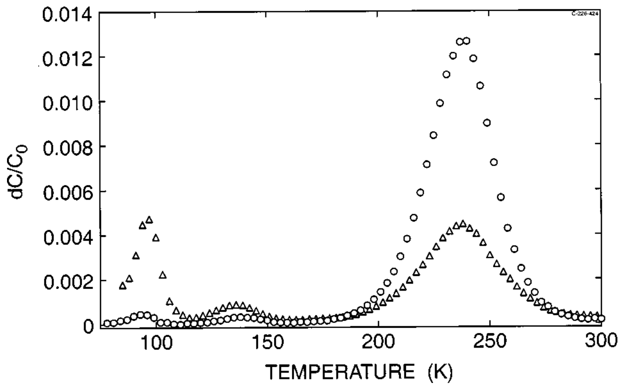

FIG. 1. DLTS spectra of a p^+n-*mesa* diode implanted at room temperature with 150 keV Ge^+ ions to a dose of $1\times10^{10}\ cm^{-2}$, before (○) and after (△) a reverse bias annealing at 380 K for 60 min at a reverse bias of −10 V. Only every third data point is shown. The DLTS spectrum was measured by pulsing from −5 to 0 V with a repetition rate of 250 Hz and a pulse width of 150 μs.

deep level transient spectroscopy (DLTS) via its acceptor level at $E_C - E_{PV} = 0.42$ eV,[8] where E_C is the energy of the bottom of the conduction band. Both p^+n-*mesa* diodes, and Au and Pt Schottky diodes were utilized. The *mesa* diodes were formed from (100)-oriented, ~2 Ω cm (2.5×10^{15} P/cm^3), *n*-type, FZ-type Si wafers with a 2000 Å thick, molecular beam epitaxially (MBE) grown, highly boron-doped (~5×10^{19} B/cm^3) p^+ top layer. Into these diodes 150 keV Ge ions were implanted to doses between 5×10^9 and $1\times10^{11}\ cm^{-2}$ with the samples tilted by 7° relative to the beam direction in order to reduce channeling effects. The lower and upper dose limits were determined by the minimum dose which we could handle in our implantation system and by the DLTS demand of a P–V concentration less than 10% of the dopant concentration, respectively. Both the Ge and the defect distributions are completely contained within the p^+ top layers, according to TRIM simulations.[9] Gold–Schottky diodes were also formed (using thermal evaporation of Au) on 1 Ω cm *n*-type, FZ-Si in which the Ge implantation had been done prior to the diode formation. Further, some results of defect introduction from Pt Schottky-diode formation by e-gun evaporation of Pt on 1 Ω cm, *n*-type, FZ-Si will be presented. We have previously demonstrated that an e-gun evaporation of, e.g., Pt is accompanied with a bombardment of low energy ions giving rise to an injection of vacancies identical to the one observed in an ion implantation process.[1] Finally, for reference purposes, 2 MeV electron irradiations were done in both FZ- and CZ-type Si *mesa* diodes.

III. RESULTS AND DISCUSSION

Typical DLTS spectra of a *mesa* diode ion implanted with 150 keV Ge to a dose of $1\times10^{10}\ cm^{-2}$ are shown in Fig. 1, before and after an annealing at 380 K. The spectrum of the as-implanted diode contains one dominating peak at a temperature of 240 K and two just discernable peaks at temperatures of 95 and 135 K. From Arrhenius plots of the electron emissivity versus reciprocal temperature, ionization enthalpies and apparent capture cross sections (the ''DLTS signatures'') have been extracted; they are collected in Table I. The extracted parameters for the dominating line is in perfect agreement with those for the *E* center in Si found in the electron irradiated FZ-Si *mesa* diodes, and we conclude that this line originates from *E* centers. The parameters of the two small lines are uncertain due to their small intensities; however, the ionization enthalpy of the line at 135 K is in agreement with that of the di-vacancy,[8] whereas that of the line at 95 K is smaller than that of the interstitial oxygen-vacancy pair (O–V or *A* center) [the *A* center is typically found in CZ-type Si after MeV-electron irradiation with an ionization enthalpy of $E_C - E_A = 0.16$ eV (Ref. 8)].

TABLE I. DLTS signatures from as-implanted *mesa* diodes: Ionization enthalpies $E_C - E_t$, relative to the bottom of the conduction band, and apparent capture cross sections σ_a extracted from Arrhenius plots of the electron emissivity, corrected for the T^2 dependence vs reciprocal temperature. The quoted uncertainties are standard error of the means from a large number of measurements.

