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Vacancy in 6H-Silicon Carbide Studied by Slow Positron Beam *

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The defect changes in 6H-SiC after annealing and 10 MeV electron irradiation have been studied by using a variable-energy positron beam. It was found that after annealing, the defect concentration in n-type 6H-SiC decreased due to recombination with interstitials. When the sample was annealed at 1400 °C for 30 min in vacuum, a 20-nm thickness Si layer was found on the top of the SiC substrate, this is a direct proof of the Si atoms diffusing to surface when annealed at high temperature stages. After 10 MeV electron irradiation, for n-type 6H-SiC, the S parameter increased from 0.4739 to 0.4822, and the relative positron-trapping rate was about 27.878 times of the origin sample, this shows that there are some defects created in n-type 6H-SiC. For p-type 6H-SiC, it is very unclear, this may be because of the opposite charge of vacancy defects.

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Nowadays, there is great interest in silicon carbide (SiC). As a semi-conduction material, silicon carbide holds great potential for power devices that are functional under extreme conditions, such as high temperature, high-frequency, and radiation environments.[1−4]. Recently, it has already been possible to grow SiC with good perfection and control to develop excellent devices.[5] In order to improve the device performance and wafer die yields, it is necessary to reveal the nature of irradiation-induced defects. Various methods have been used to study the defects induced by irradiation, such as electron spin resonance (ESR), photoluminescence (PL), deep-level transient spectroscopy (DLTS), and positron annihilation spectroscopy.[2]

Early photoluminescent lines (PL) studies[6−11] showed that a series of luminescence lines designated D_1 were observed in 3C, 4H, and 6H-SiC crystals due to the annealing at the temperature 1000–3000 °C following electron or ion irradiation. The D_1 luminescence was reported to persist even after the annealing at 1700 °C. Patrick and Choyke[7] proposed that the D_1 luminescence was related to pure defect complex, such as divacancies, since its intensity increased irrespective of irradiated ion specimens. Deep level-transient spectroscopy (DLTS) studies for nitrogen-doped 6H-SiC revealed a series of deep levels, termed E1/E2, E3/E4, and Z1/Z2, were introduced by electron or ion irradiation at room temperature.[12−14] Ballandovich and Violina showed that E1/E2 and E3/E4 can be annealed to 1100 °C,[14] while the Z1/Z2 levels remained even after annealing at 1700 °C.[12,13] To identify the defect specimens generated by irradiation, several electron spin resonance (ESR) studies have been performed.[15−20]

From the detailed analyses of the spectra, Itoh *et al.* succeeded in identifying silicon and carbon vacancies (V_{Si} and V_C) in electron-irradiated 3C-SiC.[16,17] It was revealed that these two types of defects were annealed via two major stages (at 150 °C and 750 °C) and via a single stage at approximately 200 °C, respectively. Their results also suggested the presence of Frenkel pairs. In electron-irradiated 6H-SiC, carbon and silicon vacancies were found to anneal at approximately 200 °C and 750 °C.

Positron annihilation spectroscopy is a powerful tool to detect vacancy-type defects in crystalline solids.[21] Recent developments in slow positron beam methods allow the investigation of such properties for thin films, layered structures, and at surfaces. In previous studies, many researchers have suggested that monovacancies and Frenkel pairs in SiC are stable at room temperature,[2] and divacancies have an even stability. These are quite different from the situation in conventional semiconductors such as Si.[2] Recently, results of defects in electron-irradiated 6H-SiC, obtained by using the method of positron lifetime measurements, also showed that after irradiation in nitrogen doped 6H-SiC, defects related to silicon and carbon vacancies were observed. These vacancies were found to be partly annealed at several stages below 500 °C and were ultimately diminished by high temperature annealing up to 1450 °C.[1] The motion of vacancies and the dissociation of complex between vacancies and impurities can explain the high temperature stages. Meanwhile, the low temperature stages can be explained by the recombination between vacancies and interstitials due to the motion of interstitials. This is supported by the fact that vacancies are immobile here. No positron trapping was observed in electron-irradiated p-type 6H-SiC and thus no vacancies were detected in this material. This can be caused by the positive charge of the vacancy type.[22]

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Table 1. Treatment conditions of samples and the fitted results of S parameter and $L_{\rm eff}$. The forming gas is N_2:H_2 (80%:20%).

