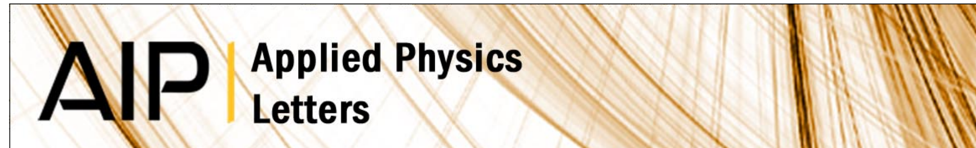

Characterization of silicon dioxide films on 4H-SiC Si (0001) face by cathodoluminescence spectroscopy and x-ray photoelectron spectroscopy

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Characterization of silicon dioxide films on 4H-SiC Si (0001) face by cathodoluminescence spectroscopy and x-ray photoelectron spectroscopy

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We measured cathodoluminescence (CL) spectra of SiO_2 films grown on 4H-SiC wafers and found that for an acceleration voltage of 5 kV, CL peaks at 460 and 490 nm, assigned to oxygen vacancy centers (OVCs), become weak by post-oxidation annealing in N_2O ambient at 1300 °C whereas the CL peak around 580 nm, related to Si-N bonding structures, becomes intense. Furthermore, the peak assigned to N-Si_3 configurations in x-ray photoelectron spectroscopy (XPS) spectra was observed in the SiO_2/SiC interface in only samples annealed in N_2O ambient. These results suggest that the interface trap densities decrease and the channel mobility in n-type MOS capacitors increases by the termination of dangling bonds by the N atom in the SiO_2/SiC interface. CL spectroscopy and XPS provide us with extensive information on OVCs and dangling bonds in the SiO_2/SiC interface on the 4H-SiC substrate. © *2012 American Institute of Physics*. [doi:10.1063/1.3688173]

Silicon carbide (SiC) is a well-known wide-bandgap semiconductor that contains native silicon dioxide (SiO_2), the presence of which makes SiC suitable for applications to high-power, high-frequency metal–oxide–semiconductor (MOS) devices. The interface trap densities (D_{it}) at the SiO_2/SiC interface and effective fixed charge density (Q_{eff}) are one to two orders of magnitude higher than those typically found at the SiO_2/Si interface (of the order of 10^{11} cm^{-2});[1] these values degrade the channel mobility (CM).[2–5] The presence of interface traps in SiC MOS field-effect transistors (FETs) is attributed to (1) excess carbon,[4,6] (2) interface defects due to the presence of threefold coordinated O and C interstitial atoms,[4,6] and (3) point defects such as Si and O vacancies that extend into the SiC layer underneath the SiO_2/SiC interface; the extending of the point defects was determined via a comparison with SiO_2 films grown on a Si substrate.[7,8] Although post-oxidation annealing (POA) by H_2,[2] NO,[9,10] or N_2O (Refs. 3 and 11–13) effectively increases the CM, few studies have focused on effect of POA on the microstructure of SiO_2 films on SiC wafers.

In cathodoluminescence (CL) spectroscopy, luminescence of a sample subjected to electron beam irradiation is observed.[14–16] CL spectroscopy provides considerable information on defects in thin SiO_2 films. In a previous study,[17] we measured the CL spectra of SiO_2 films on Si prepared by various methods and observed peaks at 445 and 480 nm, originated from oxygen vacancy centers (OVCs). The CL measurement of the cross section of a thermally grown SiO_2 film on a Si substrate indicated that the intensities of the above-mentioned peaks in the SiO_2/Si interface were stronger than that of the CL peak at 640 nm, attributed to non-bridging oxidation hole centers (NBOHCs).

X-ray photoelectron spectroscopy (XPS)[18,19] is conducted by irradiating the material to be analyzed with an x-ray beam and simultaneously measuring the kinetic energy and number of electrons that escape from the top 10 nm region from the material surface. Kurimoto *et al.*[18] studied the thermal oxidation temperature dependence of a 4H-SiC substrate using XPS and capacitance–voltage (C–V) measurements. They suggested that when SiC was thermally oxidized, silicon oxycarbides (SiC_xO_y) were first grown and then SiO_2 was grown.

