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Defect layer in SiO₂–SiC interface proved by a slow positron beam

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Abstract

The structure of the SiO₂–4H-SiC interface layer produced by dry oxidation has been studied by positron annihilation spectroscopy using slow positron beams. From Doppler broadening measurements, the interface layer was clearly distinguished from the SiO₂ and SiC layers and was observed to be defective. At the interface layer, a single long positron lifetime of 451 ps, which is close to the second lifetime in the SiO₂ layer, was obtained, thus suggesting that the structure of the interface layer resembles an amorphous SiO₂ network. A comparison was made between the obtained electron momentum distribution at the interface layer and the theoretical calculation. It was found that positrons annihilate with oxygen valence electrons. By annealing after the oxidation, the annihilation probability of the positrons with oxygen valence electrons and the number of interface traps decreased in the same temperature range, thus suggesting a correlation between interface traps and positron annihilation sites.

1. Introduction

Silicon carbide (SiC) is known as a wideband gap semiconductor that is expected to be used as a material for high power electronic devices. SiC has an attractive feature with respect to the manufacture of a metal-oxide-semiconductor (MOS) type device that can produce a SiO₂ layer by conventional thermal oxidation. However, several interface states remain near the SiO₂–SiC interface and cause a degradation of the device properties. By post-oxidation annealing (POA), the number of interface traps can be reduced [1]. However, to develop a more efficient process, the origin of the interface states must be clarified. Many extensive studies have been conducted to reveal the physical structure of the interface traps. Their results show the existence of a SiO₂–SiC interface layer containing defects such as suboxides, carbon clusters, and so on [2,3].

The correlation between the defects and interface traps has not been fully clarified.

Positron annihilation spectroscopy (PAS) using a slow positron beam is suitable for the study of vacancy type defects in a subsurface. Recently, PAS was applied to study the SiO₂–SiC interface [4]. The annihilation characteristics of the positron traps in the SiO₂–SiC interface layer are observed to be similar to those in the SiO₂–Si interface [5]. However, the atomic structure and detailed chemical environment of the positron annihilation site have not been clarified.

In this study, we attempted to investigate the defect structure in the interface layer of SiO₂–SiC formed by conventional dry oxidation. The structure and chemical environment of positron trapping sites were studied using Doppler broadening, positron lifetime, and first-principles calculation. In addition, after conducting POA, the correlation between interface traps, which were detected by capacitance-voltage (CV) measurement, and positron annihilation sites was examined.

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E-mail address: maekawa.masaki@jaea.go.jp (M. Maekawa).

2. Experimental

The samples used in this study were cut from an n-type chemical-vapor deposition (CVD) grown 4H-SiC epilayer on an 8°-off oriented 4H-SiC(0 0 0 1) substrate that was purchased from CREE Research Inc. The oxide layer was grown by dry oxidation at 1200 °C for 3 h. The thickness of the oxide layer was approximately 40 nm. Post-oxidation annealing was conducted in Ar and N_2O ambient. The energy spectrum of positron annihilation radiations (511 keV) is Doppler broadened depending on the electron momenta. The Doppler spectra were characterized by S and W parameters, which are defined as the normalized peak region $(0–20 \times 10^{-3} m_0 c)$ and tail region $(10–15 \times 10^{-3} m_0 c)$ intensities, respectively. The S and W parameters were measured as functions of incident positron energy (E) from 0.2–20 keV. The S–E or W–E curves obtained were analyzed as a layered model by using the VEPFIT code [6]. In order to obtain a detailed estimate of the chemical environments at the positron annihilation site, coincidence Doppler broadening (CDB) measurement was also carried out. To extract the fine structures, the CDB spectrum was expressed as a ratio curve divided by the spectrum of the SiC bulk. Moreover, the positron lifetime was measured using a pulsed positron beam [7] and analyzed by PATFIT-88 code [8].

3. Theoretical calculation

In order to interpret the obtained positron annihilation characteristics, the Doppler broadening of annihilation radiation was calculated by first principles. The Doppler broadening spectra were obtained by the convolution of the 1D-ACAR spectra with the resolution function of the measurement system. The 1D-ACAR spectrum is obtained by the integrating ρ along two momentum axes, where ρ is the three-dimensional electron momentum distribution and is given by $\rho = \rho_{\text{core}} + \rho_{\text{valence}}$. The valence electron wavefunction was computed using the free-distributed ABINIT 4.1.4 code [9]. For core electrons, Alatalo's manner was employed [10]. A supercell containing 48Si and 48C atoms was constructed for the 4H-SiC crystal calculation. The amorphous SiO_2 bulk structure was obtained by a simulated annealing method using a periodic cell of β-quartz containing 24 Si and 48 O atoms.