Sample	Type	Irradiation	Annealing	S parameter	$L_{\rm eff}$ (nm)
AN0	n	No	No	0.4694 ± 0.0003	59.7 (±3.4)
AN1	n	No	1400 °C 15 min in vacuum	0.4728 ± 0.0003	60.7 (±1.5)
AN2	n	No	1400 °C 30 min in vacuum	0.4696 ± 0.0003	44.6 (±3.3)
AN3	n	No	1000 °C 30 min in forming gas	0.4685 ± 0.0003	65.0 (±2.9)
AN4	n	No	1400 °C 15 min in forming gas	0.4739 ± 0.0003	87.2 (±2.5)
EN0	n	No	As above	0.4739 ± 0.0003	86.2 (±3.6)
EN1	n	1×10^{17}e$^-$/cm^2	No	0.4822 ± 0.0002	39.1 (±2.1)
EP0	p	No	No	0.4696 ± 0.0002	12.1 (±1.6)
EP1	p	1×10^{17}e$^-$/cm^2	No	0.4713 ± 0.0002	13.9 (±1.3)

Up to now, the studies of defects on 6H-SiC induced by electron irradiation of 3 MeV, 2.2 MeV and so on, have been performed. Our studies focus on the annealing behaviour of defects in the as-grown SiC wafer and the production of vacancies formed by 10 MeV electron.

The samples used in this work were cut from the modified Lely grown nitrogen-doped (n-type) and Al-doped (p-type) research grade 6H silicon carbide wafers purchased from CREE Research Inc. The doping concentrations of the n-type and the p-type materials were 1.1×10^{18} cm^{-3} and 1.8×10^{18} cm^{-3}, respectively. The samples were degreased with acetone and methanol, and then rinsed with deionization water. A series of n-type samples was annealed at different temperatures and environments, and the other two n-type and p-type samples were irradiated by 10-MeV electrons at room temperature. The irradiation dose was 1×10^{17}e$^-$/cm^2. The treatment conditions were listed in Table 1. Variable-energy positron measurements were performed for all specimens at the University of Hong Kong. The vacuum in the target chamber is 1.33×10^{-6} Pa. The Doppler broadening technique of the annihilation radiation is applied to the measurements. Photo-peak energy spectra of annihilation 511 keV γ-rays from the target were measured using a high purity Ge detector, which had an energy resolution of 1.2 keV (FWHM) at 514 keV γ-ray of ^{85}Sr. The line-shape S parameter of a spectrum is defined as the integral of γ-ray counts in the central energy region at the 511 keV divided by the total counts of spectrum, in which 5×10^5 counts is contained.

$$S = \int_{-a}^{a} c(E)\mathrm{d}E \Big/ \int_{-\infty}^{\infty} c(E)\mathrm{d}E, \qquad (1)$$

where $c(E)$ is the measured spectrum with the background subtracted, $(-a, a)$ is an energy region in the coordinate axis with original point at the peak energy 511 keV. We take an energy shift of about 1 keV at both the sides of the peak energy. The variation of the S parameter is mainly influenced by the relative counts around the peak, so it provides the information about the positron annihilating with the lower momentum electrons. At the defect region, the atoms lack in vacancy region will increase the S parameter for the larger fraction of lower momentum electrons.

All the $S - E$ curves, which were the measured relative S parameter as a function of positron incident energy E, were analysed by using the VEPFIT 5 (Ref. [23]) programme. The fitted results of the S parameter and $L_{\rm eff}$ were listed in Table 1. Here $L_{\rm eff}$ indicates effective diffusion lengths of positron in material. It is related to the trapping of the defect in the sample[3] as follow:

$$L_{\rm eff} = [D_+/(\lambda_b + k_i)]^{1/2}, \qquad (2)$$

where D_+ is the positron diffusion coefficient, λ_b is the positron annihilation rate in the bulk, k_i is the trapping rate in a concentration of defects C_i, and it is proportional to the defect-concentration, i.e., $k_i = \mu_i \times c_i$. The relative values of k_i for different samples are calculated as follows:

$$k_i = \Big(\frac{L_0}{L_i}\Big)^2 k_0 + \Big[\Big(\frac{L_0}{L_i}\Big)^2 - 1\Big]\lambda_b, \qquad (3)$$

where L_0 and L_i are the effective diffusion lengths of basic sample and compared sample respectively; k_0 is the positron trapping rate of basic sample.

In a previous study Ling *et al.*[3] have observed that when the annealing temperature is above 1000 °C, $V_{\rm Si}$ was almost annealed out in n-type 6H-SiC, and the remaining kind of vacancy was mostly to be divacancy $V_{\rm Si}V_{\rm C}$. Meanwhile, the vacancy trapping rates remain to be constant. In our case, if taking the sample annealed at 1400 °C for 15 min in the forming gas as a basic sample, $L_0 = 87.2$ nm. Following Brauer *et al.*,[5] we can take $\lambda_b = 1/\tau_{bi}$ to be 7.092×10^{-9}s^{-1} for n-type 6H-SiC. All of the relative positron trapping rates of the n-type 6H-SiC samples can be calculated by Eq. (3), and the results are listed in Table 2.

Table 2. Relative positron trapping rates of the n-type 6H-SiC samples.

