Instability of incorporated nitrogen in HfO$_2$ films grown on strained Si$_{0.7}$Ge$_{0.3}$ layers

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The interfacial characteristics and thermal stability of nitrided HfO$_2$ films grown on strained Si$_{0.7}$Ge$_{0.3}$ layers were investigated by medium energy ion scattering, high-resolution x-ray photoelectron spectroscopy, and near-edge x-ray absorption fine structure. N incorporation of HfO$_2$ films grown on Si$_{0.7}$Ge$_{0.3}$ layers was strongly related to the diffusion of Si and Ge from strained Si$_{0.7}$Ge$_{0.3}$ layers in the interfacial region between HfO$_2$ films and Si$_{0.7}$Ge$_{0.3}$ layers by the annealing treatment in NH$_3$ ambient. The chemical states of SiO$_x$N$_y$ and GeO$_x$N$_y$ were formed in the interfacial region by N incorporation, and SiO$_x$N$_y$ was dominant chemical states rather than that of GeO$_x$N$_y$. However, the incorporated N was not stable, which was mostly diffused out during the postnitridation annealing in a N$_2$ ambient. The instability of incorporated N through the additional annealing treatment extensively caused the change in the structure of HfO$_2$. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3077014]

As the aggressive scaling of the conventional SiO$_2$ gate dielectric leads to the fundamental limits, various attempts have been investigated to improve the complementary metal-oxide-semiconductor performance.[1,2] High dielectric oxides have been attractively considered due to the accomplishments of thicker insulator thickness and lower leakage current rather than the Si based oxides.[3] However, the severe problem for applying high dielectric oxide into device processing is the decrease in mobility induced by the increase in phonon scattering.[4]

Strained Si$_{1-x}$Ge$_x$ has been a promising candidate as a substitute material for Si in the enhancement of carrier transport properties because of its higher hole mobility.[5,6] Moreover, Si$_{1-x}$Ge$_x$ could be utilized in band gap engineering to provide heterostructures for a variety of Si based devices.[7] Several studies have recently reported the characteristics of HfO$_2$ on SiGe alloys because of serious degradation in the conventional thermal oxidation of Si$_{1-x}$Ge$_x$.[8,9] Even if HfO$_2$ films have a great potential as an alternative for gate dielectric oxide on SiGe alloys due to their reasonably high dielectric constant and relatively large band gap, HfO$_2$ films have an inferior evidence on the thermal stability, such as the structural evolution and the interfacial formation through high thermal budget processing.[10] Incorporation of N into HfO$_2$ films can lead to the enhancement of thermal stability in film and interface regions.[11] Therefore, the characteristics of nitrided HfO$_2$ films on Si$_{1-x}$Ge$_x$ layers and the stability of its nitrogen are crucial issues in determining the potential processing of high dielectric oxide on Si$_{1-x}$Ge$_x$.

The focus of this study is on the interfacial characteristics of nitrided HfO$_2$ films grown on strained Si$_{0.7}$Ge$_{0.3}$ layers and their thermal stability during postnitridation annealing (PNA). The results indicate that the incorporation of N has a dominant influence on the physical characteristics in the interfacial region, as evidenced by medium energy ion scattering (MEIS) and high-resolution x-ray photoelectron spectroscopy (HRXPS). The incorporation of N is originated by the reactions with Si and Ge diffused from Si$_{0.7}$Ge$_{0.3}$ layers. The incorporated N is mostly disappeared by the PNA, and it induces the structural changes in HfO$_2$ films.

The strained Si$_{0.7}$Ge$_{0.3}$ layers with a 50 nm thickness were grown by ultrahigh vacuum chemical vapor deposition on an epitaxial Si buffer layer 50 nm in thickness at 570 °C using SiH$_4$ and GeH$_4$. The surfaces were cleaned by the standard Radio Corporation of America method and dipped in dilute HF solution to remove metallic contamination and the native oxide. HfO$_2$ films were grown on Si$_{0.7}$Ge$_{0.3}$/Si heterostructures at 300 °C using atomic layer deposition. Then, HfO$_2$ films on Si$_{0.7}$Ge$_{0.3}$/Si were annealed in a NH$_3$ ambient for 1 min in order to examine the nitridation effect. In addition, the stability of incorporated N was investigated by PNA at 700 °C in a N$_2$ ambient for 1 min.

