

## Formation of Thermal Vacancies in Highly As and P Doped Si

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Using positron annihilation measurements we observed the formation of thermal vacancies in highly As and P doped Si. The vacancies start to form at temperatures as low as 650 K and are mainly undecorated at high temperatures. Upon cooling the vacancies form stable vacancy-impurity complexes such as  $V\text{-As}_3$ . We determine the vacancy formation energy of  $E_f = 1.1(2)$  eV and the migration energy of  $E_m = 1.2(1)$  eV in highly doped Si. By associating these values with the vacancy-impurity pair, we get an estimate of 2.8(3) eV for the formation energy of an isolated neutral monovacancy in intrinsic Si.

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The vacancies formed in thermal equilibrium in Si are important, since they mediate the diffusion of both lattice and impurity atoms. Their role is also prominent in the electrical properties of highly doped material, since the vacancy diffusion leads to the formation of electrically passive donor impurity clusters. However, the thermal vacancies have escaped direct experimental observation, and thus their basic thermodynamical properties have been uncertain.

Most of the information on thermal vacancies has been obtained from diffusion studies. The experiments of Bracht *et al.* gave the diffusion activation energy  $H_A = H_f + H_m$  values between 3.8 and 4.2 eV and the activation entropy  $(3-7)k_B$  [1-3], whereas Ural *et al.* reported 4.86 eV and  $12.8k_B$ , respectively [4]. Generally, it is difficult to distinguish between the contributions of vacancy formation (formation enthalpy  $H_f$ ) and migration (migration barrier  $H_m$ ) in diffusion studies. Interestingly, the recent results of Bracht *et al.* suggest that  $H_f \approx 2.1$  eV and  $H_m \approx 1.8$  eV. This value of  $H_f$  is lower than the theoretical predictions (3.1-3.3 eV [5,6]), whereas  $H_m$  is much larger than obtained in electron irradiation studies ( $< 0.5$  eV [7]).

Thermally formed defects have also been observed by applying infrared spectroscopy [8] or electrical experiments [9] in samples that have been rapidly quenched after thermal or laser annealing. These experiments, however, do not report vacancy concentrations at thermal equilibrium. Further uncertainties are associated with the defect complex identification and their formation kinetics during and after the quench.

Positron annihilation spectroscopy has been one of the major techniques used to study the formation of thermal vacancies in metals (see, e.g., Ref. [10]) and recently also in GaAs [11]. However, in Si the data are confusing. Although thermal vacancies were first reported to form above 1450 K in undoped Si [12], later careful studies concluded that this is not the case [13,14]. This indicates that their concentration is below the detection limit of  $10^{16}$  cm $^{-3}$  at 1600 K. In highly  $n$ -type Si, however, thermal vacancies may form more abundantly as pairs with donor atoms (the effect of binding energy) and in negative

charge state due to electron trapping (the effect of Fermi level) [15].

In this Letter we show that vacancies are thermally generated in highly P and As doped Si already at a temperature of 650 K. After cooling the sample to room temperature, the dominant defects can be identified as vacancies surrounded by three donor atoms, the  $V\text{-D}_3$  complexes. The analysis of our data yields experimental results for vacancy formation energies in both doped and intrinsic Si as well as estimates for the vacancy migration barrier in highly  $n$ -type material.

The positron lifetime measurements were performed with a time resolution of 230 ps and a 30  $\mu\text{Ci}$   $^{22}\text{Na}$  source [16]. The stopping profile of positrons from the  $^{22}\text{NaCl}$  source is exponential with a mean depth of 110  $\mu\text{m}$  in Si. The effect of positrons annihilating in the source material and the aluminum or nickel foil surrounding it was estimated in reference samples. Experiments were performed also by implanting positrons from a low-energy (0-38 keV) beam, in order to study the near surface layer 0-3  $\mu\text{m}$  of the samples [16].

