

Synchrotron X-ray Photoelectron Spectroscopy on interface state densities of CVD-Grown SiO₂/4H-SiC Structures Treated by Post-Deposition Treatments

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Abstract

In order to realize a high quality interface of silicon dioxide /SiC structures, we applied post-deposition treatments (PDTs) to an interface between a chemical vapor deposition grown silicon dioxide and 4H-SiC (0001) substrate. We used an Ar plasma treatment and N₂/H₂ annealing as the PDTs, and evaluated interface state densities (D_{it}) by hard X-ray photoelectron spectroscopic measurement with applying bias voltages to the samples. For as-deposited sample, D_{it} was $4 \times 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$ at conduction band minima (CBM). On the other hand, D_{it} at the CBM decreased to 3×10^{11} for the sample treated with the Ar plasma and to the value of below detection limit of the analysis for the sample annealed in N₂/H₂ ambient. However some increases of D_{it} were seen at the deep position of the bandgap. Therefore, the PDTs resulted in the reduction of D_{it} , but their extent of the reduction depended on the position of the bandgap.

1. Introduction

Silicon carbide, which exhibits superior breakdown electric field and thermal conductivity over Silicon, has attracted considerable attention for power devices such as metal-oxide-semiconductor (MOS) field-effect transistors [1]. Except for Si, SiC is only the semiconductor material that can form silicon dioxide (SiO₂) films by thermal oxidations.

However, in the thermal oxidation of SiC substrate, small amount of carbon impurities remain in the oxide films and on the SiO₂/SiC interfaces [1,2]. Consequently, the impurities cause electrical degradations of SiC devices, which is a crucial obstacle to the implementation of SiC-based power electronics. On the other hand, deposition methods (e.g. chemical vapor deposition (CVD)) can avoid the remains of carbon impurities. However, interfaces between CVD-grown SiO₂ films (CVD-SiO₂) and SiC substrates commonly have larger amount of interface states than interfaces fabricated by thermal oxidations, because of the bombardment of ions into the substrates. In order to improve the interface quality of CVD-SiO₂/Si structure, we had applied post-deposition treatments (PDTs) (e.g. Ar/O₂ plasma treatment) to the structure and confirmed the improvement of interface qualities [3].

In this study, we applied an Ar plasma treatment and N₂/H₂ annealing to CVD-SiO₂/SiC samples. We evaluated interface state densities (D_{it}) by hard X-ray photoelectron spectroscopic measurement with applying bias voltages to the samples (BA-HAXPES [4]). The PDTs resulted in the reduction

of D_{it} , but the extent of the reduction depended on the position of the bandgap.

2. Experiment

We used an as-grown 4-off-angle 4H-SiC (0001) wafer for the fabrication of MOS structure samples. Donor concentration of the wafer was $1 \times 10^{15} \text{ cm}^{-3}$. After a standard RCA cleaning and subsequent native oxide removal with a diluted hydrofluoric acid (HF) solution, a SiO₂ film was deposited on the wafer in two steps. In first step, a dry oxygen plasma treatment was used to clean the surface of the wafer. In second step, a 100 nm SiO₂ film was deposited by a CVD deposition at the temperature of 400 °C. After the deposition, the wafer cut into $4 \times 4 \text{ mm}$ pieces, and SiO₂ films were etched to 20 nm thickness with a diluted HF solution. After these preparation, samples were treated by two kinds of PDTs. One received an Ar plasma treatment (CVD + Ar plasma), the other received an N₂ (90%)/H₂ (10%) annealing (CVD + N₂/H₂ anneal). Ar plasma treatment was carried out in a micro-wave excited high-density plasma for 5 minutes at the temperature of 350 °C with the pressure of 133 Pa. N₂ (90%)/H₂ (10%) annealing was carried out in a horizontal furnace for 20 minutes at 400 °C with the atmospheric pressure. We also kept the as-deposited sample (CVD as-deposited). Ten-nanometer TiN films were deposited on samples by a sputtering.

The samples were attached an Au stage of XPS equipment with a silver paste. Au wires were connected to the TiN films with the silver paste. BA-HAXPES was carried out at Beam line 16 XU of SPring-8. X-ray energy was 8 keV and photoelectron take-off angle was 85 degree to the sample surfaces. Si 1s spectrum were measured at several bias conditions. Energy shifts of Si 1s peaks of the SiC substrates, from the zero bias condition, were estimated by a peak fitting analysis.

