Structural and stoichiometric change in nitrided HfO_2 grown on Ge(100) by atomic layer deposition

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The electronic structure and stoichiometric characteristics of postnitrided HfO_2 grown on Ge(100) were investigated by various physical measurements. N incorporation in HfO_2 grown on Ge was strongly related to the diffusion of Ge from Ge substrate into the film by the postannealing treatment in an NH_3 ambient. The diffusion of Ge into the HfO_2 film was influenced by the formation of GeO_x and GeO_xN_y in the interfacial region. The small amount of N was incorporated into the film at a nitrided temperature of 600 °C, while much larger amounts of N atoms were incorporated into the interfacial layer to form GeON at a temperature of 700 °C, resulting in the suppression of the diffusion of Ge into the film. However, the interfacial nitrided layer was not stably maintained during the postnitridation anneal, resulting in an enhanced interdiffusion of Ge and Hf into the film. [DOI: 10.1063/1.2186739]

As the aggressive scaling of Si-based complementary metal-oxide semiconductors approaches the fundamental limit, various attempts such as modified channel materials have been investigated in attempts to improve device performance by enhancing the carrier mobility in the channel region.[1] One possible modification of the channel region being considered at present involves replacing the conventionally used Si by alternative semiconductor materials, such as Ge. This has attracted considerable interest because Ge has a higher intrinsic carrier mobility.[2] The higher mobility and smaller band gap of Ge as a channel material has a number of advantages owing to the improvement in injection current density and the scaling of the supply voltage, which results in high speeds and a low power consumption.[3] Despite the excellent properties of Ge, the lack of a stable passivation oxide and the necessity of a lower temperature process have hindered the fabrication of Ge-based devices.[4] The deposition of a high-k gate dielectric on a Ge substrate has recently been demonstrated, and the results indicate superior interfacial characteristics.[2] Furthermore, improvements in gate dielectric properties have been reported by applying the various surface treatments of Ge prior to the deposition of HfO_2 films.[5,6] However, previous reports have concentrated on reducing leakage current density owing to an interfacial GeO_xN_y formed by the surface nitridation of the Ge substrate. Although interfacial GeO_xN_y plays an important in the electrical properties, our understanding of the thermal stability of N incorporated in the interfacial GeO_xN_y and the reaction of N with a HfO_2 film or a Ge substrate is limited. Moreover, the behaviors of Ge and N in HfO_2 grown on Ge during postnitridation or postannealing have not been extensively studied. Therefore, a synthetic and systematic investigation of postnitridation effects in HfO_2 grown on Ge(100) is necessary, if we are to understand the performance of interfacial GeO_xN_y.

The focus of this study was on the electronic structure and stoichiometric characteristics of postnitrided HfO_2 grown on Ge(100) substrates by atomic layer deposition (ALD). In order to clarify changes in the film and interface as the result of the incorporation of N, stoichiomeric changes in the depth direction were investigated as a function of postannealing temperature in an NH_3 ambient using various physical measurements. The results of medium-energy ion scattering (MEIS) and x-ray photoelectron spectroscopy (XPS) indicate that Ge largely diffuses from the substrate to the film after the nitridation treatment and N incorporation is closely related to the diffusion of Ge. During the postannealing treatment in an NH_3 ambient, the N is positioned at the film containing Ge at an annealing temperature of 600 °C, while it is mainly incorporated into the interfacial region at an annealing temperature of 700 °C, which inhibits the diffusion of Ge to the film. However, the incorporated N is dissociated and diffused out through the film after the postnitridation anneal, resulting in an enhanced interdiffusion between Hf and Ge at the interfacial region.

A p-type Ge (100) substrate was dipped into a dilute HF solution and rinsed in H_2O before introduction into the chamber in order to remove the surface oxide. HfO_2 with a thickness of ~3.5 nm was grown using a vertical warm wall type ALD system. The HfO_2 grown on Ge was subsequently annealed at a temperatures of 600 and 700 °C in an NH_3 ambient for 2 min. Various physical analyses were employed using MEIS, high-resolution x-ray photoelectron spectroscopy (HRXPS), and a near-edge x-ray absorption fine structure (NEXAFS) analysis. HRXPS and NEXAFS measurements were carried out at the Pohang accelerator laboratory on beamline 8A1 using a third generation synchrotron radiation source.

