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Studies of NO on 4H-SiC(0001) using synchrotron radiation

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Abstract
Detailed studies of the effects induced on the $\sqrt{3} \times \sqrt{3}$ R30° 4H-SiC(0001) surface after different NO exposures, at a substrate temperature of 800 °C, have been made. Photoemission experiments using synchrotron radiation were performed in order to study the properties of the interface formed after gas exposures. Recorded Si 2p spectra show three shifted components, besides the bulk SiC peak. These are assigned as originating from Si_3N_4 or Si^{1+} sub-oxide, N–Si–O and SiO_2. It was concluded that SiO_2 does grow on top of N–Si–O and that Si_3N_4/Si^{1+} is located at the interface. Two N 1s components are observed after NO exposures. The main one, located at around 398.05 eV, is assigned as originating from Si_3N_4 and the weaker one is suggested to correspond to N–Si–O bonding. The assignments are made with the aid of Si 2p and N 1s spectra collected after NH_3 and O_2 exposures under similar conditions. No graphite-like carbon or carbon by-product at the interface can be detected after large NO or O_2 exposures.

1. Introduction

Silicon oxynitride is an alternative to ultrathin dielectric films for use in silicon carbide based electronic devices. It has been claimed that silicon oxynitride improves the electrical reliability [1, 2]. The reason for this is still unclear, however. From our earlier studies of SiO_2/SiC samples grown by a standard dry oxidation method and by *in situ* oxygen exposures [3] we have suggested that a main reason for the high interface defect density is the presence of a Si^{1+} sub-oxide. Other groups have suggested that it is due to carbon clusters or carbon containing by-products at the interface [4, 5].

We have therefore made detailed studies of the effects induced on the $\sqrt{3} \times \sqrt{3}$ R30° 4H-SiC(0001) surface after exposures to nitrogen containing gases (NO, N_2O and NH_3) and

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also pure oxygen. Core level and valence band photoemission experiments using synchrotron radiation were performed in order to study the properties of the oxynitride/SiC, nitride/SiC and oxide/SiC interfaces formed after NO, NH_3 and O_2 exposures, respectively. Distinct differences were found between the different gases.

2. Experiment

The experiments were performed on beamline I311 at the MAX synchrotron radiation laboratory. This beamline is equipped with a modified SX-700 monochromator and an end station built up around a large hemispherical Scienta electron analyser which operates at a base pressure of about 1×10^{-10} Torr. A total-energy resolution, determined by the operating parameters used, of $\leqslant$100 meV at a photon energy of 330 eV and of $\leqslant$300 meV at 600 eV was selected in the high resolution studies of the core levels reported below.

Oxynitride layers were thermally grown *in situ* in pure flowing NO at pressures from 10^{-7} to 10^{-3} Torr. The exposures were made with the sample kept at 800 °C. Other gases (N_2O, NH_3 and O_2) were also used for comparison.

3. Results and discussion

Si 2p spectra recorded after different gas exposures are shown in figure 1 together with the results obtained after applying a curve fit procedure [6]. The spectrum shown in (a) was collected after an exposure of 10^6 L of NO, in (b) after 10^5 L of NH_3 + heat and in (c) after 10^6 L of O_2. After oxygen exposure (figure 1(c)) two shifted components corresponding to a Si^{1+} sub-oxide and SiO_2 (Si^{4+}) with shifts of 0.5 and 2.0 eV respectively are observed in agreement with earlier findings [3]. The spectrum recorded after ammonia exposure and annealing (figure 1(b)) also shows two shifted components. The one shifted by 0.4 eV to larger binding energy is suggested to correspond to Si_3N_4 [7]. The second one shifted by −0.6 eV, i.e. to lower binding energy, is suggested to correspond to one of the surface shifted components appearing on the $\sqrt{3}$ surface [3].

After NO exposure (figure 1(a)), three shifted components were found to be required in the fit. These exhibit the average shifts of 0.4, 1.4 and 2.0 eV relative to the bulk SiC peak. The largest shift we assign to SiO_2. The smallest shift (0.4 eV) is very similar to that observed for the NH_3 sample (corresponding to Si_3N_4) but also fairly similar to the shift for the Si^{1+} sub-oxide after oxygen exposure. We therefore tentatively assign this component as corresponding to Si_3N_4 or Si^{1+} since we cannot distinguish between these. The component exhibiting a shift of 1.40 eV we assign to N–Si–O, i.e. as originating from a mixture of nitrogen and oxygen bonding to the silicon. The mixed oxynitride component was found to increase somewhat after the largest exposure while the Si_3N_4/Si^{1+} component remains fairly constant. This dependence on exposure suggests that the component having the smallest shift is likely to originate predominantly from Si_3N_4. An analysis of Si 2p spectra collected at different photon energies showed that SiO_2 does grow on top of N–Si–O and that Si_3N_4/Si^{1+} is located at the interface.

