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Identification of Vacancy-Impurity Complexes in Highly *n*-Type Si

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We show that the detailed atomic structure of vacancy-impurity complexes in Si can be experimentally determined by combining positron lifetime and electron momentum distribution measurements. The vacancies complexed with a single impurity, V-P and V-As, are identified in electron irradiated Si. The formation of native vacancy defects is observed in highly As-doped Si at the doping level of 10^{20} cm^{-3}. The defects are identified as monovacancies surrounded by three As atoms. The formation of a V-As$_3$ complex is consistent with the theoretical descriptions of As diffusion and electrical deactivation in highly As-doped Si. [S0031-9007(99)08546-4]

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In the As and Sb doping of Si the concentration of free electrons saturates at the level of $\leq 5 \times 10^{20}$ cm^{-3} when the impurity concentration is increased [1]. This behavior is indicative of the formation of inactive impurity clusters or compensating defects that trap free electrons. There is presently no consensus on the detailed nature of these defects. Experimental evidence has been obtained on impurity precipitation as well as on the formation of vacancy-impurity complexes (see Refs. [2–4], and references therein). Theoretical results propose that the vacancy-impurity complexes are formed very abundantly and they may also play distinct roles in the diffusion and clustering of impurities [3]. However, the number of vacancies and impurities in these complexes has remained unresolved in the experiments. Moreover, recent calculations and x-ray absorption measurements suggest that the deactivating defects are not associated with vacancies [4]. There is thus a need for new experimental information on the atomic structure of defects in heavily n-type Si.

Positron annihilation spectroscopy is a method for the direct identification of vacancy defects [5]. Thermalized positrons in solids get trapped at neutral and negative vacancies because of the missing positive charge of the ion cores. At vacancies, positron lifetime increases and positron-electron momentum distribution narrows due to the reduced electron density. The core electron momentum distribution can be used to identify the atoms surrounding the vacancy [6]. In earlier measurements in heavily As- or Sb-doped Si, vacancy defects have been detected and the momentum distribution induced by the dopant atom surrounding the vacancy has been qualitatively observed [7–9]. However, these experiments do not reveal the open volume of the vacancies, the number of dopant atoms in their surroundings, or their concentrations.

In this paper we show that the combination of positron lifetime and core electron momentum distribution experiments yields quantitative and detailed information on the structure of vacancy-impurity complexes. We identify V-P and V-As pairs after electron irradiation and show that heavily As-doped Si contains a V-As$_3$ complex as a native defect. The electrical deactivation and diffusion properties of As in Si will be discussed and the recent theoretical models will be commented on in light of our experimental observations.

We studied Czochralski grown (Cz) Si(111) bulk crystals doped with [As] = 10^{19} and 10^{20} cm^{-3} and [P] = 10^{20} cm^{-3}. Experiments were done in as-grown samples as well as after 2 MeV electron irradiation at 300 K. The positron experiments were performed in the conventional way by sandwiching two identical sample pieces with a 30 μCi ^{22}Na positron source [5]. A fast-fast coincidence system with a time resolution of 230 ps was used in the positron lifetime experiments. The positron-electron momentum distribution was measured as a Doppler broadening of the 511 keV annihilation radiation, using a Ge detector with an energy resolution of 1.4 keV. In order to observe positron annihilations with core electrons, the experimental background was reduced by detecting simultaneously the two annihilation photons [6]. For this purpose, a NaI detector was place collinearly with the Ge detector, and a coincidence between the two detectors was electronically required.

The positron lifetime spectra in the as-grown Si([As] = 10^{19} cm^{-3}) and Si([P] = 10^{20} cm^{-3}) samples have a single component of 222 ps at 300 K. The lifetime is the same as often reported for defect-free Si (τ_B = 220 ps) [10], and depends very little on temperature (Fig. 1). This behavior is typical when all positrons annihilate at a delocalized state in the lattice, and it can be attributed to the thermal expansion [5]. The Si([As] = 10^{19} cm^{-3}) and Si([P] = 10^{20} cm^{-3}) samples are thus free of vacancies trapping positrons.