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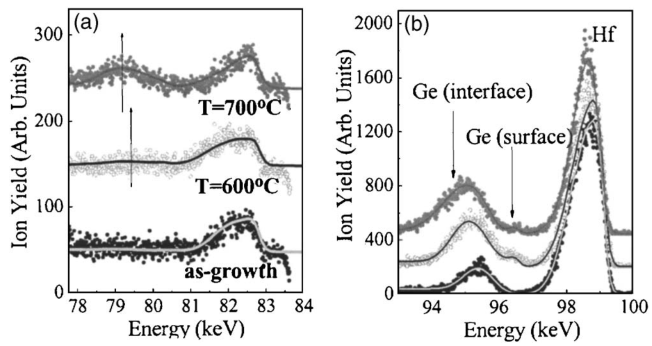

FIG. 1. MEIS spectra and fitting curves for HfO_2 grown on Ge substrates and postannealed at 600 and 700 °C in an NH_3 ambient for 2 min. (a) O and N peaks. (b) Hf and Ge peaks.

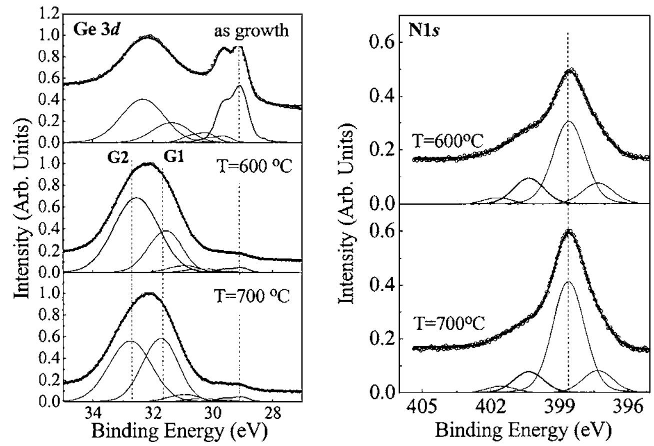

FIG. 2. XPS spectra of Ge 3*d* and N 1*s* for as-grown HfO_2 on Ge and annealed at 600 and 700 °C in NH_3 ambient for 2 min. Dotted lines indicate G2 (GeO_2), G1 (GeO_xN_y), and Ge substrates in the spectra of Ge 3*d*, respectively.

Figure 1 shows the MEIS spectra of HfO_2 grown on Ge substrate as a function of post-annealing temperature in an NH_3 ambient. The clear finding is that the Ge shoulder near a scattering energy of ~96.4 keV is evident at an annealing temperature above 600 °C, indicating the incorporation of Ge diffused from the substrate into the film surface. The quantity of Ge, calculated from the MEIS data is ~7 at. % at an annealing temperature of 600 °C, while it is reduced to ~4 at. % at 700 °C. Moreover, the increased Ge peak at ~95 keV shows that the quantity of Ge at the interfacial region is increased with annealing temperature, implying that the interfacial Ge layer with an amorphous structure is formed. The change in the position and height of the N peak suggests that the difference in the quantity of Ge between the annealed samples at 600 and 700 °C is related to the quantity of N incorporated at the interfacial region. A few atomic percent of incorporated N was found at a temperature below 600 °C, while the quantity is abruptly increased up to ~15 at. % at a temperature of 700 °C. Moreover, the change in peak position and width indicates that the incorporated N spreads through the entire film at an annealing temperature of 600 °C, while it is dominantly located at the interfacial region at 700 °C. Kim *et al.* reported that a nitrided Ge surface effectively suppresses the interaction between GeO_x and HfO_2, implying that the highly incorporated N at the interfacial region at an annealing temperature of 700 °C has the same role.[6] Thus, the amount of Ge in the annealed film at 700 °C is decreased, compared with the case of a film annealed film at 600 °C, as shown by the change in the Ge peak, because nitrided Ge layer inhibits the diffusion of Ge into the film. Another interesting finding is that the width of the O peak is decreased in the film annealed at an annealing temperature of 700 °C, compared to a film annealed at 600 °C, while the Ge peak caused by the interlayer is increased with annealing temperature. Consequently, the changes in O, N, and Ge peaks in the MEIS spectra indicates that an interfacial layer such as GeO_x is increased up to a temperature of 600 °C, while the unstable GeO_x layer is dissociated and diffuses out at a high annealing temperature of 700 °C, resulting in the growth of an oxygen-deficient GeO_xN_y interlayer. Moreover, the change in the decrease at lower energy region in the Hf peak reflects the interaction between HfO_2 and GeO_x; that is, the decline is relatively steep in the sample annealed at 700 °C, compared to the as-grown and annealed samples at 600 °C, indicating that interfacial reaction between the interfacial layer of GeO_x and HfO_2 at an annealing temperature of 600 °C is higher than that of 700 °C. The findings herein suggest that the incorporation of N is closely related to the diffusion of Ge into the film; that is, the interfacial nitrided Ge layer plays a role in suppressing interfacial reactions and blocks the diffusion of Ge into film.

