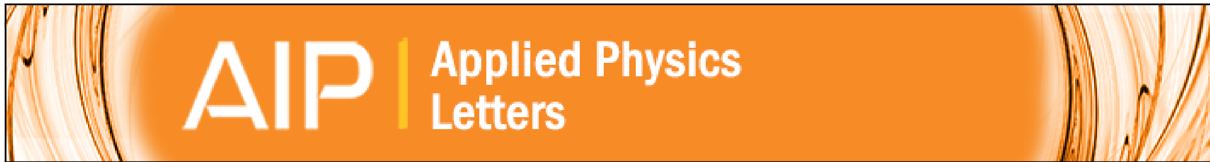

Initial stages of SiC oxidation investigated by ion scattering and angle-resolved x-ray photoelectron spectroscopies

C. Radtke, I. J. R. Baumvol, J. Morais, and F. C. Stedile

Citation: Applied Physics Letters **78**, 3601 (2001); doi: 10.1063/1.1374518
View online: http://dx.doi.org/10.1063/1.1374518
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/78/23?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in

The initial oxidation of Al–Mg alloys: Depth-resolved quantitative analysis by angle-resolved x-ray photoelectron spectroscopy and real-time in situ ellipsometry
J. Appl. Phys. **106**, 114913 (2009); 10.1063/1.3268480

A medium energy ion scattering and x-ray photoelectron spectroscopy study of physical vapor deposited thin cerium oxide films on Si(100)
J. Appl. Phys. **100**, 044103 (2006); 10.1063/1.2234820

High resolution synchrotron radiation-based x-ray photoemission spectroscopy study of the Si-rich β-SiC(100) 3×2 surface oxidation
J. Vac. Sci. Technol. B **21**, 1876 (2003); 10.1116/1.1589515

Characterization of TiAlN thin film annealed under O 2 by in situ time of flight direct recoil spectroscopy/mass spectroscopy of recoiled ions and ex situ x-ray photoelectron spectroscopy
J. Vac. Sci. Technol. A **20**, 1320 (2002); 10.1116/1.1482711

Profiling nitrogen in ultrathin silicon oxynitrides with angle-resolved x-ray photoelectron spectroscopy
J. Appl. Phys. **87**, 4449 (2000); 10.1063/1.373090

AIP Applied Physics Reviews
NEW Special Topic Sections
NOW ONLINE
Lithium Niobate Properties and Applications: Reviews of Emerging Trends
AIP Applied Physics Reviews

Reuse of AIP Publishing content is subject to the terms at: https://publishing.aip.org/authors/rights-and-permissions. Download to IP: 143.54.44.137 On: Thu, 05 May 2016 16:53:03

Initial stages of SiC oxidation investigated by ion scattering and angle-resolved x-ray photoelectron spectroscopies

C. Radtke, I. J. R. Baumvol, and J. Morais
Instituto de Física, UFRGS, Bento Gonçalves, 9500, Porto Alegre, RS, Brazil 91509-900

F. C. Stedile[a)]
Instituto de Química, UFRGS, Bento Gonçalves, 9500, Porto Alegre, RS, Brazil 91509-900

(Received 11 September 2000; accepted for publication 29 March 2001)

Initial stages of oxidation of single-crystal, Si-faced silicon carbide were investigated using ion scattering and angle-resolved x-ray photoelectron spectroscopies. The very first oxidation products are shown to be silicon oxycarbides (SiC_xO_y), while, for longer oxidation times, a mixture of SiC_xO_y and SiO_2 is formed in the near-surface region of the growing oxide film. The composition of the near-surface region of such thin films is very similar to that reported in previous investigations for the near-interface region when thicker oxides films are grown on SiC. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1374518]

Silicon carbide (SiC) is a promising material for electronic devices that involve high-power, high-temperature, high-speed, and/or high frequency. In such harsh conditions, the most used semiconductors, Si and GaAs, do not present satisfactory performance due to the uncontrolled generation of intrinsic carriers.[1,2] Besides its highly desirable properties, SiC is the only compound semiconductor that can be thermally oxidized to form SiO_2, the most studied and used dielectric. This is a great advantage since the passivation of the semiconductor surface plays an important role in device fabrication. Although similarities exist between oxides thermally grown on SiC and on Si,[3,4] the former exhibits worse electrical passivation characteristics.[5] The chemical structure of the oxide/SiC interface is altered by the presence of carbon in the film: Si–C–O compounds, named silicon oxycarbides are formed in this interface.[6] Vathulya *et al.*[7] correlated the carbon content in oxides grown on SiC to the electrical characteristics of metal–oxide–semiconductor (MOS) structures, concluding that the presence of C degrades the dielectric. In order for SiC to fulfill its potential as a large-band gap semiconductor, lower values of fixed charge densities in the oxide and interfacial trapped charge densities still must be achieved. For this reason, studies of oxidation mechanisms and composition of thermally grown oxides on SiC play a fundamental role in the understanding and control of the electrical characteristics of SiC-based devices.

