

## Effect of Surface Functionalization on TiO<sub>2</sub> ALD on Ge(100)

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Germanium is being investigated for integration into silicon-based electronic devices mainly due to its high bulk electron and hole mobilities and the lower thermal budget required for the processing.<sup>1</sup> Scaling dictates that germanium will be coupled with high- $\kappa$  dielectric materials to overcome power losses in Ge-based metal-oxide-semiconductor field effect transistors. Atomic layer deposition (ALD) is an important technique for deposition of high- $\kappa$  films. However, due to the instability and poor interfacial properties of the germanium oxide, it will be important to passivate the surface of Ge prior to ALD of a high- $\kappa$  film.<sup>1</sup> We have previously studied the passivation of germanium surfaces by halogens and alkanethiolate self-assembled monolayers (SAMs).<sup>2</sup> We have also investigated ALD of titania (TiO<sub>2</sub>) as a model dielectric system on Br-terminated Ge surfaces, and our results suggested formation of an oxide-free TiO<sub>2</sub>/Ge interface.<sup>3</sup>

In the current work, we have compared TiO<sub>2</sub> ALD on Cl- vs. Br-terminated Ge surfaces. We have also explored the ability of alkanethiolate SAMs formed on halogenated Ge surfaces to block TiO<sub>2</sub> deposition for application to area selective ALD (ASALD). Titanium tetrachloride (TiCl<sub>4</sub>) and water were employed as ALD precursors with 2 s pulse times, separated by a 10 s N<sub>2</sub> purge. Deposition was carried out over a range of substrate temperatures (100-300°C). The halogenated, thiolated, and TiO<sub>2</sub> coated Ge surface were investigated by various experimental and theoretical methods, including water contact angle (WCA) measurements, ellipsometry, transmission infrared (IR) spectroscopy, x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and density functional theory (DFT).

Ellipsometry measurements show that the film thickness of the TiO<sub>2</sub> film deposited on the halogenated Ge samples is dependent upon both the type of passivation and the temperature, with significantly higher growth rates achieved at higher substrate temperatures, most probably due to halogen desorption (Figure 1). At lower temperature (100°C), TiO<sub>2</sub> ALD was observed to a significant extent only on the Cl-passivated Ge(100) surface. This temperature-dependent trend was also separately confirmed by XPS. As shown in Figure 2(a), ~14.8% Ti was detected at the Cl-terminated Ge(100) surface at 100°C after 50 ALD cycles. Moreover, our XPS and AES results show formation of stoichiometric TiO<sub>2</sub> at this functionalized surface.

Finally, we have explored the area selective ALD of TiO<sub>2</sub> at the Ge surface. WCA, AES, XPS, and IR results show formation of well-packed 1-octadecanethiolate (ODT) SAMs after thiolation of Cl-terminated Ge(100) surfaces. Furthermore, as shown in the XP spectrum in Figure 2(b), ODT SAMs protect the Ge(100) surfaces from ALD at 100 °C (i.e. only ~<0.3% is Ti detected). Although the SAMs are stable at 100°C under ALD conditions, we have found that they decompose at temperatures above 100 °C under ALD conditions. Hence, bromination/thiolation is not compatible with ASALD of TiO<sub>2</sub> on Ge, since it would require growth at temperatures above 100°C, whereas the

chlorination/thiolation route can be employed for selective deposition of TiO<sub>2</sub> on Ge(100).

These results demonstrate a new route to Ge surface functionalization and passivation, and also demonstrate ASALD of TiO<sub>2</sub> on Ge at low temperatures.

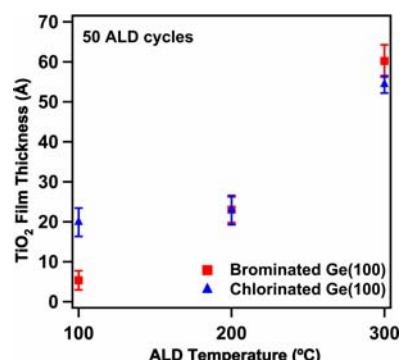


Figure 1. TiO<sub>2</sub> film thickness as a function of substrate temperature.

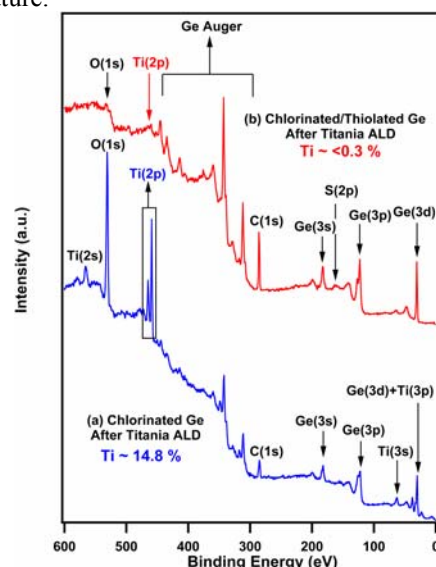


Figure 2. XP spectra of (a) chlorinated Ge(100) and, (b) thiolated Ge(100) after 50 cycles of TiO<sub>2</sub> ALD at 100 °C.

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- (2) Ardalan, P.; Musgrave, C. B.; Bent, S. F. *Langmuir* **2009**, 25, 2013-2025.
- (3) Ardalan, P.; Pickett, E. R.; Harris Jr., J. S.; Marshall, A. F.; Bent, S. F. *Appl. Phys. Lett.* **2008**, 92, 252902.