The lifetime spectra  $n(t)$  were analyzed in terms of exponential decay components  $n(t) = \sum_i I_i e^{-t/\tau_i}$ . The positron state  $i$  (e.g., delocalized state in the lattice or localized state in a vacancy) has a lifetime  $\tau_i$  and intensity  $I_i$ . The increase of the average lifetime  $\tau_{\text{ave}} = \sum_i I_i \tau_i$  above the bulk Si lattice lifetime  $\tau_B = 220$  ps shows that vacancy defects exist in the samples. The Doppler broadening of the annihilation radiation was measured using a coincidence system with Ge and NaI detectors. The shape parameters  $S$  and  $W$ , describing annihilation with valence and core electrons, respectively, were determined from the electron momentum distribution [16]. The  $S$  parameter increases and the  $W$  parameter decreases for a positron trapped at an isolated vacancy. While lifetime measurements give information about the open volume of the defect, the Doppler broadening is sensitive also to its chemical environment [17]. The vacancy concentrations were determined using the conventional positron trapping model with a trapping coefficient of  $2 \times 10^{15}$  s $^{-1}$  [16].

We studied several Czochralski-grown Si(111) bulk crystals with As and P dopings of  $10^{20} \text{ cm}^{-3}$ . The as-grown Si([As] =  $10^{20} \text{ cm}^{-3}$ ) sample contains a small concentration ( $\sim 10^{17} \text{ cm}^{-3}$ ) of native  $V\text{-As}_3$  defects [17]. In the as-grown Si([P] =  $10^{20} \text{ cm}^{-3}$ ) sample the vacancy concentration was less than  $10^{16} \text{ cm}^{-3}$  [17]. We performed both isochronal and isothermal annealings in a vacuum of  $10^{-3}$  mbar. We tested the effect of surface conditions by annealing identical samples both facing vacuum and facing each other (the so-called proximity capping). No differences in the vacancy concentrations were observed.

The average positron lifetimes are shown in Fig. 1 as a function of isochronal (30 min) annealing temperature. The positron lifetime was measured at room temperature between each annealing. The average lifetime starts increasing at 800 and 900 K in P and As doped samples, respectively, indicating that vacancy-type defects are formed. By comparing the larger lifetime component  $\tau_2$  [270(10) ps for P and 245(5) ps for As doping] with earlier measurements (Refs. [16–18]) and theoretical calculations [ $\tau(V\text{-As}_{1-3}) = 252\text{--}254$  ps [17]], the defects can be attributed to monovacancies. Coincidence Doppler measurements in the Si([As] =  $10^{20} \text{ cm}^{-3}$ ) sample give similar curves as obtained earlier [17,18] allowing one to identify the vacancy as  $V\text{-As}_3$ . The results of Fig. 1 show that thermal vacancies are formed above 900 K, and they are quenched to vacancy-impurity complexes during the annealing and cooling.

In order to observe the thermal vacancy directly we performed a positron lifetime experiment during the annealing at the equilibrium temperature (Fig. 2). The increase of the average lifetime shows that the vacancies start to form already at 650 K. After about 100 h at 750 K the

lifetime saturates to 255 ps [the lifetime component being  $\tau_2 = 280(10)$  ps] indicating that thermal equilibrium has been reached. At lower temperatures the thermal vacancies are observed, but their concentration does not saturate within the annealing time of 300 h.

We identified the structure of the vacancies in thermal equilibrium by performing Doppler broadening measurements on a Si([As] =  $10^{20} \text{ cm}^{-3}$ ) sample. A low-energy positron beam was applied to study the vacancy formation at  $0\text{--}2 \mu\text{m}$  from the surface, and to avoid source correction effects typical for high-temperature experiments performed in contact with the  $^{22}\text{NaCl}$  source. The thermal vacancies were observed again at 700 K in the conventional  $S$  and  $W$  parameters. The thermal equilibrium was reached much faster (in  $<1$  h) than in the bulk experiment of Fig. 2, as expected for vacancies generated at the surface. The decrease of annihilations with core electrons (7% in the  $W$  parameter) indicates that most of the thermal vacancies are isolated and not decorated by As.

The kinetics of the quenching of the isolated thermal vacancies to vacancy-impurity clusters is studied in Fig. 3, where positron lifetime measurements were performed at room temperature between isothermal annealings at 800–920 K. Around 900 K the thermal equilibrium is achieved much faster (order of 10 h) than in the 700–750 K measurements (Fig. 2). The Doppler broadening experiments show that the vacancy defects in Si([As] =  $10^{20} \text{ cm}^{-3}$ ) are mainly  $V\text{-As}_3$ . However, in Si([P] =  $10^{20} \text{ cm}^{-3}$ ) the vacancy defects have a positron lifetime component of 270(10) ps, which is slightly longer than expected for

