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Effects of post-deposition annealing on sputtered SiO_2/4H-SiC metal-oxide-semiconductor

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ABSTRACT

Reactive sputtering followed by N_2, NH_3, O_2, and NO post-deposition annealing (PDA) of SiO_2 on 4H-SiC was investigated in this study. The results of ellipsometry, an etching test, and X-ray photoemission spectroscopy showed that N_2 and NH_3 PDA nitrified the SiO_2. Devices using N_2 and NH_3 PDA exhibited a high gate leakage current and low breakdown field due to oxygen vacancies and incomplete oxynitride. SiO_2/4H-SiC MOS capacitors were also fabricated and their electrical characteristics measured. The average breakdown fields of the devices using N_2, NH_3, O_2, and NO PDA were 0.12, 0.17, 4.71 and 2.63 MV/cm, respectively. The shifts in the flat-band voltage after O_2 and NO PDA were 0.95 and −2.56 V, respectively, compared with the theoretical value. The extracted effective oxide charge was $-4.11 \times 10^{11}\,\text{cm}^{-2}$ for O_2 PDA and $1.11 \times 10^{12}\,\text{cm}^{-2}$ for NO PDA. NO PDA for 2 h at 1200 °C shifted the capacitance–voltage curve in the negative direction. The oxygen containing PDA showed better electrical properties than non-oxygen PDA. The sputtering method described can be applied to 4H-SiC MOS fabrication.

1. Introduction

4H-silicon carbide (SiC) is a wide bandgap material with a high breakdown voltage, a high thermal conductivity, and a fast saturation drift velocity [1–3]. Based on these characteristics, SiC-based devices are expected to replace traditional silicon devices in high-voltage, high-frequency, and high-temperature applications [4,5]. SiC can form silicon oxide (SiO_2) by oxidation, thus, facilitating metal–oxide–semiconductor (MOS) gate insulator fabrication [6,7]. However, when the gate dielectric is formed by oxidation, the residual carbon, which does not participate in the silicon/oxygen reaction, forms carbon clusters. Interface states arising from the carbon clusters deteriorate device performance [8–11]. To prevent this degradation, various nitridation methods have been investigated using nitrous oxide (N_2O) or nitric oxide (NO) gas [7,12–15], nitric acid [16], and N_2 plasma treatment [17,18]. The nitridation process breaks C—C bonding in carbon clusters and forms C—N bonds, resulting in an improvement in electrical characteristic [7,19]. Otherwise, rapid thermal processing using N_2O has introduced the oxynitridation of 4H-SiC with reduced trapped charges [20,21].

In recent years, 4H-SiC devices have been fabricated using chemical vapor deposition (CVD) [22,23] or atomic layer deposition (ALD) [4,5,24]. Gate oxides deposited by these methods suppress carbon clusters and exhibit superior MOS characteristics. However, the quality of the deposited oxide is worse than that of oxides grown by thermal oxidation, thus, requiring subsequent heat treatment to improve its quality. We have already reported that the flat-band voltage (V_{FB}) was changed by the NO post-deposition annealing (PDA) [4]. In this case the V_{FB} was 1.55, 1.36, and 1.11 V after 1, 2, and 3 hours-long PDA, respectively. On the other hand, sputtering using physical vapor deposition (PVD) is a widely used method for fabrication of thin films. Its advantages include a fast sputtering rate and low-temperature deposition [25,26]; however, there have been few reports on 4H-SiC MOS fabricated using the sputtering method. In addition, further detailed research on the gate dielectric of 4H-SiC MOS is still needed.

In this study, sputtering for fabrication of the gate dielectric in SiO_2/4H-SiC MOS capacitors was investigated. The PDA was performed to improve the gate leakage current and capacitance–voltage (*C*–*V*) characteristics after deposition of the gate oxide. N_2, NH_3, O_2, and NO-based PDA were applied to the SiO_2/4H-SiC MOS capacitors, respectively, and the oxidation and nitridation of PDA analyzed and compared.

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Table 1
Measured thickness and refractive index at 632.8 nm of the SiO_2 on 4H-SiC before and after N_2, NH_3, O_2, and NO PDA.

