Atomic Layer Deposition of the Conductive Delafossite PtCoO₂

Dirk J. Hagen, Jiho Yoon, Haojie Zhang, Bodo Kalkofen, Mindaugas Silinskas, Felix Börrnert, Hyeon Han, and Stuart S. P. Parkin*

1. Introduction

A considerable number of intriguing physical properties have been discovered in ternary and higher oxides containing metals of the platinum group during recent years. For example, the pyrochlore iridate Y₂Ir₂O₇ was one of the first proposed Weyl semimetals, although experimental investigations remained ambiguous. One reason for this is the difficulty of growing high-quality single-crystals, which is necessary for the direct proof of Weyl semimetallicity, e.g. by angle resolved photo-electron spectroscopy (ARPES).[1–9] The perovskites SrIrO₃ and SrRuO₃ were shown to exhibit a strong spin Hall effect[10,11] and to be effective materials for the shifting of magnetic domain walls by electrical currents.[12–14] respectively. Furthermore, the delafossites PdCoO₂ and PtCoO₂ turned out to be among the most conductive oxides. For example, Kushwaha et al.[15] determined a resistivity ρ as low as 2.1 μΩ cm at room temperature for PtCoO₂, the lowest value reported for an oxide thus far. Moreover, the conductivities reach values close to those of metals such as Cu, Ag, and Au at low temperatures.[15,16] These delafossites consist of two-dimensional Pd respectively Pt sheets connected by octahedrally coordinated CoO₂. Due to this structure, their electrical conductivity is strongly anisotropic and highest within the (ab) plane. Moreover, Kitamura et al.[17] predicted a large intrinsic spin Hall effect in PtCoO₂ from ab-initio calculations, which makes it an interesting material for spintronic devices such as ferromagnetic racetracks, in which the spin Hall effect is exploited for generating a spin current.[18–22]

Most of the work published thus far about these delafossites concerned bulk material. The deposition of PdCoO₂ thin films was only reported quite recently by Harada et al.[23] and Yordanov et al.[24] who used pulsed laser deposition (PLD) and by Brahlek et al.[25] who used molecular beam epitaxy (MBE). Harada et al.[23] needed a Pd-PdO target in addition to a PdCoO₂ target in order to obtain stoichiometric PdCoO₂ films at a growth temperature of 700 °C, while Brahlek et al.[25] carried out their MBE experiments at a growth temperature as low as 300 °C where they obtained amorphous films, which were crystallized by subsequent annealing. The low temperature was needed since other phases, Pd and Co₃O₄, were formed at higher temperatures. The loss of stoichiometry during PLD has also been observed for pyrochlore iridates. For example, Liu et al.[7] required a target with excess Ir for the deposition of Y₂Ir₂O₇. PtCoO₂ films have been grown by Wei et al.[26] using spin-coating of an aqueous solution and subsequent calcination at 750 °C in air. However, vacuum-based deposition techniques are usually preferred to spin-coating due to the better control of thickness and uniformity. Therefore, there is a demand for the development of alternative deposition methods for platinum metal containing oxides.

Atomic layer deposition (ALD) has been successfully implemented for the growth of a large number of ternary oxides.[27–40] For example, a review by Mackus et al.[41] from 2019 provides an extensive overview of ALD processes for ternary and higher oxides, as well as doped oxides. Interestingly, the authors list only one ALD process for such an oxide that contains a...
platinum group metal, Ru₃AlO₅. However, the reported material was rather a composite of metallic Ru and amorphous alumina than a ternary oxide phase.[42] We would like to mention that Minjauw et al.[44] reported ternary ALD processes for ruthenates during the preparation time for this article. This article focused on the low-temperature growth chemistry using RuOₓ with trimethyl aluminum and trimethyl-Pt-methyloclopenadentenyl (Me₃Pt(CpMe)) but did not report the formation of a crystalline ternary phase. One likely explanation for this lack of reported ALD processes is the difference of ALD processes for oxides of noble metals to those of non-noble metals. For noble metals, there is typically a competition between the growth of the pure metal and an oxide depending on the exact growth conditions. For example, Kim et al.[45] observed a shift from the growth of Ir to IrO₂ in an ALD process involving (ethylocyclopentadienyl) (1,5-cyclooctadiene)iridium and an Ar/O₂ mixture at 290 °C when the O₂ content in the Ar/O₂ mixture exceeded 75%. The transition pressure shifted to lower O₂ concentrations when the temperature was decreased. Hämäläinen et al.[46] reported a transition from the growth of metallic Pt to PtOₓ in a process involving Pt-bis(acetylacetonate) (Pt(acac)_2) and O₂ when the deposition was carried out at temperatures below 140 °C. Knoops et al.[47] were able to deposit PtOₓ in a much wider temperature window of 100–300 °C using Me₃Pt(CpMe) and O₂ plasma when long plasma exposures were used. From shorter plasma exposures, metallic Pt was obtained at substrate temperatures above 200 °C. Hence, the important questions are: can the platinum group metal be deposited in an oxidized state in a ternary ALD process, and has the second metal any impact on this issue.

