Silicon Carbide Surface Oxidation

Since several decades, the general trend in microelectronics is toward higher integration densities which, according to the Moore law, are supposed to double every 18 months. However, such an approach is rapidly reaching its fundamental limits with basically no known technological solution indicating that following the Moore law would still be possible in 5 to 7 years from now. In this view, one of the important issues is semiconductor surface passivation. Primarily due to the excellent properties of its native oxide (SiO_2) and to the low defect density of the SiO_2/Si interfaces, silicon is by far the most commonly used semiconductor in device technology. The SiO_2/Si interface is generally grown by thermal oxidation which results in a non abrupt interface having a SiO_2 to Si transition layer of about 30 ~ 40 Å thickness including non stoichiometric oxidation products of lower oxidation states (Si^{3+}, Si^{2+}, Si^{+}). The present downsizing approach in device technology now requires ultra thin oxide layers having thicknesses below ≈50 Å (Fig. 1). It is therefore not anymore possible to have a transition layer at the oxide/semiconductor interface having a thickness in the same order of magnitude.

Silicon carbide (SiC) is not a new material since it is actually older than the solar system. It has been discovered at the end of the 19th century by Henri Moissan (1904 Chemistry Nobel Prize laureate), on a meteorite located in the Diablo canyon (Arizona). However, SiC is definitively an advanced material with many technological applications. SiC is a IV-IV compound wide band gap (from 2.4 eV to 3.3 eV) semiconductor especially suitable in high temperature, high power, high frequency and high voltage micro-electronics devices and sensors. In addition, SiC is rather inert chemically and is resistant to radiation damages. Furthermore, due to a small mismatch between lattice parameters, SiC is an excellent substrate for the growth of the new class of III-V nitride semiconductors in both hexagonal and cubic phases.

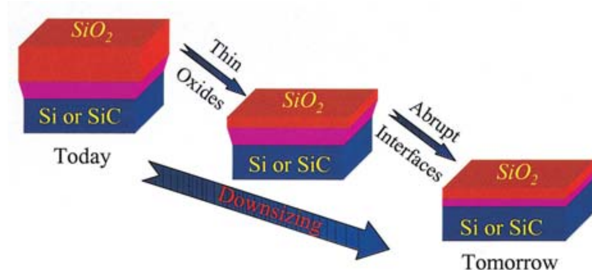

Fig. 1: Schematic of the downsizing approach in oxide thin films on Si or SiC surfaces. The transition layer including sub-stoichiometric oxides is represented in purple at the interface between SiO_2 and Si (SiC).

SiC exits in various crystallographic phases with more than 170 polytypes. Recently, thanks to advanced experimental techniques, high quality hexagonal and cubic SiC surfaces could be achieved at the atomic scale. Despite lower carrier mobilities compared to β-SiC, hexagonal 6H- and 4H-SiC polytypes are the most commonly used for devices because of good quality crystal wafer availability and larger bandgap. Surface passivation is a crucial issue in successful SiC device technology. Unlike other semiconductors except silicon, SiO_2 is the native oxide of SiC. However, SiC oxidation could result in mixed oxides products containing C species. In order to achieve high quality SiO_2/SiC interfaces, it is necessary to find alternative approaches to SiC oxidation. In particular, to avoid C intermixing into the oxide products, it is challenging to investigate the passivation process using a "gentle" surface oxidation controlled at the atomic scale.

In this report, we describe the most recent results obtained in atomic scale SiC surface oxidation and initial SiO_2/SiC interfaces formation, focusing primarily on Si-rich hexagonal 6H-SiC(0001) 3×3 surface. The investigations are performed using synchrotron-radiation-based core level photoemission spectroscopy at NSRRC. The 6H-SiC(0001) 3×3 surface is found to be highly reactive to oxygen, even at extremely low exposures with SiO_2 as the

dominant oxidation product. Initial oxygen deposition takes place below the surface, away from Si dangling bonds, close from the carbon plane with oxygen atom in Si-O-Si bridge bonded sites. The oxidation of a pre-deposited thin Si overlayer onto the 6H-SiC(0001) 3×3 surface leads to an abrupt SiO_2/SiC interface formation. In contrast, 4H-SiC(0001) 3×3 oxidation results in dominant mixed oxide products.