Si 2p spectra recorded after N_2O exposures at about 1 atm and at a substrate temperature of 900 °C showed a dominant SiO_2 component and presence of only a Si^{1+} sub-oxide. These spectra were thus very similar to those observed after oxygen exposure. No N 1s signal could be detected after these exposures, indicating oxide growth only and not the earlier suggested [8] nitrogen incorporation. The reason for this, we believe, is that 900 °C is too low a temperature to dissociate N_2O efficiently. This was unexpected since a temperature of 800 °C was sufficient for NO and NH_3.

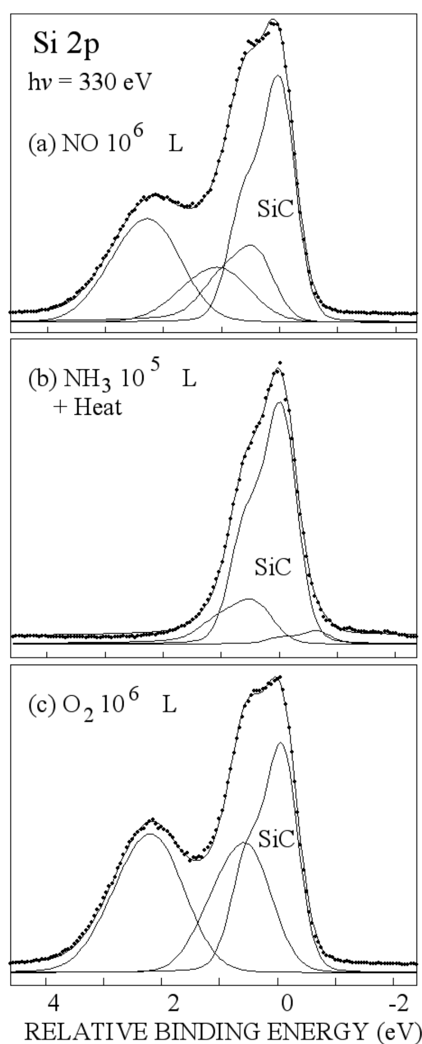

Figure 1. Si 2p spectra collected after exposures of (a) 10^6 L of NO, (b) 10^5 L of NH_3 + 1060 °C heating and (c) 10^6 L of O_2, using a photon energy of 330 eV.

The N 1s spectra recorded after a 10^5 L exposure of NH_3 and NO and after a subsequent heating to about 1060 °C are shown in figure 2. Two N 1s peaks are observed after NH_3 exposure, a main one located at a binding energy of around 398.05 ± 0.14 eV and a weaker one shifted by about 1.2 eV to higher binding energy. The main component is interpreted as corresponding to Si_3N_4 [7, 9, 10] and the shifted one, which is seen to disappear after annealing, as corresponding to NH_2 fragments adsorbed on the surface [9–11]. Two N 1s components are also observed after NO exposures. The dominant peak is located at the same binding energy as the Si_3N_4 component for the NH_3 exposed and annealed sample. The considerably weaker additional peak is shifted about 1.3 eV to higher binding energy. This peak appears stronger in the spectrum recorded at higher surface sensitivity ($h\nu = 465$ eV) and is undetectable after annealing the sample at about 1060 °C for 1 min. We suggested that it could originate from N–Si_2O bonds [12]. However, since it is considerably stronger in the more surface sensitive spectrum and disappears upon annealing we cannot exclude the possibility that it originates

