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# OBSERVATION OF 4H–SIC TO 3C–SIC POLYTYPIC TRANSFORMATION DURING OXIDATION

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**Abstract.**We have observed the formation of single and multiple stacking faults that sometimes give rise to 3C–SiC bands in a highly doped *n*-type 4H–SiC epilayer following dry thermal oxidation. Transmission electron microscopy following oxidation revealed single stacking faults and bands of 3C–SiC in a 4H–SiC matrix within the 4H–SiC epilayer. These bands, parallel to the (0001) Basal plane, were not detected in unoxidized control samples. In addition to the 3.22 eV peak of 4H–SiC, Cathodoluminescence spectroscopy at 300 K after oxidation revealed a spectral peak at 2.5 eV photon energy that was not present in the sample prior to oxidation. The polytypic transformation is tentatively attributed to the motion of Shockley partial dislocations on parallel (0001) slip planes. The generation and motion of these partials may have been induced by stresses caused either by the heavy doping of the epilayer or nucleation from defect.

## 1. INTRODUCTION

Single crystal 4H–SiC is currently the polytype of choice for the fabrication of silicon carbide high power devices, including prototype power metal–oxide–semiconductor field-effect transistors. This is largely due to its high electron mobility and the near isotropy of the mobility in directions parallel and perpendicular to the crystallographic *c* axis. Considerable progress has been made toward the improvement of the gate oxide quality in terms of reducing interface traps and improving inversion channel mobility, but significant performance and reliability deficiencies remain. The reduction of crystal defect density is also another area that has witnessed considerable progress. However, little investigation has been conducted to understand how thermally-induced surface and subsurface modification impacts device electrical characteristics.

## 2. THE EFFECTS OF OXIDATION

In studying the effects of oxidation on the surface and subsurface of 4H– and 6H–SiC of various doping levels to understand its effect on the electrical characteristics of metal/ SiC contacts, we have observed 4H–SiC to 3C–SiC polytypic transformation in heavily doped (1.731019 cm23) samples

To the best of our knowledge, the optical and structural results reported here are the first observation of a polytypic transformation of SiC ~or any other semiconductor! as a result of thermal oxidation.

A high resistivity ~4 Vcm!, 8° off-axis [from the (0001) basal plane], Si-face, *p*-type 4H–SiC substrate with a homoepitaxially grown 2 mm thick *n*-type epilayer (1.7 * $10^{19}$ $cm^{-3}$ doping) was purchased from Cree, Inc. The wafer was cut into 1 * 1 $cm^2$ pieces and cleaned in acetone/ methanol ~henceforth termed "solvent clean"!. One set was put aside after the solvent clean, while the second set was Piranha (50:50 volume ratio of sulfuric and peroxide solution) cleaned, rinsed in deionized (DI) water, and dry oxidized at 1150 °C for 4 h. The oxide was subsequently stripped in 49% HF acid and again rinsed in DI water and Piranha cleaned. A subset from each set was metallized and analyzed with cathodoluminescence spectroscopy (CLS) based on low-energy electron nanoluminescence (LEEN). Current–voltage (*I* –*V*) measurement was also performed on

this subset. The second subset without metal was analyzed with transmission electron microscopy (TEM).
LEEN-based CLS measurements taken over a range of incident electron-beam energies provide a means to identify the presence of localized states and their spatial distribution on a nanometer scale. With increasing excitation energy, *EB* , the electron cascade and resultant generation of free electron–hole pairs occur at increasing depths, ranging from 25 nm at 1 keV to 150 nm at 4 keV for the nucleon values and material densities of SiC. Electron–hole excitation rates peak at depth values, $U_0$ , which are approximately one third of the electron penetration depths.

