Thermal Stability and Electrical Properties of HfO_xN_y Gate Dielectrics with TaN Gate Electrode

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HfO_2 and HfO_xN_y films were deposited by plasma-enhanced chemical vapor deposition using $Hf[OC(CH_3)_3]_4$ as the precursor in the absence of O_2. The crystallization temperature of the HfO_xN_y films is higher than that of the HfO_2 film. Nitrogen incorporation in HfO_xN_y was confirmed by auger electron spectroscopy analysis. After post deposition annealing (PDA) at 800□, the EOT increased from 1.34 to 1.6 nm in the HfO_2 thin films, whereas the increase of EOT was suppressed to less than 0.02 nm in the HfO_xN_y. The leakage current density decreased from 0.18 to 0.012 A/cm^2 with increasing PDA temperature in the HfO_2 films. But the leakage current density of HfO_xN_y does not vary with increasing PDA temperature because an amorphous HfO_xN_y films suppresses the diffusion of oxygen through the gate dielectric.

Keywords: High-k gate dielectric, HfO_2, HfO_xN_y, TaN gate electrode

1. INTRODUCTION

A considerable interest has developed in the replacement of dielectrics for use SiO_2 in metal/oxide/semiconductor (MOS) devices in which the channel lengths are less than 100 nm[1]. The intent is to phase out conventional SiO_2 and oxynitrides due to excessive leakage current and reliability concerns. Alternative gate insulators with a higher electrical permittivity than SiO_2 are currently under widespread investigation for use in future generations of metal oxide semiconductor (MOS) transistors. Thus, high dielectric constant thin films offer the potential of increased capacitance in physically thicker films, thus providing a possible way to reduce direct tunneling[2].

Due to their thermodynamic stability when they are in contact with silicon, HfO_2 and its silicates have attracted considerable attention recently[3-5]. In addition, HfO_2 is compatible with a polysilicon gate without any barrier materials[6]. However, there are some potential concerns about low temperature crystallization, as well as the degradation of equivalent oxide thickness (EOT) due to the increase in interfacial layer thickness at high temperature. Nitrogen incorporation technology is studied to solve problems such as high leakage current density and high EOT[7-9].

In this work, nitrogen incorporation into HfO_2 films was investigated for gate dielectric applications.

2. EXPERIMENT

After standard cleaning of p-type Si (100) wafers, HfO_2 and HfO_xN_y films were deposited by plasma-enhanced chemical vapor deposition using hafnium tertiary-butoxide ($Hf[OC(CH_3)_3]_4$: Techno Semichem Co., Ltd., Korea) as the precursor in the absence of O_2. The deposition was performed at a temperature of 300□ and a pressure of 0.5 Torr. The precursor was vaporized in a bubbler maintained at 30~35□ and was carried into the reactor using argon as the carrier gas. The HfO_2 and the HfO_xN_y films were deposited in Ar and Ar+N_2 ambients, respectively with an rf power of 40 W. In order to avoid the damage at HfO_2 or HfO_xN_y/Si interface by plasma, thermal deposition of HfO_2 without plasma was performed at initial stage (around 1 minute) and then deposition by plasma was performed after 1 minute[5]. The TaN gate electrode was deposited using a reactive dc magnetron sputtering method. The deposition conditions were at a room temperature, a pressure of 5 mTorr, and a gas flow rate ratio (N_2/Ar) of 0.05. The TaN gate electrode for measurement of the electrical properties was patterned using lift-off lithography. The capacitor area for the MOS structure was 50×50 μm^2. The post deposition annealing (PDA) temperature was varied from 600 to 800□ for 1 min in a N_2 ambient. The post metal annealing (PMA) was performed at 900□ for 1 min in a N_2 ambient.

The crystal structure of HfO_2 and HfO_xN_y films was examined using x-ray diffraction (XRD; Rigaku, D/MAX-RC, Japan). The physical thickness of the HfO_2 or HfO_xN_y thin film was measured using Ellipsometry. The nitrogen incorporation into HfO_2 films was determined by Auger electron spectroscopy (AES; VG Scientific Microlab 310-D, United Kingdom). The capacitance-voltage (C-V) and current-voltage (I-V) characteristics were measured using an HP4194A impedance/gain-phase analyzer and an HP4156A semiconductor parameter analyzer, respectively.

3. RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of the 30 nm thick-HfO_2 and HfO_xN_y films annealed at various temperatures. Thicker films than those of typically used gate dielectrics were used because the crystallinity of ultrathin films cannot be identified by XRD. The annealing temperature was varied from 500 to 900℃ for 5 min in a N_2 ambient. As-deposited HfO_2 films at 300℃ (Fig. 1(a)) show broad ($\bar{1}$11), (111), and (200) peaks, indicating that the films are not crystalline in nature. Films annealed above 600℃ for 5 min in N_2 ambient were well-crystallized, showing monoclinic HfO_2 peaks of (110), ($\bar{1}$11), (111),

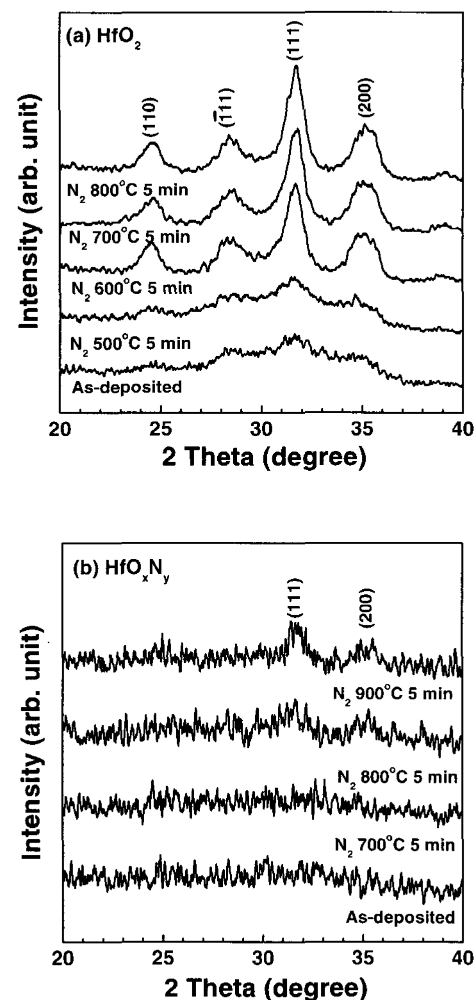

Fig. 1. X-ray diffraction patterns of (a) HfO_2 (~30 nm) and (b) HfO_xN_y (~30 nm) films annealed at various temperatures for 5 min in nitrogen ambient.

and (200) planes. On the other hand, HfO_xN_y (Fig. 1(b)) films are still amorphous after annealing at 800℃ in N_2 for 5 min. The HfO_xN_y films annealed at 900℃ show only broad (111) and (200) peaks. The crystallization temperature of HfO_xN_y is higher than 200℃ compared with that of the HfO_2 film, due to nitrogen incorporation into HfO_2.

Figure 2 (a) shows AES spectrum of HfO_2 (HfO_xN_y)/Si annealed at 600℃ in an nitrogen ambient for 1 min. Inset in Fig. 2 shows the evidence of the nitrogen incorporation into the HfO_2 film. As expected, nitrogen incorporation was detected in the case of the HfO_xN_y film. The nitrogen incorporation was observed at the interface and in the bulk of HfO_xN_y film as shown in AES depth-profile of Fig. 2 (b). The films deposited by PECVD using organometallic compounds were

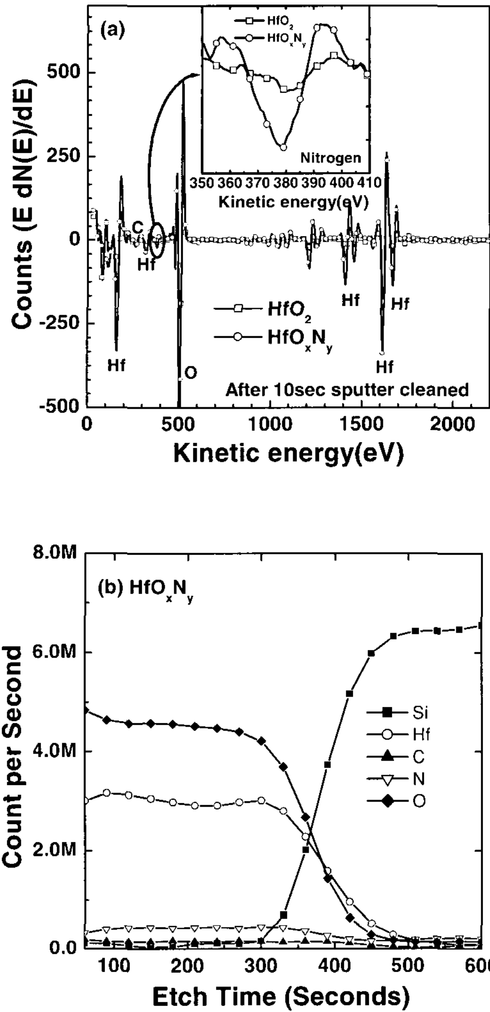

Fig. 2. (a) AES spectrum of 5.6 nm-HfO_2 (6 nm-HfO_xN_y)/Si annealed at 600℃ in nitrogen ambient for 1 min. Insert figure shows the nitrogen incorporation into HfO_2 film. (b) AES depth profile of HfO_xN_y/Si annealed at 600℃ in nitrogen ambient for 1 min.