The changes in the structure and composition of HfO$_2$(3 nm)/Si$_{0.7}$Ge$_{0.3}$(50 nm)/Si stack structures were analyzed by MEIS measurement in the depth direction as a function of nitridation temperature. Figure 1 shows the energy spectra of MEIS for as-grown and nitridation samples annealed in a NH$_3$ ambient. The structural evolutions of HfO$_2$ films after nitridation, such as the shrinkage of thickness and crystallization, have no evidence from Hf peak. However, the increase in film thickness in the interfacial region can be observed from the width of O peak as the nitridation temperature increases, i.e., the calculated total film thickness included interfacial layer was 3.5 and 4.3 nm for as-grown and nitrided films at 800 °C. In detailed depth analysis using fitting program, this increase in thickness is accompanied by the diffusions of Si and Ge from Si$_{0.7}$Ge$_{0.3}$ layers in the interfacial region. The interesting finding is that the incorporated N is also concentrated in the interfacial region. This means that the incorporation of N corresponds to the bonding of Si–N and Ge–N, formed by the diffusion of Si and Ge from Si$_{0.7}$Ge$_{0.3}$ layers.

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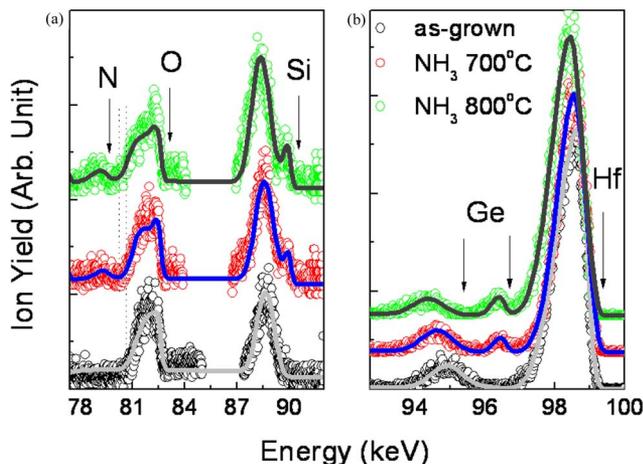
FIG. 1. (Color online) MEIS energy spectra and fitting curves of (a) Si, O, N and (b) Hf, Ge regions for HfO$_2$ films grown on Si$_{0.7}$Ge$_{0.3}$ layers as a function of nitridation temperature. The dotted lines in O region indicate the increase in interfacial thickness.

FIG. 3. (Color online) HRXPS spectra of (a) Si 2*p* and (b) N 1*s* for nitridation and PNA at 700 °C in N$_2$ ambient. The indices in N 1*s* indicate the following chemical states: N1-A_3N_4, N2-$(A_3O)_xN$, N3-A_2ON, and N4-AO$_2$N (A=Si or Ge).