In a previous paper,[20] we characterized SiO_2 films on a 4H-SiC (0001) Si face using Fourier transform infrared (FT-IR) spectroscopy and CL spectroscopy. We found that the peak frequencies of the optical phonons and CM of the SiC-MOSFET decreased roughly in proportion to the increase in the CL peak intensity at 460 and 490 nm, attributed to OVCs. This suggested that a decrease in the peak frequencies of these phonons and CM was mainly because of an increase in the number of OVCs near the SiO_2/SiC interface.

Although it is known that POA by H_2,[2] NO,[9,10] or N_2O (Refs. 3 and 11–13) ambient effectively increases CM, few studies have focused on the effect of POA on the microstructure of the SiO_2/SiC interface on SiC wafers. In order to clarify the bonding structures near the SiO_2/SiC interface, we study changes in the CL spectra of SiO_2 films on a 4H-SiC (0001) Si face for films that did and did not undergo POA by N_2O ambient and compare the result with the XPS spectra of SiO_2 films on a 4H-SiC substrate prepared by thermal oxidation with gradient etching.

Epitaxial layers (approximately 5 μm thick) were grown by chemical vapor deposition (CVD) on a 4° off-axis 4H-SiC(0001) Si face.[21] After these layers were RCA cleaned, they were thermally oxidized in dry O_2 at 1150 °C and then underwent POA in N_2O ambient at 1300 °C. The several samples were then annealed in Ar ambient at 1300 °C. The oxide thickness was measured by ellipsometry. The typical oxide

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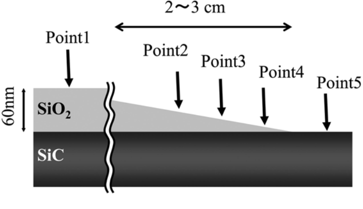
TABLE I. Thickness, oxidation condition, interface trap densities (D_{it}), effective fixed charge density (Q_{eff}), and channel mobility of thermally grown SiO_2 films on the 4H-SiC (0001) Si face.

Sample No.	Thickness (nm)	Thermal oxidation	Post-oxidation	D_{it} ($cm^{-2} eV^{-1}$) (Ec-E ∼ 0.2 eV)	Q_{eff} (cm^{-2})	Mobility (cm^2/Vs)
No. 1	100	1150 °C 12 h	—	5.0×10^{12}	-1.5×10^{12}	4
No. 2	100	1150 °C 12 h	N_2O anneal: 1300 °C 2 h Ar anneal: 1300 °C 0.5 h	5.0×10^{11}	-2.3×10^{11}	24
No. 3	100	1150 °C 12 h	N_2O anneal: 1300 °C 2 h Ar anneal: 1300 °C 5 h	4.0×10^{11}	-2.8×10^{11}	34
No. 4	100	1150 °C 12 h	Ar anneal: 1300 °C 0.5 h	1.0×10^{12}	2.6×10^{11}	5
No. 5	100	1150 °C 12 h	Ar anneal: 1300 °C 5 h	1.0×10^{12}	3.9×10^{11}	7



Point	SiO_2 thickness (nm)
1	60
2	15
3	10
4	5
5	0

FIG. 1. Schematic diagram of the points measured by XPS with gradient etching.

thickness was approximately 100 nm. D_{it} was estimated from high-frequency (1 MHz) and low-frequency (quasi-static) C–V curves of n-type MOS capacitors, and Q_{eff} of the samples was determined from the flatband voltage in the C-V curves. The voltage sweep rate in C–V measurements was 0.1 V/s. The thickness, oxidation condition, D_{it}, Q_{eff}, and channel mobility of the samples are listed in Table I.

We used a scanning electron microscope (SEM) with a Schottky-emission-type gun (HITACHI S-4300SE) as the excitation source for CL measurement.[20] We recorded the CL spectra at acceleration voltages of 3 and 5 kV at room temperature with a beam current of less than 5 nA.[20] To minimize the degradation caused by electron beam irradiation, most CL spectra were measured for 60 s. We repeated the CL measurement of each film two times and obtained reproducible CL spectra. The XPS measurements were obtained using ESCALAB220iXL (VG) with monochromatic AlKα as an excitation source ($h\nu = 1486.6$ eV).[19] A hemispherical electron analyzer was operated in fixed analyzer transmission (FAT) mode by selecting a constant pass energy of 30 eV throughout the measurements. The N1s core level was studied. The XPS spectra were measured at the take-off angle of 45°. Next, we measured the XPS spectra of the SiO_2 films on the 4H-SiC substrate prepared by thermal oxidation with gradient etching. The schematic diagram of the measured points is shown in Fig. 1.[19]

