Heteroepitaxial Hexagonal (00.1) CuFeO$_2$ Thin Film Grown on Cubic (001) SrTiO$_3$ Substrate Through Translational and Rotational Domain Matching

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Heteroepitaxy of complex oxide thin films is a significant challenge when a large mismatch in the lattice parameters (>8%) and difference in the crystallographic symmetry coexist between the film and substrate. Herein, the heteroepitaxial growth of a hexagonal delafossite CuFeO$_2$ thin film with (00.1) orientation on a cubic perovskite (001) SrTiO$_3$ substrate through translational and rotational domain matching epitaxy is reported. The rotational in-plane domain orientation relationships are CuFeO$_2$ [11.0]//SrTiO$_3$ [110] and CuFeO$_2$ [2T.0]/SrTiO$_3$ [110] with about 10% in-plane lattice mismatch. The 14.8 nm-thick (00.1) CuFeO$_2$ thin film shows high-crystalline quality with a full width at half maximum of rocking curve of about 0.24$^\circ$ and exhibits a possible indirect optical bandgap of 1.43 eV or direct optical bandgap of 1.94 eV. Herein, not only a model system demonstrating translational and rotational domain matching heteroepitaxy of complex oxides is reported, but also a way to thin-film heterostructures integrating hexagonal delafossite with cubic perovskite materials for functional oxide devices is opened.

1. Introduction

Hexagonal CuFeO$_2$ with the delafossite structure, well-known for its antiferromagnetic and multiferroic properties at low temperature, has garnered attention in studies of p-type oxide semiconductors for potential optoelectronic applications in photovoltaics since 1987,[1] and recently in photodiode devices.[2–4] CuFeO$_2$ has recently attracted extensive interest as a promising narrow-bandgap semiconductor photocathode material for solar fuel conversion,[5–14] due to the tunable and relative small optical bandgap (E$_{g}$ ≈1.5 eV) with the position of the conduction/valence bands in a useful range. In addition, CuFeO$_2$ consists of earth-abundant Cu and Fe elements, which is important for applications. Conventional photoanodes typically consist of powders of the photoactive material deposited by electrochemical deposition on a conductive substrate, which is needed as the current collector for the standard photoelectrochemical (PEC) test. However, the development of performing photoelectrodes for visible-light-driven water splitting and CO$_2$ reduction has enormous advantages using thin-film deposition technology.[15,16] Thin films can indeed be used as ideal model systems, with well-defined crystalline, crystallographic, and morphological properties, to access subtle materials’ properties whose characterization would be precluded with conventional samples. Particularly, important is for example, the role of the crystallographic surface and bulk orientation which can affect the charge transfer at the solid/liquid interface and the external quantum efficiency.[17–19] Crystalline, epitaxial thin films, of CuFeO$_2$ grown on conductive substrates, is an alternative device design that would allow us to gain complementary insights into the PEC properties of this promising material.

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It is beneficial to study the fundamental physics and chemistry of thin-film CuFeO₂ for possible technological applications. It is, therefore, desirable to deposit high-quality thin films with specific crystallographic orientation on commercial conductive single-crystal substrates or conductive epitaxial layer-buffered single-crystal substrates. The cubic perovskite SrTiO₃ doped with Nb is the only commercially available conductive single crystal metal oxide substrate widely used for growing epitaxial oxide thin films. Alternatively, epitaxial layers of cubic perovskite oxides, such as SrRuO₃,[20–22] La₅Sr₁₋ₓMnO₃,[23,24] LaNiO₃,[25–27] and SrMoO₃,[27–30] are commonly used as conductive buffer layers. The epitaxial growth of CuFeO₂ thin films has been only demonstrated with a (00.1) out-of-plane crystallographic orientation on insulating hexagonal (00.1) sapphire substrates using pulsed laser deposition.[31,32] There is no report on heteroepitaxy formed between the crystal planes of hexagonal delafossite and cubic perovskite materials. The heteroepitaxial growth of CuFeO₂ thin films on cubic perovskite SrTiO₃ substrates would not only create a platform to study the fundamental photoelectrochemical properties of CuFeO₂, but also provide a model system to demonstrate the feasibility of oxide heterostructures consisting of the two functional complex oxide families for developing oxide-based devices with novel functionalities.