The composition of oxides grown on SiC has been extensively studied by various techniques, mainly x-ray photoelectron spectroscopy, core level photoemission spectroscopy, and secondary ion mass spectrometry.[6,8–11] Önneby *et al.*[6] exposed SiC to ambient air at room temperature, yielding the formation of silicon oxycarbide species and SiO_2 at long exposure times (60 days). In another work[9] a C-free and rather abrupt SiO_2/SiC interface was achieved when an epitaxial Si overlayer (few atomic layers) was deposited on SiC before oxidation. Other authors investigated thicker oxides prepared by thermal oxidation at high temperatures of single crystal SiC (*c*-SiC) wafers, where depth profiling of the various species in these systems evidenced that the SiO_2/SiC interface is not abrupt.[6,10,11] Gradual transition between *c*-SiC and amorphous SiO_2 has been theoretically proposed by *ab initio* calculations, which showed that the topology and geometry of *c*-SiC surfaces are not suitable for abrupt interfaces.[12] In the present work, the first stages of oxidation of commercially available *n*-type 6H-SiC(0001) wafers were studied *in situ* by means of ion scattering spectroscopy (ISS) and angle resolved x-ray photoelectron spectroscopy (ARXPS). ISS gives the elemental composition of the first atomic layer while ARXPS provides information about the chemical composition of the probed material as a function of depth. In conjunction, these two techniques constitute a powerful method to characterize the first oxidation products of SiC.

A Si-faced *n*-type (nitrogen doped) 6H-SiC sample cut from a wafer with resistivity 0.075 Ω cm supplied by Cree Inc. was used in this experiment. The sample was dipped for 30 s in a 5% HF solution in ethanol, followed by a 30 s ethanol rinsing aimed at removing the native oxide. Immediately after HF etching the sample was introduced into the UHV chamber of the surface analysis facility. ISS spectra were obtained with a He^+ beam at 1000 eV aiming at surface specificity, which is only achieved when low energy rare gas ions are used.[13] Figure 1(a) shows the ISS spectrum from this sample, where one notices the presence of Si, C, N, O, and F at the surface. Since the sample had its (0001) face exposed, only Si should be detected. In order to remove contaminants and a possible native oxide, the wafer was heated to 850 °C in ultrahigh vacuum (base pressure was 3×10^{-10} mbar) for 10 min. Clean and stoichiometric β-SiC(100) surfaces have been obtained by a similar procedure carried out at higher temperatures.[14] The ISS spectrum from the resulting surface (hereafter referred as the cleaned sample) is shown in Fig. 1(b): only Si and N (dopant species) were detected. The intensity of the N signal in this spectrum is comparable to that of Si, which is a surprising observation even if one considers that the dopant concentration in SiC is usually two orders of magnitude higher than in Si.[2] Such a

[a)]Electronic mail: stedile@if.ufrgs.br

Reuse of AIP Publishing content is subject to the terms at: https://publishing.aip.org/authors/rights-and-permissions. Download to IP: 143.54.44.137 On: Thu, 05 May 2016 16:53:03

 © 2001 American Institute of Physics

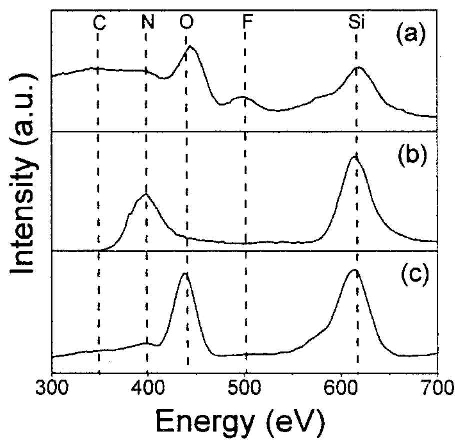

FIG. 1. ISS spectra of a SiC sample (a) after HF etching, (b) same as in (a) and then submited to heating in ultrahigh vacuum at 850 °C for 10 min, and (c) same as in (b) and then oxidized for 8.5 min in a dry O_2 pressure of 10^{-5} mbar at 850 °C. Dashed lines indicate the energy position of the elements.

