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ABSTRACT

Typical low-temperature frustrated triangular antiferromagnet CuFeO_2 is attracting extensive interest due to its narrow-band-gap semiconductor properties. High-quality and impurity-free CuFeO_2 epitaxial thin films would be preferable for fundamental studies on the physical and chemical properties. However, the heteroepitaxial growth of impurity-free CuFeO_2 thin films has been a significant challenge due to its narrow formation window in the Cu–Fe–O system as well as the metastable nature of the Cu^{1+} cations. This work reports for the first time the fabrication and characterization of high-quality and impurity-free (00.1)-oriented CuFeO_2 epitaxial thin films grown with relaxed interfaces on (00.1) sapphire substrates by pulsed laser deposition. Below the critical thickness of around 16 nm, the films exhibit a rhombohedral structure with relatively good crystalline quality where all Cu ions appear to be in the 1+ oxidation state, while the rocking curves display a narrow full width at half maximum of about 0.11° . Increasing the thickness, the (111)-oriented $\gamma\text{-Fe}_2\text{O}_3$ nanograins grow embedded in the CuFeO_2 films. Here, an excess Fe^{3+} -assisted growth mechanism is proposed to explain the iron oxide grain formation. This study provides insight into the heteroepitaxial growth of relaxed CuFeO_2 thin films with high purity and crystalline quality as an ideal sample design to characterize the fundamental properties of this material in view of potential device applications.

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I. INTRODUCTION

The delafossite structure of CuFeO_2 has a hexagonal symmetry with the space group $R\bar{3}m$ or $P63/mmc$, depending on the stacking of the Cu^{1+} cation layers along the c axis. In the past two decades, powder and single crystals of CuFeO_2 with a rhombohedral $R\bar{3}m$

structure have been widely investigated as a frustrated triangular antiferromagnet, as well as a multiferroic material exhibiting both ferroelectric and antiferromagnetic behavior at low temperature.^{1–10} Recently, CuFeO_2 has attracted extensive research interest as a p-type semiconductor photoelectrode material for solar water

splitting and CO_2 conversion owing to its optimal bandgap, good stability in aqueous solution, and its composition consisting of earth-abundant elements.^{11–18} High-quality epitaxial $\text{Cu}^{1+}\text{Fe}^{3+}\text{O}_2$ thin films without the presence of impurities containing Cu^{2+} ions would be a preferable platform to study the fundamentals of physical and chemical properties of this material. However, the heteroepitaxial growth of high-quality and impurity-free CuFeO_2 thin film turns out to be a formidable challenge owing to the complex thermodynamics and nonstoichiometry, and the coexistence of multiple phases in the Cu-Fe-O solid solution^{19–22} as well as the metastable nature of the Cu^{1+} cation in complex oxide compounds.

To date, the heteroepitaxial growth of CuFeO_2 thin film was only achieved along the (00.1) crystallographic direction using (00.1)-oriented sapphire (single crystal $\alpha\text{-Al}_2\text{O}_3$). The films were grown by pulsed laser deposition (PLD),²³ and the presence of Cu^{2+} ions was clearly observed by x-ray photoelectron spectroscopy (XPS) $\text{Cu}2p$ core-level spectra. The CuFeO_2 thin films are reported to be significantly strained at the interface with the substrate. The strain seems to relax when the film thickness is larger than 9 nm, leading to a defect-rich top layer formed on the 9-nm thick strained initial layer with less defects. The lattice mismatch between (00.1) CuFeO_2 ($a = 0.303$ nm) and (00.1) $\alpha\text{-Al}_2\text{O}_3$ (O–O distance is 0.252 or 0.286 nm) is greater than 10% in average, which is way too large to allow an epitaxial growth with high crystal quality. Ideally, a relaxed interface would produce high-quality epitaxial CuFeO_2 thin films with larger thickness.²³

This work reports the fabrication of high-quality and impurity-free (00.1) CuFeO_2 epitaxial thin films with a relaxed crystal structure. Our samples were grown on (00.1) sapphire substrates by PLD. The thickness-dependent microstructural properties are investigated and discussed.

II. EXPERIMENTAL DETAILS

The CuFeO_2 bulk target for PLD was prepared by a traditional solid-state reaction combined with pressure-less sintering. The mixed raw powders of Cu_2O (99.5% purity, Wako, Japan) and Fe_2O_3 (99.9% purity, Wako, Japan) were weighed in stoichiometric amounts, pressed to a pellet at 50 MPa and then heated in a nitrogen flow at 1000 °C for 24 h. The resulting pellet was crushed and ground into fine powders with a pestle in a mortar. The resulting powder was pressed into a pellet at 50 MPa and then sintered in nitrogen flow at 1000 °C for 24 h.

