

Chemical-state evolution and phase stability of epitaxial PtCoO₂ thin films probed by XPS, HAXPES, and *in situ* XRD

Kerry Hazeldine^{1,*}, Jean-Philippe Soulié¹, Robin Petit², Christophe Detavernier²,
Silvia Armini¹, and Christoph Adelmann¹

¹*Imec, Kapeldreef 75, 3001 Leuven, Belgium*

²*Department of Solid State Sciences, Krijgslaan 281-S1, Ghent University, 9000 Gent, Belgium*



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Epitaxial PtCoO₂ thin films were grown on Al₂O₃(0001) substrates by physical vapor deposition under back-end-of-line compatible conditions, followed by postdeposition annealing to induce crystallization. While annealing-driven structural evolution in delafossite oxides has been reported, the corresponding chemical-state evolution across crystallization and decomposition boundaries remains insufficiently understood. Here, x-ray photoelectron spectroscopy, hard x-ray photoelectron spectroscopy (HAXPES), and *in situ* x-ray diffraction are combined to track chemical states and phase stability in PtCoO₂ thin films as a function of thermal processing. This multimodal approach resolves the spectroscopic fingerprints of the metallic delafossite phase, unambiguously identifying formal Pt¹⁺ and Co³⁺ valence states. Bulk-sensitive HAXPES, reported here for PtCoO₂, mitigates surface artifacts and enables direct correlation between bulk chemistry and structural order. Annealing at 800 °C yields phase-pure, epitaxial PtCoO₂, whereas higher temperatures induce decomposition into metallic Pt and cobalt oxide phases, defining a narrow thermal stability window. Highly crystalline films down to 4.5 nm thickness exhibit low in-plane resistivities consistent with the metallic delafossite phase. These results establish a chemically specific framework for assessing phase formation and stability in PtCoO₂ thin films and demonstrate the utility of combined photoelectron spectroscopy and *in situ* diffraction for complex oxide metals.

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I. INTRODUCTION

For nearly three decades, copper (Cu) has been the primary material of choice for interconnect applications in the back end of line (BEOL) for integrated circuits due to its lower resistivity, improved reliability, and scalability compared to earlier metallization schemes [1–3]. However, continued device scaling towards sub-10 nm metal pitches is projected to drive interconnect dimensions to below its bulk electron mean free path (~40 nm) resulting in a sharp increase in line resistance that compromises performance requirements [4–7]. Surface and grain boundary scattering at these length scales leads to increased resistance-capacitive (RC) delay and energy dissipation, while further scaling exacerbates integration challenges inherent to the Cu dual-damascene scheme [8–11]. In particular, diffusion barriers and adhesion liners required to suppress electromigration and ensure dielectric compatibility occupy an increasing fraction of the conductive cross section and must continue to scale without loss of functionality [12–14].

These limitations have motivated the exploration of alternative interconnect materials that can maintain low resistivity

at reduced dimensions while minimizing or eliminating barrier layers. Among elemental metals, ruthenium (Ru) and molybdenum (Mo) offer improved scaling behavior due to their short mean free paths and demonstrated electromigration resistance; however, their higher than Cu bulk resistivity still limits performance gains [15–20].

Metallic delafossite oxides, such as PdCoO₂ and PtCoO₂, represent a less explored class of material for interconnects. These layered ternary compounds have a general formula of ABO₂ where *A* and *B* are both transition metals, where *A* is frequently a noble metal. The structure is composed of a layer of *A* atoms bonded to each other in a triangular lattice, and a layer of BO₆ octahedra in a triangular lattice, in an alternating layered rocksaltlike structure [21,22]. Most delafossite oxides are insulators and semimetals; however a few, including PtCoO₂ and PdCoO₂, are metallic, exhibiting high anisotropy with very low resistivity in the in-plane direction [23]. Despite their long mean free paths (>70 nm for PtCoO₂ at room temperature), their anisotropic conduction could suppress scattering at the surface and interfaces if the correct crystallographic orientation is acquired [22,24,25]. The low bulk resistivities of PtCoO₂ and PdCoO₂ at room temperature are comparable to that of aluminum with an in-plane value of 2.6 μΩ cm for PdCoO₂, and an even lower value of 2.1 μΩ cm for PtCoO₂ [26,27]. Nevertheless, experimental studies have overwhelmingly focused on PdCoO₂, whereas PtCoO₂, despite its lower resistivity, remains far less explored.

The deposition and growth of delafossite oxides are typically performed on sapphire substrates at temperatures

*Contact author: Kerry.hazeldine@imec.be

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TABLE I. Sample identifiers and sample specifications for the PCO thin films in this study.

Sample identifier	Film thickness (nm)	PDA (°C)	Platinum liner (nm)	Resistivity ($\mu\Omega$ cm)	Film roughness (nm)
20 nm PCO (no PDA)	22.9	—	—	Overscale	0.19
20 nm PCO (800 °C PDA)	20.2	800	—	12.6	5.74
20 nm PCO (900 °C PDA) ^a	20	900	—	Potential	11.55
2 nm Pt + 20 nm PCO (800 °C PDA)	20.4	800	2	11.0	3.20
4.5 nm PCO (800 °C PDA)	4.5	800	—	14.5	1.19

^aA reliable thickness could not be extracted from XRR due to severe film roughening and phase decomposition; therefore, the nominal deposited thickness is reported.

exceeding 700 °C, as summarized by Harada [21]. Such high processing temperatures pose significant challenges for integration with BEOL processes and conventional Si-based technology. Nevertheless, recent advances in layer transfer techniques suggest that the elevated temperatures required to form PtCoO₂ may not represent a fundamental limitation [28]. As an alternative to direct high substrate temperature deposition, this study employs low-temperature growth at 420 °C followed by postdeposition annealing (PDA) to promote crystallization, developed by Soulié *et al.* in previous work conducted by the group [29]. Similar two-step approaches have been successfully utilized for the sister material PdCoO₂ [30]. Beyond thermal budget considerations, low-temperature depositions offer practical advantages such as improved compatibility with existing fabrication tools, established process recipes, and standard semiconductor manufacturing workflows.

