Suppression of phase separation in Hf-silicate films using NH_3 annealing treatment

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The structural characteristics of Hf-silicate films and nitrogen incorporated Hf-silicate films, prepared using a NH_3 annealing treatment, were investigated by various measurements. Hf-silicate films annealed in a N_2 ambient at 900 °C show the evidence of crystallization in local regions, resulting in the phase separation of HfO_2 and SiO_2. In addition, a SiO_2 overlayer is formed on the Hf-silicate films, due to the diffusion of Si by postannealing in an ambient of N_2 at 900 °C. However, in nitrogen incorporated Hf-silicate films, prepared using a NH_3 annealing treatment, phase separation is effectively suppressed and no SiO_2 overlayer is present. The incorporated N is distributed into the film and interfacial layer, and obstructs the diffusion of Si from the substrate as well as the film. Structural changes in films affect electrical characteristics such as the dielectric constant and flatband voltage. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2175493]

The aggressive shrinkage of silicon-based devices has imposed restrictions on the use of conventional SiO_2 and SiON gate dielectrics for submicron complementary metal-oxide-semiconductor (CMOS) transistors. The scaling down of previous Si-based oxide led to technological and theoretical limits because of the resulting leakage current through direct tunneling.[1] Several studies have recently focused on investigating high-*k* gate dielectrics, which could potentially replace SiO_2 in advanced CMOS technologies. Conventional high-*k* candidates, such as Al_2O_3, ZrO_2, HfO_2, and silicates of either Hf or Zr, have been considered as alternative gate dielectric materials.[2,3] Such materials should ideally have high dielectric properties and satisfy thermal stability requirements, for example, by being resistant to interfacial reactions and structural changes after the postannealing treatment under the integration process. Unfortunately, high dielectric oxide films do not have an acceptable thermal stability because they can easily change from an amorphous structure to a polycrystalline structure and can react with the Si substrate.

In order to overcome these problems, recent efforts have focused on silicate films such as Hf and Zr based silicates due to their excellent thermal stability, adequate band gaps, and compatibility in fabrication using conventional CMOS processing.[4] However, it has been reported that Hf and Zr silicate systems can decompose into SiO_2 and metal oxide at temperature annealing above ~800 °C due to the positive enthalpy of mixing of SiO_2 and metal oxides.[5] These phase separations lead to the degradation of thermal stability, dielectric and electrical properties. Consequently, the thermal stability of the silicates and the effects of phase separation on their properties are important issues. Quevedo-Lopez *et al.* have recently investigated the enhanced thermal stability of plasma nitrided Hf-silicate films using Fourier transform infrared (FTIR) spectroscopy analysis.[6] Akbar *et al.* obtained the superior electrical results for Hf silicate by NH_3 post-deposition annealing.[7] However, the causes for the improvement in thermal stability and electrical properties as the result of nitrogen incorporation are not fully understood, although the changes in stoichiometry in the depth direction including N are closely related to structural thermal stability and phase separation.

In this letter, we report on an investigation of the structural characteristics of Hf-silicate films and nitrogen incorporated Hf-silicate films using an NH_3 annealing treatment. The findings show that the incorporation of nitrogen during the NH_3 annealing treatment effectively enhances the thermal stability and structural properties.

A *p*-type Si (100) substrate was cleaned chemically by the Radio Corporation of America method and the native oxide was removed with a dilute HF solution. A ~10 Å layer of thermal SiO_2 was prepared by a rapid thermal oxidation (RTO) process in order to stabilize and reduce the interfacial state. The Hf-silicate films were grown using an atomic layer deposition (ALD) system, which has a vertical warm-wall reactor with a showerhead and a heat susceptor. The Hf-silicate films with a thickness of ~35 Å were deposited at a temperature of 320 °C using tetrakis(ethylmethylamino)hafnium, tris(demethlyamono)silane, and H_2O, respectively, as reactant sources for Hf, Si, and O. The composition of the Hf-silicate films was determined by controlling a number of cycles for the respective source. Hf-silicate films with a 75% Hf content ($\%Hf = 100 \times [Hf]/([Hf]+[Si])$ were used in this study because phase separation became dominant as the Hf content increases.[8] After deposition of Hf-silicate films, the samples were divided into two groups for posttreatments using rapid thermal annealing. One sample was annealed in an ambient of N_2 at a temperature of 900 °C for 1 min. The other was annealed in an ambient of