Figures 2(a) and 2(b) shows the CL spectra of the samples measured at acceleration voltages of 3 and 5 kV, respectively. CL peaks were observed at 460, 490, and 660 nm for the SiO_2 films on the 4H-SiC substrate. The CL peaks at 460 and 490 nm were attributed to OVCs, whereas the CL peak at 660 nm was attributed to NBOHCs.[20] The CL spectrum of the 4H-SiC substrate is also shown in the figure for comparison. The CL peaks at 390 and 540 nm originate from a bound exciton and donor-acceptor pair, respectively.

Surprisingly, in Fig. 2(b), the CL peaks around 390 and 580 nm for sample Nos. 2 and 3, annealed in N_2O ambient are stronger than those for other samples. We measured the CL spectra for a range of silicon nitride (SiN) films prepared on Si substrates by sputtering, low-pressure (LP) CVD, and plasma CVD at 400 and 500 °C. The CL spectra of SiN films are shown in Fig. 3. As shown in Fig. 3, CL peaks are observed around 390 and 580 nm for the SiN films. A comparison between Figs. 2 and 3 indicates that the CL peak around 580 nm for sample Nos. 2 and 3 is attributed to the Si-N bonding structure.

Several groups[22,23] have studied the photoluminescence (PL) and CL spectra of SiN films. Deshpande *et al.*[22] observed the PL peaks for the SiN films at 3.0, 2.5, and

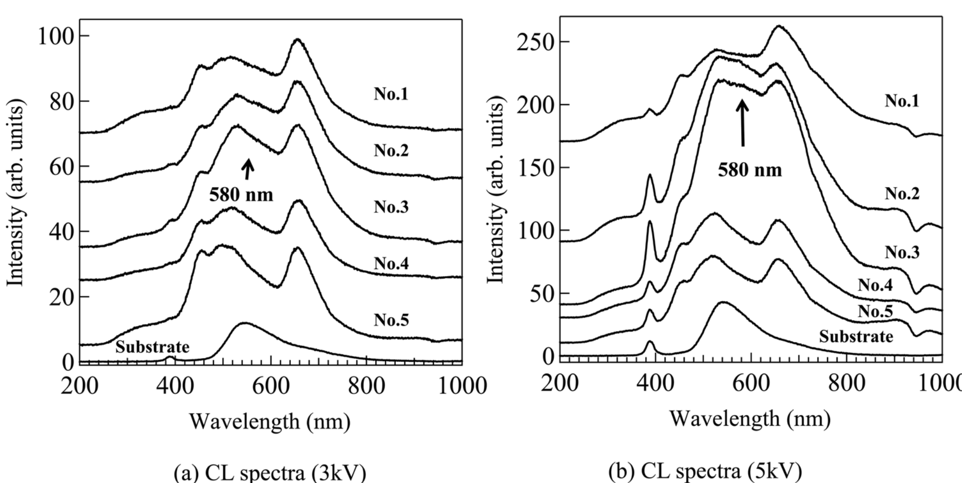


FIG. 2. CL spectra of SiO_2 films on 4H-SiC substrate measured at acceleration voltages of (a) 3 kV and (b) 5 kV.

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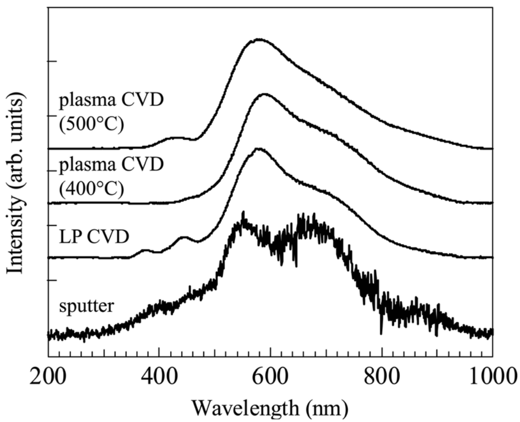

FIG. 3. CL spectra for SiN films prepared on Si substrates by sputtering, low-pressure CVD, and plasma CVD at 400 and 500 °C.

