Plasma Nitridation of 4H-SiC by Glow Discharge of N_2/H_2 Mixed Gases

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Abstract. The mixed gas of nitrogen and hydrogen was used for the plasma nitridation of SiC surface. A small amount of hydrogen was effective to activate the nitridation reaction and suppress the oxidation reaction. The interface properties were improved by using nitride layer as an interfacial buffer layer of SiC MIS structure.

Introduction

Recently, interfacial defects between SiO_2 and SiC can be passivated effectively by nitridation in NO or N_2O ambient and a SiC MOSFET has been commercially available, but the high densities of interface traps near the conduction band edge has still remained as a serious problem. It is believed that the high density of interface traps is responsible for low inversion channel mobility in SiC MOSFETs.

We have reported that a direct nitridation layer might be a successful candidate for SiC passivation[1, 2, 5]. Shirasawa et al. reported on the formation of an epitaxial silicon oxynitride SiON layer on a 6H-SiC (0001) surface, which offers great potential for device applications[6]. We have tried to form a nitride layer on the SiC surface by plasma nitridation[7]. Pure nitrogen was used as the reaction gas. It has been difficult to get the nitride layer thicker than several nm even by the direct nitridation with the nitrogen plasma. In this work, we have tried to form a nitride layer using the mixed gas of N_2 and H_2 , instead of pure N_2. The atomic ratio of N and H was 0.95 and 0.05, respectively. A nitride layer has been successfully grown on the 4H-SiC (0001) surface by this method.

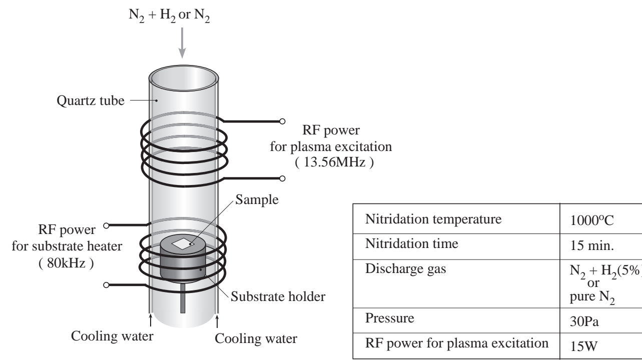
The X-ray photoelectron spectroscopy (XPS) was used to characterize the surface of nitrided SiC. The thickness of the nitride layer was several nm and too small to measure the C-V characteristics. A SiO_2 layer was formed on the nitride layer by thermal chemical vapor deposition (CVD) method using tetraethoxysilane (TEOS) to obtain sufficient thickness for interface characterization by C-V method[7].

Experimental

The substrate was a (0001) Si face of an epitaxial 4H-SiC obtained from Cree. The donor concentration was $1.5 \times 10^{16}\text{cm}^{-3}$. Immediately before the nitridation, the substrate was immersed in buffered HF to remove the native oxide on the surface.

Figure 1 shows the schematic representation of the nitridation setup.

The nitridation was carried out in the grow discharge of pure nitrogen. The plasma was excited by an inductively coupled RF power of 40W at 13.56MHz. The reaction was carried out under the pressure of 30Pa. The water cooled quartz tube was used as the reaction chamber. The substrate holder was made from graphite block and was heated by an inductively coupled RF power of 80 kHz up to 1400°C. The substrate temperature was measured by a pyro thermometer. The nitridation was tried at room temperature and at the temperature between 800°C to 1400°C for 15 min. The SiO_2 layer was deposited by the chemical vapor deposition using the TEOS as a source material to form the SiO_2/nitride/SiC structure with the insulating layer of enough thickness for the C-V measurement. Aluminum was evaporated to form a MIS diode. MIS diodes without nitride layer (SiO_2/SiC structure)



Nitridation temperature	1000°C
Nitridation time	15 min.
Discharge gas	$N_2 + H_2$(5%) or pure N_2
Pressure	30Pa
RF power for plasma excitation	15W

Fig. 1: Schematic representation of the nitridation setup.

were also prepared to examine the effect of nitridation on the interface property. In this case, the SiO_2 layer was deposited directly on the SiC surface by TEOS CVD, immediately after the treating the SiC surface with buffered HF. The TEOS CVD was carried out at 750°C for 15min. The thickness of the SiO_2 layer was estimated to be about 90nm. The XPS measurement was carried out to characterize the direct nitridation layer. The C-V characteristics of SiO_2/nitride/SiC MIS diodes and those of SiO_2/SiC MIS diodes were measured at 1 MHz to evaluate interface properties.

