

Visualization of Defects in Single-Crystal and Thin-Film PdCoO₂ using Aberration-Corrected Scanning Transmission Electron Microscopy

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Single-crystal delafossite PdCoO₂ is known to have an extremely low intrinsic impurity concentration of ~0.001%, demonstrating extraordinarily high conductivity with a mean free path of ~20 microns at low temperatures. However, when grown as thin films, the resistivity at room temperature increases by a factor of 3 to 80 times, depending on the film thickness. Using scanning transmission electron microscopy, we identify different classes of defects for the single crystal vs epitaxial thin film. The dominant defect for single-crystal PdCoO₂ is found to be ribbon-like defects. For the thin films, we identify different types of defects arising in epitaxial thin films mainly due to substrate termination that disrupt the lateral connectivity of the conducting planes. Our results are consistent with the high conductivity of single crystals and increased electrical resistivity of the thin films compared to that of single crystals, suggesting that selecting a proper substrate, improving surface quality, and reducing the step density are the keys to enhance the film quality for utilizing PdCoO₂ as a platform for future applications.

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INTRODUCTION

Bulk delafossite PdCoO₂ is known for its remarkable in-plane resistivity, as low as 8 nΩ · cm, with mean-free paths as long as 20 μm at low temperatures [1]. Recently, V. Sunko et. al. reported that such high conductivity is a result of extraordinary intrinsic purity of the materials with point defect concentrations as low as 0.001% [2]. Owing to its high conductivity, the potential of PdCoO₂ and other metallic delafossites [3] as a platform for studying quantum transport [4,5], as a component of spintronic devices [6], or as thermoelectric devices [7,8] has been of great interest. Nevertheless, the quality of epitaxial thin films, which is vital to device applications, is still at an early stage. In 2018, Harada et al. first reported the epitaxial growth of ultrathin PdCoO₂ films on *c*-plane Al₂O₃ by pulsed-

laser deposition (PLD) [9]. Shortly thereafter, the growth of PdCoO₂ thin films on *c*-plane Al₂O₃ using molecular-beam epitaxy (MBE) was reported [10, 11]. The advantages of thin PdCoO₂ films are demonstrated by the recent successful control of Schottky barrier heights using the interface dipole effect of the inserted PdCoO₂ layer in metal/ β -Ga₂O₃ junctions [12].

Compared to single crystals, PdCoO₂ thin films grown on Al₂O₃ tend to show much higher in-plane resistivities, which increase as the film thickness decreases [9-11]. This is expected for a thin film as it experiences limitations such as boundary conditions imposed at its interfaces and grain boundaries that could act as scattering centers [9, 10]. From the growth perspective, while bulk-growth processes occur near thermodynamic equilibrium conditions, thin film growth techniques are generally carried out further from equilibrium conditions. This results in the growth process being dominated by the diffusive kinetics of adatoms on the growth surfaces. As a result, thin films can easily deviate from stoichiometry, resulting in various point defects inside the film [13, 14]. The conduction of PdCoO₂ is dominated by Pd 2D-layers as CoO₂ layers are insulating [15, 16]. Thus, resistivity in bulk PdCoO₂ is expected to be dominated by defects in the conductive Pd planes. In particular, defects that disrupt continuity of the Pd planes could have detrimental effects on the electrical properties. Controlling such defects are therefore crucial to improve film properties towards bulk-like perfection, which can be achieved by first understanding the defect types that occur in this system at the atomic scale.

In this paper, we report the first atomic-resolution images of defects in PdCoO₂, both for as-grown bulk PdCoO₂, and for an 8 nm thick film of PdCoO₂ grown on *c*-plane Al₂O₃ by MBE, using aberration corrected scanning transmission electron microscopy (STEM). The transport properties of this thin film were measured, and the room temperature resistivity and residual resistivity ratio were found to be degraded with respect to the single crystal [10]. With medium-angle annular dark field (MAADF-STEM) imaging of single-crystal PdCoO₂, we observe ribbon-like defects ranging a few hundred nanometers in lateral length that are likely dislocations or stacking faults. High angle annular dark field (HAADF-) and annular bright field (ABF-STEM) imaging of thin film PdCoO₂ reveals 180° in-plane rotation twin domains created by the energetic equivalence of nucleating such PdCoO₂ domains on the (001) surface of the Al₂O₃ substrate. Meanwhile, we report that majority of defects- such as out-of-phase boundaries, Pd-rich agglomerates, and unambiguous twin domains which we are the first to report in this paper- are induced by the

substrate surface termination, which is correlated with these PdCoO₂ thin films having inferior electrical characteristics compared to single crystals. The quality of PdCoO₂ film growth dependence on the substrate surface quality can be a limiting factor for future applications, which would require specific strategies for improvement.

