Formation of Vacancy-Impurity Complexes by Kinetic Processes in Highly As-Doped Si

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Positron annihilation experiments have been applied to verify the formation mechanism of electrically inactive vacancy-impurity clusters in highly n-type Si. We show that the migration of V-As pairs at 450 K leads to the formation of V-As_2 complexes, which in turn convert to stable V-As_3 defects at 700 K. These processes manifest the formation of V-As_3 as the dominant vacancy-impurity cluster in highly n-type Si. They further explain the electrical deactivation and clustering of As in epitaxial or ion-implanted Si during postgrowth heat treatment at 700 K.

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The computing speed of microprocessors increases due to the miniaturization of the Si field-effect transistors (FETs) which act as the basic logical elements of the device [1]. The decrease of the size of the FET requires an increase in the doping density, both at the source and drain electrodes as well as in the channel [1]. Doping levels up to 10^{20} cm^{-3} are used in current device technologies. In n-type doping of Si with arsenic, however, fundamental material problems start to appear when doping increases above $\sim 3 \times 10^{20}$ cm^{-3} [2,3]. The concentration of free electrons does not increase linearly with the doping concentration, indicating that inactive impurity clusters or compensating defects are formed. Furthermore, the diffusion coefficient of As starts to increase rapidly at $[\mathrm{As}] > 3 \times 10^{20}$ cm^{-3} demonstrating that new migration mechanisms become dominant [4].

Both the electrical deactivation of dopants and the enhanced As diffusion have often been attributed to the formation of vacancy-impurity complexes [3]. According to theoretical calculations, vacancies surrounded by several As atoms (V-As_n, $n > 2$) have negative formation energies suggesting that these complexes are abundantly present at any doping level [5,6]. The formation of these defects is, however, limited by kinetic processes such as the migration of As. At very high doping concentrations ($>10^{20}$ cm^{-3}) the diffusion of V-As pairs is enhanced by another As at the fifth neighbor site or closer (the vacancy percolation model) [4,7]. The calculations predict that also the V-As_2 complex is mobile at relatively low temperatures enabling the formation of higher order V-As_n complexes [6,8]. In fact, vacancy complexes have been observed in positron annihilation experiments [9] and recently their dominant structure has been identified as V-As_3 in Czochralski (Cz) Si doped up to $[\mathrm{As}] = 10^{20}$ cm^{-3} [10].

In this Letter we apply positron annihilation spectroscopy to verify experimentally the formation mechanism of V-As_3 complexes in highly n-type Si. Positrons get trapped at vacancy defects with subsequent changes in their annihilation characteristics. The positron lifetime gives direct information on the open volume of the defect. The Doppler broadening of the annihilation radiation is sensitive to the atomic environment of the vacancy. The combination of these techniques thus allows the identification of both the open volume of the defect and the atoms surrounding it. The present results indicate that the mobile V-As pairs form V-As_2 complexes at 450 K in highly n-type Si. The V-As_2 defects become mobile at 700 K and create subsequently stable V-As_3 complexes by migration. This process manifests experimentally the formation mechanism of V-As_3 in highly n-type Si at high growth temperatures. It further explains how the electrical deactivation and clustering of As take place in low-temperature (300–500 K) grown Si during postgrowth heat treatment at about 700 K.

We studied Si(111) bulk crystals grown with the Czochralski (Cz) method and doped with As concentrations $[\mathrm{As}] = 10^{19}$ and 10^{20} cm^{-3}. The as-grown materials have been characterized earlier by positron spectroscopy [10]. No vacancies were detected in Si($[\mathrm{As}] = 10^{19}$ cm^{-3}). The other sample Si($[\mathrm{As}] = 10^{20}$ cm^{-3}) was found to contain native vacancies complexed with three As atoms (V-As_3 defects) at concentrations of $\sim 10^{17}$ cm^{-3}. In this work, the samples were irradiated with 2 MeV electrons at 300 K in order to create vacancy defects above thermal equilibrium concentration and to study their annealing and migration processes. The irradiation fluences were 1×10^{18} and 5×10^{18} cm^{-2} for the samples Si($[\mathrm{As}] = 10^{19}$ cm^{-3}) and Si($[\mathrm{As}] = 10^{20}$ cm^{-3}), respectively. After irradiation the samples were annealed isochronally (30 min) at 300–900 K and all positron experiments were done at 300 K.