Although structural evolution during annealing has been reported previously [31,32], the accompanying chemical-state evolution, particularly during crystallization and decomposition, remains insufficiently understood where prior x-ray photoelectron spectroscopy (XPS) interpretations have often overlooked multiplet splitting and surface oxidation effects. In this work, we address these limitations by combining XPS, *in situ* x-ray diffraction (XRD), and hard x-ray photoelectron spectroscopy (HAXPES) measurements to resolve chemical-state evolution during crystallization and decomposition. This work presents a HAXPES investigation of PtCoO₂ thin films, enabling bulk-sensitive identification of oxidation states and stoichiometry. This multimodal approach allows us to identify the spectroscopic fingerprints of the Pt¹⁺ and Co³⁺ delafossite phase, track chemical-state evolution through processing, and define a narrow thermal window separating crystallization from decomposition. Finally, we demonstrate scalability by achieving highly crystalline PtCoO₂ films down to 4.5 nm thickness with resistivity values competitive with state-of-the-art interconnect materials.

PtCoO₂ will be referred to as PCO from here on out.

II. METHODS

All PCO thin films were grown via PVD onto a *c*-axis oriented (0001) Al₂O₃ substrate (*c*-sapphire) through reactive cosputtering from Pt and CoO targets under a flow of Ar (15 sccm) and O₂ (50 sccm) with a working pressure of 1.7×10^{-3} mbar inside the chamber. The substrate was held at a temperature of 420 °C during the deposition with a deposition rate of 0.06 nm/s. After growth, some films were

transferred to an Annealsys AS-One furnace for a postdeposition anneal (PDA) at either 800 °C, under 1 bar O₂, for 60 min; or at 900 °C under the same conditions. The heating rate for the PDA was 7 °C/s. For one of the samples that underwent a PDA of 800 °C, a 2 nm liner of Pt was deposited *in situ* via PVD onto the *c*-sapphire substrate prior to deposition of PCO. Sample identifiers, specifications, and film thickness as measured by x-ray reflectivity (XRR), and film roughness can be found in Table I.

XPS and HAXPES spectra were acquired in angle integrated mode with an exit angle of 45° using a Ulvac-Phi Quantes instrument equipped with a monochromatic Al *K* α source ($h\nu = 1486.6$ eV) for XPS measurements providing an information depth of approximately 5–8 nm, and a monochromatic Cr *K* α source ($h\nu = 5414.7$ eV) for HAXPES measurements providing an information depth of approximately 15–20 nm. Charge neutralization and a spot size of 100 μ m was used during the measurements. XPS and HAXPES analysis was conducted using casaxps where the binding energy of the XPS spectra was calibrated to the C-C peak of adventitious carbon (AdC) of the C 1s at 284.8 eV. HAXPES spectra were binding energy calibrated to the main peak in the Pt 4f peak in the XPS spectra as no C 1s spectra were recorded. A Shirley background type was used for all spectra except when there was a flat or increasing background where in this case, a linear background type was used. For symmetric peaks, a pseudo-Voigt line shape with a Gaussian-Lorentzian (GL) ratio of 70:30 was used. For asymmetric peaks, notably, the metallic peaks in the Pt 4f, a Lorentzian finite (LF) line shape was used. For atomic percentage composition quantification, the in-built database of relative sensitivity factors for the Ulvac-Phi Quantes instrument was used.

High-resolution $2\theta/\omega$ scans were conducted on a Rigaku SmartLab instrument equipped with a HyPix-3000 high energy resolution 2D HPAD detector. The Rigaku SmartLab was also used to conduct XRR measurements to confirm the thickness of the PtCoO₂ thin films.

In situ XRD (IS XRD) measurements during ramp annealing were conducted in a custom-built heating stage in a mixture of He (20%) and O₂ (80%) at a heating rate of 0.2 °C/s. The heating stage, mounted on a goniometer equipped with a one-dimensional (1D) x-ray detector, enabled 2θ - ω XRD measurements using Cu *K* α radiation, allowing for the *in situ* monitoring of PCO XRD patterns as a function of annealing temperature. The IS XRD was measured at a 2θ angle of 35° and VERDI software [33] was used for IS XRD analysis.

Transmission electron microscopy (TEM), high-angle annular dark field imaging scanning transmission electron microscopy (HAADF STEM), and energy dispersive spectroscopy (EDS) were performed using a FEI Titan G2 microscope operating at 200 kV. TEM specimens were prepared using a Helios Hydra plasma focused ion beam (FIB) lift-out system. Protective spin-on carbon and Pt capping layers were deposited prior to milling.

Atomic force microscopy (AFM) was conducted on a Bruker Dimension Edge scanning probe microscope in tapping mode.

Resistivity was calculated from the product of the sheet resistance measured using a Four Dimensions 280SI four-point probe; film thickness was measured by XRR. Sheet resistance was measured at room temperature under ambient conditions. For the 20 nm PCO (900 °C), film thickness could not be measured by XRR and therefore a nominal value is used.

III. RESULTS AND DISCUSSION

The results reveal three major stages in the structural and chemical evolution of PCO:

1. As-deposited PCO is amorphous and comprises oxidized Pt (PtO_x) and Co predominantly in the 2+ and 4+ and 2+ oxidation states, respectively.
2. Crystallization of PCO is achieved through PDA at 800 °C forming Pt¹⁺ and Co³⁺.
3. At higher annealing temperatures, PCO decomposes into Pt⁰ and cobalt oxide (CoO_x).

In the following sections, it is shown how XPS, HAXPES, and XRD are used to identify these transitions and to correlate chemical-state evolution with crystallinity and resistivity.

Five PCO samples are investigated (Table I): three annealed at the optimum PDA temperature of 800 °C, one annealed at 900 °C, and one left unannealed. The 800 °C set includes a 4.5 nm film, a 20 nm film, and a 20 nm film deposited on a 2 nm Pt liner. This sample set enables direct comparison of crystallization and decomposition processes, revealing a narrow thermal window for phase-pure PCO formation.