Sample	AN0	AN1	AN2	AN3	AN4	EN0	EN1
k_i/k_0	10.172	9.606	23.841	7.422	1	1.189	33.147

It can be seen that when the sample was annealed at 1000°C for 30 min (AN3) in the forming gas, its relative trapping rate was about 73% of the as-grown one (AN0), this indicates that some vacancies in the sample were eliminated after annealing, which is probably due to the migration of the pure silicon vacancies. The ESR studies have shown that pure silicon vacancies become mobile at around 750 °C.[15] The mobile silicon vacancies seem to annihilate at sinks or to form complexes of silicon vacancies and nitrogen atoms. Probably, after the sample was annealed at 1000 °C, more complexes of silicon vacancies and nitrogen vacancies were formed, thus the total concentration decreased. Compared the samples that annealed at 1400 °C for 15 min in the forming gas (AN4) and in vacuum (AN1) respectively, it is obvious that the relative positron-trapping rate annealed in vacuum was 9.606 times of that annealed in the forming gas. This implies that the vacancies concentration annealed in the former was much larger than that in the latter, which may be caused by different diffusion behaviour of the Si atoms annealed at different environments. At the high temperature 1400 °C, some of the Si atoms diffuses to the surface and then V_{Si} vacancy can form. This process can be completed with the recovery of original V_{Si} during the annealing. More Si atoms can diffuse to the surface of sample when it was annealed in vacuum than that annealed in the forming gas. Considering the curve of the sample that annealed at 1400 °C for 30 min in vacuum, we could observe that the S parameter increased with the increasing energy when the energy increased to about 1 keV, Considering this part of the $S-E$ relations in AN2, we found that they have the same tendency with that of the original Si as previous work obtained.[25] According to the above explanation that the Si atoms would diffuse to surface when annealed at high temperature, we can conclude that some Si films can be formed when the sample was annealed at 1400 °C for 30 min in vacuum. Using a three-layer model (Si/Interface/SiC), a good fitting can be given out. It was found that a 20-nm thickness Si layer formed on the top. It is a direct proof that the Si atoms diffused to the surface when annealed at high temperature. According to its high relative positron-trapping rate $k_i/k_0 = 23.841$, we can also see that because of the diffusion of the Si atoms to surface, more vacancies were created.

Ling *et al.*[3] showed that when the annealing temperature is higher than 1000 °C in the forming gas, the positron-trapping rate remains to be constant. However, in our case, when the sample was annealed at 1000 °C for 30 min in the forming gas (AN3), its relative positron-trapping rate was 7.422 times of that annealed at 1400 °C for 15 min in the forming gas (AN4). These different results may mostly be caused by the different measurement methods. Ling *et al.* used the positron annihilation lifetime method. The positrons came from the ^{22}Na source can be implanted about 0.5-mm depth of the SiC substructure. The slow positron beams can only detect the vacancies information of near the surface in the sample. In our experiment, the detecting range is about 1 μm below the surface for incident positron energy of 16 keV. To some extent, during the annealing process, two reactions exist: the creation of the Si vacancies induced by some Si atoms diffusing to the surface, and the annealing out of the Si vacancies because of annihilating at sinks or forming complexes of silicon vacancies and nitrogen atoms. The former is stronger near the surface than that in bulk, so the V_{Si} concentration near the surface was larger than that in bulk. All these reasons cause the great differences between the results of ours and Ling *et al.* However, the results of positron lifetime spectra presented the information of the bulk samples.

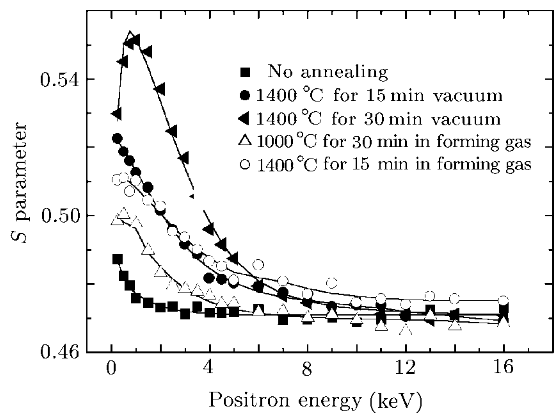

Fig. 1. Mean S parameter as a function of incident positron energy E for the n-type SiC specimens AN0-AN4. The solid lines are the fitted curves.

The $S-E$ curves of the as-grown samples (no irradiation) and the 10-MeV electron irradiated n-type 6H-SiC are included in Fig. 2. The calculated relative positron trapping rates were listed in Table 2. The S parameter of irradiated sample increased from 0.4739 to 0.4822. It is shown that after 10 MeV electron irradiated, more vacancies have been created. Dannefaer *et al.*[24] found that two vacancy types have been created after electron irradiated, but the balance between these two defects is energy dependent.

