

# Photoemission Spectroscopy and In-Situ Spectroscopic Ellipsometry Studies on the Ar Post-Oxidation-Annealing Effects of Oxide/SiC Interfaces

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## Abstract

The effect of post-oxidation annealing in Ar atmosphere (Ar-POA) on 4H-SiC/oxide interfaces has been studied by photoemission and ellipsometry measurements. It was shown by angle-resolved x-ray photoelectron spectroscopy (AR-XPS) and ultraviolet photoelectron spectroscopy (UPS) measurements that the concentration of Si<sup>3+</sup> and C-C bond and the structures of O2p twin peaks changed remarkably around 600 °C. It was also found from the in-situ spectroscopic ellipsometry studies that there exist interface layers having higher refractive index than those of stoichiometric SiO<sub>2</sub> and SiC and the refractive indices of the interface layers also decrease by Ar-POA at the temperatures above 600 °C. It has been reported by *C-V* measurements on SiC metal-oxide-semiconductor (MOS) capacitors that the magnitude of flat-band shift decreases by Ar-POA around the same temperature as that observed by photoelectron and optical measurements mentioned above. These results suggest that the structural changes at the interfaces observed by photoemission spectroscopy and ellipsometry are the origins that bring about the flat-band voltage shift in *C-V* properties by Ar-POA.

## I. Introduction

The physical properties of silicon carbide (SiC), such as a wide band gap and high-breakdown electric field, make SiC attractive for electronic device applications including high-power and high-frequency devices whose specifications are hard to be obtained by using Si or GaAs. In addition, SiC can be thermally oxidized to grow insulating SiO<sub>2</sub> layers, which are known to have superior dielectric properties for metal-oxide-semiconductor (MOS) applications, similar to Si.[1] However, SiC MOSFETs have some problems to be solved before practical use, such as their higher on-resistances than those predicted from material properties. It has been reported that[2] the reason for this degradation is due to the low channel mobility  $\mu_{ch}$  in inversion layer of SiC MOSFET, and the small  $\mu_{ch}$  is resulted from high interface trap density and high oxide-trapped charges estimated by capacitance-voltage (*C-V*) measurements with respect to SiC-MOS capacitors. It has been reported that some post-oxidation processes, such as NO annealing[3] and re-oxidation[4], improve electrical properties of SiC MOS capacitors or/and MOSFETs. We have reported that[5][6], in the results of x-ray photoelectron spectroscopy (XPS) measurements for slope shaped oxide films with various post-oxidation processes, several differences in photoemission peaks among the samples with various

processes were observed. However, so far it was hard to specify the origins bringing about these differences in the electrical properties.

In our recent work[7], we focused on Ar post-oxidation-annealing (Ar POA) first of all as one of the post-oxidation processes to clarify the effects of them for interfacial structures. It was found by the results of *cycle C-V* measurements that the flat-band voltage  $V_{fb}$  shifts toward higher gate-bias voltage side with increasing starting gate-bias voltage, which is called as *cycle  $V_{fb}$  shift* here. Also, the magnitude of *cycle  $V_{fb}$  shift* becomes smaller with increasing POA temperature. We have also studied SiC/oxide interface optically by use of a spectroscopic ellipsometry, and found there exist interface layers, around 1nm in thickness, having large refractive indices compared with those of SiO<sub>2</sub> and SiC. It was also found the refractive indices of the interfaces decrease by Ar POA at 950 °C.

In this report, we examined the changes in the interfacial structures of SiC/oxide interface by Ar-POA at various temperatures using angle-resolved x-ray and ultraviolet photoelectron spectroscopy (AR-XPS/UPS). We also tried to observe the changes by Ar-POA optically using specially a designed in-situ spectroscopic ellipsometer, by which the changes of the optical properties of interfaces can be observed in real time without fear of the influence of surface contamination. Finally, we will discuss about the structural changes of the SiC/oxide interfaces by Ar-POA, based on the results of photoemission and ellipsometric measurements, as well as those of *C-V* measurements.

