

Unveiling the effect of the starting precursor on Ge₂Sb₂Te₅ atomic layer deposition

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Chalcogenide materials like Ge₂Sb₂Te₅ (GST) are widely studied for application in memory devices [1]. To address the material needs resulting from the architectural device challenges within storage class memory (SCM), atomic layer deposition (ALD) has emerged as a prominent solution. Pore et al. have demonstrated a low temperature ALD process for GST using GeCl₂.C₄H₈O₂, SbCl₃, and Te[(CH₃)₃Si]₂ as precursors [2]. This process comprises the two binary ALD processes of GeTe and Sb₂Te₃ in a specific ratio to target the desired Ge₂Sb₂Te₅ composition, using either GeCl₂.C₄H₈O₂ or SbCl₃ as the first precursor pulse. This first pulse could affect the final film composition, and as such affect device performance.

In this work, we therefore study how the starting precursor influences the GST growth behavior and layer composition when deposited on SiO₂. The deposition on the SiO₂ substrate is initially Ge-rich, irrespective of the starting precursor, and gradually evolves to the desired 2:2:5 Ge:Sb:Te ratio when the thickness increases. The ideal composition is reached after 36 cycles. The interfacial Ge content is slightly higher when the GST ALD process starts with a GeCl₂.C₄H₈O₂ reaction as compared to starting with a SbCl₃ reaction, according to X-ray Fluorescence (XRF) (Fig. 1).

The chemical reactions at the GST/SiO₂ interface are investigated more thoroughly through chemisorption experiments, where we apply a single precursor reaction and measure the surface concentration of either Ge, Te or Sb ex-situ by means of total reflection XRF (TXRF). The results indicate that GeCl₂.C₄H₈O₂ has a higher reactivity towards SiO₂ than SbCl₃, as the concentration of Ge is ~4 times higher than the concentration of Sb. Almost no Te was observed after a single Te[(CH₃)₃Si]₂ reaction, indicating very low reactivity. We also investigate the subsequent Ge, Te, and Sb precursor reactions after a first Sb, Te, or Ge precursor reaction on SiO₂ and analyze the results assuming that only ligand exchange reactions take place, according to the model in [3] (Fig. 2-3). Based on the concentration of Ge, Te, and Sb, we propose that Ge could react with two surface hydroxyl groups on the SiO₂ surface. On the other hand, due to the lower reactivity of SbCl₃, we propose that there are still unreacted surface hydroxyl groups after the SbCl₃ reaction that can react with GeCl₂.C₄H₈O₂ during the next pulse. This model leads to an overall Ge-rich GST at the interface, irrespective of the starting precursor.

References:

1. T. Kim et al., IEEE Trans Electron Devices **67**, 1394 (2020).
2. V. Pore et al., J Am Chem Soc **131**, 3478 (2009).
3. R. L. Puurunen, Chemical Vapor Deposition **11**, 79 (2005).

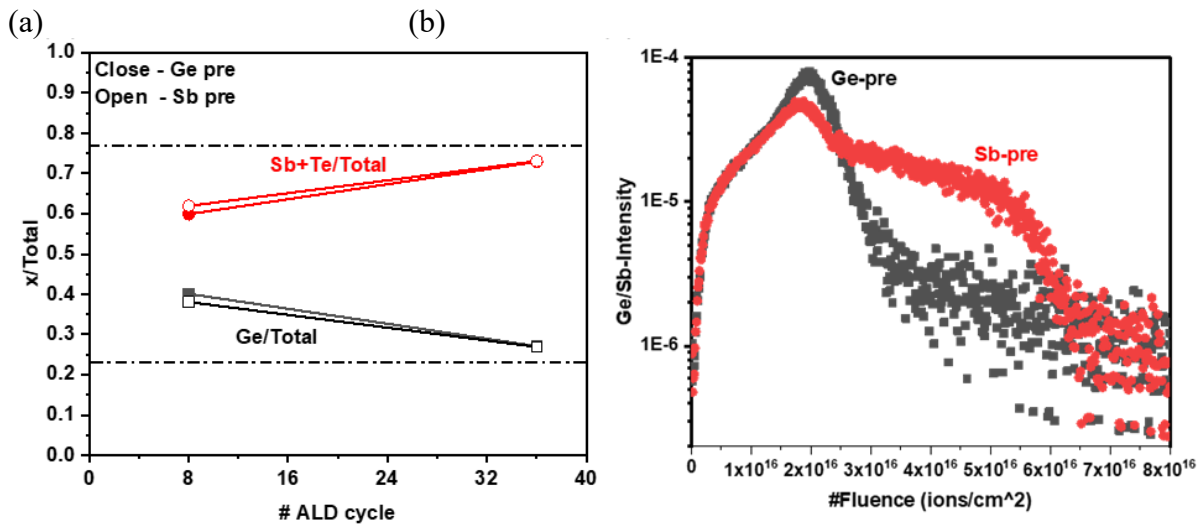


Figure 1(a) GST composition using XRF and (b) ToF-SIMS data of GST showing the Ge/Sb intensity ratio with sputtering flux, for different starting precursors.

