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Intermixing between HfO_2 and GeO_2 films deposited on Ge(001) and Si(001): Role of the substrate

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Thermally driven atomic transport in HfO_2/GeO_2/substrate structures on Ge(001) and Si(001) was investigated in N_2 ambient as function of annealing temperature and time. As-deposited stacks showed no detectable intermixing and no instabilities were observed on Si. On Ge, loss of O and Ge was detected in all annealed samples, presumably due to evolution of GeO from the GeO_2/Ge interface. In addition, hafnium germanate is formed at 600 °C. Our data indicate that at 500 °C and above HfO_2/GeO_2 stacks are stable only if isolated from the Ge substrate. © *2011 American Institute of Physics*. [doi:10.1063/1.3574093]

There is a current research effort on high-mobility semiconductors due to their potential applications in high performance metal-oxide-semiconductor field effect transistors (MOSFETs).[1] Germanium (Ge) is a particularly relevant candidate for next generation pMOSFETs.[2] The necessary surface passivation, however, is still under investigation. Thermal instability of the native germanium oxide (GeO_2), which is also water soluble, and the technological requirement of about 1 nm equivalent SiO_2 thickness have made the goal of high quality surface passivation a major challenge. Use of a high-k dielectric has been demonstrated to some extent,[3] and HfO_2, now incorporated to advanced Si technology, is one of the most promising dielectrics for Ge.

It has been reported that HfO_2 films on Ge can react with the substrate during the deposition process and subsequent thermal annealing. This produces beneficial effects, such as increase in the HfO_2 permittivity[4] and decrease in oxygen diffusion in the film,[5] but also deleterious ones, such as increase in the density of interface states. Therefore, it is necessary to understand the atomic transport of different species during deposition and thermal annealing in order to control the complex interplay between high-k film and Ge substrate. Since deposition often produces GeO_2 between HfO_2 and the Ge substrate, $HfO_2/GeO_2/Ge$ stacks are an integral part of the problem. In the present work, we compare HfO_2/GeO_2 stacks on Ge and Si with respect to thermally driven atomic transport. The combined use of ion beam analysis and photoelectron spectroscopy indicates that Ge from the substrate drives instabilities observed at the HfO_2/GeO_2 interface.

Si(001) and Ge(001) substrates were cleaned in an ultrasonic acetone bath and then etched in a 40% HF aqueous solution for 1 min. The Si substrates were immediately loaded in a remote plasma enhanced chemical vapor deposition (RPECVD) reactor, where a 5 nm layer of GeO_2 was deposited followed by a 3 nm layer of HfO_2, leading to a $HfO_2/GeO_2/Si(001)$ structure. The Ge substrates were loaded in resistively heated quartz tube furnace that was pumped down to 2×10^{-7} mbar and then pressurized with 200 mbar of O_2 enriched to 97% in the ^{18}O rare isotope. The use of ^{18}O (whose natural abundance is 0.2%) allows one to distinguish it from ^{16}O incorporated during ulterior processing and exposure to the atmosphere. The Ge substrates were annealed at 450 °C for 2 h in order to thermally grow a 5 nm layer of Ge $^{18}O_2$. Following this step, a 3 nm layer of HfO_2 film was deposited, leading to a $HfO_2/Ge\ ^{18}O_2/Ge(001)$ structure.

As-deposited samples were submitted to thermal annealing in 1 atm of N_2 at 500 or 600 °C for 1–4 h. The resulting depth distributions of ^{18}O were determined by resonant nuclear reaction analysis using the $^{18}O(p,\alpha)^{15}N$ reaction at 151 keV,[6] which yields a depth resolution of 1 nm close to the sample surface. Ge and Hf amounts were measured by channeling Rutherford backscattering spectrometry (c-RBS) using He^+ ions at 1 MeV, with a sensitivity of 10^{14} at per square centimeter and accuracy of 10%.[7] X-ray photoelectron spectroscopy (XPS) was performed using Mg $K\alpha$ radiation and a take-off angle of 80°. Low energy ion scattering (LEIS) measurements were performed using He^+ ions at 1 keV.