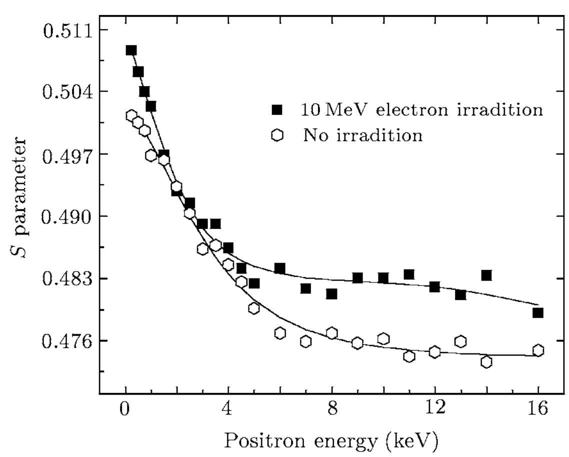

Fig. 2. Mean Doppler broadening parameter S as a function of incident position energy E for n-type SiC of specimens EN0-EN1. The solid lines are the fitted curves.

Change of the S parameter after 10-MeV electron irradiation in our case was about 1.75%, which is lower than the result presented by Dannefaer *et al.* This may be caused by the lower irradiation dose for our sample. Kawasuso *et al.*[1] found that the trapping rates of positrons in vacancies increased linearly with the dose in the initial stage of irradiation. After the linear increase, the trapping rates were proportional to the square root of the dose for n-type 6H-SiC. We obtained that $L_{\rm eff}$ decreased from 86.2 nm to 39.1 nm after irradiated, thus the relative positron-trapping rate of the irradiated sample was about 27.878 times of the origin sample. This means that the concentration of vacancies increased after irradiated.

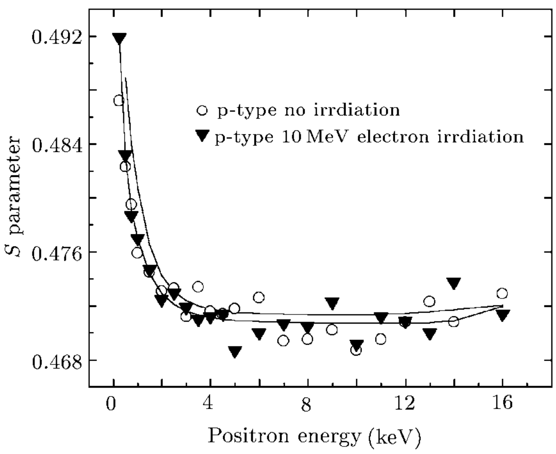

Fig. 3. Mean Doppler broadening parameter S as a function of incident position energy E for p-type SiC of specimens EP0-EP1. The solid lines are the fitted curves.

For p-type 6H-SiC, the sample was irradiated under the same condition with the n-type one. Figure 3 shows the $S-E$ data and the fitting curves. The fitting $L_{\rm eff}$ and the S parameter were listed in Table 1. It is interesting that different behaviour of $L_{\rm eff}$ occurs in p-type. Here $L_{\rm eff}$ increased from 12.1 nm of the as-grown sample to 13.9 nm after the same irradiation. The S parameter only slightly changed from 0.4696 to 0.4713. This may be explained by the fact that irradiation-introduced vacancies $V_{\rm Si}$ and $V_{\rm C}$ in the p-type were positively charged, thus they are not capable of trapping positrons. This is distinctly possible since Itoh *et al.* detected a paramagnetic resonance signal they ascribed to a positive charged carbon vacancy $V_{\rm C}^{+}$ only in p-type 3C-SiC; and in the previous study, Ling *et al.*[3] pointed out that in the p-type 6H-SiC material, the Fermi level was close to the valence band, which probably made the silicon vacancy $V_{\rm Si}$ positively charged and the acceptor neutrally charged. The second reason is that the introduction rate of vacancies may be much smaller in materials than that in n-type, since the p- or n-type dependences on irradiation damage is commonly observed for semiconductors. To make the process of irradiation in p-type SiC clear, more experiments should be carried out.

In summary, we have investigated the vacancy concentration changes in 6H-SiC induced by annealing and 10-MeV electron irradiation with the slow positron beams. It was found that after the sample was annealed at 1000 °C and 1400 °C respectively, the vacancies concentration in n-type 6H-SiC decreased because of the reduction of the vacancies duo to recombination with interstitials during annealing, and the longer annealing time would strongly enhance the process of annealing effect. Studying the samples irradiated by 10 MeV electrons, we found that the concentration in n-type 6H-SiC increased, this shows that there are some vacancies created or induced by irradiation. For p-type 6H-SiC, it is unclear that there are vacancies created, this may be caused by the introduced vacancies of positively charged, so this material is not suitable for using positron as a detector.

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