# Interfacial characteristics of $HfO_2$ grown on nitrided Ge (100) substrates by atomic-layer deposition

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The microstructural and electrical properties of Ge-based metal–oxide–semiconductor capacitors containing high-*k* gate dielectric layers were investigated with and without the presence of a $GeO_xN_y$ interface layer. The effect of this nitrided layer on thermal stability of the metal oxide/Ge structures was probed by medium energy ion energy spectroscopy (MEIS). Atomic-layer deposited $HfO_2$ on a chemical oxide-terminated Ge (100) surface exhibited poor capacitance–voltage behavior; however, direct substrate surface nitridation at 600 °C in $NH_3$ ambient before $HfO_2$ deposition improved the carrier trapping characteristics. Diffusion of metal impurities (including Hf) into the interfacial oxide/Ge-substrate may be an important source of the measured degradation of electrical properties. MEIS results suggested that the $GeO_xN_y$ interface layer may inhibit Hf diffusion into the underlying semiconductor at the temperatures investigated. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1797564]

As the continued scaling of Si complementary metal–oxide–semiconductor (CMOS) devices approaches its fundamental limits, various modified channel materials, such as a strained Si,[1] are being investigated to increase the drain current by improving the carrier mobility in the channel region. Among the possible modifications being studied at present, the conventional Si (100) substrate may be replaced by an alternative semiconductor material with higher intrinsic carrier mobility, such as Ge. Because of its higher low-field carrier mobility for improved injection current density and smaller band gap for supply voltage scaling, there have been many attempts to use Ge as a channel material in high-speed field effect transistors.[2,3] Unfortunately, during device manufacturing, the lack of a sufficiently stable thermal oxide of germanium has made obtaining a high quality surface passivation extremely difficult. Recently, however, Ge-based MOS capacitors and transistors incorporating deposited high-*k* gate dielectrics which show superior electrical properties have been demonstrated.[2–4] In addition, surface nitridation (Ge-oxynitride passivation) of Ge (100) surfaces has been investigated and has provided improvements in the electrical properties of high-*k*/Ge gate stacks.[5] However, the mechanism responsible for these improvements and a systematic comparison of the different surface passivation conditions have not been reported.

In this letter, the microstructural and electrical characteristics of $HfO_2$ dielectric layers grown by atomic-layer deposition (ALD) on a chemical oxide and a Ge-oxynitride layer are presented and compared. In order to understand the role of the interfacial $GeO_xN_y$ layer formed by direct-nitridation of HF-cleaned Ge substrate in a $NH_3$ ambient, medium energy ion scattering (MEIS) analysis was performed. The MEIS technique is a lower energy version of Rutherford backscattering in which the energy and angular distributions of scattered ions are used, and it is a powerful technique to obtain detailed information about atomic composition in the topmost 5–20 nm of a gate stack.[6]

Four inch diameter *p*-type ⟨100⟩ Ge wafers having 0.25 (Ω cm) resistivity were used as substrates. Either a vendor-supplied chemical oxide ($GeO_x$) or a nitrided interface oxide was used as a surface passivation layer prior to the high-*k* dielectric deposition. For surface nitridation, the initial oxide present on the Ge substrates was removed using a cyclic rinsing of 50:1 HF solution and de-ionized water, and the samples were nitrided for 1 min at 600 °C in $NH_3$ ambient using an AG4108 RTP system. After the surface passivations, the Ge wafers were immediately transferred to a cold wall-type high vacuum ALD system and deposition of 4.4-4.6-nm-thick $HfO_2$ was performed at 300 °C using alternating surface-saturating reactions of $HfCl_4$ and $H_2O$. Each precursor was pulsed for 2 s and $N_2$ purging followed for 30 and 60 s after each $H_2O$ and $HfCl_4$ pulse, respectively. Various sizes of 50-nm-thick Pt gate electrodes for electrical measurements were deposited by the room temperature e-beam evaporation through shadow mask and, subsequently, Al was deposited on the back side of the Ge wafers to reduce the contact and series resistance of the samples. Capacitance–voltage ($C-V$) measurements were performed without any postannealing using an HP4284A precision LCR meter. Current–voltage ($I-V$) measurements were performed using a Keithley 230 programmable voltage source and 6512 programmable electrometer. The thickness and film microstructures of selected samples were analyzed by cross-sectional transmission electron microscopy (TEM—Philips CM20 FEG-TEM). MEIS analysis was performed with a 100 keV proton beam in a detector alignment so as to reduce the contributions from the crystalline Ge substrate, allowing deconvolution of spectra into contributions from the $HfO_2$ layer, Ge-containing underlayer, and Ge substrate. The inci-