Samples	Thickness (nm)		Refractive index at 632.8 nm	
	Before annealing	After annealing	Before annealing	After annealing
As-dep.	47.04	–	1.51	–
N_2 PDA	46.90	38.80	1.51	1.48
NH_3 PDA	46.43	33.70	1.51	1.67
O_2 PDA	45.19	47.38	1.51	1.47
NO PDA	45.46	38.90	1.52	1.47

2. Experimental

The SiO_2/4H-SiC MOS capacitors were fabricated with a 12-µm-thick n-epitaxial layer on 4-off-axis Si face *n*-type 4H-SiC wafers. The dopant in the epitaxial layer was nitrogen at a doping concentration of $5 \times 10^{15}\,cm^{-3}$. The surface of the 4H-SiC was cleaned using sulfuric acid and RCA to remove impurities, and then the 4H-SiC was transferred to a sputtering chamber. The contamination should influence the experimental results. The chamber was maintained at a base pressure, which was less than 9×10^{-7} Torr for reducing contaminants. The pre-sputtering was also performed to reduce the contamination of the target before main deposition. A pure silicon target and O_2/Ar mixed gas as the oxidant were used for reactive sputtering of SiO_2. The sputtering process was performed under a pressure of 6×10^{-3} Torr at room temperature. The SiO_2 in all devices was sputtered at same time. The SiO_2 on 4H-SiC was annealed in a tube furnace. Post-deposition annealing (PDA) was then conducted under ambient N_2, NH_3, O_2, and NO at 1200 °C for 2 h each. The thickness of the SiO_2 (t_{ox}) before PDA was within the range 45–47 nm, and the value of t_{ox} was changed by the PDA, as shown in Table 1. The 100-nm-thick Ni gate was evaporated by an electron beam. After photolithography, the Ni was etched with a solution of sulfuric, nitric, and acetic acid. The gate area of all capacitors was $1.3 \times 10^{-3}\,cm^2$ which was measured optical microscope. Finally, Al with a thickness of 100 nm was deposited on the backside using a thermal evaporator to form an Ohmic contact. The pressure, temperature, and time of the chamber were 600 s, 40 °C, and 2×10^{-5} Torr, respectively. The thermal process did not proceed to suppress the degradation of the surface contact. The *C–V* and time-zero dielectric breakdown characteristics were measured using a 4200-SCS analyzer (Keithley, Cleveland, OH, USA) at room temperature. A total of 20 MOS capacitors were measured and *C–V* measurements were conducted at a frequency of 1 MHz. To reliably measure the accumulation and inversion regions, a gate voltage from −6 to 10 V was applied in a reverse sweep. Interface trap density (D_{it}) was also measured by conductance method using HP4194A.

3. Results and discussion

Physical and chemical properties of sputtered SiO_2 on 4H-SiC were investigated. The thickness and refractive index were measured using spectroscopic ellipsometry (ESM-300, J. A. Woollam Co., Inc.). When the angle of incidence was 65 and 75°, the spot size of the ellipsometry was 7 and 12 mm in the diameter of longitudinal direction, respectively. The refractive index and thickness (t_{ox}) of SiO_2 before and after N_2, NH_3, O_2, and NO PDA are listed in Table 1. The N_2, NH_3, and NO PDA decreased t_{ox} by 17, 27, and 17% compared with a nontreated sample. The O_2 PDA increased slightly t_{ox} due to oxidation. For the cases of N_2 and NH_3 PDA, it is presumed that some part of the silicon, which was not chemically bonded with oxygen, dissociated from SiO_2 at high temperature. Si-N bonds were revealed by X-ray photoemission spectroscopy (XPS) and were attributed to strong nitrogen radicals inherent in NH_3 PDA that broke Si—O bonds to form Si—N bonds. In contrast, after O_2 PDA, t_{ox} increased, due to the reaction of the residual silicon with oxygen resulting in SiO_2 formation.

