

Home Search Collections Journals About Contact us My IOPscience

Synchrotron radiation studies of the  $SiO_2$  /SiC(0001) interface

This article has been downloaded from IOPscience. Please scroll down to see the full text article. 2004 J. Phys.: Condens. Matter 16 S3423 (http://iopscience.iop.org/0953-8984/16/33/002)

View the table of contents for this issue, or go to the journal homepage for more

Download details: IP Address: 129.252.86.83 The article was downloaded on 28/05/2010 at 07:54

Please note that terms and conditions apply.

J. Phys.: Condens. Matter 16 (2004) S3423-S3434

PII: S0953-8984(04)81036-1

# Synchrotron radiation studies of the SiO<sub>2</sub>/SiC(0001) interface

## L I Johansson and C Virojanadara

Department of Physics and Measurement Technology, Linköping University, S-58183 Linköping, Sweden

E-mail: lij@ifm.liu.se

Received 20 May 2004 Published 6 August 2004 Online at stacks.iop.org/JPhysCM/16/S3423 doi:10.1088/0953-8984/16/33/002

#### Abstract

Two questions thought to have a significant effect on SiC-MOS device characteristics are treated. The existence of carbon clusters or carbon containing by-products and the existence of sub-oxides at the SiO<sub>2</sub>/SiC interface. Results of photoemission studies using synchrotron radiation of the interface of the Siterminated surface of n-type SiC(0001) crystals are presented. The results show that no carbon clusters or carbon containing by-product can be detected at the interface of in situ or ex situ grown samples with an oxide layer thickness larger than  $\sim 10$  Å. The presence of sub-oxides at the SiO<sub>2</sub>/SiC interface was predicted in a theoretical calculation and has been revealed in Si 2p core level data by several groups. These results were not unanimous; significant differences in the number of sub-oxide and shifts were reported. A study also including the Si 1s core level and Si KLL Auger transitions was therefore made. These data show the presence of only one sub-oxide at the interface, assigned to Si<sup>1+</sup> oxidation states. The SiO<sub>2</sub> chemical shift is shown to exhibit a dependence on oxide thickness, similar to but smaller in magnitude than the thickness dependence earlier revealed for SiO<sub>2</sub>/Si.

# 1. Introduction

Because of the limitations of Si based devices in high power, high temperature, and high frequency applications, the wide band gap semiconductor silicon carbide (SiC) has for some years been considered a very attractive alternative material for such applications [1]. A high quality SiO<sub>2</sub>/semiconductor interface with a low defect density is of crucial importance for the performance of metal-oxide–semiconductor (MOS) devices. For silicon surfaces the SiO<sub>2</sub>/Si interface properties have been intensively studied [2] in the past and interfaces with low defect

densities have been achieved. The Si-terminated (0001) surface of hexagonal SiC crystals of the 4H (and 6H) polytype has to date been considered the most promising [1, 3, 4] for device applications. The high defect density both in the SiC wafers and at the SiO<sub>2</sub>/SiC interface has been identified as two major obstacles to overcome before SiC can be successfully realized as a new electronics material.

The formation of carbon clusters and/or carbon containing by-products at the SiO<sub>2</sub>/SiC interface has been suggested [4–6] to be the important factor for the high defect densities. Recent experimental efforts utilizing synchrotron radiation to prove if carbon or carbon containing by-products can be detected at the SiO<sub>2</sub>/SiC interface are presented and discussed. It is shown that no carbon clusters or carbon containing by-products can be detected at the SiO<sub>2</sub>/Si interface of *in situ* or *ex situ* grown samples with an oxide layer thickness larger than ~10 Å. It is moreover shown that surface carbon deliberately created by *in situ* high temperature anneals can be reduced to below the detection limit by *in situ* oxidation and heating cycles.