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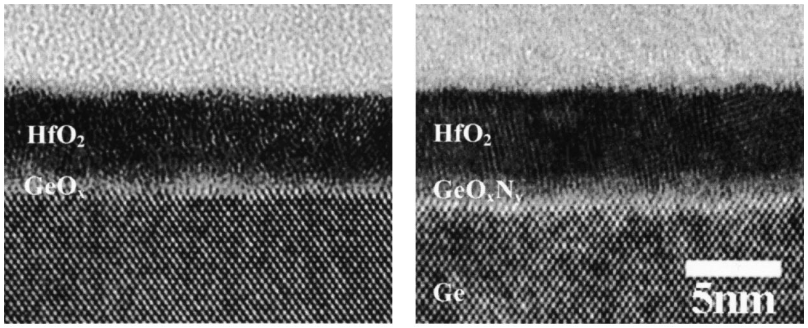


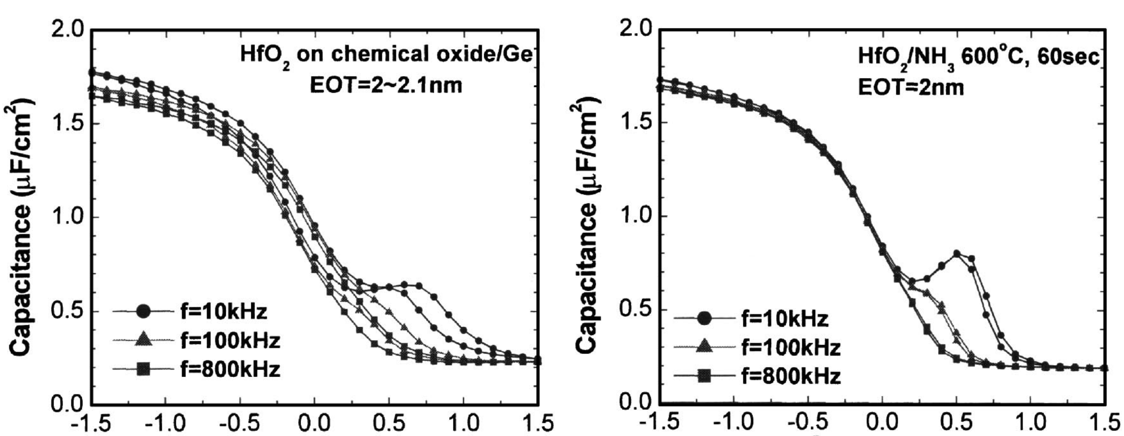

(a) (b)

FIG. 1. Cross-sectional high resolution-TEM images of ALD-$HfO_2$ (4.4–4.6 nm) on Ge with different surface treatments: (a) chemical oxide (0.8–0.9 nm) and (b) $GeO_xN_y$ (1.1–1.2 nm) grown at 600 °C for 1 min in $NH_3$.

dent ions were directed along the $[11\overline{1}]$ direction in the $(1\overline{1}0)$ plane and the scattered ions were along the [001] direction with a scattering angle of 125°. Quantitative depth profiles for different species were extracted with a resolution of less than 0.5 nm in the near-surface region.