strong N signal could be due to a segregation of N, a fact already observed after oxidation of SiC.[15] Quantification of this segregation and study of N chemical environment in the initial stages of SiC oxidation will be the subject of a forthcoming publication. The cleaned sample underwent *in situ* subsequent oxidation steps for total times of 5.0, 8.5, or 23.5 min in a dry O_2 pressure of 10^{-5}mbar at 850 °C. After each oxidation step ISS and ARXPS measurements were accomplished.

The ARXPS analyses were conducted using Mg Kα excitation ($h\nu$=1253.6 eV). Detection angle θ of the photoelectrons, with respect to the normal to the sample surface (takeoff angle), was varied from 25° (bulk sensitive mode) to 70° (surface sensitive mode). All spectra were fitted assuming a Shirley background.[16] Lines were fitted by 80% Gaussian + 20% Lorentzian functions, setting for each line a value of full width at half maximum. The Si 2p doublet was simulated by two lines with a branching ratio $2p_{1/2}/2p_{3/2}$ of 0.5 (the statistical ratio) and a spin-orbit splitting of 0.6 eV. The component of the Si 2p photoelectron spectrum corresponding to SiC was used as the binding energy reference: all other binding energies are given with respect to this one.[6,10,11]

Figure 2 shows Si 2p and C 1s regions from cleaned, 5.0 and 23.5 min oxidized SiC samples. One notices broadenings in both regions after oxidation which are attributed to the formation of oxygen bearing compounds. The first fitting procedure of the Si 2p regions of the oxidized samples consisted of assuming two components, corresponding to SiO_2 and SiC. The SiO_2 component was constrained to a binding energy 2.7 eV higher than the SiC component. This procedure evidenced the presence of a third component with binding energy between those corresponding to SiO_2 and SiC. It was attributed here to silicon oxycarbide (SiC_xO_y) compounds since C is less electronegative than O. C 1s regions were fitted with two components: one corresponding to C in SiC and another one lying at binding energies 1.2 eV higher. This last component was also attributed to silicon oxycarbide since other possible C compounds, usually attributed to sample contamination, should lie at least 1.6 eV apart from that of C in SiC.[10] These contaminants were indeed eliminated after the *in situ* cleaning, as shown in the ISS spectrum of Fig.1(b).

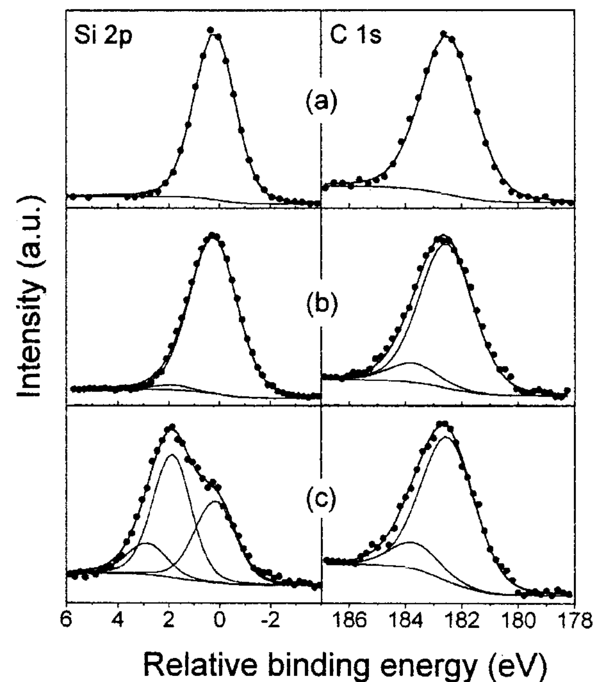

FIG. 2. Si 2p (left column) and C 1s (right column) regions of XPS spectra corresponding to (a) cleaned, (b) 5.0 min oxidized, and (c) 23.5 min oxidized SiC samples recorded with a takeoff angle of 70°. Points represent experimental data. Solid curves correspond to fitting components, Shirley background, and their sum. The components at binding energies 0.0 and 182.5 eV were assigned to silicon carbide, those at 2.0 and 183.7 eV were assigned to silicon oxycarbide, and the component at 2.7 eV was assigned to silicon oxide.

