Clustering of Vacancies in Semi-Insulating SiC Observed with Positron Spectroscopy

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Abstract. Positron annihilation radiation Doppler broadening spectroscopy was used to study defects in semi-insulating (SI) silicon carbide (SiC) substrates grown by high-temperature chemical vapour deposition (HTCVD). The Doppler broadening measurements show (i) that the measured samples contain vacancy clusters (ii) that the positron trapping to the clusters is increased in annealing (iii) that the chemical environment of the defects in the un-annealed samples is different from those of the annealed samples.

Introduction

Semi-insulating (SI) SiC substrates are needed for example for SiC MESFETs for high-power microwave applications. SI SiC substrates can be realized by pinning the Fermi-level of the samples to near the middle of the band gap. This can be done by introducing deep levels to the material. Previously this has been realized by doping the material with vanadium. The semi-insulating material can also be produced by lowering the concentration of residual impurities enough to allow the pinning of the Fermi-level to the intrinsic defects of the material. High-Temperature Chemical Vapor Deposition (HTCVD) [1, 2] is a commercial method for growing high-purity (vanadium free) semi-insulating SiC. In this study we have measured HTCVD grown 4H-SiC samples with positron annihilation line Doppler broadening spectroscopy.

Positron spectroscopy allows studying vacancy type defects in solid materials [3, 4]. Positrons are repulsed by positive ion cores, and thus they tend to get trapped and localized in vacancies which lack the ion core. In the annihilation the momentum of the annihilated electrons is conserved and transferred to a pair of γ-quanta created. By measuring the energies of these quanta, one can gather information on the chemical environment of the annihilation site.

Experimental

The studied HTCVD samples are of 4H polytype grown under either hydrocarbon rich or poor growth conditions. The samples were studied before and after annealing for 1 h at 1600°C in H_2 ambient. The samples were grown at Okmetic, Linköping, Sweden. The C rich samples are n-type and the Si rich samples semi-insulating. Additionally we have measured p-type reference samples (which come from a different supplier).

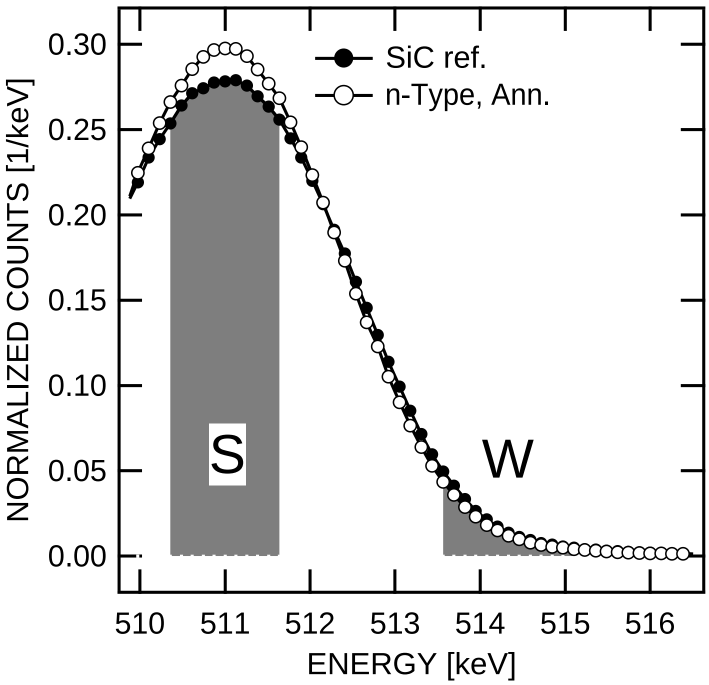

Figure 1: Measured positron annihilation line Doppler broadening spectra in bulk reference and annealed n-type samples (measured at 100 K). In the figure are presented also windows for determining the S- and W-parameters. From the figure one can observe that the annihilation line in the annealed n-type sample is narrower than that of the reference sample. In this case the S-parameter is increased and the W-parameter is lowered. The result indicates positrons annihilating on average with electrons with lower momenta than those of the bulk - i.e. the samples contain vacancies.

The measurements have been performed as a function of temperature between 20 and 540 K. The samples have been in a "sandwich" configuration with $\approx 10\ \mu$Ci ^{22}Na positron sources deposited on folded $1.5\ \mu$m Al foil. The annihilation line energy spectra have been measured with a High Purity germanium γ detector with a 1.19 keV (FWHM @511 keV) energy resolution. The measured spectra contain more than 3×10^6 counts in the peak.