Survey and high-resolution core level spectra show signals from Pt, Co, and O, along with adventitious carbon (AdC) and trace Al from the substrate. Atomic compositions extracted from XPS and HAXPES (Table II and Supplemental Material (SM) Table I [34]) closely match the expected Pt : Co : O = 1 : 1 : 2 ratio within the typical ~20% uncertainty of photoemission-based quantification. Slightly elevated oxygen contents arise from surface oxidation and AdC; however these contributions are suppressed in the more bulk-sensitive HAXPES, which revealed the expected stoichiometry for films annealed at 800 °C. Small quantities of Al are detected in the annealed samples by both XPS and HAXPES, with a higher concentration measured by HAXPES owing to its greater information depth. This observation is consistent with substrate-related contributions arising from localized voids and interfacial Al diffusion as discussed below. The Al signal is most clearly observed in the Al 1s

TABLE II. Atomic percentage compositions extracted from XPS and HAXPES (in bold) showing that close to the expected stoichiometry of Pt:Co:O was achieved. Oxygen was extracted from the O 1s and cobalt was extracted from the Co 2p_{3/2} for both XPS and HAXPES, while platinum was extracted from the Pt 4f for XPS and the Pt 3d_{5/2} for HAXPES.

Sample	Oxygen	Cobalt	Platinum
20 nm PCO (800 °C PDA)	55.3 50.7	23.0 23.7	21.7 25.6
20 nm PCO (no PDA)	59.0 51.8	19.4 25.8	21.6 22.4
20 nm PCO (900 °C PDA)	55.3 56.9	23.4 18.9	21.3 24.2

HAXPES spectra (SM Fig. 1 [34]), as contributions from Al 2p are significantly attenuated by the lower photoionization sensitivity of this core level under Cr K α excitation.

A. As-deposited PCO (no PDA)

To establish a baseline for annealing-induced phase evolution, the chemical and structural states of the as-deposited films were examined.

The Pt 4f core-level spectrum of the 20 nm PCO (no PDA) [Fig. 1(ai)] consists of three symmetric doublets, with no contribution from metallic Pt (Pt⁰) which would exhibit an asymmetrical line shape. Despite using a metallic Pt sputter target, all components correspond to oxidized Pt species formed during deposition in a partially oxygenated environment, as confirmed by reference films sputtered in Ar versus Ar/O₂ (SM Figs. 2(a) and 2(b) [34]). The three peaks are assigned as Pt(OH)₂/PtO_{ads} at 72.8 eV, PtO at 74.2 eV, and PtO₂ at 74.7 eV. Corresponding HAXPES spectra [Fig. 2(ai)] confirm that oxidation extends into the bulk, with reduced hydroxide and absorbed oxygen contributions, consistent with postdeposition air exposure [35].

Deconvolution of the 2p core level spectra of first row transition metals such as Co 2p often poses many challenges due to multiplet splitting, asymmetry, and satellite features. Due to the presence of this multiplet splitting, peak fitting which assigns a singular 2+ or 3+ peak, or a singular 2+ or 3+ peak with a "shoulder" component, does not sufficiently resolve the spectral features. The curve fitting procedures proposed by Biesinger *et al.*, with supporting data from Yang *et al.*, were used for the deconvolution of Co in PCO in this study [36,37]. The fitting was additionally supported by fitting parameters of reference Co oxides provided by the Walton group.

The Co 2p_{3/2} core level spectrum [Fig. 1(bi)] exhibits a line shape characteristic of Co²⁺ but with deviations from literature or reference CoO or Co(OH)₂, indicating the presence of mixed cobalt oxide phases. The spectrum does not resemble literature or reference spectra for Co₃O₄, suggesting a convolution of CoO_x phases formed during reactive sputtering of the Co oxide target at elevated temperatures [37–39]. Comparable line shapes in XPS and HAXPES [Fig. 2(bi)] indicate minimal surface-specific modification, supporting a predominately bulk Co²⁺ contribution.

