Remote NH$_3$ plasma passivation on the interface between the remote plasma Al$_2$O$_3$ atomic layer deposited and 6H SiC substrate

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We investigated the effects of remote NH$_3$ plasma passivation on the interfacial properties between 6H SiC substrate and Al$_2$O$_3$ gate dielectric deposited by remote-plasma atomic layer deposition in a metal-oxide-semiconductor device. X-ray photoelectron spectroscopy and Auger emission spectroscopy analysis reveal that nitrogen is clearly incorporated into the Al$_2$O$_3$/SiC interface. Atomic force microscopy shows negligible damage on the plasma treated SiC surface. A lower leakage current and higher breakdown voltage are attained by the remote plasma passivation. The interfacial state density of the as-deposited sample with the NH$_3$ treatment is about 4 times lower than that of sample without nitrogen passivation and post forming gas annealing improves the interface quality further.

Keywords: SiC, ALD Al$_2$O$_3$, Plasma Passivation.

Introduction

Increasing interest in attaining higher energy efficiency leads to look for alternative materials and devices. In particular, wide band gap (WBG) materials have been strongly investigated as enablers to achieve a higher efficiency and used for power device applications due to their excellent material properties. Of the WBG materials being investigated, silicon carbide (SiC) is the most attractive material because SiC has a large band gap energy (3.2 eV for 4H-SiC, 3.0 eV for 6H-SiC) and its dielectric breakdown field strength is up to 10 times as high as that of silicon (Si). Furthermore, SiC has a high thermal conductivity and saturated electron drift velocity compared to Si. Owing to these superior electrical properties, a SiC-based metal-oxide-semiconductor (MOS) device becomes a strong candidate for high power, high temperature and high frequency devices [1-3]. In particular, one of the main advantages of SiC against other WBG semiconductor materials such as GaN and diamond is that silicon dioxide (SiO$_2$) for a gate dielectric can be thermally grown on SiC substrates, which have been commonly used for Si-based MOS devices.

However, it turns out that the thermally grown SiO$_2$ on SiC has at least one or two orders of magnitude higher interfacial state density ($D_{it}$) than that of a SiO$_2$/Si interface [4-6]. Alexey Gavrikov et al. [7] and Deak et al. [8] have suggested the mechanisms of defect generation causing a higher $D_{it}$. In general, incomplete oxidation and intrinsic oxygen deficiency are considered as the main reasons for a higher $D_{it}$ [9]. Incomplete oxidation causes the accumulation of carbon clusters and leads to defects at the interface between SiO$_2$ and SiC during the oxidation process. These effects degrade the electrical properties in MOS devices such as electron mobility because defects act as electron trap sites.

Various passivation techniques have been proposed to reduce $D_{it}$. Nitrogen passivation at the interface between SiO$_2$ and SiC has been reported by either oxidation or pre-/post-oxidation annealing under nitric/nitrous gases [10-11]. Hydrogen passivation has also been suggested [12]. A plasma pretreatment with a nitrogen or hydrogen ambient has been proposed as an alternative passivation technique [13-14]. Despite the suppressed $D_{it}$ with the aid of thermal or plasma passivation techniques, poor interfacial quality could be induced to the area between thermally grown insulators and SiC substrates due to carbon precipitates or lattice mismatch during the high temperature oxidation step. Therefore, gate insulators with a high dielectric constant (high-k dielectrics) such as HfO$_2$, Al$_2$O$_3$, MgO, Gd$_2$O$_3$ and SiN using a deposition method have been investigated as an alternative gate dielectric to replace the thermally grown SiO$_2$ for further $D_{it}$ reduction [15-20].

Recently, atomic layer deposition (ALD) has been widely used for gate dielectric deposition due to the precise thickness control and uniform film properties [21]. Compared to conventional thermal ALD, plasma-enhanced ALD (PEALD) provides several advantages such as a lower deposition temperature and higher film
density due to a higher reactivity of the precursor while a direct plasma could induce damage on the deposited film or substrate. However, alternative remote plasma ALD (RPALD) is proposed to minimize the direct plasma effect because a plasma formed away from the substrates induces less damage on the films [22]. Among the numerous high-k dielectrics being studied, Al₂O₃ is a promising gate dielectric due to a reasonably high k (~10) [23], excellent lattice mismatch with SiC, good thermal stability and large conduction band offset in the SiC-Al₂O₃ system. However, despite several attempts to investigate an ALD Al₂O₃/SiC system with interfacial passivation [24-28], a RPALD Al₂O₃/SiC system in conjunction with remote NH₃ plasma passivation has not been studied yet. In addition, the remote plasma treatment causes less damage compared with the direct plasma treatment. It is expected to obtain a better smooth surface and interfacial quality using a RPALD high-k gate dielectric on a SiC substrate with the remote plasma passivation. Therefore, it is worthwhile to evaluate interfacial properties between RPALD Al₂O₃ and remote plasma passivated SiC in a MOS device for potential power device applications.