In this work, we approach this problem for the example of PtCoO₂ as for both Pt/PtOₓ and CoOₓ well-established ALD processes exist.[28,29,47–51] We first investigate the ALD of PtCoO₂ thoroughly using Me₃Pt(CpMe), Co-bis(N-t-butyl-N'-ethylpropanimidamidate) (Co-AMD), and O₂ plasma, which is generated by a remote inductively-coupled-plasma (ICP) source. We have chosen these precursors because we used them in earlier work for the deposition of Pt, CoO₂, and Co-P.[52] Next, we explore the formation of the delafossite phase by annealing in different atmospheres and analyze the crystal structure. Finally, we investigate the suitability of PtCoO₂ for spintronic applications and the possibility to coat three-dimensional structures conformally.

2. Results and Discussion

2.1. Film Growth

As discussed above, the growth of PtOₓ instead of Pt was observed in literature when the deposition temperature was lowered and when the oxygen exposure was increased. We, therefore, investigated if PtOₓ can be grown at a low sub-strate temperature of 120 °C, and observed a transition from the growth of Pt to PtOₓ when the pressure during the oxygen plasma exposure was reduced from 100 to 20 mTorr. This can be explained by the higher density of reactive species above the substrate when the ICP is generated at a lower pressure.[53,54] Therefore, we choose this temperature for the investigation of the ternary PtCoO₂ process by varying the growth parameters and measuring thickness and composition. Similarly to the binary process, the pressure during the oxygen-plasma exposure was a critical value as PtCoO₂ films could be readily obtained at a pressure of 50 mTorr and below with a growth per cycle (GPC) of about 0.7 Å while GPC and Pt concentration decreased significantly for 100 mTorr and further for 200 mTorr, where the films contained very little Pt (Figure 1d). Apparently, the influence of the pressure on the PtOₓ part-process is much bigger than on the CoO₂ part-process. Interestingly, the impact of the plasma power was much less significant as a noticeable decrease of the GPC was only observed for very low powers (25 W) (Figure S1, Supporting Information). The plasma-exposure time for the process to reach saturation was 4 s (Figure 1c). The strong plasma conditions made it very difficult to avoid a parasitic chemical-vapor-deposition (CVD) component during the CoO₂ sub-cycle, and we had to modify the purging conditions (15 s purge after Co-AMD exposure, 20 s purge after plasma exposure, pressure-control valve completely open, plasma exposure 10 s) to ensure saturation during the pulse with the oxygen sensitive Co-AMD (Figure 1b). In contrast, the growth saturated after about 1s exposure of Me₃PtCpMe (Figure 1a).

The contrasting behavior of the two part-processes highlights the difficulty of the ALD of ternary oxides containing two dissimilar metals. We then used 20 mTorr plasma pressure for investigating how growth rate and composition change with the substrate temperature. As can be seen in Figure 1e, both remain nearly constant within the investigated temperature window from 100 to 320 °C, which is remarkable given the limited stability of Pt oxides. Furthermore, we demonstrated that the composition changes steadily with the ratio of the Pt and Co subcycles (Figure 1f).