## II. Experimental procedure

### II-1. Analysis of oxide/SiC interfaces by photoemission spectroscopies

Epitaxial wafers of 4H-SiC with 8° off-oriented (0001) Si-face, *n*-type,  $N_d - N_a = 4 \times 10^{15} \text{ cm}^{-3}$  were used in this study. After standard RCA cleaning, the surface of the SiC epitaxial layer was oxidized up to 50 nm of oxide thickness in pure dry O<sub>2</sub> flow at 1200 °C. After oxidation, one sample was quenched (a), the others were annealed in Ar for 3 hours at the temperatures; 500 °C (b), 600 °C (c), 950 °C (d). All four samples (a)-(d) must be etched off in order to be thinner than escape depth of photoelectrons  $\lambda_e \sim 2.3 \text{ nm}$  for XPS or  $\sim 1.5 \text{ nm}$  for UPS. However, a few atomic layers of SiO<sub>2</sub> must be left on the interfacial layer because the interface could be changed in quality if it is exposure to the air. Taking account for the thickness of interfacial layer  $\sim 1 \text{ nm}$ [5][8], oxide thickness was determined around 2 nm. Based on these considerations, we etched the samples by buffered HF solution and obtained the oxide thickness of (a), (b), (c), (d) = 1.63, 2.30, 1.76, 1.87 nm, respectively, measured by a spectroscopic ellipsometer. AR-XPS measurements were done with Mg-K $\alpha$  line (= 1253.6 eV) as a light source and semi-spherical analyzer as an electron spectrometer. Here, in-take angle of photoelectron is indicated by  $\theta_e$ , which is regarded as an angle from the sample surface. After AR-XPS measurements were carried out, a part of all the samples are deposited by Au thin film with multi-dot pattern for the reference of energy (horizontal) axis by referring the Au 5p peak. The thickness of Au thin films was around 8 nm. UPS measurements were performed with HeII line (= 40.8 eV) as a light source.

### II-2. Optical observations of the effects of Ar POA by a in-situ spectroscopic ellipsometry

Epitaxial wafers of 4H-SiC with the same specification as those used in photoemission experiments were used for the optical measurements. After the standard RCA cleaning, the samples were loaded on the sample stage in the vacuum chamber of an in-situ spectroscopic ellipsometer and were heated by IR ramp in vacuum at 500 °C for 15 min for thermal cleaning. Ellipsometric measurements were carried out in the wavelength range between 250 and 850 nm in vacuum in order to obtain the optical constants of SiC, which is necessary to analyze the optical properties of SiC/oxide systems. Then, the samples were oxidized thermally at 1100 °C in pure oxygen flow with the flow rate of 500 sccm in an oxidation furnace. After 6 hours oxidation, the sample was cooled down

immediately as for thermally quenched, and was reloaded in the vacuum chamber of the ellipsometer. Before annealing, ellipsometric measurements were performed in vacuum. Then, the sample was heated at 600 °C by IR ramp in Ar flow for 30 minutes. After sufficient time to cool down to room temperature passed, ellipsometric measurement was done in vacuum. The same measurement was carried out after the sample was reheated for 90 minutes. Then, the oxide layer was etched off and the same procedure from the oxidation to the ellipsometric measurement was done at the annealing temperatures of 750 and 900 °C.

### III. Result and Discussion

#### III-1. AR-XPS and UPS measurements

The spectrum of Si2p region and that of C1s region from the quenched sample (a) at  $\theta_e = 45^\circ$  were shown in Fig. 1(a) and (b), respectively. The elemental peaks divided by deconvolution process with Gaussian peaks and fitting curve were indicated together with measured spectrum. One may point out that some elemental peaks were including arbitrariness, however, they have been confirmed by the differential spectra which were derived by two spectra at different  $\theta_e$  each other. Intensities of elemental peaks with respect to photoelectron escape depth as a function of Ar POA temperature were plotted in Figs.2. However, it is noted that only the bonds, which depend on Ar POA temperature, were indicated in Figs.2 and plotting was omitted when the peak was weak up to below the noise level, also, atomic concentration was calculated by a following simple equation,

$$I_i / \sigma^n I_m, \quad (1)$$

where  $I_i$ ,  $I_m$  and  $n$  indicate the intensity of the corresponding elemental peak, the intensity of an elemental peak and the number of elements, respectively. From the results of  $C-V$  measurements, cycle  $V_{fb}$  shift described above becomes lower abruptly at 600 °C. It is found from Figs.2 that  $Si^{3+}$  and C-C bonds behave such temperature dependence.