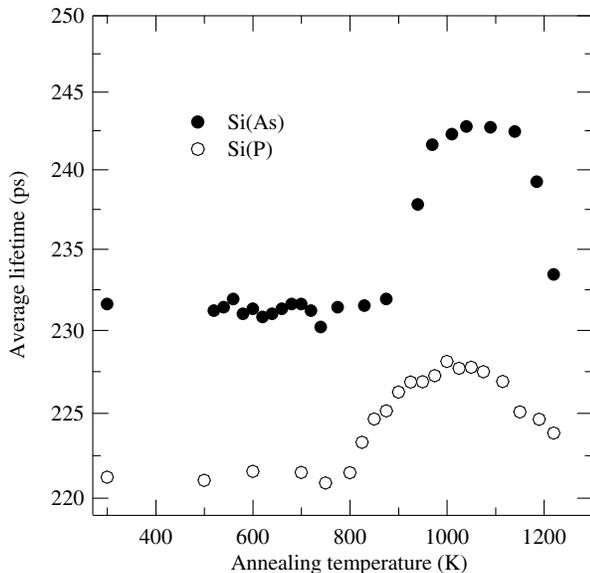


FIG. 1. Average positron lifetime as a function of annealing temperature. The annealing time at each point was 30 min. The lifetime measurement was done at 300 K.

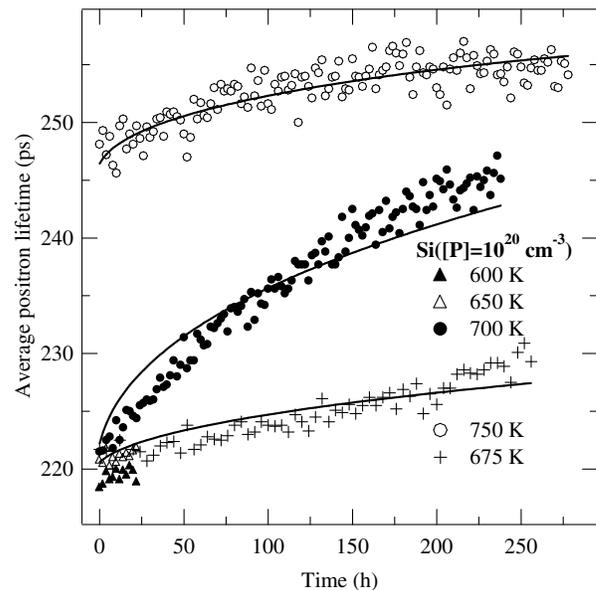


FIG. 2. Average positron lifetime as a function of measurement time for different measurement temperatures in the Si([P] =  $10^{20} \text{ cm}^{-3}$ ) sample. The same sample has been used in all measurements, except for the 675 K measurements where a new sample was used. The lines are from the solution of the diffusion equation.

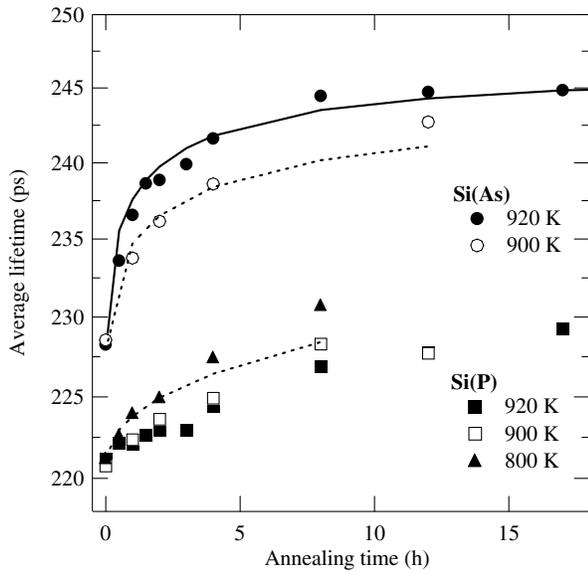


FIG. 3. Average positron lifetime measured at room temperature as a function of annealing time at annealing temperatures 800, 900, and 920 K. The lines are from the solutions of the diffusion equation.

monovacancy-impurity complexes [17,18]. A fraction of the thermal vacancies is thus quenched in as divacancy complexes.