METHODS

Single crystals of PdCoO₂ were grown in sealed quartz tubes as described in [2]. The as-grown crystals had platelet forms and were 3-8 μm in thickness and 300-700 μm in lateral dimensions. Thin film of PdCoO₂ with a thickness of 8 nm was grown on *c*-plane sapphire at 480 °C (measured by a thermocouple in the vicinity of the substrate, but not in thermal contact with it) under a background partial pressure of 10^{-5} Torr of distilled ozone (80% O₃ + 20% O₂) in a Veeco Gen10 MBE system. (001) oriented Al₂O₃ substrates (CrysTec GmbH) with a miscut angle of $\pm 0.1^\circ$ are annealed in air at 1050°C for 6 hours prior to growths to yield a step-and-terrace morphology. More information on detailed growth conditions, surface characterization and electrical transport results for the thin films can be found in [10].

Cross-sectional [210], plan-view TEM specimens of single-crystal and cross-sectional [100] TEM specimens of thin film PdCoO₂ were prepared using a FEI Strata 400 Focused Ion Beam (FIB), where a PdCoO₂ lamella with a typical volume of ~ 20 (width) \times 5 (height) \times 2 (thickness) μm^3 was extracted and thinned down to $\sim 18 \times 5 \times 0.05 \mu\text{m}^3$ by Thermo Fisher Helios G4 UX FIB with a final milling step of 5 keV to reduce damage. Carbon and platinum layers were sputtered on the sample surface prior to FIB thinning to minimize potential damage from ion milling. The samples were then examined by scanning transmission electron microscopy (STEM), using an aberration-corrected Titan Themis operating at 300 keV for atomic-resolution imaging and also a Tecnai F20 at 200 keV for wide-field surveys. A convergence angle of 21 mrad was used on the Titan, and 9 mrad on the Tecnai. High-angle annular dark field (HAADF-STEM) imaging was done with an inner cutoff angle of 40 mrad, while MAADF-STEM imaging was performed with an inner cutoff angle of around 30 mrad in Tecnai F20 to obtain strain-sensitive images.

RESULTS AND DISCUSSIONS

Defects in Pure Single Crystals

Using STEM, we investigated single crystals of PdCoO_2 , looking at a total volume of $36 \mu\text{m}^3$ by preparing six cross-sectional TEM samples and two plan-view TEM samples extracted from four different crystals. Figures 1(a) and 1(b) show simultaneously-acquired atomic resolution HAADF-STEM and ABF-STEM cross-sectional images, respectively. Pd and Co sites are resolved in Fig. 1(a), while the ABF signal of Fig. 1(b) resolves the oxygen atoms as well. Typical TEM samples prepared by FIB have a thickness ranging from 20-50 nm, which is along the direction that we see in projection. Thus, the atomic contrast we get is an average over ~ 50 -150 atoms along each resolved column. Compared to 2D monolayers such as MoS_2 or graphene, detection of a single vacancy or an interstitial therefore becomes more difficult as it is only $\sim 1/100$ atoms here, comparable to our detection limits (See Fig. S1 for more details [17]). The electron beam also experiences channeling as it propagates along the column, so the same number of point defects can yield different intensities depending on the location they occupy along the column [18]. As we were not able to observe any measurable contrast differences from point defects in the images, we thus believe the concentration of isolated point defects—vacancies or interstitials—are less than the detection limit of HAADF-STEM ($\sim 1\%$ /atom column). Much thinner samples would be needed for single atom sensitivity, at which point vacancies could be detected and counted, and a more useful upper bound could be placed.