The thin films were grown on $10 \times 10 \times 0.5$ mm³ (00.1) sapphire (single crystal $\alpha\text{-Al}_2\text{O}_3$) substrates (MTI, USA) by pulsed laser deposition (PLD, Pascal Co. Ltd., Japan) using a 248 nm KrF excimer laser (Coherent COMPex 102, USA) operating at 3 Hz. The laser fluence on the target surface is about 3.5 J/cm² (laser energy of 125 mJ, spot size of 3.6 mm²). The background vacuum was 1×10^{-4} Pa and the ambient O_2 pressure was 0.07 Pa. The target to substrate distance was 4.5 cm. The substrates (face downward) were heated to the targeted deposition temperatures from 700 to 900 °C (according to the manufacturer's calibration) from behind using IR lamp radiation. A 0.5 mm thick silicon piece was attached on the backside of sapphire substrates to facilitate effective heating of the substrate from the IR lamp.

The crystal structure of the thin films was investigated by x-ray diffraction (XRD), performing out-of-plane symmetrical $2\theta/\omega$ scans and rocking curves using a diffractometer (Rigaku SmartLab

9 kW AMK, Japan) with a five-axis goniometer, a Cu rotating anode source, and a two-bounce Ge (022) monochromator. The in-plane orientation relationship of the films with respect to the substrate was assessed by performing ϕ -scan (ϕ -scan) without the monochromator. The thicknesses of thin films were calibrated using x-ray reflectometry (XRR). The surface morphology and roughness of the films were studied by atomic force microscopy (AFM, Shimadzu SPM-9700, Japan). Cross-sectional lamella of thin film samples was prepared for transmission electron microscopy (TEM) via the “lift-out” technique using a dual-beam focused ion beam/scanning electron microscope (FIB/SEM, Nanolab 600i, FEI Company, USA). The cross-sectional transmission electron microscopy (TEM) and selected area electron diffraction (SAED) characterizations of thin films were performed using a TECNAI G2 F30 FEG TEM (FEI Company, USA) at an acceleration voltage of 300 kV. The cross-sectional morphology of the thin film was also analyzed by using scanning transmission electron microscopy (STEM) with a high-angle annular dark field (HAADF) detector and integrated energy-dispersive x-ray spectroscopy (EDS) operated at 200 kV for mapping elemental distributions. Raman spectra were recorded using a Raman spectroscope (Horiba LabRAM HR Raman system, France) with 532 nm laser with 1 mW of power and a 30 s signal acquisition. The optical transmission measurements of the films were conducted using an ultraviolet-visible-near infrared (UV-VIS-NIR) spectrophotometer (Shimadzu UV-3600, Japan). Rutherford backscattering spectrometry (RBS) was performed to determine the chemical composition (Fe/Cu atomic ratio) of the thin films. The samples were irradiated with a 2 MeV ^4He beam, and the backscattered ^4He particles were detected with a silicon PIN diode detector under an angle of 168° toward the incident beam. Data collected by RBS were analyzed by the RUMP program.²⁴ X-ray photoelectron spectroscopy (XPS) measurements were performed using a scanning x-ray photoelectron spectrometer (PHI 5000 VersaProbe II, Physical Electronics Inc., USA) with a monochromatic Al $K\alpha$ x-ray source. A charge neutralizer was used to neutralize the charge effect, and a 0.05 eV scan step energy was selected for the core scan. After Shirley-type background subtraction, the raw XPS spectra were fitted for the composition analysis. The binding energy shifts of the $\text{Cu}2p$ core-level due to relative surface charging were corrected by using the $\text{C}1s$ level of adventitious carbon at 285.0 eV as a reference and the Cu^{1+} (CuFeO_2) and Cu^{2+} (CuFe_2O_4) levels at 932.5 eV and 933.7 eV as the internal standards, respectively. All the operations were carried out at room temperature.

III. RESULTS AND DISCUSSION

The thin films were deposited at different temperatures from 700 to 900 °C for 10 min to identify the optimal deposition temperature. The XRD pattern of the film deposited at 700 °C is shown in Fig. 1(a). The peaks of (222), (333), and (444) series assigned to the cubic spinel structure of CuFe_2O_4 are clearly visible, together with the (01.2) and (00.6) peaks of rhombohedral CuFeO_2 phase. This indicates a mixture of randomly oriented CuFeO_2 grains and (111)-oriented CuFe_2O_4 grains. As shown in Fig. 1(a), all films deposited at temperatures above 750 up to 900 °C exhibit a single phase rhombohedral CuFeO_2 phase with [00.1] orientation. The interference fringes visible around the (00.6) peaks indicate the very

FIG. 1. (a) XRD patterns of CuFeO_2 thin films deposited at different temperatures, (b) selected (00.6) peaks, (c) rocking curves around the (00.6) peaks, and (d) XPS $\text{Cu}2p$ core-level spectra of CuFeO_2 thin films deposited at 700 °C, 750 °C, and 850 °C.