Next, we deposited a thicker film (60 nm) in order to investigate composition and morphology more thoroughly. As can be seen from the X-ray photoelectron spectroscopy (XPS) depth profile in Figure S5, Supporting Information, the composition is very close to the stoichiometry PtCoO₂ nearly throughout the whole profile. X-ray diffraction (XRD) as well as transmission electron microscopy (TEM) showed that the film is amorphous (Figure 3a and Figure S7, Supporting Information). Furthermore, no indications for separated PtOₓ-rich and CoO₂-rich phases could be observed. The determination of the chemical states of the elements from the high-resolution XPS scans is rather challenging. First, the Co 2p signals for the various oxides are very similar, so it is not possible to discriminate between a Co(III), Co(II), or mixed state from our data (Figure S4, Supporting Information). Second, the XPS signals are strongly dominated by the surface region and thus by potential post-deposition reactions in the atmosphere and by the final ALD step, which is oxygen plasma exposure. The Pt 4f₇/₂ and 4f₅/₂ peaks of the as-deposited film are quite sharp and centered at 74.3 and 77.6 eV, respectively (Figure S3, Supporting Information). Thus, they are between the literature values for PtO and PtO₂, respectively.[55] After sputtering, the spectrum broadens, showing the coexistence of different oxides with the lowest 4f₇/₂ signal at 72.2 eV, which is consistent with Pt(I) in PtCoO₂.

Finally, we investigated the suitability of our ALD process for coating three-dimensional structures. Figure 2 shows
micrographs of a film deposited on Si which was structured with trenches of different sizes (obtained from an industry partner). High-resolution micrographs are shown for the narrowest trenches, which were 20 nm wide and 150 nm deep. It can be clearly seen that the coating is indeed very conformal with the ratio of the film thicknesses at the trench bottom and the top ranging between 0.8 and 1, highlighting the potential of our ALD process.

2.2. Crystallization

Samples with a 60 nm thick amorphous PtCoO2 film were subjected to thermal treatments in different atmospheres. Annealing in Ar led to a phase separation and the formation of a Pt surface layer (Figures S8, S9, Supporting Information). In contrast, the delafossite PtCoO2 phase could clearly be identified from grazing incidence XRD (GIXRD) patterns after annealing at temperatures between 700 and 800 °C in O2 (Figure 3a). When the temperature was further increased to 900 °C, the films decomposed to CoOx and Pt. These temperature transitions are similar to those reported for bulk PtCoO2. An unexpected result was obtained when we tested the crystallization of much thinner films as these showed a strong (001) texture (Figure 3b). Therefore, we evaluated the films more extensively using TEM and (S)TEM (S = scanning). The micrograph of the ~60 nm thick film in Figure 4a together with its Fourier transform in the inset confirms its polycrystalline nature without any apparent texture. In contrast, two-dimensional Pt planes nearly parallel to the surface are clearly visible in the high-angle annular dark-field (HAADF) STEM image in Figure 4c. Wei et al. made similar observations in their solution-growth studies as they obtained strong (001) orientations for thin films but a loss of this orientation when thicker films were deposited. However, these researchers performed epitaxial growth on sapphire while the film in Figure 4c is grown on the amorphous native oxide of Si. A high anisotropy of the surface energy is the most likely explanation for this phenomenon. We want to highlight that such strongly oriented layers are quite rare for ALD-grown films.