Once the fitting procedure of the ARXPS was defined, the areas of the various components of Si 2p regions were determined. Figure 3 shows the dependence of the relative areas of SiO_2 and SiC_xO_y components (normalized by the areas of the SiC component) with the cosine of the takeoff angle. The horizontal axis can be related to the analyzed

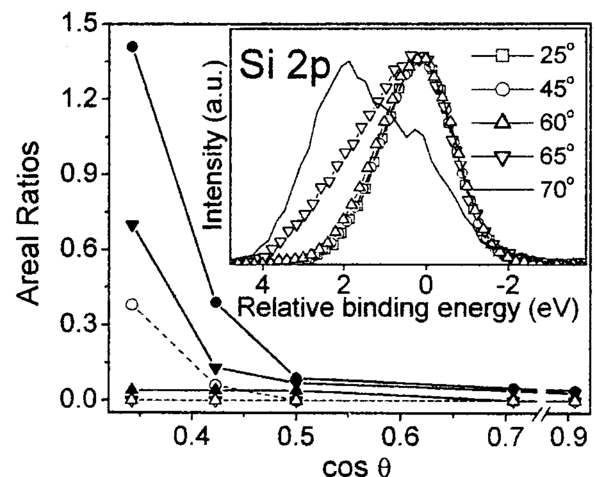

FIG. 3. Si 2p components areal ratios (normalized to the SiC component) as a function of the cosine of the takeoff angle. Oxidation times were 5.0 (up triangles), 8.5 (down triangles), and 23.5 min (circles). Open symbols stand for the SiO_2/SiC ratios while solid symbols stand for SiC_xO_y/SiC ratios. Si 2p experimental regions recorded for the sample oxidized for 23.5 min at different takeoff angles are showed in the inset. All regions were normalized to the same maximum intensity after subtraction of the background.

Reuse of AIP Publishing content is subject to the terms at: https://publishing.aip.org/authors/rights-and-permissions. Download to IP: 143.54.44.137 On: Thu, 05 May 2016 16:53:03

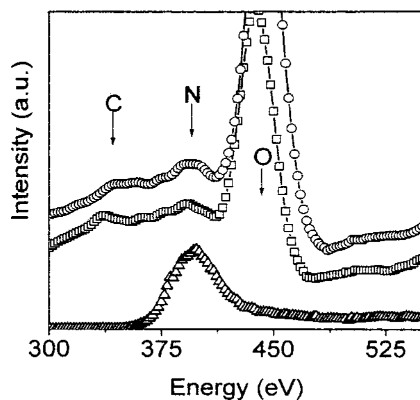

FIG. 4. ISS spectra of the cleaned (triangles), oxidized for 5.0 min (squares), and oxidized for 23.5 min (circles) SiC sample. Arrows indicate the energy position of the elements.

depth by $X = d \cos\theta$ where X is the probed depth, d is the escape depth of photoelectrons, and θ is the takeoff angle. Assuming the escape depth of Si 2*p* photoelectrons to be 1.8 nm—an approximate value obtained from the universal curve of electron mean free path[17]—one can see significant changes in the areal ratios occurring in the first nanometer below the sample surface. Greater amounts of oxygen compounds are observed as the oxidation time is increased: (i) SiC_xO_y is detected already for the shortest oxidation time and has a pronounced increase for longer oxidation times; (ii) stoichiometric SiO_2 is detected only after the longest oxidation time, and even in this case it is less abundant than silicon oxycarbide. The variation of the areal ratios of the three components in the Si 2*p* regions as the takeoff photoelectron emission angle is varied can also be clearly seen in the inset of Fig. 3, which stands for the sample oxidized for 23.5 min. As the takeoff angle is raised a marked asymmetry towards higher binding energy values is observed, an effect of the increasing contribution of oxidized species. Only at a 70° takeoff angle the contribution due to SiO_2 to the Si 2*p* region is remarkable. The amounts of silicon oxycarbide components calculated from the C 1*s* regions are consistent with the picture depicted in Fig. 3.

Composition of the surfaces after oxidations was accessed by ISS. Figure 1(c) shows the sample oxidized for 8.5 min: besides Si and some N, already present in the cleaned sample, O and some C were also detected. In Fig. 4, one can see more clearly the presence of C, N, and O at the surface of SiC oxidized for 5.0 and 23.5 min, corroborating the incorporation of C in the growing oxide films already observed by ARXPS.

