HF Chemical Etching of SiO$_2$ on 4H and 6H SiC

M.B. JOHNSON, M.E. ZVANUT, and OTHA RICHARDSON

University of Alabama at Birmingham, 310 Campbell Hall, 1300 University Blvd., Birmingham, AL 35294-1170

Thickness and etch rate of SiO$_2$ films thermally grown on hexagonal SiC substrates were compared to results obtained from SiO$_2$/Si samples. The data confirm that profilometry and ellipsometry yield the same thickness values for oxides grown on Si and SiC. Within the accuracy of our measurements, oxides grown on different polytypes and faces of SiC etch at the same rate in a HF acid solution. The etch rate using a 50:1 H$_2$O:HF(50%) solution at room temperature is 0.1 nm/s and is uniform throughout the thickness of the SiO$_2$ films. The rate is the same as that obtained for SiO$_2$ grown on Si.

**Key words:** Chemical etching, SiO$_2$/SiC, SiO$_2$ etch rate, oxidized silicon carbide

**INTRODUCTION**

SiC is being investigated as a potential replacement for Si in specialty applications because SiC has a higher melting point and thermal conductivity than Si. Also, SiC is one of the few wide band gap semiconductors which produces an insulating SiO$_2$ film, crucial to metal oxide semiconductor (MOS) technology. Many investigations have addressed the chemical and structural composition of SiO$_2$ films thermally grown on SiC.\(^1\)\(^-\)\(^7\) Several of the physical properties of SiC, including oxidation, depend on which face of the SiC sample is being analyzed.\(^1\)\(^,\)\(^2\)\(^,\)\(^10\) For instance, the carbon face of SiC is known to oxidize one and a half to three times faster than the silicon face of SiC.\(^1\) It should not be surprising that the composition of the oxide layer formed on the two faces is different, especially in the region near the interface. For example, ellipsometry studies of Ramberg and coworkers reveal that for SiO$_2$ films grown on the Si-face, the index of refraction increases as the film thickness decreases. No change is observed for oxides grown in the C-face.\(^2\) Angle resolved x-ray photoelectron spectroscopy work by Horentz and coworkers shows layers of Si-C-O near the SiC surface of each oxidized face, but the stoichiometry and the thickness of the layers is different for the two SiC faces.\(^5\)

Aside from composition and structure, the thickness of the SiO$_2$ film must be known for all microelectronic applications. Ellipsometry is the technique commonly used by the semiconductor industry for measuring the thickness of SiO$_2$ films on a Si substrate. Calculation of film thickness from ellipsometric data depends on the values of the optical constants of both the substrate and film. Given that most reports suggest that a layer of undetermined thickness and composition exists at the SiO$_2$/SiC interface, it is not clear that the optical constants for bulk, free standing SiO$_2$ and SiC will yield a reasonable thickness for an SiO$_2$ film thermally grown on a SiC substrate. In this work, we compare thickness measured by ellipsometry with that obtained from profilometry. Profilometry is a mechanical method that measures the amount of SiO$_2$ on the substrate by physically touching the system, and therefore is not dependent on assumptions about the type of material being investigated. By comparing ellipsometric and profilometry data we verify that the indices of refraction for bulk SiO$_2$ and SiC yield physically realistic thickness values, at least for oxide layers between 20 nm and 120 nm thick.

Once grown, SiO$_2$ films on Si are often chemically etched to form windows for further processing. Thus, at least an approximate value for the etch rate as well as its degree of uniformity is important to microelectronic processing. Previous work on SiO$_2$/Si structures has shown that etching is sensitive to the density and composition of the SiO$_2$.\(^9\) For example, an HF solution has been used to investigate differences of SiO$_2$ layers grown on silicon.\(^10,\)\(^11\) Our studies employ HF etching and ellipsometry to investigate the etch rate of SiO$_2$ as film thickness varies and to compare the etch rates of oxides grown on Si and the two faces of hexagonal SiC. The results show that the etch rate
of SiO$_2$ on 4H and 6H silicon carbide are uniform, and the etch rates of SiO$_2$ grown on different SiC faces and polytypes is the same as that measured for SiO$_2$/Si samples.

**EXPERIMENTAL**

Wafers of p-type 6H SiC doped with 5.0 \times 10^{15} \text{ cm}^{-3} Al and oriented 3.5° off the (0001) direction were used in the study. Oxides were also grown on 1.9 \times 10^{18} \text{ cm}^{-3} Al doped epitaxial layers deposited on (0001) 4H SiC. A commercial grade Si sample which was p-type, 300 ohm-cm, Boron doped, and oriented along the (100) direction was used for comparison to the SiC. The samples were cleaned ultrasonically using consecutive baths of trichloroethane, xylene, acetone, methanol, and deionized water. The samples were oxidized at 1150°C for 10 min to 6 h in flowing O$_2$ that was passed over boiling water. The same substrates were used repeatedly in all the etch rate experiments. After the oxidation, the oxides were left to cool on the edge of the furnace for approximately 10 min, where the ambient air was rich in O$_2$ and the temperature was 200°C. This procedure avoided formation of a thin layer that could not be etched in a 9:1 H$_2$O:HF(50%) solution, but could be removed if we etched the sample using an HF(50%) solution and cleaned it with the series of ultrasonic baths noted at the beginning of this section.

A Tencor Instruments Alpha-Step 500 Surface Scan Profilometer was used to measure the thickness of the oxide, and the results were compared to measurements made using a Sentech ellipsometer. The ellipsometer has a HeNe laser with a wavelength of 632.8 nm. The angles of incidence used in our experiments were 50°, 60°, and 65°. The complex indices of refraction measured on a cleaned piece of 6H and 4H SiC, which had only the native oxide present on them, were 2.66–0.151 i, and 2.62–0.132 i, respectively. The index of refraction of SiC used in studies of SiO$_2$ films is 2.65–0.05 i. Assuming that the discrepancy between the measured value and the accepted value was due to the presence of the native oxide, we used 2.65–0.05 i for our measurements. Also, in keeping with accepted values, the index of refraction for SiO$_2$ and Si were taken to be a 1.46, and 3.874–0.016 i, respectively. Both the 4H and 6H samples were originally polished on both sides. In order to use ellipsometry on these samples we first had to abrade the face opposite the face we wished to measure. The single wavelength ellipsometry measurements do not provide sufficient information to properly assess the interfacial region where stoichiometry and composition are uncertain. At the same time, profilometry becomes increasingly inaccurate as the film gets thinner. For these reasons our analysis did not include oxide thickness below approximately 5 nm.

In determining the etch rate uniformity throughout the oxide, we used a solution of 50:1 H$_2$O:HF(50%) at room temperature. To calculate the etch rate we plotted the thickness of the oxide against the time etched and used a least squares regression program to

**Fig. 1.** (a) Thickness of oxide layers grown on Si measured by ellipsometry (●), and profilometry (○); thickness of oxide layers grown on 6H SiC carbon face measured by ellipsometry (●), and profilometry (○); (b) thickness of oxide layers grown on 6H SiC silicon face measured by ellipsometry (●) and profilometry (○).