Figure 2 displays a set of representative Si 2p and C 1s core levels for clean and oxygen exposed (0.25 L and 0.5 L) 6H-SiC(0001) 3×3 surfaces. The Si 2p core level for the clean 6H-SiC(0001) 3×3 surface reconstruction exhibits two surface shifted components SS1 and SS2 and one bulk component. SS1 is related to the Si ad-atom while SS2 corresponds to the Si trimer + Si ad-layer. One can see here that SS1 and SS2 are not at all affected which indicates no oxygen interaction with the Si surface atoms, in excellent agreement with the picture derived from STM measurements. Instead, one can observe the growth of a chemically shifted component (Si^{+}) already at a very low 0.25 L O_2 exposure and high oxidation states formation (Si^{2+} and Si^{3+}) at only a slightly higher O_2 exposure of 0.5 L. This indicates the formation of oxidation products already at room temperature and at oxygen exposures 3 orders of magnitude smaller than that, e.g., for Si surfaces.

We now look at the SiC oxidation process in a

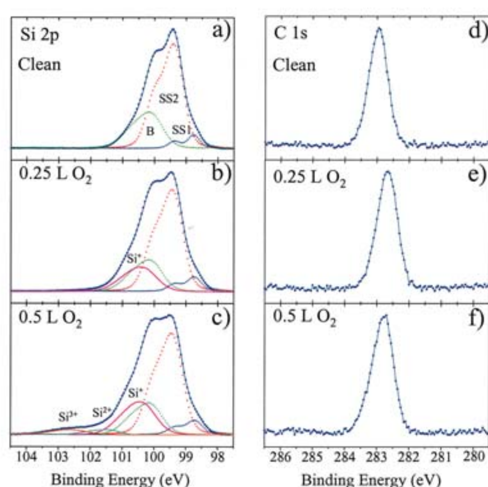

Fig. 2: Si 2p core level for the 6H-SiC(0001) 3×3 a) clean surface and oxygen exposed at b) 0.25 L and c) 0.5 L in the surface sensitive mode (hν = 150 eV and emission angle and θ_e = 30°). d), e), f): C 1s core level for the same surfaces as in a), b) and c) (hν = 330 eV and emission angle and θ_e = 60°).

totally different regime, focusing on the initial insulator/SiC interface formation. We study the effect of a 1000 L of O_2 exposure at 500℃ on the 6H-SiC(0001) 3×3 surface reconstruction. Figure 3a shows the Si 2p recorded in a surface sensitive mode at a photon energy of hν = 150 eV and grazing emission angle. The three peaks A, B and C correspond to the clean Si 2p surface (SS1 and SS2) and bulk shifted components respectively. As can be seen from Fig. 3a, the silicon dioxide (Si^{4+}) is the dominant spectral feature. However, we can also notice the presence of important amounts of sub-stoichiometric oxide components clearly indicating a non-abrupt SiO_2/6H-SiC(0001) 3×3 interface. These sub-stoichiometric oxide components have binding energies corresponding to the Si^{3+}, Si^{2+} and Si^{+} oxidation states. Looking in Fig. 3b at the Si 2p in the bulk sensitive mode (hν = 300 eV and normal emission angle), one can see that the peak corresponding to Si^{2+} is now the dominant spectral feature. However, such a large intensity does not result from Si^{2+} only but from oxygen atoms bonded to both C and Si species, forming a carbonate mixed oxide product, as previously observed for the cubic 3C-SiC(100) 3×2 surface oxidation. Further support for this assignment to the presence of mixed oxides can be found by looking in Fig. 3c at the C 1s core level for the same oxygen exposure with a C 1s broadening by 26%. Therefore, this indicates the strong involvement of carbon atoms in the oxidation process and, together with the Si 2p core level results, suggests the formation of carbonate oxidation products with SiO_2 presence at the top surface of the passivation layer. Such a non-abrupt SiO_2/SiC interface would probably result in a high density of interface states.