1.8 eV. They assigned these PL peaks to the defects in the films, based on Robertson's theoretical predictions.[24,25] On the other hand, Pundur *et al.*[23] observed two additional CL peaks at 2.0 and 1.75 eV. They proposed a model based on the Si-Si (σ-σ^*) bonds separated by 4.6 eV, representing the band edges and additional electron and hole traps with the gap, and ascribed the CL peaks at 2.0 and 1.75 eV to the electron and/or hole traps within the gap. Based on their results, we considered the CL peak around 580 nm, which we observed in the SiO_2/SiC interface, to originate from Si-N bonds or from defects related to Si-N bonds.

Figures 4(a) and 4(b) shows the CL spectra of samples measured at acceleration voltages of 3 and 5 kV, respectively. These spectra are subtracted by the CL spectrum of the 4H-SiC substrate shown in Figs. 3(a) and 3(b) and normalized by the intensity of the CL peak at 640 nm. A comparison between Figs. 4(a) and 4(b) indicates that the CL peak at 580 nm for sample Nos. 2 and 3, which is assigned to Si-N bonding structures, is stronger at the acceleration voltages of 5 kV than at 3 kV. Monte Carlo simulations indicated that the penetration depths of electrons in thin SiO_2 films at acceleration voltages of 3 and 5 kV were approximately 30 and 60 nm, respectively. However, the penetration depth of electrons in thin SiO_2 films at the acceleration voltage of 5 kV is considered to be greater than the Monte Carlo simulation results because the CL peaks are observed for the 4H-SiC substrate (as in Fig. 2(b)), when measured at 5 kV. By comparing the penetration depth and sample thickness, the intensity of the CL peak at 580 nm is considered to increase in the SiO_2/SiC interface. This suggests that Si-N bonds are formed in the SiO_2/SiC interface.

In order to clarify the bonding structures near the SiO_2/SiC interface, we measured XPS spectra of the SiO_2 films on the 4H-SiC substrate with gradient etching.[21] Figures 5(a)–5(d) shows the N1s spectra of sample Nos. 1–4. As shown in Fig. 5, the peak assigned to N-Si_3 configurations[9] was observed at about 397.2 eV in the SiO_2/SiC interface for only sample Nos. 2 and 3 annealed in N_2O ambient. Furthermore, we detected no peak assigned to N-Si_3 configurations in the sample No. 5. On the other hand, on measuring the Si2p spectra of sample Nos. 1–5, we could not significantly find any difference among the Si2p spectra of the samples.

As given in Table I, the D_{it} of sample Nos. 2 and 3 is lower than that of other samples and the CM of sample Nos. 2 and 3 is higher than that of other samples. A decrease in D_{it} and an increase in CM for sample Nos. 2 and 3 is caused by the POA in N_2O ambient at 1300 °C. In Figs. 2(a) and 4(a), the CL peaks at 460 and 490 nm, attributed to OVCs, become weak by POA in N_2O ambient at 1300 °C whereas the CL peak around 580 nm related to Si-N bonding structures becomes intense. This tendency can be clearly observed in Figs. 2(b) and 4(b) for an acceleration voltage of 5 kV. Furthermore, for sample Nos. 2 and 3, the CL peak at 640 nm ascribed to NBOHCs appears to be weaker than the CL peak around 580 nm when measured at an acceleration voltage of 5 kV. Considering these results, we conclude that the number of OVCs in the SiO_2/SiC interface decreases by POA in N_2O ambient at 1300 °C and that the number of NBOHCs and/or the dangling bonds in the SiO_2/SiC interface decreases by termination by the N atom, resulting in a decrease in D_{it} and an increase in CM.

In summary, we measured CL and XPS spectra of SiO_2 films grown on a 4H-SiC wafer and found that the CL peaks at 460 and 490 nm, attributed to OVCs, become weak by POA in N_2O ambient at 1300 °C whereas the CL peak around 580 nm, related to Si-N bonding structures, becomes intense for the acceleration voltage of 5 kV. The peak assigned to N-Si_3 configurations in the XPS spectra was observed at 397.2 eV in the SiO_2/SiC interface for only sample Nos. 2 and 3 annealed in N_2O ambient. Furthermore, for sample Nos. 2 and 3, the CL peak at 640 nm, ascribed to NBOHCs, appears to be weaker than the CL peak around 580 nm for the acceleration voltage of 5 kV. These results show that a decrease in D_{it} and an increase in CM are caused by the

