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Modification of the Oxide/Semiconductor Interface by High Temperature NO Treatments: a Combined EPR, NRA and XPS Study on Oxidized Porous and Bulk n-type 4H-SiC

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Abstract. The effect of thermal treatments in nitric oxide (NO) on the paramagnetic defects at the 4H-SiC/SiO_2 interface are analyzed by EPR in oxidized porous samples. The results on ultrathin thermal oxides show that the NO treatment at 1000°C is insufficient for an efficient reduction of the two dominant paramagnetic interface defects: P_{bC} centers and carbon clusters. From the NRA and XPS analysis of bulk samples treated under the same conditions we attribute the weak effect to the low nitrogen concentration of only 1% at the interface.

Introduction

The beneficial modifications of semiconductor/dielectric interfaces by nitrogen incorporation have been widely studied in the past for (100)Si/SiO_2 interfaces with ultrathin oxides where they give rise to reduced interface defect concentrations (D_{it}) and increased stability against degradation [1].High temperature post oxidation treatments in NO have been shown to be particularly interesting due to the exclusive incorporation of the N at the interface. A particlarly interesting result was the reduction in the intrinsic concentration of paramagnetic P_b centers without the involvement of hydrogen passivation [2].

In the case of 4H-SiC/SiO_2 interfaces, where typically an order of magnitude higher interface defects (D_{it}) concentrations are encountered, the same treatments have also been investigated. A reduction in the D_{it} has been observed but is still insufficient as the reduced defect concentration is still in the $10^{12}cm^{-2}eV^{-1}$ range [3-5]. The question why the nitrogen treatments as well as the hydrogen passivation schemes are much less successful than for Si/SiO_2 is still under discussion and further information on the incorporation processes is required. A particular handicap in the case of 4H-SiC/SiO_2 is the fact that the microscopic structure of the interface defects is not well known due to the absence of detailed EPR results. Whereas in the case of Si/SiO_2 the P_b centers have been identified as the main interface defects by this technique, EPR results on bulk 4H-SiC/SiO_2 have given only minimal information [6].We have shown recently [7] that the use of oxidized porous 4H-SiC can greatly improve the situation for EPR studies. A carbon related Pb center has been identified as the dominant interface defect. In addition, a carbon related isotropic center, attributed to carbon clusters in the oxide, has been observed [7]. The observation of the interface defects with a high signal to noise ratio is related to the high internal surface area in a porous sample. The porous sample is still monocristalline, but the orientation of the internal surfaces are no longer related to the external surface; they depend on the electrochemical dissolution process. Very often facetting with preferential surface orientation is nevertheless observed. In particular, in porous layers with the so-called 'dendritic structure' [8] the external (0001) surface has been found to be also a dominant internal surface in the porous layer.

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Experimental Details:

Free standing porous 4H-SiC layers were prepared by electrochemical dissolution from n-type 4H (0001) oriented bulk substrates. Details of the pore structure and dissolution conditions can be found elsewhere [8]. Single crystal bulk (0001) 4H-SiC:N samples, both sides polished, were used for the NRA and XPS measurements. The porous layers and the bulk samples were oxidized together in dry oxygen at 1000°C under 30mbar of $^{18}O_2$ for typically 10min. The resulting oxide thickness is estimated to be in the 1-2nm range. The samples were then treated in $^{15}N^{18}O$ gas at 1000°C and 10mbar for 30min, 2h, 4h and 8h.

The X-band (9.6GHz) EPR measurements have been performed at 300K. The XPS measurements were performed on the bulk samples with a spectrometer equipped with a non-monochromatic Al Kα source and a hemispherical electron energy analyzer. The binding energy scale was calibrated assigning the energy of the bulk component of the Si 2p spectrum ($Si2p^0$) to 100.2eV. The O1s, N1s, C1s and Si2p core levels were studied. In order to evaluate the surface or volume character of the centers, the XPS spectra were measured at two different take off angles: 0° (normal) and 70° (grazing). The ^{18}O and ^{15}N concentrations were determined on the bulk samples by nuclear reaction analysis (NRA).

Experimental Results and Discussion.

In the as oxidized state the porous samples show a high intensity EPR spectrum (fig.1) which can be decomposed into two distinct spectra related to two different defects: the first is a SiC/SiO_2 interface defect, the carbon dangling bond P_b center and the second has been attributed to a carbon cluster related center in the oxide [7]. Whereas these centers can be easily detected due to the high internal surface area in oxidized porous samples they are not observed in the oxidized n-type bulk samples at 300K. NRA measurements of the oxidized bulk samples (fig.2) show an ^{18}O density of $1.5x10^{16}cm^{-2}$ for both the Si and the C side. From the ^{18}O area concentrations we can estimate the oxide thickness of 1-2 nm.