The positron average lifetime is clearly higher in the as-grown Si([As] = 10^{20} cm^{-3}) sample, τ_{av} = 232 ps at 300 K. Furthermore, the lifetime spectrum has two components, the longer of which is $\tau_2 = 250 \pm 3$ ps. Both τ_{av} and τ_2 are almost constant as a function of temperature. The two-componential lifetime spectrum and the increase of τ_{av} above the bulk lifetime τ_B are clear signs that native vacancies exist in the Si([As] = 10^{20} cm^{-3}) sample. The second lifetime component $\tau_2 = 250 \pm 3$ ps is characteristic for the positron annihilations at the vacancy [5].

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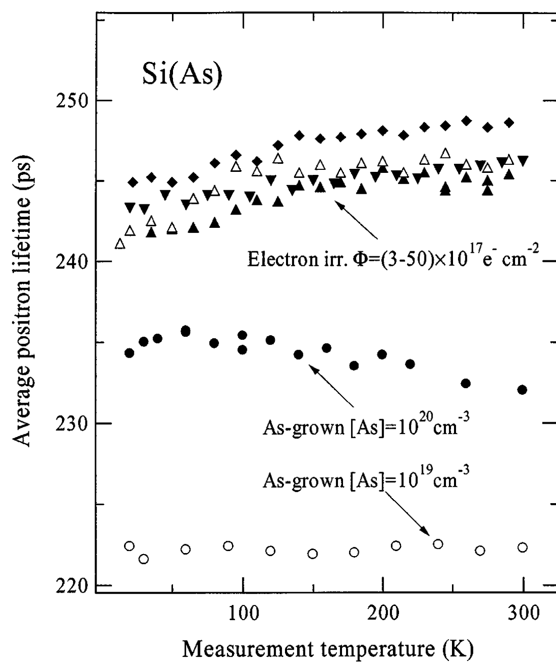

FIG. 1. The average positron lifetime vs temperature in as-grown and electron irradiated Si(As). The irradiation fluences are 3×10^{17} cm^{-2} (△) for the Si([As] = 10^{19} cm^{-3}) sample and 3×10^{17} cm^{-2} (▲), 1×10^{18} cm^{-2} (▼), and 5×10^{18} cm^{-2} (◆) for the Si([As] = 10^{20} cm^{-3}) sample.

In all electron irradiated samples the average positron lifetime is longer than in as-grown samples, indicating that irradiation-induced vacancies are observed. In the Si(P:10^{20}) sample irradiated to the fluence $\Phi = 5 \times 10^{17}$ cm^{-2}, the lifetime spectrum can be decomposed and the vacancy component $\tau_2 = 250 \pm 3$ ps is thus obtained. Both irradiated Si([As] = 10^{20} cm^{-3}) samples have only a single positron lifetime of about 247 ± 2 ps, almost independently of the irradiation fluence (Fig. 1). This behavior can be explained by a total positron trapping at irradiation-induced vacancy defects. When the vacancy concentration exceeds 10^{18} cm^{-3} [5,10], all positrons annihilate at the irradiation-induced vacancy defects with the lifetime 247 ± 2 ps, and no annihilations take place at the delocalized bulk state or at the native vacancies detected only before irradiation. The vacancy concentration of $\sim 10^{18}$ cm^{-3} is consistent with the expected introduction rate in electron irradiated heavily n-type Si [10–12]. We checked with electrical measurements that the conductivity of the samples remains practically unchanged in the irradiation, indicating that the concentration of electrically active As is much larger than that of vacancies.

The same positron lifetime at the vacancy, $\tau_V = 248 \pm 3$ ps, is thus observed for three different types of samples: (i) As-grown Si([As] = 10^{20} cm^{-3}), (ii) electron irradiated Si([As] = 10^{20} cm^{-3}), and (iii) electron irradiated Si([P] = 10^{20} cm^{-3}). The positron lifetime at the vacancy characterizes the open volume of the defect. According to experiments [10,11] and theoretical calculations [13], the lifetime of 248 ± 3 is typical for the single vacancy in Si, whereas for a divacancy much larger values of about 300 ps are observed [13–15]. In all three systems listed above, the open volume of the dominant vacancy defect is the same, and equal to that of a monovacancy.