flat surfaces and interface with the substrate. The thickness of the films deposited at temperatures of 750–900 °C is evaluated to be around 8 nm with calibration by x-ray reflectivity (XRR) analysis (not shown). All 2 θ -scan patterns were calibrated with alignment of (00.6) sapphire at 41.700° ($c = 1.298$ nm). From Fig. 1(b), it can be seen that there is no evidence of any angular peak shift for all films grown above 750 °C. The calculated c -lattice constant is approximately 1.711 nm that is in line with the reported bulk value range from 1.709 to 1.717 nm,^{2,25} indicating no significant strain present in the films. The value of the full width at half maximum (FWHM) of the rocking curve of the film deposited at 850 °C is 0.105° [Fig. 1(c)], smaller than the value of 0.16° reported in the literature.²³ The rocking curves of films deposited below 800 °C and above 850 °C show a much larger degree of misalignment between adjacent grains. The combination of higher diffraction peak intensity, smaller FWHM of rocking curve, and more fringes around the (00.6) diffraction peak suggests that 850 °C is the optimal deposition temperature for growing high-quality pure CuFeO_2 thin films. The XPS $\text{Cu}2p$ core-level spectra of the films in Fig. 1(d) confirm the pure Cu^{1+} state in CuFeO_2 thin films grown above 750 °C, while the presence of cubic spinel CuFe_2O_4 impurity (Cu^{2+}) in the film grown at 700 °C is evident.

The in-plane orientation relationship between the films and the substrates was determined by Phi scans around the (10.2) peaks of the 8.5 nm CuFeO_2 thin film grown at 850 °C and the (10.4) peaks of the substrate, as shown in Fig. 2. Six peaks at 60° intervals can be observed for the film, indicating a sixfold symmetry of the film and the presence of an in-plane twin crystallographic structure. The sixfold peaks of the film are rotated by 30° with respect to the threefold peaks from the substrate, confirming the in-plane

epitaxial matching of (00.1) CuFeO_2 thin film on (00.1) sapphire substrate. The atomic-scale schemes of (00.1) CuFeO_2 and (00.1) sapphire ($\alpha\text{-Al}_2\text{O}_3$) crystal planes are illustrated in Fig. 3 to reveal the in-plane epitaxial matching relationship between the thin film and the substrate. The out-of-plane orientation relationship is evidently $[00.1] \text{CuFeO}_2 // [00.1] \text{Al}_2\text{O}_3$, while there should be three possible in-plane epitaxial matching relationships as shown in Fig. 3.

Epitaxial (00.1)-oriented CuFeO_2 thin films with thicknesses from 3.8 to 28.4 nm were grown on (00.1) sapphire substrates at

FIG. 2. Phi-scan of (10.2) and (10.4) peaks for 8.5 nm CuFeO_2 film deposited at 850 °C and sapphire substrate, respectively.

Possible in-plane matching relationship:

[10.0]Al₂O₃//[11.0]CuFeO₂ and [11.0]Al₂O₃//[01.0]CuFeO₂ (*a*_{AO}-*b*_{AO} axis)
 or [10.0]Al₂O₃//[21.0]CuFeO₂ and [11.0]Al₂O₃//[10.0]CuFeO₂ (*a'*_{AO}-*b'*_{AO} axis)
 or [10.0]Al₂O₃//[12.0]CuFeO₂ and [11.0]Al₂O₃//[11.0]CuFeO₂ (*a''*_{AO}-*b''*_{AO} axis)

FIG. 3. Schematic of in-plane epitaxial matching relationship between (00.1) CuFeO₂ and (00.1) Al₂O₃ crystal planes. Crystallographic data of crystal planes and surface atomic terminates of (00.1) hexagonal CuFeO₂ and (00.1) hexagonal *a*-Al₂O₃ from the Cambridge Structure Database (CSD). Atomic-scale structures are visualized using VESTA.²⁶

850 °C to investigate the thickness-dependent microstructural properties. Figure 4 shows the XRD patterns and rocking curves of the films with different thicknesses calibrated by XRR analysis (not shown). From Fig. 4(a) and 4(b), it can be seen that the 3.8–15.3 nm thick thin films exhibit a single phase rhombohedral CuFeO₂ structure with only one orientation along [00.1]. Conversely, a series of peaks that can be assigned to a cubic spinel

structure appear in the XRD plot of the 16.9–28.4 nm thick films. A critical thickness around 16 nm seems to exist for the formation of the impurity phase. From Fig. 4(c), there is no apparent shift observed on (00.6) reflexes of the 3.8–28.4 nm thick films, and the calculated *c*-lattice constant is approximately 1.711 nm similar to the bulk value, indicating that no significant strain formed in the films. Figure 4(d) shows the rocking curves of all films measured