4. Results and discussion

4.1. As-oxidized state

Fig. 1 shows the S and W parameters as functions of the incident positron energy after oxidation. The constant S and W parameters at $E > 15$ keV indicate positron annihilation in the SiC layer. The enhancement in the S parameter around $E = 1$ keV occurs due to positronium formation in the SiO_2 layer [11]. A slight reduction in the S parameter at $E = 0.2$ keV indicates positron annihilation at
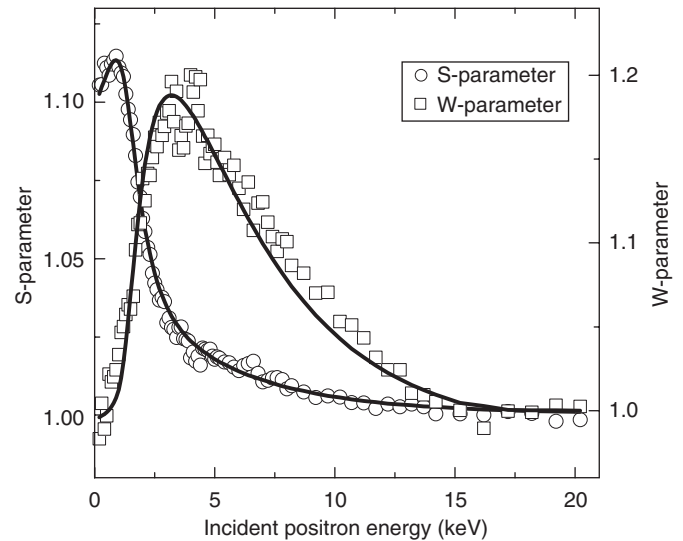

Fig. 1. Open circles and squares are Doppler broadening S parameter and W parameter for the as-prepared SiO_2–SiC sample as a function of incident positron energy. Solid lines are the best fittings by the VEPFIT code.

the surface. Between the SiO_2 and SiC layer, the W parameter dramatically increases around $E = 3-6$ keV. This energy range corresponds to the SiO_2–SiC interface. Hence, the structure of this SiO_2–SiC sample may be modeled as a combination of four layers—SiO_2 surface, SiO_2 layer, SiO_2–SiC interface layer, and bulk SiC region. The solid lines in Fig. 1 represent the results of the VEPFIT analysis of this model. The interface layer should exist in order to obtain physically valid fittings. The thickness of this layer is obtained as 3.9 nm, which is in agreement with that reported by other techniques [12]. The extremely short diffusion length (1.8 nm) in the interface layer indicates that the diffusion of positrons is suppressed, i.e., the SiO_2–SiC interface layer contains many defects.

To investigate the properties of this defective interface layer, positron lifetime measurement and CDB measurement were carried out at $E = 3.7$ keV. Only a single lifetime component (451 ps) was obtained from the lifetime measurement. Since this lifetime is similar to the second lifetime of the SiO_2 layer [11], the structure of the interface layer is analogous to the open-volume structure of the amorphous SiO_2 layer. Fig. 2(a) shows the ratio curve of the obtained interface layer. The enhanced intensity at $p = 10-15$ mrad causes the high W parameter in the interface layer. The reasons considered to cause this enhancement are as follows: (1) The different chemical environments of the positron annihilation sites in Si and C atoms. Oxygen valence electrons have higher momenta because of their compact wave function [13]. Since positrons have a strong affinity for oxygen atoms, a positron tends to annihilate preferentially with oxygen valence electrons. (2) The effect of the second Brillouin zone [14]. When positrons are localized at defects, the discontinuous distribution at the second Brillouin zone of a perfect crystal tends to
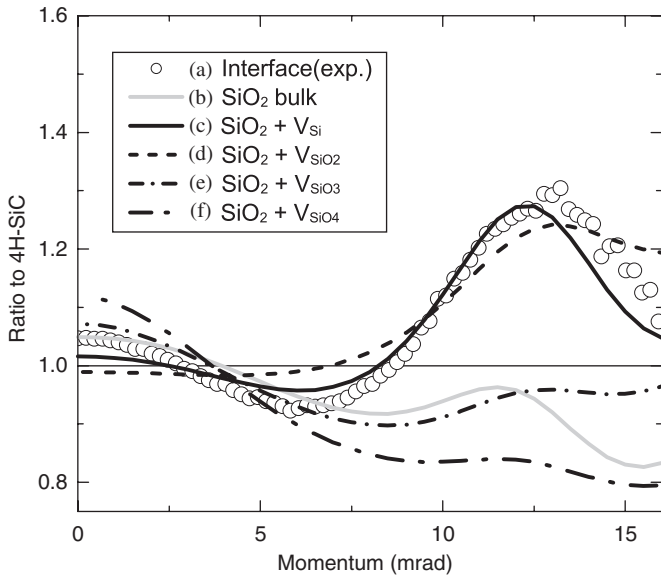
Fig. 2. Open circles (a) are CDB spectra for the interface layer of the as-prepared SiO_2/SiC sample. Lines (b)–(f) represent the calculated ratio curves for the amorphous SiO_2 and amorphous SiO_2 introducing defects. These spectra are expressed as a ratio curve divided by the spectrum of the SiC bulk.