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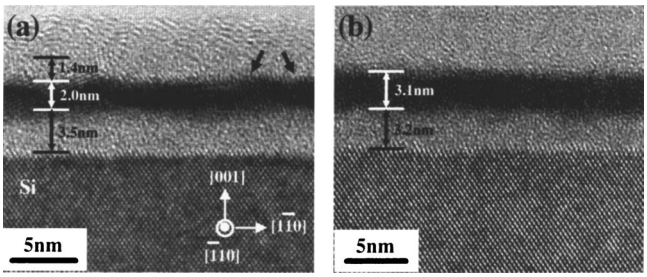

FIG. 1. HRTEM images of Hf-silicate films (a) annealed in an ambient of N_2 at 900 °C and (b) annealed in an ambient of NH_3 at 900 °C: the arrows indicate the crystallization of HfO_2 in several local regions due to the phase separation.

NH_3 at a temperature of 900 °C for 1 min. Interfacial and structural characterizations of Hf-silicate films were performed using high-resolution transmission electron microscopy (HRTEM), medium energy ion scattering (MEIS), and near edge x-ray absorption fine structure (NEXAFS) analysis. The electrical characteristics of Hf-silicate films depending on the structural changes were obtained by capacitance-voltage (*C-V*) measurements.

The HRTEM images in Fig. 1 show the structural stability of Hf-silicate films: (a) annealed in an ambient of N_2 at 900 °C, (b) annealed in an ambient of NH_3 at 900 °C. The total stack thickness increases, but the thickness of the silicate film decreases after annealing in an ambient of N_2 at 900 °C. The interfacial layer of SiO_2 is somewhat increased from 10 to 15 Å after ALD growth, which could be related to the ALD process or diffusion of oxygen in the interface due to oxygen vacancies in the film.[9] In addition, the formation of another layer on the Hf-silicate films, which is regarded as an oxide layer caused by the diffusion of Si, was observed in the films annealed in N_2. Another interesting finding is that crystallization of Hf-silicate films after annealing in N_2 occurs in several local regions. The crystalline structure is the monoclinic phase of HfO_2, calculated from the fringe of the crystallite in the HRTEM image. These indicate that the phase of the Hf-silicate films was separated with HfO_2 and SiO_2 through high temperature annealing, in agreement with previously reported results.[5] On the contrary, no crystalline phase was observed in the Hf-silicate films annealed in an ambient of NH_3 at 900 °C, even if an increase in interfacial layer thickness occurred. Moreover, the thickness of Hf-silicate films is maintained in the thickness of the as-deposited films. Therefore, phase separation of Hf-silicate films could be effectively suppressed by a postannealing treatment in an ambient of NH_3.

To investigate changes in structure and concentration in the depth direction, a MEIS analysis was performed as shown in Fig. 2. The width of the O peak in Hf-silicate films is dramatically increased after annealing in an ambient of N_2 at 900 °C, compared with as-deposited films. This indicates that the thickness of the interfacial region was increased, resulting in an increase in total film thickness. The surface Si peak near an energy of ~90.2 keV is also increased, indicating that the quantity of Si in the surface region is increased. In addition, O and Si peaks are shifted in a high energy direction in the case of annealing in N_2, compared with as-deposited films and films annealed in an ambient of NH_3. This relative movement in the energy spectrum could be due to the fact that an overlayer related to Si and O was formed on the Hf-silicate films. The lower energy shift of the Hf peak also confirms the existence of an overlayer associated with Si and O. However, in the case of Hf-silicate films annealed in NH_3, Si in the interfacial region is slightly increased and N is incorporated into the entire film structure including the interfacial layer, without the formation of overlayer. For further information on a detailed quantity, MEIS spectra were simulated using the Kido program.[10] Figure 2(b) shows the compositional depth profile for as-deposited films, films annealed in an ambient of N_2 and in NH_3 at 900 °C, respectively. The total thickness of Hf-silicate films annealed in N_2 and NH_3 is increased to ~67 and ~61 Å, respectively, which is analogous of the HRTEM results. The noteworthy result, is that the SiO_2 overlayer with a thickness of ~15 Å is formed on the Hf-silicate films, coincident with the HRTEM results. The important change in compositional distribution is that a N quantity of ~20% is incorporated over the entire film and the quantity of O is decreased in parallel with the increase in N concentration. The compositional change progresses, regardless of the quantity and compositional distribution of Hf. This tendency implies that the incorporation of N by the NH_3 annealing treatment is strongly related to the Si, O bondings such as SiON, which is analogous to results obtained for HfSiON using sputtering.[11]

