Growth of PdCoO$_2$ by ozone-assisted molecular-beam epitaxy

Cite as: APL Mater. 7, 121112 (2019); https://doi.org/10.1063/1.5130627
Submitted: 05 October 2019 • Accepted: 08 December 2019 • Published Online: 27 December 2019

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Submitted: 5 October 2019 • Accepted: 8 December 2019 • Published Online: 27 December 2019

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ABSTRACT

We report the in situ, direct epitaxial synthesis of (0001)-oriented PdCoO$_2$ thin films on c-plane sapphire using ozone-assisted molecular-beam epitaxy. The resulting films have smoothness, structural perfection, and electrical characteristics that rival the best in situ grown PdCoO$_2$ thin films in the literature. Metallic conductivity is observed in PdCoO$_2$ films as thin as $\sim 2.0$ nm. The PdCoO$_2$ films contain 180$^\circ$ in-plane rotation twins. Scanning transmission electron microscopy reveals that the growth of PdCoO$_2$ on the (0001) surface of Al$_2$O$_3$ begins with the CoO$_2$ layer.

The delafossite PdCoO$_2$ is distinguished by having the lowest in-plane resistivity ($\rho_{ab}(4K) = 7.5$ n$\Omega$ cm) and longest mean free path ($\ell_{ab}(4K) = 21.4$ $\mu$m) of all known oxide materials. Its conductivity at room temperature is even higher than elemental copper per carrier. Moreover, this family of compounds hosts large spin-orbit coupling (SOC). A spin splitting of 60 meV and 120 meV of surface-derived bands arising from Rashba-like splitting has been observed on PdCoO$_2$ and PdRhO$_2$, respectively, using angle-resolved photoemission spectroscopy (ARPES). The combination of a layered structure, long mean free path, low density of states (for a metal), and large SOC makes PdCoO$_2$ a promising candidate for the next generation of spintronic devices, such as in the proposed Magneto-Electric Spin-Orbit (MESO) logic architecture.

The physics of PdCoO$_2$ and related metallic delafossites has been primarily studied using flux-grown single crystals that, despite decades of research, are still limited in size ($\sim 3$ mm in diameter). To facilitate further studies of its physical properties, particularly as its thickness is decreased down to a single formula unit, and the assessment of proof-of-principle spintronic devices, single crystals with large area and smooth surfaces in the form of thin films are needed. So far, PdCoO$_2$ has been synthesized in thin film form using sputtering, pulsed-laser deposition (PLD), and molecular-beam epitaxy (MBE). Already the advantages of the thin-film growth have been demonstrated by the realization of a high-performance electronics device based on PdCoO$_2$ films grown by PLD.

A major challenge to the growth of PdCoO$_2$ is oxidizing the palladium. If we look to synthesis routes that have achieved high-quality PdCoO$_2$, the original method took place under 3000 atm of oxygen at 800$^\circ$C for 12 h. Such conditions are clearly far from being compatible with vacuum deposition methods used to produce thin films, but subsequently a lower-pressure route was found that yields PdCoO$_2$ single crystals up to 3 mm in size involving the...
reaction $\text{PdCl}_2 + 2 \text{CoO} \rightarrow \text{PdCoO}_2 + \text{CoCl}_2$ in a sealed quartz tube at 700 °C for 40 h.\textsuperscript{5,6}

Compared to the growth of bulk $\text{PdCoO}_2$, the pressures at which $\text{PdCoO}_2$ thin films have been made are much lower. Early sputtered films were deposited at pressures of $2 \times 10^{-7}$ Torr in an amorphous state. They were subsequently annealed at about 700 °C in 1 atm of air or oxygen to form $\text{PdCoO}_2$.\textsuperscript{7} By PLD, $\text{PdCoO}_2$ has been formed directly during growth at pressures ranging from $10^{-3}$ to 2 Torr.\textsuperscript{8,9} In the case of MBE, pressures of $4 \times 10^{-6}$ Torr have been used.\textsuperscript{7} The use of low pressures in MBE arises from the necessity of maintaining a mean-free-path that exceeds the distance from the sources to the substrate (typically ~20 cm) in order to preserve the molecular beams.\textsuperscript{7}

