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Positron trapping kinetics in thermally generated vacancy donor complexes in highly As-doped silicon

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We have measured positron lifetime and Doppler broadening in highly As-doped silicon containing thermally generated V-As_3 defect complexes (vacancy is surrounded by three arsenic atoms). We observe positron detrapping from the V-As_3 defect complex and determine the binding energy of 0.27 eV of a positron to the complex. The results explain why 85% of the thermal vacancies formed in highly As-doped Si at temperatures over 700 K are invisible to positron measurements at elevated temperatures.

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I. INTRODUCTION

Miniaturization of field-effect transistors requires higher and higher doping densities to maintain a sufficient conductance of the source and drain areas.[1] In the case of arsenic, problems arise when the donor concentration is increased above $\sim 3\times 10^{20}$ cm^{-3}.[2] At doping levels this high, the free electron concentration stops increasing linearly with the doping density and saturates.[2,3] At the same time, a new As-migration mechanism becomes dominant.[4] Both these effects have been attributed to the formation of vacancy impurity complexes such as V-As_3, i.e., vacancy surrounded by three donor atoms.[3]

Thermal vacancies that form during processes at high temperatures can mediate the diffusion of impurity atoms in silicon. This diffusion leads to the formation of electrically passive donor impurity clusters, thus playing a significant role in electrical deactivation of the material. Recently, thermal vacancies have been directly observed with the positron annihilation spectroscopy in highly n-type silicon.[5]

Positron annihilation spectroscopy is suitable for observing thermal vacancies directly at high temperatures where they form. In intrinsic silicon, the concentration of thermal vacancies is still below the detection limit of positron measurements ($\sim 10^{16}$ cm^{-3}) even at 1600 K.[6,7] However, in highly n-type Si thermal vacancies form more abundantly as pairs with donor atoms and in negative charge state due to electron trapping, which both lower the formation energy.[3]

Measurements carried out in P-doped Si show the increase in positron lifetime as the thermal vacancies diffuse from the surface (where they form) into the bulk.[5] In heavily As-doped Si, however, the effect is greatly reduced, since most of the thermally generated vacancies ($\sim$85%) seem to be invisible as far as positron measurements are concerned.[8] In this work we show that this is due to positrons escaping from vacancy-impurity complexes at high temperatures and determine the binding energy of 0.27(3) eV of a positron to the V-As_3 complex.

II. METHOD

A. Experimental details

Our samples were Czochralski-grown Si(111) bulk crystals with an As doping of 1×10^{20} cm^{-3}. The untreated sample (1) contained a small concentration ($\sim 10^{17}$ cm^{-3}) of native V-As_3 defects, as shown in Ref. 9. The samples 3 and 4 have been annealed at 900 and 920 K until the thermal equilibrium vacancy concentration has been achieved and then quenched to room temperature, as reported in Ref. 5. One sample pair (2) was then annealed during positron lifetime measurements at 700, 750, and 800 K. The details of the samples are collected into the Table I.

The positron lifetime experiments were carried out using a conventional fast-fast lifetime spectrometer with a time resolution of 260 ps and a ^{22}NaCl source with a positron activity of 10 μCi. The positron annihilations in the source material, in the Ni-foil covering the source, and as positronium were determined using a reference sample and subtracted from the lifetime spectra before the analysis. The sample temperature during the measurements was controlled by liquid nitrogen cooling and resistive heating systems.

The lifetime spectra $n(t)=\Sigma_i I_i \exp(-t/\tau_i)$ were analyzed as a sum of exponential decay components convoluted with the Gaussian resolution function of the spectrometer. The indexes i correspond to the different lifetime components in the spectra with individual lifetimes τ_i and intensities I_i. The increase of the average lifetime τ_{ave} above the bulk lifetime τ_B=218 ps in Si is an indication of vacancies being present in the material.[10] This parameter coincides with the center of

TABLE I. Samples were annealed at different temperatures to thermally create vacancy impurity complexes. T is the annealing temperature and t the duration of the annealing. The vacancy concentration $[V]$ has been calculated from the positron lifetime measurements after the annealing at room temperature assuming a single monovacancy defect with As decoration, for which the defect lifetime is 248 ps.