In most samples from the single crystal, we were able to observe pristine areas ranging from several microns in lateral dimensions as in Fig. 1(c). To obtain enhanced contrast from strained areas, MAADF-STEM imaging was used in Fig. 1(d), revealing regions with thin, long defects extending about 200-300 nm in lateral dimension but only about 2 nanometers wide. The contrast from these defects tend to disappear during STEM observation even with small sample tilts, indicating that the depths of the defect should be at the scale of a few nms. The density of these defects are approximately calculated to be slightly less than 0.001% in volume, in good agreement with [2]. These defects only appear as strain fields in low magnification TEM images without any visible change in lattice structure. When magnified, the lattice structure is not so different from the bulk structure of Fig. 1(a). This is related to the fact that we are observing a projection of 20-50 nm in thickness, where the atomic arrangements of an

embedded defect can be obscured if the defects are very thin. As plan-view [001] TEM imaging of the specimen also showed similar results, we suspect that the defects are likely to be very thin ribbon-like defects, such as dislocations or stacking faults. Since we were not able to see much change in the lattice structure by HAADF-STEM imaging, understanding its formation mechanism by detailed, careful observation of the atomic arrangements should be done in the future -perhaps by scanning electron beam nano diffraction which is capable of capturing small local changes in atomic arrangements without beam damage.

Defects in Thin-Film PdCoO₂

While the room-temperature in-plane resistivity of single-crystal PdCoO₂ is 2.6 $\mu\Omega\cdot\text{cm}$, when grown as thin films with varying thicknesses from 10 nm down to 3 unit cells (1.6 nm), the resistivity at room temperature increases by a factor of 3 to 80 times respectively, with the resistivity reaching a plateau with increasing film thickness [10]. The resistivity of our 8-nm-thick film of PdCoO₂ which we will discuss later in this paper, is 11 $\mu\Omega\cdot\text{cm}$ at room temperature [10]. Further, the residual resistivity ratio, ($\text{RRR} = \rho_{300\text{K}}/\rho_{4\text{K}}$), which is as high as 347 for single crystals, was significantly reduced to 2 for the 8-nm-thick film. The increase in resistivity is a common feature for thin films of metallic oxides due to confinements imposed by the thin film geometry, reducing the mean free path of conduction electrons by increased surface scattering effects [19, 20]. However, in light of the high defect density of these films (described below), it would be necessary to understand the types of defects.

The (001)-oriented epitaxial growth of PdCoO₂ on (001) Al₂O₃ follows from its lattice match (-2.9% when the crystal structures are rotated in-plane by 30° with respect to each other), trigonal crystal symmetry, and the chemically isomorphic CoO₂ surface termination of PdCoO₂ [9, 10]. PdCoO₂ films grow with the expected 30° in-plane rotation to the underlying substrate, but it is energetically equivalent for both a +30° rotation angle and a -30° rotation angle. The result is that both $\pm 30^\circ$ nuclei form and in doing so, the film consists of two non-equivalent twin domains related by an in-plane rotation of 180° [9, 10]. Figure 2 shows an example of rotational twinning at the interface of PdCoO₂ and Al₂O₃. The HAADF-STEM image in Fig. 2(a) shows heavy Pd and Co atomic layers. The simultaneously acquired ABF-STEM image in Fig. 2(b) gives less contrast between both heavy and light atoms,

making it possible to simultaneously detect the oxygen atoms, resolving the CoO_2 layer and therefore the O-Co-O bonding directionality (See Fig. S2 in [17] for raw ABF-STEM image without overlaid graphics). At the interface we observe two distinct twin domains with 180° rotated bonding directions as highlighted by the yellow lines overlaid on O-Co-O bonds (two regions where the film structure is 30° and -30° rotated from the substrate). These two twin domains, namely domain 1 (D1) and domain 2 (D2) are specified by the crystal schematics in Fig. 2(c). The twin domain structures are shown to alternate between D1 and D2 along the growth direction. Also, twin boundaries are not perpendicular to the interface, but rather switch continuously at different locations at each in-plane CoO_2 layer creating meandering twin boundaries which we discuss later in this study.