In this paper, therefore, we fabricated a MOS device with a Pt/RPALD Al₂O₃/remote NH₃ plasma passivation/SiC structure and evaluated the effects of the remote NH₃ plasma passivation using a remote plasma ALD system.

Experimental

(0001) Si faceted n-type 6H-SiC substrates were used for the device fabrication. First, the samples were dipped into a dilute hydrofluoric acid (HF) solution with de-ionized (DI) water (HF (47%) : DI water = 10 : 1) for 1 minute, followed by DI water rising and N₂ gas drying. Prior to gate dielectric deposition, the sample received the remote plasma passivation. The sample was irradiated with a NH₃ plasma (denote “NH₃” sample) under 0.5 torr (66.7 Pa) gas pressure, 200 sccm gas flow rate and 250 W RF power for 20 minutes in the remote plasma chamber. It is expected that the remote plasma treatment would give less damage compared to the direct plasma treatment. The substrate was heated up to 300°C during the plasma treatment. For comparison, the other sample (denote “HF-Last” sample) was not exposed to plasma passivation. Subsequently, the samples were loaded into the RPALD chamber for Al₂O₃ preparation using a trimethyl-aluminum (TMA, Al(CH₃)₃) source, O₂ oxidant gas (50 sccm) and Ar purging gas (80 sccm) under 0.5 torr (66.7 Pa) working pressure. TMA and O₂ pulse time was 1 s and 6 s, respectively. The plasma exposure process started just after 1 s O₂ gas injection. The total exposure time for 1 cycle was 5 s. Our RPALD process was conducted at 100 W RF power for 130 cycles and the substrate was heated to 350°C during Al₂O₃ deposition. 100 nm-thick Pt was then evaporated as a gate electrode and a lift-off process was adopted for electrode patterning. After back-side Ohmic contact formation, forming gas annealing (FGA) was performed at 400°C for 30 minutes in N₂ + H₂ (5%). Using an ellipsometer (Nano-view SE MG-1000), 175 Å and 167 Å thicknesses of Al₂O₃ were measured for “HF-last” and “NH₃” samples, respectively. Atomic force microscopy (AFM, park systemsXE-100) images were taken to investigate the plasma induced-damage on the surfaces of the SiC substrates during the passivation process with a non-contact mode. X-ray photoelectron spectroscopy (XPS, ESCA Lab-2220I, VG) with a Mg source and Auger emission spectroscopy (AES, PHI 680) were used to analyze the chemical composition and depth profiles at the Al₂O₃/NH₃ plasma passivated SiC interfaces. For electrical characterizations, capacitance-voltage (C-V), leakage current density-voltage (J-V) using a probe station (MS-TEC) and a semiconductor analyzer (Agilent B1500A) were used. The C-V measurements were conducted at 100 kHz. Finally, Dₓ values were attained using conductance method.

Results and Discussion

Figure 1 (a) and (b) shows AFM images of “HF-Last” and “NH₃” treated SiC substrates, respectively. Root-mean-square (RMS) roughness values are 4.04 Å and 2.59 Å for “HF-last” and “NH₃” samples, respectively. It is clearly confirmed that the “NH₃” plasma pretreatment did not cause damage on the SiC surface during the passivation steps and even relatively improved the surface roughness compared with the non-plasma passivated “HF-Last” sample.

XPS spectra of Si 2p and N 1s of the “HF-Last” and “NH₃” samples are shown on Figure 2 (a) and (b), respectively. XPS spectra of the samples are calibrated by using the binding energy of the C 1s peak (285 eV) as a reference. Si 2p peaks of the “HF-Last” sample consist of three peaks which are located at 98.49 eV, 100.34 eV, and 101.64 eV and 102.74 eV for Si-Si, Si-C, Si-O and Si-N bonds. However, Si 2p peaks of the “NH₃” sample exhibit four different peaks at 98.49 eV, 100.34 eV, 101.64 eV and 102.74 eV for Si-Si, Si-C, Si-O and Si-N bonds.