The positron lifetime measurements were performed using a conventional fast-fast coincidence system with a time resolution of 210 ps (for technical details see, e.g., Ref. [11]). The lifetime spectra $n(t)$ were analyzed in terms of exponential decay components $n(t) = \sum_i I_i \exp(-t/\tau_i)$. The positron in state i (e.g., delocalized state in the lattice or localized state at a vacancy) annihilates with lifetime τ_i and intensity I_i. The increase of the average lifetime $\tau_{\mathrm{ave}} = \sum_i I_i \tau_i$ above the bulk Si lattice lifetime $\tau_B = 218$ ps shows that vacancy defects exist in the samples. The Doppler broadening of the annihilation radiation was measured using Ge detectors. The coincidence detection of both 511 keV photons

emitted from the $e^+ - e^-$ annihilation was accomplished by a two-parameter multichannel analyzer. An energy resolution of 0.9 keV and peak-to-background ratio of 2×10^6 were achieved in the coincidence mode.

After irradiation at 300 K the average positron lifetime in both samples is 242–245 ps. The lifetime spectra have one dominant component of about $\tau_V = 240$ ps, but a longer lifetime of $\tau_{V2} = 300$ ps with a small intensity ($I_{V2} \sim 10\%$) is also observed. The average lifetime is almost independent of irradiation fluence in the range $\Phi = (3-50) \times 10^{17}$ cm^{-2} [10]. As explained earlier [10], these results indicate that almost all ($\geq$90%) positrons annihilate as trapped at monovacancies ($\tau_V = 240$ ps), although a minor contribution from divacancies ($\tau_{V2} = 300$ ps [11] and intensity I_{V2}) is also detected. The monovacancies can be identified as vacancy-arsenic pairs [10] (the so-called E centers) which are formed when irradiation-induced primary vacancies migrate and get trapped by As impurities [12]. Their concentration is $\geq 10^{18}$ cm^{-3}, which is compatible with that of primary vacancies [$\approx 3 \times 10^{18}$ cm^{-3} for the fluence of 10^{18} cm^{-2} (see, e.g., [13])]. A large fraction of the vacancies thus survive recombination with interstitials and migrate to form E centers.

The average positron lifetimes are shown as a function of annealing temperature in Fig. 1. Between 300 and 400 K τ_{ave} is almost constant in both samples, but starts to decrease above 400 K. Some vacancy defects thus disappear from the sample, as can be expected since the recovery of the E centers starts at 400 K [12]. After annealing at 440–500 K both the average lifetime and the intensity I_{V2} increase (Fig. 1). Divacancies are thus formed as a result of the annealing but I_{V2} shows that their concentration remains an order of magnitude smaller than that of V-As pairs. In agreement with earlier studies [12], all divacancies disappear at 500–550 K as indicated by the decreasing τ_{ave} and I_{V2} in Fig. 1.

After annealings above 600 K the positron lifetime spectra in Si([As] = 10^{20} cm^{-3}) have only a single component indicating saturated positron trapping at monovacancies with the lifetime $\tau_V = 240$ ps. No evident decrease in their concentration was observed between 300 and 500 K since the changes seen in τ_{ave} can be totally attributed to divacancies (I_{V2} in Fig. 1). On the other hand, the average lifetime decreases more in Si([As] = 10^{19} cm^{-3}), first between 400 and 600 K (Fig. 1), and then up to 900 K. The positron trapping rates $\kappa = \tau_B^{-1}(\tau_{\text{ave}} - \tau_B)/(\tau_V - \tau_{\text{ave}})$ show that the vacancy concentration decreases by an order of magnitude between 650 and 900 K. Vacancy defects thus survive the annealings better in the samples with higher doping.

