Low-temperature oxidation of 4H-SiC using oxidation catalyst SrTi$_{1-x}$Mg$_x$O$_{3-δ}$

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A thermal oxidation method with SrTi$_{1-x}$Mg$_x$O$_{3-δ}$ as a catalyst is proposed to oxidize the 4H-SiC surface at low temperatures. The rate constant for the interfacial reaction of the 4H-SiC(0001) Si-face at 800 °C is enhanced by approximately two orders of magnitude from that of conventional dry oxidation. The method enables the production of a gate SiO$_2$ layer of a MOSFET at temperatures below 900 °C. Electrical characterization of the MOS interface suggests that the catalytic oxidation produces similar interface state densities to those produced by conventional dry oxidation in the energy range of 0.2–0.5 eV from the conduction band edge at 1300 °C.

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The wide-band-gap (3.263 eV) property of 4H-type silicon carbide (4H-SiC) results in a critical field for avalanche breakdown about 10 times larger than that of Si. In addition, SiC is a unique wide-band-gap semiconductor material that can be oxidized by thermal oxidation to form SiO$_2$ at the surface, similarly to Si. These properties of SiC offer a power-switching metal–oxide–semiconductor field-effect transistor (MOSFET) with an on-state resistance that is more than 100 times lower than that of Si MOSFETs. Recent progress has, in fact, demonstrated specific on-state resistance of less than 2 mΩ cm$^2$ with a 1200 V blocking voltage and fast switching of current over 150 A.

While intensive research and development are in progress for practical applications, the low-channel-carrier mobility of the 4H-SiC MOSFET still remains to be solved. The experimentally observed electron mobility in the channel is approximately 40 times lower than that in the bulk. The electron mobility is significantly degraded by the presence of electron trap states generated at and near the 4H-SiC/SiO$_2$ interface during the formation of the gate SiO$_2$ layer using thermal oxidation. While post oxidation thermal treatments such as nitridation and incorporation of phosphorus in the interface have been shown to be effective in reducing the density of interface traps $D_{it}$, the origin of the high interface state density for SiC is not well understood. It has been found, from thermal oxidation study carried out at 1120 °C, that high-temperature thermal oxidation causes a metamorphic oxidation of the SiC at the MOS interface to the so-called carbon cluster, which generates interface electron traps. It has been reported that residual carbon in SiO$_2$ thermally grown at 1300 °C can be reduced by 40% compared with the case of 1080 °C. On the other hand, it has been shown that lowering the oxidation temperature results in reduced $D_{it}$. Additionally, it has been reported that low-temperature oxidation in oxygen ambient applied to high-temperature oxidized 4H-SiC is effective in reducing $D_{it}$. Thus, low-temperature oxidation is worth investigating from the perspective of not only reducing the processing temperature for surface passivation but also forming gate oxide. However, most of the previous studies of oxidation including MOSFET characterization have employed oxidations at temperatures higher than 1100 °C. The reason for this is that the surface of 4H-SiC, particularly the (0001) Si-face which gives a much lower interface trap density than the (0001) C-face, is difficult to oxidize at temperatures below 1000 °C.

In this letter, we report a new oxidation method that is able to significantly enhance the thermal oxidation rate of 4H-SiC. Oxide growth at 800 °C up to 34 nm thickness on the 4H-SiC(0001) Si-face surface is presented. The impact of low-temperature oxidation on the interface property is also investigated.