In order to identify the monovacancies in greater detail, we have performed Doppler broadening experiments using the two-detector coincidence technique [6]. These measurements yield the one-dimensional momentum distribution of electrons as seen by the positron. In the samples containing vacancy defects we obtain the superimposed distribution $\rho(p) = (1 - \eta)\rho_B(p) + \eta\rho_V(p)$, where $\rho_B(p)$ and $\rho_V(p)$ are the momentum distributions in the lattice and at the vacancy, respectively. The lifetime results (Fig. 1) can be used to determine the fraction of positrons annihilating at vacancies $\eta = (\tau_{av} - \tau_B)/(\tau_V - \tau_B)$. Since the momentum distribution in the lattice $\rho_B(p)$ can be measured in the reference sample, the distributions $\rho_V(p)$ at vacancies can be decomposed from the measured spectrum $\rho(p)$. They are shown in Fig. 2 for the monovacancies observed in as-grown Si([As] = 10^{20} cm^{-3}) as well as in irradiated Si([As] = 10^{20} cm^{-3}) and Si([P] = 10^{20} cm^{-3}).

The momentum distributions $\rho_V(p)$ at vacancies indicate large differences in the higher momenta ($p > 12 \times 10^{-3} m_0 c$), where the annihilation with core electrons is the most important contribution (Fig. 2). Since the core

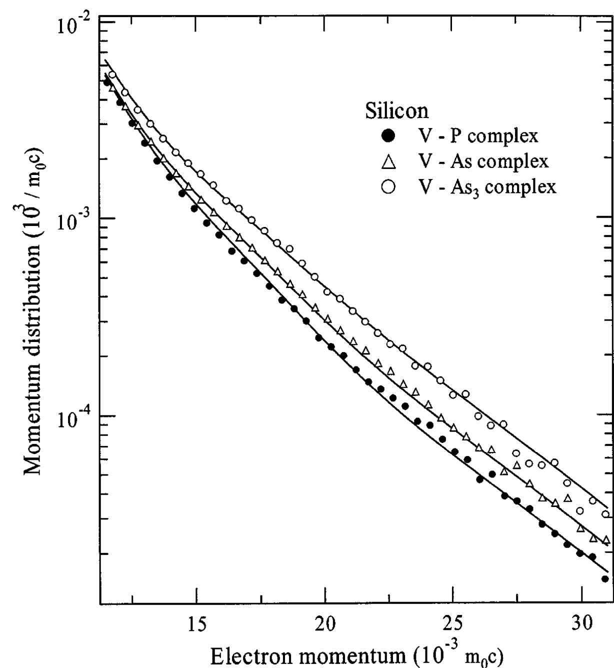

FIG. 2. The high-momentum part of the positron-electron momentum distribution at the various vacancy-impurity pairs, identified in electron irradiated Si([P] = 10^{20} cm^{-3}) (●) and in as-grown (○) and irradiated (△) Si([As] = 10^{20} cm^{-3}). The results of theoretical calculations are shown by the solid lines.

electron momentum distribution is a specific characteristic of a given atom, the differences between the spectra in Fig. 2 indicate different atomic environments of the vacancy in each of the three cases. Because in both Si ($Z = 14$) and P ($Z = 15$) the $2p$ electrons constitute the outermost core electron shell, the core electron momentum distributions of these elements are very similar. The crucial difference in the core electron structures of Si, P, and As is the presence of $3d$ electrons in As. The overlap of positrons with the As $3d$ electrons is much stronger than with the more localized Si or P $2p$ electrons. The large intensity of the core electron momentum distribution is thus a clear sign of As atoms surrounding the vacancy.

The 2 MeV electron irradiation creates vacancies and interstitials as primary defects, both of which are mobile at 300 K [12]. In heavily n-type Si the donor atom may capture the vacancy and form a vacancy-impurity pair [12]. The monovacancy detected in heavily P-doped Si is thus the V-P pair. Similarly, it is natural to associate the electron irradiation-induced vacancy in Si([As] $= 10^{20}$ cm^{-3}) with a V-As pair surrounded by a single As atom. The influence of As next to the vacancy is clearly visible as the enhanced intensity in the high momentum region (Fig. 2). Since an even stronger signal from As is seen in the as-grown Si([As] $= 10^{20}$ cm^{-3}), we can conclude that this monovacancy is surrounded by at least two As atoms.