FIG. 4. (a) and (b) XRD patterns of CuFeO₂ thin films with different thicknesses deposited at 850 °C, (c) selected (00.6) peaks, and (d) rocking curves around the (00.6) peaks.

around the (00.6) reflexes. The FWHM values of the rocking curves of the 3.8–15.3 nm thick CuFeO_2 films are all about 0.11° . Larger FWHM values are observed for the 16.9–28.4 nm thick films, as well as the evidently broader and higher peak tails. The latter likely indicates the presence of a two-layered film with different concentrations of crystalline defects, most probably a top defect-rich layer and a bottom defect-poor layer.²³ Undoubtedly, the formation of an impurity phase leads to more defects and results in worse crystal quality of films. Considering the large lattice mismatch, greater than 10%, between the (00.1) surfaces of film and substrate, there is no way to form a (semi)coherent interface between these two materials. An incoherent and disordered interface is formed, and any potential strain arising from the lattice mismatch is expected to be fully released by introducing misfit dislocations and other types of defects.

Figure 5 shows the XPS Cu2p and Fe2p core-level spectra of selected CuFeO_2 thin films with the thickness from 3.8 to 28.4 nm. All films show a pure Cu^{1+} oxidation state as shown in Fig. 5(a). The comparison of XRD and XPS analysis reveals that the 3.8–15.3 nm thick films are composed of pure CuFeO_2 without Cu^{2+} impurities and that the cubic spinel structure identified in the XRD plot of the

FIG. 5. XPS (a) Cu2p and (b) Fe2p core-level spectra of CuFeO_2 thin films with different thicknesses.

FIG. 6. Simulation of the interference fringes around the (00.6) diffraction peak of the 11.9 nm thick CuFeO_2 film.

thicker films does not belong to CuFe_2O_4 , since in such a case, the presence of Cu^{2+} ions would have been revealed by XPS. Alternative candidates to account for the cubic spinel impurity would be Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$, which have similar crystal structures as CuFe_2O_4 .^{27,28} Figure 5(b) shows evidence of Fe^{3+} in all films,^{2,29–31} suggesting that the cubic spinel $\gamma\text{-Fe}_2\text{O}_3$ is the impurity phase that is formed in the films above the critical thickness of about 16 nm.

Figure 6 shows Laue fringes around the (00.6) diffraction peak of the CuFeO_2 thin film with a thickness of 11.9 nm as measured by XRR. The red line in Fig. 6 is the simulation of the interference fringes around the diffraction peak. A remarkably good agreement between the simulation and measurement is obtained considering that the interference fringes are arising from the presence of 21 crystal planes parallel to the substrate surface. The unit cell of the c axis oriented CuFeO_2 ($c = 1.711$ nm) is a layered structure consisting of three subunit cells of equal size stacked along the c axis with

FIG. 7. Raman spectra of the (00.1) CuFeO_2 thin films with different thicknesses.

FIG. 8. (a)–(e) AFM surface morphologies images ($1 \times 1 \mu\text{m}^2$) of heteroepitaxial (00.1) CuFeO₂ thin films with different thicknesses: (a) 6.7 nm, (b) 11.9 nm, (c) 15.3 nm, (d) 18.9 nm, and (e) 28.4 nm. (f) Curve of RMS surface roughness vs thin film thickness.

FIG. 9. (a) Long-scale TEM cross-sectional image, (b) HAADF cross-sectional image with EDS mappings of (c) Cu, (d) Fe, and (e) O elements, (f) SAED pattern of interface from ~200 nm lateral length scale, (g) magnified image of a selected interface region in (h) HRTEM cross-sectional interface image, and (i)–(k) FFT patterns of the 28.4 nm thick CuFeO₂ film.

$c' = 0.57$ nm. Considering c' as the spacing between the adjacent crystal planes of the layered structure, the out-of-plane stacking of 21 lattice planes would result in a total thickness of about 11.97 nm. This value, estimated by fitting the interference fringes in the XRD plot, is in very good agreement with the value of 11.9 nm measured by XRR. This result can be obtained with all films and is an indication of very good crystal quality with a long range biaxial order.

Raman spectroscopy was performed to characterize the CuFeO₂ thin films grown at 850 °C. Delafossite (space group $R\bar{3}m$) CuFeO₂ has two Raman active vibrational modes with E_g and A_{1g} symmetry. Figure 7 shows the Raman spectrum acquired with a 532 nm laser at room temperature. Two clear vibrational modes at 350 and 690 cm^{-1} are visible, in good agreement with the results obtained for a single crystal and polycrystals.^{32,33} As the thickness increases from 3.8 to 13.5 nm, there is no evidence of shift in the peak position and the FWHM values of the E_g and A_{1g} mode peaks do not seem to broaden. The Raman analysis further confirms the high crystal quality of the heteroepitaxial impurity-free CuFeO₂ thin films with a low density of structural defects.