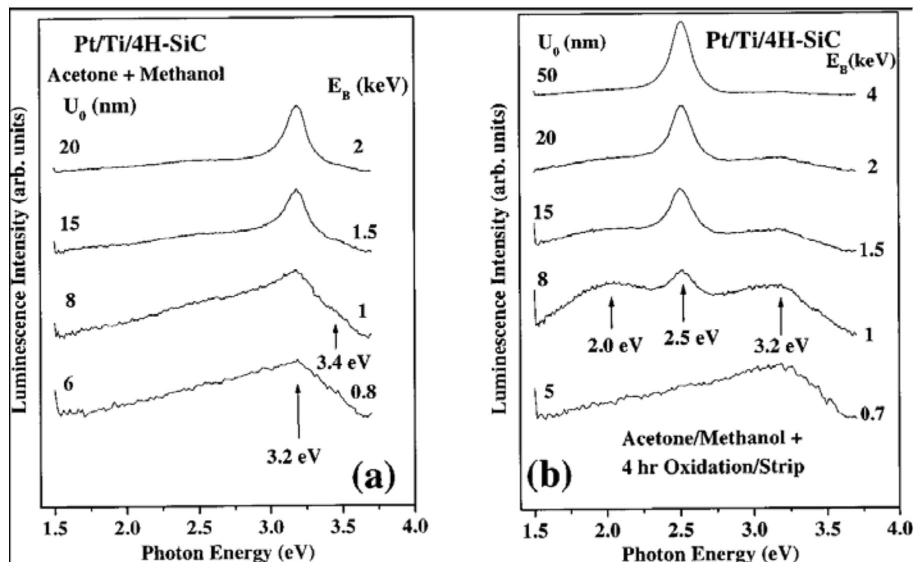


***FIG. 1. Depth-resolved LEEN spectra of (a) the acetone/methanol cleaned 4H–SiC sample depicts the 3.22 eV photon energy of 4H–SiC, and (b) of 4H–SiC sample after 4 h of oxidation followed by oxide removal in 49% HF acid and pirhana clean. A sharp 2.47 eV photon peak corresponding to 3C–SiC extends at least 50 nm deep into the epilayer.***

These electron–hole pairs excite band-to-band and band-to-defect transitions that are detected optically, even through the thin Pt(20 nm)/Ti (10 nm) /contact layer on the SiC. Thus, it is possible to excite luminescence selectively, either at the metal/SiC interface, in the near surface region extending tens of nanometers into the SiC epilayer, or beyond this region well into the SiC epilayer. Figure 1(a) depicts the LEEN spectra of the unoxidized sample. A 3.22 eV photon energy peak is observable at *EB*50.8 keV ~*U*056 nm, including the metal!, which peaks more sharply at higher *EB* with further penetration into the epilayer. This energy corresponds to the near band edge emission of 4H–SiC, and it is the only such peak evident in this sample. Emission observed at lower photon energies corresponds to a broad distribution of states in the band gap confined to the near-interface region. After 4 h of oxidation followed by oxide stripping, the spectra changed dramatically as shown in Fig. 1(b). A sharp 2.5 eV photon peak appears at all excitation depths except $U_0$=5 nm and *EB* 50.7 keV from the metal/SiC interface, while a broad 3.2 eV photon peak slowly decays over the first 20 nm excitation depth. The 2.5 eV emission at all depths except $U_0$=5 nm indicates the occurrence of a substantial structural change in a large volume fraction of the oxidized 4H–SiC sample.

The cross sectional TEM image of the solvent-cleaned sample shown in Fig. 2 indicates an undisturbed cross section, consistent with LEEN spectra, to be 4H–SiC. However, the TEM image shown in Fig. 3 of the sample that was oxidized for 4 h and the oxide stripped reveals dramatic structural changes over the entire thickness of the

epilayer, consistent with the dramatic changes observed by LEEN. Referencing from the surface, transformation bands of 3C– SiC can be seen to propagate into the 4H–SiC epilayer. However, all these bands will terminate at their thickest point nearly 2 mm from the top surface at the region that roughly corresponds to where the epilayer/substrate interface should reside. High-resolution transmission electron microscopy ~HRTEM! of Fig. 4 offers a closer look at one of the 3C bands with the corresponding magnified inset. The image shows seven Si–C bilayers with a 3C–SiC periodicity sandwiched between 4H–SiC.

Multiple $I - V$ measurements showed the solvent-cleaned sample to be symmetrically nonohmic. The ideality factor, $n$, was extracted from the slope of the linear region of the semilogarithmic $I - V$ plot under condition of low injection between 0.025 and 0.05 V, with the resultant value of $n = 1.37$. The deviation from ideality can possibly be attributed to the presence of adventitious carbon compounds as observed by x-ray photoelectron spectroscopy (XPS), which could act as recombination centers known to degrade channel mobility at the oxide/SiC interface of SiC metal–oxide–semiconductor devices.

The ohmic contact on the oxidized sample with oxide stripped and piranha cleaned showed a substantial reduction in adventitious carbon when analyzed with XPS prior to metallization.