In order to improve the interfacial quality, we now proceed to the oxidation of a pre-deposited Si thin film on 6H-SiC(0001). As can be seen from Fig. 4a, the Si 2p core level recorded in the surface sensitive mode, silicon dioxide (Si^{4+}) is the dominant oxide product, but the amount of sub-stoichiometric (Si^{3+}, Si^{2+} and Si^{+}) and mixed (Si-O-C) oxides has decreased dramatically. Unlike the case of direct oxidation (Fig. 3b), stoichiometric SiO_2 is the dominant oxide product in the bulk sensitive mode, as can be seen in Fig. 4b while the C 1s core level (Fig. 4c) for the clean and oxygen exposed at 500℃ Si/6H-SiC(0001) surface keeps the same full width at half

maximum (FWHM = 0.68 eV) indicating that the C atoms are not significantly affected by the oxidation process. Overall, the results indicate the formation of carbon free SiO_2. In addition, the oxidation of a Si ultra thin film (≈10 Å) pre-deposited onto the 6H-SiC(0001) 3×3 surface leads to an abrupt SiO_2/6H-SiC(0001) interface formation, with C atoms bonded to both Si and C species at the interface. This situation significantly differs from the direct surface oxidation as seen above. The resulting oxide layer thus grown is thicker than one could expect from the oxidation of the silicon thin film only. This indicates that the latter also plays an active role into the oxidation of the underlying silicon carbide surface. The structure of this silicon thin film grown on hexagonal SiC is indeed of special relevance into the oxidation process of the SiC surface since it as an unexpected cubic 4×3 surface array and is highly sensitive to oxygen.

For all polytypes, direct SiO_2/SiC interface formation is achieved already at room temperature and extremely low oxygen exposures. However, the two 6H- and 4H-polytypes have significantly different behaviors with larger amounts of oxide products having higher oxidation states for the 6H-SiC(0001) 3×3 surface, while mixed oxides including carbon species (Si-O-C) are the dominant oxide products for the 4H polytype surface.

In all cases, the oxygen uptake remains significantly larger for the 6H polytype when compared to the 4H one as can be derived from O1s core level in Fig. 5. The very different behavior of the 6H and 4H polytypes seems to originate, at least in part, from the presence of two domains in the bulk for the 4H polytype, which

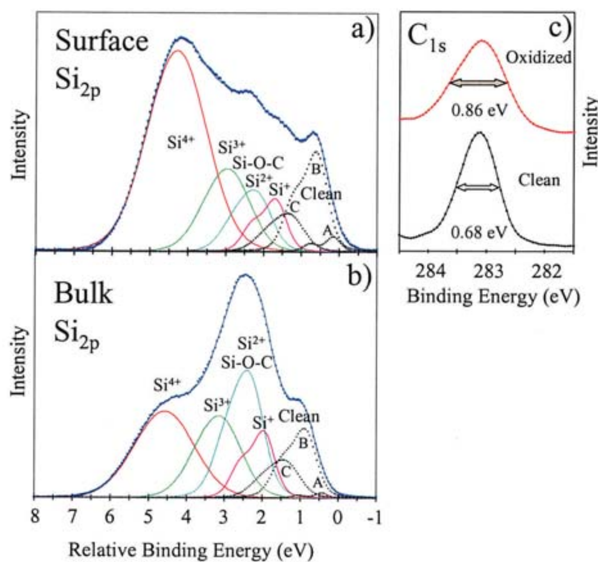

Fig. 3: 1000 L of O_2/6H-SiC(0001) 3×3 at 500°C: a) Si 2p core level recorded at a photon energy of hν = 150 eV and grazing emission angle (surface sensitive mode). The binding energy scale is relative to Si 2p binding energy (99.2 eV) for a silicon surface. The surface and bulk shifted components A, B, and C (dotted line) and the chemically shifted components (continuous line) are also displayed. b) Si 2p core level recorded at a photon energy of hν = 300 eV and normal emission angle (bulk sensitive mode). The binding energy scale is relative to Si 2p binding energy (99.2 eV) for a silicon surface. The surface and bulk shifted components A, B, and C (dotted line) and the chemically shifted components (continuous line) are also displayed. c) C 1s core level shift for clean and oxidized (as above) surfaces recorded at a photon energy of hν = 330 eV and grazing emission angle (surface sensitive mode).