As discussed in [10, 21], the lattice mismatch between Al_2O_3 and PdCoO_2 along the (001) direction can lead to the formation of out-of-phase boundaries (OPBs) [22] as the palladium planes can be out of registry depending on where the CoO_2 layer starts to nucleate on the sapphire substrate. In Fig. 3 (a), abrupt termination of a Pd layer is caused by surface steps at the interface. Although the Pd/ CoO_2 layers grown above are not highly affected, in (b) they have formed a broad OPB, but still maintains partially intact conductive Pd-layers. Figure 3 (c) shows OPBs caused by the surface steps that resulted in disruption of the Pd layer, which could be more detrimental to the electrical properties than the previous two cases.

Point defects can also affect the electrical properties, especially when they disrupt the continuity of conductive Pd layers. The most energetically stable Pd interstitial position for PdCoO_2 is calculated to be when a Pd atom is positioned to bond to two oxygen atoms above and two Pd atoms below or vice versa (See Fig. S3 in [17]) [2]. Although we were not able to observe a single interstitial located at this position, a similar configuration was observed in Fig. 4, where we can see multiple Pd viewed in projection, located at the interstitial position, collected into a line defect (e.g., such as one might expect at a dislocation core [23]). On average these were observed with a spacing of roughly once every 220 nm (± 7 nm). With the aid of ABF imaging, we observe that these agglomerates tend to occur at the twin boundaries along with surface steps, as shown in Fig. 4 (a). The atomic step of the interface is outlined by a white line (Raw image available in Fig. S4 [17]). Here, we can see that these agglomerates are located on top of the atomic step, where a twin boundary also occurs. Atomic steps may be low-energy nucleation

locations for twin boundaries as well as for Pd interstitials. The different O-Co-O bond directionality for the two twin domains that meet at the twin boundary creates a wider gap between the neighboring Pd atoms. This allows a much wider space available for an interstitial to be positioned, which would also lower the overall formation energy. The schematics are presented in Fig. S4 [17]. Local non-stoichiometry, which results from relatively low growth temperature with limited adatom mobilities, can also aid formation of such interstitials. The regions boxed in blue in the HAADF-STEM image shows a shorter Co-Co distance compared to other regions. This is due to the overlap of twin domains D1 and D2. As a result, in the ABF-STEM image we can observe a discrete zigzag structure of the overlapped CoO_2 structure. Figure 4 (b) shows a similar case where the agglomerates has formed on top of an atomic step at the interface. These Pd-rich agglomerates also occur frequently far away from the interface as shown in Fig. 4(c), which is formed along the twin boundaries. Here, we can see meandering twin boundaries as the twin domains switch continuously at different locations in each CoO_2 layer. Since these agglomerates are formed perpendicular to the Pd conductive planes, these would appreciably contribute to the increase in resistivity.

Our observations indicate that in order to improve the film properties, we would need a suitable buffer layer to mitigate defects and use other trigonal substrates with better lattice mismatch to relieve and eliminate the twinning. This has been recently discussed by Ok et.al., where they have seen higher quality growths of PdCrO_2 when grown on a monolayer-thick CuCrO_2 buffer layer [24, 25]. However, the CuCrO_2 buffer layer was found to form $\text{CuCr}_{1-x}\text{Al}_x\text{O}_2$ delafossite at the $\text{CuCrO}_2/\text{Al}_2\text{O}_3$ inducing homogenous and stable nucleation with delafossite symmetry, where this preferential nucleation by Al substitution only occurs for Cu-based delafossites [24]. Therefore, more research is needed to find an optimal buffer layer for Pd-based delafossites. Extending the delafossite buffer layer concept further, the ideal substrate for the growth of delafossite films is likely to be a chemically and structurally compatible delafossite single crystal. Single crystals of the delafossite CuFeO_2 with a diameter of 10 mm and several centimeters in length were recently produced [26]. This size is sufficient to be used as substrates for the growth of thin films.

The formation of OPBs and frequent Pd agglomerates due to surface steps suggests that the growth of PdCoO_2 benefits from perfectly flat substrate surface, or more ideally, a substrate with controllable surface termination to obtain high quality thin films [10, 21]. Another recent study reported the growth of a single domain CuCrO_2 film,

on a high miscut SrTiO_3 (111) substrate that can benefit from controllable surface termination through chemical etching [21]. The applicability of similar substrates to the epitaxial growth of Pd-, Pt- based metallic delafossites should be further studied. In addition, as mentioned in [10], to decrease the overall defect densities a higher growth temperature might be beneficial, although it can also lead to the formation of Co_3O_4 due to PdO volatility. The PdCoO_2 film in this study was measured to be stoichiometric by Rutherford backscattering spectrometry, having a Pd:Co ratio of 1:1 with an accuracy of $\pm 2\%$. Therefore, we can expect that if the film is slightly more off-stoichiometric, the defect density would increase even further.