The presence of sub-oxides was a major issue for the SiO<sub>2</sub>/Si interface. That three suboxides (Si<sup>1+</sup>, Si<sup>2+</sup> and Si<sup>3+</sup>) besides the fully developed SiO<sub>2</sub>(Si<sup>4+</sup>) can exist at the SiO<sub>2</sub>/Si interface is well known [2]. A theoretical calculation predicted [7] that sub-oxides inevitably do exist also at the SiO<sub>2</sub>/SiC interface. Whether sub-oxides are formed at the SiO<sub>2</sub>/SiC interface, and if so, which ones, has therefore attracted considerable attention during the last few years. Recent findings are presented and discussed. For the Si-terminated SiC(0001) surface it is shown that one sub-oxide (Si<sup>1+</sup>) besides the fully developed SiO<sub>2</sub>(Si<sup>4+</sup>) does exist at the SiO<sub>2</sub>/SiC interface. Experimental evidence that the sub-oxide is located at the interface is presented. The SiO<sub>2</sub> chemical shift is shown to exhibit a dependence on the oxide thickness, similar to but smaller in magnitude compared to the dependence earlier reported [2] for SiO<sub>2</sub>/Si samples.

## 2. Experimental details

The photoemission results presented below have all been collected using synchrotron radiation at different beam lines at MAX lab and HASYLAB. The beam lines covered differed photon energy ranges and allowed high resolution studies of not only the Si 2p, C 1s and O 1s core levels (energy resolution of  $\leq 20-100$  meV at photon energies from 130 to 330 eV and of  $\leq 300$  meV at 600 eV) but also of the Si 1s core level and of Si KLL Auger transitions (3.0 keV photon energy with an overall energy resolution of  $\leq 0.5$  eV) which proved to be advantageous.

The SiC(0001) surface of the 4H and 6H polytypes is polar, i.e. either Si- or C-terminated. Our data were always collected from 8° off-cut 4H-SiC crystals. The presentation below is focused on the Si-terminated surface since it is the one commonly used for device fabrication. In MOS devices oxide thicknesses of one to two thousand angströms are typically used, but by photoemission the interface can only be directly studied for considerably thinner oxides layers, typically  $\leq 50-100$  Å. Therefore many of the studies reported to date have been focused on the initial oxide growth after *in situ* oxygen exposures. The preparation of the initial clean surface is then a crucial step. For the Si-terminated SiC(0001) surface two different methods have commonly been applied to prepare clean and well ordered surfaces. An ex situ chemical preparation is combined with *in situ* heating cycles [8] to produce a  $\sqrt{3} \times \sqrt{3}$  reconstructed surface, originating [8, 9] from Si adatoms on top of the Si-terminated bulk truncated crystal for both 4H and 6H polytypes. The other method combines in situ heating and Si-deposition cycles to produce a Si-rich  $3 \times 3$  reconstructed surface, originating [10, 11] from three Si-layers on top of the bulk truncated crystal. The effects induced by oxygen exposure of these surfaces at different substrate temperatures have been investigated and these results are compared and discussed.

For making devices an *ex situ* dry oxidation process in a furnace is commonly used, which enables the growth of thick oxide layers. Such *ex situ* grown samples are shown to have a small hydrocarbon contamination on the surface, preventing a very sensitive probing of carbon species at the interface. They are, however, very useful for investigating the presence of eventual sub-oxides at the interface since they bridge the gap between real MOS interfaces and interfaces produced by *in situ* oxide growth. In the latter case the maximum oxygen partial pressure that can be used is normally limited so only fairly thin oxide layers, typically less than ~20 Å, can be grown.

# 3. Results and discussion

#### 3.1. Carbon by-products at the SiO<sub>2</sub>/SiC interface?

Characterizations of oxide layers thermally grown on SiC have been studied using different techniques [5, 6, 12, 13]. The results showed homogeneous carbon free SiO<sub>2</sub> layers with well defined interfaces to SiC. However, the presence of quite a large amount of carbon containing by-products at the SiO<sub>2</sub>/SiC interface was suggested [5, 12]. This was surprising and initiated further studies.

