Al2O3 prepared by atomic layer deposition as gate dielectric on 6H-SiC(0001)

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Al2O3 films were deposited as alternative gate dielectric on hydrogen-terminated 6H-SiC(0001) by atomic layer chemical vapor deposition and characterized by photoelectron spectroscopy (PES) and admittance measurements. The PES results indicate an abrupt interface free of significant Si–suboxide contributions where the Al2O3 layer is connected to SiC by bridging oxygen atoms. The admittance measurements yield an interface state density which is lower than that of the thermally formed oxide and show in particular no increase toward the conduction band edge. Furthermore, a nearly symmetrical band alignment of Al2O3 on 6H-SiC with offsets of 2.2 and 1.8 eV is determined for the valence and conduction bands, respectively. This makes Al2O3 a serious competitor to thermal oxides as gate insulator in SiC devices. © 2003 American Institute of Physics.

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SiO2 is the first choice gate dielectric for silicon carbide (SiC)-based metal–oxide–semiconductor (MOS) devices because it forms naturally on SiC upon heating to 1100 °C in oxidizing atmospheres thermal oxidation. It turns out, however, that the SiC/SiO2 interface thus formed has a density of electronically active interface states (Dit) which is at least one to two orders of magnitude higher than that of the corresponding Si/SiO2 interface. This renders the as-grown thermal oxide rather useless as dielectric for SiC-based MOS devices.1,2 Two principle reasons have been suggested for this behavior.3 Incomplete oxidation of the carbon atoms in SiC leads to the formation of carbon clusters which are believed to contribute to Dit on account of their graphitic and therefore semimetallic nature. The steep increase in Dit toward the conduction band edge Ec, especially in 4H-SiC—is due to so-called near interface traps (NITs). Their microscopic origin is as yet unclear but it was suggested that they are due to an oxygen deficiency.2 These states act as interface traps for electrons and reduce the channel mobility of electrons in MOS devices. Attempts to reduce Dit significantly by postoxidation treatments such as nitridation have met with limited success so far.1–5 Here we report the preparation and properties of an alternative dielectric, Al2O3, on 6H-SiC with atomic layer chemical vapor deposition (ALCVD) technique. Al2O3 is one of the few dielectrics exhibiting a large dielectric constant (ε ~ 10) and a large band gap, that can be grown by ALCVD technique with high quality.6,7 We show that the 6H-SiC/Al2O3 interface so formed yields a density of interface states in the upper half of the gap that is significantly lower than that of the thermally grown SiC/SiO2 interface and lacks in particular the interface traps associated with the steep increase of Dit toward Ec. In our opinion, three aspects are responsible for this improvement. First, the gentle deposition of Al2O3 at low temperatures (300 °C) by ALCVD rather than the high temperature oxidation does not lead to a disruption of the SiC lattice and the concomitant defects. In particular, the formation of carbon clusters has been avoided completely. Second, the choice of Al2O3 instead of SiO2 avoids the formation of Si–Si bonds and with it the detrimental near interface traps. Finally, a special treatment of the SiC substrate before Al2O3 deposition makes for particularly defect-free surfaces and thus interfaces.

Al2O3 is deposited onto the 6H-SiC(0001) surface (Si-face) from the gas phase of trimethylaluminium [Al(CH3)3 (TMA)] and water vapor according to the overall reaction

\[ 2 \text{Al(CH}_3\text{)}_3 + 3 \text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6 \text{CH}_4. \]

In the ALCVD process, this overall reaction is split into two half reactions by admitting consecutively TMA and H2O to the substrate held at 300 °C for 1 s each and purging with N2 for 2 s in-between. The deposition conditions are chosen so that each step leads in a self-limiting reaction to the deposition of an effective monolayer of Al followed by crosslinking of this layer by oxygen atoms. This insures a complete reaction to Al2O3 and at the same time a very homogenous, conformal coverage of the substrate. The total Al2O3 thickness is a strictly linear function of the number of deposition cycles. From ellipsometric thickness measurements for layer thicknesses between 50 and 200 nm, we determine a growth rate of 0.10 ± 0.01 nm Al2O3 per deposition cycle in excellent agreement with other reports.6–8

In order to achieve the best possible SiC/Al2O3 interface, it is mandatory that the SiC(0001) surface itself is defect-free and stoichiometric to start with. To this end we treat the n-6H-SiC(0001) wafer in ultrapure (8N) hydrogen.