CONCLUSIONS

In this paper, we have looked at bulk single crystal and thin-film PdCoO_2 using aberration-corrected STEM to understand the types and structures of unintentional defects. We have only observed ribbon-like defects in single crystals which require further investigation to determine the atomic details of their structures. On the other hand, epitaxially grown thin-film PdCoO_2 shows a myriad of defects including twin domains, OPBs, and Pd-rich agglomerates. The high concentration of defects indicates that improvements in film quality can be expected. Specific strategies identified to reduce the concentrations of the defects seen include using a substrate with a better structural match, as well as the insertion of a suitable delafossite buffer layer that can be grown at higher temperature than PdCoO_2 to reduce its defect density before transitioning to PdCoO_2 , which can only be grown at relatively low temperature by vacuum deposition methods. We hope our findings can lead to a deeper understanding of these fascinating materials while providing ideas to improve the growth of thin films of PdCoO_2 and other delafossites for fundamental investigations as well as proof-of-principle device studies.

SUPPLEMENTARY MATERIAL

See supplementary material for more information on HAADF-STEM detection limit on point defects and additional figures.

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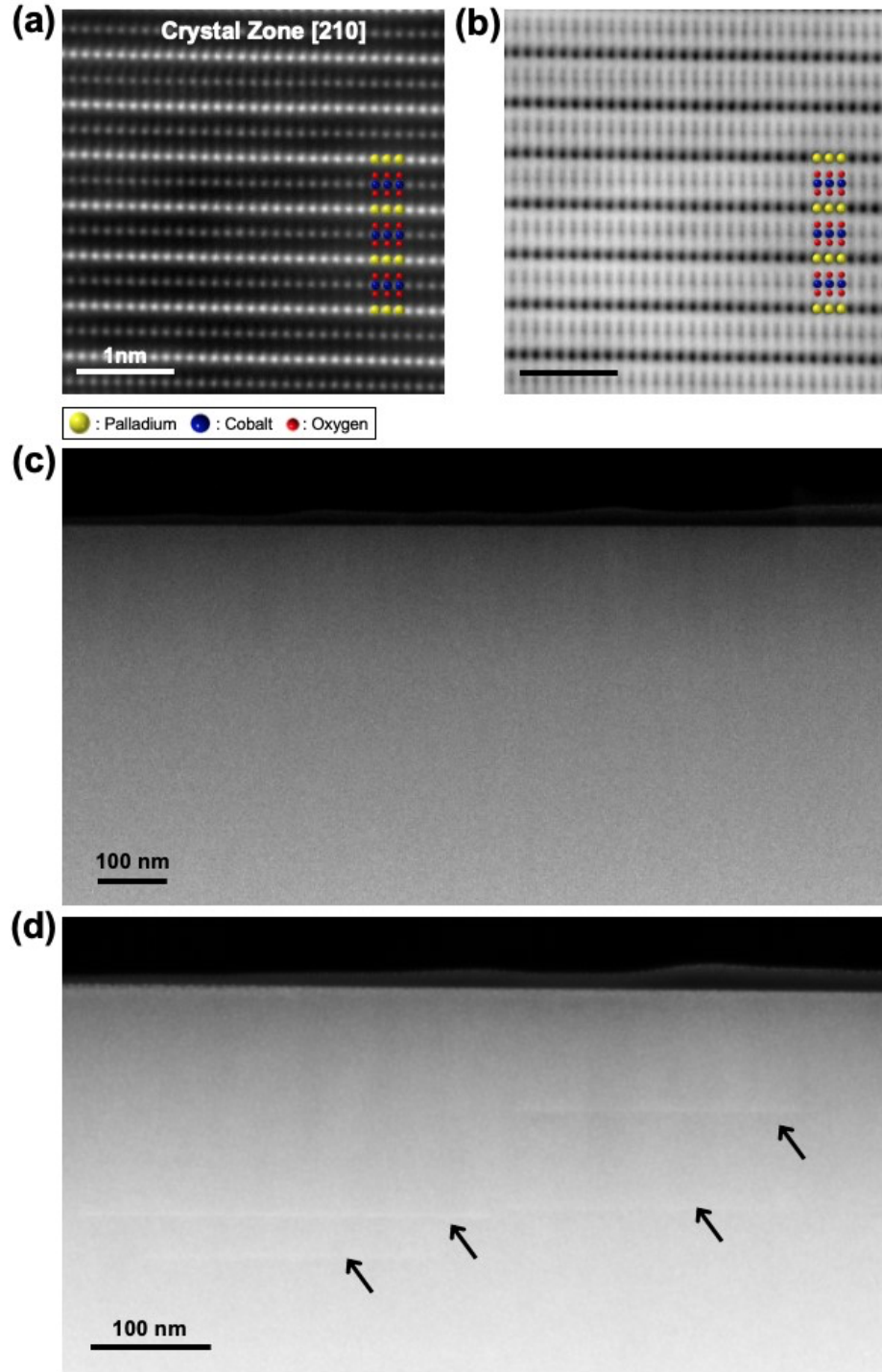