A direct and simultaneous probing of fairly thick oxide layers, the interface and the SiC substrate is possible when using a high photon energy. This was utilized in studies [14] of about 50 Å thick oxide layers grown using a standard *ex situ* dry oxidation process. These samples had, however, to be stored for some time before the measurements. A graphite-like C 1s component was observed on these samples but it was found to originate from carbon on top of the oxide and not at the interface. Hydrocarbon contamination during storage was assumed to be the reason, and the possibility that this contribution actually shadowed a weaker contribution from carbon at the interface could not be excluded. In addition, the oxide thickness used in applications is typically  $\ge 1000$  Å, and this could also be of importance for the quality of the interface. Therefore a different method [15] was tried. The same ex situ oxidation process was applied but thicker oxide layers, around 1000 Å, were grown. The oxide layer was then chemically etched down, using diluted HF and a spinner, just prior to load-locking the samples into the end station for measurements. Si 2p and C 1s core level spectra recorded [15] at different electron emission angles, using a photon energy of 3 keV, from one of these samples are shown in figure 1. Two peaks are clearly visible in the Si 2p spectrum, the one at lower binding energy corresponding to bulk SiC and the one at larger binding energy to  $SiO_2$ . In the C 1s spectrum the SiC bulk peak dominates but at the largest emission angles a weak contribution from a graphite-like C 1s peak located at higher binding energy is also discernable. Both spectra have been normalized to the low binding energy peak so it is only the relative intensity of the two components with emission angle that are displayed. The relative intensity variation can be utilized to determine from where in the sample the graphite-like carbon signal originates. The intensities of the components in the Si 2p and C 1s spectra were extracted using a curve fitting procedure [16]. These values allowed a determination of the intensity ratio between the  $SiO_2$  and the SiC peak (labelled Si) and the ratio between the graphite-like and the SiC peak for C 1s level (labelled C) at each emission angle. The ratios obtained are shown in figure 2, and the relative intensity of the Si 2p and C 1s peaks originating from SiO<sub>2</sub> and graphite-like carbon are seen to increase with increasing emission angle. When applying a simple layer attenuation model this indicates that the graphite-like carbon signal originates from a carbon containing layer at the surface and not at the interface. The solid curves show the calculated emission angle dependence for an oxide layer thickness of 25.5 and a 0.05 Å thick surface graphite-like layer, when electron attenuation lengths [17] of 45 and 50 Å for the



Figure 1. Si 2p and C 1s core level spectra recorded from an *ex situ* grown SiO<sub>2</sub>/SiC sample at different electron emission angles using a photon energy of 3 keV.

C 1s and Si 2p photoelectrons, respectively, are assumed. The experimental and calculated intensity variations are seen to agree fairly well. Load-locking the sample immediately after the chemical etching thus considerably reduced the surface carbon contribution but did not completely eliminate it. We could, however, not observe any carbon containing by-product at the interface. If it existed, the concentration was below the detection limit. The results shown in figures 1 and 2 were used to estimate [15] that an approximately 0.5 Å thick carbon containing compound like Si<sub>4</sub>C<sub>2</sub>O<sub>2</sub>, or a 0.12 Å thick graphite-like layer, would be required at the interface in order to be detectable. It could thus be concluded that if such a carbon containing layer did exist it was definitely considerably thinner than the thickness of 8 Å, proposed in the earlier investigation [5]. The above results showed that no carbon by-product could be observed at the interface of *ex situ* prepared samples possibly because of a small but unavoidable hydrocarbon contamination on load-locked samples.

In situ oxidation experiments were therefore tried [18, 19] instead. Carbon spectra were then recorded using a photon energy of 330 eV in order to obtain the highest possible surface sensitivity. It was found that clean oxide surface/interface/layers could be obtained, where no signal from carbon clusters or carbon by-product at the interface could be detected. This is illustrated in figure 3. Only the bulk SiC peak is observed in the C 1s spectrum recorded after a  $1.2 \times 10^6$  L oxygen exposure with the sample at 800 °C. The C 1s spectrum from the initial  $\sqrt{3} \times \sqrt{3}$  reconstructed surface contains three components. The component labelled S1, at about 0.7 eV lower binding energy than the bulk SiC component, is interpreted [20, 21] to originate from the uppermost Si–C bilayer of the reconstructed surface. The component labelled S2, at about 1.3 eV higher binding energy than the bulk component, originates from carbon clusters (graphite-like carbon) on the surface, possibly at steps and domain boundaries [9]. This initial  $\sqrt{3}$  surface was actually prepared at a slightly higher temperature than needed for the purpose to obtain a pronounced S2 carbon component on the surface before