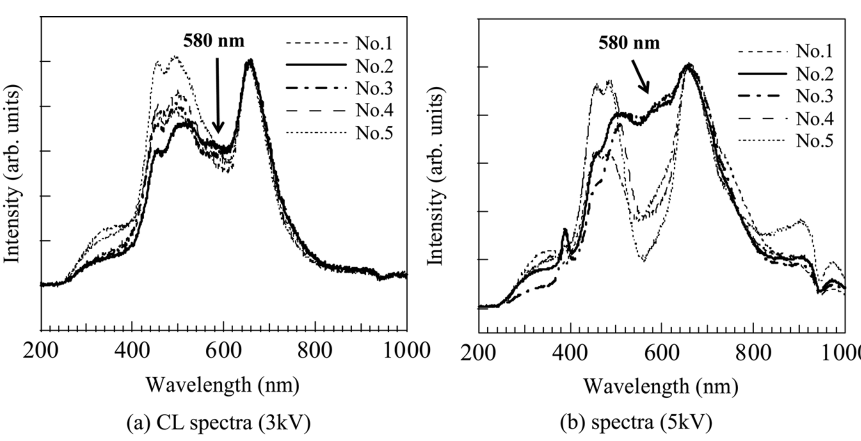

FIG. 4. CL spectra of samples subtracted by CL spectrum of 4H-SiC substrate and measured at acceleration voltages of (a) 3 kV and (b) 5 kV.

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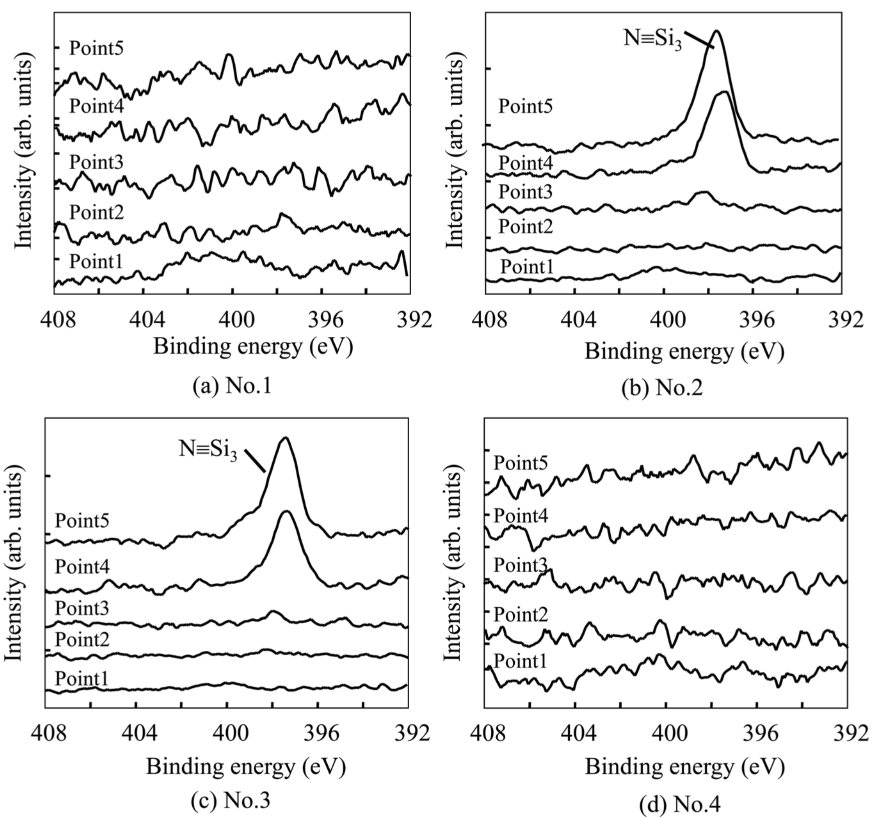

FIG. 5. N1s spectra of samples (a) No. 1, (b) No. 2, (c) No. 3, and (d) No. 4.

termination of NBOHCs and/or the dangling bonds by the N atom in the SiO_2/SiC interface. CL spectroscopy and XPS provide us with a large amount of data on OVCs and dangling bonds in the SiO_2/SiC interface on the 4H-SiC substrate.

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