In order to study the depth profile of thermal vacancies, we first annealed a Si([P] =  $10^{20}$  cm $^{-3}$ ) sample for 1 h at 800 K, and thereafter etched 20–30  $\mu$ m from the surface. The positron experiment shows a decrease of the average lifetime from 224.0(2) to 222.1(2) ps by etching, indicating that more than 50% of the thermally generated vacancy complexes could be removed. The vacancies are thus created at the surface, and the kinetics of Figs. 2 and 3 describe the vacancy migration into the bulk. Interestingly, the lifetime component of positrons trapped at vacancies decreases to 247(8) ps after etching. This lifetime is expected for monovacancies complexed with P atoms, such as  $V\text{-P}_3$  [17,18]. The profile of quenched-in divacancy complexes is thus much narrower than that of the monovacancy complexes. This is reasonable since the formation of the stable  $V\text{-P}_3$  defect is proportional to the vacancy concentration, whereas the divacancy formation is proportional to the square of the vacancy concentration.

The annealing results show that the concentration of stable vacancy-impurity clusters decreases when the annealing temperature is above 1100 K in Fig. 1 or above 900 K in the P doped sample in Fig. 3. At these temperatures the  $V\text{-As}_3$  and  $V\text{-P}_3$  defects dissociate according to our electron irradiation studies [19]. Stable defect complexes could thus be formed only during the cooling. This is consistent with our previous results in epitaxial Si(As) samples where the cooling rate was seen to influence the final defect concentration [20].

The concentrations of thermal vacancies are shown in Fig. 4. The data have been collected from either equilib-

rium temperature measurements (Fig. 2) or from experiments after long annealings below the dissociation temperatures of vacancy-impurity complexes (Fig. 3). The vacancy concentration  $c = N_A e^{S_f/k_B} e^{-E_f/k_B T}$  follows the Arrhenius behavior ( $N_A$  is the density of lattice sites). The fitted formation energy is  $E_f = 1.1(2)$  eV and entropy  $S_f = 5(3)k_B$ .

The data of Figs. 2 and 3 indicate that the thermal equilibrium requires very long annealings. In order to take the migration and depth profile of vacancies  $c(x, t)$  into account in the analysis, we solved the diffusion equation  $\frac{d}{dt}c(x, t) = D \frac{d^2}{dx^2}c(x, t)$  at conditions equivalent to the measurements. The vacancies were assumed to have the thermal equilibrium concentrations at the surface layers, from where they migrate into the bulk with the diffusion coefficient  $D = \frac{1}{8}\Gamma_s a^2$ , where  $a$  is the lattice constant,  $\Gamma_s = \nu_0 e^{-E_m/k_B T}$  is the jump frequency, and  $\nu_0$  is the Debye frequency  $10^{13}$  s $^{-1}$ . The diffusion model was fitted to the average positron lifetime data by calculating the overlap of the vacancy concentration  $c(x, t)$  and the positron stopping profile.

The analysis of the data in Figs. 2 and 3 yields a value of  $E_m = 1.2(1)$  eV for the migration energy in both As and P doped samples. The migration energy of a pure vacancy is expected to be less than 0.5 eV [7]. However, our result  $E_m = 1.2(1)$  eV is equal to the migration barrier of simple  $V\text{-As}$  and  $V\text{-P}$  pairs, whereas the vacancies complexed with more donor impurities have higher migration energies [18,21,22]. Although the  $V\text{-As}$  and  $V\text{-P}$  pairs are not stable at 700–900 K, we can conclude that the thermal vacancy, on average, diffuses in highly  $n$ -type Si under the Coulomb attraction of a single impurity atom. By fixing a formation entropy of  $S_f = 5k_B$ , the diffusion model also yields the

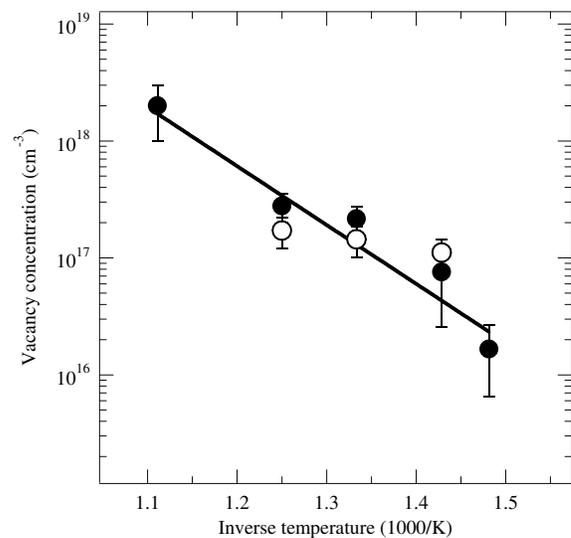


FIG. 4. Concentration of thermal vacancies vs the inverse temperature. The results have been obtained with conventional lifetime experiments (filled symbols) and Doppler broadening experiments with a positron beam (open symbols).

formation energy of vacancies as  $E_f = 1.1(2)$  eV, which is in good agreement with the data of Fig. 4.