Temperature of DLTS line (K)	$E_C - E_t$ (eV)	σ_a (cm^2)
95	~0.13	
135	~0.24	
240	0.415 ± 0.003	$(2.0\pm0.4)\times10^{-15}$

The depth profile of the *E* centers is shown in Fig. 2 measured by the double-pulse DLTS technique. It appears that the *E*-center distribution extends to a depth of about 1 μm and peaks towards the surface. Thus, vacancies migrating from the ion implanted surface layer into the Si crystal interact predominantly with P^+ ions to form *E* centers and, to a much lesser extent, with each other to form di-vacancies. The depth distribution shown in Fig. 2 is most probably determined by the interaction of the migrating vacancies with P^+ ions (trap-limited migration) and not by the vacancy-diffusion coefficient, as discussed in Ref. 2. The depth region from 0 to ~0.3 μm of Fig. 2 is the depletion region of the *mesa* diode. The charge state of the migrating vacancies in this region depends on the position of the (0/−)-acceptor level of the vacancy in the band gap; as this level is probably situated in the middle of the gap[8] both neutral and singly

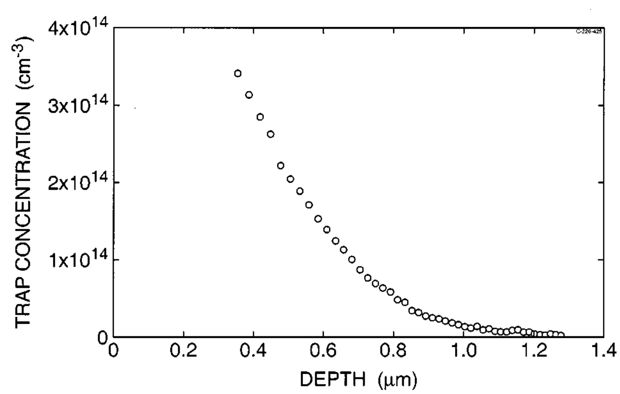

FIG. 2. Depth profile of the *E* center of a p^+n-*mesa* diode implanted with 150 keV Ge^+ ions to a dose of $1\times10^{10}\ cm^{-2}$ measured with the double pulse DLTS technique using $\Delta U = 0.5$ V corresponding to a depth resolution of ~600 Å.

charged negative vacancies can be assumed in this region. In the field-free region of the diode, from ~0.3 μm and further in, the charge state of the vacancy is either singly or doubly negative depending on the position of the (−/=)-acceptor level of the vacancy. If this level is situated at 0.28 eV from the conduction band as suggested in Ref. 10, a major fraction of the migrating vacancies will be doubly negative charged. Thus, the interaction between vacancies and P^+ ions will be strongest in the field-free region, and the profile can be anticipated to somehow level-off towards the surface. These considerations are in agreement with P–V profiles measured in Schottky diodes where the diode is formed after ion implantation and where, consequently, the vacancies have migrated all the way in a field free region. In this case fewer P–V pairs are found compared to those in the *mesa* diodes at similar depths indicating that more vacancies have been trapped in the near surface layer. An integration of the profile of Fig. 2 yields a total P–V concentration of $1\times10^{10}\,\mathrm{cm}^{-2}$. As the implanted dose was also $1\times10^{10}\,\mathrm{cm}^{-2}$, and considering the above discussion on the shape of the P–V profile in the depletion layer, it can be concluded that at least one vacancy is injected per implanted Ge ion; similar values were found in the whole dose range investigated. This value is much higher than the value of $\sim10^{-4}$ which Privitera *et al.*[4] found from the *P*-deactivation experiments after 40 keV Si implantations to doses in the $10^{13}\,\mathrm{cm}^{-2}$ range. However, Privitera *et al.* observed an increasing value with decreasing dose, probably reflecting the increase in complexity of the damage with increasing dose and, hence, an increasing trapping of the point defects in the damage, as also discussed by Privitera *et al.*