To analyze quantitatively the chemical environment of the monovacancies we define the conventional W parameter as an integral of the momentum distribution at $20 \times 10^{-3} < p/m_0c < 25 \times 10^{-3}$. The relative quantities W_V/W_B as well as the positron lifetimes are given in Table I. Because of the similar core electron structures of Si and P the value $W_V/W_B = 0.71$ measured for the V-P pair is expected to be close to that of an isolated vacancy (for a theoretical verification, see below). The W_V/W_B increases by 0.28 between the V-P pair (isolated vacancy) and the V-As pair found in electron irradiated Si([As] $= 10^{20}$ cm^{-3}). For the vacancy in as-grown Si([As] $= 10^{20}$ cm^{-3}) the ratio $W_V/W_B = 1.49$. The change of W_V/W_B from the irradiation-induced V-As pair to the native V-As$_n$ complex is thus about twice the difference between the V-P (isolated vacancy) and V-As defects. A linear extrapolation of the W_V/W_B ratio on the number of neighboring As atoms thus indicates that the native complex is V-As$_3$, i.e., the vacancy is surrounded by *three* As atoms.

TABLE I. Experimental (expt) and theoretical (theor) positron annihilation characteristics at vacancy-arsenic complexes in Si. The leftmost column indicates the number of As atoms neighboring the vacancy. τ_V, W_V, and W_B are the positron lifetime and the high electron-momentum parameters in the bulk (subscript B) and at the vacancy (subscript V), respectively.

No. of As atoms	τ_V (ps) (expt)	τ_V (ps) (theor)	W_V/W_B (expt)	W_V/W_B (theor)
0	248(3)	257	0.71(3)	0.74
1	248(3)	254	0.99(3)	0.98
2	···	253	···	1.23
3	248(3)	252	1.49(3)	1.49
4	···	250	···	1.76

The As atoms modify the momentum distribution at the vacancy also at $p < 10 \times 10^{-3} m_0c$, where the annihilations with valence electrons dominate. Figure 3 shows the differences $\rho_{V\text{-As}}(p) - \rho_{V\text{-P}}(p)$ and $\rho_{V\text{-As}_3}(p) - \rho_{V\text{-P}}(p)$, which emphasize the effect of substituting the Si (or P) atoms by As atoms in the lattice sites neighboring the vacancy. When the number of As atoms increases, the valence electron momentum distribution broadens.

In order to put the above ideas on a firmer basis we calculated the momentum distributions of annihilating electron-positron pairs theoretically [13,16]. The valence electron densities were calculated self-consistently, employing the plane-wave pseudopotential method. Atomic wave functions were used for core electrons. A supercell of 64 atomic sites in a periodic superlattice was used to describe defects which were assumed to be ideal, i.e., the atoms were at the ideal lattice sites. Only the neutral defect states were considered in the calculations. The ensuring positron states and annihilation characteristics were calculated within the local density approximation for electron-positron correlation (parametrizations by Boronski and Nieminen [17] were used). The state-dependent enhancement scheme [16] was used in calculating momentum distributions. We tested that the use of the pseudowave functions instead of all-electron wave functions for valence electrons and the cutoff of the plane-wave

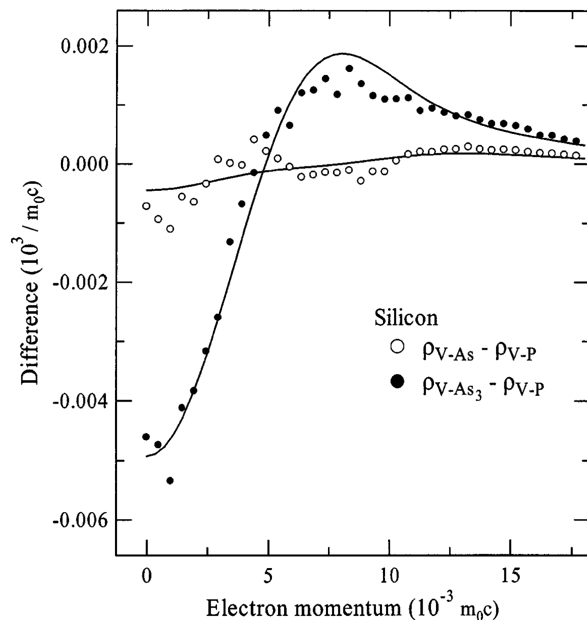

FIG. 3. The momentum difference of V-As and V-As$_3$ complexes with respect to the momentum distribution at the V-P complex. The theoretical calculations are shown by the solid lines.

expansions does not affect the momentum distributions in the momentum regions considered.