Figures 8(a)–8(e) show the surface morphologies of the CuFeO₂ films with different thicknesses as observed by atomic force microscopy (AFM), and Fig. 8(f) shows the curve of RMS surface roughness vs film thickness. The 6.7–15.3 nm thick thin films show similar grains with an average size around 20 nm while the 18.9 and 28.9 nm films show much larger grains. The RMS roughness of surfaces increases as the thickness increases and is less than 3% of the film thickness for all films, indicating flat surfaces.

The cross-sectional morphology of the 28.4 nm CuFeO₂ thin film was investigated by scanning transmission electron microscopy (STEM) together with energy-dispersive x-ray spectroscopy (EDS), as shown in Fig. 9. The high-angle annular dark field (HAADF) image [Fig. 9(b)] and EDS elemental mapping images

FIG. 10. HRTEM cross-sectional image of the 28.4 nm thick CuFeO₂ film, with the inserted FFT pattern of the selected region.

[Figs. 9(c)–9(e)] clearly reveal the distribution of Cu, Fe, and O. The selected area electron diffraction (SAED) pattern [Fig. 9(f)] obtained from ~ 200 nm lateral length scale confirms that the in-plane crystal orientation relationship between the film and substrate is $[11.0]\text{CuFeO}_2//[1\bar{1}.0]\text{Al}_2\text{O}_3$, which is consistent with the x-ray diffraction analysis [Fig. 2] and the schematic atomic-scale matching relationship structure shown in Fig. 3. Figure 9(h) shows a high-resolution transmission electron microscopy (HRTEM) image of the interface between the CuFeO₂ film and Al₂O₃ substrate. Figure 9(g) exhibits the magnified image of the interface region, revealing that the film-to-substrate interface is characterized by a very high density of misfit dislocations. Such interfacial

FIG. 11. (a)–(d) RBS analysis of heteroepitaxial (00.1) CuFeO₂ thin films with different thicknesses: (a) 6.7 nm, (b) 10.0 nm, (c) 13.5 nm, and (d) 28.4 nm. (e) Curve of Fe/Cu atomic ratio vs film thickness from RBS analysis.

morphological features are likely to lead to a relaxed crystal structure of the film, which would be consistent with the result of the XRD analysis discussed above. The Fast Fourier Transform (FFT) patterns [Figs. 9(i)–9(k)] from the HRTEM image [Fig. 9(h)] also confirms the in-plane orientation relationship. Figures 9(i)–9(k) show the Fourier transforms of the data in framed areas A, B, and C in Fig. 9(h), respectively. The results of the substrate [Fig. 9(i)], the interface between substrate and film [Fig. 9(j)], and the film itself [Fig. 9(k)] represent the same in-plane epitaxial relationship as shown in Fig. 9(f).

As shown in Fig. 10, TEM analysis clearly identifies a cubic spinel grain embedded into the 28.4 nm CuFeO₂ film near the surface. This cubic spinel impurity is here assumed to be γ -Fe₂O₃ with pure Fe³⁺ in agreement with the XPS spectra shown in Fig. 5. The γ -Fe₂O₃ grain exposes very flat crystal planes to form atomically flat interfaces with the matrix of (00.1) CuFeO₂ thin film. Its bottom-side crystal plane appears perfectly parallel to the interface plane between CuFeO₂ film and sapphire substrate. The distance between the bottom sides of γ -Fe₂O₃ grain and sapphire substrate is approximately 16 nm, which is consistent with the proposed critical film thickness around 16 nm above which the impurity phase appears. Summarizing, the samples below the critical thickness of about 16 nm are high-quality and impurity-free (00.1) CuFeO₂ epitaxial thin films, while above the critical thickness, the films are composed of two layers including a bottom layer of pure (00.1) CuFeO₂ and a top composite layer of (111) γ -Fe₂O₃ nanograins embed in the (00.1) CuFeO₂ matrix.

To rationalize the existence of a critical film thickness above which the impurity phase starts to form, we propose a mechanism of excess Fe³⁺-assisted growth of impurity-free CuFeO₂ film. The excess Fe³⁺-O cations or clusters exist at the frontier surface of the growing film to assist the formation of a pure CuFeO₂ phase, where Fe is present only in the 3+ oxidation state. Increasing the thickness, the surface concentration of Fe³⁺ ions progressively increases leading to the formation of γ -Fe₂O₃ nanograins. The observed atomically flat interfaces between the (111)-oriented facets of γ -Fe₂O₃ nanograins and the (00.1)-oriented surface of CuFeO₂ may help reduce the energy barrier for self-assembling of γ -Fe₂O₃ nanograins. To further support this hypothesis, it is worth noticing that in high-temperature processing of Cu-containing oxides, the presence of excess Fe₂O₃ can hinder the formation of copper oxides with Cu²⁺ ions, such as CuO and CuFe₂O₄. It is, therefore, reasonable to assume that the excess Fe³⁺ ions may play the same role during the growth of CuFeO₂ thin films by PLD.