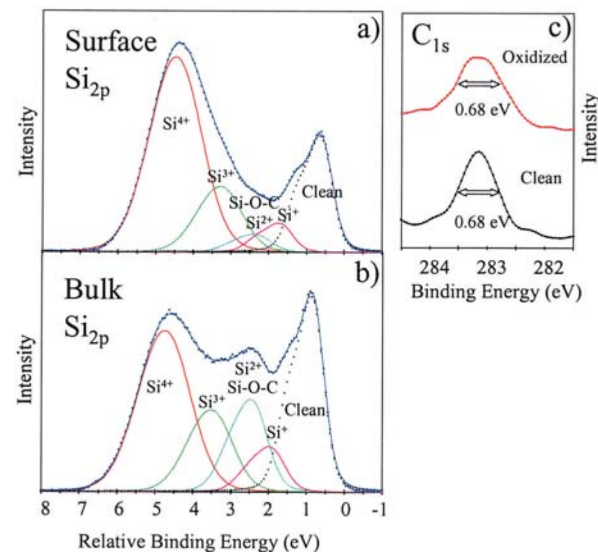

Fig. 4: 1000 L of O_2/Si/6H-SiC(0001) at 500°C: a) Si 2p core level recorded at a photon energy of hν = 150 eV and grazing emission angle (surface sensitive mode). The binding energy scale is relative to Si 2p binding energy (99.2 eV) for a silicon surface. The Si 2p for SiC (dotted line) and the chemically shifted components (continuous line) are also displayed. b) Si 2p core level recorded at a photon energy of hν = 300 eV and normal emission angle (bulk sensitive mode). The binding energy scale is relative to Si 2p binding energy (99.2 eV) for a silicon surface. The Si 2p for SiC (dotted line) and the chemically shifted components (continuous line) are also displayed. c) C 1s core level shift for clean and oxidized (as above) surfaces recorded at a photon energy of hν = 330 eV and grazing emission angle (surface sensitive mode).

limits the oxygen insertion into the 4H-SiC lattice. Instead the 6H polytype has only one bulk domain with a single Si 2p bulk component. Abrupt SiO_2/6H-SiC interfaces could be achieved by thermal oxidation of a pre-deposited Si overlayer onto the surface leading to have oxide thicknesses ranging from 10 Å up to 80 Å after post-oxidation with a transition layer of less than 5 Å. These studies show that, using a "gentle" initial oxidation approach at low temperatures and low oxygen exposures allow high quality SiO_2/SiC interfaces with oxides resistant to radiation damages as the result of a low temperature process. It also brings interesting novel insights into the understanding of polytype crucial effect in SiC surface oxidation.

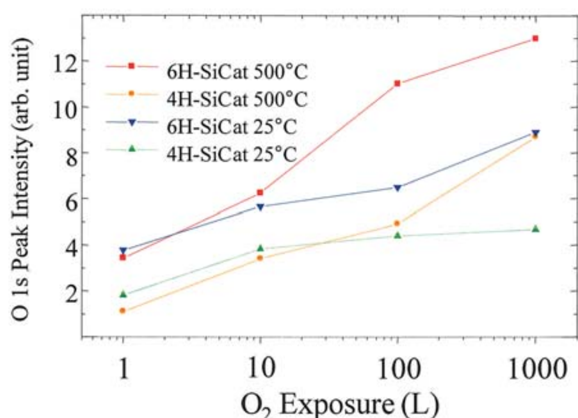

Fig. 5: Comparison of the oxygen uptake on the 4H-SiC(0001) 3×3 and 6H-SiC(0001) 3×3 surfaces at 25 ˚C and 500˚C. O 1s peak intensity is displayed using arbitrary units and corresponds to the integrated surface of the core level peak.

Beamlines:

20A1 High Energy SGM beamline

08A1 Low Energy SGM beamline

Experimental Station:

Photoelectron spectroscopy end station

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