Figure 1 shows a cross-sectional TEM image of $HfO_2/GeO_xN_y/Ge$ structure compared with $HfO_2$ upon chemical oxide passivated Ge without any surface cleaning. A relatively thinner (0.8–0.9 nm) interfacial oxide remained in the case of $HfO_2$ deposition on chemical oxide-terminated Ge substrate compared to $HfO_2$ on a similarly passivated Si substrate (1.4–1.5 nm interfacial layer). Also, cross-sectional TEM micrographs obtained from the interface between the $HfO_2$ film and the interfacial layer (chemical oxide) were consistent with greater interface roughness than is typically observed in the $HfO_2/SiO_2$ case.[7] It is believed that inhomogeneous dissociation of Ge-oxide[8] or, possibly, a partial reaction between the $HfO_2$ and Ge oxide may occur even at the relatively low ALD deposition temperature, thus decreasing the interface layer thickness and producing the observed roughness. For nitrided Ge samples, a uniform 1.1–1.2-nm-thick interfacial $GeO_xN_y$ layer was observed, as shown in Fig. 1(b). This layer may block chemical interactions between the deposited $HfO_2$ film and the substrate more effectively than a Ge oxide layer, in keeping with the well-known diffusion barrier characteristics of silicon nitride and similar materials.

Figure 2(a) shows *C–V* characteristics of ALD-$HfO_2$ film on a Ge (100) surface passivated with a chemical oxide. Significant hysteresis and dispersion associated with slow states near the conduction band edge of Ge band gap were observed. The root source of these inferior *C–V* characteristics may be a significant number of interfacial defects originating from the poorly passivated bonding or the diffusion of metal impurities from the gate dielectric into the substrate. It is well known that the incorporation of nitrogen into gate dielectrics, such as $SiO_2$ (Ref. 9) or high-*k* dielectrics[10] can improve dielectric integrity and also inhibit impurity diffusion of contaminant species from either the gate dielectric or the top gate electrode into the channel. A Ge oxynitride layer was incorporated into the Ge MOS structure through direct nitridation of the Ge. *C–V* characteristics of Pt/ALD-$HfO_2/GeO_xN_y/Ge$ MOS structures given various different nitridation treatments (rapid thermal $NH_3$ nitridation at 500–700 °C) were measured, and nitridation at 600 °C was found to exhibit the most promising results. Representative *C–V* data are shown in Fig. 2(b). Although a significant density of slow states still exists near the Ge conduction band edge, an outstanding improvement of *C–V* characteristics was achieved through the $NH_3$ nitridation of the Ge surface before the high-*k* deposition. Higher nitridation temperatures resulted in a significant increase in the capacitance signature of these slow states and an increase of the capacitance in the inversion bias regime. According to XPS studies, the N incorporation into the $GeO_xN_y$ linearly increased with nitridation temperature and approximately 25 at. % N was detected from $GeO_xN_y$ layer nitrided at 600 °C.[5] The nitrided layer is believed to act as a diffusion barrier or a passivation layer reducing the density of defects which originate from the poor quality of Ge-based oxides. However, the oxynitride layer may itself generate other trap levels, to which the observed slow states can be attributed. A high




(a) (b)

FIG. 2. *C–V* characteristics of $Pt/HfO_2/Ge$ capacitors with different surface treatments: (a) chemical oxide (0.8–0.9 nm) and (b) $GeO_xN_y$ (1.1–1.2 nm) grown at 600 °C for 1 min in $NH_3$.

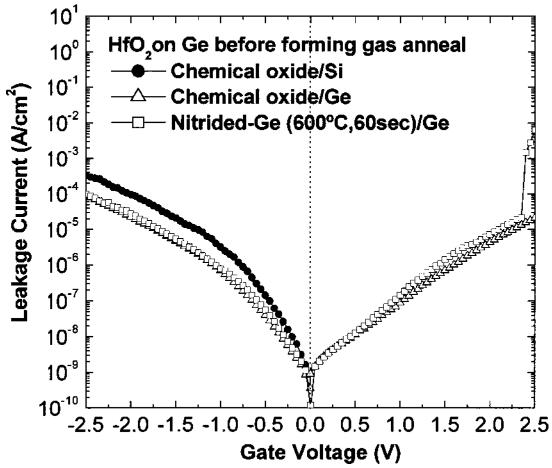



FIG. 3. $J-V$ characteristics of $Pt/HfO_2/Si$ and $Pt/HfO_2/Ge$ capacitors with different surface passivations (the physical thickness of $HfO_2$ is identical; 4.4–4.6 nm).

density of N-related defects has also been observed in silicon nitride films directly deposited on Si (100) substrates.[11]

Figure 3 shows the leakage current densities of ALD-grown $HfO_2$ films on Ge substrates treated with different surface passivation methods. Although there were significant differences in $C-V$ characteristics for the surface passivation conditions used, the leakage current densities were identical for both polarities and were similar to or even lower than those of ALD-$HfO_2$ films deposited on Si substrates having identical physical thickness of $HfO_2$.