3. Result

Figure 1 shows Si 1s spectrum under bias conditions. The bias voltages were applied to the SiC substrates with respect to the TiN films, and were restricted to keep voltage drops, caused by leakage currents, across the surfaces of TiN films one-tenth less than the applied voltages. The right peaks are corresponding to SiC substrates and left ones are corresponding to SiO₂ films in figure 1. Applying positive bias voltages shifted the substrate peaks toward a higher binding energy. On the other hand, applying negative voltages shifted the substrate peaks toward a lower binding energy.

Figure 2 shows the energy shifts of substrate peaks as a function of bias voltages. The bias-induced shifts were completely

reversible which mean these shifts were caused by a band bending and accumulation/release of electrons at interface states by the bias voltages. The energy shifts were in the same manner for the three samples, but the features of the graphs depend on the samples. From the slopes of graphs, D_{it} can be evaluated by the method which has been proposed by Kobayashi et al. (see references [4] for the details).

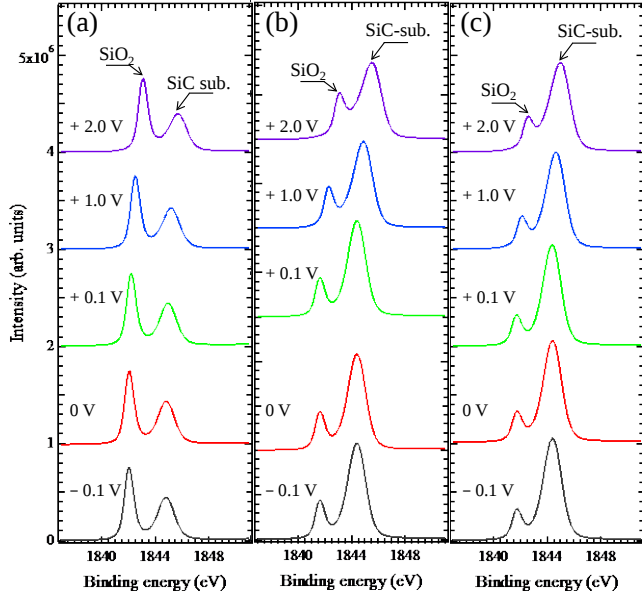


Fig. 1 Si 1s spectrum for the TiN/CVD-SiO₂/SiC samples. (a) CVD as-deposited, (b) CVD + Ar plasma, (c) CVD + N₂/H₂ anneal.

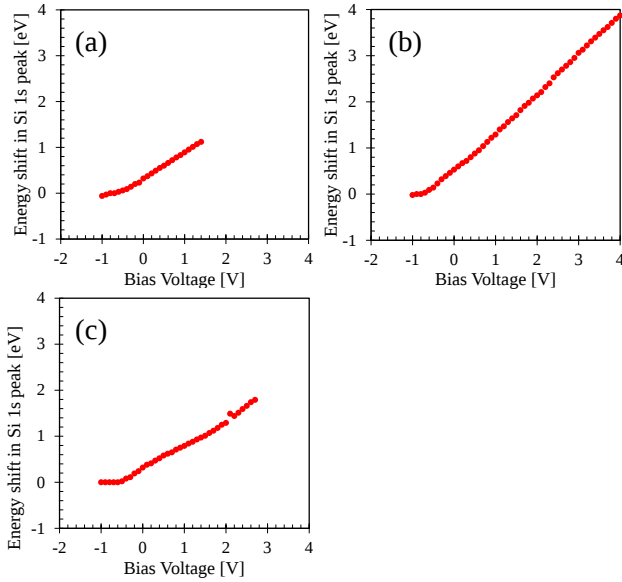


Fig. 2 Energy shifts in Si 1s peaks compared to the energy at zero bias (a) CVD as-deposited, (b) CVD + Ar plasma, (c) CVD + N₂/H₂ anneal.

