Growth and Polymorphism of Insulating Delafossites

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Abstract

Silver cobalt oxide ($AgCoO_2$) , a delafossite-structure material, was synthesized with molecular-beam epitaxy (MBE).The films were characterized using high-energy electron diffraction (RHEED), X-ray diffraction (XRD) and atomic force microscopy (AFM) to analyze their structure and surface quality. Both the rhombohedral and hexagonal polymorphs were observed in our samples. In this work we were able to successfully interface $AgCoO_2$ with $PdCoO_2$ in both orientations, demonstrating $AgCoO_2$'s potential as a pseudosubstrate for future applications. .

Introduction

Delafossite are a class of layered materials with the general formula ABO_2, where A is a monovalent metal such as Ag^+ or Pd^+, B is a trivalent transition metal such as Co^{3+}, and O represents oxygen(1). Depending on the elements involved, delafossites can range from semi-metallic to insulating, and some even have transparent properties(1). Their unique combination of structural and electronic characteristics makes them promising for a variety of electronic and magnetic applications. For example, $PdCoO_2$ and $PtCoO_2$ have higher conductivity than their constituents(2); $AgFeO_2$ is known for its magnetic applications; and $CuFeO_2$ and $CuCrO_2$ have been shown as p-type transparent semiconductor (3).

Two crystal polymorphs exist within this family: rhombohedral ($R\bar{3}m$) and hexagonal ($P6_3/nmc$). In the rhombohedral structure the oxygen atoms follow the A-B-C stacking pattern, while in the hexagonal structure they follow an A-B stacking pattern. The primary difference between these structures lies in the stacking pattern in the middle BO6 octahedral layers, however both share alternating A layers and octahedral layers, which is key to the delafossite structure(1). Like all materials, delafossites can contain structural defects. One specifically is twinning, which is a grain boundary in which you have two identical crystal structures, but one is flipped or rotated relative to the other. Twinning is commonly observed in delafossite thin films grown on c-plane sapphire due to a lattice mismatch; for c-plane sapphire, which has a hexagonal structure, and $AgCoO_2$, which has a rhombohedral structure, this mismatch is +/- 4.5%. The alternating termination of the sapphire substrate makes two in-plane domain orientations energetically equivalent, and combined with the different geometries of the unit cells, both orientations readily form leading to twinning (see Fig. 1.) This defect is undesirable because it can degrade electronic properties (4). We hypothesize that growing films in the hexagonal polymorph may suppress twinning due to the stacking difference eliminating the energetic degeneracy.

Within this broader class, we focused on silver cobalt oxide ($AgCoO_2$), a relatively understudied compound. $AgCoO_2$ has been proposed as a p-type transparent semiconductor and has also been shown to be insulating in bulk at room temperature (1,5). However, its conductivity in thin-film form remains largely unexplored. In this work, the goal is to better understand the growth and electronic properties of $AgCoO_2$ thin films. Insulating $AgCoO_2$ can serve as a high-quality delafossite template for growing other

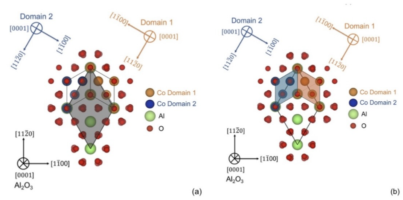

Fig. 1. (a) Schematic adapted from (3) source, highlights the hexagonal unit cell of the substrate. (b) Schematic showing the rhombohedral unit cells of the two domains in the material.

delafossites that do not grow well on c-plane sapphire or other commonly available substrates. It's important that the template is insulating so it does not affect the electronic properties of the material grown on top. In addition to optimizing growth conditions and characterizing $AgCoO_2$ thin films, this work also investigates its polymorphism, conductivity and compatibility with $PdCoO_2$.

Methods

To grow the samples, molecular-beam epitaxy (MBE) was used. All samples were grown on c-plane sapphire substrates with a constant flow of distilled ozone introduced into the MBE chamber as the oxidation source at a pressure of 8 x 10-6 Torr. For deposition, shutter growth was used, a method where each element is introduced for a specific time to precisely control the film's thickness and composition.

To use this method effectively, the sources' fluxes were calibrated to determine the time required to deposit a single monolayer of atoms. During growth, Reflection high-energy electron diffraction (RHEED) images were collected to monitor and analyze the surface structure and quality of the samples in situ. The main analysis techniques used to characterize the samples were X-ray diffraction (XRD) and atomic force microscopy (AFM).