Due to the similar crystal symmetry, a heteroepitaxial interface between cubic (111) crystal plane and hexagonal (00.1) crystal plane can be obtained, and several examples are reported in literature.[33–38] A few examples of heteroepitaxy between cubic (001) and hexagonal (00.1) planes of metal oxides are La(Sr)MnO₃ (001) [110]//ZnO (00.1) [10.0],[39,40] and BaTiO₃ (001) [110]//ZnO (00.1) [10.0],[39,41] in which the occurrence of domain rotations is the consequence of mismatch of the rotational symmetries of the cubic (100) and hexagonal (00.1) crystal planes.[39] And both cases are characterized by a relatively small in-plane lattice mismatch along the [110]//[10.0] directions of about 2% and 0.5%, respectively. However, in the case of interest for this study, the lattice mismatch between hexagonal (00.1) CuFeO₂ (a = 3.033 Å, both Fe–Fe and O–O distances are 3.033 Å) and cubic (001) SrTiO₃ (a = 3.905 Å, O–O minimum distance is 2.761 Å) is about 10%,[42,43] which is far too large to allow heteroepitaxial growth with a coherent interface.

In systems with a large lattice mismatch of above 8%, the film and substrate with similar crystal symmetry may form a heteroepitaxial interface through domain matching epitaxy, where a periodic array of dislocations forms along the interface to accommodate the lattice mismatch.[44] In some cases, a structurally modified transition layer has been reported to be formed at the interface to facilitate the heteroepitaxial growth.[45,46] Recently, domain matching epitaxy was observed for orthorhombic (111) Hf₀.₅Zr₀.₅O₂ (HZO) thin films grown on cubic (001) La₂/₃Sr₁₋ₓMnO₃ (LSMO) epitaxial layer through the introduction of arrays of interface dislocations with short periodic spacing.[47] In this unique case, the crystal planes of the film and substrate show an apparent symmetry dissimilarity, whereas the lattice mismatches along two in-plane matching orientations of HZO [211]//LSMO [110] and HZO [022]//LSMO [110] are calculated to be about 10% and 58%, respectively. Although the domain rotational heteroepitaxy could form between the two crystal planes without symmetry similarity, typical examples are normally observed only for systems with small lattice mismatch.[41] The complex chemical interface composition and chemical interactions, together with large lattice mismatches and dissimilar crystal symmetries, makes heteroepitaxy of complex oxides systems very challenging. To date, the examples of heteroepitaxial growth of complex oxides thin films with symmetry dissimilarity and large lattice mismatch (above 8%) are limited.

Understanding the interfacial structures in complex oxide heterostructure systems with symmetry dissimilarity and large lattice mismatch is crucial for studying complex oxide heterostructures and developing oxide thin-film devices. The CuFeO₂/SrTiO₃ heterostructure can indeed be considered as a prototypical example of this kind of oxide heterostructures. This work demonstrates the heteroepitaxy of a hexagonal (00.1) CuFeO₂ thin film grown on a cubic (001) SrTiO₃ substrate through translational and rotational domain matching epitaxy.

2. Results and Discussion

The CuFeO₂ thin films were grown on single-crystal (001) SrTiO₃ substrates using pulsed laser deposition (PLD). The preparation of the CuFeO₂ bulk target for PLD and the effects of deposition parameter on the growth of CuFeO₂ thin films are reported in our previous work on heteroepitaxial (00.1) CuFeO₂ films grown on sapphire substrates.[32] We have selected the film thickness of 14.8 nm because we could show in our previous work,[32] that pure phase (00.1) CuFeO₂ epitaxial films grown on (00.1) sapphire substrates could only be obtained with a maximum film thickness of about 16 nm, above which a second phase of Fe₂O₃ nanograins is formed. As we used the same PLD conditions in this study, to grow the epitaxial (00.1) CuFeO₂ thin films on (001) SrTiO₃ substrates, we limited the film thickness to less than 16 nm, to achieve the heteroepitaxy between hexagonal (00.1) delafossite and cubic (001) perovskite crystal planes through translational and rotational domain matching. In this work, the thin-film deposition was carried out using a laser fluence of 3.5 J cm⁻² with a 3 Hz repetition rate for a deposition time of 40 min. The oxygen partial pressure was kept at 0.07 Pa and the substrate was held at a set temperature of 900 °C.

Figure 1a shows a representative out-of-plane X-ray diffraction (XRD) pattern of the CuFeO₂ thin films. The 2θ–ω scans were aligned and calibrated using the (002) SrTiO₃ reflection at 46.470° (2θ = 3.905 Å). The film exhibits a series of peaks assigned to the (00.3), (00.6), (00.9), and (00.12) planes of the hexagonal delafossite structure of CuFeO₂. The rocking curves of the thin-film XRD reflexes show a full width at half maximum (FWHM) of about 0.24°, as shown in Figure 1b, suggesting a very good crystalline quality for a heteroepitaxial oxide thin film with a large lattice mismatch of about 10%. Figure 1c shows Laue fringes around the (00.6) diffraction peak of a 14.8 nm thick film, with a simulation of fitting the interference fringes.[48] The thickness of film is measured by X-ray reflectivity (XRR), as shown in the insert of Figure 1c. The evaluated deposition rate of the film is about 0.02 Å per pulse (about 0.37 nm min⁻¹). (A 0.01) interplanar distance between two Fe–O layers of one subunit cell is evaluated to be 5.714 Å according to the 2θ value of 31.280° for the (00.6) reflections in Figure 1a,c. The c-lattice constant is calculated to be 1.714 nm that is in line with the bulk value range