The new oxidation method uses SrTi$_{1-x}$Mg$_x$O$_{3-δ}$ as a catalyst to produce atomic oxygen from an oxygen molecule (O$_2$) in an oxidation furnace at elevated temperatures. Preliminary results of oxidation enhancement achieved by using Si are reported elsewhere. Figure 1(a) shows the unit cell of SrTi$_{1-x}$Mg$_x$O$_{3-δ}$. The oxygen vacancies are produced by replacing Ti$^{4+}$ with Mg$^{2+}$ in the SrTiO$_3$ lattice of the basic ABO$_3$ perovskite structure. When O$_2$ molecules are intro-
duced, an oxygen atom occupies the oxygen vacancy as an O\(^-\) ion. The O\(^-\) ion is a metastable state, so that it is desorbed from the material as an active oxygen species (O\(^+\)) to form an oxygen vacancy (V\(_{O}\)). The emission of O\(^-\) occurs at temperatures above 400 °C. Therefore, O\(^-\) oxidation can be realized by simply placing the oxidation catalyst together with the oxidation target (SiC) in an oxidation furnace. SrTi\(_{1-x}\)Mg\(_x\)O\(_3\) has been demonstrated as a high-performance catalyst for the oxidative coupling of methane.\(^{20,21}\) It has also been applied as an oxygen sensor material because of its high oxygen absorption ability.\(^{21}\)

The SrTi\(_{1-x}\)Mg\(_x\)O\(_3\) catalyst was prepared by mixing SrCO\(_3\), TiO\(_2\), and MgO powders at various molar ratios with respect to the composition x. The mixed powders were then sintered at 1100 °C in air for 3 h. Figures 1(b) and 1(c) show X-ray diffraction (XRD) patterns of SrTiO\(_3\) and SrTi\(_{0.4}\)Mg\(_{0.6}\)O\(_3\) respectively. In the XRD pattern of SrTi\(_{0.4}\)Mg\(_{0.6}\)O\(_3\), several peaks are observed near the 20 diffraction angles of 31–33, 43, and 62° in addition to the peaks of SrTiO\(_3\). These peaks indicate the formation of new phases\(^{20,21}\) caused by the replacement of Ti\(^4+\) with Mg\(^2+\).

Temperature-programmed desorption (TPD) was conducted to investigate the ability of SrTi\(_{1-x}\)Mg\(_x\)O\(_3\) to produce active oxygen species. The catalyst samples were preheated in a 50 mL/min flow of pure O\(_2\) up to 800 °C for 2 h. After cooling to room temperature, TPD measurements were performed in a He flow at 30 mL/min. Figure 1(d) shows mass signal intensity spectra for mass number of 16 measured for 0.7 g of SrTiO\(_3\) and SrTi\(_{0.4}\)Mg\(_{0.6}\)O\(_3\) samples. Comparison of the spectra clearly reveals that the density of the oxygen adsorption sites on SrTi\(_{0.4}\)Mg\(_{0.6}\)O\(_3\) is much higher than that on SrTiO\(_3\). SrTiO\(_3\) also shows the emission of oxygen atoms owning the presence of oxygen vacancies produced as unintentional crystallographic defects.

To evaluate the enhancement of the oxidation of 4H-SiC using the catalyst material, an oxidation experiment was conducted using the setup shown in Fig. 2(a). SrTi\(_{1-x}\)Mg\(_x\)O\(_3\) catalyst powder was placed in a rectangular quartz dish and covered with a 1 mm-thick quartz plate in which a 7 × 7 mm\(^2\) window was fabricated. A 4H-SiC wafer was set face-down on the quartz plate. The entire set was loaded into the quartz tube of an electric furnace. Oxidation was performed at 800 °C under atmospheric pressure with an O\(_2\) flow rate of 1 L/min. The 4H-SiC wafer used was the (0001)-oriented Si-face n-type with a 6.6-μm-thick epitaxial layer. The doping concentration of the epitaxial layer was 2 × 10\(^{16}\) cm\(^{-3}\). Prior to oxidation, the sample wafer was dipped in diluted HF and rinsed with deionized water to remove native oxides at the surface. The thickness of the SiO\(_2\) layer after oxidation was measured by spectroscopic ellipsometry (Horiba AutoSE).

