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Effective electrical passivation of Ge(100) for high-*k* gate dielectric layers using germanium oxide

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In search of a proper passivation for high-*k* Ge metal-oxide-semiconductor devices, the authors have deposited high-*k* dielectric layers on GeO₂, grown at 350–450 °C in O₂. ZrO₂, HfO₂, and Al₂O₃ were deposited by atomic layer deposition (ALD). GeO₂ and ZrO₂ or HfO₂ intermix during ALD, together with partial reduction of Ge⁴⁺. Almost no intermixing or reduction occurs during Al₂O₃ ALD. Capacitors show well-behaved capacitance-voltage characteristics on both *n*- and *p*-Ge, indicating efficient passivation of the Ge/GeO_x interface. The density of interface states is typically in the low to mid-10¹¹ cm⁻² eV⁻¹ range, approaching state-of-the-art Si/HfO₂/matal gate devices. © 2007 American Institute of Physics. [DOI: 10.1063/1.2773759]

Si/SiO₂ based transistors are unable to accommodate the severe scaling requirements for sub-45 nm complementary metal oxide semiconductor (MOS) devices. To further improve performance, alternative materials are considered. Germanium is introduced as a channel material due to its higher electron and hole mobility as compared to silicon. As alternative gate dielectric layers, high-k materials show reduced tunneling currents at an equivalent SiO₂ thickness. About five years ago, the successful combination of a high-k dielectric film in Ge-based transistors was demonstrated.¹ Today, it is, however, still not straightforward to get a sufficiently low interface state density at the Ge/high-k interface.^{2,3} Also, the Ge/GeO₂ interface is generally considered to be more defective than the Si/SiO₂ interface, although reports are scarce. Currently, more effort is being made to investigate and reduce the interface state density of the Ge/GeO₂ interface.^{4,5}

In this work, we have investigated thermally grown GeO_2 as passivation layer for high-*k* layers deposited by atomic layer deposition (ALD). The electrical quality of GeO_2 can be affected by air exposure and thermal process steps because GeO_2 is hygroscopic and thermally unstable (GeO desorbs at 420 °C in N₂ or vacuum). Therefore, we have avoided air exposure between surface preparation, oxidation, and ALD. Germanium oxidation and high-*k* deposition were performed at low temperature to avoid decomposition of GeO_2 and desorption of GeO. Efficient electrical passivation of the Ge/GeO_x interface will be demonstrated.

Ge(100) substrates were cleaned in HF solution. The subsequent surface preparation, germanium oxidation, and high-*k* deposition were performed in a Polygon® 8200 cluster⁶ without air breaks between these process steps (unless where mentioned otherwise). The Polygon cluster is equipped with an EPSILONTM reactor for thermal treatments and an ALCVDTM PULSAR® 2000 reactor. The samples were first annealed in H₂ at 650 °C for 10 min to desorb O or C that can be present after HF cleaning.⁷ Oxidations were subsequently performed in the same reactor in O₂ at 700 Torr at 350 or 450 °C. ZrO₂, HfO₂, and Al₂O₃ were

deposited at 300 °C in the ALD reactor from ZrCl₄, HfCl₄, or Al(CH₃)₃ with H_2O . Some samples were annealed in N_2 at 550 °C for 5 min to simulate the thermal budget of device processing. X-ray photoelectron spectroscopy (XPS) was performed on a Theta300 system (Thermo Instruments) in parallel angle-resolved mode with monochromatized Al K_a radiation. Analysis was based on the Ge 3d or Ge 3p peaks. Thicknesses were calculated assuming a two- or three-layer model (Ge/GeO₂/high-k). Air exposure between sample preparation and XPS analysis was limited to 15 min or less. The areal density of Hf (Hf/nm²) on GeO₂ was measured by rutherford back scattering (RBS) in a RBS400 end station with a 1 MeV He⁺ beam. Electrical measurements were performed on MOS capacitors with TiN gates. The TiN gate was deposited ex situ by physical vapor deposition. Gate patterning was done by lithography, followed by resist strip, TiN etching, and dielectric removal. The devices were annealed at 550 °C in N2 to activate dopants. The electrical characteristics were measured with a Keithley K4200 semiconductor parameter analyzer and an HP4284 LCR meter.