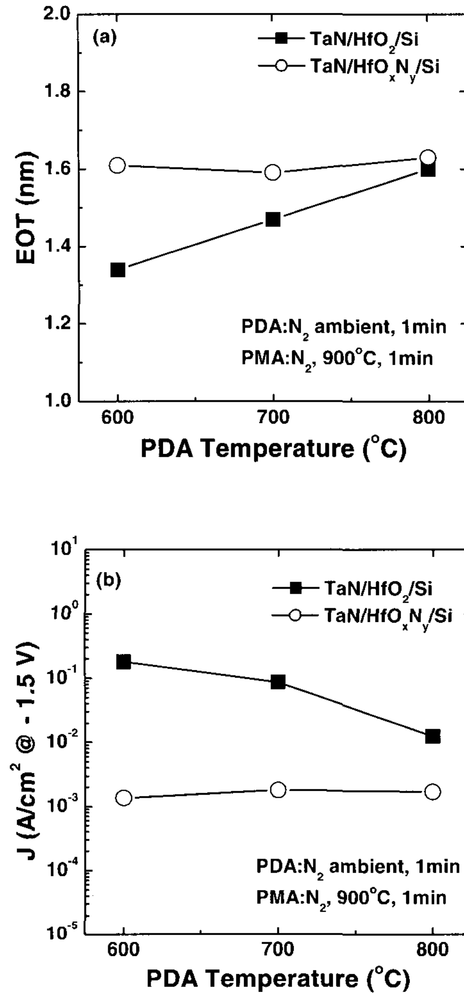

Fig. 3. (a) EOT and (b) leakage current density of TaN/HfO_2 (HfO_xN_y)/Si capacitors annealed at various post deposition annealing (PDA) temperatures for 1 min in N_2 ambient. The post metal annealing (PMA) was performed at 900□ for 1 min in a N_2 ambient.

contaminated by carbon in films because PECVD was performed at low temperature. Even though PECVD was performed at low temperature, carbons dissociated from the precursors in plasma atmosphere are activated enough to react with oxygen of the $Hf[OC(CH_3)_3]_4$ precursor and easily evaporated as carbon monoxide or carbon dioxide.

Figure 3 (a) shows EOT of TaN/HfO_2 (HfO_xN_y)/Si capacitors annealed at PDA temperatures for 1 min in N_2 ambient. The EOT values were extracted from the accumulation capacitance (-2 V) of *C–V* curves at 1 MHz and include the quantum mechanical deduction using the North Carolina State University CVC program [10]. After PDA at 800℃, the EOT increased from 1.34 to 1.6 nm in the HfO_2 thin films, whereas the increase of EOT was suppressed to less than 0.02 nm in the HfO_xN_y films. The excellent thermal stability of HfO_xN_y can be explained by incorporation of nitrogen. Figure 3 (b) shows the leakage current density of TaN/HfO_2 (HfO_xN_y)/Si capacitors annealed at PDA temperature for 1 min in N_2 ambient. The leakage current density decreased from 0.18 to 0.012 A/cm^2 with increasing PDA temperature in the HfO_2. The reduction in leakage current density can be explained by the increase of silicon dioxide thickness. On the other hand, the leakage current density of HfO_xN_y does not change with increasing PDA temperature because the HfO_xN_y films keep an amorphous state at high temperature.

Figure 4 shows the variation of the EOT of HfO_2 and

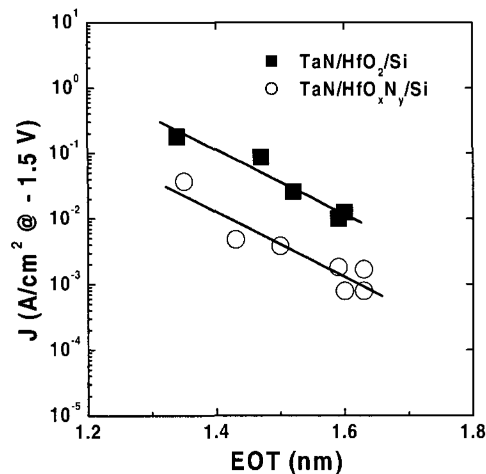

Fig. 4. Leakage current density vs. EOT of HfO_2 and HfO_xN_y. HfO_xN_y dielectrics show lower current density compared to HfO_2.

HfO_xN_y films as a function of leakage current density at −1.5 V. All the data in Fig. 4 were collected by PDA (N_2, 600~800℃, 1 min) and PMA treatment (N_2, 900℃, 1 min). The leakage current density of HfO_xN_y films is approximately one order of magnitude lower than HfO_2 at the same EOT.

4. CONCLUSION

HfO_2 and HfO_xN_y thin films for use in gate dielectric were deposited at 300□ on p-type Si (100) substrates using $Hf[OC(CH_3)_3]_4$ as the precursor by plasma enhanced chemical vapor deposition. Compared with HfO_2, HfO_xN_y show excellent properties including high crystallization temperature, low leakage current density, and good thermal stability. Leakage current density of HfO_xN_y is approximately one order of magnitude lower than that of HfO_2 for the same EOT. The excellent electrical properties of HfO_xN_y can be explained by incorporation of nitrogen into HfO_2.

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