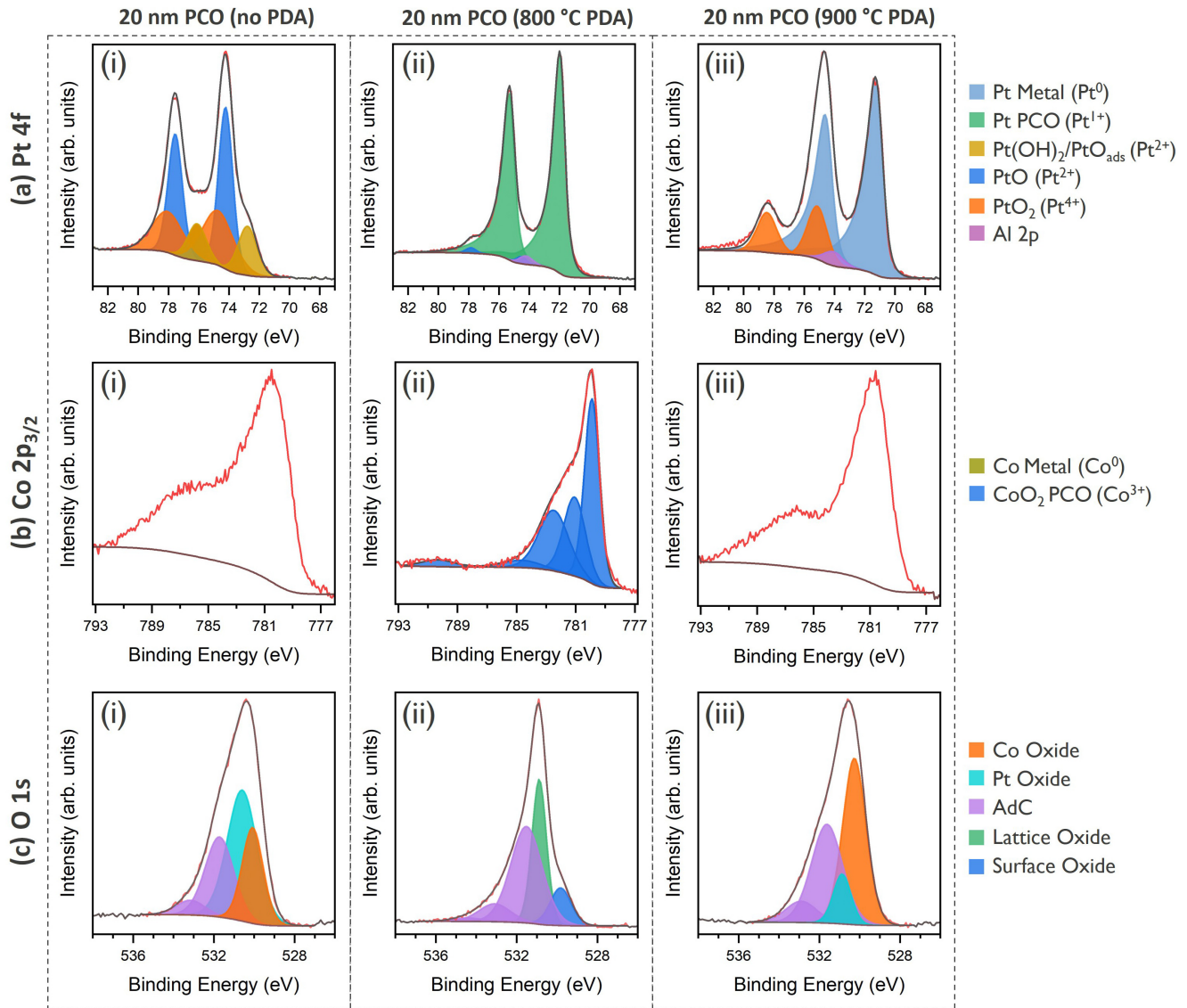


FIG. 1. (a) XPS Pt 4f core-level spectra of the (i) 20 nm PCO (no PDA), (ii) 20 nm PCO + 800 °C, and (iii) 20 nm PCO + 900 °C PDA. (b) XPS core-level Co $2p_{3/2}$ spectra of the (i) 20 nm PCO (no PDA), (ii) 20 nm PCO + 800 °C, and (iii) 20 nm PCO + 900 °C PDA. (c) XPS core-level O 1s spectra of the (i) 20 nm PCO (no PDA), (ii) 20 nm PCO + 800 °C, and (iii) 20 nm PCO + 900 °C PDA.

The O 1s spectrum [Fig. 1(c)] consists of two metal-oxide components and AdC. The lower-binding-energy peak at 530.1 eV (FWHM = 1.3 eV) is assigned to CoO_x , while the broader feature at 530.6 eV (FWHM = 1.8 eV) arises from overlapping platinum oxide (PtOx) species, consistent with Pt reference spectra [40]. The dominance of the PtOx contribution reflects surface Pt enrichment.

Cross-sectional transmission electron microscopy (TEM) and XRD corroborate the amorphous nature of the as-deposited films. TEM [Fig. 3(a)] reveals continuous film with an absence of distinct layer stacking and a rough surface layer consisting of differently orientated grains. The interface between the PCO and the substrate is sharp, while the diffraction pattern, although very weak, indicates interfacial crystallographic templating by the Al_2O_3 (0001) substrate while the film remains predominantly amorphous. High-angle annular dark-field scanning transmission electron microscopy (HAADF STEM) and energy-dispersive x-ray spectroscopy

(EDS) [Figs. 3(b) and 3(c)], show uniform bulk composition with no Al diffusion. A Pt-rich surface layer (~ 3 nm) attributed to Pt oxide/hydroxide formation, is observed resulting in a Co-rich subsurface.

XRD patterns [Figs. 4(a) and 4(b), blue trace] show no PtCoO_2 (0001) reflections, with only substrate peaks and broad features at 37.9° and 68.8° present, confirming the absence of long-range crystallinity. Although no long-range crystallinity is detected by XRD, the low deposition rate results in a deposition process lasting approximately 110 min for a 20 nm film combined with the high substrate temperature, providing an opportunity for surface diffusion during growth. Such diffusion may promote short-range Pt-O-Co ordering and interface equilibrium, contributing to the local crystallographic registry observed by TEM fast-fourier transform (FFT) despite the amorphous nature of the film. The Pt-rich surface layer identified by EDS may further indicate redistribution of Pt- and Co-containing species driven by