The theoretical results reproduce well the experimental observation that the positron lifetime is rather insensitive to the substitutional impurities surrounding the vacancy (Table I). The calculations verify further that nearly the same W parameter is obtained for an isolated vacancy and a V-P pair. The theoretical and experimental momentum distributions are in good agreement at high momenta (Fig. 2). The theoretical W_V/W_B ratio increases by about 0.26 for each As atom added. This is the same difference as deduced above from the experimental results for V-P and V-As pairs and used further to identify the V-As_3 native defects. The calculated W_V/W_B ratio for the V-As_3 complex is in very good agreement with the experimental result, whereas those for V-As_2 and V-As_4 are much too small or large, respectively. In the valence electron-momentum range, the calculated difference curves for V-As and V-As_3 fit very well with the experiment (Fig. 3), but for V-As_2 and V-As_4 a strong disagreement is found. The broadening of the momentum distribution with the substitution of Si by As (Fig. 3) can be interpreted as an increase of valence electron density seen by the positron. To conclude, the theoretical calculations strongly support the experimental defect identifications that (i) vacancies complexed with single donor impurities are detected in electron irradiated P and As-doped Si, and (ii) the native defect in Si($[\mathrm{As}] = 10^{20}\ \mathrm{cm}^{-3}$) is a vacancy surrounded by three As atoms.

The existence of V-As_3 complexes in heavily As-doped Cz Si is consistent with the defect formation and diffusion mechanisms described theoretically by Ramamoorthy and Pantelides [3]. The calculated formation energies of V-As_n ($n > 2$) complexes are negative, suggesting that total deactivation of As takes place at any doping level [2,3]. The n-type conductivity of Si(As) is possible only because the creation of defect complexes is limited by kinetic processes such as the migration of defects. At high temperature, the diffusion of As starts with the formation of V-As pairs, which can migrate if two As atoms are fifth neighbors or closer to each other, thus enabling the formation of V-As_2 complexes [18]. The calculations predict that this complex can diffuse fast through the sample even at moderate temperatures [3]. At the high growth temperature of Cz Si, the V-As_2 complexes thus migrate until they stop at the substitutional As forming the V-As_3 complex. In perfect agreement with this theoretical scheme, the stable V-As_3 complex is observed in the experiments in the Si($[\mathrm{As}] = 10^{20}\ \mathrm{cm}^{-3}$) sample. Furthermore, no V-As_3 are found at the lower doping level of $[\mathrm{As}] = 10^{19}\ \mathrm{cm}^{-3}$, most likely because the average distance between the donor atoms is too large to form the migrating V-As_2 in the process described above.

The concentration of free electrons in heavily doped Si saturates at $\leq 5 \times 10^{20}\ \mathrm{cm}^{-3}$ due to the formation of compensating defects [1]. The deactivation has been theoretically explained by the creation of vacancy-impurity complexes V_m-As_n, but there is no agreement on the value of m and n [2,3,19]. The present results show that V-As_3 is the dominant vacancy defect in Cz grown Si($[\mathrm{As}] = 10^{20}\ \mathrm{cm}^{-3}$), i.e., $m = 1$ and $n = 3$. The concentration of V-As_3 in our samples is $\sim 10^{17}\ \mathrm{cm}^{-3}$, which is a typical value for compensating centers at the doping level of $1 \times 10^{20}\ \mathrm{cm}^{-3}$ [1,4,9,19]. Recently, the deactivation of dopants has been attributed to the formation of defects containing pairs of dopant atoms without vacancies [4]. The present experiments do not give information on these defects, because the open volume in them is too small to trap positrons.

In conclusion, the present results show that positron lifetime and core electron momentum distribution experiments can yield detailed information on the open volume and atomic surrounding of vacancy-impurity complexes in Si. In electron irradiated material, we identify vacancies complexed with single P and As impurities. In as-grown Si we observe the formation of vacancy defects when the As doping level increases up to $10^{20}\ \mathrm{cm}^{-3}$. The native defect is identified as a monovacancy surrounded by three As atoms. The formation of a V-As_3 complex is consistent with the theoretical predictions on the As diffusion and electrical deactivation in highly doped Si.

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