Also shown in Fig. 1 is a DLTS spectrum of the *mesa* diode after a reverse-bias annealing at 380 K for 60 min. The annealing results in a significant reduction of the intensity of the *E*-center line, a slight increase of the di-vacancy line, and a large increase of the small line at 95 K. It is well established that both the O_i–V pair and the C_i–C_s pair have characteristic DLTS lines at or near 95 K (Ref. 8) for the present measuring conditions. However, only small C and O concentrations are expected in these crystals and, in addition, no characteristic C_i line was observed at lower temperature prior to the appearance of this new line (C_i is produced in irradiation experiments by the $Si_i+C_s\rightarrow C_i$ replacement mechanism; it becomes mobile at about 320 K and transforms into the C_i–C_s pair[8]). Thus, C_i–C_s is excluded as the cause of this new line. The electron emission from the center associated to this line is strongly dependent on the electric field (the emission shows Poole–Frenkel effect[8]); this is not a diode artifact as demonstrated in Fig. 3 where the electron emissivity is displayed versus the electric field for both the *E* center and the new center measured in the same diode: the emission rate of the new center increases with increasing electric field whereas that of the *E* center is independent of the field as it should be for electron emission from the (0/−)-acceptor level of the *E* center. A similar analysis of the *A* center produced in CZ-type Si after a 2 MeV electron irradiation (not shown) gives also an electric-field-independent emission rate, as expected as this *A*-center level is known to be a (0/−)-acceptor level. Thus, we conclude that the new

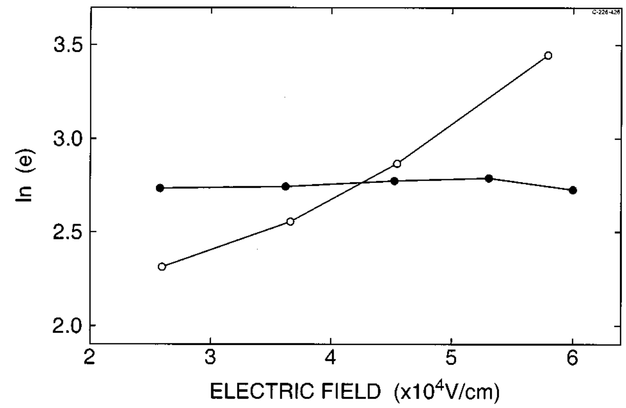

FIG. 3. Electron-emission rate vs electric field of the (0/−)-acceptor level of the *E* center (●) and the $E_C-E_t\approx0.15$ eV level of the new center (○) measured in a p^+n-*mesa* diode implanted with 150 keV Ge^+ ions to a dose of $1\times10^{10}\,\mathrm{cm}^{-2}$ annealed at 450 K for 30 min. The new defect line was measured at a temperature of 93 K and the *E*-center line at 227 K.

center is not the *A*-center and, furthermore, that the level under investigation is a donor level. Curves like the one shown in Fig. 3 for the new line have been measured at different temperatures and the emission rate at zero field have been estimated. These values were plotted versus reciprocal temperature and the ionization enthalpy extracted from the slope of this Arrhenius plot was found to be $E_C-E_t=(0.15\pm0.02)$ eV; (for the *A* center in the electron-irradiated CZ-Si *mesa* diodes, we find $E_C-E_A=(0.16\pm0.01)$ eV.

The new line grows in according to an almost one-to-one ratio with the disappearance of the *E* center, as demonstrated in Fig. 4. However, one should be cautious about this one-to-one ratio as the *E*-center distribution in the depletion layer of the diode might interact with the *E*-center distribution in the field-free region during annealing. In the experimental situation of Fig. 4, the *E*-center concentration is expected to be higher in the depletion region than in the field-free region as part of the vacancy in-diffusion has taken place without the presence of a depletion layer (the depletion layer develops during the e-gun deposition). Thus, a certain in-diffusion

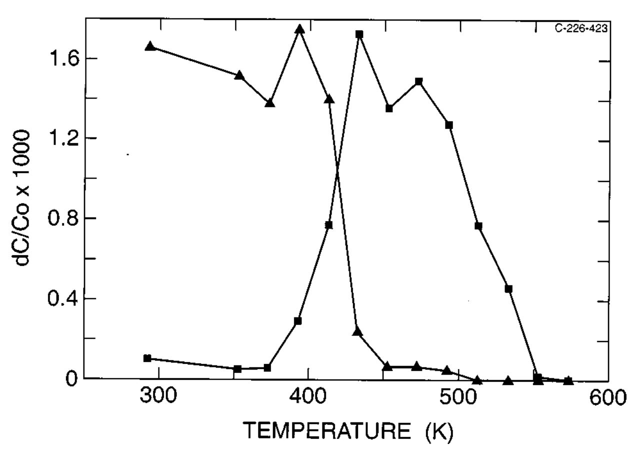

FIG. 4. DLTS intensities of the *E*-center line (▲) and the new line (■) as a function of anneal temperature for a 30 min isochronal annealing. The diode was a Pt Schottky diode in which the Pt had been e-gun evaporated (see Ref. 1). The spectrum was measured with a repetition rate of 250 Hz.

of *E* centers from the depletion layer into the field-free region might be anticipated during annealing and the almost exact one-to-one ratio of Fig. 4 is most probably a coincidence; in ion-implanted *mesa* diodes conversion ratios of 70% are typically found. The new center has completely annealed at a temperature of 550 K [this is also the anneal temperature of the C_i-C_s pair whereas the *A* center anneals at about 650 K (Ref. 8)].