When growing materials that are difficult to oxidize by MBE, a common approach to achieving oxidation at pressures within the MBE regime is to use activated oxidants, such as the reactive species emitted from an oxygen plasma source or concentrated ozone.\textsuperscript{10} Brählek et al.\textsuperscript{11} used an atomic oxygen plasma in their recent MBE work. They found that they could oxidize the elemental constituents to form $\text{PdCoO}_2$ at substrate temperatures up to 300 °C, but that at higher growth temperatures, the $\text{PdCoO}_2$ spontaneously decomposed.\textsuperscript{12} To improve the structural perfection and electrical transport properties of their films, Brählek et al.\textsuperscript{11} performed an \textit{ex situ} anneal on their films. The best electrical properties were achieved following a 10 h anneal in 1 atm of oxygen at 800 °C. Although this anneal drastically improved the electrical transport, it also caused the film surface to roughen.\textsuperscript{13}

In this study, we apply ozone-assisted MBE to the growth of $\text{PdCoO}_2$. Ozone is an excellent oxidant for use in MBE because it can be distilled and delivered with high purity to the substrate (~80% ozone with the remainder being oxygen).\textsuperscript{14} In this concentrated ozone ambient, we find that $\text{PdCoO}_2$ films can be grown by MBE at substrate temperatures up to nearly 500 °C. At these significantly higher temperatures, the surface mobility of the adatoms is dramatically increased, leading to films with improved smoothness and structural perfection. Importantly, the films do not need to be annealed \textit{ex situ} after growth. Our work thus opens the door to the growth of heterostructures and superlattices containing $\text{PdCoO}_2$ with an atomic-layer control as well as the possibility of achieving layers of sufficient quality that they can be characterized using in-vacuum techniques such as ARPES.\textsuperscript{15}

The $\text{PdCoO}_2$ thin films are synthesized on $c$-plane sapphire at 480 °C (measured by a thermocouple close to, but not in direct contact with the substrate) under a chamber background pressure of $10^{-5}$ Torr of distilled ozone (~80% $\text{O}_3$ + 20% $\text{O}_2$) in a Veeco Gen10 MBE system. Palladium (99.999% purity) and cobalt (99.95% purity) are evaporated from Langmuir cells (free evaporation from crucibles with large orifices). The palladium and cobalt shutters are opened and closed sequentially under a continuous supply of ozone to supply monolayer doses of palladium and cobalt following the sequence of atomic layers along the $c$-axis of the crystal structure of $\text{PdCoO}_2$. Prior to the growth, the $c$-plane sapphire substrates (CrysTec GmbH) are annealed at 1050 °C under 1 atm of air for 6 h to obtain a step-and-terrace morphology. The planes of the substrates are all oriented within 0.2° of (0001). A summary of the samples studied, including thicknesses and electrical characteristics, is provided in Table I.

\textit{In situ} reflection high-energy electron diffraction (RHEED) is employed to monitor the evolution of surface structures and reconstructions during growth. Figures 1(a) and 1(b) show the RHEED patterns of a bare $c$-plane sapphire substrate viewed along high symmetry directions where sharp diffraction streaks and Kikuchi lines are visible. Upon deposition of the first cobalt oxide monolayer followed by a palladium monolayer, the diffraction patterns change to those shown in Figs. 1(c) and 1(d). With the deposition of another cobalt oxide monolayer to complete the dumbbell O-Pd-O linear coordination along the $c$-axis (the direction of growth) of the bulk $\text{PdCoO}_2$ crystal structure, the diffraction patterns change again as shown in Figs. 1(e) and 1(f). Figures 1(g) and 1(h) show the RHEED patterns at the end of the growth of sample A, a 10.2 nm thick film. The latter RHEED patterns correspond to those of $\text{PdCoO}_2$ without any surface reconstruction, in contrast to the surface reconstructions present in Figs. 1(e) and 1(f) for the ultrathin $\text{CoO}_2$-$\text{Pd-CoO}_2$ film. Following two repeated cycles of supplying a monolayer of cobalt followed by a monolayer of palladium to the growing surface (under a continuous flux of ozone), the diffraction streaks are relatively sharp (and not spotty) indicating that our films are relatively smooth and epitaxial. In addition, we also observe splitting of the diffraction streaks into doublets which we do not yet fully understand, but attribute to the presence of in-plane rotational twins that are described below.