**Figure 2.** Experimentally extracted intensity ratios C (graphite-like carbon/SiC), Si (SiO<sub>2</sub>/SiC) and C/Si (multiplied by 20) for the *ex situ* grown SiO<sub>2</sub>/SiC sample are shown by filled squares, circles and triangles respectively. The solid lines show calculated intensity ratios when assuming the model of the element distribution shown by the inset.

the oxygen exposure. After exposure the S2 and S1 components are no longer observable within the detection limit of the experiment. This indicates that if carbon clusters are present at the interface the concentrations is so low (less than about 1-2% of a monolayer) that they are not detectable using photoemission. The upper curve in figure 3 shows the C 1s spectrum recorded after the oxidized sample had been heated *in situ* at 1120 °C for about a minute. The S1 component but not the S2 component does reappear. No oxygen signal was detectable after the heating, and the sample showed a very clear and intense  $\sqrt{3}$  low energy electron diffraction pattern. We were thus able to prepare a clean and well ordered  $\sqrt{3}$  reconstructed surface by first growing an oxide layer on the surface and then removing it by high temperature annealing. The *in situ* oxidation results thus show that no carbon clusters or carbon containing by-product can be detected at the interface after oxygen exposures in the 10<sup>6</sup> 1 range, and also that a very clean  $\sqrt{3}$  reconstructed surface can be prepared by *in situ* oxidation and annealing cycles.

#### 3.2. Sub-oxides at the interface?

On elemental Si surfaces it is well known [2] that three sub-oxides (Si<sup>1+</sup>, Si<sup>2+</sup> and Si<sup>3+</sup>) besides the fully developed SiO<sub>2</sub>(Si<sup>4+</sup>) can form upon oxidation. Photoemission spectra [2] show four shifted Si 2p components which, assuming a formal oxidation state model, correspond to a shift of about one eV per nearest neighbour O atom. For the SiO<sub>2</sub>/SiC interface, however, very different interpretations concerning the number of oxidation states present have been reported. In *in situ* oxidation studies [18, 19] of the  $\sqrt{3} \times \sqrt{3}$  reconstructed 4H-SiC(0001) surface we could experimentally verify the existence of only one sub-oxide, besides the fully developed SiO<sub>2</sub>. This is illustrated in figure 4, where Si 2p spectra recorded [18] before and after an oxygen exposure of 0.9 × 10<sup>6</sup> L at a substrate temperature of 600 °C are shown. The change in shape of the main Si 2p peak after oxidation, and also the difference spectrum, indicates the presence of at least one additional Si 2p component located between the SiO<sub>2</sub>(Si<sup>4+</sup>) and bulk SiC(Si<sup>0+</sup>) components. Results obtained after curve fits [16] to Si 2p spectra are shown in figures 5(a) and (b). Since only two additional components, besides the SiC bulk peak, are visibly resolved in the recorded spectra, only two additional Si 2p components were applied



**Figure 3.** C 1s spectra recorded at  $h\nu = 330$  eV from the initial  $\sqrt{3} \times \sqrt{3}$  reconstructed surface, after an oxygen exposure of  $1.2 \times 10^6$  L and after the surface has been regenerated by *in situ* heating. See the text for details.

**Figure 4.** Si 2p spectra recorded at hv = 330 eV from the clean  $\sqrt{3} \times \sqrt{3}$  reconstructed 4H-SiC(0001) surface and after oxidation to a total oxygen exposure of  $0.9 \times 10^6$  L. The difference spectrum between after and before oxidation is shown by the bottom curve.

in the fitting procedure. This was found to produce fits of good quality, and indicated the presence of only one sub-oxide. Since the shift of this additional component,  $\sim 0.5 \text{ eV}$ , was about one fourth of the shift of SiO<sub>2</sub>(Si<sup>4+</sup>) it was assigned [18] to originate from Si<sup>1+</sup> oxidation states. A study [19] including the effects of smaller and larger oxygen exposures and different substrate temperatures showed the same, i.e. that only one intermediate oxidation state could be experimentally verified to be present.