Thus, the evolution of the thermal oxidation products determined by ARXPS shows that the first step of oxygen incorporation in SiC is the formation of silicon oxycarbides. Hornetz *et al.*[10] have proposed that a compound formed by Si, C, and O is the first reaction product of a Si–C double layer with molecular O_2, consistent with the present results. For longer oxidation times, Si is progressively oxidized until stoichiometric SiO_2 is detected in the near-surface region. As evidenced by ISS and ARXPS, silicon oxycarbides are still present in this region and therefore a complete layer of pure, stoichiometric SiO_2 is not formed, indicating that even the longest oxidation time used here still represents the first stages of SiC oxidation. Thus, at these initial stages Si is bonded to a variable number of C and O atoms originating a region very similar to the previously described transition layer between SiC and SiO_2.[6,10]

Summarizing, we have investigated the first stages of SiC oxidation using ISS and ARXPS. The results showed that the first oxidation products are silicon oxycarbides. The amount of such compounds increases for longer oxidation times within the first nanometer below the surface. As more oxygen is supplied to the system (longer oxidation times) a mixture of silicon oxycarbides and SiO_2 is detected near the surface. These initial stages of oxidation portrait the reaction environment of the dielectric/semiconductor interface during further thermal oxidation stages of SiC.

The authors would like to thank R. P. Pezzi for performing ARXPS and ISS measurements and for helpful discussions. This work was supported in part by CNPq and FAPERGS.

[1] R. R. Siergiej, R. C. Clarke, S. Sriram, A. K. Agarwal, R. J. Bojko, A. W. Morse, V. Balakrishna, M. F. MacMillan, A. A. Burk, Jr., and C. D. Brandt, Mater. Sci. Eng., B **61–62**, 9 (1999).
[2] H. Morkoç, S. Strite, G. B. Gao, M. E. Lin, B. Sverdlov, and M. Burns, J. Appl. Phys. **76**, 1363 (1994).
[3] M. B. Johnson, M. E. Zvanut, and O. Richardson, J. Electron. Mater. **29**, 368 (2000).
[4] K. McDonald, M. B. Huang, R. A. Weller, L. C. Feldman, J. R. Williams, F. C. Stedile, I. J. R. Baumvol, and C. Radtke, Appl. Phys. Lett. **76**, 568 (2000).
[5] G. G. Jernigan, R. E. Stahlbush, M. K. Das, J. A. Cooper, Jr., and L. A. Lipkin, Appl. Phys. Lett. **74**, 1448 (1999).
[6] C. Önneby and C. G. Pantano, J. Vac. Sci. Technol. A **15**, 1597 (1997).
[7] V. R. Vathulya, D. N. Wang, and M. H. White, Appl. Phys. Lett. **73**, 2161 (1998).
[8] Z. Zheng, R. E. Tressler, and K. E. Spear, J. Electrochem. Soc. **137**, 854 (1990).
[9] F. Amy, P. Soukiassian, Y.-K. Hwu, and C. Brylinski, Appl. Phys. Lett. **75**, 3360 (1999).
[10] B. Hornetz, H.-J. Michel, and J. Halbritter, J. Mater. Res. **9**, 3088 (1994).
[11] H.-F. Li, S. Dimitrijev, D. Sweatman, H. B. Harrison, P. Tanner, and B. Feil, J. Appl. Phys. **86**, 4316 (1999).
[12] R. Buczko, S. J. Pennycook, and S. T. Pantelides, Phys. Rev. Lett. **84**, 943 (2000).
[13] D. G. Armour, in *Methods of Surface Analysis*, edited by J. M. Walls (Cambridge University Press, Cambridge, 1989), pp. 263–298.
[14] M. R. Chudoba, P. Soukiassian, C. Jaussaud, and S. Dupont, Phys. Rev. B **51**, 14 300 (1995).
[15] J. W. Palmour, R. F. Davis, H. S. Kong, S. F. Corcoran, and D. P. Griffis, J. Electrochem. Soc. **136**, 502 (1989).
[16] D. A. Shirley, Phys. Rev. B **5**, 4709 (1972).
[17] M. P. Seah and W. A. Dench, Surf. Interface Anal. **1**, 2 (1979).

Reuse of AIP Publishing content is subject to the terms at: https://publishing.aip.org/authors/rights-and-permissions. Download to IP: 143.54.44.137 On: Thu, 05 May 2016 16:53:03