The morphology of the film surface is also characterized \textit{ex situ} by atomic force microscopy (AFM) carried out using an Asylum Cypher ES Environmental AFM. Figure S1(a) in the supplementary material shows the step-and-terrace morphology of an annealed sapphire substrate with a root-mean-square (rms)

\begin{table}[h]
\centering
\caption{Summary of the samples studied in this letter and their features, including thickness, electrical characteristics, and the characterization techniques performed on them.}
\begin{tabular}{|c|c|c|c|}
\hline
Sample & Thickness (nm) & $\rho_\text{ab}(300 \text{ K})$ ($\mu\Omega$ cm) & RRR & Characterization \\
\hline
A & 10.2 ± 0.2 & 9.3 & 2.2 & XRD, $R$ vs $T$, RHEED \\
B & 8.0 ± 0.1 & 11 & 1.8 & XRD, $R$ vs $T$, AFM, STEM, RBS \\
C & 5.4 ± 0.1 & 16 & 1.6 & XRD, $R$ vs $T$ \\
D & 4.1 ± 0.2 & 18 & 1.4 & XRD, $R$ vs $T$ \\
E & 3.2 ± 0.1 & 38 & 1.2 & XRD, $R$ vs $T$ \\
F & 2.0 ± 0.1 & 66 & 1.1 & XRD, $R$ vs $T$ \\
G & 1.6 ± 0.1 & 80 & 220 & Insulating XRD, $R$ vs $T$, AFM \\
\hline
\end{tabular}
\end{table}
roughness of 0.08 nm. After the deposition of the first three monolayers, deposited in the sequence cobalt, palladium, and cobalt in a continuous flux of ozone, the PdCoO$_2$ film has fully covered the substrate (the initial nuclei are fully coalesced), while the substrate steps are still apparent underneath, as shown in Fig. S1(b). At the end of the growth of sample B, the surface remains smooth with an rms roughness of 0.13 nm, as shown in Fig. S1(c) and in the magnified image in Fig. 2. Our films are the smoothest among PdCoO$_2$ thin films reported in the literature, which will facilitate the controlled integration of this delafossite material with other materials as well as venturing into the atomic layer engineering of delafossites, which is now commonplace for perovskite oxides.

X-ray diffraction (XRD) measurements were carried out using Panalytical Empyrean and Panalytical X’Pert Pro diffractometers with Cu-K$_{α1}$ radiation. In the coupled θ-2θ scans in Fig. 3(a), only 000ℓ reflections corresponding to the bulk crystal structure of PdCoO$_2$ together with substrate reflections were observed, indicating that our films are c-axis oriented, epitaxial, and phase pure. Moreover, Laue oscillations around the film reflections are clearly visible, indicating that the films have a well-defined thickness, i.e., not only a smooth surface but also a smooth film-substrate interface. This is corroborated by the scanning transmission electron microscopy (STEM) image shown later in this letter. To study the structural perfection, we performed symmetric rocking curve measurements of the 0006 film and substrate reflections of sample B, using a triple-axis geometry. As shown in Fig. 3(b), the full width at half-maximum (FWHM) of the rocking curves in ω of the film and substrate reflections are comparable: both are 9 arc sec. This is the instrumental resolution of our diffractometer. Such a narrow rocking curve indicates the high degree of structural perfection in terms of a low out-of-plane mosaicity. In contrast to the narrow rocking curve in ω, the FWHM of the asymmetric ϕ scan shown in Fig. 3(d) is much larger for the film than that of the substrate (4800 arc sec and 470 arc sec, respectively). This indicates that the mosaic spread is highly anisotropic: there is far greater in-plane mosaic spread (twist) between PdCoO$_2$ subgrains than out-of-plane mosaic spread (tilt). Such asymmetry is observed in other heteroepitaxial systems such as GaN on (0001) Al$_2$O$_3$ and SrTiO$_3$ on (100) Si.$^{17,18}$ Both systems exhibit narrow out-of-plane ω-scan rocking curve widths and broader asymmetric ϕ-scan widths.