Figure 3(a) shows UPS spectra of 4H-SiC without Au (solid line) and with Au (dotted line). By setting 0 eV of the energy axis into SiC valence band maximum (VBM) and compared with 'with Au' of 'without Au', we can determine that the peaks with a small split around 5.5 eV and the peak at 10.5 eV are originated from Au 5p<sub>3/2</sub> peak, which is including unpaired electron, and Au 5p<sub>1/2</sub> peak,

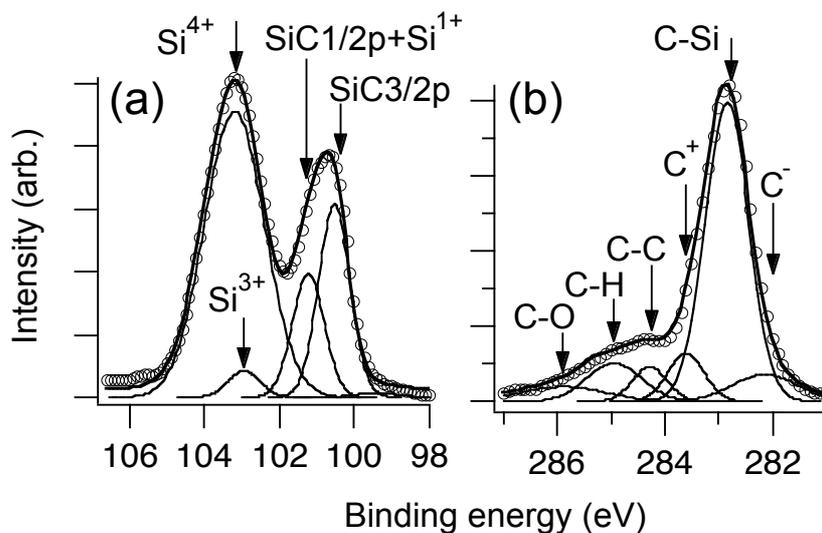


Fig.1 XPS spectra of sample (a) quenched,  $\theta_e = 45^\circ$  (a) Si2p (b) C1s.

respectively. Therefore, the energy difference between Fermi Edge of Au and that of SiC was obtained as 5.6 eV in our experiments. This value was used as a reference for the following experiments. Figure 3(b) shows UPS spectra of samples (a)-(d) mentioned before at  $90^\circ$  in intake angle  $\varphi_e$  without photoemission signal from Au film. We can see three peaks in Fig. 3(a), broadened one around 3.0 eV, biggest one around 10.5 eV and one at the highest relative energy side ( $\sim 15$  eV). The broadest peak around 3.0 eV is considered to be originated from hybridized Si 3s + 3p orbital[9], i.e. Si3sp<sup>3</sup>. Tabe et al. reported in case of oxide on Si that[10] two peaks at the energy region larger than 6 eV are originated from O2p. It is noted that the structure of O2p peak depends on the Ar POA temperature and changes in the peak energy shift, intensity and intensity ratio of O2p peaks. The lowest temperature at which the structure of O2p changes, i.e. 500-600 °C, agrees well with that at which the magnitude of *cycle*  $V_{fb}$  shift in *C-V* measurements changes[7]. On the other hands, the change of UPS spectra does not concern with oxide. Therefore, the structural change of O2p bond can be confirmed as one of the origin of *cycle*  $V_{fb}$  shift in *C-V* measurements. We have measured also in case of  $\varphi_e = 45^\circ$ . The shift and the intensity reduction of O2p peak by Ar POA, like as the case of  $\varphi_e = 90^\circ$ , were not observed at all contrary the case of  $\varphi_e = 90^\circ$ . This suggests that the structure of oxide layer was changed by Ar POA not at oxide layer side but just above top-most SiC layer, since the measurement at  $\varphi_e = 45^\circ$  is more surface sensitive than that at  $\varphi_e = 90^\circ$  in general for amorphous material.