Doppler broadening measurements were performed to identify the atomic structure of monovacancies after various annealings. The conventional W parameter gives the probability of positron annihilations with core electrons at high momenta [in this work at $(10-16) \times 10^{-3} m_0 c$, where m_0 is the rest mass of electron and c is the speed of light]. To remove the influence of positron annihilations at bulk lattice from the Doppler spectra, we calculated the fraction of annihilations at vacancies $\eta = (\tau_{\text{ave}} - \tau_B)/(\tau_V - \tau_B) = (W - W_B)/(W_V - W_B)$ from the positron lifetime data and solved thereafter the characteristic W_V parameter at vacancies ($W = W_B$ in defect-free Si). This parameter is shown as scaled to W_B in Fig. 2.

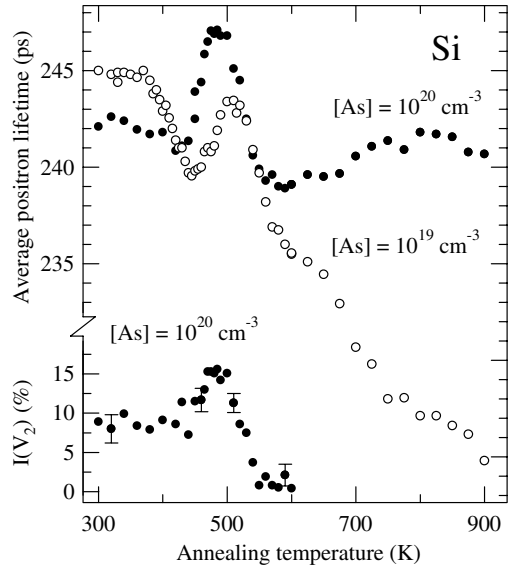

FIG. 1. Average positron lifetime and the intensity I_{V2} of the divacancy lifetime component ($\tau_{V2} = 300$ ps) as a function of annealing temperature. All measurements were done at 300 K. I_{V2} has been determined by fixing $\tau_{V2} = 300$ ps in the analysis of positron lifetime spectra.

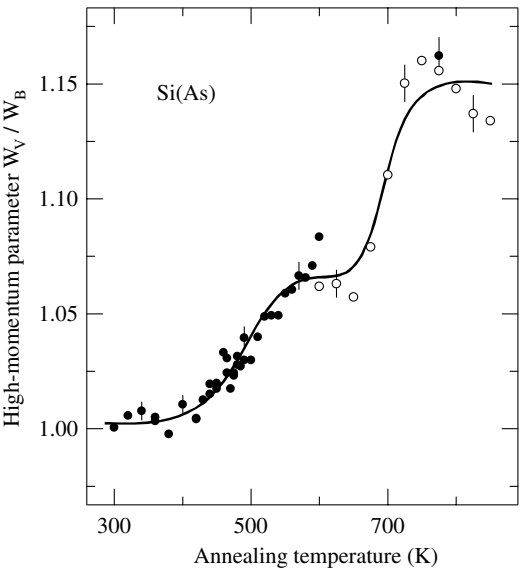

FIG. 2. Relative W parameter of the vacancy defect as a function of annealing temperature. Solid points are measured in sample Si([As] = 10^{20} cm^{-3}) and open circles in Si([As] = 10^{19} cm^{-3}).

The W_V/W_B parameter stays at a constant value of 1.00 up to 400 K. In the V-As pair the value of W_V is equal to W_B since the decrease of the core electron density at the vacancy is compensated by the $3d$ electrons of the As atom adjacent to the vacancy [10]. At the recovery stage of E centers at 400–500 K the W_V parameter starts to increase towards $W_V/W_B = 1.07$, and a further step up to $W_V/W_B = 1.15$ is seen at 650–750 K. In both these recovery stages the probability of positron annihilations with core electrons increases indicating that more As atoms appear in the atomic surroundings of the monovacancies. This is the dominant effect because the divacancies seen in the lifetime results (Fig. 1) obviously contribute very little to the W parameters in Fig. 2.