As illustrated in Fig. 3(c), by overlaying the in-plane crystal structures of c-axis oriented PdCoO$_2$ and Al$_2$O$_3$, we find a lattice
mismatch of $-2.9\%$ under a $30^\circ$ in-plane rotation,

$$
c = \frac{a_{\text{Al}_2\text{O}_3} - \sqrt{3}a_{\text{PdCoO}_2}}{\sqrt{3}a_{\text{PdCoO}_2}} = \frac{4.76 \text{ Å} - 4.902 \text{ Å}}{4.902 \text{ Å}} = -2.9\%.
$$

One implication that arises from this epitaxial orientation relationship is that there are two equivalent ways to lay the film crystal structure with respect to the substrate that are $180^\circ$ rotated from each other. If this orientation relationship were true, we would expect rotational twinning in our films. We plot stereographic projections of the asymmetric 01·8 peaks of Al$_2$O$_3$ and PdCoO$_2$ in Fig. S2 where one only expects to see three equivalent poles for both the substrate and the film if both are untwinned single crystals. We performed an off-axis $\phi$ scan around the film and substrate 01·8 reflections of sample A. In addition to the three substrate peaks, six film peaks are present, as shown in Fig. 3(d). The film peaks are interpreted as two sets of peaks corresponding to domains that are $30^\circ$ rotated from the substrate and $180^\circ$ rotated from each other, which validates the orientation relationship proposed. The six peaks are all the same height, indicating equal populations of the two twin variants. These $180^\circ$ in-plane rotation twins are consistent with prior studies of epitaxial PdCoO$_2$ grown on (0001) Al$_2$O$_3$ substrates.$^{8,10}$ The presence of these twin boundaries is likely detrimental to the electrical characteristics of our films, as discussed below.

High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was performed on sample B using an aberration-corrected FEI Themis Titan microscope operating at 300 kV. Sample preparation was carried out by a focused ion beam (FIB) lift-out method using a Thermo Fisher Helios G4 UX FIB. From the cross-sectional HAADF-STEM images in Fig. S3 (low magnification) and Fig. 4(a) (high magnification), we observe an abrupt and smooth interface between the substrate and film,
consistent with the observation of the Laue oscillations mentioned earlier. Overlaid on the enlarged HAADF-STEM image near the film-substrate interface in Fig. 4(b) are an annular bright field (ABF-STEM) image and the schematics of the crystal structures of PdCoO$_2$ and Al$_2$O$_3$. We observe that the film structure is $30^\circ$ rotated from the substrate, which is consistent with the XRD $\phi$ scans and prior reports. From the XRD and STEM results, the epitaxial orientation relationship between the substrate and the film is determined to be (0001) PdCoO$_2$ || (0001) Al$_2$O$_3$ with [1120] PdCoO$_2$ || [1100] Al$_2$O$_3$ as well as a second in-plane twin variant with [1120] PdCoO$_2$ || [1100] Al$_2$O$_3$. Owing to the atomic number contrast in the HAADF imaging mode, when combined with the ABF image, the brighter (dimmer) dots in the image and the orange (blue) spheres in Fig. 4(b), respectively. We observe that the first monolayer in contact with the sapphire substrate is indeed a CoO$_2$ layer followed by a palladium plane, which corresponds to the deposition sequence mentioned earlier. Note that the first monolayers in the PLD and ex situ annealed MBE films are also CoO$_2$ layers, suggesting the commonality of this feature in the heteroepitaxial PdCoO$_2$/Al$_2$O$_3$ system. During growth we observe that if we deposit the palladium monolayer first or if we do not deposit a full cobalt monolayer, the resulting film is semicrystalline with weak diffracted features and a relatively intense diffuse background in RHEED, as shown in Fig. S4. This RHEED pattern does not improve with in situ annealing at temperatures up to 900 °C. This suggests that the palladium terminated surface of PdCoO$_2$ does not provide the low-energy interface in contact with c-plane sapphire; rather the CoO$_2$-terminated surface is the more stable interface with (0001)-oriented sapphire.