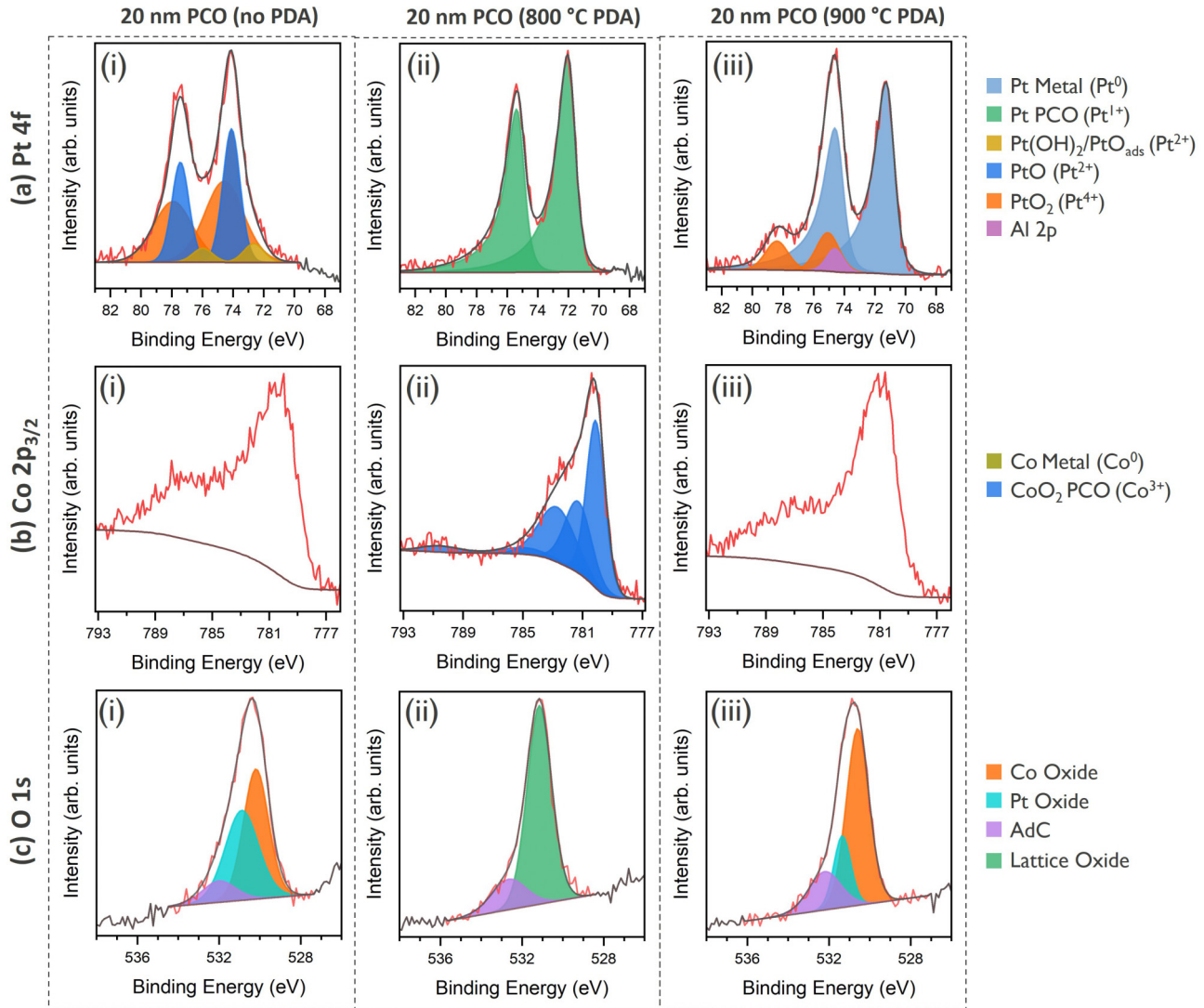


FIG. 2. (a) HAXPES Pt 4f core-level spectra of the (i) 20 nm PCO (no PDA), (ii) 20 nm PCO + 800 °C, and (iii) 20 nm PCO + 900 °C PDA. (b) HAXPES core-level Co 2p_{3/2} spectra of the (i) 20 nm PCO (no PDA), (ii) 20 nm PCO + 800 °C, and (iii) 20 nm PCO + 900 °C PDA. (c) HAXPES core-level O 1s spectra of the (i) 20 nm PCO (no PDA), (ii) 20 nm PCO + 800 °C, and (iii) 20 nm PCO + 900 °C PDA.

differences in surface energies, which could influence both the film morphology and the crystallization pathway during subsequent PDA. Nevertheless, these processes are insufficient to induce formation of the delafossite phase during growth, as evidenced by the absence of PtCoO₂ reflections in XRD. Consistent with this lack of crystallization, sheet-resistance measurements yielded overscale values. Together, these results demonstrate that deposition at 420 °C does not induce PtCoO₂ crystallization, necessitating higher-temperature thermal processing.

B. Optimized film—800 °C PDA

Postdeposition annealing at 800 °C induces a pronounced transition in both the chemical states and crystallinity of PCO, corresponding to the formation of phase-pure, epitaxial PtCoO₂, and the emergence of low resistivity. Following annealing, the Pt 4f core level spectrum of the 20 nm PCO film [Fig. 1(a)] exhibits a dominating asymmetric doublet

centered at 71.9 eV, approximately 0.7–0.8 eV higher than cited binding energy positions for Pt⁰, which is observed at 71.2 eV for the reference sample (SM Figs. 2(ai)) [34][40,41]. This feature is distinct from Pt oxide species, which appear at higher binding energies (>72.0 eV) and exhibit symmetric line shapes [42–44]. Considering the asymmetric line shape, binding energy position, and the known delafossite formal valency ($A^{1+}B^{3+}O_2^{2-}$) this component is assigned to conducting Pt¹⁺ within the Pt triangular lattice layers of PtCoO₂ [45].

A minor symmetric component at 74.5 eV is attributed to surface Pt⁴⁺ species and accounts for ~1% of the Pt 4f signal in the 20 nm film. The absence of this component in the corresponding HAXPES spectra [Fig. 2(a)] confirms its surface-localized origin. Comparable Pt 4f line shapes are observed across all films annealed at 800 °C (SM Figs. 3(a) and 3(b) [34]), with increased surface oxide contributions in thinner films, consistent with the relative probing depths of XPS and HAXPES.

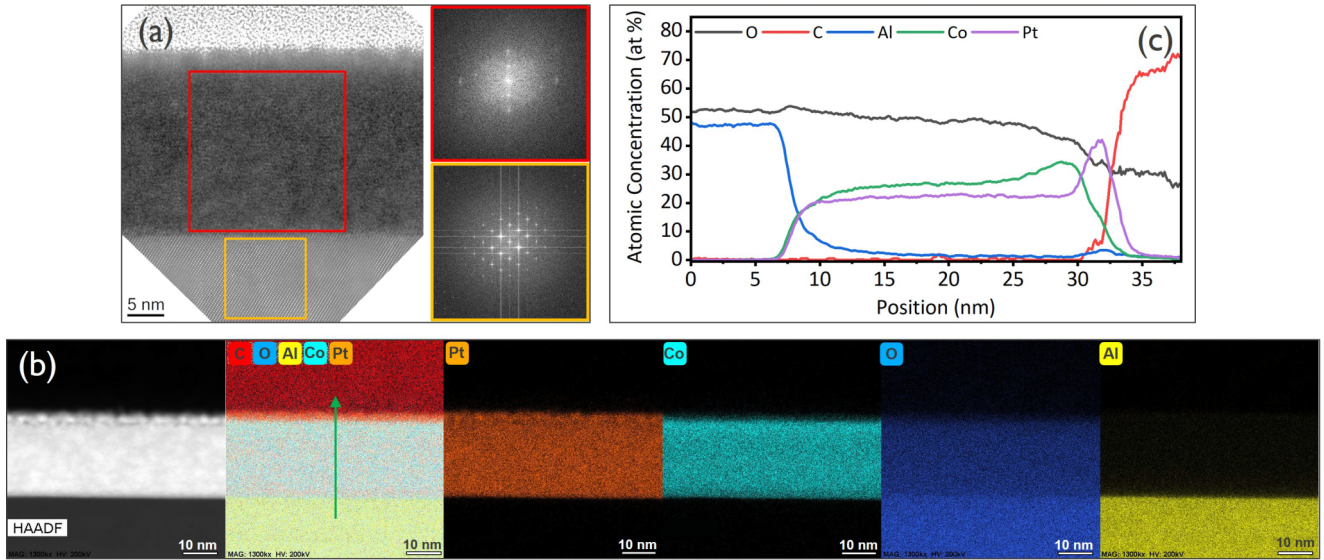


FIG. 3. (a) Cross-sectional TEM of 20 nm as-deposited PCO and fast-Fourier transform (FFT) of PCO (red box) and c-sapphire substrate (yellow box). (b) HAADF STEM EDS mapping of as-deposited PCO. (c) Extracted atomic concentration profiles of the area as denoted by the green arrow in the HAADF STEM EDS image (b).