This proposed mechanism would inevitably lead to a hypothesis that the excess Fe³⁺ cations remain in the resulting impurity-free CuFeO₂ thin films while the relative Fe content increases as the film thickness increases up to the critical thickness of about 16 nm. In order to verify the change in the composition of the films as the thickness increases, we carried out RBS measurements to determine the atomic ratios of Fe/Cu in the films. Figures 11(a)–11(d) show the RBS analysis results of the CuFeO₂ thin films, and Fig. 11(e) exhibits the curve of Fe/Cu atomic ratio vs film thickness from the RBS analysis. The Fe/Cu atomic ratio is slightly larger than 1.0 in

FIG. 12. (a) UV-VIS-NIR transmission spectra of epitaxial (00.1) CuFeO₂ thin films with different thicknesses. (b)–(d) Tauc-plots from transmission spectra for the first and second optical bandgaps.

the 6.7 and 10.0 nm thin films and apparently increases as the thickness increases from 10.0 nm to 13.5 nm, supporting the above described hypothesis. Combined with the analysis results from above, it can be concluded that an excess Fe^{3+} -assisted growth mechanism results in high-quality and impurity-free (00.1) CuFeO_2 epitaxial thin films with a critical thickness around 16 nm, above which the (111)-oriented $\gamma\text{-Fe}_2\text{O}_3$ nanograins self-assemble to be embedded in the films.

The lack of impurity-free samples with high crystallographic quality makes it difficult to probe fundamental characteristics of the CuFeO_2 thin film, such as its optical bandgaps that are of critical importance for any potential photoelectrical and photoelectrochemical applications. UV-VIS-NIR spectrometry was used to characterize the optical bandgaps of our films. These measurements were performed in the transmission mode using the thin films grown on double-side polished substrates. The acquired spectra of epitaxial (00.1) CuFeO_2 thin films with different thicknesses are shown in Fig. 12(a), and the resulting Tauc-plots are shown in Figs. 12(b)–12(d). From Fig. 12(b), the 3.8–13.5 nm thin films exhibit the first indirect bandgap of about 1.25 eV and a possible second indirect bandgap around 2.3–2.4 eV. Although Fig. 12(c) shows a possible first direct bandgap around 1.55 eV, a recent work has verified the first indirect bandgap of CuFeO_2 through time-resolved optical spectroscopy combined with band structure calculation.¹⁸ Figure 12(d) shows a possible second direct bandgap around 1.9–2.0 eV. The 18.9 and 28.9 nm thick films show smaller bandgaps, which is probably attributed to the comparatively lower crystal quality and the defects formed with impurity phase grains in the films. The bandgap of $\gamma\text{-Fe}_2\text{O}_3$ is evaluated to be around 2.0 eV by experiment and calculation,^{34,35} which is similar to the second bandgap of CuFeO_2 thin films and may cause problems in evaluating the effect.

IV. CONCLUSIONS

In summary, this work demonstrates the heteroepitaxial growth of high-quality and impurity-free (00.1) CuFeO_2 thin films with a relaxed interface on (00.1) sapphire substrates by pulsed laser deposition. The microstructural characterization supports the proposed excess Fe^{3+} -assisted growth mechanism. The high-quality and impurity-free (00.1) CuFeO_2 epitaxial thin films exhibit a critical thickness of around 16 nm, above which (111)-oriented $\gamma\text{-Fe}_2\text{O}_3$ nanograins self-assemble to be embedded in the CuFeO_2 films. The Fe/Cu atomic ratio is slightly larger than 1.0 in the 6.7 and 10.0 nm thin films and apparently increases as the thickness increases from 10.0 nm to 13.5 nm. The 6.7–15.3 nm thick films show similar grains with an average size around 20 nm while the 18.9 and 28.9 nm films show apparently much larger grains. The RMS roughness of the surfaces increases as the thickness increases and is less than 3% of the film thickness for all the films. The 3.8–13.5 nm thin films exhibit the first indirect bandgap of about 1.25 eV, and either a possible second indirect bandgap around 2.3–2.4 eV or a possible second direct bandgap around 1.9–2.0 eV.