Rutherford backscattering spectrometry (RBS) using 1.4 MeV He$^{+}$ ions was used to assess the stoichiometry of the films. The results were analyzed using the software program RUMP. The RBS spectrum of sample B is shown in Fig. S5. The Pd:Co ratio of this film is 1.105. Considering the accuracy of the RBS measurement for these films (±2%) and that the growth was both initiated and completed with a CoO$_2$ monolayer, we conclude that the film is stoichiometric within the error bars of the RBS measurement.

We are particularly interested in exploring the transport in this two-dimensional electron system, PdCoO$_2$, at the ultrathin limit, a regime that is inaccessible using bulk crystals. We measured the transport properties of the MBE-grown films using a 4-point van der Pauw geometry in a quantum design physical property measurement system (PPMS). Figure 5(a) shows the temperature dependence of the in-plane resistivity as a function of film thickness. The films are metallic down to $\sim$2 nm and only becomes insulating at $\sim$1.6 nm. This latter thickness contains fewer than 3 palladium planes along the c-axis of the film.

The residual resistivity ratio (RRR = $\rho_{300 K}/\rho_{4 K}$) is a sensitive probe to structural disorder as low temperature resistivity arises primarily from defects. As shown in Fig. 5(c), the RRRs of our films scale almost linearly with thickness, indicating that surface scattering has a large contribution to electrical resistance. For thin films, such boundaries include film-substrate interfaces and twin boundaries. The RRR of 2.2 of our thickest film ($\sim$10.2 nm) is comparable to the values of PLD-grown films at similar thicknesses, but drastically inferior to the values of 16 and 347 for ex situ annealed MBE-grown films (180 nm thick) and single crystals, respectively.

Note that the step height of our annealed sapphire substrate is $\sim$0.26 nm, which corresponds to the Al-Al distance along the c-axis of sapphire, while the Co-Pd distance along the [0001] direction in PdCoO$_2$ is $\sim$0.30 nm. This mismatch in the c-axis lengths could lead to the formation of out-of-phase boundaries when palladium planes that nucleate on different steps of the sapphire substrate coalesce. The resulting discontinuities in palladium planes could disrupt the conduction pathways and deteriorate the electrical properties, which has been observed for other two dimensional metallic thin films. The room temperature in-plane resistivity of our thickest film ($\sim$10.2 nm) is $\sim$9.3 $\mu$Ω cm, which is several times larger than the single crystal value of 2.6 $\mu$Ω cm. The room-temperature resistivity of our films increases quickly, however, with decreasing thickness reaching 220 $\mu$Ω cm at $\sim$1.6 nm, as shown in Fig. 5(b). The increase in resistivity could also be attributed to a reduction in conduction pathways due to out-of-phase boundaries.

Besides out-of-phase boundaries and twin boundaries, the comparatively poorer electrical characteristics of our films could...
FIG. 5. Electrical transport measurements of PdCoO$_2$ films (samples A-G). (a) Temperature dependence of the in-plane resistivity showing the preservation of metallicity down to $\sim$2 nm, which contains fewer than 4 palladium planes along the out-of-plane direction of the film. (b) Thickness dependence of the room-temperature in-plane resistivity showing an increase in resistivity at smaller thickness. (c) Thickness dependence of the residual resistivity ratio (RRR). RRR is seen to scale linearly with thickness, consistent with surface scattering.

arise because of additional crystallographic defects such as point defects associated with slight nonstoichiometry and dislocations due to the large lattice mismatch with the sapphire substrate. The higher defect densities of our films compared to the ex situ annealed MBE films could be attributed to the lower deposition temperature of 480 °C in our case vs the annealing temperature of 800 °C used in the latter work.$^{10}$ Higher annealing or growth temperature may aid the removal of defects to help improve the electrical properties. On the other hand, PdO becomes volatile at higher temperatures and we observe the formation of Co$_3$O$_4$ at growth temperatures higher than 500 °C. Indeed, the removal of crystallographic defects without losing PdO in single-step, in situ synthesis remains an open challenge. The other major contributors to low temperature resistivity, as mentioned earlier, are the twin boundaries.

