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Silicon displacement threshold energy determined by electron paramagnetic resonance and positron annihilation spectroscopy in cubic and hexagonal polytypes of silicon carbide

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Abstract

Both for electronic and nuclear applications, it is of major interest to understand the properties of point defects into silicon carbide (SiC). Low energy electron irradiations are supposed to create primary defects into materials. SiC single crystals have been irradiated with electrons at two beam energies in order to investigate the silicon displacement threshold energy into SiC. This paper presents the characterization of the electron irradiation-induced point defects into both polytypes hexagonal (6H) and cubic (3C) SiC single crystals by using both positron annihilation spectroscopy (PAS) and electron paramagnetic resonance (EPR). The nature and the concentration of the generated point defects depend on the energy of the electron beam and the polytype. After an electron irradiation at an energy of 800 keV v_{Si} mono-vacancies and v_{Si}–v_C di-vacancies are detected in both 3C and 6H–SiC polytypes. On the contrary, the nature of point defects detected after an electron irradiation at 190 keV strongly depends on the polytype. Into 6H–SiC crystals, silicon Frenkel pairs v_{Si}–Si are detected whereas only carbon vacancy related defects are detected into 3C–SiC crystals. The difference observed in the distribution of defects detected into the two polytypes can be explained by the different values of the silicon displacement threshold energies for 3C and 6H–SiC. By comparing the calculated theoretical numbers of displaced atoms with the defects numbers measured using EPR, the silicon displacement threshold energy has been estimated to be slightly lower than 20 eV in the 6H polytype and close to 25 eV in the 3C polytype.

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1. Introduction

Silicon carbide is an important material, both for its electronic and physical properties. Due to its high thermal conductivity, high temperature stability, chemical inertness and small neutron capture

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cross-section, SiC has potential uses in nuclear applications. It has been proposed for the encapsulation of fissile material in high temperature nuclear reactors of the fourth generation. To simulate and evaluate the behavior of SiC in reactors, fundamental data on the effect of irradiation in SiC have to be determined. One of these fundamental data is the displacement threshold energy, which is essential to foresee the formation of defects in materials under irradiation. Several experimental or theoretical studies have already been performed to determine the displacement energy thresholds for silicon and carbon in SiC. The mean values of the threshold displacement energies E_d have been calculated by molecular dynamics (MD) in 3C–SiC by Devanathan and Weber [1] (classic MD) and by Lucas and Pizzagalli [2] (MD ab initio): $E_d(\mathrm{Si}) = 35$ eV and $E_d(\mathrm{C}) = 20$ eV. For 6H–SiC this value is still in debate, as recent experimental studies have given very different results. Steeds et al. [3] found a value close to 19 eV using the electron beam of a transmission electron microscope associated with the photoluminescence technique to characterize the generated point defects, while Rempel et al. [4], using a Van de Graaff accelerator and positron annihilation techniques, proposed that it is higher than 30 eV.

In this work positron annihilation spectroscopy (PAS) and electron paramagnetic resonance (EPR) were used to investigate the properties of vacancy defects produced by low energy electron irradiation and to propose a value of the silicon displacement energy in both 3C and 6H polytypes.

2. Experimental

2.1. Materials and irradiation conditions

Two SiC polytypes have been studied: 170 μm thick 3C–SiC N-doped ($N_D - N_A = 8.4 \times 10^{15}$ cm^{-3}) (001) oriented single crystals, and 420 μm thick 6H–SiC N-doped ($N_D - N_A \approx 1 \times 10^{18}$ cm^{-3}) (0001) oriented single crystals. 3C–SiC crystals have been grown by the HOYA Company using CVD on Si(111) substrates, and then polished by NovaSiC using a mechano-chemical process. The characterization of the 3C–SiC as-grown crystals using positron annihilation spectroscopies [5] has shown that the two faces are very different. On the 'growth' face no defects have been detected while vacancy defects are present in a layer close to the Si/SiC interface. 6H–SiC crystals have been grown by CEA-LETI using the modified Lely method. Their characterization by positron annihilation spectroscopy shows that these crystals are homogeneous as a function of depth, but contain a quite high concentration of negatively charged non-vacancy defects.