Sample	T (K)	t (h)	τ_{ave} at RT (ps)	$[V]$ (10^{18} cm^{-3})
1			226	0.4(1)
2	700	25		
	750	188		
	800	88	234	1.2(1)
3	900	17	243	5.2(5)
4	920	168	243	5.2(5)

mass of the lifetime spectrum and is insensitive to the decomposition process. Changes even as low as 1 ps can be reliably measured. The vacancy concentrations were determined from the average positron lifetime using the conventional positron trapping model with a trapping coefficient of $\mu_D = 2 \times 10^{15}$ s^{-1}.[11]

The Doppler broadening of the annihilation radiation was measured simultaneously with positron lifetime using a Ge detector with an energy resolution of 1.3 keV at 511 keV. The Doppler broadened momentum distribution was analyzed using the conventional shape parameters S and W, which describe the positron annihilation fraction with low momentum electrons ($|p_z| < 3 \times 10^{-3}\ m_0 c$) and with high momentum electrons ($9 \times 10^{-3}\ m_0 c < |p_z| < 15 \times 10^{-3}\ m_0 c$), respectively.[10] The Doppler technique gives information not only on the vacancy concentration, but also about chemical surroundings of the vacancy.[9]

B. Positron trapping at defects

The positron annihilation rate λ_i in a state i is proportional to the electron density at the site of the positron. Each state has thus a characteristic lifetime τ_i defined as $\tau_i = 1/\lambda_i$. The experimental positron lifetime spectrum can be decomposed into several lifetime components allowing the determination of the fractions of positrons annihilating in various states. The average lifetime, when N lifetime components can be separated from the experimental spectrum, is

$$\tau_{ave} = \sum_{j=1}^{N} I_j \tau_j, \tag{1}$$

where I_j is the intensity of the lifetime component. In the common case of one type of defect with a specific lifetime τ_D and no detrapping, the higher lifetime component $\tau_2 = \tau_D$ gives directly the defect lifetime and the smaller lifetime component is the modified bulk lifetime[12] $\tau_1 = (\tau_B^{-1} + \kappa_D)^{-1}$.

The lifetime components change, however, if the positrons escape from the trap. In the case of one type of defect and taking into account the detrapping, the lifetime components τ_1 and τ_2 depend on the trapping parameters as[12]

$$\frac{1}{\tau_{1,2}} = \frac{1}{2}\{\tau_B^{-1} + \tau_D^{-1} + \kappa + \delta \pm [\,(\tau_B^{-1} + \kappa - \tau_D^{-1} - \delta)^2 + 4\kappa\delta)]^{1/2}\}. \tag{2}$$

The escape rate δ at a temperature T is given by[13]

$$\delta = \mu_D \left(\frac{2\pi m^* k_B T}{h^2}\right) \exp\left(-\frac{E_b}{k_B T}\right), \tag{3}$$

where E_b is the binding energy of the positron to the trap and m^* is the effective mass of the positron ($m^* \approx m_0$). The trapping rate of positrons to the vacancies κ is proportional to the defect concentration c_D (Ref. 10)

$$\kappa = \mu_D c_D, \tag{4}$$

where μ_D is the trapping coefficient.

