**BAPVC Annual Project Report**

**Project Title:** Improving the Long-Term Stability of Perovskite Solar Cells
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## Summary:

We have been developing conformal, atomic layer deposited (ALD) titanium oxide ($TiO_2$) barrier layers to prevent volatile organic components of methylammonium lead iodide ($MAPbI_3$) from leaving perovskite solar cells to improve their thermal and long term stability. Conditions for low temperature ALD deposition of $TiO_2$ were determined in order to reduce damage to the perovskite during deposition. We have also deposited our first titanium oxide films on the perovskites and are working to further reduce damage to the perovskite during deposition.

## Key Accomplishments:

We did preliminary research on ALD-$TiO_2$ protection of perovskite absorbers ($CH_3NH_3PbI_3$), which indicated that the perovskite material is not stable when the deposition temperature is above 100 °C. As typical ALD temperatures for $TiO_2$ are 150°C -170 °C, it was necessary to develop a low temperature ALD $TiO_2$ growth process for our project. To better understand the electronic and basic material properties of this material, we first studied low temperature ALD $TiO_2$ growth on crystalline silicon substrates. We used tetrakis(dimethylamino) titanium (TDMAT) as the titanium precursor and water as the oxygen source to try to deposit $TiO_2$ on silicon at 45 °C. We demonstrate that even at these low temperatures, the growth is quite linear, consistent with self-limiting precursor surface reactions (**Figure 1, left)**. X-ray photoelectron spectroscopy (XPS) measurements show a relatively small nitrogen concentration in the films, which indicates the organic component of the TDMAT leaves the film with little residue during deposition at 45°C. Electrical characterization (**Figure 1, right**) of this material shows that the leakage current decreases as the thickness increases. To test whether there are pin-holes in the film, we performed Auger analysis. The data shows that there is no signal present from the silicon substrate on which we deposit 10 nm $TiO_2$, which indicates good surface coverage for this film thickness. Further experiments are needed (e.g. conductive AFM) to test for pinholes in thinner low-temperature ALD-$TiO_2$ films.

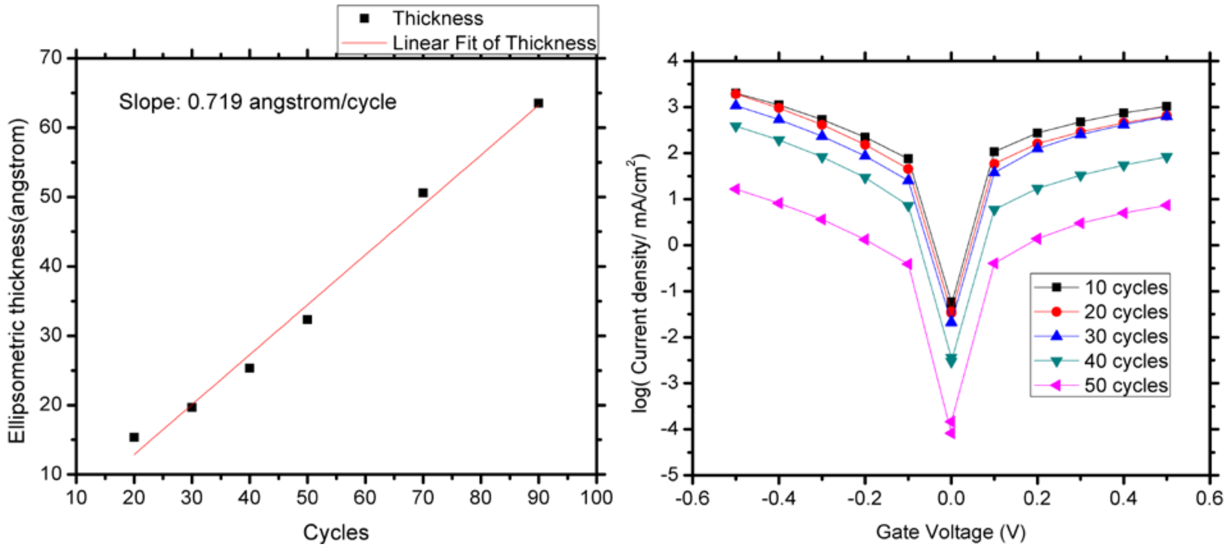


**Figure 1. (left)** Ellipsometric thickness of $TiO_2$ as a function of ALD cycles. **(right)** Current-voltage measurements of the silicon samples after ALD.

We have begun to deposit $TiO_2$ on top of perovskite films using this process. XPS measurements show the titanium signal increases roughly in proportion to the number of ALD cycles, indicating there is no problem initiating $TiO_2$ growth on top of the perovskite. However, X-ray diffraction (XRD) measurements show the presence of lead iodide ($PbI_2$), indicating that the perovskite is partially degraded after only 15 cycles of ALD. Optimization of the $TiO_2$ growth conditions is our current focus in order to develop conformal protective thin $TiO_2$ films which do not disrupt the quality of the underlying perovskite material and allow for efficient solar cell performance.

**Future Work:**

In the coming six months we will explore other $TiO_2$ ALD deposition conditions to minimize damage to the perovskite. In particular, we will try using other chemistries, such as ozone, that do not involve using water as the oxygen source, as water moisture is known to degrade the perovskite into lead iodide. Successful deposition will be determined by the lack of lead iodide peaks in the XRD pattern. We will also deposit $C_{60}$ on top of the perovskite prior to titania deposition to try to protect the perovskite, as well as improve electron extraction in full solar cells. We may need to incorporate zinc nanoparticles into the $C_{60}$ to help seed the titania growth to improve coverage. Additionally, we are beginning measurements using a residual gas analyzer (RGA) to identify the volatile compounds that leave perovskite films and solar cells when exposed to vacuum or heated. These studies will help inform the design of barrier materials and encapsulants to prevent the egress of these species.