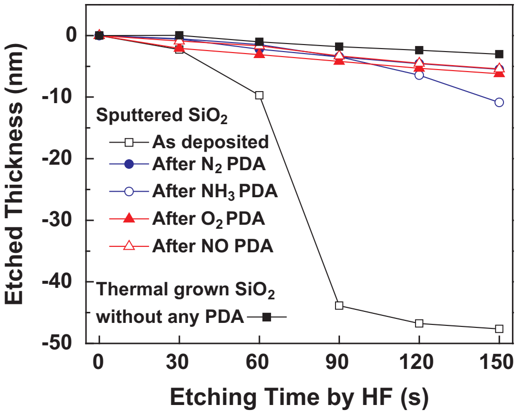

Fig. 1. Measured etching rate of the SiO_2 on 4H-SiC before and after N_2, NH_3, O_2, and NO PDA by dilute HF.

For SiO_2 on 4H-SiC after NO PDA, we expected an increase in t_{ox} due to oxidation. However, t_{ox} after NO PDA was comparable to t_{ox} after N_2 PDA because of a densification of sputtered SiO_2 and coexisting N radicals. Note that the refractive index of as-deposited oxide is 1.51, which is higher than the ideal value of SiO_2, 1.46. This indicates that the as-deposited oxide is not in the stoichiometric state of SiO_2. After N_2, O_2, and NO PDA, the dissociation or oxidation of residual silicon reduced the refractive index to 1.48, 1.47, and 1.47, respectively, which is close to the ideal refractive index of SiO_2. The N_2 PDA dissociated Si—Si bonds while the O_2 and NO PDA dissociated Si—Si bonds and formed Si—O bonds. The refractive index increased from 1.51 to 1.67, after NH_3 PDA; this value is almost identical to the refractive index [27] of nitrided SiO_2 by NH_3, indicating that a nitridation reaction occurred on 4H-SiC during NH_3 PDA.

An SiO_2 etching test using dilute HF (0.5% in H_2O) was performed for analysis; the measured etching rate is shown in Fig. 1. A low etching rate indicates a dense film. For comparison, SiO_2 was also grown on 4H-SiC using dry oxidation and the etching rate measured. Compared with other results, the t_{ox} value of as-deposited SiO_2 immediately decreased after dipping in the etchant due to porous and non-stoichiometric oxides. However, the etching rate of SiO_2 after PDA was reduced significantly, indicating that PDA stabilizes SiO_2 by a densification process and chemical reaction. The etching rate of SiO_2 after PDA was slightly higher than that of grown SiO_2 by dry oxidation. The thickness reduction of SiO_2 over time by HF dipping had a linear relationship with etching time. However, the etching rate of SiO_2 after NH_3 PDA increased as it went inward from the surface; it is likely that SiO_2 after NH_3 PDA is an unstable oxynitride rather than a stable silicon nitride.

For analysis of the chemical bonding at the SiO_2/4H-SiC interface, XPS was conducted using monochromatic Al *Kα*. Si 2p and N 1s spectra were recorded. The SiO_2 on 4H-SiC after N_2, NH_3, O_2, and NO PDA was etched using dilute HF (1% in H_2O). The etching time of SiO_2 after N_2, NH_3, O_2, and NO PDA was 155, 155, 510, and 360 s, respectively, because the t_{ox} of each sample was different. The remaining SiO_2 thickness was 5 nm for the samples of N_2 and NH_3 PDA after etching. The thickness of SiO_2 in the samples using O_2 and NO PDA was 7 nm. The measured XPS data were aligned to the peak of the 4H-SiC substrate [28]. Si 2p and N 1s spectra of the samples after N_2, NH_3, O_2, and NO PDA is shown in Fig. 2. Chemical bonding in each peak was analyzed based on the literature [26,28–31]. After N_2 and NH_3 PDA, the resulting samples showed an Si—N peak, while the sample after O_2 PDA did not. This confirms that N_2 and NH_3 PDA formed silicon nitride (SiN_x) at the interface, as evidenced by the N 1s spectrum. On the other hand, the thickness of SiO_2 can affect the shoulders of the XPS spectra and distort the intensity of SiN_x. Our group has reported that the SiN_x was detected