To investigate the in-plane structure of the thin PtCoO2 films, we deposited ~10 nm PtCoO2 on an amorphous SiNx membrane and annealed the sample at 700 °C in O2. Figure 4b shows an overview HAADF STEM image of such a film. The grain structure is readily visible with a pronounced bright spot
in the middle of each grain as the grain nucleation point and small holes in black at the grain borders. The mean grain size is about 1 \( \mu m \). Similar grain sizes were also observed in atomic force microscopy (AFM) investigations (Figure S6, Supporting Information). Diffraction patterns from large sample areas show discrete rings confirming a strong (001) orientation but a distribution of in-plane rotated grains. On these samples, we performed dark-field TEM imaging to obtain crystal orientation maps. Figure S10a in Supporting Information shows an orientation map constructed from three dark-field images with the respective diffraction-plane aperture positions indicated in the diffraction ring on the right. Due to the hexagonal symmetry of the diffraction pattern, the indicated aperture positions cover the complete set of orientations. Also, the area of a single aperture covers a range of diffraction spots originating from different neighboring orientation angles, thus, a single color in the orientation map indicates a certain set of orientations. Nevertheless, we find a distribution of single-crystalline grains with a typical size on the order of 1 \( \mu m \). We checked this by recording selected-area diffraction patterns using an image-plane aperture selecting areas of 0.7 \( \mu m \) diameter often resulting in very narrow angular distributions of the diffraction patterns indicating a strain in the single crystals (Figure S10b, Supporting Information).

Next, we explored the possibility of epitaxial growth using (0001) sapphire substrates. As can be seen in Figure 3b the pattern of the Bragg-Brentano scan of the film on sapphire is similar to that on silicon indicating highly relaxed growth.

Figure 2. TEM micrographs of patterned Si sample coated with PtCoO2.

Figure 3. XRD analysis of PtCoO2 films; a) GIXRD of \( \approx \)60 nm thick film annealed in O\(_2\) at different temperatures, b) scans in Bragg-Brentano geometry of \( \approx \)5 nm thick films deposited on Si and sapphire and annealed at 700 °C. Asterisks denote substrate diffractions. The inset in (b) shows a phi scan on the (012) diffraction peak for the film on sapphire. (PDF cards: 00-027-1339, 00-042-1467, 00-004-0802).
There is a small additional peak at 36.8°, which can be from PtCoO₂ (101) or Co₃O₄ contamination. The in-plane relationship between the sapphire substrate and the PtCoO₂ film was explored with a phi scan on the (012) diffraction. The PtCoO₂ film shows diffraction peaks at distances −30° and 30° from the substrate peaks, which is similar to the observations by Wei et al. [26] for solution processed films which indicates the coexistence of two epitaxial grain configurations, triangle, and inverted triangle.

The crystallization is accompanied by change of the chemical environment of the Pt cations as can be seen from the XPS investigation in Figure S3b, Supporting Information. The signals arising from Pt(I) become dominant, although small contributions from higher oxidation states are still present.

2.3. Electrical Characterization

The interest in PtCoO₂ is largely due to its excellent electrical properties. [16,15] Therefore, we measured the temperature-dependent electrical resistivity of a 10 nm thick PtCoO₂ film annealed at 700, 750, and 800 °C using the van-der-Pauw configuration (Figure 5a). The room-temperature resistivity values increase with increasing annealing temperature from 35 to 60 µΩcm; thus, they are one order of magnitude higher than the values reported for bulk single-crystals. The resistivity decreases with decreasing temperature as it is expected for metallic conduction, although the residual resistivity is quite high with residual resistivity ratios (RRR) ρ_{300K}/ρ_{15K} of about 1.3. An interesting detail is a slight increase of resistivity below 5 K. Kushwaha et al. [15] observed a similar increase at low temperatures but were not able to interpret it as they ruled out possible explanations such as the Kondo effect. The reasons for the high resistivity can be the polycrystalline nature of the film and the resulting grain-boundary scattering and the small deviation from the surface parallelism of the Pt sheets which can be seen from the STEM micrograph in Figure 4b. This limits the channel that electrons can move within the two-dimensional layers to dimensions smaller than the electron mean free path reported for single-crystalline PtCoO₂ (about 20 µm at low temperatures). [16]

In addition, Nandi et al. [16] reported a significant magnetoresistance for their PtCoO₂ crystals. For the comparison, we also performed temperature-dependent electrical resistivity measurements in the presence of an out-of-plane magnetic field with a magnitude of 9 T. As can be seen in Figure 5a, however, there is no indication for a similar field dependence of the resistivity. This might be explained by the reduced conductivity as the magnetoresistance is usually associated with high charge-carrier mobilities. [57]