Figure 1(a) shows a cross-sectional transmission electron microscopy (XTEM) image of the as-deposited sample on Ge. A well defined interface is observed between amorphous HfO_2 and GeO_2. Figure 1(b) presents Hf 4*f* photoelectron spectra for samples on Ge and Si, both as-deposited and annealed at 600 °C for 1 h. The spectral component at a binding energy of 19.8 eV (Hf $4f_{5/2}$) can be assigned to Hf–O bonding in stoichiometric HfO_2,[8] indicating that HfO_2 and the GeO_2 underlayer do not react during the RPECVD deposition at 300 °C. This result is consistent with Fig. 1(a). After annealing, only Hf–O bonding was observed in all Si samples and Ge samples annealed at 500 °C. Ge samples annealed at 600 °C irrespective of time showed an additional spectral component assigned to Hf–O–Ge bonding.[5] This result indicates that the substrate onto which the HfO_2/GeO_2 stacks are deposited plays a major role regarding thermal stability. The process that triggers chemical in-

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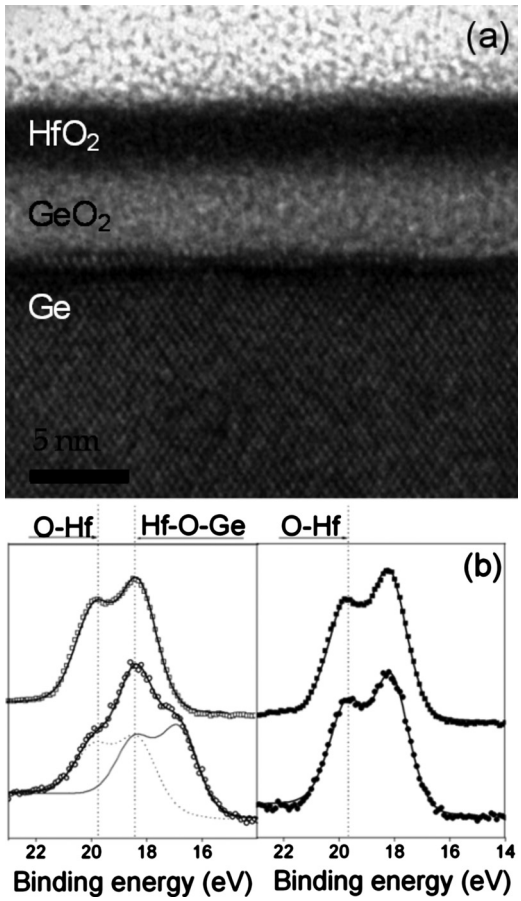

FIG. 1. (a) XTEM image of the $HfO_2/GeO_2/Ge$ as-deposited sample. (b) Hf 4*f* XPS spectra of HfO_2/GeO_2 layers on Ge (left-hand side and open symbols) and on Si (right-hand side and full symbols) in samples as-deposited (squares) and annealed at 600 °C for 1 h (circles).