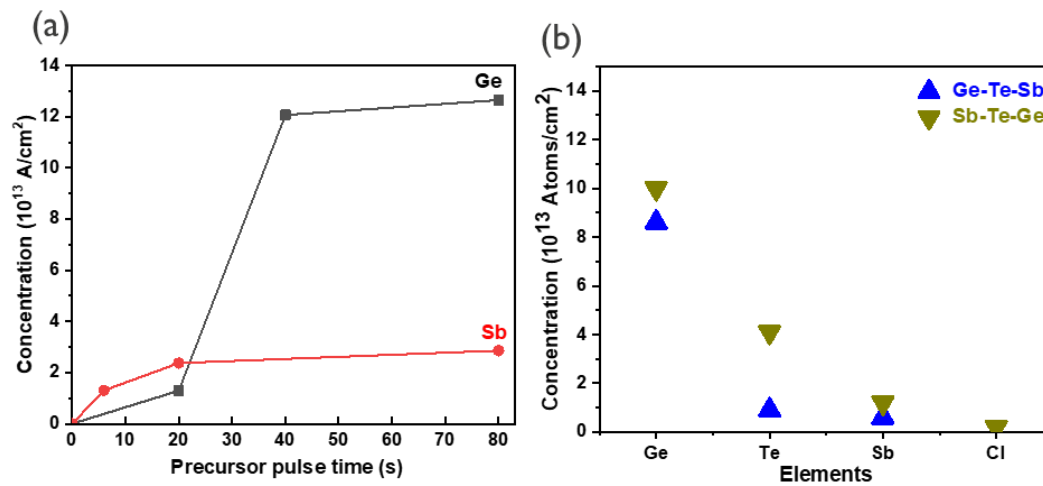


Figure 2 (a) Concentration of Ge and Sb with pulse time and (b) concentration of Ge, Te, Sb and Cl for the Ge-Te-Sb and Sb-Te-Ge precursor sequences using T-XRF.

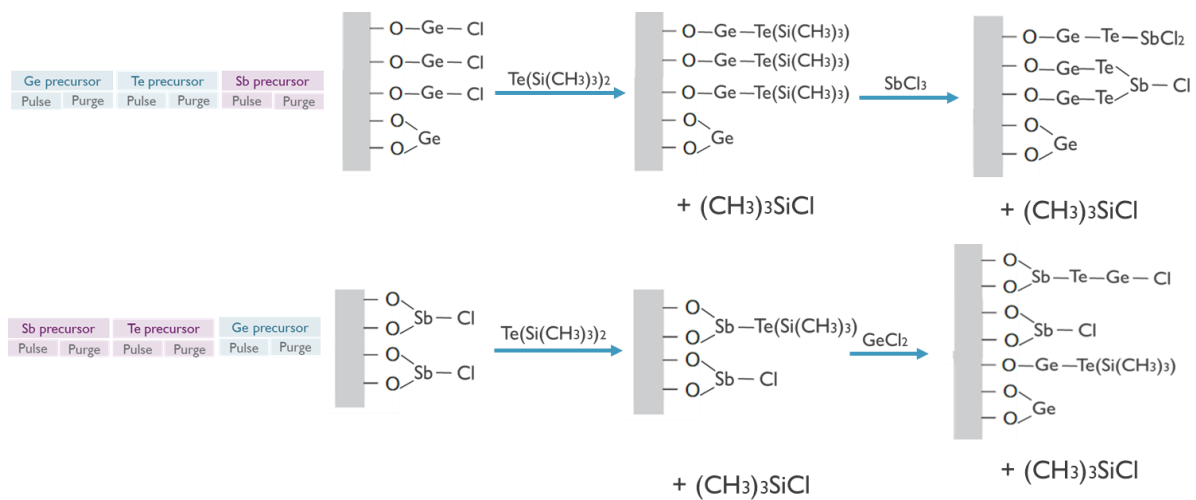


Figure 3 Proposed reaction mechanism for the (a) Ge-Te-Sb and (b) Sb-Te-Ge precursor sequence.