Preparation and Characterization of Nitridation Layer on 4H SiC (0001) Surface by Direct Plasma Nitridation

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Abstract. A nitride layer was formed on a SiC surface by plasma nitridation using pure nitrogen as the reaction gas at temperatures from 800°C to 1400°C. The surface was characterized by XPS. The XPS measurement showed that an oxynitride layer was formed on the SiC surface by plasma nitridation. The high process temperature seemed to be effective to activate the nitridation reaction. A SiO₂ film was deposited on the nitridation layer to form SiO₂/nitride/SiC structure. The interface state density of the SiO₂/nitride/SiC structure was lower than that of the SiO₂/SiC structure. This suggested that the nitridation was effective to improve the interface property.

Introduction

The formation of SiO₂ layer on SiC by the conventional oxidation is one of the attracting factors of SiC as a material for power electronics devices. The high densities of interface states are believed to be responsible for the low inversion channel mobility in n-channel metal-oxide semiconductor field effect transistors (MOSFETs). Many efforts have been carried out to reduce or to passivate these interface states. It has been reported that such interfacial defects can be passivated effectively by nitridation in nitric oxide (NO) ambient [1].

However, the density of interface states at SiO_2/SiC interfaces has remained one or two orders of magnitude larger than that at SiO_2/Si interfaces. Silicon nitride is another candidate for the insulating layer of SiC MIS devices. Few papers have reported about nitridation of SiC surface. We have proposed that a direct nitridation layer might be a candidate for SiC passivation [2, 3, 4]. 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 [5]. Devyncka et al. focused on the electronic properties of the interface structure composed of an epitaxial silicon oxynitride layer on 6H-SiC (0001), using a density functional scheme[6].

We have tried to form an insulating nitride layer on SiC by direct nitridation[2,3,4]. Chai et al also reported a Si_3N_4 passivation layer grown on the 4H-SiC (0001) surface by direct atomic source nitridation at various substrate temperatures [7]. Although the direct nitridation seemed to be an attractive method to form insulating layer on SiC, it has been difficult to get the nitride layer thicker than several nm by direct nitridation method.

In this work, we have tried to form a nitride layer through exposure of SiC surfaces to nitrogen glow discharge plasma. A nitridation layer has been successfully grown on the 4H-SiC (0001) surface by this method. The chemical property of the nitridation layer was measured by X-ray photoelectron spectroscopy (XPS). However, the thickness of the nitride layer was several nm and too small to prepare the sample for the the capacitance–voltage (C–V) measurement. A SiO₂ layer was formed on the nitride layer by chemical vapor deposition (CVD) method using tetraethoxysilane (TEOS) to obtain sufficient thickness for interface characterization by C–V method. The C-V characteristics were measured at 1 MHz to evaluate interface properties.

Experimental

The substrate was a (0001) Si face of an epitaxial 4H-SiC obtained from Cree. The donor concentration was 1.5×10^{16} cm⁻³. Immediately before the nitridation, the substrate was immersed in buffered HF to remove the native oxide on the surface. The nitridation was carried out in the glow discharge of pure nitrogen. The plasma was excited by an inductively coupled RF power of 40W at 13.56 MHz. The reaction was carried out under the pressure of 30 Pa. 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 85 kHz up to 1400°C. The substrate temperature was measured by a pyro thermometer. The nitridation was carried out at room temperature and at temperature between 800°C to 1400°C for 15 min. The SiO₂ layer was deposited by the chemical vapor deposition using the TEOS as a source material to form the SiO₂/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 (SiO₂/SiC structure) were also prepared to examine the effect of nitridation on the interface property. In this case, the SiO₂ 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 SiO₂ layer was estimated to be about 90nm.

The XPS measurement was carried out to characterize the direct nitridation layer. The C-V characteristics of SiO₂/nitride/SiC MIS diodes and those of SiO₂/SiC MIS diodes were measured at 1 MHz to evaluate interface properties.