FIG. 1. STEM images of single crystal PdCoO₂. (a) HAADF-STEM image of pristine PdCoO₂ imaged along the [210] zone axis resolving Pd and Co atomic sites. (b) Simultaneously taken ABF-STEM image of PdCoO₂ resolving Pd, Co, and also O. Overlaid yellow, blue, and red spheres in the crystal structure correspond to Pd, Co, and O, respectively. (c) Image of a pristine region taken at low magnification. (d) Defects in pure PdCoO₂ are captured by MAADF-STEM imaging.

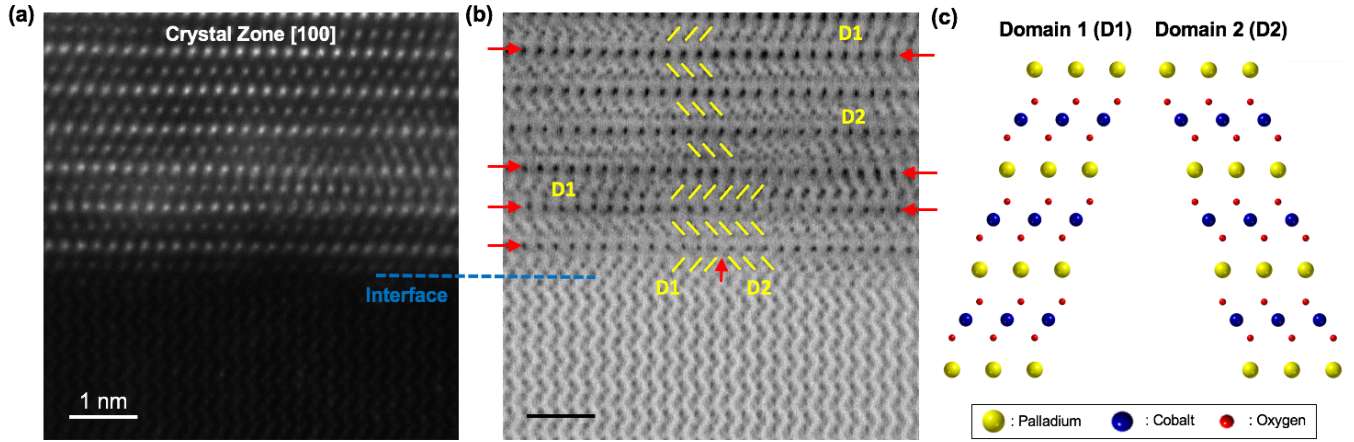


FIG. 2. Formation of twin domains in PdCoO_2 at the interface and inside the film. (a) HAADF-STEM image along the $[100]$ zone axis. (b) Simultaneously acquired ABF-STEM image reveals the CoO_2 layer that has different bonding directionalities, revealing the location of two different twin domains denoted as Domain 1 (D1) and Domain 2 (D2). Twin boundaries are distinguished by red arrows. Raw ABF-STEM image is provided in [17]. (c) Crystal schematics for two different twin domains D1 and D2, related by a 180° in-plane rotation from each other.