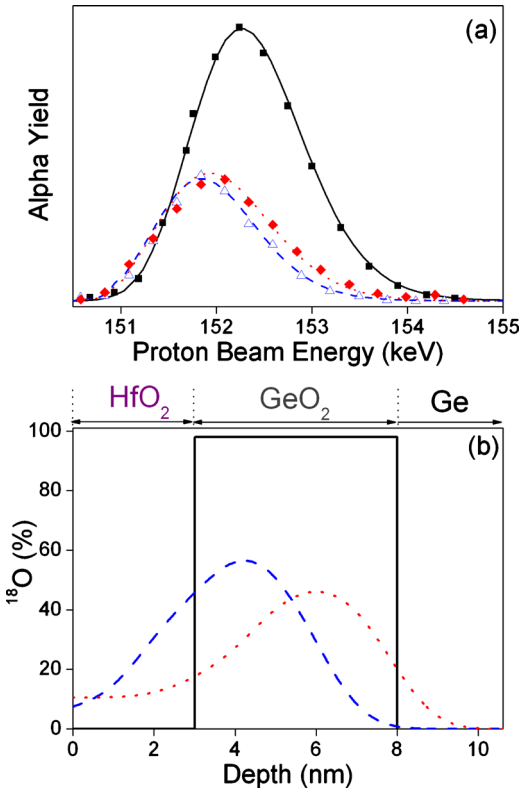

FIG. 2. (Color online) (a) Measured excitation curves (symbols) of the $^{18}O(p,\alpha)^{15}N$ nuclear reaction around the resonance energy $E_r=151$ keV and the corresponding simulations (lines) for samples as-deposited (full squares and solid line), annealed at 500 °C for 1 h (full lozenges and dotted line), and 500 °C for 4 h (open triangles and dashed line). (b) ^{18}O profiles assumed in the simulations presented in (a); line types are the same as in (a).

teraction between HfO_2 and GeO_2 on Ge above 500 °C is absent on Si.

Figure 2(a) presents measured (symbols) and simulated (lines) excitation curves for the $^{18}O(p,\alpha)^{15}N$ nuclear reaction applied to samples on Ge; Fig. 2(b) shows the ^{18}O profiles assumed in the simulations. The as-deposited sample presents a boxlike ^{18}O profile compatible with 5 nm of Ge $^{18}O_2$ under 3 nm of HfO_2, in agreement with Fig. 1(a). Annealing at 500 °C for 1 and 4 h produces two distinct effects: (i) reduction in the ^{18}O concentration in both samples by similar amounts and (ii) incorporation of ^{18}O to the original HfO_2 overlayer. Regarding (i), previous work[9,10] showed that annealing the GeO_2/Ge structure may lead to a solid state reaction producing GeO. The latter, volatile compound can diffuse to the ambient, thus we attribute the decrease in ^{18}O concentration to volatilization of Ge ^{18}O. The rate of GeO generation should depend on annealing conditions (time, temperature, and ambient), GeO_2 thickness, and presence of a capping layer such as HfO_2.

Regarding item (ii) above, we suggest that ^{18}O incorporation into HfO_2 is due to trapping of Ge ^{18}O during transport to the sample surface, so (i) and (ii) would be directly related. Direct evidence of Ge incorporation into HfO_2 was provided by the LEIS spectra shown in Fig. 3. The technique, which is essentially sensitive only to the outermost atomic layer at the sample surface, revealed Hf as the only heavy element in the as-deposited stack on Ge; both Hf and Ge in a sample annealed at 500 °C; and only Ge after annealing at 600 °C. These results support the integrity of the as-deposited sample and the transport of Ge to the surface during annealing. Regarding the absence of Hf–O–Ge bonding in samples annealed at 500 °C [Fig. 1(b)], we hypothesize that higher temperatures are necessary to provide the activation energy for chemical reaction between HfO_2 and GeO. The observation of a surface composed solely of germanium oxide after treatment at 600 °C was clarified with the use of Rutherford backscattering.

Figure 4 presents the amount of germanium on top of the Si(001) and Ge(001) single-crystalline substrates as deter-

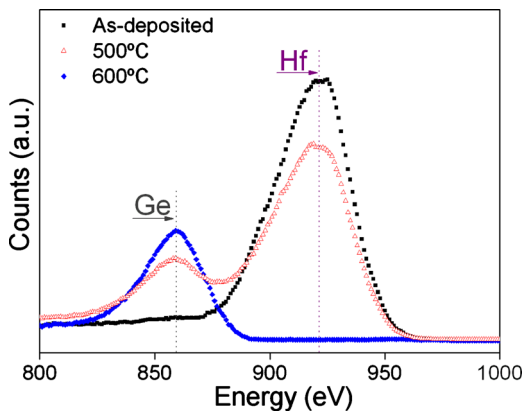

FIG. 3. (Color online) LEIS spectra for the as-deposited sample (full squares) and annealed at 500 °C for 4 h (open triangles) and at 600 °C for 4 h (full lozenges). a.u. stands for arbitrary units. The energy positions for Ge and Hf are indicated.