Results

One challenge during growth was oxidizing silver in its +1 oxidation state, which is difficult to achieve. This is why distilled ozone was essential as a highly reactive oxidizing agent. To control the silver content in the samples, an $AgCoO_2$ shutter time series was performed. All samples were 15 unit cells (UC) thick and were grown at 400C and 8 x 10-6 Torr. At low shutter times, there was no additional silver metal in the sample, but the overall sample quality was poor. At higher shutter times, silver peaks appeared despite overall sample quality improving (see Fig. 2). Regardless of the silver content deprived, all samples remained insulating, which aligned with the intended goals.

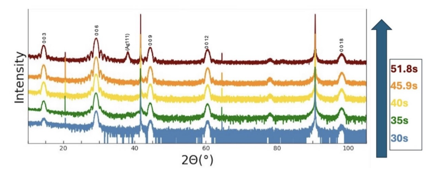

Fig. 2. XRD plot showing that the short shutter times resulted in lower silver peaks and poor sample quality, while long shutter times produced more pronounced silver peaks and improved film quality.

After addressing the challenge of controlling silver content, another concern was the growth of thicker samples, which required re-optimization of growth conditions. For this series, a range from 5 to 50 UC was grown, revealing a decline in crystal quality and the appearance of silver impurities at 50 UC (see Fig. 3). This indicated that re-optimization of growth conditions was necessary to produce high-quality thicker samples.

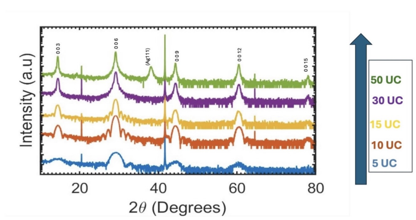

Fig. 3. XRD plot showing that as the sample thickness increased, silver peaks became more pronounced and the over film quality declined

After re-optimization, a high-quality thick sample was obtained. AFM images for the sample revealed the presence of two polymorphs (see Fig. 4). Phi scans, an X-ray diffraction method, was performed to identify twinning and confirm the polymorphs. In Figure 5, six peaks are observed for the rhombohedral structure, where only three are expected. This was confirmed by measuring the strong off-axis peak (0-18), which is forbidden in the hexagonal polymorph, indicating twinning. In Figure 6, six peaks appear for the hexagonal polymorph; this was confirmed by measuring an off-axis peak (105) forbidden in the rhombohedral polymorph. These results suggest that these polymorphs could potentially be stabilized and serve as templates in the future.

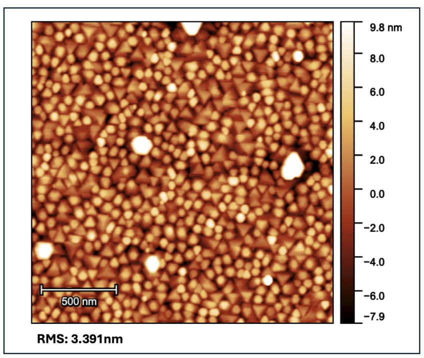

Fig. 4. AFM image showing indications of two polymorphs: rhombohedral regions appear as triangles and hexagonal regions appear as hexagons.

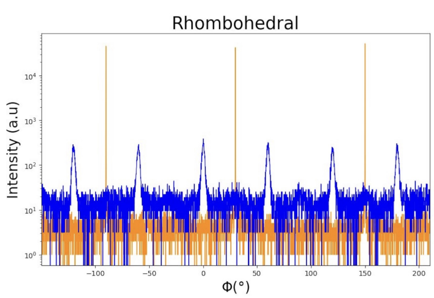

Fig. 5. Phi scan of the rhombohedral polymorph showing six peaks instead of the expected three indicating that there, indicating twinning. The similar heights of the peaks suggest similar domain populations. Orange represents the substrate, and blue represents the smaple.

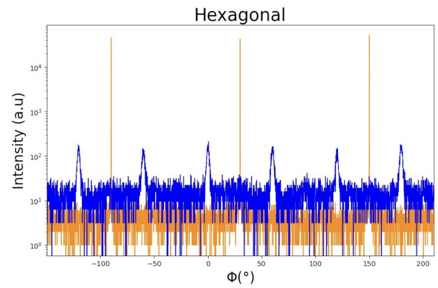

Fig. 6. Phi scan of the hexagonal polymorph showing six peaks, as expected, indicating the presence of this polymorph.. Orange represents the substrate, and blue represents the smaple

An initial investigation into $AgCoO_2$'s compatibility with other delafossites was performed by interfacing it with $PdCoO_2$. $PdCoO_2$ was chosen because it is a well-studied delafossite, and high-quality films have been demonstrated via MBE in previous works (4,6). First, $AgCoO_2$ was grown on top of $PdCoO_2$ while collecting RHEED images during growth. The middle and outermost streaks are what we expect to see for delafossites, while the fainter streaks indicate twinning or the presence of a different polymorph. In Figures 7(c) and 7(d), the streaks appear slightly bumpier, suggesting that the film surface is rougher. As seen in Figure 8, all the expected XRD peaks for both materials are present, with only a very small silver peak, indicating a successful attempt to stabilize the bi-layer.

