Resistive capillary array calorimetry method for ALD and ALE processes

Calorimetry is an essential analytical technique for determining the thermodynamics of chemical reactions. In-situ calorimetry during atomic layer deposition and etching (ALD/ALE) processes would be a valuable tool to probe the surface chemical reactions that yield self-terminating growth and removal of material at the atomic scale. Besides this, in-situ calorimetry would reveal the partitioning of chemical energy between the individual half-reactions that constitute the ALD or ALE cycle. Here we present a calorimetry strategy that utilizes the temperature-induced resistance changes in ALD thin films. Our calorimetry approach utilizes an ALD nanocomposite resistive thin film deposited conformally on the inner surfaces of microcapillary array substrates. These substrates are fabricated using borosilicate glass capillaries, 3D-printing, or through-substrate interposers. The ALD nanocomposite layer has a high resistivity and a well-defined thermal coefficient of resistance (TCR), both of which can be fine-tuned by adjusting the nanocomposite layer composition via ALD process parameters.

In practice, the resistive capillary array (RCA) calorimeter is installed in the ALD system and electrically biased to produce a current that is recorded in real time. During the ALD/ALE surface reactions, heat exchanged with the coating produces transient current features due to the non-zero TCR of the nanocomposite resistive layer. These transient features are highly reproducible and can be used to calculate the reaction enthalpies of the individual surface reactions based on the TCR value and the thermo-physical properties of the capillary array substrates. The RCA calorimeter is highly sensitive due to the high surface area of the microcapillary array substrate, the rapid response of the nm-scale resistive coating, and the tunable TCR value. Moreover, the calorimeter device is relatively low cost and can be easily integrated into ALD/ALE systems for precursors reaction monitoring.

To demonstrate the RCA calorimetry method, we performed in-situ calorimetry measurements for a range of ALD processes including Al_2O_3, AlF_3, $Al_xO_yF_z$, ZnO, MgO, TiO_2, and ZrO_2 as well as ALE processes including Al_2O_3, TiO_2, MoS_2, and HfO_2. We also studied the nucleation behavior when transitioning between ALD processes and from ALD to ALE processes. We find good agreement between reported enthalpy changes for ALD reactions and the values measured by in-situ RCA calorimetry. We believe that RCA calorimetry is a versatile in situ method to study the thermodynamics of ALD/ALE surface reactions and a convenient diagnostic for real-time ALD/ALE process monitoring in a manufacturing environment. For an instance, this RCA calorimetry method is useful for ALD/ALE process optimization, e.g., gas flow monitoring, precursor dose /flux monitoring over ultra-high aspect ratio large wafers, precursor distribution from a showerhead, reaction byproduct monitoring at the outlet of the reactor and after pump exhaust system. Briefly, we will also discuss the challenges and limitations of RCA calorimetry method.