 GeO_2 is grown when Ge(100) is oxidized at low temperature, as evidenced by the XPS Ge 3*d* spectra [Fig. 1(a)].



FIG. 1. XPS Ge 3*d* spectra for (a) germanium oxide grown at different temperatures and times and (b) 1.3 nm GeO₂ (450 °C, 5 min) covered with 2 nm Al₂O₃ with and without post deposition anneal (PDA) (N₂ 550 °C).

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FIG. 2. XPS Ge 3p spectra of 1.3 nm GeO₂ (450 °C, 5 min) before and after 2 nm HfO₂ and ZrO₂ ALD. (b) Growth per cycle (GPC) as a function of the number of cycles for HfO₂ and ZrO₂ ALD on 1.3 nm GeO₂ (450 °C, 5 min) and 0.3 nm GeO_x (HF cleaned Ge) and O-free Ge.

The difference in binding energy of the oxide and substrate peaks is 3.3 eV, indicating Ge⁴⁺.⁸ No significant components of lower oxidation states are detected. Oxidation at 450 °C yields 1.3 and 2.3 nm of GeO₂ after 5 and 18 min, respectively, in agreement with oxidation studies in similar conditions reported previously.⁹ At 350 °C, 1.1 nm of GeO₂ was grown in 60 min.

During Al₂O₃ ALD on GeO₂, the main oxidation state of Ge remains Ge⁴⁺, as indicated by the Ge 3*d* spectrum [Fig. 1(b)]. The binding energy shift of the oxidized Ge 3*d* peak remains 3 eV, and the contributions of Ge in oxidation states lower than 4+ are small. The reconstructed composition depth profile from angle-resolved XPS intensities indicates sharp interfaces between Al₂O₃ and GeO₂ (not shown). Post-deposition annealing in N₂ at 550 °C results in a slight increase of the GeO₂ component in the Ge 3*d* spectrum. The main oxidation state of Ge remains 4+, although a small shift of the oxide component is observed [Fig. 1(b)].

During ALD of HfO₂ or ZrO₂ on GeO₂, the GeO₂ and HfO₂ or ZrO₂ layers partly intermix. Unfortunately, the Ge 3*d* peak is located at a binding energy very close to O 2*s* (from HfO₂, 32.5 eV) and Zr 4*p* (27.1–28.5 eV) and was, therefore, not analyzed.¹⁰ Ge 3*p* has no overlap with HfO₂ or ZrO₂ peaks and indicates a binding energy shift of the Ge 3*p*_{1/2} oxide component of 0.4 eV with respect to samples without high-*k* dielectric. The reconstructed composition depth profiles from angle-resolved XPS indicate partial intermixing of GeO₂ and HfO₂ or ZrO₂ (not shown).

Intermixing has been observed previously for GeON and HfO_2 deposited by ALD, either from $HfCl_4/H_2O$ at 350 °C or from hafnium-alkylamide/H₂O at 150 °C.^{11,12}

It has been reported previously that GeO_x surfaces enhance the growth per cycle in the first reaction cycle of the HfO₂ ALD.¹³ The growth enhancement also occurs for HfO₂ and ZrO₂ ALD on thermally grown GeO₂ [Fig. 2(b)]. In the first reaction cycle, 6.5 Hf/nm² and 12.8 Zr/nm² are deposited on GeO₂. The reaction mechanism proposed to account for the growth enhancement was an agglomeration mechanism in which HfCl₄ exchanges Cl with OH from the starting