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REFERENCES

- ¹M. Mekata, N. Yaguchi, T. Takagi, T. Sugino, S. Mitsuda, H. Yoshizawa, N. Hosoi, and T. Shinjo, "Successive magnetic ordering in CuFeO_2 —A new type of partially disordered phase in a triangular lattice antiferromagnet," *J. Phys. Soc. Jpn.* **62**(12), 4474–4487 (1993).
- ²V. R. Galakhov, A. I. Poteryaev, E. Z. Kurmaev, V. I. Anisimov, S. Bartkowski, M. Neumann, Z. W. Lu, B. M. Klein, and T.-R. Zhao, "Valence-band spectra and electronic structure of CuFeO_2 ," *Phys. Rev. B* **56**(8), 4584–4591 (1997).
- ³S. Mitsuda, N. Kasahara, T. Uno, and M. Mase, "Partially disordered phase in frustrated triangular lattice antiferromagnet CuFeO_2 ," *J. Phys. Soc. Jpn.* **67**(12), 4026–4029 (1998).
- ⁴M. Hasegawa, M. I. Batrashevich, T. R. Zhao, H. Takei, and T. Goto, "Effects of oxygen nonstoichiometry on the stability of antiferromagnetic phases of $\text{CuFeO}_{2+\delta}$ single crystals," *Phys. Rev. B* **63**, 184437 (2001).
- ⁵T. Kimura, J. C. Lashley, and A. P. Ramirez, "Inversion-symmetry breaking in the noncollinear magnetic phase of the triangular-lattice antiferromagnet CuFeO_2 ," *Phys. Rev. B* **73**, 220401 (2006).
- ⁶T. Arima, "Ferroelectricity induced by proper-screw type magnetic order," *J. Phys. Soc. Jpn.* **76**(7), 073702 (2007).
- ⁷S. Seki, Y. Yamasaki, Y. Shiomi, S. Iguchi, Y. Onose, and Y. Tokura, "Impurity-doping-induced ferroelectricity in the frustrated antiferromagnet CuFeO_2 ," *Phys. Rev. B* **75**, 100403 (2007).
- ⁸N. Terada, T. Nakajima, S. Mitsuda, H. Kitazawa, K. Kaneko, and N. Metoki, "Ga-substitution-induced single ferroelectric phase in multiferroic CuFeO_2 ," *Phys. Rev. B* **78**, 014101 (2008).
- ⁹Y. Tanaka, N. Terada, T. Nakajima, M. Taguchi, T. Kojima, Y. Takata, S. Mitsuda, M. Oura, Y. Senba, H. Ohashi, and S. Shin, "Incommensurate orbital modulation behind ferroelectricity in CuFeO_2 ," *Phys. Rev. Lett.* **109**, 127205 (2012).
- ¹⁰N. Terada, D. D. Khalyavin, P. Manuel, T. Osakabe, P. G. Radaelli, and H. Kitazawa, "Pressure-induced polar phases in multiferroic delafossite CuFeO_2 ," *Phys. Rev. B* **89**, 220403 (2014).
- ¹¹C. G. Read, Y. Park, and K.-S. Choi, "Electrochemical synthesis of p-type CuFeO_2 electrodes for use in a photoelectrochemical cell," *J. Phys. Chem. Lett.* **3**, 1872–1876 (2012).
- ¹²J. Gu, A. Wuttig, J. W. Krizan, Y. Hu, Z. M. Detweiler, R. J. Cava, and A. B. Bocarsly, "Mg-doped CuFeO_2 photocathodes for photoelectrochemical reduction of carbon dioxide," *J. Phys. Chem. C* **117**, 12415–12422 (2013).
- ¹³M. S. Prevot, N. Guijarro, and K. Sivula, "Enhancing the performance of a robust sol-gel-processed p-type delafossite CuFeO_2 photocathode for solar water reduction," *ChemSusChem* **8**, 1359–1367 (2015).
- ¹⁴M. S. Prevot, X. A. Jeanbourquin, W. S. Bouree, F. Abdi, D. Friedrich, R. van de Krol, N. Guijarro, F. L. Formai, and K. Sivula, "Evaluating charge carrier transport and surface states in CuFeO_2 photocathodes," *Chem. Mater.* **29**, 4952–4962 (2017).
- ¹⁵A. Yengantiwar, P. S. Shinde, S. Pan, and A. Gupta, "Delafossite CuFeO_2 photocathodes grown by direct liquid injection chemical vapor deposition for efficient photoelectrochemical water reduction," *J. Electrochem. Soc.* **165**, H831–H837 (2018).
- ¹⁶J. Husek, A. Cirri, S. Biswas, A. Asthagiri, and L. R. Baker, "Hole thermalization dynamics facilitate ultrafast spatial charge separation in CuFeO_2 solar photocathodes," *J. Phys. Chem. C* **122**, 11300–11304 (2018).
- ¹⁷Y. Oh, W. Yang, J. Tan, H. Lee, J. Park, and J. Moon, "Boosting visible light harvesting in p-type ternary oxides for solar-to-hydrogen conversion using inverse opal structure," *Adv. Funct. Mater.* **29**, 1900194 (2019).