The core electron regions of the Doppler broadening spectra were recorded more accurately using a coincidence setup of two Ge detectors. This allows the measurement of high-momentum events at $(15–40) \times 10^{-3} m_0 c$ (Fig. 3) where annihilations with either the Si $2p$ or As $3d$ electrons dominate. The curve obtained after electron irradiation at 300 K corresponds to the V-As pairs. It has higher intensity than that in isolated vacancies or V-P pairs (shown in Ref. [10]) due to the $3d$ electrons of the As atom [10].

The annealing at 600 K increases the intensity of the momentum distribution by ~25% (Fig. 3) indicating stronger overlap between positrons and As $3d$ electrons. By combining experiments and theory, the increase of exactly 25% can be expected when a vacancy is surrounded by two As atoms instead of one [10]. Further, the curve after 775 K annealing has ~50% larger intensity than obtained for the V-As pair. The comparison with theoretical calculations [10] implies that the vacancy has three As atoms as its nearest neighbors. In fact, the momentum distribution after annealing at 775 K is similar as we have previously measured for V-As_3 complexes formed during the growth (Fig. 3 and Ref. [10]). Notice that this complex is present also at concentrations of 10^{17} cm^{-3} in the Si([As] = 10^{20} cm^{-3}) material before irradiation. However, the concentration of V-As_3 defects is $>10^{18}$ cm^{-3} after irradiation and annealing at 775 K (see Fig. 1), indicating that the possible contribution of the native V-As_3 is negligible.

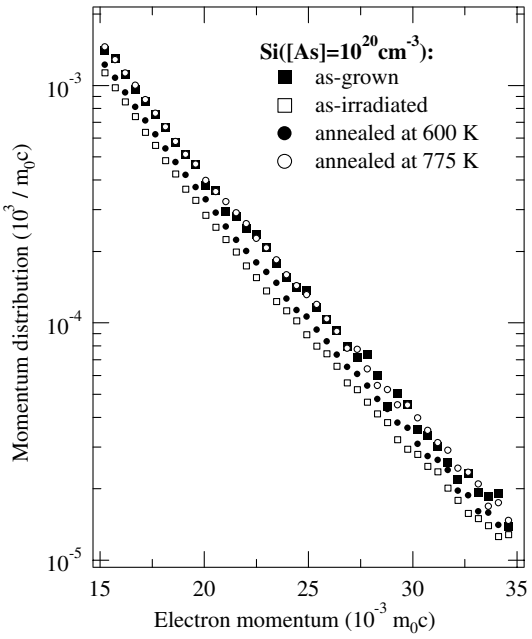

FIG. 3. Core electron momentum distribution for native (black squares) or irradiation-induced (other markers) vacancies in sample Si([As] = 10^{20} cm^{-3}). In the as-grown Si the figure shows the decomposed spectrum where annihilations in the defect-free Si lattice have been removed [10].

The annealing sequences of irradiation-induced point defects manifest the migration mechanisms of vacancy-impurity complexes in heavily As-doped Si. After annealing at 400 K the V-As pairs become unstable and start to convert to V-As_2 complexes as indicated by the increasing W_V in Fig. 2. The V-As_2 defect is naturally formed when V-As migrates as a pair until trapped by an isolated As impurity. During further annealing at 700 K, V-As_2 centers are converted to V-As_3 defects. Again, this obviously takes place when the V-As_2 complexes become mobile and migrate until they find an As atom in the lattice. At high As concentrations ([As] = 10^{20} cm^{-3}) the formation of V-As_2 and V-As_3 is likely and their concentration is thus comparable with that of V-As after irradiation at 300 K ($>10^{18}$ cm^{-3}). When the impurity concentration is lower ([As] = 10^{19} cm^{-3}), however, the dissociations of V-As and V-As_2 dominate because roughly 10 times more migration steps are required for the formation of V-As_2 and V-As_3. As seen in the lifetime results (Fig. 1), the migration or dissociation processes also create some divacancies which are stable at 440–500 K.