The Co $2p_{3/2}$ spectrum after annealing [Fig. 1(bii)] exhibits a markedly different line shape compared to the as-deposited films and can be described by a single Co^{3+} multiplet structure with the primary feature at 779.9 eV. Notably, the shake-up satellite feature characteristic of high-spin Co^{2+} ($\sim 786 - 787$ eV) is strongly suppressed, indicating the formation of low-spin Co^{3+} in an octahedrally coordinated environment [46–48]. The spectra closely resemble other materials where Co is in the 3+ oxidation state including LiCoO_2 , which shares the same ABO_2 layered structure of PCO, and $\text{CoO}(\text{OH})$ [37,49–51]. Identical Co $2p_{3/2}$ line

shapes in both XPS and HAXPES [Figs. 1(bii) and 2(bii)] indicate uniform chemical states throughout the film thickness. The O $1s$ spectrum [Fig. 1(cii)] can be deconvoluted into three components: a lattice oxygen peak at 530.8 eV with a narrow FWHM of 0.85 eV, a broader surface oxide component at 529.8 eV, and AdC at positions > 531.5 eV. The surface oxide contribution is absent in HAXPES [Fig. 2(cii)] and increases slightly in thinner films, consistent with surface oxidation. The narrow lattice oxygen peak reflects the high crystallinity of the PCO phase.

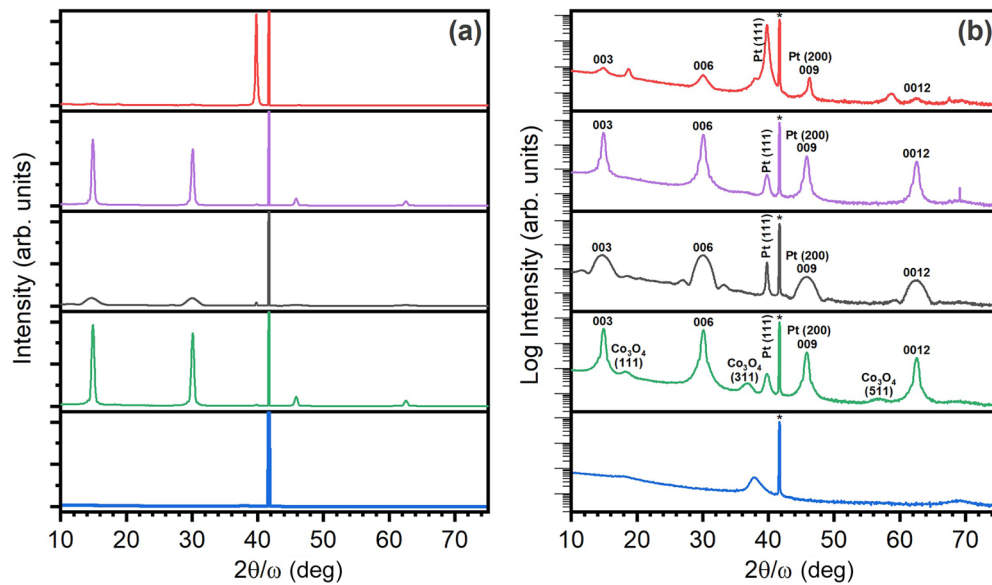


FIG. 4. (a) Linear intensity and (b) logarithmic intensity XRD patterns of PCO films with intensity plotted on a logarithmic scale: 20 nm PCO with no PDA (blue), 20 nm PCO with 800 °C PDA (green), 2 nm Pt + 20 nm PCO with 800 °C PDA (black), 4.5 nm PCO with 800 °C PDA (purple), and 20 nm PCO with 900 °C PDA (red). The logarithmic scale highlights the weak secondary-phase reflections, while the linear scale emphasizes the dominance of the PtCoO_2 diffraction peaks and the comparatively low intensity of the secondary phases.

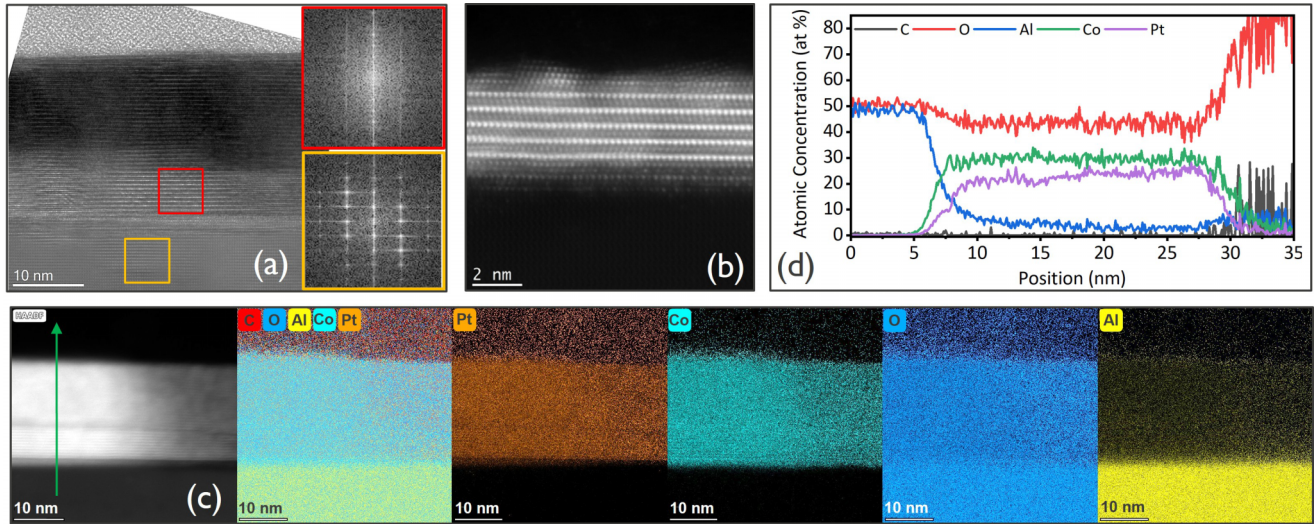


FIG. 5. (a) Cross-sectional TEM of 20 nm PCO (800 °C) with the FFTs of the PCO (red box) revealing epitaxial growth on the *c*-sapphire substrate (yellow box). (b) HAADF STEM of 4.5 nm PCO showing the high contrast between the Pt and CoO₂. (c) HAADF STEM and EDS mapping of PCO showing homogeneous dispersion of platinum, cobalt, and oxygen in the PCO bulk. (d) Atomic concentration line scan of the area as denoted by the green arrow in the HAADF STEM image in panel (c).