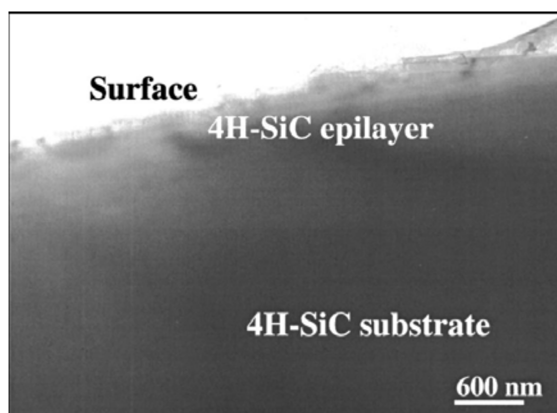


***FIG. 2. Cross section TEM of as-received, unoxidized 4H–SiC sample shows no indication of polytypic transformation.***

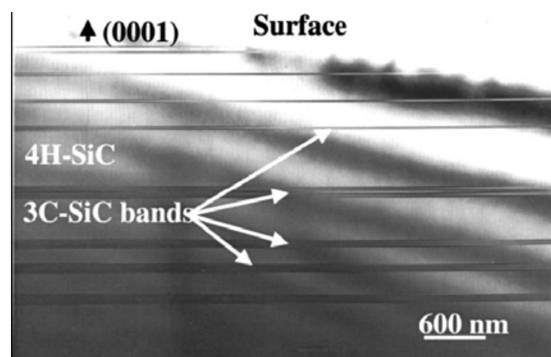


***FIG. 3. Cross section TEM shows 3C–SiC bands propagating parallel to the 8°-tilted basal plane. The bands terminate at a consistent vertical depth approximately 2 mm beneath the surface, the region that roughly corresponds to the substrate/epilayer interface.***

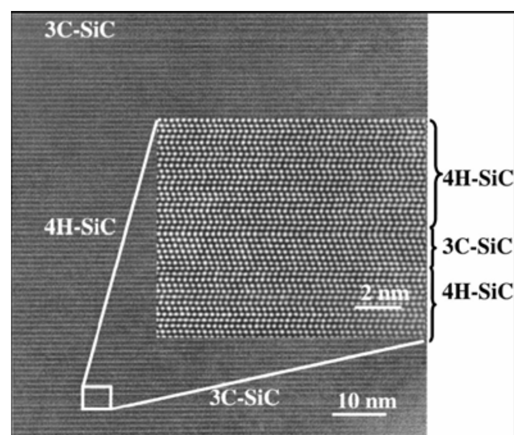


***FIG. 4. HRTEM image of 4H–SiC and 3C–SiC within a band shows two 3C–SiC subbands separated by 4H–SiC. Further magnification ~inset! reveals that one of the 3C–SiC subbands is made up of seven Si–C bilayers.***

While the significant reduction of adventitious carbon may be the reason for the ohmic contact formation, another possibility may be due to the modification of the band structure associated with the observed 4H–SiC to 3C–SiC polytypic transformation. No detectable change in dopant concentration was observed between samples as analyzed by secondary ion mass spectroscopy, which eliminated the possibility of nitrogen outdoping as observed in the case of Vlaskina and Shin11 in 6H–SiC (under much different experimental conditions from this work). It was determined that the role of oxidation as a driving mechanism for this transformation is not significant. Samples taken from the same wafer were thermally treated in argon ambient for 4 h at 1150 °C. The LEEN spectra also depicted the shift from the 3.2 eV phonon energy corresponding to 4H–SiC to the 2.5 eV observed when previous samples were oxidized under the same conditions.

## 3. CONCLUSIONS

In conclusion, we have determined that single and multiple layers of stacking faults form close to the oxide/4H– SiC interface in highly doped 4H–SiC at temperatures as low as 1150 °C during thermal oxidation. In the cases where stacking faults form on neighboring ~0001! planes, bands of 3C–SiC form the 4H/3C polytypic transformation occur in highly doped 4H–SiC at temperature as low as 1150 °C during thermal oxidation. There is the possibility that the transformation may have resulted in the ohmic contact by a change in the band structure to that of 3C–SiC. While investigations continue, we tentatively suggest that the observed stacking fault layers and polytypic transformation may be the result of nucleation and propagation of 1/3^101¯ 0& Shockley partial dislocations on basal ~0001! planes. These may act as a mechanism of relieving the strain produced by the stresses due to heavy doping (1.731019 cm23) of the epilayer on a lightly doped substrate, or due to the stresses produced during oxidation of the 4H–SiC. Given the crucial role anticipated for 4H–SiC in high power electronics, it becomes imperative that this observed transformation phenomenon in the crystal be critically investigated further.

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