Based on the results of photoemission spectroscopic measurements, let us consider the

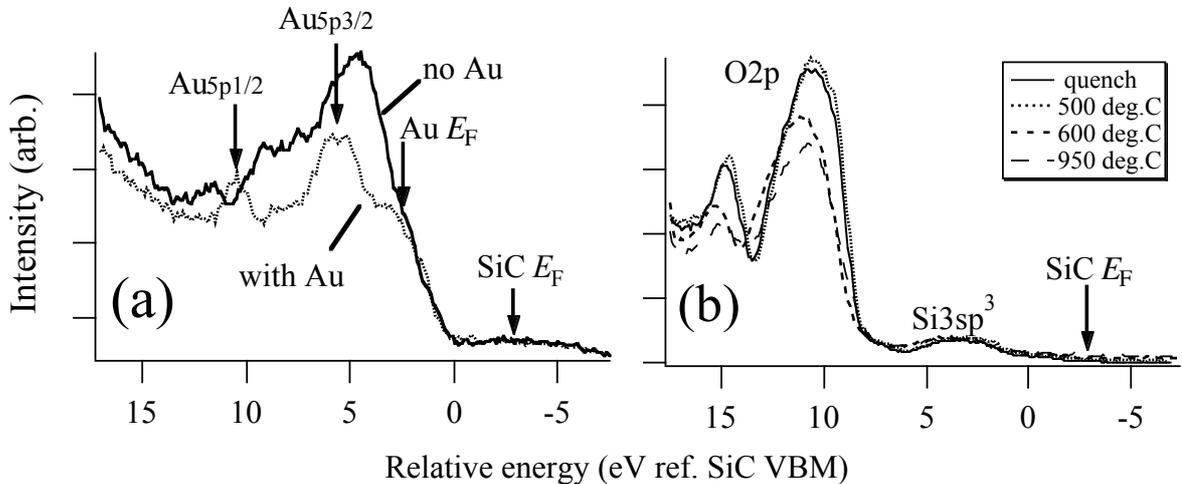


Fig.3 UPS spectra ( $\varphi_e=90^\circ$ ) of (a) SiC (b) Ar POA temperature dependence of oxide films with  $\sim 2$  nm in thickness.