![AFM images for SiC surfaces with “HF-Last” treatment (a) and “NH₃” plasma passivation (b). RMS values of “HF-Last” and “NH₃” samples are 4.04 Å and 2.59 Å, respectively.](image-url)
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N bonds, respectively. N 1s peak is observed only on the “NH$_3$” sample and has 399.06 eV for the N-C bond and 397.21 eV for the N-Si bond. The Si-N bond in the Si 2p peaks and N 1s peaks of the “NH$_3$” sample from this XPS analysis indicate that nitrogen is incorporated into the Al$_2$O$_3$/SiC interface and a resultant interfacial layer is formed.

In addition, Al, O, N, Si and C elements through the Al$_2$O$_3$/SiC system are detected by AES depth profile analyses as shown in the figure 3. AES analysis supports the idea that nitrogen piles up at the Al$_2$O$_3$/SiC interface. Therefore, the NH$_3$ plasma treatment on SiC prior to RPALD Al$_2$O$_3$ is proven to be an effective passivation technique.

Figure 4 (a) and (b) shows C-V and J-V characteristics of the “HF-Last” and “NH$_3$” samples, respectively. Compared with the as-deposited “HF-Last” sample, a lower flatband voltage (V$_{FB}$) is observed with the as-deposited “NH$_3$” sample, indicating an interfacial layer (IL) such as SiN or SiON formation and nitrogen induced positive fixed charge generation. However, after the annealing, the shift of the C-V curve from the “NH$_3$” sample is not substantial while a noticeable negative C-V shift with the “HF-Last” sample is observed. The thermally induced V$_{FB}$ instability of a MOS device with noble metals such as Pt and high-k gate dielectrics are well known phenomena [29-30]. The negative V$_{FB}$ shift after annealing can be explained by the modified energy band diagram. Thermally generated oxygen vacancies and charges due to oxygen diffusion from the high-k metal oxide during annealing cause the newly formed electrostatic potential, leading to a band bending [31-32]. However, it can be speculated that SiN or SiON IL produced by the NH$_3$ treatment can block oxygen out-diffusion and reduce oxygen vacancy generation, resulting in negligible V$_{FB}$ shift. From the J-V characteristics of “HF-Last” and “NH$_3$” samples after FGA, a lower leakage current density and higher breakdown voltage (V$_{bd}$) are obtained from the “NH$_3$” sample than the “HF-Last” sample. Inset in figure 4 (b) represents V$_{bd}$ distribution for the “HF-Last” and “NH$_3$” samples. A wider V$_{bd}$ distribution is observed with the “NH$_3$Last” while a tighter V$_{bd}$ distribution is attained with the “NH$_3$” samples, indicating a poor interface with the wet-chemically
cleaned SiC substrate.

The Dit distribution as a function of energy levels for the “HF-Last” and “NH₃” samples without and with FGA is shown on figure 5. E_c and E_t are the energy levels of the conduction band and trap in the 6H-SiC substrate, respectively. It is found that the interfacial state density of the as-deposited sample with a NH₃ plasma treatment is about 4 times lower than of a sample without nitrogen passivation and subsequent post forming gas annealing improves the interfacial quality by more than one order of magnitude in Dit.

Before the annealing, the Dit values attained at E_c - E_t = 0.5 eV are 1.24 × 10¹⁴ and 3.38 × 10¹³ eV⁻¹ cm⁻² for the “HF-Last” and “NH₃” samples, respectively. And Dit after FGA are significantly decreased to 7.05 × 10¹² and 8.78 × 10¹¹ eV⁻¹ cm⁻² for the “HF-Last” and “NH₃” samples, respectively. A steeper Dit increase as the energy approaches E_c, which is attributed to near interfacial traps, is also substantially suppressed with the NH₃ plasma treatment. Regardless of FGA, lower Dit values with the NH₃ plasma passivation indicate the Al₂O₃/SiC interface is effectively passivated with nitrogen leading to a suppressed interfacial state density.

Conclusions

In summary, we have investigated the effects of remote NH₃ plasma passivation on SiC MOS capacitors with an Al₂O₃ gate dielectric prepared by remote-plasma ALD. Negligible surface damage and improved surface roughness are attained from “NH₃” remote-plasma passivation. Nitrogen incorporation into the interface between Al₂O₃ and SiC was confirmed by XPS and AES analysis. A lower leakage current, higher breakdown voltage and suppressed interfacial state density were attained by the remote NH₃ plasma nitridation in conjunction with FGA. Remotely processed ALD high-k oxide and NH₃ treatment could improve SiC surfaces and are applicable to achieve better power device performance. However, further process optimization such as exposure time, intensity and different gases are taken into consideration to improve SiC interfacial quality.

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References

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