Figure 2 shows XPS spectra of Ge 3*d* and N 1*s* as a function of postannealing temperature in an NH_3 ambient. The spectra of an as-grown film for Ge 3*d* shows that there are many peaks arising from the interfacial GeO_x layer with Ge bulk peaks (~29.2 eV). As the nitridation temperature increases, the intensity of the Ge bulk peaks dramatically decrease, while that of the high binding peaks, regarded as GeO_xN_y increases. Through a more detailed curve fitting analysis, the spectra of the nitrided film at the temperature of 600 and 700 °C can be deconvoluted into two different Ge components: ~31.7 eV (G1) and ~32.7 eV (G2). The deconvolution shows an increase in the G1 peak with annealing temperature, indicating the growth of a nitrided Ge layer. This is consistent with the MEIS data, which show that interfacial layers such as GeO_xN_y are grown with increasing annealing temperature. In addition, the increase of the major peak of N 1*s* near 398.8 eV with the annealing temperature supports the growth of nitrided Ge interlayer. From the connection with the results obtained from MEIS data, the peaks can be assigned to oxygen-deficient GeO_xN_y (G1) and GeO_x (G2), respectively. In the case of the Hf peak, nitrogen incorporation causes the peak shift to a lower binding energy because incorporated N diminishes the effect of ionic bonding between Hf and O. However, the shift in binding energy in our data can be measured with difficulty even if not shown here. Thus, we conclude that the incorporation of N occurs mainly in the interfacial GeO_x and unstable oxygen is exchanged with N, resulting in an increase in the oxygen deficient GeO_xN_y layer in the interfacial region as a function of annealing temperature in an NH_3 ambient.

The detailed properties of the molecular structure as a function of nitridation temperature were examined using NEXAFS. NEXAFS spectra of the O *K* edge and N *K* edge in the HfO_2 film are shown in Fig. 3. The spectra of the O *K* edge clearly represent three peaks caused by unoccupied hybridized orbitals assuming an octahedral symmetry of HfO_2.[7] These three peaks can be assigned to e_g(Hf $5d$+O $2p\sigma$), t_{2g}(Hf $5d$+O $2p\pi$), and $(a_{1g}+t_{1u})$ (Hf $6sp$+O $2p$). A specific

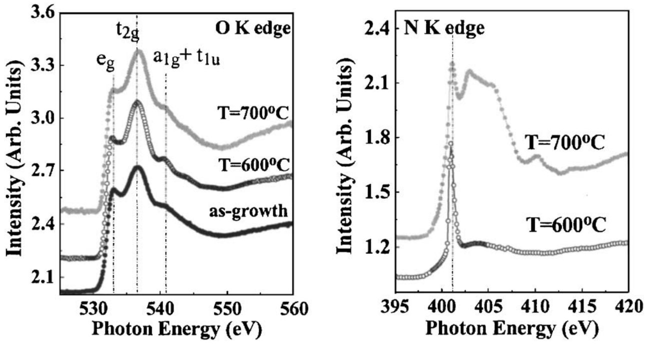

FIG. 3. NEXAFS spectra of the O K edge and N K edge for as-grown HfO_2 on Ge and annealed at 600 and 700 °C in an NH_3 ambient for 2 min. Dotted lines indicate O1, O2, and O3 from lower photon energy, respectively.