Figure 2(b) shows the thickness distribution of SiO\(_2\) on 4H-SiC formed by oxidation at 800 °C for 10 h with the SrTi\(_{0.4}\)Mg\(_{0.6}\)O\(_3\) catalyst. It is noteworthy that signals from Sr, Ti, and Mg were not detected at the surface of the samples using electron probe micro analyzer (EPMA).
of dry oxidation, which suggests that enhanced oxidation is a result of an enhanced reaction owing to O\(^{−}\) generated in the oxidation ambient by the SrTi\(_{1−x}\)Mg\(_{x}\)O\(_3−δ\) catalyst.

In the following, the quantitative validity of the proposed method is discussed. We assume that oxides are formed by the reaction of SiC with O\(^{−}\). The linear rate constant B/A at 800 °C with the use of the catalyst with x = 0.6 is extracted from the experimental results to be 2.3 × 10\(^{-3}\) μm/h = 6.4 × 10\(^{-4}\) nm/s. Since the molar density of SiO\(_2\) is 3.66 × 10\(^{-2}\) mol/cm\(^3\) and the sample size was about 0.7 × 0.7 cm\(^2\), the reaction rate of O\(^{−}\) with Si is estimated to be 2.3 × 10\(^{-12}\) mol/s. The same amount of C as Si is consumed as a result of oxidation. Assuming that C forms oxides and desorbs as CO from the surface, leaving SiO\(_2\) behind, the required arrival rate of O\(^{−}\) is estimated to be 3.45 × 10\(^{-12}\) mol/s. On the other hand, the emission rate of O\(^{−}\) from the SrTi\(_{0.4}\)Mg\(_{0.6}\)O\(_3−δ\) catalyst is estimated as follows. According to the previous report,\(^{21,25}\) the amount of oxygen adsorption of SrTi\(_{1−x}\)Mg\(_x\)O\(_3−δ\) is 8.8 × 10\(^{-4}\) mol/g. This value was obtained by scanning the temperature from 570 to 770 K for 20 min. Therefore, the emission rate of O\(^{−}\) is estimated to be 8.8 × 10\(^{-6}\) / 1200 = 7.3 × 10\(^{-9}\) mol/g-s. In our experiment, the amount of SrTi\(_{0.4}\)Mg\(_{0.6}\)O\(_3−δ\) catalyst placed in the test bench was 0.06 g, which gives the O\(^{−}\) emission rate of 4.43 × 10\(^{-10}\) mol/s. This value satisfies the required arrival rate of O\(^{−}\), described above, to account for the oxidation enhancement.

Figure 5 shows \(D_a\) evaluated by the high-low method.\(^{26}\) Besides the gate oxide prepared using SrTi\(_{1−x}\)Mg\(_x\)O\(_3−δ\) catalyst at 850 °C for 2.5 h, a gate oxide was prepared by using dry oxidation without the catalyst at 1300 °C for 1 h. For the catalytic oxidation sample, post-oxidation annealing (POA) in O\(_2\) at 800 °C for 5 min was carried out. The catalytic oxidation sample prepared at 850 °C gives slightly higher \(D_a\) in the energy level of 0.2–0.5 eV than the sample prepared by dry oxidation at 1300 °C.

In summary, a novel thermal oxidation method using an oxidation catalyst was proposed to enhance the oxidation rate of 4H-SiC at temperatures below 900 °C. Experiments were conducted using SrTi\(_{1−x}\)Mg\(_x\)O\(_3−δ\) catalyst for the oxidation of the 4H-SiC(0001) Si-face. Experimental results indicated that the growth rate of SiO\(_2\) is enhanced by about two orders of magnitude compared with that in the case of conventional dry oxidation. In the temperature range of 800–900 °C and in the SiO\(_2\) thickness range less than 60 nm, the growth is limited by the reaction rate at the SiO\(_2\)/4H-SiC interface and the activation energy for the reaction is reduced by using the oxidation catalyst, which strongly suggests that the active oxygen species produced by the catalyst enhances the oxidation rate. The electrical characterization indicated that the oxidation at 850 °C using the catalyst produces interface traps at a density similar to that in the case of conventional dry oxidation at 1300 °C. Therefore, the low-temperature oxidation using the catalyst is of great interest for application to surface passivation of a device.

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