- ¹⁸C.-M. Jiang, S. E. Reyes-Lillo, Y. Liang, Y.-S. Liu, G. Liu, F. M. Toma, D. Prendergast, I. D. Sharp, and J. K. Cooper, "Electronic structure and performance bottlenecks of CuFeO₂ photocathodes," *Chem. Mater.* **31**, 2524–2534 (2019).
- ¹⁹A. E. Katkov and A. A. Lykasov, "Spinel phase relations in the Fe₃O₄-CuFe₂O₄ system," *Inorg. Mater.* **39**(2), 171–174 (2003).
- ²⁰A. V. Khvan, O. B. Fabrichnaya, G. Savinykh, R. Adam, and H. J. Seifert, "Thermodynamic assessment of the Cu-Fe-O system," *J. Phase Equilib. Diff.* **32**, 498–511 (2011).
- ²¹D. Shishin, T. Hidayat, E. Jak, and S. A. Decterov, "Critical assessment and thermodynamic modeling of the Cu-Fe-O system," *Calphad* **41**, 160–179 (2013).
- ²²J. Schorne-Pinto, L. Cassayre, L. Presmanes, and A. Barnabe, "Insights on the stability and cationic nonstoichiometry of CuFeO₂ delafossite," *Inorg. Chem.* **58**, 6431–6444 (2019).
- ²³T. Joshi, T. R. Senty, R. Trappen, J. Zhou, S. Chen, P. Ferrari, P. Borisov, X. Song, M. B. Holcomb, A. D. Bristow, A. L. Cabrera, and D. Lederman, "Structural and magnetic properties of epitaxial delafossite CuFeO₂ thin films grown by pulsed laser deposition," *J. Appl. Phys.* **117**, 013908 (2015).
- ²⁴L. R. Doolittle, "A semiautomatic algorithm for Rutherford backscattering analysis," *Nucl. Instrum. Meth. B* **15**, 227–231 (1986).
- ²⁵A. Pabst, "Notes on the structure of delafossite," *Am. Mineral.* **31**, 539–546 (1946).
- ²⁶K. Momma and F. Izumi, "VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data," *J. Appl. Cryst.* **44**, 1272–1276 (2011).
- ²⁷M. Boudeulle, H. Batis-Laddoulsi, Ch. Leclercq, and P. Vergnon, "Structure of γ -Fe₂O₃ microcrystals: Vacancy distribution and superstructure," *J. Solid State Chem.* **48**, 21–32 (1983).
- ²⁸E. H. Nickel, "The new mineral cuprospinel (CuFe₂O₄) and other spinels from an oxidized ore dump at Baie Verte, Newfoundland," *Can. Mineral.* **11**, 1003–1007 (1973).
- ²⁹Y. Gao and S. A. Chambers, "Heteroepitaxial growth of α -Fe₂O₃, γ -Fe₂O₃ and Fe₃O₄ thin films by oxygen-plasma-assisted molecular beam epitaxy," *J. Cryst. Growth* **174**, 446–454 (1997).
- ³⁰C. R. Brundle, T. J. Chuang, and K. Wandelt, "Core and valence level photoemission studies of iron oxide surfaces and the oxidation of iron," *Surf. Sci.* **68**, 459–468 (1977).
- ³¹T. Fujii, F. M. F. de Groot, G. A. Sawatzky, F. C. Voogt, T. Hibma, and K. Okada, "In situ XPS analysis of various iron oxide films grown by NO₂-assisted molecular-beam epitaxy," *Phys. Rev. B* **59**, 3195–3202 (1999).
- ³²S. P. Pavunny, A. Kumar, and R. S. Katiyar, "Raman spectroscopy and field emission characterization of delafossite CuFeO₂," *J. Appl. Phys.* **107**, 013522 (2010).
- ³³O. Aktas, K. D. Truong, T. Otani, G. Balakrishnan, M. J. Clouter, T. Kimura, and G. Quirion, "Raman scattering study of delafossite magnetoelectric multiferroic compounds: CuFeO₂ and CuCrO₂," *J. Phys. Condens. Matter* **24**, 036003 (2012).
- ³⁴J. K. Vassiliou, V. Mehrotra, M. W. Russell, E. P. Giannelis, R. D. McMichael, R. D. Shull, and R. F. Ziolo, "Magnetic and optical properties of γ -Fe₂O₃ nanocrystals," *J. Appl. Phys.* **73**, 5109–5116 (1993).
- ³⁵R. Grau-Crespo, A. Y. Al-Baitai, I. Saadoune, and N. H. De Leeuw, "Vacancy ordering and electronic structure of γ -Fe₂O₃ (maghemite): A theoretical investigation," *J. Phys. Condens. Matter* **22**, 255401 (2010).