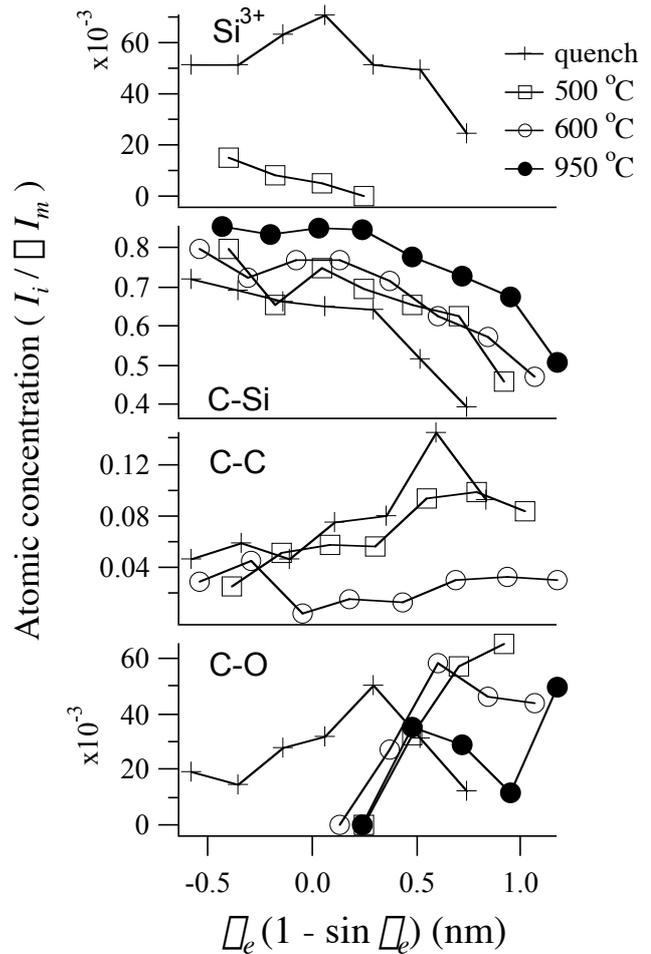


Fig.2 Atomic concentrations as a function of escape depth. (Plotting was omitted when the signal was very weak)

composition and bonding structure of oxide/SiC interfaces, and the effects of Ar POA for the interfaces. In general, it is considered that high temperatures beyond 1000 °C are necessary to oxidized SiC because Si-C connections at the oxidation front must be broken away, and the oxidation temperature of SiC is resulting in much higher than that of Si. Therefore, it is predicted that heating process “without the advance of oxidation front” after oxidation is necessary to fabricate an abrupt interface with carbon free. According to ref. 7, there exists acceptor-like defects at the interface, which bring about *cycle*  $V_{fb}$  shift. It can be speculated that the origin of these defects is some carbon bond since the electron negativity of carbon is higher than that of Si. On the other hands, it is reported that[10], in case of very thin oxide film (< a few nm) on Si, the peak intensity ratio between O2p twin peaks is concerned with the composition  $x$  of  $\text{SiO}_x$ . The value of  $x$  becomes bigger with increasing the ratio of the peak at higher energy side to another peak at lower energy side ( $I_l/I_l+I_h$ ). In our results,  $I_l/I_l+I_h$  is changed from  $\sim 0.35$  to 0.18 by Ar POA at 500-600 °C. Taking account for XPS results as well, it can be considered that  $\text{Si}^{3+}$  bonds replaced to  $\text{Si}^{1+}$  bonds by Ar POA, which brings about low  $x$ . Further, the three back bonds of Si with insertions of oxygen, i.e. Si-O<sub>3</sub>-C<sub>3</sub> networks, may be left when quenched, and they are removed and replaced to Si-O-Si network by Ar POA.

### III-2. In-situ spectroscopic ellipsometry

Figures 4 show the wavelength dependences of  $\tan \Psi$  and  $\cos \Psi$  for the oxide films before and after Ar-POA for 30 minutes. Both the values of  $\tan \Psi$  and  $\cos \Psi$  change by Ar-POA, especially in the shorter wavelength region, as shown in the enlarged inset. There were little difference in the values for 90 minutes Ar-POA from those for 30 minutes Ar-POA, which suggests the changes by Ar-POA finish within 30 minutes.

We have derived the refractive indices of the interface layer by assuming that the oxide film is composed of two layers, a  $\text{SiO}_2$  layer with stoichiometric composition, i.e., having the same refractive indices as those of fused quartz, and an interface layer, 1 nm in thickness, the refractive indices of which follow Sellmeier's dispersion law,

$$n = \sqrt{1 + \frac{(A^2 - 1)\lambda^2}{\lambda^2 - B}} \quad (2)$$

and extinction coefficient  $k = 0$ . We have obtained the refractive indices of the interface layer by curve fitting between observed and calculated  $\tan \Psi$  and  $\cos \Psi$  spectra, where the Sellmeier's parameters  $A$  and  $B$  and the thickness of the  $\text{SiO}_2$  layer were used as fitting parameters. The values of  $A$  and  $B$  correspond to