Electron irradiations have been performed in liquid hydrogen ($T = 20$ K) at LSI laboratory using a Van de Graaff accelerator at two different beam energies (350 keV and 1 MeV). During irradiations the samples are placed in a 10 μm thick copper foil dived in liquid hydrogen. Before reaching the SiC samples, the electrons have to cross the different materials (i.e. a 25 μm thick steel window, 2 mm of liquid hydrogen and a 10 μm thick copper foil). The mean energies at the entrance of the crystals are 190 keV for the lowest beam energy and 880 keV for the highest one. At 880 keV, electrons cross the crystals, while 190 keV electrons stop into the samples. The electron fluence depends on the electron beam energy: it is 3×10^{19} cm^{-2} for the lowest energy, and 5×10^{18} cm^{-2} for the highest one.

2.2. X-band electronic paramagnetic resonance measurements

They were performed using an EMX BRUKER spectrometer in the 120–290 K range. The spectra were decomposed using numerical simulation into different lorentzian shape components. The spin numbers in the irradiated crystals were determined at 290 K by comparison with a $CuSO_4$ standard sample.

2.3. Positron lifetime spectroscopy measurements (PALS)

The PALS technique was used to study the nature of vacancy defects created in the bulk of the 880 keV electron irradiated 3C–SiC crystals. Positron lifetime is the time between the entrance of the positron and its annihilation in the material. Positron lifetime measurements were performed using a conventional fast–fast coincidence spectrometer with a time resolution of 230 ps. A ^{22}Na positron source was sandwiched between two identical samples. The time intervals between the detection of the 1.27 MeV β^+ decay photon simultaneously emitted with positron and the 0.511 keV annihilation photons are measured as a function of the temperature in the 15–295 K range. Approximately two million events are collected for each spectrum. After subtracting the source and background components, the lifetime spectra is the convolution of the resolution of the spectrometer $R(t)$ with the probability that the positron annihilates at the time t *which is the sum of decreasing exponentials*

$$L(t) = R(t)\sum_i I_i \exp\left(\frac{-t}{\tau_i}\right). \quad (1)$$

These spectra were fitted with one or two components using a modified version of the software PosFiT [6]. For a two-component decomposition Eq. (1) becomes

$$L(t) = R(t)\left[I_1 \cdot \exp\left(\frac{-t}{\tau_1}\right) + I_2 \cdot \exp\left(\frac{-t}{\tau_2}\right)\right], \quad (2)$$

where I_1 and I_2 are the intensities ($I_1 + I_2 = 1$), and τ_1 and τ_2 are the lifetime components of the spectra. The average lifetime is calculated as follows:

$$\tau_{av} = (I_1 \cdot \tau_1) + (I_2 \cdot \tau_2). \quad (3)$$

It increases when the size or/and the concentration of vacancy defects increases.

3. Theoretical calculations

Both PENELOPE [7] and POLY-SMOTT [8] programs have been used to calculate respectively the electron energy loss during SiC irradiation and the atomic displacement cross-sections. The PENELOPE program permits to simulate the energy loss of the electrons along their range in a material that is considered as amorphous. Using PENELOPE program, the electron energy distribution and the beam angular dispersion, at the entrance of SiC and as a function of depth into SiC, were obtained. The program takes into account the different materials crossed before reaching SiC (i.e. a 25 μm thick steel window, 2 mm of liquid hydrogen and a 10 μm thick copper foil). POLY-SMOTT programs give the displacements cross- sections as a function of the electron energy in polyatomic solids for different values of the displacement threshold energies E_d. It has to be underlined that these programs take into account the indirect collisions that can occur during irradiation (displacement cascades). The combination of the PENELOPE and POLY-SMOTT programs gives an estimation of the number of displaced atoms, as a function of the electrons incident energy and as a function of the depth into SiC, in both 3C–SiC and 6H–SiC single crystals. The number of displaced atoms into the crystal N, can therefore be estimated from the following expression:

$$N = \phi \cdot S \cdot N_A \int_0^L \int_0^{E_{max}} p(E,x) \cdot \sigma(E) \cdot dE \cdot dx, \quad (4)$$

where A is Si or C, N_A is the A atoms concentration (cm^{-3}), ϕ is the electrons fluence (cm^{-2}), S is the irradiated surface (cm^2), L is the sample thickness (cm), $p(E,x)$ is the energy and depth electrons distribution, and $\sigma(E)$ the displacements cross-section. In the Table 1, the N values obtained for the silicon sublattice in the 3C and 6H polytypes irradiated at the mean energy of 880 and 190 keV, respectively, and with the fluence of 5×10^{18} and 3×10^{19} cm^{-2}, respectively, are reported. N is given in each case for different displacement threshold energies E_d(Si) fixed in the 15–30 eV range.