Fig. 3. The schematic drawing of the atomic structure of V_{Si} and V_{SiO4}.

Fig. 4. W–E plots for the SiO_2–SiC sample after Ar-POA and N_2O-POA treatment. For references, W parameters obtained for the as-prepared states are also shown. Solid lines are the best fittings of Ar-POA sample obtained by the VEPFIT code.

disappear due to the lack of translational symmetry. In the ratio curve, a bump may appear at the second Brillouin zone boundary. These two possibilities are examined through a comparison with the theoretical calculations using appropriate models.

The atomic structures at the interface are not derived a priori because of the difficulty in theoretical modeling. The above-mentioned experimental findings reveal that the interface structure resembles the SiO_2 amorphous network and contains several defects. Thus, we examined the amorphous SiO_2 structure introduced various defects. To change the number of the silicon and oxygen dangling bonds at a defect, V_{Si}–V_{SiO4} was introduced. A schematic drawing of the defects is shown in Fig. 3. The solid lines in Figs. 2(b)–(e) represent the calculation results. V_{SiO4} is considered instead of oxygen vacancy (V_O) due to the weak localization of the positron wave function at V_O. The positron wave function was strongly localized at the defect. However, in the case of V_{SiO4}, the ratio curve is not representative of the experiment. The intensity at $p = 10-15$ mrad is especially weak. This shows that the enhancement of $p = 10-15$ mrad cannot be explained only as an effect of positron localization (effect of Brillouin zone). On the other hand, it was found that the intensity at $p = 10-15$ mrad increased with the number of oxygen dangling bonds. In the case of V_{Si}, the intensity at $p = 10-15$ mrad increased sufficiently and the curve shape was rather similar to that obtained from the experiment. It is possible that positrons preferentially annihilate with oxygen dangling bonds contained in the SiO_2 amorphous network.
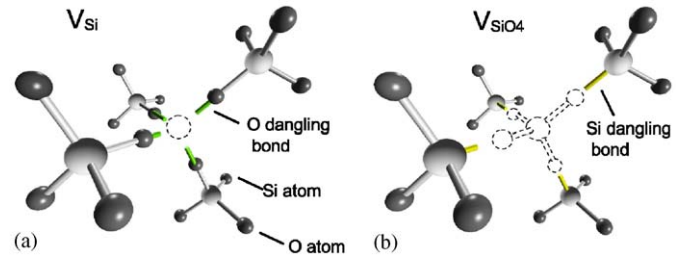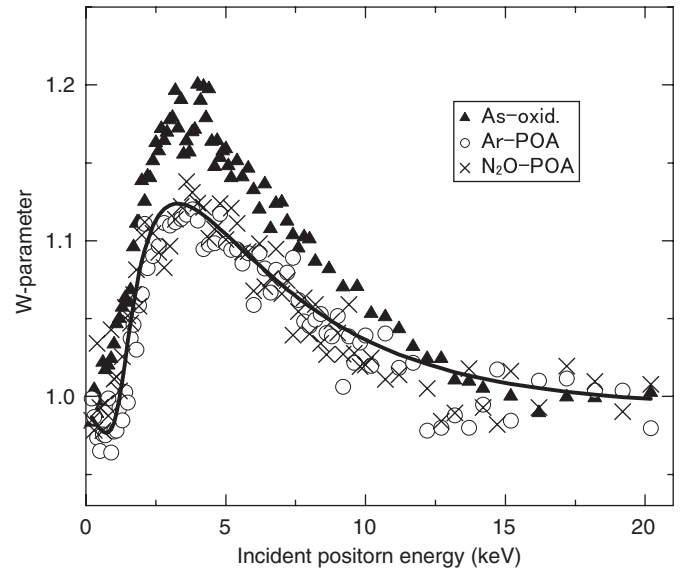
4.2. Effect of post-oxidation annealing