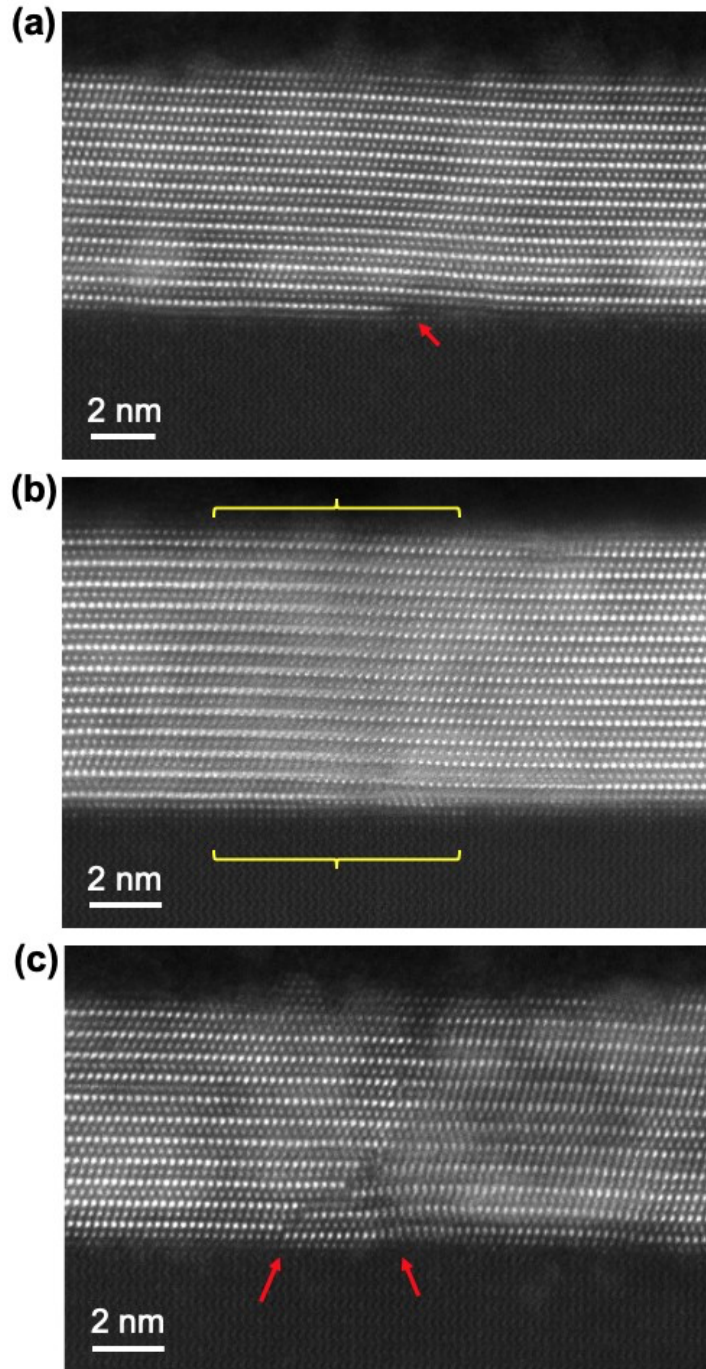


FIG. 3. Stacking defects in PdCoO₂ films. (a) Termination of one Pd layer by a step edge in the substrate. (b) Out-of-phase boundaries (in yellow brackets) are formed from step edge at the interface, but the Pd layers remain partially connected. (c) Large lattice mismatch along the *c*-axis from atomic steps at the interface can result in the formation of OPBs with disconnected Pd layers (red arrows).