In order to determine the electronic structure of HfO$_2$ films on Si$_{0.7}$Ge$_{0.3}$ layers after the nitridation annealing, the measurement of HRXPS was performed using a synchrotron radiation source at Pohang Acceleration Laboratory (PLS) in Korea. The changes in HRXPS spectra for Si 2*p* and Ge 3*d* between as-grown and nitrided HfO$_2$ films are shown in Fig. 2. The spectra of Si 2*p* and Ge 3*d* were carefully deconvoluted into various chemical states with suboxidation states of Si and Ge.[12,13] Both spectra for Si and Ge clearly show the increase in suboxidation states of Si and Ge after nitridation treatment. The remarkable point is that the deconvoluted peak intensity of Si^{2+}, Si^{3+} and Ge^{2+}, Ge^{3+}, related to the oxidation states of SiO$_x$N$_y$ and GeO$_x$N$_y$, is dominantly increased after nitridation annealing, as indicated in the changes in deconvoluted peaks of Si and Ge in Fig. 2. However, the increment in suboxidation states in Si is much higher than that in Ge. The other oxidation states of Si^{4+} related to SiO$_2$ are distinctly increased after nitridation, as well. On the other hand, the oxidation states of Ge except the GeO$_x$N$_y$ state have almost similar features to as-grown films after nitridation. This tendency and small increase in GeO$_x$N$_y$ state imply that the nitridation of Ge is not easily generated
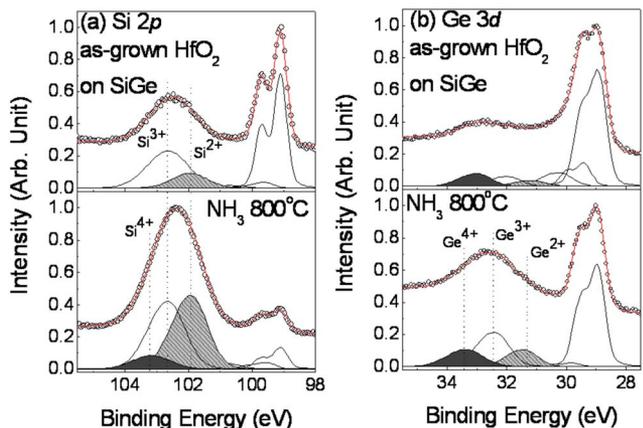
as comparing to the nitridation of Si because the formation and dissociation of GeO$_x$N$_y$ are simultaneously occurred by the decomposition of GeO$_x$ and GeN$_x$ above 600 °C.[14,15] The correlations between MEIS data and HRXPS spectra are that the N incorporation of HfO$_2$ on Si$_{0.7}$Ge$_{0.3}$ layers is dominantly focused on the interfacial region and strongly related to the formation of SiO$_x$N$_y$.

Although N incorporation is the beneficial manner to improve the thermal stability of dielectric stack structure, the stability of incorporated N during PNA is another important issue because unstable N states can provide the possibility of changing the properties of films.[16] To characterize the thermal stability of incorporated N, the chemical states of Si 2*p* and N 1*s* were analyzed by HRXPS spectra after PNA treatment in a N$_2$ ambient at 700 °C. The chemical states of N bonding are mostly disappeared after PNA, as shown in N 1*s* in Fig. 3, and the oxidation states of Ge (not shown in here) related to GeO$_x$N$_y$ in Ge 3*d* are completely gone. The outdiffusion of N in the chemical states of GeO$_x$N$_y$ is generated by the dissociation of Ge–N and Ge–O bondings. Moreover, the preferential breaking of unstable Ge–N and Ge–O bondings in the networks of Si–Ge–O–N could result in the disappearance of SiO$_x$N$_y$ states and the enhancement of its removal, considered by the reduction in the states of Si^{2+} and Si^{3+}.

Finally, near-edge x-ray absorption fine structure (NEXAFS) spectra of the O *K*-edge and N *K*-edge in Fig. 4 clearly show the changes in molecular structure after PNA treatment. In the spectra of O *K*-edge, the molecular structure of HfO$_2$ films has no changes after nitridation. However, the spectral changes in O *K*-edge induced by the crystal field splitting occur after PNA. HfO$_2$ has the molecular structure constructed by the hybridization between Hf metal *d* states and O 2*p* orbitals, resulting in three representative states caused by unoccupied hybridized orbitals: e_g(Hf 5*d* +O 2*p*π), t_{2g}(Hf 5*d*+O 2*p*σ), and $(a_{1g}+t_{1u})$(Hf 6*s*,6*p* +O 2*p*) in an octahedral symmetry.[17] The crystal field splitting corresponds to the changes in the hybridized molecular orbitals by their structural changes, such as the formation of crystalline.[18] The sharp energy states around 400 eV represent N$_2$ molecule states by a N 1*s* to 2*p* π* transition. The spectra of N *K*-edge were collected by two different take-