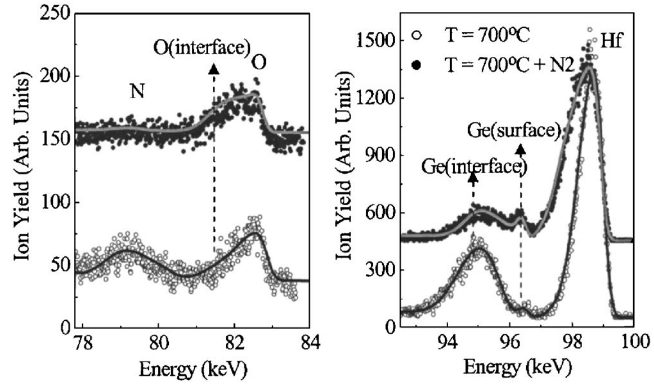

FIG. 4. MEIS spectra of HfO_2 grown on Ge after being additionally annealed at 700 °C in a N_2 ambient after nitridation at 700 °C. The enlargement of O and N region (left side) and the Hf and Ge region (right side).

change in the spectra is not observed, while the intensity of the t_{2g} and $(a_{1g}+t_{1u})$ peaks changes slightly with annealing temperature. The minor change reflects the incorporation of small amounts of N into the HfO_2 film because the incorporated N is dominantly concentrated in the interfacial layer, as shown in the MEIS spectra. Since the peaks are also caused by O $2p$ states hybridized with Ge $4sp$ orbitals due to the octahedral arrangement of rutile GeO_2,[8] the minor change in O K edge spectra with annealing temperature can be caused by a change in the interfacial layer, as shown in the previous MEIS and XPS data; that is, the relative change in GeO_x and GeO_xN_y causes a decrease in the intensity of t_{2g} and $(a_{1g}+t_{1u})$ peaks at a higher temperature. In addition to a O K edge spectra, the N K edge data reflect the molecular structure of N in the HfO_2 film. The sharp peak near 401 eV is carefully assigned to the N_2 molecular states in the film because of the position of the energy and the sharpness of peak, as reported by Feifel *et al.*[9] The increase in peak size with annealing temperatures implies that the formation is related to the thermodynamical reaction factor between the incorporated N into interfacial layer and the recombination process of N atoms. Another interesting finding is that the peak positioned in the region of higher photon energy above 402 eV is drastically increased at a temperature of 700 °C. The possible change can be attributed to the transition related to (Hf $6sp$+N $2p$) and (Ge $4sp$+N $2p$), which is consistent with the position of the energy.[10] However, previous MEIS and NEXAFS data exclude the incorporation of N into a HfO_2 film. Thus, the sudden change in the region of higher photon energy at an annealing temperature of 700 °C can be considered to be due to the formation of a nitrided Ge layer, generated by the incorporation of N into the interfacial GeO_x layer.

Finally, we investigated the thermal stability of N incorporated at the interfacial layer by an additional annealing treatment of the nitrided HfO_2 film at 700 °C. The additional annealing process was achieved at an annealing temperature of 600 °C in a N_2 ambient for 1 min. The MEIS data in Fig. 4 show that the quantity of N is dramatically decreased after the additional annealing process. In the MEIS spectra, a shoulder at ~96.4 keV caused by the diffusion of Ge into the film surface is increased, while the Ge peak at ~95 keV owing to interfacial GeO_xN_y is significantly decreased, implying the outdiffusion of N in the GeO_xN_y layer. In addition, the outdiffusion of N at the interfacial region has a significant effect on the diffusion of Ge into the film surface, resulting in a change in the shape of the Hf peak. The lower-energy edge and width of the Hf peak (~97.5 keV) are explicitly increased and the maximum height of Hf peak is decreased, which can be attributed to the formation of a mixed structure composed of Hf, Ge, and O in the interfacial region. Compared to the amount of Ge at the film surface, the level of Ge at the interfacial region is not high, indicating that the mixed structure formed at the interfacial region is caused by the diffusion of Hf into the interfacial region. Therefore, based on these results, we conclude that the N incorporated in the interfacial region is unstable and the interdiffusion of Ge and Hf in the HfO_2 film on Ge substrate cannot be durably blocked during the additional annealing treatment.

In summary, postnitridation of HfO_2 grown on Ge (100) substrates was investigated using various physical measurements. N incorporation of HfO_2 grown on Ge was strongly related to the diffusion of Ge from the Ge substrate into the film by the postannealing in an NH_3 ambient. The incorporated N greatly affects the change in chemical state related to GeO_xN_y in the interfacial region. However, nitrogen that is incorporated at the interfacial region is unstable and diffuses out during the additional annealing process. Moreover, the absence of nitrided Ge oxide in the interfacial region results in the diffusion of Hf atoms into the underlying layer.

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