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indicating that there is no significant strain in the films. Considering that the interference fringes are arising from the presence of 26 parallel crystal planes with an interplanar distance of 5.714 Å, the simulation is in a remarkably good agreement with the measurement. The unit cell of layered structure CuFeO$_2$ consists of three subunit cells of equal size stacked along the c-axis, a total thickness of out-of-plane stacking of 26 subunit cells would be about 14.856 nm, which is very close to the evaluated value of 14.8 nm obtained by XRR. These results indicate a very flat surface and interface as well as excellent crystal quality with long-range biaxial order.

The phi scans were carried out to determine the in-plane orientation relationship. As shown in Figure 1d, 12 peaks of CuFeO$_2$ film are separated by 30° intervals and are rotated by 15 or 75° with respect to the four peaks from SrTiO$_3$ substrate. This indicates four distinct orientation relationships with the SrTiO$_3$ substrate, which can be denoted as

\[ \text{CuFeO}_2{}\text{[11.0]}/\text{SrTiO}_3{}\text{[110]} \]  
(1)

\[ \text{CuFeO}_2{}\text{[11.0]}/\text{SrTiO}_3{}\text{[110]} \]  
(2)

\[ \text{CuFeO}_2{}\text{[21.0]}/\text{SrTiO}_3{}\text{[110]} \]  
(3)

\[ \text{CuFeO}_2{}\text{[21.0]}/\text{SrTiO}_3{}\text{[110]} \]  
(4)

The (1) and (2) relationships as well as the (3) and (4) relationships represent mirror inverted variants of each other. The relation between (1) with (4) and between (2) with (3) is a 30° in-plane rotation. This result is similar to the phi scan result of heteroepitaxial ZnO(00.1)/BaTiO$_3$(001) films grown on (001) SrTiO$_3$ substrates, suggesting that a rotational domain heteroepitaxy probably forms between (00.1) CuFeO$_2$ and (001) SrTiO$_3$ crystal planes. From Figure 1e, the in-plane XRD analysis result confirms the presence of the in-plane orientation relationship, and the CuFeO$_2$[11.0]/[21.0] directions are parallel to SrTiO$_3$[110] direction. There are completely separate satellite peaks observed near the (11.0) CuFeO$_2$ peaks. Figure 1f shows the intensity ratios of satellite versus (11.0) CuFeO$_2$ reflection from the data in Figure 1e as a function of incident angle. As the incident angle, \( \omega \) increases, the penetration depth of the X-ray also increases, indicating that the satellite peak may originate from deeper in the layer at the interface and may indicate a modulated strain region at the interface. According to the typical interface mode in domain matching epitaxy, the strain is localized in a region at the interface and should relax abruptly within several unit cells (around 1–2 nm) through the formation of a high concentration of interfacial dislocations.

Figure 2 shows the atomic-scale schemes of (00.1) CuFeO$_2$ and (001) SrTiO$_3$ crystal planes for revealing in-plane atomic lattice matching. There are two possible in-plane matching relationships: CuFeO$_2$[11.0]/SrTiO$_3$[110] and CuFeO$_2$[21.0]/SrTiO$_3$[110]. The latter coexists with the orientation relationship of CuFeO$_2$(01.0)/SrTiO$_3$(110). The two sets of mirror inverted variants ((1) with (2) as well as (3) with (4)) as discussed earlier, belonging to the orientation relationships of CuFeO$_2$[11.0]/SrTiO$_3$[110] and CuFeO$_2$[21.0]/SrTiO$_3$[110], present identical Fe-terminating planes with the SrTiO$_3$ surface. The in-plane lattice mismatch along CuFeO$_2$(11.0)/SrTiO$_3$(110) direction between (00.1) CuFeO$_2$ (3.033 Å) and (001) SrTiO$_3$ (O–O distance is 2.761 Å) planes is about 10%.
SrTiO$_3$[110] direction, although the lattice misfit is about 90% with the SrTiO$_3$ lattice, it is about 5% misfit of one CuFeO$_2$ lattice distance with respect to two SrTiO$_3$ lattice distances for achieving domain matching. While the in-plane lattice mismatch along the CuFeO$_2$[01.0]/SrTiO$_3$[110] direction is about 10%. These translational and rotational domain matching relationships are in good agreement with the domain rotation rule in heteroepitaxy.\textsuperscript{[41]} The XPS core-level spectra of Cu$2p$ and Fe$2p$ for the CuFeO$_2$ thin film are shown in Figure 3. The film shows a pure Cu$^{1+}$ oxidation state and evidence of Fe$^{3+}$, suggesting that the film is composed of a pure CuFeO$_2$ phase.\textsuperscript{[3,4,32,49]}