Cross-sectional TEM and HAADF STEM [Figs. 5(a) and 5(c)] show a high-quality, uniform thin film of 20 nm PCO where the distinct alternating Pt and CoO₂ layers can be observed. In addition to crystallization of the delafossite phase, localized voids extending to the substrate are observed in AFM following annealing (SM Fig. 4 [34]). These voids are absent in the as-deposited films and likely arise from the substantial structural rearrangement and densification that accompanies crystallization. Their formation also contributes to the increase in surface roughness following PDA (Table I). FFT analysis confirms epitaxial growth of PtCoO₂(0001) onto Al₂O₃(0001), with the expected $R\bar{3}m$ delafossite structure. While a thin interfacial layer exhibiting Al diffusion and slight Co enrichment is observed, the PCO bulk remains compositionally uniform with minimal Al incorporation.

The deposition of a 2 nm Pt liner prior to PCO growth results in a more spatially confined interface region, evidenced by the narrower Al diffusion profile observed by STEM EDS (SM Fig. 5(c) [34]), and suppresses Co₃O₄ formation as indicated by the lack of Co₃O₄ diffraction peaks in Fig. 4, yielding a phase-pure bulk film.

High-resolution XRD further confirms the formation of (0001) epitaxial PCO [Figs. 4(a) and 4(b), green trace]. Laue thickness fringes indicate uniform film thickness and a high degree of structural coherence. Weak secondary reflections corresponding to Pt(111) and Co₃O₄ are observed at intensities approximately two orders of magnitude lower than the primary PCO peaks, indicating that the film is dominated by the delafossite oxide. When considering the detection limits of XPS (~ 1 at. % [52]), these secondary phases are not expected to yield resolvable components in the photoemission core level spectra. Consistent with microscopy, these secondary phases are located at the surface and substrate interface. Previous pole figure measurements performed by our group on PtCoO₂ film prepared using the same growth and annealing conditions revealed a sixfold rotational symmetry, confirming a well-defined in-plane epitaxial relationship in addition

to the out-of-plane PtCoO₂(0001) orientation observed here [29]. Despite the relatively large in-plane lattice mismatch of approximately 5.9% between PtCoO₂ ($a = 2.83$ Å) and Al₂O₃(0001) ($a = 2.77$ Å), crystallization proceeds with a well-defined epitaxial relationship.

Electrical measurements reflect the structural and chemical improvements achieved after 800 °C PDA. The 4.5 and 20 nm PCO films exhibit resistivities of 14.5 and 12.6 $\mu\Omega$ cm, respectively, while incorporation of a Pt liner further reduces the resistivity to 11.0 $\mu\Omega$ cm likely due to improved interface quality, suppression of secondary oxide phases, and reduced void formation. These values are comparable to state-of-the-art alternative interconnect metals, Ru and Mo, at similar dimensions [7].

C. Crystallinity versus decomposition—900 °C PDA

Annealing at 900 °C drives a marked departure from the delafossite phase, enabling identification of the chemical signatures that distinguish crystallization from decomposition and thereby defining the upper limit of the processing window.

The Pt 4*f* spectra of the PCO film annealed at 900 °C [Fig. 1(a_{iii})] are dominated by an asymmetric doublet at 71.2 eV, coincident with the binding energy of metallic Pt⁰ observed in the Pt reference film. In contrast to films annealed at 800 °C, this peak is accompanied by a pronounced symmetric Pt⁴⁺ component at 75.1 eV, accounting for approximately 19% of the Pt signal. The persistence of this oxidized component in HAXPES [Fig. 2(a_{iii})], with a comparable relative intensity ($\sim 15\%$), indicates that Pt oxidation occurs throughout the bulk rather than being confined to the surface. These spectral changes provide direct evidence for the reduction of Pt¹⁺ to Pt⁰ and the breakdown of the delafossite lattice at elevated temperature. This decomposition is believed to be driven by the volatility of Pt at higher temperatures [53–56] and has previously been observed by Hagen *et al.*, for their films deposited by atomic layer deposition (ALD) [31].

