Characterization of Metal-Insulator-Semiconductor Capacitors with Insulating Nitride Films Grown on 4H-SiC

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Nitrided layers were grown on a 4H-SiC(0001) by plasma nitridation method using NH₃. Nitridation was enhanced with increasing RF power and with decreasing growth pressure. However, the exact Capacitance-Voltage properties of the nitride layer/SiC interface could not be determined because of the leakage current. The SiO₂ film was deposited on the nitrided layer by thermal chemical vapor deposition method using Tetraethoxysilane (TEOS) omit obtain an insulating film with sufficient thickness and an exact interface property. The interface state density Dᵢ was evaluated from C-V characteristics by the Terman method. It was indicated that Dᵢ near the mid gap of the TEOS oxide/nitride layer structure was higher than those of the TEOS-SiO₂ films and thermal oxide film. The Dᵢ of the oxide/nitride layer successfully decreased by post NH₃ annealing.

KEYWORDS: SiC, MIS, nitridation, SiN, interface state density

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1. Introduction

The excellent electrical and physical properties of silicon carbide (SiC) and its ability to form an insulating silicon dioxide (SiO$_2$) layer by thermal oxidation make it a very attractive material for high temperature and high power metal-oxide-semiconductor (MOS) devices. In the case of Si, MOS technology is based on the thermally grown SiO$_2$, as a gate dielectric material, due to its high reliability, very low interface defect density and high resistivity. However, both 6H-SiC and 4H-SiC MOS field-effect transistors (MOSFETs) suffer from low electron mobility in n-channel inversion layers.$^{1-4}$

Several research groups pointed out that severe degradation of the surface electron mobility in 6H-SiC and 4H-SiC MOS devices is due to the high density of interface electron traps close to the conduction band edge.$^{1-4}$

To realize SiC based MOS devices, it is important to fabricate the high quality gate oxide and SiC/SiO$_2$ interface with minimum defect density. At present, the defect state density ($D_{it}$) at the SiO$_2$/4H-SiC interface has been reduced to $10^{11}$-$10^{12}$ eV$^{-1}$cm$^{-2}$, which is not enough for device applications.$^{5}$ As a solution, post-annealing of thermal oxide in N$_2$O or NO has been reported to be effective in improving the SiO$_2$/4H-SiC interface.$^{6}$ Nitrogen atoms can form strong Si≡N bonds which passivate interface traps originating in dangling and strained bonds.

On the other hand, the silicon nitride (Si$_3$N$_4$) films have been studied as a potential material in replacing silicon-dioxide (SiO$_2$).$^{7-9}$ Their main advantages are low density of surface state and high dielectric permittivity.

Previously, we reported that the nitride layer could be grown on the SiC surface by a plasma nitridation method using mixed gasses of NH$_3$ and N$_2$.$^{10}$ However, the thickness of the sample was about several nm. In this work, a SiO$_2$ layer on the nitride layer formed by thermal CVD method using tetraethylxysilane(TEOS) in order to obtain enough thickness for interface characterization by C-V method.

2. Experimental

The nitride layer was formed on the silicon-faced n-type 4H-SiC(0001) wafers (Cree Research Inc., Research grade, $\sim 0.1\Omega$cm). The carrier concentration was estimated to be
2.5 \times 10^{17} \text{cm}^{-3} \) from C–2V plot of Schottky contact. As the pretreatment, the substrates were thermally oxidized for 2h at 1000°C in O_{2}+H_{2}O atmosphere and then were etching in a 5% hydrofluoric acid to obtain a damage free surface. After the pretreatment, the substrate was immediately set in the nitridation furnace.

The nitridation furnace was consisted of water-cooled double quartz tubes and a graphite substrate holder. The graphite susceptor was heated by an induction coil. An optical thermometer was used to measure the temperature of the substrate. The substrate temperature reported in this article is the surface temperature of the substrate. Before the nitridation, the furnace was evacuated by a rotary pump and was purged several times with N_{2} to reduce the residual oxygen. The plasma nitridation was carried out at substrate temperatures of 800°C in a NH_{3} atmosphere for 1h. The NH_{3} gas was diluted to 50% with N_{2}. The flow rate was maintained at 50 sccm during the nitridation process. The pressure during the nitridation varied from 0.5 to 5 Torr, and the RF power for the plasma generation varied from 7 to 70 W.

The SiO_{2} films were deposited on the nitride layer by a thermal CVD using TEOS. The thermal CVD system consists of a hot wall quartz furnace, a graphite susceptor and a TEOS cylinder in the thermostatic bath. The TEOS vapor was introduced in the furnace by bubbling with carrier N_{2} gas. The N_{2} flow rate and growth pressure were maintained at 20 sccm and 1 atm, respectively. The temperature of the substrate and TEOS cylinder were 750°C and 75°C, respectively.

The Al electrode of 0.5 mm in diameter was deposited on the insulating layer to form the MIS diode. The ohmic contact was formed on the back surface by depositing Ni layer and annealing at 1000°C for 15 min.

X-ray photoelectron spectroscopy(XPS) and C-V measurement were used to characterize the insulator layer. A capacitance meter (HP 4280A) was used to measure the C-V characteristics. The signal level was 30 mV at 1MHz. The interface state density was estimated by Terman method.\textsuperscript{11)
3. Results and Discussions

Figure 1 shows the dependence of the film composition on the RF power. The concentration ratio of Si-C configuration decreased and the N content increased with increasing RF power. This means that the nitridation is enhanced with increasing RF power. Thus, it was suggested that the NH$_x$ radicals increased with increasing RF power.