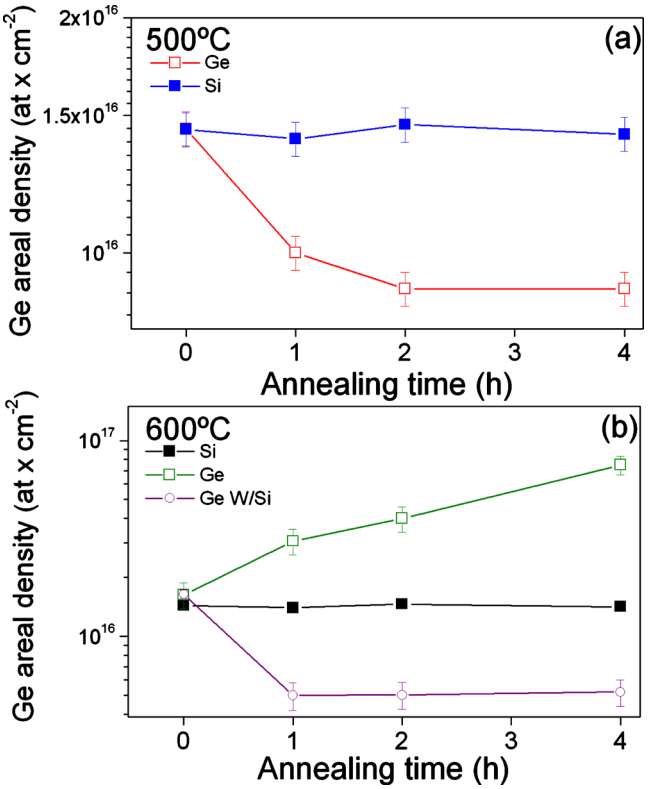

FIG. 4. (Color online) Ge areal densities obtained from c-RBS as a function of annealing time for samples deposited on silicon (full symbols), germanium (open symbols), and germanium with Si backlayer (open circles). Samples annealed at (a) 500 °C and (b) 600 °C.

mined by c-RBS. As before, no instability was observed in Si samples. Regarding the Ge substrate, annealing at 500 °C [Fig. 4(a)] led to the loss of Ge in the initial GeO_2 film, which again supports volatilization of GeO from the samples. Treatment at 600 °C [Fig. 4(b)] originally produced a contrasting result, i.e., a significant increase in the amount of Ge on top of Ge(001), which nevertheless agreed with the LEIS data in Fig. 3. Previous works[11,12] indicate the possibility of surface deposition of GeO generated in the annealing chamber due to oxidation of the back side of the Ge substrate. In this work, such oxidation would be due to residual oxygen in the furnace. To confirm this hypothesis we performed the same processing at 600 °C on Ge samples that had the back side coated with 300 nm of Si. As shown in Fig. 4(b), Ge loss became clearly detectable, pointing to accelerated evolution of GeO at this temperature.

In summary, we investigated the stability of HfO_2/GeO_2 structures deposited on Ge(001) or Si(001) when submitted to thermal annealing in N_2. Combined use of photoelectron spectroscopy and ion beam analysis revealed that the HfO_2/GeO_2 stack deposited on Si is stable at up to 600 °C. Annealed samples on Ge yielded direct evidence of migration and loss of both Ge and O. This was understood as due to the formation of volatile GeO at the GeO_2/Ge interface. Despite the transport of Ge into HfO_2 already at 500 °C, effective formation of a germanate occurred only at 600 °C. Given the occurrence of GeO as the origin of all instabilities, they should also be observed for HfO_2/Ge structures annealed at these temperatures in the presence of O_2.

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