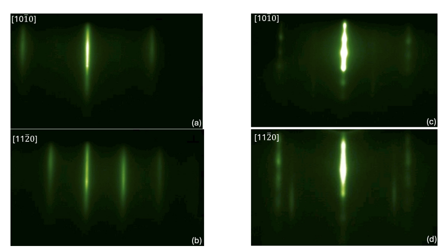

Fig. 7. (a) and (b) RHEED images of $PdCoO_2$ showing sharp streaks typical of a delafossite structure. (c) and (d) RHEED images of AgCoO2 grown on $PdCoO_2$, where the streaks appear bumpier indicating a slightly rougher film surface.

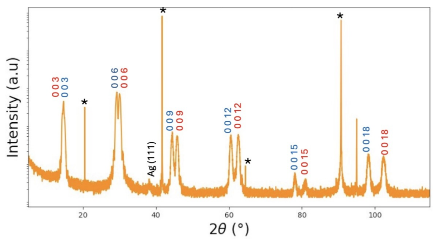

Fig. 8. XRD plot of $AgCoO_2$ grown on $PdCoO_2$, where the blue is ACO and red is PCO. All expected peaks for both materials are present, and the minimal silver metal peak indicates a high-quality sample.

Next, the growth order was by growing $PdCoO_2$ on $AgCoO_2$. RHEED for this sample can be seen In Figures 9(c) and 9(d), the streaks also are bumpy, again suggesting a rougher film surface. XRD measurements of this sample are shown in Figure 10, revealing all expected peaks. The sample quality is somewhat lower compared to the previous growth, likely because $PdCoO_2$ requires higher growth temperature, making it more challenging to grow on top of AgCoO2 due to intercalation at the interface. A small silver peak is seen in the XRD, but overall, these results still indicate potential for $AgCoO_2$, once further optimized, to serve as a template for other delafossites.

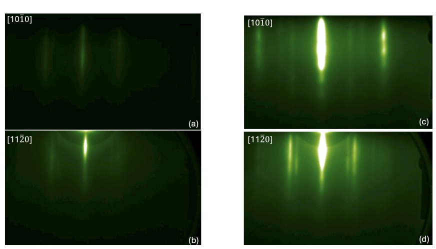

Fig. 9. (a) and (b) RHEED images of $AgCoO_2$ showing sharp streaks typical of a delafossite structure. (c) and (d) RHEED images of $PdCoO_2$ grown on $AgCoO_2$, where the streaks appear bumpier indicating a slightly rougher film surface.

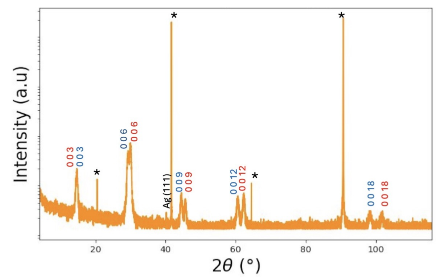

Fig. 10. XRD plot of $PdCoO_2$ grown on $AgCoO_2$, where the blue is ACO and red is PCO. All expected peaks for both materials are present, and the minimal silver metal peak indicates a good-quality sample.

The ACO peaks match perfectly with their expected positions, while the PCO peak for $PdCoO_2$ grown on $AgCoO_2$ is slightly shifted, likely due to the lower quality of that sample. Since the peak positions did not significantly shift, this suggests the films are relaxed and not strained. This small shift, combined with the successful observations of all expected peaks for both materials indicates that the interfacing of $AgCoO_2$ and $PdCoO_2$ was successful and demonstrates strong potential for advancing $AgCoO_2$ as a template for other delafossites.

Conclusion and Next Steps

We optimized the growth conditions of $AgCoO_2$, and found that regardless of the amount of silver deprived, the samples remained insulating. We successfully interfaced $AgCoO_2$ with $PdCoO_2$ in both ways, moving a step closer to using $AgCoO_2$ as a delafossite template for growing other delafossites. Additionally, our RHEED images and Phi scans revealed evidence of twinning and the presence of a mix of polymorphs in our $AgCoO_2$. The next steps are to improve the surface quality of our $AgCoO_2$ samples. This will allow for further testing to determine whether they can be interfaced with other delafossites for use as a template. We also plan to stabilize our polymorphs. One step is enhancing substrate preparation, through cleaning or annealing, to create a more suitable surface for nucleation. Additionally, a slower growth rate could also promote step-flow growth. These results highlight the potential of $AgCoO_2$ and similar delafossites, paving the way for future studies and applications in electronics and energy devices, and demonstrating why this class of materials is so compelling to explore.

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