Another unusual observation by Nandi et al. [16] was the presence of two different regimes of the Hall resistivity at high and low fields for temperatures in the range of 50 to 200 K. However, we did not make similar observations in our Hall measurements but observed a linear slope of the Hall resistivity in response to an applied field ranging from −9 to 9 T (Figure S11, Supporting Information). Therefore, we used a simple single-carrier-type model to calculate the electron density nₑ. As can be seen in Figure 5b, nₑ is about 2 × 10²⁸ m⁻³ which is on the order of magnitude for typical metallic
systems. Furthermore, $n_e$ differs very little on the annealing temperature and shows only a weak temperature dependence. Combining the results from the resistivity and the Hall measurements, we calculated the electron mobilities $\mu_e$ (inset Figure 5b). For the film that was annealed at 700 °C, $\mu_e$ increases from about 8 cm$^2$ Vs$^{-1}$ at room temperature to 12 cm$^2$ Vs$^{-1}$ at 50 K. The $\mu_e$ values for the films annealed at 750 and 800 °C are slightly lower.

### 2.4. Exploration of Spintronic Properties

A large part of the spintronic devices, which are eagerly investigated at the moment, relies on the interaction between thin films of a magnetic material and a conductor that exhibits strong spin-orbit coupling (SOC). Here, the SOC can be responsible for the generation of spin currents via the spin Hall effect and the stabilization of certain spin textures in the magnetic layer via interfacial effects such as Dzyaloshinskii–Moriya interaction (DMI). Containing the 5d element Pt, the SOC in PtCoO$_2$ is considerably large, and its role in the formation of a single-band Fermi surface was demonstrated by Kushwaha and coworkers for example.$^{[15]}$ Moreover, a theoretical work by Kitamura et al.$^{[17]}$ indicated that the material shows a strong spin-Hall effect, although an experimental verification has thus far been obstructed by the difficulties of preparing thin-film structures suitable for typical experiments such as ferromagnetic-resonance measurements. In this work, we prepared two types of heterostructures: a multilayer consisting of 0.3 nm Co, 0.7 nm Ni, 0.3 nm Co and 3 nm TaN was deposited by magnetron sputtering on top of a 5 nm thick PtCoO$_2$ film, which had been annealed at 700 °C, and $\approx$10 nm PtCoO$_2$ was deposited on (111)-oriented yttrium iron garnet (Y$_3$Fe$_5$O$_{12}$, YIG), a ferrimagnetic insulator. The metallic multilayer is similar to magnetic layers regularly applied, e.g., by our group, for the fabrication of SOT-driven racetrack memories.$^{[18,21,22,58,59]}$ Here, the spin-injection layer has typically been a regular heavy metal such as Pt, Ir, or W. It is important to note the magnetic texture and therefore the functionality of these structures is extremely sensitive to details of the films including texture and interface sharpness. For example, perpendicular magnetic anisotropy (PMA) is readily induced by the growth on a strongly (111) textured Pt layer by interfacial magnetocrystalline effects.$^{[18,60–62]}$ Magnetic insulators such as YIG have attracted interest because spin can be transferred over wide distances such as a few $\mu$m via magnons.$^{[63–66]}$

Figure 6a shows magnetic hysteresis curves of the PtCoO$_2$/Co/Ni/Co/TaN film stack measured at room temperature with

![Figure 6](image-url)

**Figure 6.** Analysis of the interaction of PtCoO$_2$ with magnetic materials: a) magnetic hysteresis loops of Co/Ni/Co multilayer deposited on a PtCoO$_2$ film; b) resistance of PtCoO$_2$ layer deposited on YIG under magnetic fields directed in varying angles $\alpha$ toward the current-flow direction.
the magnetic field applied parallel (in-plane, IP) as well as perpendicular (out-of-plane, OOP) to the surface using vibrating sample magnetometry (VSM). The nearly rectangular shape around the origin with a coercive field of 0.33 kOe the OOP loop proofs a magnetic easy axis along the surface normal. Con- gruently, the IP curve is mainly S-shaped indicating a hard axis in the film plane. However, the magnetic loop shows a substantial coercive field. Thus, a small part of the film might exhibit in-plane anisotropy. This might be caused by small impurity phases such as Co3O4 or differing magnetocrystalline effects whether the PtCoO2/Co interface consists of a Pt sheet or a Co–O2 plasma over a wide tempera-
tion window from 100–320 °C. The as-deposited amorphous films were converted into the delafossite phase via annealing in oxygen at temperatures between 700 and 800 °C, while annealing in an inert atmosphere caused a phase separation and the formation of a Pt surface layer. We showed with XRD and TEM that thin films exhibited a strong (001) texture and consisted of grains with a horizontal size of about 1 μm while thicker films were randomly oriented. The films showed metallic conduction, and the resistivity decreased with decreasing temperature.