Figure 3 shows energy distributions of D_{it} for the samples. For CVD as-deposited, D_{it} were $4 \times 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$ at conduction band minima (CBM) and $2 \times 10^{12} \text{ eV}^{-1} \text{ cm}^{-2}$ at $E_c - 1.0 \text{ eV}$. Here, E_c is the energy level of the CBM. D_{it} of this sample is as low as those in interfaces fabricated by thermal oxidations reported in previous literatures [5]. On the other hand, for CVD + Ar plasma, D_{it} were $3 \times 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$ at the CBM and

$4 \times 10^{12} \text{ eV}^{-1} \text{ cm}^{-2}$ at $E_c - 1.0 \text{ eV}$. For CVD + N₂/H₂ anneal, D_{it} were the value of below the detection limit of this evaluation at the CBM and $2 \times 10^{12} \text{ eV}^{-1} \text{ cm}^{-2}$ at $E_c - 1.0 \text{ eV}$. In addition, D_{it} of over $4 \times 10^{12} \text{ eV}^{-1} \text{ cm}^{-2}$ was extracted around the mid-gap. Although the clear mechanism has not been elucidated, the PDTs were able to decrease D_{it} at the CBM, but exacerbated D_{it} at the deep positions of bandgap.

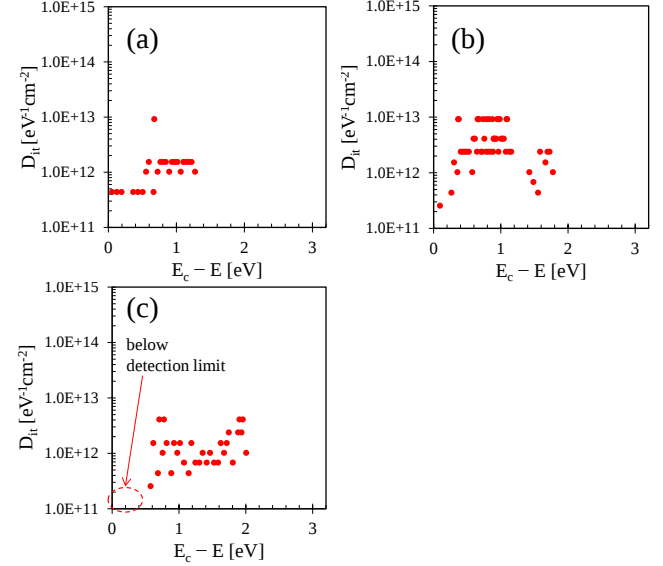


Fig. 3 Energy distributions of the interface states for (a) CVD as-deposited, (b) CVD + Ar plasma, (c) CVD + N₂/H₂ anneal.

4. Conclusion

We applied PDTs to CVD-SiO₂/SiC interfaces and evaluated D_{it} of the samples by BA-HAXPES. For as-deposited sample, D_{it} was $4 \times 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$ at the CBM. On the other hand, D_{it} at the CBM decreased to $3 \times 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$ for the sample treated with the Ar plasma and to the value of below detection limit of the analysis for the sample annealed at the temperature of 400 °C in N₂/H₂ ambient. Our BA-HAXPES analysis revealed that the PDTs were able to decrease D_{it} at the CBM, but also increased D_{it} at the deep positions of bandgap. An improvement of treatment conditions to realize lower interface state densities is the next topic in order to obtain a guideline for superior SiC-MOS devices.

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References

- [1] T. Kimoto, Jpn. J. Appl. Phys. **54** (2015) 040103.
- [2] T. L. Biggerstaff, C. L. Reynolds Jr., T. Zheleva, A. Lelis, D. Habersat, S. Haney, S.-H. Ryu, A. Agarwal and G. Duscher, Appl. Phys. Lett. **95** (2009) 032108.
- [3] K. Kawase, A. Teramoto, H. Umeda, T. Suwa, Y. Uehara, T. Hattori and T. Ohmi, J. Appl. Phys. **111** (2012) 034101.
- [4] H. Kobayashi, Y. Yamashita, T. Mori, Y. Nakato, T. Komeda and Y. Nishioka, Jpn. J. Appl. Phys., Part 1 **34** (1995) 959.
- [5] H. Watanabe, T. Hosoi, T. Kirino, Y. Kagei, Y. Uenishi, A. Chanthaphan, A. Yoshigoe, Y. Teraoka and T. Shimura, Appl. Phys. Lett. **99** (2011) 021907.