FIG. 3. Capacitance-voltage characteristics of (a) p-Ge/GeO_x/HfO₂ and (b) p-Ge/GeO_x/Al₂O₃ gate stacks (1.3 nm GeO₂ was grown at 450 °C during 5 min) measured at 100 Hz, 10 kHz, and 1 MHz. The inset in (a) shows the normalized conductance as a function of frequency at V_G =0.65 V.

surface. Intermixing could occur by this mechanism if Ge is included in the volatile hafnium hydroxychloride intermediate that readsorbs on the surface. Very little or no intermixing with Ge was observed when HfO_2 is deposited directly on Ge(100) but intermixing occurred during O_2 annealing at 500 °C.¹⁴

As germanium oxide is hygroscopic, we have investigated the effect of air exposure between Ge oxidation and ALD. When GeO₂ is exposed to air, the intermixing between GeO₂ and HfO₂ or ZrO₂ also occurs, while the interface with Al₂O₃ remains sharp.

The frequency dependent capacitance-voltage (*C-V*) characteristics of *p*-Ge/GeO_x/HfO₂ and *p*-Ge/GeO_x/Al₂O₃ gate stacks are shown in Figs. 3(a) and 3(b), respectively. Well-behaved *C-V* characteristics are observed for both gate stacks with minimal frequency dispersion, minimal stretch out, and the absence of bumps near the flatband voltage. This indicates the efficient electrical passivation of the Ge/GeO_x interface obtained for high-*k* gate dielectric ALD on thermally grown GeO₂ (air exposure between oxidation and ALD was avoided). Similar results were observed on *n*-type Ge substrates (not shown). The density of interface states, estimated from conductance measurements as a function of frequency [inset of Fig. 3(a)], is about 3×10^{11} cm⁻² eV⁻¹, approaching state-of-the-art Si/SiO_x/HfO₂/metal gate stacks (typically mid to high 10^{10} cm⁻² eV⁻¹).

The equivalent oxide thickness (EOT), extracted from the fits of the *C*-*V* characteristics with a Ge-based simulator, is about 1.5 and 2.4 nm for the GeO_x/HfO₂ and GeO_x/Al₂O₃ gate stacks, respectively. This leads to an EOT contribution of about 0.7–0.8 nm for 1.3 nm GeO_x, assuming EOT contributions of 0.8 nm for 4 nm HfO₂ and 1.6 nm for 4 nm extra based on the provided method of the distance consistent with the value reported by Scott.¹⁵

Hysteresis of the flatband voltage ($\Delta V_{\rm FB}$) of the GeO_r/Al_2O_3 $(\sim 200 \text{ mV})$ and GeO_r/HfO_2 stacks $(\sim 900 \text{ mV})$ is observed when the gate voltage is swept from inversion to accumulation and back to inversion. We point out that the maximum gate voltage reached in accumulation during the C-V measurement corresponds to the same electric field in the GeO_r interfacial layer for both gate stacks (fixed at ~ 10 MV/cm), assuring a fair comparison of hysteresis between gate stacks with different EOTs. The large C-V hysteresis observed for these devices, more specifically for GeO_x/HfO_2 stacks, is caused by bulk oxide traps and is not related to the passivation of the Ge interface. Partial intermixing of GeO₂ and HfO₂, as shown by XPS, could create more bulk oxide traps (slow states), leading to a larger C-Vhysteresis for HfO_2 as compared to Al_2O_3 gate stacks. The choice of the high-k material, its deposition process, and/or device processing have to be investigated further to reduce the hysteresis.

To conclude, many studies have focused on the passivation of Ge with elements other than oxygen (N, Si, S),^{16–18} as GeO₂ is commonly believed to be a poorly passivating oxide. In this work, we have shown that thermally grown GeO₂ can act as a good electrical passivation layer for high-*k* dielectrics deposited by means of ALD. Downscaling the GeO₂ thickness while maintaining good passivation properties will be the subject of further investigation.

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