These values will be compared in the discussion with the defect concentrations determined by electron paramagnetic resonance.

4. Experimental results

For the two polytypes, the EPR signals depend on the irradiation conditions, but the same EPR spectra were observed for different measurement temperatures in the 120–290 K range. In the 190 keV irradiated 6H–SiC crystal, EPR measurements show a spectrum (Fig. 1) characterized by an isotropic superhyperfine (SHF) interaction with 6 equivalent NNN Si and a g-factor of 2.0030 (when the magnetic field is parallel to the (0001) axis). This spectrum

Table 1
Numbers of silicon atoms displaced in the 3C–SiC and 6H–SiC crystals under electron irradiations as a function of the silicon displacement threshold energy and of the irradiation conditions

SiC polytype	Thickness (μm)	Electron irradiations		E_d(Si) (eV)			
		Energy (keV)	Fluence (cm^{-2})	15	20	25	30
3C–SiC	157	880	5×10^{18}	1.0×10^{16}	4.6×10^{15}	1.7×10^{15}	3.6×10^{14}
6H–SiC	420	190	3×10^{19}	9.8×10^{15}	1.4×10^{15}	1.9×10^{14}	5.4×10^{13}

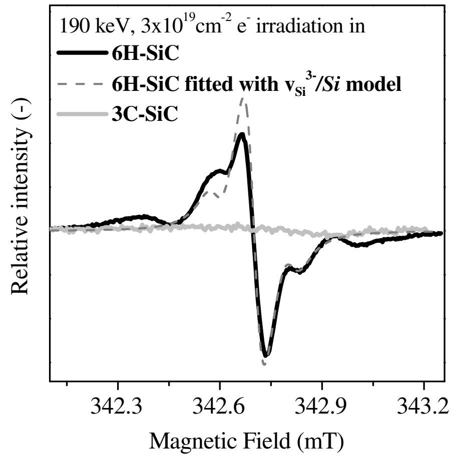

Fig. 1. EPR signal measured when the magnetic field is parallel to the (1000) axis in 6H–SiC and when the magnetic field is parallel to the (001) axis in 3C–SiC after electron irradiation at an energy of 190 keV at a fluence of 3×10^{19} cm^{-2}.

has already been attributed to the v_{Si}^{3-}/Si Frenkel pair by Von Bardeleben et al. [9] and Kerbiriou et al. [10]. The number of Frenkel pairs detected in the 190 keV 3×10^{19} cm^{-2} irradiated crystal is $(1.9\pm0.2)\times10^{15}$ (corresponding to a concentration of 9.4×10^{17} cm^{-3}). For 3C–SiC, the well-known isolated v_{Si}^{-} mono-vacancy [11], characterized by its SHF interaction with 12 equivalent Si atoms, is detected by EPR (Fig. 2) in the 880 keV 5×10^{18} cm^{-2} electron irradiated crystal, and the number of v_{Si}^{-} is $5.0\pm0.5\times10^{14}$ (corresponding to a concentration of 1.6×10^{17} cm^{-3}). After a 190 keV irradiation at a fluence of 3×10^{19} cm^{-2} (Fig. 1), no irradiation-induced spectrum is observed in the 3C–SiC crystal.

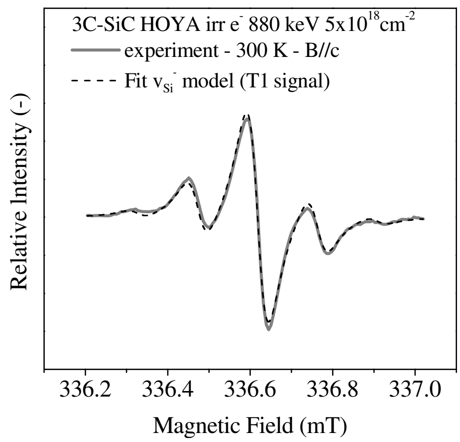

Fig. 2. EPR signal measured when the magnetic field is parallel to the (001) axis in 3C–SiC after electron irradiation at 880 keV at a fluence of 5×10^{18} cm^{-2}.