Fig. 4 shows the W–E curves for the SiO_2–SiC samples annealed at 950 °C. Table 1 summarizes the W parameters from the VEPFIT analyses, positron lifetimes, and number of interface traps (N_{it}). N_{it} values are in the order of As-Oxid > Ar-POA > N_2O-POA. This is because interface states are passivated by heating; furthermore, the N-atom effectively terminates the interface states [15,16]. On the other hand, positron lifetimes remain constant while the W parameter significantly decreases post Ar-POA. As shown above, this reduction in the W parameter is caused by the flattening of the bump at $p = 10-15$ mrad, i.e., by the reduction of oxygen dangling bonds at the positron annihilation site. The porous structures in the interface layer are scarcely affected by POA. Despite conducting N_2O-POA, the W parameter and the lifetime were almost the same as in the case of Ar-POA. The effect of POA on positron annihilation is a purely thermal effect. Thus, a change in W parameter does not entirely correspond to the interface states. This indicates that the interface states do not necessarily originate from the oxygen dangling bond.

Table 1

W-parameters, positron lifetimes and number of interface traps(N_{it}) obtained for SiO$_2$–SiC samples

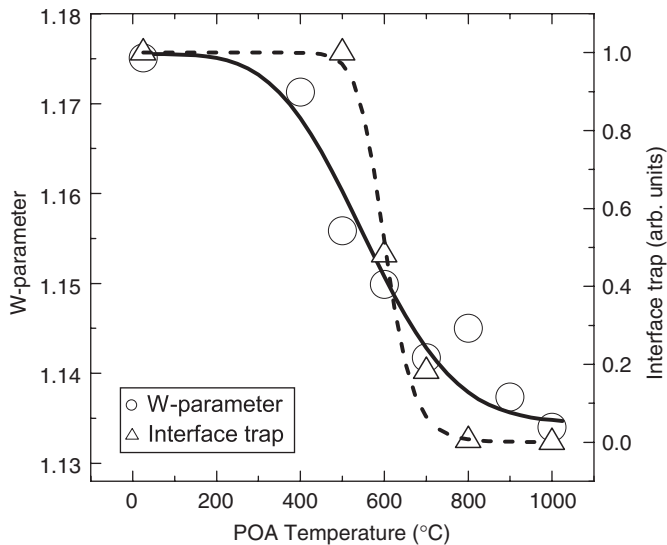|	*W*-parameter	Positron lifetime (ns)	Nit (cm^{-2})
As-oxid.	1.25	451	5.1×10^{12}
Ar-POA	1.17	462	4.6×10^{11}
N$_2$O-POA	1.18	468	1.6×10^{11} [15]

Fig. 5. The correlation of *W* parameter and interface trap density obtained from the CV measurements as a function of annealing temperature.

Isochronal annealing was carried out to investigate the correlation between oxygen dangling bonds and interface states. Fig. 5 shows the temperature dependence of the *W* parameter and the number of interface traps; both exhibit a dramatic decrease in the same temperature range. It is suggested that the recovery of the interfacial defects accompanies the rearrangement of oxygen dangling bonds. When the oxidation process comes to an end, both the interface defects and the unreacted oxygen atoms persist at the interface layer. It is possible that in the POA process the interface defects are reoxidized by these excess oxygen atoms. The interface states might originate from unreacted silicon or carbon atoms that can react with the excess oxygen atoms. Unreacted silicon exists as suboxides [3] and carbon atoms cause clustering [2]. If carbon clusters disappear due to POA, microvoids appear in the form of marks. However, no changes in the positron lifetime were observed. It is inferred that a reduction in the interface states is related to the reduction in suboxides near unreacted oxygen by reoxidation.

5. Summary

The SiO$_2$–SiC interface layer prepared by the dry oxidation method has been studied using PAS measurements. Many defects were detected in the interface layer. The layer is rather porous due to the positron lifetime. This layer, which was seldom considered in other techniques, depicted a preferential annihilation of positrons with oxygen valence electrons. On the application of POA, a reduction in the *W* parameter of the interface layer was observed. The annihilation behavior of oxygen valence electrons decreased due to POA at around 600 °C. The interface trap density, as detected by CV measurement, decreased in the same temperature range. It is suggested that the recovery of the interfacial defects accompanies the rearrangement of oxygen dangling bonds.

Acknowledgements

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