In summary, we have grown c-axis oriented PdCoO$_2$ on c-plane sapphire using in situ MBE with distilled ozone as an oxidant. Our films are smooth and phase pure with a high degree of structural perfection and electrical characteristics similar to other in situ grown PdCoO$_2$ thin films in the literature. Using an ozone-assisted MBE approach, we have grown PdCoO$_2$ films exhibiting metallic conductivity as thin as in previous PLD work.$^{7}$ It is metallic at a film thickness of $\sim$2.0 nm with fewer than 4 palladium monolayers along the out-of-plane direction. This ozone-assisted in situ MBE process provides the beginning of a pathway to atomically engineer delafossites for fundamental science purposes and to make and evaluate proof-of-principle device heterostructures.

See the supplementary material for additional characterization of the PdCoO$_2$ films by AFM, XRD, HAADF-STEM, RHEED, and RBS.

This work was primarily supported by the U.S. Department of Energy, Office of Basic Sciences, Division of Materials Sciences and Engineering, under Award No. DE-SC0002334. Materials synthesis was performed in a facility supported by the National Science Foundation [Platform for the Accelerated Realization, Analysis, and Discovery of Interface Materials (PARADIM)] under Cooperative Agreement No. DMR-1539918. This work made use of a Helios FIB supported by NSF (DMR-1539918) and the Cornell Center for Materials Research (CCMR) Shared Facilities, which are supported through the NSF MRSEC Program (Grant No. DMR-1719875). We would like to thank Malcolm Thomas, John

APL Mater. 7, 121112 (2019); doi: 10.1063/1.5130627
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Grazul, and Mariena Silvestry Ramos for assistance in the Electron Microscopy CCMR facilities. The FEI Titan Themis 300 was acquired through Grant No. NSF-MRI-1429155, with additional support from Cornell University, the Weill Institute, and the Kavli Institute at Cornell. This work also made use of the CESI Shared Facilities partly sponsored by the NSF (Grant No. DMR-1338010) and the Kavli Institute at Cornell. Substrate preparation was performed in part at the Cornell NanoScale Facility, a member of the National Nanotechnology Coordinated Infrastructure (NNCI), which is supported by the NSF (Grant No. ECCS-1542081).

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Supplementary Information

Figure S 1 – AFM images of (a) a bare (annealed) c-plane sapphire showing the step-and-terrace morphology with rms roughness of ~0.08 nm and (b) a similar c-plane sapphire substrate upon which Co-Pd-Co monolayers have been deposited. The ~0.6 nm thick PdCoO$_2$ film has completely coalesced while the substrate morphology underneath is still visible. The rms roughness is ~0.12 nm. (c) At end of the growth of an 8.0 nm thick PdCoO$_2$ film (sample B). The rms roughness is ~0.13 nm.
Figure S 2 - Stereographic projection of the 01•8 peak of single crystals of c-axis oriented (a) Al₂O₃ and (b) PdCoO₂. In both cases three equivalent poles are present, i.e., three peaks are expected in the Φ scan for an untwinned single crystal of either of these materials.

Figure S 3 - Low magnification cross-sectional HAADF-STEM of sample B showing an abrupt film-substrate interface.
Figure S 4 - RHEED patterns of semi-crystalline films resulting from Pd-rich deposition condition. (a) and (b) are patterns taken along the two in-plane high symmetry directions indicated.

Figure S 5 - Rutherford backscattering spectrum (RBS) of sample B, an 8.0 nm thick PdCoO$_2$ film grown on (0001) sapphire. The Pd:Co ratio was found to be 1:1.05 indicating that the film is stoichiometric within the resolution of RBS.