Characterizing Epitaxial Growth of Nd$_2$Ir$_2$O$_7$ Pyrochlore Thin Films via HAADF-STEM Imaging and EDX


1. Department of Materials Science and Engineering, The Ohio State University, Columbus, OH, USA
2. Department of Physics, The Ohio State University, Columbus, OH, USA
3. Department of Chemistry, The Ohio State University, Columbus, OH, USA

Much interest has been given to the 5d transition metal oxides because of their strong spin-orbit coupling, leading to the prediction of new exotic phases of matter, including the Weyl semimetal, topological Mott insulator, and spin liquid [1–4]. The pyrochlore iridates with the general formula of A$_2$Ir$_2$O$_7$ have been predicted to show the Weyl semimetal and topological insulator phases under epitaxial strain [5,6]. These theoretical predictions have motivated the study and growth of epitaxial thin films of such pyrochlore iridates. In this work, we report the synthesis of Nd$_2$Ir$_2$O$_7$ and growth of epitaxial thin films using off-axis magnetron sputtering and ex-situ post-growth annealing. Using aberration corrected high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and energy dispersive X-ray spectroscopy (EDX), the growth mechanisms of Nd$_2$Ir$_2$O$_7$ are characterized. A thermodynamic explanation of the observed mechanisms is presented.

Phase-pure powders of Nd$_2$Ir$_2$O$_7$ were created via a mixture of Nd$_2$O$_3$ and IrO$_2$ with a slight excess of IrO$_2$. Synchrotron X-ray diffraction (XRD) confirms stoichiometric pyrochlore powders with a lattice constant of $a = 10.373$ Å and slight oxygen inhomogeneity. The powders were pressed into a target for sputtering in ultra-high vacuum. Films were deposited on (111) yttria-stabilized zirconia (YSZ) at room temperature. The as-deposited films were amorphous with stoichiometric ratios of Nd, Ir, and O. A 12-hour ex-situ post-growth anneal at 750°C was used to fully crystallize the films. XRD and STEM imaging show a lattice constant of $a = 10.387$ Å and an epitaxial relationship between the film and the substrate, where $<111>_{\text{Nd}_2\text{Ir}_2\text{O}_7} || <111>_{\text{YSZ}}$ and $<110>_{\text{Nd}_2\text{Ir}_2\text{O}_7} || <110>_{\text{YSZ}}$.

In some cases, HAADF-STEM imaging reveals a cloudy interfacial layer between the fully annealed films and the substrate, as seen in Fig. 1, in spite of the fact that images filtered by fast Fourier transform prove that there is a continuous epitaxial interface. In order to explain this, an annealing study was performed for post-growth anneal times shorter than 12 hours. A quick 5-minute anneal with the same ramp rate, hold temperature, and atmosphere resulted in isolated crystalline islands within the amorphous as-deposited film. HAADF-STEM imaging revealed clear pyrochlore ordering within the islands and confirmed that the remaining material was amorphous, Fig. 2. EDX line scans with experimentally determined Cliff-Lorimer $k$-factors showed that the crystalline and amorphous materials both remain stoichiometric, Fig. 3. Void spaces were observed around crystalline island/amorphous/substrate interface in which 2 nm metallic Ir nanocrystals were found to agglomerate. These same crystallites were also found to be the cause of the cloudy interfacial layer that was sometimes seen between the film and the substrate.

Given the heat capacities of both Nd$_2$O$_3$ and IrO$_2$, it can be shown that during the 750°C post-anneal, temperatures at the growth front can exceed the decomposition temperature of IrO$_2$, resulting in the metallic Ir nanocrystals. We assert that the inconsistent observation of a cloudy layer between the film and the substrate is dependent on the location from which the TEM sample was taken using the focused ion beam (FIB). When a FIB foil is taken near the coalescence of two or more grains, it may contain
some of these Ir nanocrystals, clouding the interface; whereas, FIB foils taken from the center of a grain will not.

[7] Funding for this research was provided by the Center for Emergent Materials at the Ohio State University, an NSF MRSEC (Award Number DMR-1420451).

![Figure 1: Nd$_2$Ir$_2$O$_7$/YSZ interface showing apparent epitaxy in spite of the cloudy interface](image1.png)

![Figure 2: Crystalline Nd$_2$Ir$_2$O$_7$ islands nucleating at the YSZ interface after a 5-minute *ex-situ* anneal from the amorphous, as-deposited film](image2.png)

![Figure 3: EDX line scan across the amorphous/crystalline Nd2Ir2O7 interface, showing that both materials have the same stoichiometry](image3.png)