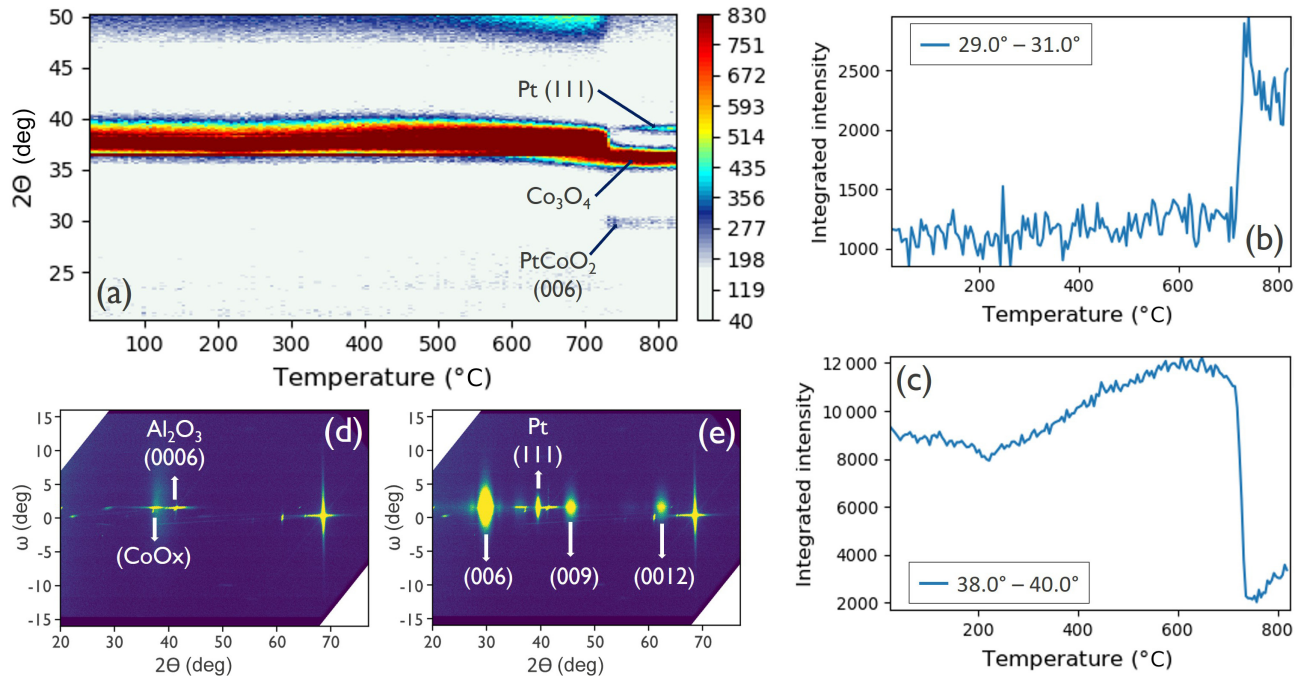


FIG. 6. (a) 2D heat map of XRD 2θ vs temperature during *in situ* anneal of PCO to 825 °C under oxygen atmosphere. Extracted intensity of the (b) PtCoO₂(006) and (c) Pt(111) with annealing temperature. 2D ω - 2θ XRD heat maps of PCO (d) before *in situ* annealing, and (e) after *in situ* annealing.

Consistent with this behavior, the Co $2p_{3/2}$ core level spectrum [Fig. 1(biii)] evolves towards a line shape characteristic of the oxidation state of Co shifting towards the 2+ state, resembling CoO and Co(OH)₂ [36,37]. As with the as-deposited film, the spectrum likely reflects a convolution of multiple CoO_x phases, rather than a single stoichiometric oxide, although the reduced intensity of the high-spin Co²⁺ shake-up satellite suggests partial retention of higher-valency Co environments. The redistribution of Co oxidation states further supports decomposition of the ordered CoO₂ layers.

The O 1s spectrum [Fig. 1(ciii)] similarly reflects phase segregation. While both PtO_x and CoO_x contributions remain present, the dominant O 1s component corresponds to CoO_x, with a binding energy and FWHM comparable to the as-deposited film. The PtO_x contribution is narrower than that observed in the as-deposited film, consistent with the presence of a single bulk Pt species rather than mixed surface oxidation states. Together with the Pt 4f results, this indicates partial oxidation accompanying Pt metal segregation during decomposition.

XRD measurements corroborate the spectroscopic evidence for phase breakdown. In films annealed at 900 °C, the intensity of Pt(111) and Co₃O₄ reflections increases significantly relative to PtCoO₂ peaks [Figs. 4(a) and 4(b), red trace], confirming decomposition into metallic and oxide phases. Electrical measurements yield a non-Ohmic (“potential”) response, consistent with the formation of an insulating oxide layer and loss of a continuous conductive delafossite phase.

To directly capture the onset of decomposition, *in situ* XRD (IS XRD) [Fig. 6(a)] is employed during ramp annealing under oxygen atmosphere. At low temperatures, there is a broad band between 36° and 40° associated with amorphous or poorly crystalline CoO_x/PtO_x [57]. Above 700 °C, the

broad feature splits into separate Pt(111) and Co₃O₄ peaks, concurrent with the appearance of PtCoO₂(006), marking the onset of crystallization. At temperatures just below 800 °C, the PtCoO₂ intensity decreases while the Pt(111) intensity rises again, signaling the onset of decomposition where the strongest Pt(111) signal occurs near the maximum annealing temperature of ~ 825 °C [Figs. 6(b) and 6(c)]. Pre- and postanneal ω - 2θ maps confirm the formation and subsequent degradation of epitaxial PtCoO₂ [Figs. 6(d) and 6(e), respectively]. Although a small offset between the crystallization temperature observed in IS XRD and the optimum *ex situ* PDA temperature is present due to differences in heating conditions, both measurements consistently demonstrate a narrow thermal window separating amorphous growth, phase-pure crystallization, and decomposition. This rapid transition underscores the sensitivity of PtCoO₂ to thermal processing and highlights the need for precise control over annealing conditions.

D. Interpreting chemical-structural evolution

The combination of Pt¹⁺ asymmetry at a distinct higher binding energy than Pt⁰, and the Co³⁺ multiplet splitting with the suppression of the high-spin Co²⁺ shake-up satellites provides an unambiguous spectroscopic fingerprint of phase-pure PtCoO₂. These features change sharply at temperatures greater than 800 °C, making them practical indicators of changes within the film. In particular, the emergence of any Pt⁰ and/or Co²⁺ surface or bulk contributions can signal the onset of film decomposition, allowing rapid process tuning. In addition, the presence of oxidized Pt and Co not in a 3+ oxidation state can indicate the deposition of amorphous PCO and subsequently indicate the need for crystallization of the film.

IV. CONCLUSIONS

This work delivers a comprehensive chemical-structural evolution of PtCoO₂ using a multimodal characterization approach, including the first HAXPES measurements, which resolve bulk chemical states and mitigate surface artifacts inherent to conventional XPS. Coupled with *in situ* XRD, these insights reveal a narrow thermal window between crystallization and decomposition, underscoring the need for precise process control, and convert spectroscopic characterization into a practical tool for optimizing thermal budgets.

Epitaxial PtCoO₂ films with a formal valency of Pt¹⁺ and Co³⁺ form during postdeposition annealing at 800 °C, while annealing at 900 °C induces partial decomposition as evidenced by the emergence of metallic Pt⁰ and mixed Co^{2+/3+} states alongside the formation of PtOx. This is corroborated by both *in situ* and *ex situ* XRD which shows the transition from the delafossite oxide to segregated oxide and metallic phases. The decomposition at higher temperatures is attributed to the volatility of Pt, disrupting the Pt-CoO₂ layers, highlighting the critical need for precise thermal control during integration.

Electrical characterization demonstrates competitive resistivity values, 12.6 μΩ cm for 20 nm films and 14.5 μΩ cm for 4.5 nm films, comparable to leading interconnect candidates such as Ru and Mo. Resistivity of 20 nm films is further reduced to 11.0 μΩ cm with the deposition of a Pt liner layer. These findings demonstrate the potential of PtCoO₂, which offers low in-plane resistivity, as an alternative to conventional metals for interconnects such as Mo and Ru, provided that precise control over phase and stoichiometry is maintained during processing.

Beyond validating PtCoO₂ as a promising alternative to conventional metals, this work underscores the importance of advanced characterization in guiding material selection and process optimization for next-generation nanointerconnects.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [58].

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