doi:10.1017/S1431927620015287

Microsc. Microanal. 26 (Suppl 2), 2020

# Oxygen Annealing Driven Structural Evolution in $PdCoO_2$ Films Through Electron Microscopy

Debangshu Mukherjee[1], Gaurab Rimal[2], Raymond Unocic[1], Ho-Nyung Lee[1], Seongshik Oh[2] and Matthew Brahlek[1]

[1]Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States, [2]Rutgers University, Piscataway, New Jersey, United States

$PdCoO_2$ is a layered delafossite crystal where the palladium, cobalt and oxygen atoms are arranged in alternate layers – with each layer possessing three-fold symmetry [1]. Because of its' layered structure delafossites in general and $PdCoO_2$ in particular, possess highly anisotropic electronic and thermal transport behavior. The in-plane resistivity for bulk single crystal $PdCoO_2$ along the palladium layers was reported as 5μΩcm at room temperature, which decreases to a residual resistivity of 0.51μΩcm at 30K [2]. This approaches conductive metals like copper or silver which have electrical resistivities of the order of 1μΩcm and is actually lower than pure palladium's room temperature resistivity of 11μΩcm. This makes $PdCoO_2$ an attractive material for applications that require high conductivity in oxygen rich environments. The origin for this high electronic conductivity arises due to delocalized bonding from hybridized Pd *4d* orbitals [3]. The out of plane resistivity of $PdCoO_2$ has been reported to be 100-150 times higher than the in plane resistivity, however $PdCoO_2$'s resistivity in both directions is metallic as the magnitude increases monotonically with temperature [2]. These properties have led to significant interest in synthesizing $PdCoO_2$ films, on the *c*-plane of either $Al_2O_3$ or $Ga_2O_3$ substrates - both of which are hexagonal crystals [4].

Recent work has demonstrated the successful growth of $PdCoO_2$ on $Al_2O_3$ (sapphire) substrates through molecular beam epitaxy (MBE) [5]. However, since $PdCoO_2$ is unstable at high temperatures (above $300^oC$) and low oxygen partial pressures – a two-step growth methodology was adopted, where the films were initially grown at low temperatures (below $300^oC$) and then subsequently annealed at higher temperatures ($700^oC$ to $800^oC$) in pure oxygen. To understand the effect of growth and subsequent annealing on the film morphology we performed aberration corrected scanning transmission electron microscopy (STEM) on both the as grown and the oxygen annealed films. **Fig. 1(a)** demonstrates the as grown film before oxygen annealing. We observed the presence of two interfacial layers of $Co_2O_3$ between the $PdCoO_2$ film and the sapphire substrate (inset) which was epitaxial to the substrate. The annealed films on the other hand (**Fig. 1(b)**) show voids between the $PdCoO_2$ film and the sapphire substrate with the $Co_2O_3$ layer missing – indicating that this layer is air unstable and decomposes during annealing. The unannealed $PdCoO_2$ is also polycrystalline, with layered regions embedded in amorphous regions, while the annealed film was observed to be single crystalline in the entire region of observation. However, we observed the presence of multiple mirror twin walls in the annealed $PdCoO_2$ film as could be observed in **Fig. 1(b)**, with **Fig. 1(c)** showing a zoomed-out section of the image marked by the black rectangle in **Fig. 1(b)**. The twin wall can be clearly observed through the rotation of the cobalt layers as compared to the palladium layers.

Thus, we demonstrate here that while *ex-situ* oxygen annealing can create highly monocrystalline films, the interfacial quality actually degrades due to the formation of $Co_2O_3$ during initial growth and its' subsequent decomposition. The unannealed $PdCoO_2$ is overall epitaxial near the interface with regions of disordered with non-oriented grains predominately away from the interfaces; the annealed film was, however, observed to be single crystalline in the entire region of observation [6].

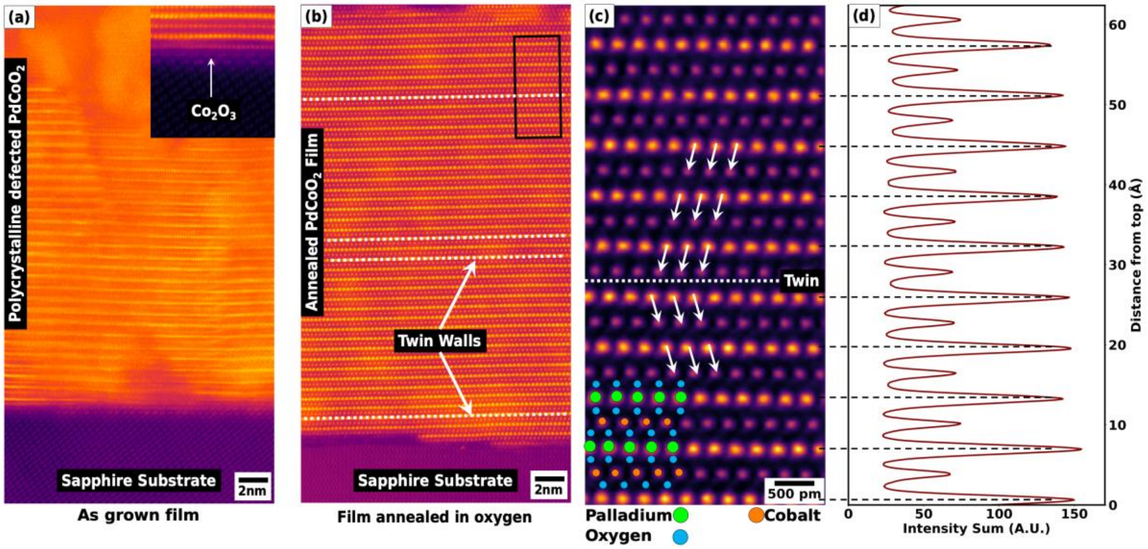

**Figure 1.** (a) STEM imaging of as-grown PdCoO2 on Al2O3 substrate, with the inset showing the presence of double cobalt layers at the film-substrate interface. (b) Oxygen annealed film showing voids between the film and substrate and the presence of multiple twin walls. (c) Zoomed in section of the film, showing the Pd-Co layer direction rotation at a twin wall. (d) Intensity profile of Fig. 1(c) demonstrating the presence of layered Pd-Co-Pd structure.

References
[1] Shannon et. al., Inorganic Chemistry, **10**(1971) p. 719.
[2] Tanaka et. al., Journal of the Physical Society of Japan, **65**(1996) p. 3973.
[3] Okabe et. al., Journal of Applied Physics, **93**(2003) p. 7258.
[4] Harada et. al., APL Materials, **6**(2018) p. 046107.
[5] Brahlek et. al., Physical Review Materials, **3**(2019) p. 093401.
[6] Research supported by ORNL's Laboratory Directed Research and Development Program, which is managed by UT-Battelle, LLC for the U.S. Department of Energy (DOE). Electron microscopy was conducted as part of a user proposal at Oak Ridge National Laboratory's Center for Nanophase Materials Sciences (CNMS), which is a U.S. DOE Office of Science User Facility.