The high-resolution transmission electron microscopy (HR-TEM) was carried out to characterize the interface between the SrTiO$_3$ substrate and CuFeO$_2$ thin film. Figure 4a shows a HR-TEM interface image with a fast Fourier transform (FFT) of the substrate region. The TEM section was fabricated using a focused ion beam (FIB) using the “lift-out” method. The TEM analysis confirms the thickness of the film and the

\begin{figure}
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\includegraphics[width=\textwidth]{figure2.png}
\caption{Schematic of atomic scale in-plane lattice matching relationship between (00.1) CuFeO$_2$ and (001) SrTiO$_3$ crystal planes. Crystallographic data of crystal planes and surface atomic terminations of (00.1) hexagonal delafossite CuFeO$_2$ and (001) cubic perovskite SrTiO$_3$ from Cambridge Structure Database (CSD).\textsuperscript{[42,43]} Atomic-scale structures are visualized using VESTA.\textsuperscript{[52]}}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{a,b) XPS core-level spectra of Cu$2p$ (a) and Fe$2p$ (b) for the CuFeO$_2$ epitaxial thin film.}
\end{figure}

\begin{figure}
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\includegraphics[width=\textwidth]{figure4.png}
\caption{a) Cross-sectional HRTEM image of the 14.8 nm-thick (00.1) CuFeO$_2$ epitaxial thin film grown on a (001) SrTiO$_3$ substrate, the inserted FFT pattern taken from region of substrate with reflections indexed, and the image with annotated lines to help visualize the incoherent interface. b) AFM surface morphology image of the film, with an inserted 3D surface morphology image.}
\end{figure}
crystallographic orientation, as measured by XRR and XRD. From the image in Figure 4a, the interface appears sharp and incoherent, with no presence of secondary phases observed and significant amounts of strain. The section marked within the dashed lines has been Fourier filtered and is shown in the inset. An array of edge dislocations is observed along the interface, as expected from the large lattice mismatch between SrTiO$_3$ and CuFeO$_2$. These results are in good agreement with the typical interface characteristic in domain matching epitaxy. Figure 4b shows an atomic force microscopy (AFM) 2D surface morphology image with an inserted 3D surface morphology image of the epitaxial thin film, which is very similar to the surface morphology of epitaxial (00.1) CuFeO$_2$ thin films with a similar thickness grown on (00.1) sapphire substrates.$^{[32]}$

Figure 5 shows the UV–vis–near infrared (NIR) transmission spectrum and the resulting Tauc plots of the 14.8 nm-thick (00.1) CuFeO$_2$ epitaxial thin film grown on (001) SrTiO$_3$ substrate. The results are close to the experimental results of the epitaxial (00.1) CuFeO$_2$ thin films grown on sapphire substrates$^{[32]}$ indicating the high quality, single phase, and low defect density of the heteroepitaxial CuFeO$_2$ thin film. The data analysis indicates a possible indirect optical bandgap of 1.43 eV or a possible direct optical bandgap of 1.94 eV, which are consistent with the reports for films prepared by magnetron sputtering showing a 1.43 eV indirect optical bandgap.$^{[18]}$ and the polycrystalline bulk samples exhibiting a direct optical bandgap of 2.03 eV.$^{[1]}$

3. Conclusions

This study demonstrates heteroepitaxial growth of hexagonal (00.1) CuFeO$_2$ thin film on a cubic (001) SrTiO$_3$ substrate through translational and rotational domain matching. The FWHM value of rocking curve of the thin film is about 0.24°, and four distinct in-plane orientation relationships are identified. A 14.8 nm-thick film shows a possible indirect optical bandgap of 1.43 eV or direct optical bandgap of 1.94 eV. This work provides new insights into the heteroepitaxial oxide systems with crystallographic symmetry dissimilarity and large lattice mismatch.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

CuFeO$_2$, heteroepitaxial thin films, rotational domain matching, SrTiO$_3$.

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Figure 5. a) UV–vis–NIR transmission spectrum of the 14.8 nm thick (00.1) CuFeO$_2$ thin film and b,c) Tauc plots from the transmission spectrum.

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