Results and Discussions

Figure 2(a) shows XPS spectra form SiC surface after plasma direct nitridation in pure nitrogen plasma or in the mixed gas plasma of nitrogen and hydrogen. The nitridation was carried out at 1000°C for 15 min. The O1s peak was smaller on the XPS spectrum of the sample prepared in the mixed gas than on that prepared in the pure N_2 gas, as shown in Fig. 2(a). The N1s peak was clearly detected on the spectrum for the sample prepared in the mixed gas.

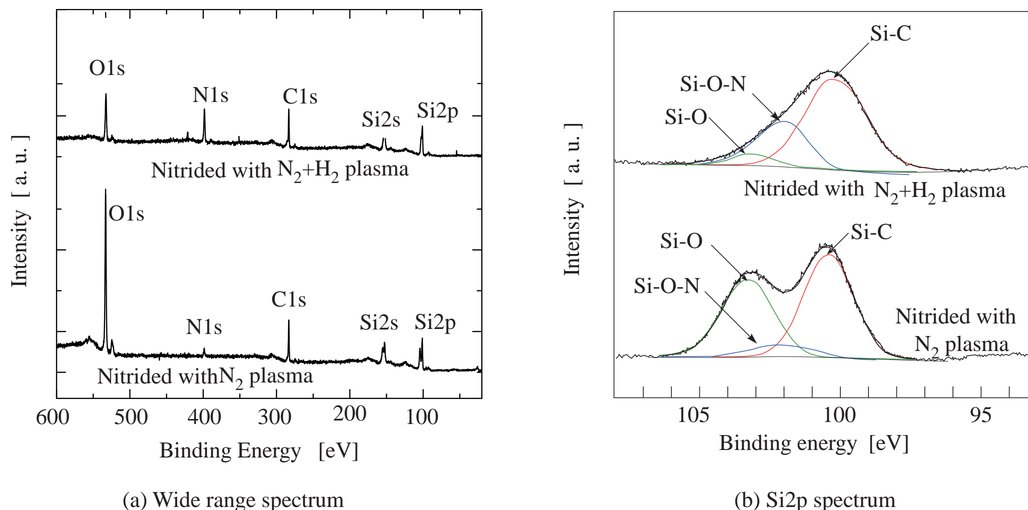
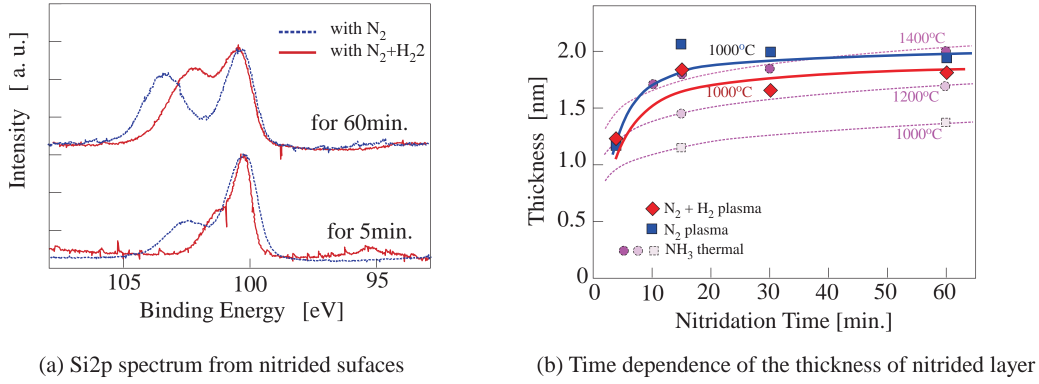


Fig. 2: XPS spectrum of the sample nitrided in the grow discharge plasma of mixed gases of N_2 and H_2(5%) or pure N_2.

Figure 2(b) shows Si2p spectra from nitrided SiC surfaces. It was apparent that the Si-O peak and the Si-O-N peak were from the nitride layer at the surface and the Si-C peak was from the substrate. The Si-O component was remarkable on the spectrum of the sample prepared using pure N_2 gas. On the other hand, the Si-O-N component was larger than Si-O component on the data of the sample prepared