The motion of the annihilating $e^+ - e^-$ pair causes a Doppler shift $\Delta E_\gamma = \frac{1}{2} c p_L$, where p_l is the longitudinal momentum component of the pair in the direction of the annihilation photon emission. This causes the broadening of the $m_0 c^2 = 511$ keV annihilation line. Since during the annihilation the positron is thermalized, its momentum is negligible and the Doppler shift is caused predominantly by the momentum of the annihilating electron. Examples of the measured Doppler spectra are presented in Fig. 1. From the spectra one can see clearly that in the case of the annealed n-type sample, the Doppler broadening spectrum is narrower than for the reference sample, indicating more annihilations with the low-momentum (valence) electrons. This is a typical situation in the case the positrons are localized in vacancies (i.e. the overlap of the e^+ wave function and the tightly bound (high momentum) core electrons is diminished).

In order to help plotting the information of the multiple spectra measured, we define the annihilation spectrum line shape parameters in a conventional way as ratios between the number of counts in specified energy windows to the total counts in the peak. The low momentum annihilation parameter S (shape) is defined in the region $|E_\gamma - m_0 c^2| < 0.64$ keV and high momentum parameter W (wing) in the region $2.56\ \mathrm{keV} < |E_\gamma - m_0 c^2| < 4.1\ \mathrm{keV}$. Because of the electron momenta contributing to the different regions of the Doppler broadening spectra, the S- and W-parameters are often called valence- and core annihilation parameters, respectively. The energy windows defined to determine the S and W parameters are shown in fig. 1.

Each annihilation state has its characteristic S and W parameters. If fraction η_i of the positrons annihilate in a state with lineshape parameter S_i, the total lineshape parameter is a superposition $S = \sum_i \eta_i S_i$ (similarily for the W). If the samples contain only one defect type, the positrons have two different possible annihilation states: bulk lattice (S_B, W_B) and the defect (S_D, W_D). In this case the equations for the lineshape parameters simplify into

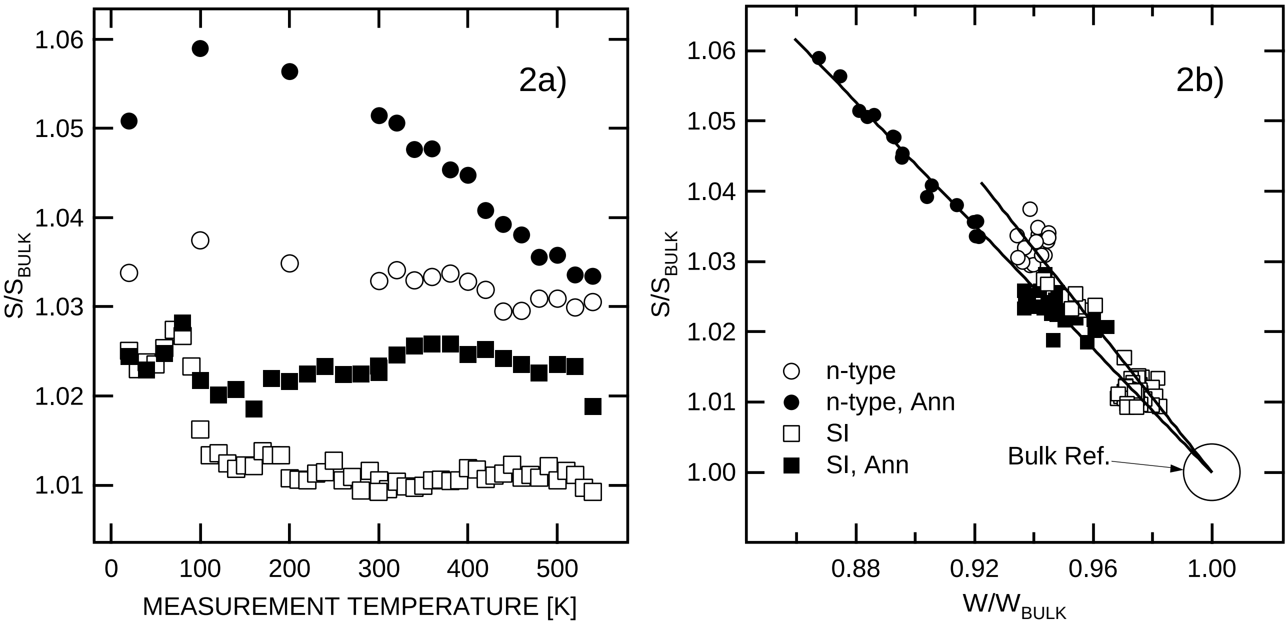

Figure 2: The normalized S-parameters as a function of the measurement temperature (2a) and as the function of the normalized W-parameter (2b). From the reference sample: $S_B = 0.380(1), W_B = 0.0637(1)$.