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at 1000 °C for 15 min. This yields a clean, unreconstructed, H-terminated surface of the highest crystallographic perfection that is furthermore chemically inert for up to 2 days in air. The hydrogenated surfaces are chemically and electronically passivated as described elsewhere.9,10 The chemical and atomic structure of the SiC/Al$_2$O$_3$ interface was probed by soft x-ray photoelectron spectroscopy (~SXPS) employing synchrotron radiation from the BESSYII storage ring. High-resolution (~0.3 eV full width at half maximum) Al 2$p$ core level spectra of five cycles Al$_2$O$_3$ film on 6H-SiC recorded with different sampling depths reveal only the signal due to Al$_2$O$_3$ and no other components corresponding to metallic Al or suboxides. Si 2$p$ spectra of the same sample with effective sampling depths $\lambda_{eff}$ between 1.6 and 5.3 Å are shown in Fig. 1(a). Using a standard peak fitting routine,10 the Si 2$p$ spectra are deconvoluted into two doublet corresponding to the Si atoms from the bulk SiC substrate and to Si atoms in the formal oxidation state Si$^+$, respectively. The variation in relative intensity of these two components with sampling depth $\lambda_{eff}$ is consistent with a structural model in which the Si$^{1+}$ atoms form a monolayer on top of SiC and below Al$_2$O$_3$, i.e., right at the interface. The structural model compatible with these observations is schematically indicated in Fig. 1(b). The Al$_2$O$_3$ layer is attached by bridging oxygen atoms to the topmost Si layer of the bulk-terminated 6H-SiC(0001) surface. The Si–O bond accounts for the formal oxidation state 1+ of silicon atoms at the interface between Al$_2$O$_3$ and SiC. Contributions of silicon atoms in higher oxidation states to the spectra of Fig. 1(a) that would indicate suboxides SiO$_x$(1 < $x$ < 2) and SiO$_2$ remain below the equivalent of 5% of a monolayer. Similar measurements of the C 1$s$ core level indicate adventitious carbon. The behavior of this signal upon changes of surface sensitivity suggests that it is due to hydrocarbon contamination on top of the Al$_2$O$_3$ layer due to a short exposure to air prior to the SXPS measurements. The same observations were made with the H-terminated 6H-SiC(0001) surface.9 The excellent structural properties of the SiC/Al$_2$O$_3$ interface are born out by the $D_{it}$ data of Fig. 2. $D_{it}$ in the upper half of the 6H-SiC gap was determined from admittance measurements as explained in Refs. 2 and 5. The $D_{it}$ values are about one order of magnitude lower than the average of $D_{it}$ for the thermal SiC/SiO$_2$ interface as also indicated schematically in Fig. 2. Moreover, there is no indication of a rise in $D_{it}$ toward $E_c$ due to the absence of NITs usually found in thermally formed SiO$_2$. The possibility to improve the interface between the as-deposited Al$_2$O$_3$ and SiC by various postannealing treatments is under investigation. Even a very low density of interface trap ($D_{it}$) would not qualify an insulator as a useful gate dielectric for a MOS device unless it provides sufficiently high barriers for electrons and holes to prevent carrier tunneling through the gate dielectric. This requirement is harder to meet for the wide band gap SiC than it is for Si. The band alignment between Al$_2$O$_3$ and 6H-SiC is derived from the valence band offset $\Delta E_v$ and the gap energy of Al$_2$O$_3$. These have been determined as follows.12–14 Figure 3 shows the valence band (VB) spectrum of about 15 Å (15 deposition cycles) Al$_2$O$_3$ on top of 6H-SiC. Also shown are the VB spectra of H-terminated 6H-SiC and a thick Al$_2$O$_3$ layer. The overlayer spectrum is well described by the weighted sum of the two constituent VB spectra provided the constituent spectra have been
FIG. 3. Valence band spectrum of 15 cycles 6H-SiC(0001)/Al₂O₃ system as measured (solid line) and as synthesized by a weighted superposition of the 6H-SiC(0001) and Al₂O₃ spectra (dashed line). The difference of the fitted curve and experimental spectrum is also given underneath.

aligned in energy according to the valence band offset between Al₂O₃ and 6H-SiC. Hence, the valence band offset ΔEV is read off as the energy separation of the extrapolated leading edges of the two spectra and this yields ΔEV = 2.2 ± 0.1 eV. The conduction band offset ΔEC follows once the band gap EG of Al₂O₃ is known. The latter was determined from the onset of inelastically scattered electrons following the O 1s core line spectrum (Fig. 4) following Miyazaki et al. 14

The lowest energy loss mechanism for hot photoelectrons in insulators is the electron-hole excitation across the band gap. In Fig. 4 this excitation threshold shows up as a clear onset in the spectral intensity on the low kinetic (high binding) energy side of the O 1s core level of Al₂O₃ due to inelastically scattered O 1s electrons. From the energy separation between the main O 1s line and the loss threshold, we determine a gap of 7.0±0.1 eV for the 1200-Å-thick Al₂O₃ film. The same value, albeit with somewhat less accuracy, is obtained for a very thin Al₂O₃ film of only 3 Å. This agreement not only confirms the outstanding homogeneity of the Al₂O₃ film down to the first few angstroms but also demonstrates the exceptional sensitivity of this method to determine EG for ultrathin insulators.

Combining ΔEV and EG, we arrive at the band diagram of Fig. 5 which attests to a nearly symmetrical disposition of the band gap of Al₂O₃ with respect to that of 6H-SiC. Using known values for the gap of 4H-SiC and a vanishing valence band offset between the two polytypes, 2 we have extended the band diagram to include the 4H-SiC/Al₂O₃ interface. In either case, the conduction and valence band barriers confirm the utility of Al₂O₃ as gate dielectric on SiC in this respect.

In summary, we have synthesized uniform and conformal dielectric Al₂O₃ films on H-terminated 6H-SiC(0001) by ALCVD technique. The photoelectron spectroscopy results indicate an atomically smooth and abrupt interface free of significant Si-suboxide and SiO₂ contributions. The Al₂O₃ layer is connected to SiC by bridging oxygen atoms. Electrical measurements yield a density of interface states, DN, in the upper half the gap that is lower than that for the thermally formed oxide. There is in particular no increase toward the conduction band edge. Furthermore, Al₂O₃ is shown to provide energy barriers in excess of 1.5 eV for electrons and holes for 6H-SiC as well as 4H-SiC.