(a) Si2p spectrum from nitrided sufaces

(b) Time dependence of the thickness of nitrided layer

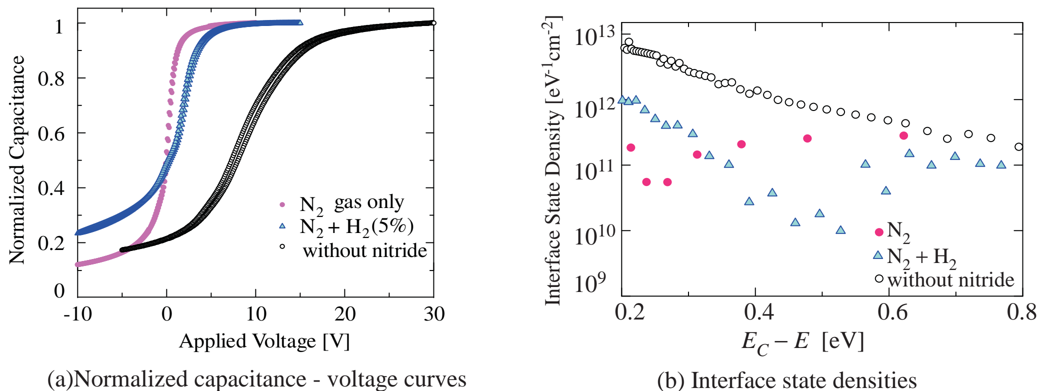
Fig. 3: Time dependence of the nitride thickness estimated from the Si2p spectra.

using mixed gases. These results indicated that the introducing H_2 gas was effective to activate the nitridation reaction, and also to suppress the oxidation reaction.

Figure 3(a) shows Si2p spectra for the samples prepared at 1000°C for 15 or 60min. The height of the Si-O or Si-N-O peak increased as increasing the nitridation time. The XPS signal form the substrate was still observed clearly after the nitridation for 60 min. This indicated that the thickness of the nitridation layer was very small. The thickness of the surface layer can be estimated from XPS data[3].

Figure 3(b) shows the time dependence of the nitride thickness estimated from Si2p spectrum, together with the data of the samples prepared by the thermal nitridation in N_2 and NH_3 mixed gases reported by Sakai et. al.[4]. The effective attenuation length of the photoelectron was assumed to be 2.5 nm in the surface nitride layer[3]. The thickness increased as increasing the reaction time until 15min. Almost no increase was observed in the thickness of nitridation layer after the nitridation time of 15min. The maximum thickness was estimated to be less than 2 nm, and was almost same to the value of the sample prepared by thermal nitridation with N_2 and NH_3 at 1400°C.

The thickness of the nitridation layer prepared with N_2 and H_2 mixed gases was slightly smaller than that of the sample prepared by pure N_2. This may be because the small diffusion constant of reaction species in nitride as compared to that in oxide. The oxynitride layer was formed by the plasma nitridation with N_2 and H_2 mixed gases as suggested by the data in Fig. 2(a). On the other hand, the oxide was the main component of the surface layer formed by the plasma nitridation with N_2. This resulted in the smaller diffusion constant of reaction species in the surface layer and the thinner surface layer of the sample layer prepared by the plasma nitridation with N_2 and H_2 mixed gases.



(a)Normalized capacitance - voltage curves

(b) Interface state densities

Fig. 4: Capacitance voltage curves and interface state densities of SiO_2/nitride/SiC MIS diodes.

The thickness of the nitride layer estimated from the XPS data was less than 2 nm and it is difficult to accurately characterize the interface because of the leakage current originating from the extremely thin nitride layer. As a solution, a SiO_2 film was deposited on the nitride layer by thermal CVD using TEOS to obtain an insulator film with sufficient thickness[5]. The nitride layer was expected to reduce the interface state density in the SiC MIS structure by acting as an interfacial layer between SiC and the insulating film such as SiO_2. The SiO_2/nitride/SiC MIS diode was fabricated to show the promising properties of the nitride as the interface layer between SiC and SiO_2.

Figure 4(a) shows the C-V curves of the samples prepared in the plasma of pure N_2 nitrogen or in the plasma of mixed gas of nitrogen and hydrogen. The frequency was 1MHz. The thickness of the SiO_2 was about 80 nm. For the sample prepared in the mixed gas plasma, the flat band voltage was about 3V, and was slightly higher than that of the sample prepared in pure nitrogen.

Figure 4(b) shows the interface state density estimated by Terman method from C-V curves shown in Fig. 4(a). Figure 4(b) indicated that the nitride layer was effective to improve the interface properties of the SiC MIS structure. Near the conduction band edge, the interface state density was slightly higher for the sample prepared in the plasma with N_2 and H_2 mixed gases than for the sample prepared with N_2.

Summary

The mixed gas of nitrogen and hydrogen was used for the plasma nitridation of SiC surface. A small amount of hydrogen was effective to activate the nitridation reaction and suppress the oxidation reaction. The nitride layer was effective to improve the interface properties of the SiC MIS structure. The remarkable improvement could not be observed on the interface properties by suing N_2 and H_2 mixed gases instead of the pure N_2.

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