Finally, the intensities in Eq. (1) are given by[12]

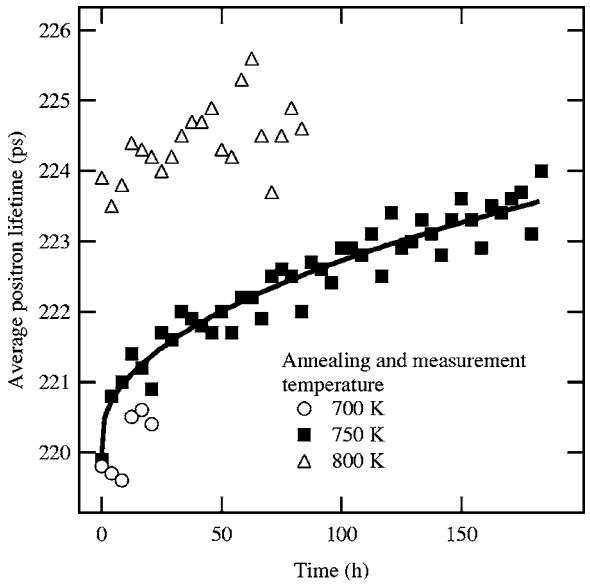

FIG. 1. Average positron lifetime as a function of isothermal annealing time for different temperatures in Si([As]$=10^{20}$ cm^{-3}) sample 2. The measurements were performed at the annealing temperature. The solid curve is from the solution of the diffusion equation as explained in Ref. 5.

$$I_1 = \frac{\lambda_B - \lambda_2}{\lambda_1 - \lambda_2} = \frac{\tau_1(\tau_2 - \tau_B)}{\tau_B(\tau_2 - \tau_1)}, \tag{5}$$

$$I_2 = \frac{\lambda_1 - \lambda_B}{\lambda_1 - \lambda_2} = \frac{\tau_2(\tau_B - \tau_1)}{\tau_B(\tau_2 - \tau_1)}. \tag{6}$$

III. RESULTS

A. Lifetime measurements during annealing

The average positron lifetime measured at room temperature in the untreated sample 2 (the same as 1) before annealings was $\tau_{ave} = 226$ ps. When the temperature during the positron measurements was increased to 700 K the average positron lifetime decreased to $\tau_{ave} \sim 220$ ps. Figure 1 shows the average positron lifetime as a function of isothermal annealing time at temperatures 700, 750, and 800 K. The measurements were carried out *in situ* at the annealing temperatures. The positron lifetime starts to increase already at 700 K. During 180 h at 750 K, the average positron lifetime increases to the value of $\tau_{ave} \approx 224$ ps. At 800 K the curve shows signs of saturation to about 225 ps.

Interestingly, after the long annealing at 800 K, the average positron lifetime after cooling down to room temperature increased to a value of $\tau_{ave} = 234$ ps. This lifetime is much larger than that observed during the 800 K annealing and suggests that only a small fraction of the vacancy defects trap positrons at 750 and 800 K. The samples annealed at 900 and 920 K (3 and 4) were measured only after cooling down.

B. Lifetime measurements after annealing

In order to understand what causes the increase in the average positron lifetime after cooling down from the an-