In initial oxidation studies of the Si-rich  $3 \times 3$  reconstructed SiC(0001) surface [22, 23] four shifted Si 2p components were reported, i.e. the presence of four Si oxidation states, with energy separations similar to those observed on oxidized elemental Si surface. The presence of mixed oxides including carbon species (Si–O–C) was also claimed for both the 6H and 4H polytypes, and found [23] to be the dominant among the oxide products for the 4H surface. Different results were reported in an XPS study [24] of oxidation of the Si-rich  $3 \times 3$ , and the C-rich  $6\sqrt{3} \times 6\sqrt{3}$ , reconstructed 6H-SiC surface. After thermal oxide growth to a thickness of around 50 Å no sub-oxides or carbon species could be observed at the interface (within their detection limit), and a shift of 2.5 eV was determined for the SiO<sub>2</sub>(Si<sup>4+</sup>) component. From the results they suggested that it should be possible to obtain nearly ideal SiO<sub>2</sub>/SiC



Figure 5. Si 2p spectra recorded using two different photon energies in (a) and (b) and after two different oxygen exposures in (a) and (c). The curves through the data points show the result of curve fits and the curves underneath show the components used.

interfaces on flat SiC terraces. In a recent angle resolved study of initial oxidation of the  $\sqrt{3} \times \sqrt{3}$  reconstructed 6H-SiC(0001) surface [25] the presence of three additional oxidation states, besides SiO<sub>2</sub>, was suggested. That was contrary to our earlier findings [18, 19] and therefore we also made such angle resolved investigations [26]. Si 2p spectra recorded at different electron emission angles from a 4H-SiC(0001) sample exposed to 50 L of oxygen at a substrate temperature of 800 °C are shown in figure 6. The dots show the raw data and the solid curve in the bottom spectrum illustrates fitted results using two shifted Si 2p components. The vertical lines indicate the positions of the oxide components. Shifts of 2.1 and 0.5 eV were obtained, in agreement with our earlier findings [18, 19] but in disagreement with the results from the 6H-SiC(0001) surface [25]. The  $\sqrt{3} \times \sqrt{3}$  reconstruction originates [8, 9] from Si adatoms on top of an Si-terminated bulk truncated crystal for both 4H and 6H crystals, and therefore the different polytypes used cannot explain the suggested difference in oxidation states on these surfaces. In [25] four oxidation states were assumed in the analysis and also



Figure 6. Si 2p spectra from an *in situ* grown SiO<sub>2</sub>/SiC sample recorded at different electron emission angles using a photon energy of 140 eV. The dots show the raw data and the curve through the data points in the bottom spectrum shows the result of a curve fitting procedure using two shifted Si 2p components. The vertical lines indicate the peak positions. See the text for further details.

equal energy intervals between the  $Si^{i+}$  and  $Si^{(i+1)+}$  states, although so many components were not visibly resolved in the data collected. We made no such *a priori* assumptions in our analysis [18, 19, 26]. Instead we tried to determine how many shifted components do the experimental results indicate to be present and how many are required to adequately model recorded spectra. Despite a good energy resolution in our angle resolved spectra only two shifted oxide related components could be visibly resolved and two shifted components were only required to adequately model recorded spectra. The different results obtained originate thus mainly from the different strategies used in the curve fitting procedure applied. The oxide related structures are fairly wide and overlap quite strongly, so one cannot hope to resolve them in greater detail even if the experimental resolution is further increased. It is therefore not meaningful to debate which of the methods used appears most reliable. What appeared more fruitful instead was to investigate if other levels than the Si 2p could provide additional information concerning the number of oxidation states present. Studies using higher photon energies so measurements of the Si 1s level and the Si KLL Auger transitions could be included were therefore made [26].