The positron lifetime measurements were performed as a function of the sample temperature (15–295 K) in the 880 keV irradiated and in the non-irradiated 3C–SiC crystals. The value of the average positron lifetimes τ_{av} obtained from the decomposition of the spectra for the 880 keV irradiated 3C–SiC crystals increases from 192 ± 1 ps at 15 K up to 201 ± 1 ps at 295 K (Fig. 3(a)). The decomposition of the spectra gives two lifetimes plotted as a function of the measurement temperature in Fig. 3: the short lifetime component is approximately $\tau_1\approx130\pm15$ ps and is independent of the temperature, while the long lifetime component τ_2 increases from 210 ± 4 ps at low

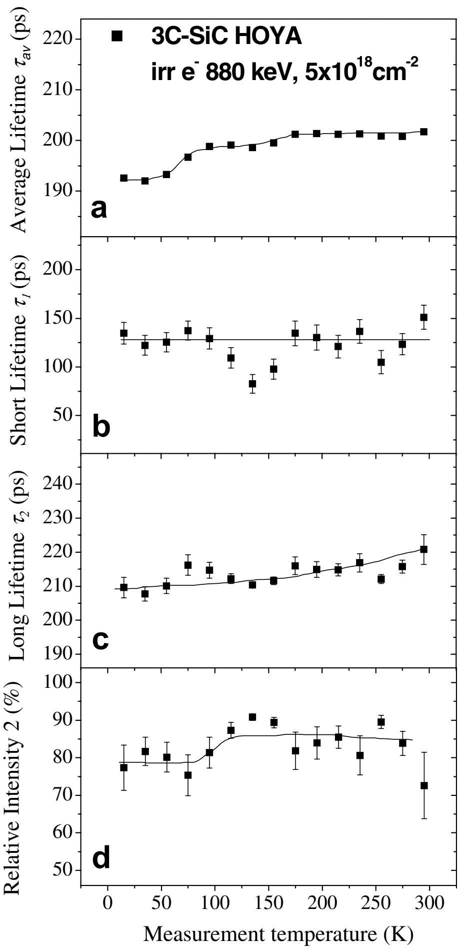

Fig. 3. Temperature dependence of the positron lifetime components obtained for the 880 keV electron irradiated 3C–SiC crystals: (a) average lifetime τ_{av}; (b) lifetime τ_1 of the shortest component; (c) lifetime τ_2 of the longest component; (d) its intensity I_2. The solid lines are guides to the eyes.

temperature up to 220 ± 7 ps at 295 K. The intensity I_2, relative to the long lifetime component τ_2 is first constant at $80 \pm 5\%$ from 15 to 75 K, then it increases very slightly up to $86 \pm 5\%$ at 105 K and it finally remains constant up to 295 K. Consequently, the intensity I_1 relative to the short lifetime component τ_1 that is given from the formula $I_1 = 100\% - I_2$ decreases as the temperature increases. In the non-irradiated 3C–SiC crystals, the average positron lifetimes τ_{av} slightly decreases from 150 ± 1 ps at 15 K up to 147 ± 1 ps at 295 K.

5. Discussion

EPR measurements show a strong signal attributed to the v_{Si}^{3-}/Si Frenkel pair in the 190 keV irradiated 6H–SiC crystal (at a fluence of $3 \times 10^{19}\ cm^{-2}$). On the contrary, no irradiation-induced defects are detected by EPR in the 3C–SiC crystal irradiated in the same conditions (190 keV, $3 \times 10^{19}\ cm^{-2}$). It indicates that either v_{Si} is created (but in a charge state which is not detectable by EPR), or the minimum electron beam energy needed to displace a silicon atom in 3C–SiC is higher than in 6H–SiC. Moreover, Doppler broadening measurements performed in the 190 keV 3C–SiC irradiated crystal have been previously reported [10] and it has been proposed that the main detected defect is the carbon mono-vacancy. These results suggest a difference concerning the silicon displacement threshold energy for the polytypes 3C and 6H. This energy could be higher for the polytype 3C than for the polytype 6H.