The dependence of concentration ratio on the growth pressure is shown in Fig. 2. The N ratio increased with decreasing growth pressure. Thus, the nitridation reaction could be enhanced with decreasing growth pressure. The result implies the enhancement of the N extraction reaction with increasing growth pressure.

Figure 3 shows C-V curve of nitrided layer. Sahin and his co-workers reported anomalous peaks in the C-V curves of p-Si metal-interface layer-semiconductor (MIS) Schottky diode,\textsuperscript{12} which were similar to that on the C-V curve in Fig. 3. They showed that the forward biased C-V plot of Schottky diode exhibited a peak due to the substrate series resistance. The current seemed to flow through the thin nitride layer in the sample shown in Fig. 3, and the diode exhibit the C-V characteristics similar to the MIS Schottky contact. In order to estimate the interface states density, the leakage current must be reduced to the low value enough to C-V measurement.

The thickness of nitride layer estimated from C-V characteristics and TEM images was about 5nm. Thus, it is difficult for exact characterization of interface because of the leakage current originating in extremely thin nitride layer. As a solution, a SiO$_2$ film was deposited on the nitride layer by thermal CVD using TEOS in order to obtain an insulator film with enough thickness.

Figure 4 shows C-V characteristics of the SiO$_2$ film on the nitride layer. The leakage current was confirmed to be reduced by SiO$_2$ film deposition and the C-V characteristics could be estimated. The flat band voltage of the SiO$_2$/nitride layer was larger than the other oxide films. It is suggested that the nitride layer has negative fixed charge. This charge results in increase of threshold voltage of n-channel MIS FET. The electrons trapped at the interface states may one of the origins of the positive flat band voltage. The post annealing was effective to decrease the flat band voltage as shown in Fig. 6.
The distribution of $D_{it}$ on the surface potential is shown in Fig. 5. The $D_{it}$ of the nitride layer was higher than that of the other oxide layer. The high value of interface state density suggested that traps were formed at and/or near the interface between SiC and nitride layer. The interfaces traps seemed to be introduced during nitridation, because lower interface state density was detected for the sample using the single layer of TEOS CVD SiO$_2$ as the insulator. The traps between nitrided layer and SiO$_2$ might be another reason for the high interface state density, because lower interface state density was detected for the sample with the double layer of thermal SiO$_2$ and TEOS CVD SiO$_2$.

In order to improve the interface, the post NH$_3$ annealing was tried. It is widely known that the SiO$_2$/SiC interface improved by post annealing in N$_2$O, NO or H$_2$ atmosphere. It is considered that an annealing effect from both nitrogen and hydrogen is provided using NH$_3$. Figure 6 shows $D_{it}$ values of the oxide/nitride layer before and after NH$_3$ annealing. The $D_{it}$ value decreased after annealing. Thus, it is found the NH$_3$ annealing can also improve the interface property.

Jamet and his co-workers reported that nitridation of carbon clusters was effective to improve the interface properties of SiC MIS structure.$^6$ The same result seemed to be obtained in this work. The flat band voltage was decreased by post annealing in NH$_3$ atmosphere as shown in Fig. 4. This indicated that the fixed charges also decreased at/or near the interface. The formation of Si-N bond was detected by FTIR measurement after the post annealing. This may be another reason for decrease of flat band voltage. The interface state density was decreased by the NH$_3$ annealing, but the value was still higher than the values reported for other methods.$^6$,$^{13}$ Further improvements are necessary to use this structure to the SiC MISFET. The details are now under investigations.

4. Conclusion

We tried the nitride layer growth on 4H-SiC by plasma nitridation method. Nitridation was enhanced with increasing RF power and with decreasing growth pressure. The interface characteristics of ultra thin SiC nitride layer could be evaluated by depositing SiO$_2$ film on the nitride layer. The interface properties improved by the post NH$_3$ annealing technique.
References

Figure captions

Fig. 1. Concentration ratio vs RF power.

Fig. 2. Concentration ratio vs growth pressure.

Fig. 3. C-V curve of nitrided layer.

Fig. 4. C-V curve of SiO$_2$ layer on nitride layer.

Fig. 5. $D_{it}$ values of the SiO$_2$/nitride layer structure.

Fig. 6. $D_{it}$ values of the oxide/nitride layer before and after annealing.
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5

Figure 5 shows a plot of $D_{it}$ [eV$^{-1}$cm$^{-2}$] versus $(E - E_C)$ [eV] for three different layers: TEOS SiO$_2$ film, TEOS SiO$_2$ on thermal oxide layer, and TEOS SiO$_2$ on nitride layer. The data is represented by different markers: circles for TEOS SiO$_2$ film, triangles for TEOS SiO$_2$ on thermal oxide layer, and squares for TEOS SiO$_2$ on nitride layer. The x-axis represents the energy difference from the conduction band edge ($E - E_C$) in eV, while the y-axis represents the density of interface states ($D_{it}$) in eV$^{-1}$cm$^{-2}$. The graph also includes a notation for mid gap.
Figure 6