The suitability of PtCoO2 for spintronic applications was tested in two ways: the magnetic anisotropy was measured for a Co/Ni/Co trilayer deposited onto PtCoO2 and the angle-dependent magnetoresistance was determined for a PtCoO2 film deposited on the magnetic insulator YIG. In the former experiment, we observed a strong PMA as it is required for applications such as ferromagnetic racetracks while the second experiment provided indications for the presence of a significant spin Hall effect as the resistance showed a sine-like variation under rotation in an in-plane magnetic field. Finally, we demonstrated the conformal deposition into trenches with an aspect ratio of 7.5:1 (20 nm wide, 150 nm deep) highlighting the potential of our ALD process.

As this work demonstrates for the first time an ALD process for a ternary oxide containing a platinum-group metal, it opens the potential for the development of ALD processes for further materials of this group. This includes further delafossites, particularly those based on Pd, pyrochlores (e.g., of iridium), and perovskites such as strontium ruthenate and strontium iridate, which exhibit phenomena such as non-trivial topology and non-collinear antiferromagnetism.

3. Conclusions

The ALD of the ternary oxide PtCoO2 was accomplished with Me3Pt(CpMe), Co-AMD, and O2 plasma over a wide temperature window from 100–320 °C. This process was characterized by varying the substrate temperature (Ts), the plasma power (P), and the pressure during the plasma exposure (p). While varying one parameter, the others were kept as follows: Ts = 120 °C, tCo = 3 s, tPt = 2 s, tO2 = 15 s, P = 300 W, and p = 20 mTorr. The number of supercycles was 150. Exceptions are noted in the text. For studying the formation of crystalline phases, films were annealed in a UniTemp RTP-100 oven using an O2 or Ar atmosphere at temperatures ranging from 300 to 900 °C.

4. Experimental Section

Film Growth: A schematic of the ALD experiments is depicted in Figure 7. The depositions were performed with an Oxford Instruments FlexAL reactor, which has a base pressure of about 1.5 × 10−6 Torr. Substrates were transferred via a load-lock. The working pressure during process steps can be controlled with a butterfly valve between 250 mTorr and about 10 mTorr at typical gas flow conditions. The reactor is equipped with a remote ICP source with a maximum power of 300 W which was used to generate O2 plasma. The Co precursor Co-AMD was heated to 80 °C and the Pt precursor Me3PtCpMe to 40 °C. Both were stored in stainless steel bubblers, and Ar was used as carrier gas. Between the precursor and plasma exposures, the reactor was purged with N2 and Ar. The ALD process consisted of the following sequence: [(Co-AMD pulse (tCo)–purge (5 s)–O2-flow stabilization (4 s)–O2 plasma exposure (tO2)–purge (7 s))–(Me3PtCpMe pulse (tPt)–purge (5 s)–O2-flow stabilization (4 s)–O2 plasma exposure (tO2)–purge (5 s))]. The expressions in the parentheses are called subcycles and that in the square brackets is called a supercycle. In this work, x = y = 1 was considered except noted otherwise, and n was used to name the number of cycles. The ALD process was characterized by varying the substrate temperature (T), tCo, tPt, tO2, the plasma power (P), and the pressure during the plasma exposure (p). While varying one parameter, the others were kept as follows: T = 120 °C, tCo = 3 s, tPt = 2 s, tO2 = 15 s, P = 300 W, and p = 20 mTorr. The number of supercycles was 150. Exceptions are noted in the text.
Characterization: The film composition was determined by XPS using a Thermofisher K-alpha spectrometer equipped with an Al source. Depth profiles were obtained by sputtering with Ar using an energy of 500 eV and the “low-current” mode. XRD in Bragg-Brentano as well as in grazing-incidence geometry was carried out in a Bruker D8 DISCOVER diffractometer for the determination of crystalline phases. The same tool was also used for X-ray reflection (XRR) to confirm the thickness measurements conducted with spectrometric ellipsometry (J. A. Woollam ESM 366). Furthermore, the morphology of the films was evaluated with AFM (Supporting information).