The equality between the theoretical number of displacements (Table 1) and the experimental number of v_{Si}^{3-}/Si detected by EPR in the 190 keV irradiated 6H–SiC crystal ($1.9 \pm 0.2 \times 10^{15}$) is obtained for a value of the silicon displacement threshold energy slightly lower than 20 eV (but higher than 15 eV). This result is in good agreement with the $E_d(Si)$ value of 19 eV proposed by Steeds et al. [3].

For the 3C–SiC 880 keV irradiated crystals, positron lifetime measurements show that τ_{av} is longer than the value obtained in the virgin crystal, indicating that the electron irradiation has generated vacancy defects. The average lifetime τ_{av} increases from 192 ± 1 ps at 15 K up to 201 ± 1 ps at 295 K. It indicates that positrons annihilate in several annihilation states and that their distribution (nature and/or concentration) changes with the measurement temperature. The short lifetime $\tau_1 \approx 130 \pm 15$ ps is quite close to the SiC lattice one ($\tau_L = 140$ ps) [5], but it remains lower, which indicates that a fraction of positrons annihilate in the lattice delocalized state and thus a partial trapping of the positrons. Moreover, the intensity I_1 relative to this short lifetime component τ_1 decreases as the temperature increases. The τ_1 value close to the SiC lattice lifetime and this I_1 decrease can be explained by the presence of an acceptor and non-vacancy-like defects called 'negative ions'. Indeed, the trapping coefficient of positrons at these 'negative ions' decreases as the temperature increases [12] and their detrapping increases with temperature due to their low binding energy into such traps. These defects were not present in the virgin crystal, which suggests that they have been generated during irradiation. The long lifetime component τ_2 is characteristic of the vacancy defects. τ_2 value measured in the 880 keV irradiated 3C–SiC crystal slightly varies as a function of the temperature from 210 ± 4 ps up to 220 ± 7 ps, indicating the positron trapping in at least two different vacancy defects. It is longer than the characteristic lifetime that has been proposed for the silicon mono-vacancies v_{Si} ($\tau = 202$ ps) in SiC [13]. It indicates that vacancy defects with larger open volume are detected in these irradiated 3C–SiC crystals. As already proposed by Kerbiriou et al. [10] for the 880 keV irradiated 6H–SiC crystals, both mono-vacancies v_{Si} – with characteristic lifetime $\tau = 202$ ps- and di-vacancies v_{Si}–v_C – with characteristic lifetime $\tau = 225$ ps could be the vacancy defects detected in these crystals. EPR measurements show the presence of v_{Si}^{-} in these 880 keV irradiated 3C–SiC crystals. The equality between the theoretical number of displacements (Table 1) and the experimental number of v_{Si}^{-} detected by EPR in the 880 keV irradiated 3C–SiC crystal is obtained for a value of the silicon displacement threshold energy included between 25 and 30 eV. Nevertheless, this value does not take into account the creation of other v_{Si} related defects by irradiation, such as the di-vacancies that are detected by PALS measurements in these samples. $E_d(Si)$ should then be slightly lower than the value evaluated from the direct comparison of the calculated numbers of displaced atoms and the generated v_{Si}^{-} number measured by EPR. $E_d(Si)$ is therefore proposed to be close to 25 eV. The maximum displacement energy transferred to Si atoms with a 190 keV electron beam corresponds to the value of 18 eV. It is then coherent with the non-detection of the silicon Frenkel pair in the 190 keV irradiated 3C crystals.

According to Devanathan and Weber [1] and its Molecular Dynamics calculations, the silicon displacement threshold energies in equivalent directions are 5 eV higher for the 3C polytype than for the 6H polytype. The difference of the silicon displacement threshold energies between the polytypes determined from the experimental studies described in this paper is therefore in agreement with the one calculated by Devanathan et al.

6. Conclusion

EPR measurements show that v_{Si}^{3-}/Si Frenkel pairs and v_{Si}^{-} are respectively created in the 6H–SiC 190 keV electron irradiated and in the 3C–SiC 880 keV electron irradiated crystals. Moreover, PAS results show that v_{Si}–v_{C} di-vacancies are detected in addition to v_{Si}^{-} in the 880 keV irradiated 3C–SiC crystals. The comparison of the numbers of defects measured by EPR with the theoretical calculations indicates that the silicon displacement threshold energy is higher in 3C–SiC ($\approx$25 eV) than in 6H–SiC (slightly <20 eV).

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