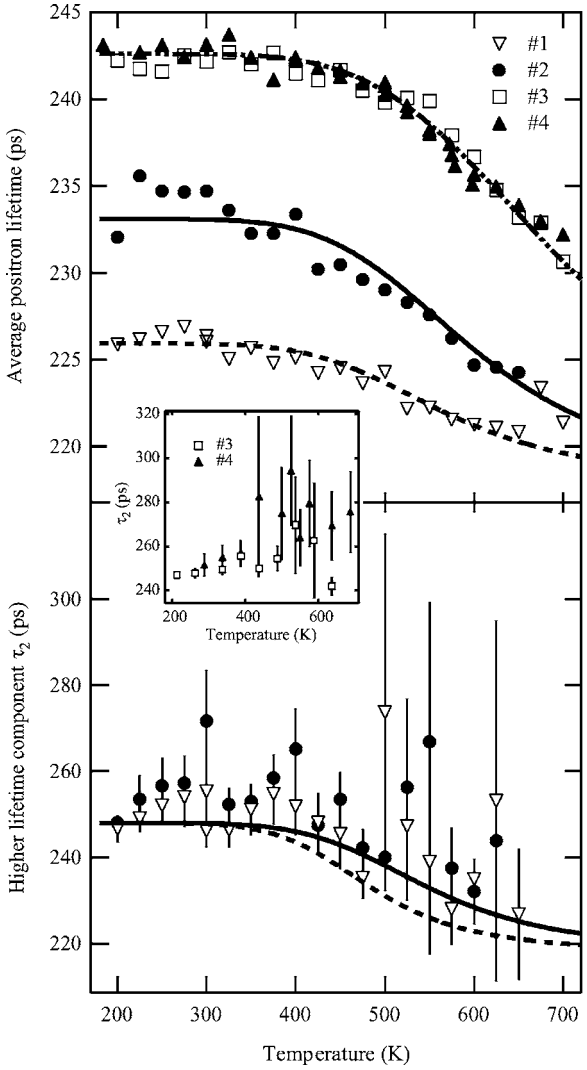

FIG. 2. The average positron lifetime and the larger lifetime component as a function of measurement temperature. The numbers in the legend correspond to the sample numbers in the text. The lines have been fitted to the average lifetime data using the kinetic trapping model. The lines among the higher lifetime data have been calculated from the fits to the average lifetime data. The inset shows the larger lifetime component in samples 3 and 4, where the lifetime shows no decreasing behavior.

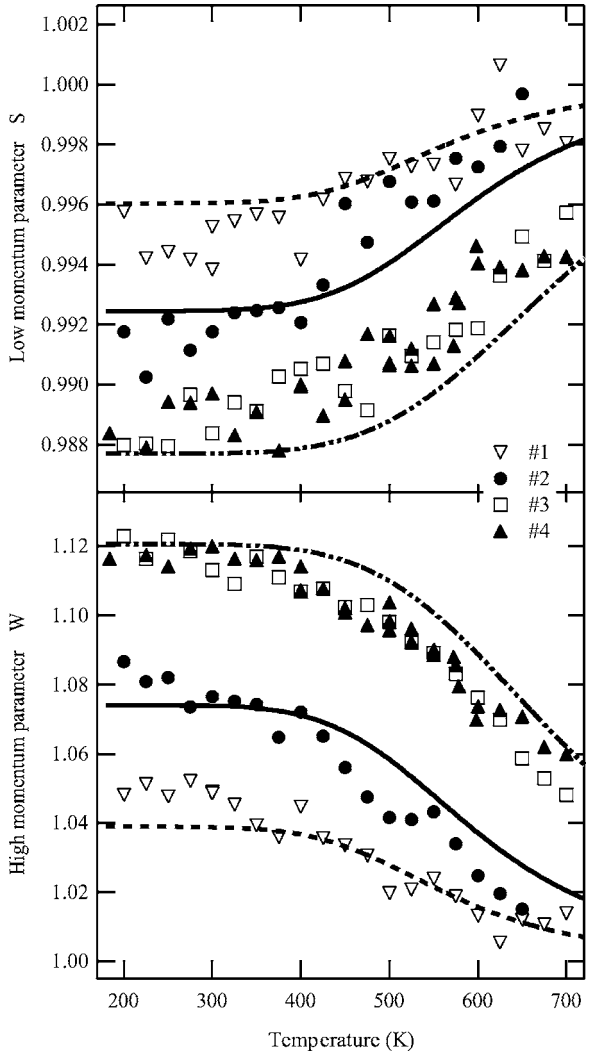

FIG. 3. The low momentum Doppler parameter S and the high momentum Doppler parameter W as a function of measurement temperature. The numbers in the legend correspond to the sample numbers in the text. The parameters are shown as scaled to the bulk values. The lines have been calculated from the fitting to the average lifetime data.

nealing temperature, we measured the positron lifetime in the temperature range from 180 to 700 K after completing the isothermal annealing experiments. The results are shown in Fig. 2. The four samples have different thermal histories and thus different vacancy concentrations, which increase the average positron lifetime from the bulk value at room temperature.