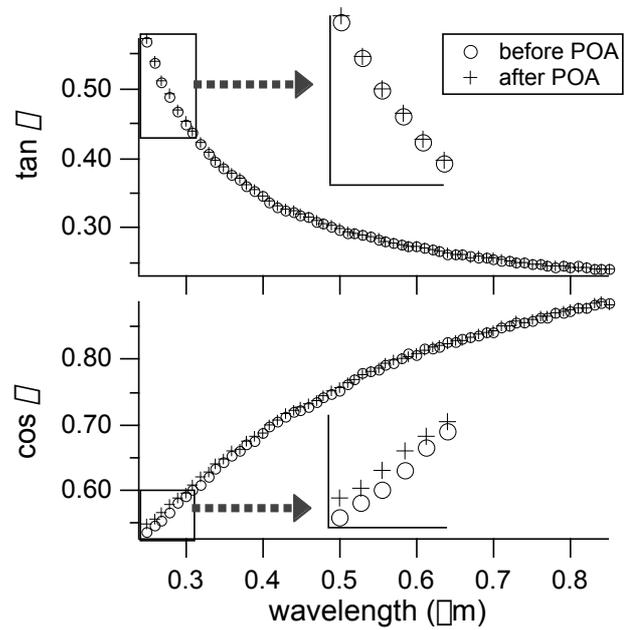


Fig.4  $\tan \Psi$ ,  $\cos \Psi$  vs. wavelength for before and after POA at 950 °C.

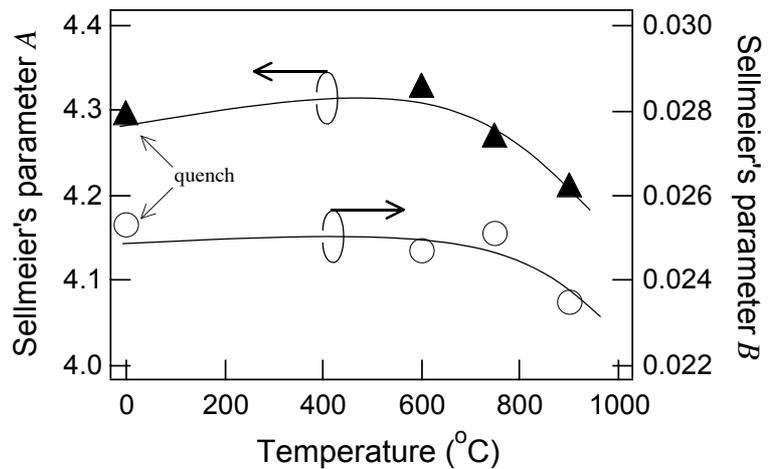


Fig.5 Sellmeier's parameter  $A$ ,  $B$  at  $\lambda = 300$  nm of the interface layer between oxide film and SiC as a function of POA temperature.

the refractive index at infinite wavelength and the square of characteristic oscillation wavelength, respectively. Figure 5 shows the values of  $A$  and  $B$  for various Ar-POA temperatures. Comparing with those for the sample before annealing, i.e., as quenched sample, both  $A$  and  $B$  decrease with increasing temperature above 600 °C. The reduction of the values of  $A$  means the reduction of refractive indices. This means Ar-POA reduces the origins which bring about the large refractive indices or large dielectric dipole moments at the interface, like Si-Si bonds, SiO<sub>x</sub> ( $x < 2$ ) phase and so on. The changes of the refractive indices start at around 600 °C, which is in good agree with the changes observed by AR-XPS/UPS and  $C-V$  measurements. These results suggest that the origins of the changes observed optical, electrical and photoelectron emission measurements are same or closely related each other.

#### IV. Summary

We have studied the effects of Ar-POA on SiC/oxide interfaces by AR-XPS/UPS and in-situ spectroscopic ellipsometry, for the first time. It was found from both the measurements that the structures of the interface change above 600 °C, which is also in good agreement with the results obtained by  $C-V$  measurements. We have discussed about the origins of these changes in terms of bonding states and dipole moments of the molecules and/or atoms at the SiC/oxide interface.

#### Acknowledgments

This work was partially supported by the management of FED as a part of the METI Project (R & D of Ultra-Low-Loss Power Device Technologies) supported by NEDO and the Ministry of Education, Culture, Sports, Science and Technology through a 2001-2002 grant-in-aid for Scientific Research (B) (No. 13450120).

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