There are two serious candidates to the center associated to this new DLTS line, namely, the P_2-V and $P-V_2$ centers. In the field-free region of the diodes, which is the region under investigation, the only defects, prior to the annealing, of any significant concentrations are the P^+ ions and the negatively charged P–V pairs; thus, it will be natural to look for candidates among combinations of these defects. It can be concluded from the small growth of the di-vacancy during annealing (Fig. 1) that part of the *E* centers dissociates during annealing. Whether they all disintegrate or only a small fraction does we cannot decisively conclude from the present experiments. Previous investigations of the annealing of the *E* center favor the diffusion to traps as the main cause of the disappearance of the *E* center during annealing with some additional annealing due to other defect reactions.[11–13] A trapping of mobile, probably neutral,[14] P–V pairs by already existing P^+ ions would then lead to P_2-V centers and can in a straightforward way explain the observed very high conversion efficiency of 70%–100% as only one P–V pair is needed for this reaction. The P_2-V center has previously been argued to be responsible for the NL1 spectrum observed by Sieverts and Ammerlaan[15] in electron-paramagnetic resonance (EPR) studies of electron-irradiated silicon containing high phosphorus concentrations. A formation of $P-V_2$ centers by trapping of mobile, negatively charged vacancies by stationary, negatively charged P–V pairs seems less probable from a Coulomb-repulsion argument. It would also demand a high degree of dissociation of the P–V pairs during annealing as they are the only source of vacancies; because of that a conversion efficiency of at most 50% could be expected. Thus, we favor the P_2-V complex as the center associated to the new line. As its level, situated at $E_C-E_t=0.15\,\mathrm{eV}$, is a donor level it will be fully ionized at room temperature. However, because it includes two P atoms it will nevertheless deactivate the P dopants to almost the same degree (70%–100%) as the neutral *E* centers do. This is then most probably the explanation as to why Kyllesbech Larsen *et al.*[2] observed that the electrical de-activation of the P dopants was stable above the anneal temperature of the *E* center.

An obvious question to be asked is whether P_2-V complexes are also formed when *E* centers, formed by MeV-electron irradiation, anneal. This point has been only briefly addressed in the present investigation, and only in the case of FZ Si. It is found that a small fraction of the annealing *E* centers converts into P_2-V complexes, however, the predominant fraction of the *E* centers simply disappear without the appearance of a new complex. We speculate that interstitial-type defects produced in the irradiation process participate in this annealing process.

We have estimated a lower limit for the vacancy-diffusion coefficient at RT by performing the DLTS measurement as soon as possible after a Ge-ion implantation of a *mesa* diode to a dose of $1\times10^{10}\,\mathrm{cm}^{-2}$. The ion implantation itself took 45 s and 4 min after the finishing of the ion implantation the measurement of the intensity of the DLTS *E* center line was performed. It was found that already at that time the *E*-center-DLTS line had achieved its full intensity and the *E*-center-depth profile its final form. Thus, from this measurement we can only make an estimate of the lower bound of the vacancy-diffusion coefficient at room temperature of $\sim4\times10^{-11}\,\mathrm{cm}^2/\mathrm{s}$ which is then for the vacancy being predominantly doubly negatively charged. This charge state of the vacancy is known from low temperature irradiation experiments to be more mobile than the neutral charge state.[8]

IV. CONCLUSION

In summary, we have demonstrated that following a Ge ion implantation to a low dose of the outermost surface layer of a *n*-type FZ-silicon single crystal, a large number of vacancies migrate deep into the Si crystal where they interact with P^+ ions to form P–V pairs. When the P–V pairs anneal a new DLTS line appear in an almost one-to-one fashion with the disappearance of the P–V pairs; the corresponding level is situated at $E_C-E_t=0.15\,\mathrm{eV}$ and shows donor character. We argue that the defect associated to this new line is most probably the P_2-V complex. From these experiments, a lower limit of the RT-diffusion coefficient of the doubly charged, negative vacancy is estimated to be $4\times10^{-11}\,\mathrm{cm}^2/\mathrm{s}$.

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