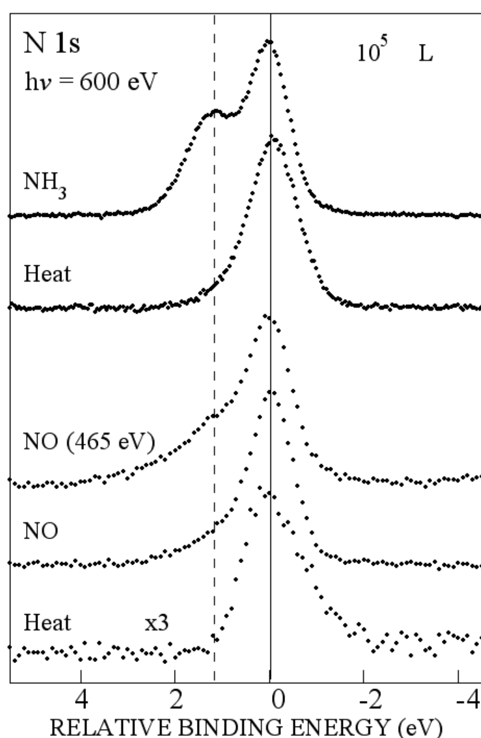

Figure 2. N 1s spectra recorded after an exposure of 10^5 L of NH_3 and NO and after a subsequent heating to about 1060 °C.

from either NO adsorbed on the surface or from N–Si–O bonding at the surface rather than within the oxynitride layer. The N 1s peak shape is seen to change after the heating of the NO exposed sample. An asymmetry on the low binding energy side is then clearly visible which can be interpreted as the appearance of a new weak N 1s peak shifted about 1.0 eV to lower binding energy. No O 1s signal could be detected after the heating at 1060 °C so no N–O bonds remain. We therefore suggest that this asymmetry, a weak additional peak, originates from a reduced nitride, possibly Si_4N_3 [13], formed when the oxide evaporated from the surface during the annealing. Nitrides remain on the surface since a higher thermal energy is required to break the Si–N bonds.

Valence band spectra recorded from clean $\sqrt{3}$ and after an exposure of about 10^6 L to the three different gases are shown in figure 3. After NO and O_2 exposures the valence band spectra appear very similar, with dominant contributions from O 2s and O 2p states, while after NH_3 exposure, contributions from N 2s and N 2p states appear instead. No carbon by-product could be detected in the C 1s data collected after large NO, N_2O and O_2 exposures.

3.1. Summary and conclusion

Effects induced by NO exposures of the $\sqrt{3} \times \sqrt{3}$ R30° reconstructed 4H-SiC(0001) surfaces are reported. Recorded Si 2p spectra showed three shifted components, besides the bulk SiC peak. These were assigned as originating from SiO_2, N–Si–O and Si_3N_4/Si^{1+} (since we could not distinguish between Si_3N_4 and an Si^{1+} oxidation state). It was concluded that SiO_2 grows on top of N–Si–O and that Si_3N_4/Si^{1+} is located at the interface. Two N 1s components were

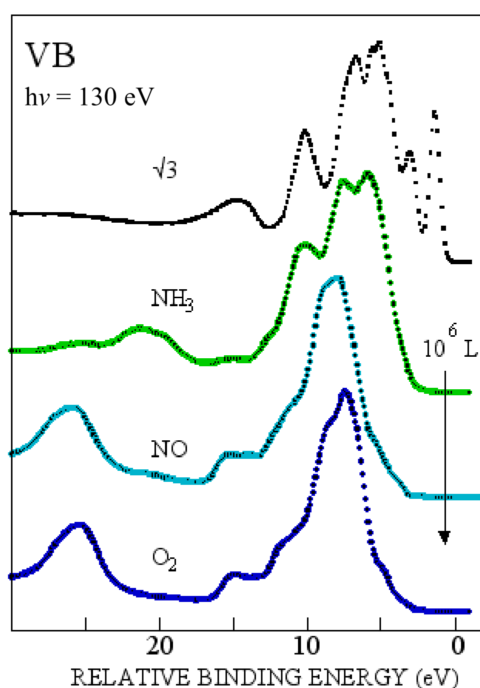

Figure 3. Valence band spectra collected from a clean $\sqrt{3}$ reconstructed surface and after a 10^6 L exposure to NH_3, NO and O_2.

(This figure is in colour only in the electronic version)

observed after NO exposures. A main one, located at around 398.05 eV, assigned as originating from Si_3N_4 and a weaker one suggested to correspond to N–Si–O bonding. The assignments were made using Si 2p and N 1s spectra collected after NH_3 and O_2 exposures under similar conditions. No graphite-like carbon or carbon by-product at the interface could be detected after large NO, N_2O or O_2 exposures. Oxide growth only and no nitrogen incorporation were observed after the N_2O exposures. This indicated that the selected temperature of 900 °C was too low to efficiently dissociate N_2O and promote nitrogen incorporation at the interface.

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