In order to understand the role of the interfacial $GeO_xN_y$ layer formed by $NH_3$ nitridation of HF-cleaned Ge substrates, MEIS analysis was used. Two samples with ~4-nm-thick ALD-$HfO_2$ films were deposited onto two different Ge substrates: one with chemical oxide passivation and the other nitrided at 600 °C in $NH_3$ for 1 min after cyclic HF stripping. Figure 4 shows the measured MEIS spectra and the fitting results for both samples. The overall shapes of both spectra were similar except for a difference in the lower energy edge of the Hf signal as shown in the insets of Fig. 4. This corresponds to the Hf signal collected from depths near the substrate surface and beneath the $HfO_2$ film. For the $HfO_2$ film deposited on chemical oxide-passivated Ge, a distinct shoulder which is consistent with diffusion of Hf into the underlying layers of the gate stack was observed even though no post-thermal treatment was performed after the 300 °C ALD $HfO_2$ film growth. On the contrary, no significant signal associated with Hf atoms in the interfacial layer and substrate was observed within the MEIS detection limit $(<5\ \text{at.}\ \%)$ in spectra obtained from the $GeO_xN_y$-containing gate stack. Although there is as yet no definitive explanation for the improvement of electrical characteristics of $HfO_2$/nitrided Ge MOS capacitors, these results suggest that blocking of Hf outdiffusion into the Ge substrate as observed in MEIS may be a significant contributor to the observed improvement in properties.

In summary, the deposition and characterization of ALD-$HfO_2$ dielectric films deposited on Ge substrates with and without substrate nitridation were discussed. Chemical oxide passivation of Ge substrates before the high-$k$ deposition yielded poor electrical results, including large $C-V$ hysteresis. Rapid thermal nitridation of the HF-last Ge surface at

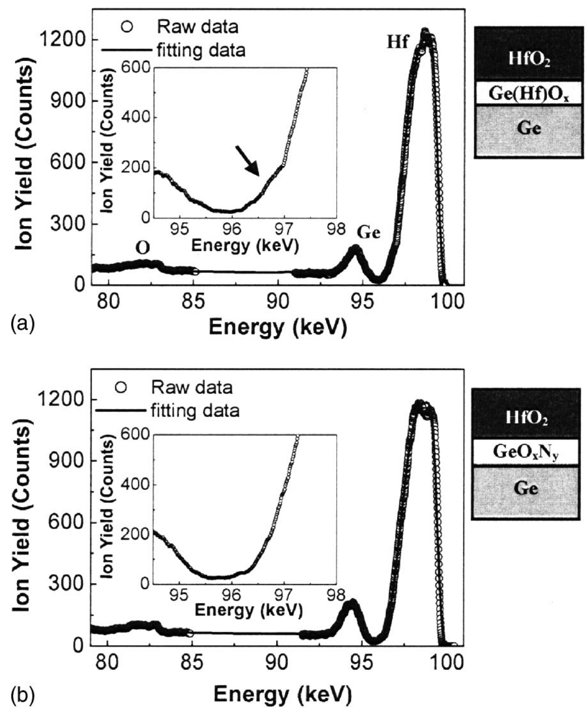



FIG. 4. MEIS spectra and fitted curves, and the corresponding model structure of (a) $HfO_2$ on Ge substrate with chemical oxide and (b) $HfO_2$ on Ge substrate nitrided at 600 °C for 1 min in $NH_3$ ambient after cyclic HF-stripping.

600 °C using $NH_3$ effectively passivated surface defects measured in MOS capacitor electrical testing. MEIS analysis suggested that the presence of a thin $GeO_xN_y$ interposed between the high-$k$ dielectric and Ge (100) substrate behaved as a diffusion barrier for metal species from the metal oxide dielectric into the Ge surface region.

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