$$S = (1 - \eta_D)S_B + \eta_D S_D, \tag{1}$$

$$W = (1 - \eta_D)S_B + \eta_D S_D. \tag{2}$$

This means that when the lineshape parameters obtained from different measurement points (e.g. as a function of temperature) are plotted on a plane, the measured points fall on this line between (S_B, W_B) and (S_D, W_D) with slope characteristic to the defect type. On the other hand, if the points do not fall on this line, this is an clear indication that more than two different annihilation states are detected i.e. more than one defect type exists in the sample.

Results

In the two panels of Fig. 2, the measured S-parameter values are presented as a function of measurement temperature (2a) and as a function of the W-parameter (2b) (when the temperature is the running parameter). One can see that in all samples the S parameter values are above the bulk value. This indicates positrons annihilating in states with lower electron momenta than in the bulk, i.e. the samples contain vacancies. The highest S-parameter measured in any of the samples is $S/S_B = 1.06$, which corresponds to vacancy clusters (for clusters typically $S_D/S_B > 1.05$) [3]. In fact, vacancy clusters have been directly observed in similar samples with positron lifetime spectroscopy [5, 6]. The S-parameter increases in the annealing for both samples. This can be attributed to enhanced trapping of positrons to the vacancy clusters. The clusters have been shown to grow due to the annealing [6], which can explain also the behavior of the S-parameter in the annealing. Above temperature 100 K the S-parameter of the measured samples (with the exception of the annealed n-type sample) stays approximately constant indicating constant fraction of positrons trapping to the defects. The most obvious explanation for this is that the defects are neutral and thus the positron trapping to them is temperature-independent. On the other hand, at T > 100 K, the lowering of the S-parameter in the annealed n-type sample indicates lowered positron trapping to the clusters. This can have two different explanations: (i) (a part of) the clusters of the sample are in negative charge state or (ii) the clusters in these samples are sufficiently large and of low concentration to cause diffusion-limited positron trapping.

In Fig. 2b, the measured S-parameters are presented as a function of the W-parameter. One can see that the measured (S,W) points of the annealed samples fall on a line including the bulk reference point. This means that the Doppler broadening results for the two annealed samples can be explained as superpositions of positron annihilations in vacancy clusters and in the bulk SiC. On the other hand, the points of the non-annealed n-type sample do not fall on this line, which indicates that the sample contains other vacancy type defects with different chemical environment than the clusters in the annealed samples. Also, the points of the as-grown SI sample measured below 100 K ($S/S_{\mathrm{BULK}} >$ 1.02 in the Fig. 2b do not fall on this line, but rather on a line connecting the as-grown n-type samples and the bulk, which shows that also this sample contains defects whose chemical environment is different from that of the clusters in the annealed samples.

The relative changes of S- and W parameters can be used to determine $R = |\Delta S/\Delta W|$, which does not depend on the fraction of trapped positrons. The fitted R-parameter curve for the annealed samples is presented in Fig. 2b from which we get $R = 0.44(1)$. Determined in a similar way, the R-parameter for the non-annealed samples is $R = 0.53(1)$. The different R-parameters reflect again different vacancy defect species before and after annealing. As shown in [6], the annealing both increases the open volume of the vacancy clusters and reduces the concentration of the point defects such as mono- or divacancies. These processes also explain the changes of Doppler broadening results of fig. 2.

Summary

To summarize, the positron annihilation line Doppler broadening measurements in semi-insulating HTCVD SiC samples reveal the presence of vacancy clusters. The positron trapping to the clusters is enhanced in annealing, which is evidently caused by the growth of these clusters in annealing. For the clusters in the annealed samples, we determine an energy-window independent R-parameter of $R = 0.41(1)$ and for the as-grown case $R = 0.53(1)$. Both as-grown samples contain defects which have different chemical environment compared with the clusters observed after annealing.

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