A NEXAFS analysis is a sensitive method for detecting bonding changes that might be associated with phase separation. The O *K* edge of Hf-silicate films can be represented as an overlap of features due to SiO_2 and HfO_2.[5] If the SiO_2 and HfO_2 phases are separated, O K edge of Hf-silicate films would be changed to a different feature from the mixture of SiO_2 and HfO_2. Figure 3(a) represents O *K*-edge spectra depending on the ambient used in the postannealing. Four representative peaks reflect the hybridized states between Hf and O; $P1:e_g$(Hf $5d$+O $2p\sigma$), $P2:t_{2g}$(Hf $5d$+O $2p\pi$), and $P3,P4:(a_{1g}+t_{1u})$(Hf $6sp$+O $2p$).[12] Peak $P2$ also coincides with the energy position of the main peak in amorphous SiO_2 (Si $3sp$ state), thus resulting in an overlap of the second *d*-state peak ($P2$) from HfO_2 with the main peak of SiO_2.[13] The as-deposited films and films annealed in an ambient of NH_3 at 900 °C have similar features. However, the O *K* edge of the films annealed in an ambient of N_2 at 900 °C is dramatically changed. The peaks are separated into four peaks representing the typical feature related to the O *K* edge of HfO_2. From the different changes of the O *K* edge between films annealed in N_2 and in NH_3, it can be concluded that the incorporation of N by the NH_3 annealing treatment suppresses the phase separation of Hf-silicate films. The chemi-

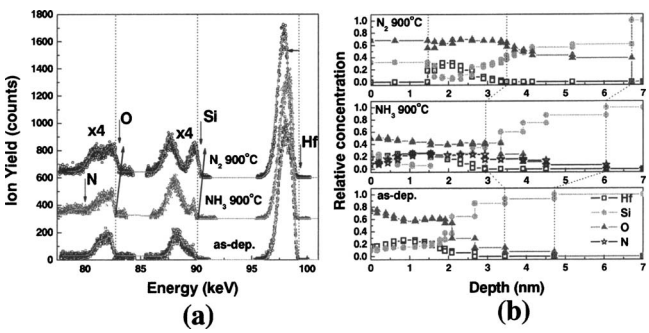

FIG. 2. (a) MEIS energy spectra for Hf-silicate films depending on the annealing ambient at 900 °C. (b) Compositional depth profile for Hf-silicate films depending on the annealing ambient at 900 °C.

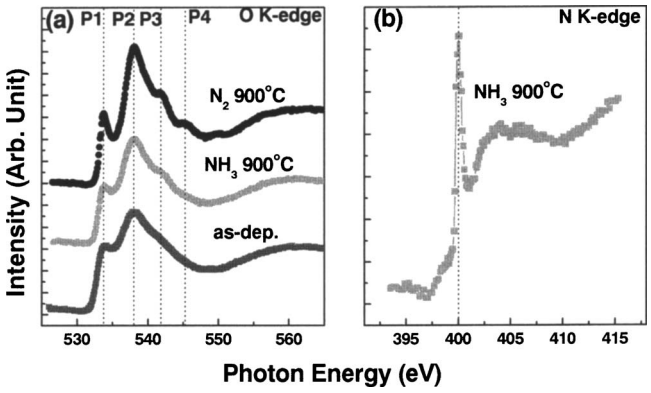

FIG. 3. NEXAFS spectra of the (a) O *K* edge for Hf-silicate films depending on the annealing ambient at 900 °C and (b) N *K* edge for Hf-silicate films annealed in an ambient of NH_3 at 900 °C. Dotted lines indicate $P1$, $P2$, $P3$, and $P4$ from lower photon energy.