# 3.3. Oxide components observed in Si 1s spectra

Angle resolved studies of the Si 1s level were carried out on SiO<sub>2</sub>/SiC samples with oxide thickness values ranging from 7 to 118 Å. Si 1s spectra recorded at three different emission angles using a photon energy of 3.0 keV from a sample with a 7 Å thick oxide layer are shown



Figure 7. Si 1s spectrum recorded at three different electron emission angles using a photon energy of 3 keV. The solid curves show fitted results assuming two oxide related components. A total oxide thickness of 7 Å was determined for this sample.

in figure 7. The shift of the SiO<sub>2</sub> component is seen to be somewhat larger for the Si 1s level (about 2.6 eV). The Si 1s spectrum consists of singlets and is simpler to model than the Si 2p spectrum consisting of doublets. Both these facts are advantageous for extracting the oxidation states present despite the larger intrinsic 1s line width and the reduced energy resolution at high photon energies. For the thickest oxide the  $SiO_2$  component dominated the spectrum. Its line shape parameters were determined and then used in the fits for the samples with thinner oxides. Clean SiC surfaces, prepared by in situ heating, were also investigated. This allowed a determination of the line shape parameters for the bulk Si 1s peak. The determined line width parameters of the Si<sup>0+</sup> and the Si<sup>4+</sup> components were then used for all fits of the Si 1s spectra. Only the number of additional components and their widths were varied in the fitting procedure. It was found [26] that only one additional shifted component was needed to obtain the best fits to the recorded spectra, as illustrated by the fitted curves in figure 7. For all samples investigated a similar quality of the fit was obtained, so the Si 1s data also indicated the presence of only two oxide related shifted components, corresponding to Si<sup>4+</sup> and Si<sup>1+</sup> oxidation states. From the angle resolved data the location of the sub-oxide could also be deduced. The peak areas of the three different components, see figures 6 and 7, were extracted and the variation versus electron emission angle was analysed using a layer attenuation model [26]. This showed that the sub-oxide is located at the interface.

#### 3.4. Oxide components observed in Si KL<sub>2,3</sub> L<sub>2,3</sub> Auger spectra

We also investigated if Si  $KL_{2,3}L_{2,3}$  spectra could provide additional information concerning the number of oxidation states present [26]. Si  $KL_{2,3}L_{2,3}$  spectra from clean SiC at normal



**Figure 8.** Si  $KL_{2,3}L_{2,3}$  spectra from clean SiC at normal emission (C) and from a sample with a 7 Å thick oxide at normal (Ia) and at 75° emission (Ib). The two bottom curves show the difference curves Ib - Ia and Ib - C.

emission (C) and from a sample with a 7 Å thick oxide at emission angles of 0° (Ia) and 75° (Ib) are shown in figure 8. The Auger spectrum from SiC and also from SiO<sub>2</sub> consists of two major peaks (final state multiplet components), a main one at high kinetic energy and a weaker one at around 6 eV lower kinetic energy. The SiO<sub>2</sub> structures, indicated by arrows, are clearly discernable in the spectra from the oxidized sample, but the presence of lower oxidation states is not. A pronounced asymmetry is, however, seen on the low kinetic energy side of the main SiC peak, particularly in the  $75^{\circ}$  spectrum where the oxide contribution is enhanced. This asymmetry is oxide related since the spectra for clean SiC showed no angle dependence. The shape of the KLL multiplet structure is not known accurately enough to allow a reliably peak fitting analysis. Therefore the oxide components were extracted also from difference curves as illustrated by Ib – Ia and Ib – C in figure 8. They both exhibit, in addition to the two  $SiO_2$ related structures, a pronounced structure around 1612 eV and a weaker one around 1606 eV. These were again interpreted [26] to originate from the presence of an Si<sup>1+</sup> oxidation state since the main component showed a shift of about one quarter of the shift for the main SiO<sub>2</sub> component. The same result was obtained when analysing Si KLL spectra in a similar way from samples with oxide thickness values of 10, 14 and 25 Å, although the relative strength of the Si<sup>4+</sup> state then became gradually more dominant. These Si KLL results are consistent with the analysis of Si 2p and Si 1s spectra made above which indicated that only a Si<sup>1+</sup> sub-oxide is present besides Si<sup>4+</sup> on the SiO<sub>2</sub>/SiC samples investigated.