The film properties were also investigated with (S)TEM. For this, cross-section samples were prepared by a focused ion beam lift-out route using a Tescan GAIA3 dual beam instrument. Plane-view samples were produced by growing the film directly on amorphous SiN, membranes. Electron microscopy data was taken with a FEI Titan 80–300 (scanning) transmission electron microscope equipped with a CEOS CESCOR third-order axial geometric aberration corrector and a Gatan UltraScan 1000 slow-scan CCD camera. The primary electron energy was 300 keV. The homogeneity distribution of the constituents was checked by energy-dispersive X-ray spectroscopy (EDS) (supporting information).

Electrical and Magnetic Measurements: The temperature-dependent electrical resistivity was measured using a Quantum Design Dynacool 9T physical-property-measurement system (PPMS). The samples were cut to about 5 × 5 mm² sized squares and contacted in van-der-Pauw geometry by wire bonding. The currents were supplied by Keithley 6221 current sources, and the voltages were measured with Keithley 2182A nanovoltmeters. The measurements were controlled with a LabView program. The resistance values were recorded with increasing temperature for two comprehensive wiring geometries and the resistivity $\rho$ was determined via

$$\rho = \frac{md}{I^2} R_{A,B,C,D} \quad (1)$$

where $d$ is the film thickness, $f$ is the geometry-dependent correction factor (for fairly to highly symmetric geometries close to unity) and $R_{A,B,C,D}$ is the resistance measured with the current applied through the contacts $A$ and $B$ and the voltage measured between the contacts $C$ and $D$. The contacts are placed at the corners of the sample and numbered counterclockwise. $R_{A,B,C,D}$ has defined accordingly. The same instrumentation was also used to measure the Hall coefficient $R_H$ at various temperatures, by cycling the magnetic field $B$ between 9 and −9 T and measuring the voltage with an applied current $I = 100 \mu A$:

$$R_H = \frac{V_{DE,AC} + V_{AC,BD}}{2IB} \quad (2)$$

where $V_{DE,AC}$ is the voltage measured between $A$ and $C$ with the current applied through the contacts $D$ and $B$. From $R_H$, the charge carrier density $n_c$ assuming only one type of carriers (electrons) is calculated:

$$n_c = \frac{1}{eR_H} \quad (3)$$

Here, $e$ is the elemental charge. Finally, the electron mobility $\mu_e$ is obtained:

$$\mu_e = \frac{1}{en_c\rho} \quad (4)$$

In order to evaluate the potential of PtCoO₂ as spin-injection material for spintronic devices a Co/Ni/Co trilayer plus a TaN capping layer were deposited on a PtCoO₂-coated sample (annealed at 700 °C) using physical vapor deposition (PVD). The out-of-plane and in-plane magnetization was then measured with a Lake Shore Cryotronics 8800 Series vibrating-sample magnetometer (VSM). Furthermore, PtCoO₂ (10 nm, 120 °C, 3 s Co-AMD, 2 s Me₆PcPhMe, 15 s plasma, 20 mTorr) was deposited on YIG (200 nm on GGG, Matesy GmbH, Jena) and annealed at 720 °C. Hall bars with a length of 265 µm and a width of 80 µm were fabricated using laser maskless optical lithography and Ar-ion beam etching. The samples were contacted by wire bonding and placed in a PPMS with the surface parallel to the magnetic field. The resistance was then measured while rotating the sample around the axis perpendicular to the surface.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

ALD, atomic layer deposition, conductive oxides, delafossites, PtCoO₂ topological materials

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