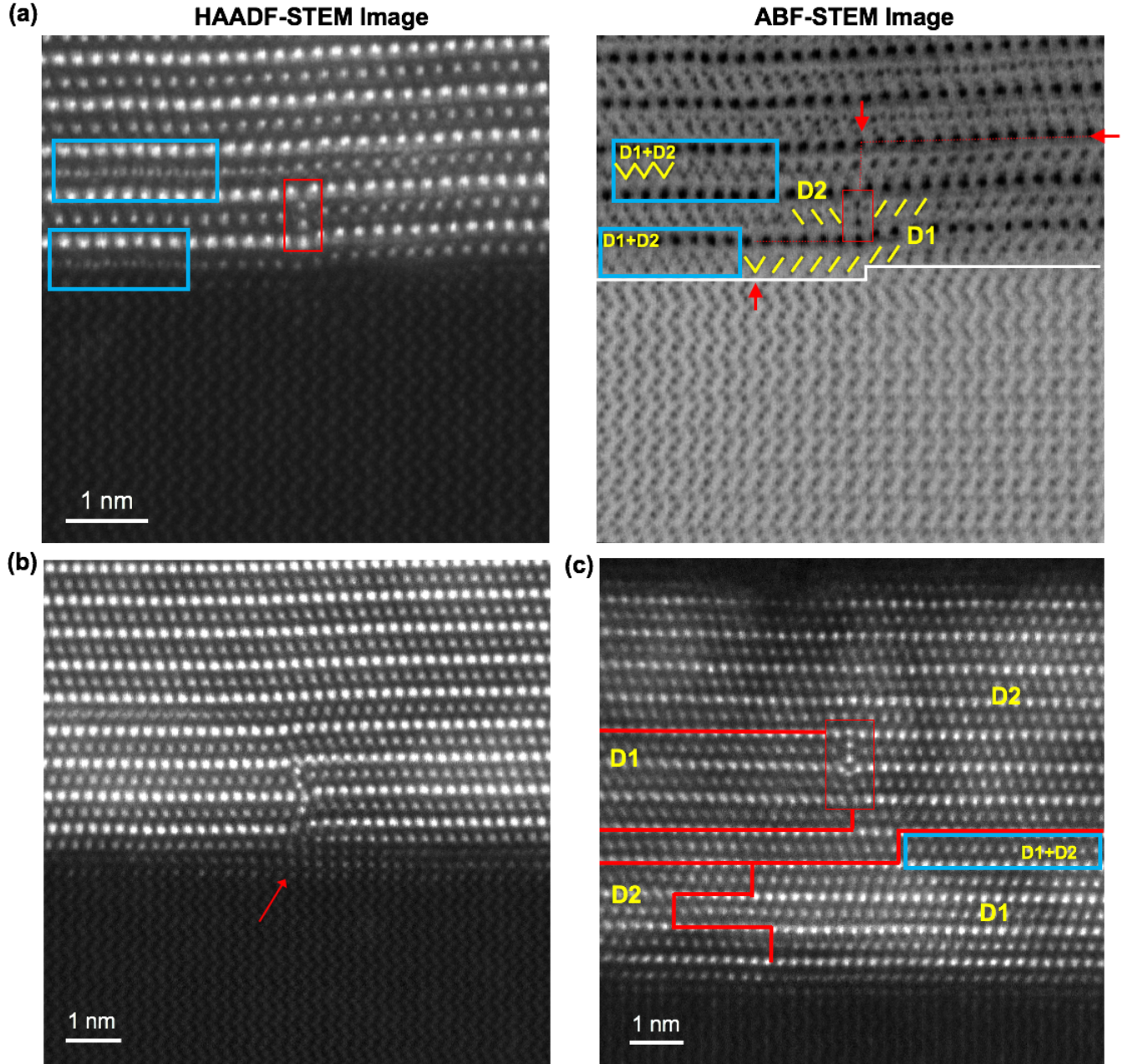


FIG. 4. Pd agglomerates formed along the growth direction. ABF-STEM image in (a) shows twin domain boundary (along the red lines) outlined by comparing the CoO_2 bonding directionality. Twin domain variants are labelled as D1 or D2. Agglomerates are frequently observed near twin boundaries as shown inside the red boxed region in (a). Red arrows show the domain boundaries. Raw ABF-STEM image is provided in [17]. Boxed region in blue shows an overlapped lattice structure of domains D1 and D2 along the beam direction. (b) shows agglomerates formed along the atomic step at the interface (red arrow). (c) shows agglomerates formed along the twin boundaries (inside the boxed region in red) without atomic steps or edge dislocations at the interface.