The average positron lifetime remains constant up until 400 K, at which temperature it starts decreasing. The decrease continues up to 700 K, where the lifetime in the samples 1 and 2 shows signs of saturation. The decrease is visible in all the measured samples and it is much stronger than the normal temperature dependence ($T^{-1/2}$) of the trapping coefficient for negatively charged defects at these temperatures.[14] This behavior is reversible with temperature, which cancels out the possibility of defects annealing out.

The higher lifetime component τ_2 also presented in Fig. 2 decreases with temperature in the two samples with smaller vacancy concentration. This can be explained by positrons escaping from the defect at high temperatures. The higher lifetime component in the samples annealed at 900 and 920 K does not decrease with temperature. In the sample annealed at 900 K, τ_2 remains constant whereas in the 920 K annealed sample τ_2 even increases. This can be explained by trapping of positrons to an additional defect in these two samples.

C. Doppler broadening results

The S and W parameters measured in the samples as a function of temperature are presented in Fig. 3. The parameters have been scaled to the values in the bulk

(S_B=0.4296, W_B=0.04229). At room temperature the S parameter is lower and the W parameter is higher than in the bulk. This is due to 3d electrons of three As atoms decorating the vacancy, which increase the relative intensity of the core electron momentum distribution.[9,15]

The S parameter in the case of V-As is clearly above the bulk value with the chosen energy window. The addition of another As around the vacancy lowers the S parameter to the bulk level. Finally, in the case of V-As_3 the S parameter drops below the bulk value.[9] At the same time, the W parameter increases in steps with each As atom added around the vacancy. The effect of As on the W parameter has been demonstrated in Refs. 16 and 17. From the values of S and W, it can be confirmed that the dominant defect in these samples is the monovacancy surrounded by three As atoms (V-As_3), as shown earlier.[5,9]

As the temperature is increased, the S parameter increases and the W parameter decreases. Both parameters thus approach bulk values of 1, which indicates that the signal from As atoms decreases. The solid and dashed curves presented in Fig. 3 have been calculated from the fits to the lifetime data using

$$P = \frac{\tau_{ave} - \tau_B}{\tau_D - \tau_B}(P_D - 1) + 1, \quad (7)$$

where the parameter P corresponds to the shape parameters S and W and P_D the parameter values in the defect state (scaled to the bulk value of 1). The calculated curves show that the Doppler results are in good agreement with the lifetime data.

IV. DISCUSSION

The increase in the average positron lifetime in Fig. 1 is due to thermal vacancies diffusing from the surface into the bulk Si similarly as observed previously in P-doped Si.[5] Interestingly, the average positron lifetime is much lower at 700 K than at room temperature both before and after the annealings at high temperature. This indicates that only a small fraction ($\sim$15%) of thermal vacancies is visible to positron measurements at temperatures above 700 K. However, after the long annealing at 750 and 800 K (Fig. 1) the V-As_3 concentration increased from 4×10^{17} to 1×10^{18} cm^{-3} showing that, although invisible at high temperature, thermal vacancies form abundantly and remain in vacancy impurity complexes after cooling down.

The fit to the lifetime data measured at 750 K has been obtained using the diffusion equation assuming vacancy formation at the surface followed by migration into the bulk. The formation entropy was fixed to the value of $5k_B$ similarly as in Ref. 5 and the defect lifetime was assumed to be 248 ps, which corresponds the positron lifetime in the As-decorated Si monovacancy. The fit gives a formation energy E_f=0.8(2) eV and a migration energy E_m=1.5(1) eV. These values are comparable to those obtained earlier in P-doped Si.[5] The migration energy appears to be slightly larger in As-doped Si, which reflects the lower diffusivity of vacancies in As-doped than in P-doped Si.

