Expitaxizing Untwinned $PdCoO_2$ Films by MBE

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Abstract

$PdCoO_2$ is a metallic delafossite material with a layered triangular structure and high in-plane conductivity, even higher than Pd metal itself. Thin film $PdCoO_2$ grown with Molecular Beam Epitaxy (MBE) on Al_2O_3 (0001) substrates currently has some structural defects that increase its resistivity. One of them is called "twinning," where the triangular structures go in two different directions 180 degrees opposite to each other. To solve the twinning problem, our Al_2O_3 substrates went through surface reconstruction from one-monolayer step height to two-monolayer step height before growth. However, after-growth characterizations such as Atomic Force Microscopy (AFM) and X-ray φ-scans still indicated twinning in our films grown on Al_2O_3 (0001) with two-monolayer step height. Alternatively, we have successfully achieved untwinned $CuCrO_2$ films on STO (111) substrates. Our future direction is to grow $PdCoO_2$ films on untwinned $CuCrO_2$ as buffer layers to eliminate twinning.

Introduction

Delafossite materials have a layered triangular structure with chemical formula *AB*O_2, mainly divided into insulating and metallic delafossites. $PdCoO_2$ [Fig. 1(a)] is one of the metallic delafossites with high in-plane conductivity, in room temperature comparable to aluminum and gold and even higher than pure palladium metal itself [1].

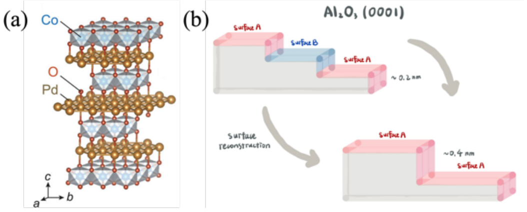

Figure 1. *Structure information. (a) Crystal structure of $PdCoO_2$ [2]. (b) Al_2O_3 (0001) substrate surface reconstruction description.*

Growing $PdCoO_2$ thin films by Molecular Beam Epitaxy (MBE), we can control growth size based on the substrate size (10×10mm) which is much larger than growing single crystals in the scale of only 1mm [3]; however, structural defects contribute to higher resistivity, one of them called "twinning"—$PdCoO_2$ has triangular structures 180 degrees opposite from each other. This happens on Al_2O_3 (0001) substrates, where the crystal structure in each one-monolayer high steps face in a different direction alternately, resulting in $PdCoO_2$ growing on top of them having triangular structures in two different directions. In order to solve twinning, surface reconstruction was performed on the Al_2O_3 substrates, making the steps from one-monolayer high to two-monolayer high [Fig. 1(b)]. As the steps from the substrate are now all facing in the same direction, we hoped to grow $PdCoO_2$ with triangles in the same direction, thus achieving untwinned films.

Alternatively, $PdCoO_2$ films are expected to grow untwinned on an untwinned insulating $CuCrO_2$ buffer layer. $CuCrO_2$ can be grown on STO (111) substrate which does not have a twinning problem; however, $PdCoO_2$ fails to grow directly on top of STO (111), requiring an oxidizing pressure too high to reach.

Methods

Specially treated Al_2O_3 substrates were provided by our collaborators by annealing in high temperature. We used MBE for growth, monitored by Reflection High Energy Electron Diffraction (RHEED). Growth methods were absorption control growth and shuttering control growth. After-growth characterizations included X-ray Reflectivity (XRR), X-ray Diffraction (XRD), X-ray φ-scan, and Atomic Force Microscopy (AFM). φ-scan and AFM were especially important for twinning analysis. From φ-scan, in the range of 360 degrees in-plane, three peaks were expected for the triangular structure; six peaks would indicate twinning in the film. From AFM, triangles oriented in two opposite directions would suggest twinning.

Results and Discussion

One of the specially treated Al_2O_3 substrates was scanned with AFM before growth [Fig. 3(a)]. Step height measured was around 0.449 nm, which is two monolayers as expected.

With same $PdCoO_2$ growth conditions on regular Al_2O_3 substrates, impurities appeared when growing on specially treated substrates. With absorption control growth, the impurities were palladium and Co_3O_4 [Fig. 2(a)]; with shuttering control growth, the impurities were PdO and Co_3O_4 [Fig. 2(b)]. This suggested that the surface energy of the Al_2O_3

substrate changed. New growth conditions are required to be found to attain pure $PdCoO_2$ films.