# 3.5. The SiO<sub>2</sub> chemical shift

The SiO<sub>2</sub> shift determined [26] from the curve fits of the core level and Auger spectra are plotted versus the oxide thickness in figure 9. The circles indicate oxide samples grown to the specified thickness, while the open diamonds indicate oxide samples grown as thick as 1000 Å and then etched down prior to measurements. The uncertainty in the determination of the shift was estimated to be  $\pm 0.05$  eV, so a trend with oxide thickness is clearly visible.



**Figure 9.** The SiO<sub>2</sub> shift for the (a) Si 1s, (b) Si 2p, and (c) Si KL<sub>2,3</sub>  $L_{2,3}$  lines versus oxide thickness. The uncertainty of  $\pm 0.05$  eV in the determination of the shift is shown only for the thickest oxide.

The shift increases gradually with increasing oxide thickness up to around 25 Å and remains fairly constant for the thicker oxides. The additional values included in figure 9(b) for the Si 2p level, and indicated by the open triangles, belong to thinner oxide samples studied using lower photon energy. These values, together with earlier findings [19], indicate that the shift appears to be fairly constant also for oxides thinner than about 10 Å. This variation of the SiO<sub>2</sub> shift in the Si 2p level with oxide thickness has long been known [2] for SiO<sub>2</sub>/Si samples, and several suggestions for the cause of it have been given. The presence of different Si-O-Si bond angles (strained  $SiO_2$ ) near the interface, chemical modifications of the oxide film near the SiO<sub>2</sub>/Si interface, a second-nearest-O-neighbour effect, electric charging due to the photon irradiation, or an effect due to electrostatic screening have been proposed. It was argued that all these factors may have an influence on the measured chemical shift but that one has to be aware of charging effects. For SiO<sub>2</sub>/Si an electrostatic image charge potential model has been shown [27] to qualitatively explain the oxide thickness dependence of the energy shifts which indicated that there is no need to assume additional chemical modifications in the oxide layer or at the interface. Also for SiO<sub>2</sub>/Si the Si<sup>4+</sup> shift was found to increase with oxide thickness up to about 25 Å and then to be fairly constant for thicker oxides. The main difference observed for SiO<sub>2</sub>/SiC, compared to SiO<sub>2</sub>/Si, is that the overall energy shift with oxide thickness is about a factor of two smaller. This applies both to the core level and Auger energy shifts.

#### 4. Summary and conclusions

The existence of carbon clusters or carbon containing by-products and the existence of suboxides at the  $SiO_2/SiC$  interface are two questions believed to have a significant effect on MOS device characteristics. Oxidation studies of SiC surfaces, using photoemission and synchrotron radiation, have therefore often focused on these two issues. In this paper recent progress concerning such characterizations on Si-terminated surfaces of hexagonal n-type SiC(0001) have been presented and discussed.

Results presented from *ex situ* and *in situ* grown SiO<sub>2</sub>/SiC samples showed that no carbon clusters or carbon containing by-product could be detected at the interface of samples with an oxide layer thickness larger than about 10 Å. For thinner oxide layers the presence of carbon containing by-products at the interface has been reported [19, 23], however. These carbon by-products were shown [19, 24] to be possible to eliminate by larger oxygen exposures, and

it was also shown [19] that a clean and well ordered SiC(0001)- $\sqrt{3} \times \sqrt{3}$  surface could be re-created by *in situ* heating of the oxidized sample.

The presence of sub-oxides at the SiO<sub>2</sub>/SiC interface had been revealed in recorded Si 2p core level spectra by several groups. The results were not unanimous, however. Different numbers of sub-oxides and also shifts had been reported. Therefore results of a recent angle resolved study [26] including also the Si 1s core level and Si KLL Auger transitions were presented. These together with earlier Si 2p data show the presence of one sub-oxide only, besides the fully developed SiO<sub>2</sub>(Si<sup>4+</sup>). The sub-oxide was assigned to Si<sup>1+</sup> oxidation states. From the oxide/SiC peak intensity ratios extracted versus electron emission angle it could be concluded that the sub-oxide is located at the interface. The SiO<sub>2</sub> chemical shift was found to exhibit a characteristic oxide thickness dependence, both in the core levels and Auger transitions [26]. This dependence was found to be similar, but smaller in magnitude, compared to the thickness dependence earlier revealed for SiO<sub>2</sub>/Si samples [2].