We fitted the average lifetime data presented in Fig. 2 using the kinetic trapping model [Eqs. (1)–(5)]. Using the defect lifetime of τ_D=248 ps (average at 180–350 K) and the bulk lifetime τ_B=218 ps, the fit gives a binding energy of 0.27(3) eV and defect concentrations of 4×10^{17}, 1×10^{18}, 5×10^{18}, and 5×10^{18} cm^{-3} for the untreated sample (1) and samples annealed at 800, 900 and 920 K (2, 3, and 4), respectively.

The solid and dashed curves in the lower part of Fig. 2 have been calculated from the fits to the average lifetime data and demonstrate that in the samples 1 and 2 the higher lifetime component decreases as expected assuming positrons escape the trap. However, in the samples annealed at 900 and 920 K the higher lifetime component (Fig. 2) does not decrease as expected in the case of detrapping. In these samples the defect concentration is close to 10^{19} cm^{-3}, which suggests that the vacancy concentration approaches the limit where all the As atoms are part of V-As_3 complexes, the doping concentration being $\sim10^{20}$ cm^{-3}. The V-As_3 complex is formed when a diffusing V-As_2 complex meets yet another As atom.[16] When the V-As_3 concentration approaches the concentration of free As atoms, the diffusing V-As_2 is as likely to find a ready-made V-As_3 complex as a separate As atom and form a V_2-As_5 complex. Similar defect complexes have been reported in highly As doped silicon earlier and it has been confirmed that the relative amount of V_2-As_5 increases dramatically during annealings at 800 °C.[15] This is consistent with the fact that the effect of V_2-As_5 shows in the two samples with the highest annealing temperatures.

The V_2-As_5 complexes are not observed at room temperature because the V-As_3 dominate, but as the positrons escape from V-As_3 above 400 K, they may still trap into V_2-As_5. However, as the overall trapping at vacancy defects still decreases, τ_{ave} decreases with temperature similarly as in the case of the samples annealed at lower temperatures. The characteristic positron lifetime at V_2-As_5 is likely to be close to the lifetime in an undecorated Si divacancy, about 290 ps,[18] or slightly lower due to the As-decoration. From the fact that τ_2 is highest in sample 4, it can be concluded that the concentration of V_2-As_5 is highest in this sample that has been annealed the longest time in the highest temperature. In the V_2-As_5 complex the S parameter is higher and the W parameter lower than in the case of V-As_3, explaining also why the S parameter increases and the W parameter decreases with increasing temperature more rapidly than expected from the lifetime data in samples 3 and 4 (see curves in Fig. 3).

The positron trapping at V-As_3 can be compared with the results obtained from the vacancy-impurity complexes in P-doped Si. Specifically the results in Fig. 1 can be compared with similar data from the P-doped samples.[5] In both cases the average positron lifetime increases as a function of measurement time as the vacancies diffuse from the surface into the bulk of the sample. However, the effect is much larger in magnitude in P-doped Si. This indicates that the positrons do not escape from the V-P_3 complex at these temperatures. This is in agreement with the earlier results from positron measurements in P-doped Si.[19] As positrons escape efficiently from the V-As_3 at high temperatures, the vacancy defects observed during the annealing at high temperatures are therefore monovacancies decorated with only one or two As atoms and divacancies decorated with As atoms such as the V_2-As_5 complex.

V. CONCLUSIONS

We have carried out positron lifetime and Doppler broadening experiments in highly As-doped silicon containing thermally generated V-As_3 complexes. We observed thermal escape of positrons from the V-As_3 complex at high temperatures. The detrapping starts at 400 K and from the temperature dependence of the positron lifetime we determine the binding energy of positrons to V-As_3 as 0.27(3) eV. The formation of V-As_3 complexes from diffusing thermal vacancies and subsequent detrapping of positrons from the V-As_3 complex explains why the increase in the average positron lifetime due to thermal vacancies is clearly smaller in As-doped Si than in P-doped Si at high temperatures, in spite of the similarity of the vacancy formation energies in the two materials.

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