Results and Discussions

Figure 1 shows XPS spectrum from the plasma nitridation layer on SiC. Small peaks corresponding to N1s signal were appeared in the XPS spectrum as shown in Fig. 1. This suggested that a thin nitride layer was formed on SiC surface by the plasma nitridation. Although pure nitrogen was used as the reaction gas, the peak from O1s appeared in the XPS spectrum as shown in Fig. 1. The residual oxygen seemed to result in the formation of oxynitride layer by the plasma nitridation, because the background pressure was about 0.24Pa, even if the careful purging was carried out before the nitridation. The intensity of the O1s peak slightly decreased after the sputter etching with Ar ion in the XPS chamber.



Fig. 1 XPS spectra from SiC surface after the direct plasma nitridation at the substrate temperature of 1200°C.



Fig. 2 XPS spectra near the Si2p peak from SiC suface after the nitridation at the substrate temperature of 1200 °C.



Fig. 3 XPS spectra near Si2p peaks from SiC surface after the nitridation at the substrate temperture from RT to 1400°C. The surface was etched with Ar ion for 5sec.

Fig. 4 XPS spectra near N1s peaks rom SiC surface after the nitridation at the substrate temperture from RT to 1400°C. The surface was etched with Ar ion for 5sec.

Figure 2 shows the XPS spectrum from Si2p. The peak seemed to consist of Si-O, Si-O-N and Si-C bond. The component corresponding to Si-C bond was observed in the Si2p peak form the nitride layer. This was because the nitride layer was so thin that the photo electron from the substrate appeared at the surface of the sample through the nitride layer. The intensity of the peak corresponding to Si-O bond also slightly decreased after sputter etching the surface by Ar ion. This suggested that the surface of the nitride layer was oxidized during the transportation of the sample from the reaction chamber to the XPS chamber in the air.

Figure 3 shows the Si2p spectrum of the samples prepared at the temperature form 800°C to 1400°C, and at room temperature. The intensity of the peak from Si-O bond decreased and that of the peak from Si-N increased with the increasing process temperature. Figure 4 shows N1s peaks from the surface of the nitride sample at temperature from 800°C to 1400°C, and at room temperature. The high process temperature seemed to be effective to activate the nitridation reaction. The temperature of 1400°C was almost the upper limit of the nitridation system used in this work.



Fig. 5 High frequency C-V curves of SiO₂/nitride/SiC MIS diodes and a SiO₂/SiC MIS diode.



Fig. 6 Interface state densities of $SiO_2/nitride/SiC$ MIS structure and a SiO_2/SiC MIS diode estimated from C-V curves shown in Fig. 5.

Figure 5 shows C-V curves of the samples prepared at temperatures from 800°C to 1400°C, and also that of the sample without nitridation layer. The closed circles indicate the data of MIS diode without nitridation layer. The flat band voltage shifted toward the negative direction with increasing process temperature. The value of flat band voltage indicated that positive charges were formed near the interface by plasma nitridation at the higher temperature than 1200°C. C-V curves suggested that the interface property was improved by the plasma nitridation. Figure 3 and 4 indicate the Si-O-N bond or the nitrogen content increased as increasing the nitridation temperature. This may have some effect on the improvement of interface property.

The interface state density was estimated from these curves by Terman method to discuss the effect of the substrate temperature on the interface property. This method has been thought to contain inaccuracy especially near the conduction band, but it may be useful for the discussions based on relative comparisons. Figure 6 shows the interface state density estimated from the C-V curves shown in Fig. 5. The closed circles indicate the interface state density of MIS diode without nitridation layer. The interface state densities of SiO₂/nitride/SiC structures were almost one order of magnitude lower than that of the SiO₂/SiC suture. It was apparent that the nitridation was effective to reduce the interface state density. It was difficult to discuss the result by comparing with reported values obtained by other methods such as NO annealed SiO₂, because of the inaccuracy of Terman method.

Summary

The XPS measurement showed that the oxynitride layer was formed on the SiC surface by plasma nitridation. The high process temperature seemed to be effective to activate the nitridation reaction. The result suggested that the nitridation was effective to improve the interface property.

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