FIG. 2. (Color online) HRXPS spectra of (a) Si 2*p* and (b) Ge 3*d* for asgrown HfO$_2$ on Si$_{0.7}$Ge$_{0.3}$ layers and the films annealed at 800 °C in a NH$_3$ ambient. Spectra were deconvoluted into the detailed chemical states of suboxidation.
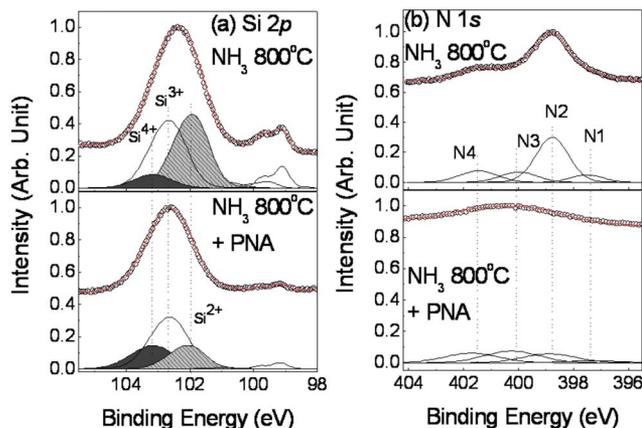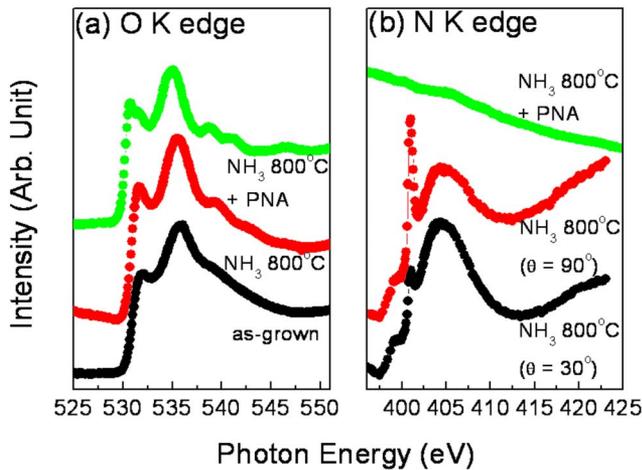
FIG. 4. (Color online) NEXAFS spectra for (a) O *K*-edge after nitridation and PNA and (b) N *K*-edge with the different takeoff angles of 30° (films region) and 90° (interface region) and after PNA treatment.

angles, i.e., 30° is relatively focused on the films and 90° is on the interface. The directional relation between the electric field vector and orbital vector can lead the angular dependence of N_2 molecule states. However, considered with the depth distribution of N in the previous MEIS data, the results of N *K*-edge for two different takeoff angles could be regarded that N is intensively incorporated in the interfacial region. The molecular states of N are unstable and completely disappeared after PNA treatment, which coincide to the HRXPS spectra in Fig. 3. Considering the spectra of O *K*-edge and N *K*-edge after PNA, the out-diffusion of unstable N results in the changes in molecular structure of HfO_2 films.

In summary, the interfacial characteristics and thermal stability were investigated in the nitrided HfO_2 films grown on strained $Si_{0.7}Ge_{0.3}$ layers by nitridation and PNA. N incorporation of HfO_2 films grown on $Si_{0.7}Ge_{0.3}$ layers is closely related to the diffusion of Si and Ge from strained $Si_{0.7}Ge_{0.3}$ layers in the interfacial region between HfO_2 films and $Si_{0.7}Ge_{0.3}$ layers. The chemical states of SiO_xN_y are dominant states rather than that of GeO_xN_y as a result of the decomposition of unstable GeO_x and GeO_xN_y. However, the incorporated N is not stable, which is mostly diffused out by the PNA. The instability of incorporated N is correlated with unstable chemical states of GeO_x and GeO_xN_y. In addition, the out-diffusion of the incorporated N through the additional annealing treatment causes the changes in molecular structure of HfO_2.

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