We interpret the low formation energy  $E_f = 1.1(2)$  eV as that of a vacancy-impurity pair in highly  $n$ -type Si. When the vacancy is created next to a donor atom, the formation energy is lowered by the binding energy,  $E_b = 1.3(1)$  eV [22,23]. In our case the Fermi level is at the conduction band edge and the vacancy-impurity pair is created in a negative charge state. This gives an additional energy gain equal to the ionization energy of 0.44 eV [24]. We can thus estimate the formation energy of a neutral vacancy in intrinsic Si as  $E_f(V^0) = E_f + E_b + 0.44$  eV = 2.8(3) eV.

In intrinsic Si no vacancies are observed with positron annihilation at temperatures up to 1600 K [13,14]. Thus the vacancy concentration must be less than the detection limit of  $10^{16}$  cm $^{-3}$  at these temperatures. Our estimate of  $E_f(V^0) = 2.8(3)$  eV is in agreement with this conclusion only if the vacancy formation entropy is less than  $5k_B$ . This value can thus be taken as an upper limit for the formation entropy of a neutral vacancy in intrinsic Si. Moreover, it is in agreement with our estimate based on the data of Fig. 4 and with the results of diffusion studies [1–3].

The estimated formation energy  $E_f(V^0) = 2.8(3)$  eV is in reasonable agreement with the theoretical results 3.17 eV [5] and 3.3 eV [6]. It is also within the error limit to the value of 2.1(7) eV obtained by Bracht *et al.* [3]. The activation energy for Si self-diffusion via vacancy mechanism has been estimated to be  $E_a = E_f(V^0) + E_m(V^0) = 4.1$  eV [1–3]. Taking  $E_f(V^0) = 2.8(3)$ , we get that the vacancy migration energy would be  $E_m(V^0) = 1.3(4)$  eV at high temperature. This result is in agreement with that of Bracht *et al.* [ $E_m(V^0) = 1.8(5)$  eV], and supports the idea [3] that the vacancy migration is significantly slower than at low temperature where  $E_m(V^0)$  is below 0.5 eV [7]. We can use our values also to estimate the activation energy of the diffusion of the As impurities via vacancy mechanism at low As concentrations. We get  $E_f(V^0) + E_m = 2.8(3) + 1.2(1) = 4.0(4)$  eV, which is in good agreement with the result of 3.81 eV from the radiotracer experiment of Laitinen *et al.* [25].

The defects that are present in the samples after high-temperature annealings are mainly the  $V$ -As $_3$  and  $V$ -P $_3$  complexes, the same as those observed earlier in highly doped as-grown material [17,20]. These defects are likely to be significant for the electrical deactivation detected at high doping concentrations [20,26]. In electron irradiation studies [18,19] their formation has been explained by the migration of vacancies decorated by one or two donor impurities. It seems that similar migration mechanisms take place in the as-grown samples during the annealing at temperatures where the thermal vacancies are formed, and also during the cooling. The moving vacancies first find a donor atom ( $D$ ) to form the  $V$ - $D_1$  pair, which subsequently move to form the larger  $V$ - $D_2$  and finally  $V$ - $D_3$  complexes.

In conclusion, we have studied the formation of thermal vacancies in highly P and As doped Si. It was observed that the formation starts already at 700 K and at high temperatures the vacancies are mainly isolated from impurities. Upon cooling the vacancies are quenched to stable vacancy-impurity complexes such as  $V$ -As $_3$  and  $V$ -P $_3$ , which act as electrically compensating defects. The vacancy formation and migration energies are estimated as  $E_f = 1.1(2)$  eV and  $E_m = 1.2(1)$  eV, respectively. The low value of  $E_f$  can be explained by vacancy formation next to the dopant atoms, resulting in an energy gain due to attractive binding. Taking the vacancy-impurity interaction into account we can estimate a formation energy of 2.8(3) eV for the neutral monovacancy in intrinsic Si.

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