Electrical Interconnects Based on Delafossite Thin Films

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Primary CNF Tools Used: Veeco Savannah ALD, Woollam RC2 Spectroscopic Ellipsometer,

Rapid Thermal Anneal - AG Associates Model 610, Everbeing SR-4 4-Point Probe Station

Abstract:

The dramatic increase in the resistivity of threedimensional (3D) metal interconnects with decreasing dimensions presents a significant bottleneck for further downscaling of integrated circuits [1]. This rise in resistivity is due to increased interface electron scattering as the interconnect dimensions approach their electron mean free path. Metallic delafossite oxides, specifically PtCoO₂ and PdCoO₂, present an alternative solution due to their Quasi-2D nature which mitigates interface electron scattering due to a 2D Fermi surface (Figure 1). Synthesis of high quality single-crystal delafossite thin films has been previously demonstrated by molecular beam epitaxy (MBE) [2], however, the challenge remains to demonstrate similarly high quality growth with a back-end-of-the-line (BEOL) synthesis technique such as atomic layer deposition (ALD).

We want to realize high quality single-crystal ALD synthesis of $PtCoO_2$ for which we need to develop a ternary ALD process made up of the PtO and Co_xO_y binary cycles, with overlapping processing conditions. In this study, we will present on the development of the Co_xO_y binary cycles under favorable conditions for ternary $PtCoO_2$ growth. We optimized Co_xO_y growth with respect to temperature, Co-pulse length, O_3 exposure time, purging conditions, adhesion layer, and the number of cycles. We characterized the growth with ellipsometry, X-ray diffraction, and X-ray reflectivity.

Summary of Research:

To grow high-quality, single-crystal $PtCoO_2$ films, we had to determine the optimal ALD conditions for the $PtCoO_2$ process, which combined Co_xO_y and PtO binary cycles. The Co_yO_y binary cycle was calibrated at

a substrate temperature suitable for deposition of PtO to support our ternary deposition process. Temperature windows with the Cobalt precursor Bis(N,N"-di-i-propylacetamidinato)cobalt(II) [Co(iPr-MeAMD)₂] and O₃ as a co-reactant are documented above 200°C [3] while the Pt deposition process is characterized above 175°C at the Cornell NanoScale Science and Technology Facility (CNF) using the same deposition tool where we calibrated our Co_xO_y cycle.

We found growths per cycle (GPC) of $\text{Co}_x \text{O}_y$ films at 150 and 175°C that were greater than growth values documented in literature at higher temperatures using similar processes (Figure 2). Increased GPC was observed by splitting up long precursor pulses into shorter, successive pulse/purge sub-cycles that resulted in the same cumulative precursor exposure (Figure 3). Linear GPC at substrate temperature of 150°C growth was observed without saturating O_3 vapor pressure, which indicated ALD growth, but yielded growth rates an order of magnitude lower than with a saturated O_3 pulse (Figure 4).

Deposition of $Co_x O_y$ was calibrated on an Al_2O_3 adhesion layer as well as native SiO₂ layer and no difference in film growth was observed. The N₂ flow rate of the chamber was determined not to affect the film growth because the ratio of precursor to carrier gas remained constant and residence time of the precursor did not increase. With an unsaturated O₃ co-reactant vapor pressure, we found Co saturation at 0.5 seconds, but with very low GPC.

 $PtCoO_2$ films were grown via ALD at an increased O_3 vapor pressure, but preliminary anneals in oxygen — measured using X-ray diffraction (XRD) — did not yield crystalline PtCoO₂ films.

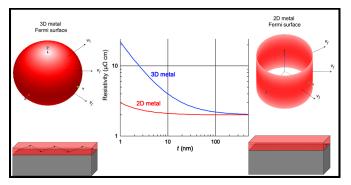


Figure 1: The quasi-2-dimensional crystal structure of the metallic delafossite oxides yield a nearly cylindrical Fermi surface with limited electron mobility out-of-plane. 3D metals (such as Cu) have a nearly spherical Fermi surface. We expect to see that the thickness of these interconnects will have a less dramatic impact on the resistivity of our quasi-2D material films.

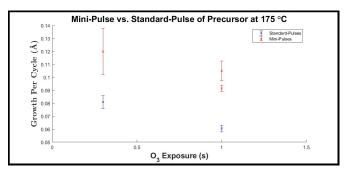


Figure 3: Increased GPC is shown using mini-precursor-pulses and multiple O_3 exposures.

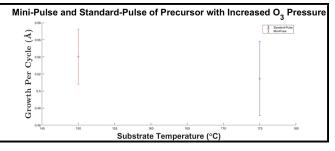


Figure 2: GPC plotted against substrate temperature at an increased O_3 pressure showing a growth rate greater than literature values documented at higher substrate temperatures.

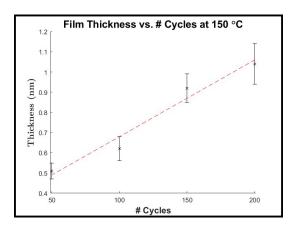


Figure 4: Average $Co_x O_y$, film thickness vs. number of cycles at 150°C substrate temperature. $Co_x O_y$, film thickness was measured at 65 points across a wafer using ellipsometry with a fixed refractive index. $Co_x O_y$ thickness accounts for any adhesion layer (Al_2O_3) and native SiO₂.

Conclusions and Future Steps:

So far, we have shown $\text{Co}_x \text{O}_y$ ALD growth at suitable temperature for ternary PtCoO₂ supercycle and determined that mini-precursor-pulses greatly increase GPC of binary ALD processes. We have also calibrated this cycle at 150°C, which we believe would overlap with the PtO binary cycle.

We must now calibrate the PtO binary cycle to determine the ratio between binary cycles in our supercycle that will yield optimal PtCoO₂ films. After we deposit amorphous PtCoO₂, we must anneal the films to achieve our desired crystallinity. We must calibrate the annealing conditions of these films to produce single-crystal PtCoO₂ films without PtO or Co_xO_y contamination. We will also measure the electrical properties of these films at varying thickness to assess the resistivity scaling curves of these materials at decreasing dimensions.

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