#### Acknowledgment

The authors gratefully acknowledge support from the Swedish Research Council.

# References

- [1] Morkoc H, Srite S, Gao G B, Lin M E, Sverdlov B and Burns M 1994 J. Appl. Phys. 76 1363
- [2] Iwata S and Ishizaka A 1996 J. Appl. Phys. 79 6653 and references therein
- [3] Afanasev V V, Bassler M, Pensel G and Schultz M J 1997 Phys. Status Solidi a 162 321
- [4] Li H F, Dimitrijev S, Sweatman D, Harrison H B, Tanner P and Feil B 1999 J. Appl. Phys. 86 4316
- [5] Hornetz B, Michel H-J and Halbritter J 1994 J. Mater. Res. 9 3088
- [6] Chang K C, Nuhfer N T, Porter L M and Wahab Q 2000 Appl. Phys. Lett. 77 2186
- [7] Buczko R, Pennycook S J and Pantelides S 2000 Phys. Rev. Lett. 84 943
- [8] Owman F and Mårtensson P M 1995 Surf. Sci. 330 L639
- [9] Coati A, Sauvage-Simkin M, Garreau Y, Pinchaux R, Argunova T and Aid K 1999 Phys. Rev. B 59 12224
- [10] Starke U, Schardt J, Bernhardt J, Franke M, Reuter K, Wedler H, Heinz K, Furthmüller J, Käckel P and Bechstedt F 1998 Phys. Rev. Lett. 80 758
- [11] Reuter K, Bernhardt J, Wedler H, Schardt J, Starke U and Heinz K 1997 Phys. Rev. Lett. 79 4818
- [12] Wahab Q, Hultman L, Willander M and Sundgren J E 1995 J. Electron. Mater. 24 1345
- [13] Wahab Q, Turan R, Hultman L, Willander M and Sundgren J-E 1996 Thin Solid Films 287 252
- [14] Johansson L I, Glans P-A, Wahab Q, Grehk T M, Eickhoff Th and Drube W 1999 Appl. Surf. Sci. 150 137
- [15] Virojanadara C, Glans P-A, Johansson L I, Eickhoff Th and Drube W 2001 Appl. Surf. Sci. 172 253–9
- [16] Mahowald P H, Friedman D J, Carey G P, Bertness K A and Yeah J J 1987 J. Vac. Sci. Technol. A 5 2982
- [17] Cumpson P J and Seah M P 1997 Surf. Interface Anal. 25 430
- [18] Virojanadara C and Johansson L I 2001 Surf. Sci. 472 L145
- [19] Virojanadara C and Johansson L I 2002 Surf. Sci. 505 358
- [20] Johansson L I, Owman F and Mårtensson P 1996 Phys. Rev. B 53 13793
- [21] Muehlhoff L, Choyke W J, Bozack M J and Yates J T Jr 1986 J. Appl. Phys. 60 2842
- [22] Amy F, Enriquez H, Soukiassian P, Storino P-F, Chabal Y J, Mayne A J, Dujardin G, Hwu Y K and Brylinski C 2001 Phys. Rev. Lett. 86 4342
- [23] Amy F, Soukiassian P, Hwu Y K and Brylinski C 2002 Phys. Rev. B 65 165323
- [24] Simon L, Kubler K, Ermolieff A and Billon T 1999 Phys. Rev. B 60 5673
- [25] Hoshino Y, Nishimura T, Yoneda T, Ogawa K, Namba H and Kido Y 2002 Surf. Sci. 505 234
- [26] Johansson L I, Virojanadara C, Eickhoff Th and Drube W 2003 Surf. Sci. 529 515
- [27] Browning R, Sobolewski M A and Helms C R 1998 Phys. Rev. B 38 13407