The pair diffusion of V-As is generally explained by the ring mechanism, where the binding between the positive As impurity and the negative vacancy plays a crucial role. At the saddle point the vacancy has moved away from the As atom to a third-nearest neighbor site, from where it can return next to As along a different path, in order to complete an elementary migration step of the pair. Monte Carlo simulations suggest that the vacancy-assisted As diffusion is totally dominated by the ring mechanism at temperatures below 1300 K [14]. Similar diffusion mechanism has been proposed for V-As_2, which migrates when the vacancy moves around the sixfold ring occupying two As atoms. According to recent *ab initio* calculations the migration barriers of the V-As and V-As_2 are 1.19 and 2.0 eV, respectively [8].

Experimental estimates for the migration energies E_m of V-As and V-As_2 can be deduced from the temperatures at which these complexes become mobile. We write the number of diffusion jumps simply as $N = \nu_0 \Delta t \exp(-E_m/kT)$, where $\nu_0 \approx 10^{13}$ s^{-1} is the jump attempt frequency [15] and $\Delta t = 1800$ s is the annealing

time. Assuming that the vacancy takes typically $N = 10^1 - 10^3$ jumps before forming a higher order V-As_n complex, we can convert the migration temperatures to energy barriers E_m. Our experimental estimates for V-As and V-As_2 are $E_m(V\text{-As}) = 1.3(2)$ eV and $E_m(V\text{-}As_2) = 2.0(2)$ eV, respectively, where the errors include realistic uncertainties in the number of diffusion jumps N and frequency ν_o. Both of these values are in excellent agreement with the theoretical calculations of Xie and Chen [8]. Our estimate for V-As is also close to that (1.1 eV) determined in electron paramagnetic resonance (EPR) experiments [15].

Previous results obtained with deep level transient spectroscopy (DLTS) [16] and EPR [17] suggest that the migration of E centers leads to the formation of vacancies surrounded by two P atoms in heavily P-doped Si. The present results verify this process in As-doped Si. Our data allow us to suggest further that the disappearance of the V-P_2 signal in DLTS measurements at 550 K [16] takes place because this defect starts to migrate and forms V-P_3 clusters when trapped at a P impurity.

The present positron experiments thus give strong support for the scenarios of As diffusion, clustering, and electrical deactivation via ring mechanisms. The diffusion of As takes place rapidly when V-As and V-As_2 complexes are present, but stops when V-As_3 defects are formed. This complex is dominant in Cz Si($[As] = 10^{20}$ cm^{-3}) bulk samples grown at high temperatures [10], and it is stable according to theoretical calculations [6,8]. Furthermore, samples prepared by epitaxial techniques [18] or ion implantation at 300–500 K followed by laser treatment [2] show evidence of the impurity clustering and subsequent electrical deactivation when they are annealed at 700–800 K [2]. The activation energy for this process is 2.0 eV [2]. At 700–800 K we see that V-As_2 becomes mobile, with a migration barrier of 2.0 eV, and passivates isolated As donors by binding them to V-As_3 complexes. The deactivating V-As_3 complexes may break in annealings at 1100–1300 K, since partial recovery of electrical activity is observed [19]. This mechanism should be verified by positron experiments in the future.

In conclusion, our positron annihilation experiments give direct information on kinetic processes leading to the formation of vacancy-arsenic complexes in highly n-type Si. The V-As pairs become mobile at 450 K [activation energy 1.3(2) eV] and migrate until stopped by substitutional As to form V-As_2 complexes. Subsequently the V-As_2 complexes start to diffuse at 700 K and create stable V-As_3 complexes by migration [activation energy 2.0(2) eV]. These processes manifest the formation of higher-order vacancy-impurity clusters by the ring diffusion mechanism. They further explain (i) the presence of electrically inactive V-As_3 complexes as dominant vacancy defects in heavily n-type Si and (ii) the electrical deactivation of low-temperature grown Si by heat treatment at 700 K.

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