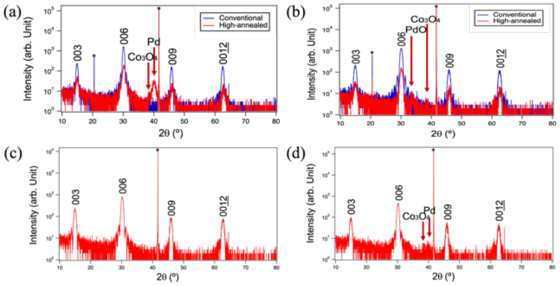

Figure 2. *XRD data for $PdCoO_2$. * = 006 peak of Al_2O_3 (0001) substrate. (a) Same absorption control growth condition on conventional and special Al_2O_3. (b) Same shuttering control growth condition on conventional and special Al_2O_3. (c) Best absorption control growth sample. (d) Best shuttering control growth sample.*

AFM images were taken for different impurities. A typical AFM image showed big dots of around 30nm high and around 100nm wide [Fig. 3(b)], another showed small dots of around 8nm high and around 60nm wide [Fig. 3(c)]. After comparing with the corresponding XRD images, the former was recognized to be palladium impurity, and the latter was recognized to be PdO impurity. The impurities guide direction towards modifying growth conditions.

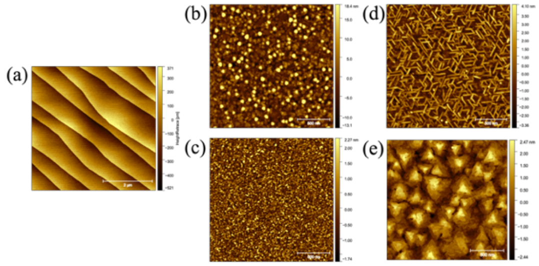

Figure 3. *AFM images. (a) For specially treated Al_2O_3 substrate. (b) For $PdCoO_2$ with Pd impurity. (c) For $PdCoO_2$ with PdO impurity. (d) For $PdCoO_2$ on special Al_2O_3. (e) For $PdCoO_2$ on conventional Al_2O_3.*

With improvement, we achieved almost pure $PdCoO_2$ films. For absorption control growth, the XRD image [Fig. 2(c)] contained strong peaks with clear fringes and no impurities. The AFM image [Fig. 3(d)] showed no dots suggesting pure films; however, there were three-fold strips on the surface, which is different from triangles we usually see for $PdCoO_2$ grown on regular Al_2O_3 substrates [Fig. 3(e)]. It was difficult to read whether there was twinning from the three-fold strips instead of oriented triangles. For shuttering control growth, $PdCoO_2$ film quality was also good, where there were only very weak Pd and Co_3O_4 impurity peaks shown on XRD [Fig. 2(d)].

X-ray φ-scans were conducted on the high-quality $PdCoO_2$ films grown on special Al_2O_3 substrates. From the results [Fig. 4(a)], there were still six peaks instead of three with equal intensity, indicating twinning.

With the alternative solution of growing $PdCoO_2$ on an untwinned buffer layer of $CuCrO_2$, we chose to find the optimal growth condition for $CuCrO_2$ films first. We achieved pure $CuCrO_2$ films on STO (111) substrate as proved by XRD [Fig. 4(b)]. What is especially exciting is that by φ-scan [Fig. 4(c)] there were only three $CuCrO_2$ peaks, confirming we have successfully achieved untwinned $CuCrO_2$ films. It is promising that we will be able to attain untwinned $PdCoO_2$ films in the future.

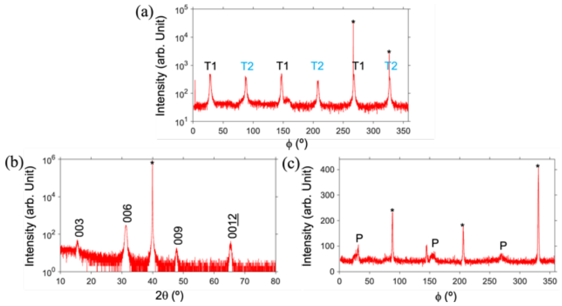

Figure 4. *X-ray data. (a) φ-scan for $PdCoO_2$ on special Al2O3. (b) XRD for $CuCrO_2$. (c) φ-scan for $CuCrO_2$.*

Conclusions and Future Work

Growth conditions for $PdCoO_2$ films changed after surface reconstruction was performed on the Al_2O_3 (0001) substrates to two-monolayer step heights. As seeking for the best growth conditions, we were able to distinguish various impurity phases in AFM. Finally, we have almost achieved pure $PdCoO_2$ films, but the twinning problem still exists.

Our future directions will be growing $PdCoO_2$ on untwinned $CuCrO_2$ buffer layer to solve the twinning problem. There is hope as we have successfully grown untwinned $CuCrO_2$ films on STO (111) substrates.

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