After the NO treatments we observe significant modifications of the EPR spectra. Both EPR spectra change in intensity (fig.3) and the P_{bC} center spectrum shows a monotonous decrease in the width of the individual lines (fig.4).However, the variations in the spin concentrations are quite different from the case of Si/SiO_2 NO treated interfaces, where a monotonic decrease in the P_b center density had been observed[2]. On the contrary, we observe here for the initial phases of NO

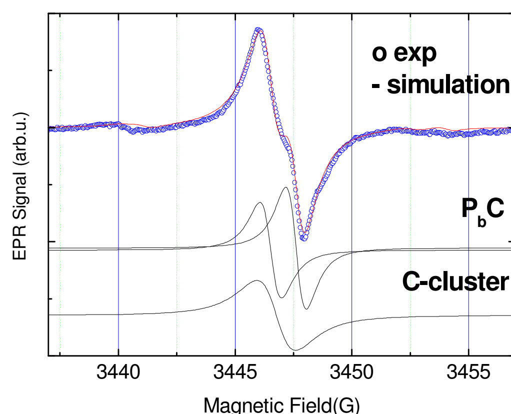

Fig.1: EPR spectra of as oxidized porous 4H-SiC sample,; T=300K, B//c

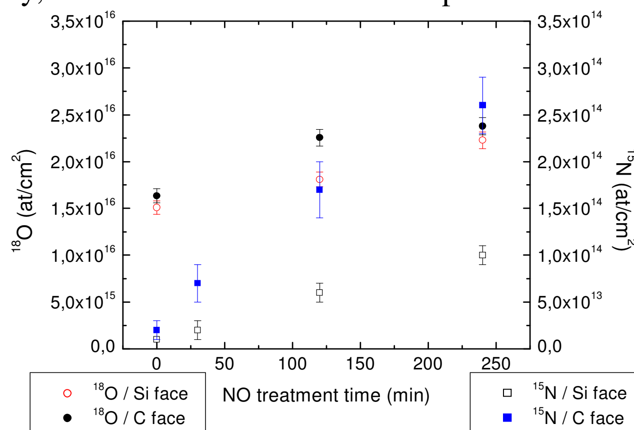

Fig.2 ^{18}O and ^{15}N area concentrations determined by NRA as a function of annealing time

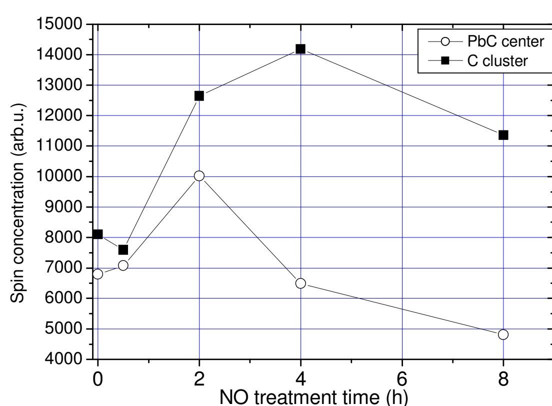

Fig.3 Spin concentrations as a function of NO annealing time in porous 4H-SiC

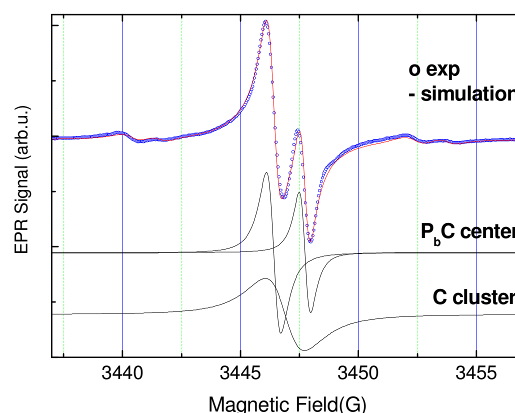

Fig.4: Experimental and simulated EPR spectra in a 8h NO annealed porous 4H-SiC sample

treatment a strong increase in the concentration of both centers. It is only for t>2h and >4h respectively that the spin concentrations decrease and the decrease is rather weak. If we analyze this evolution within the NRA results obtained on the bulk samples, we find the following: the NO treatments of 2h and 4h lead for both surfaces (C, Si) to an increase in the ^{18}O area concentration of about 25% and 50%. This means that the treatment leads to a significant oxide growth without a notable incorporation of ^{15}N. Indeed, after 4h treatment the ^{18}O area concentration has increased by $7x10^{15}cm^{-2}$ whereas the ^{15}N concentration is only $1x10^{14}cm^{-2}$ for the Si face and $2.6x10^{14}cm^{-2}$ for the C face. Clearly and distinctly from the Si/SiO_2 case the NO treatment does not lead to an incorporation of the NO molecule as a whole; in the NO dissociation process apparently only a small fraction of N atoms is incorporated at the interface contrary to the O atoms which give rise to an ongoing oxidation and a continuously "moving" interface.