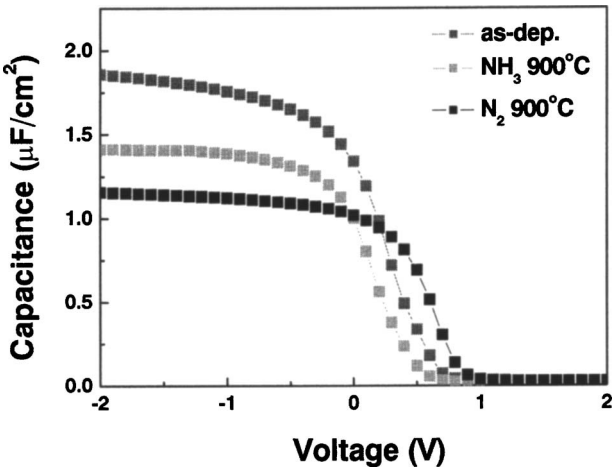

FIG. 4. *C-V* curves for Hf-silicate films depending on the annealing ambient at 900 °C.

cal structure of the incorporated N for films annealed in NH_3 was obtained from the spectra of the N *K* edge as shown in Fig. 3(b). The sharp peak near 400 eV is the N $1s \rightarrow \pi^*$ absorption spectra assigned as molecule-like N_2 states in the films.[14]

Finally, the electrical characteristics of Hf-silicate films corresponding to structural changes were measured in a MOS cap with a Pt electrode as shown in Fig. 4. The dielectric constant of as-deposited films is ~15, calculated from the accumulation capacitance serially connected to the interfacial SiO_2 layer and Hf-silicate films. The accumulation capacitance of Hf-silicate films annealed in an ambient of NH_3 at 900 °C is reduced, due to the increased interfacial layer. In the case of Hf-silicate films annealed in an ambient of N_2 at 900 °C, the accumulation capacitance is dramatically reduced, compared with the as-deposited films. This can be attributed to the SiO_2 overlayer on the Hf-silicate films in addition to the increase in interfacial layer, as shown in the HRTEM and MEIS results. The change in flatband voltage of Hf-silicate films annealed in NH_3 shows a negative shift, indicating an increase in positive trap charge, compared with as-deposited films. This is caused by the incorporation of N in the Hf-silicate films because the nitridation of SiO_2 by NH_3 treatment induces a negative shift in the flatband voltage.[15] The positive shift in flatband voltage of Hf-silicate films annealed in N_2 could be due to two factors. One is the decrease in positive trap charge in as-deposited films due to the improvement in interface state by the out-diffusion of impurities and an increase of an interfacial layer through the high temperature annealing.[16] The other is an increase in negative trap charge in the films after annealing due to the increase of a grain boundary, caused by phase separation and the formation of another interface by the SiO_2 overlayer on the Hf-silicate films.[8]

In summary, the structural characteristics of Hf-silicate films and nitrogen incorporated Hf-silicate films using NH_3 annealing treatment were investigated. The Hf-silicate films show crystallization in local regions, resulting in phase separation and the regrowth of a SiO_2 overlayer due to the diffusion of Si by postannealing at high temperature in an ambient of N_2. The thermal stability of Hf-silicate films is strongly enhanced and the phase separation of Hf-silicate films is effectively suppressed by nitrogen incorporation via the NH_3 annealing treatment. The improvement in thermal stability using NH_3 annealing treatment affects various electrical characteristics such as the dielectric constant and flatband voltage.

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