To investigate in which form the N is incorporated we have performed XPS measurements on the same bulk samples. The Si2p spectrum exhibits two main components. In our experimental conditions, the spin orbit degeneracy of this level is not resolved and the Si2p spectra were successfully fitted with only two Gaussian lineshapes. The first line is the SiC bulk component, centered at 100.2 eV with a full width at half maximum (FWHM) of 1.25eV. The second line is located at 102.4 eV and has a FWHM of about 1.8eV. This component is attributed to the Si^{4+} oxidation state. It slightly shifts to higher binding energy for the longest oxi-nitridation time, but the energy difference Si^{4+}-O1s remains constant at 429.45 eV, the same value as for pure Si/SiO_2 structure. Consequently, this small shift is certainly due to a weak charge effect in the dielectric for the larger thickness. The rather small energy difference between the Si^0 and Si^{4+} lines render the study of the interfacial intermediate oxidation states difficult. Because of the small difference of the N and O electronegativity, and the low N/O ratio (<0.01) in our experimental conditions, we did not identify any core levels states explicitly associated with Si-N bonds.

The Si^{4+}/Si^0 ratio is 0.56 after 30 minutes of treatment and reaches 0.81 for 2 hours and 0.78 after 4 hours of NO annealing. Based on previous studies of the Si/SiO_2 interface, we estimate the corresponding oxide film thickness to vary from 1.3 to 2.0 nm.

The C1s spectra could also be simulated by two Gaussian lines. The first one is centred at 282.2 eV (FWHM: 1.1eV) and is the SiC bulk component. The second line, located at 283.8 eV, is broader and increases at large take off angle. Consequently, it is attributed to surface carbon contamination.

Fig. 5 displays the N1s core level spectrum measured after 30 minutes, 2 hours and 4 hours of NO annealing. For the shortest treatment time, the N1s spectrum is asymmetric, revealing the

existence of at least two overlapping components. The spectra could be simulated using two Gaussian lines separated by 1.8eV. The first one, at 397.1 eV, has a FWHM of 1.25 eV and is

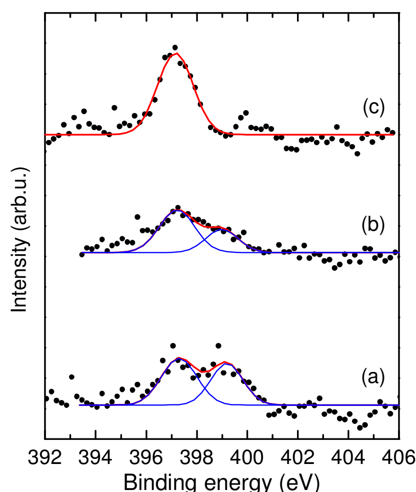

Fig.5 N1s core level spectra in bulk 4H-SiC after (a) 30min, (b) 2h, (c) 4h NO anneal

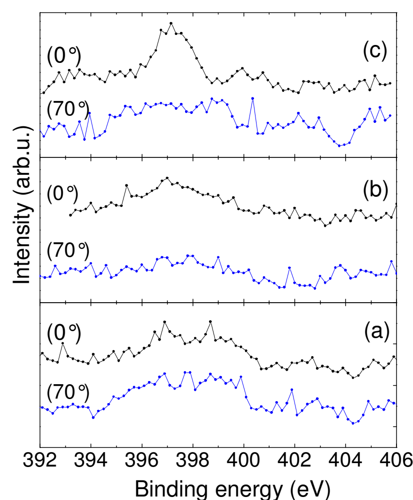

Fig.6 N1s core level spectra of samples a,b, c for normal (0°) or grazing (70°) analysis

characteristic for N-Si_3 configurations. The second line is slightly broader (FWHM: 1.4eV) and centred at 398.9 eV. This line could be attributed to N-Si_2O [9] or N-C configurations [10]. The existence of N-O bonds can be ruled out as this would lead to a much larger chemical shift. This second component decreases during NO treatment and is no longer observed after 4 hours.To get information about the distribution of these components within the dielectric layer, we performed XPS measurements at grazing take off angle. Fig. 6 compares the N1s spectra observed in normal and grazing geometries. We find that the component with a high binding energy is distributed throughout the films whereas the more stable Si-N_3 configuration is located at the SiC/SiO_2 interface.

Summary

Our EPR results on ultrathin, dry thermal oxides show that the P_{bC} center and carbon cluster densities are not significantly reduced by the low pressure $^{15}N^{18}O$ treatments at 1000°C. The NRA and XPS results suggest that the reason for this weak effect is the small Si_3N_4 fraction at the interface combined with the strong reoxidation. In the case of NO treated Si/SiO_2 with minimum interface defect concentrations Si_3N_4 fractions of up to 50% had been obtained at the interface [2].

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