Epitaxial stabilization of the hexagonal polymorph of ScFeO₃

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Abstract

Magnetoelectric multiferroic materials exhibit both ferromagnetic and ferroelectric behavior with coupling between the two properties. Hexagonal rare earth ferrites (h-**R**FeO₃) are a group of materials that have shown this multiferroic behavior at temperatures below the Néel temperature (T_N). While hexagonal scandium ferrite (h-ScFeO₃) has been predicted to have a Néel temperature significantly higher than other rare earth ferrites, previously produced results have not been as high as expected. By using molecular beam epitaxy (MBE), h-ScFeO₃ films were deposited on C-plane Al₂O₃ (0001) substrates. Well-ordered single-phase h-ScFeO₃ films of up to 70 nm thickness were obtained with negligible impurities as determined through the use of in-situ and ex-situ characterization.

Introduction

Multiferroic materials are of significant interest due to their ability to exhibit multiple spontaneous and switchable (ferroic) properties through the application of an external force. In particular, multiferroics that have both ferroelectric and ferromagnetic order with coupling between the two, known as magnetoelectrics, are of particular interest due to their potential for electronic and magnetic devices[1]. However, these types of materials are very rare since the forces behind ferroelectricity and ferromagnetism are typically mutually exclusive[2]. As a result, coupled multiferroics are often ferroelectric and weakly antiferromagnetic, with their multiferroic properties only appearing below a specific transition temperature, the Néel temperature (T_N)[2].

A group of materials that have been shown to exhibit multiferroic behavior are the hexagonal rare earth ferrites (h-**R**FeO₃). From previous reports, the Néel temperature of the rare earth ferrites has shown a linear increase relating to the decrease in ionic radius of the A-site rare earth[3]. Scandium has been shown to form this hexagonal rare-earth ferrite structure[4], and due to its much smaller ionic radius than other rare earth ferrites, it was expected to have a significantly higher Néel temperature. However, previous attempts to deposit h-ScFeO₃ films have resulted in Néel temperatures that are much lower than predicted[3]. This indicates that more precise growth methods are required to deposit phase pure, properly ordered h-ScFeO₃.

The goal of this project was to epitaxially stabilize single-phase h-ScFeO₃ on C-plane Al₂O₃ (0001) using molecular beam epitaxy, a highly controllable deposition technique that enables deposition of alternating Sc and Fe layers that form the hexagonal ferrite structure. From in-situ and ex-situ characterization, phase pure h-ScFeO₃ weas successfully deposited.

Experimental

For ScFeO₃ to be epitaxially stabilized, a substrate of suitable lattice mismatch is necessary. C-plane Al₂O₃ (0001), a commonly used substrate with a lattice parameter of 4.8Å, was chosen due to its availability and lattice mismatch of 5.3% with the minimum coincidence parameter of h-ScFeO₃ (~5.06Å).

To deposit the h-ScFeO₃ thin films, MBE was used with the shuttered deposition method, where the Sc and Fe elemental sources were alternatingly opened to the growth chamber to create the hexagonal ferrite structure. To determine the best growth conditions and critical thickness for h-ScFeO₃, the substrate temperature (800-1000°C) and deposition time were varied to create a series of samples with different thicknesses.

During the growths, in-situ reflection high-energy electron diffraction (RHEED) was performed to determine if the film was in the correct hexagonal phase, and to prevent impurities from forming due to source drift. Once deposition was finished, the samples were then analyzed using x-ray reflectivity (XRR) and x-ray diffraction (XRD) to assess the thickness and phase purity of the film. X-ray reciprocal space mapping and rocking curve analysis was also performed to assess the crystallinity of the h-ScFeO₃, and atomic force microscopy (AFM) was used to characterize the surface roughness.

Results and Discussion

RHEED analysis was carried out immediately after growth of the h-ScFeO₃ films both at growth temperature (850 °C) and after cooling to ~500 °C, as shown in Fig. 1. The RHEED patterns at the [100] and [1$\bar{1}$0] azimuths at these temperatures allow for the

determination of the crystal structure of the film surface and any impurities that are present. The spacings between the major diffraction lines displayed by the film and the faint tripling that appears during cooling at the $[1\bar{1}0]$ azimuth is consistent with RHEED of other hexagonal ferrites, indicating that h-ScFeO$_3$ was successfully deposited.

70 nm h-ScFeO$_3$ on Al$_2$O$_3$ (0001)
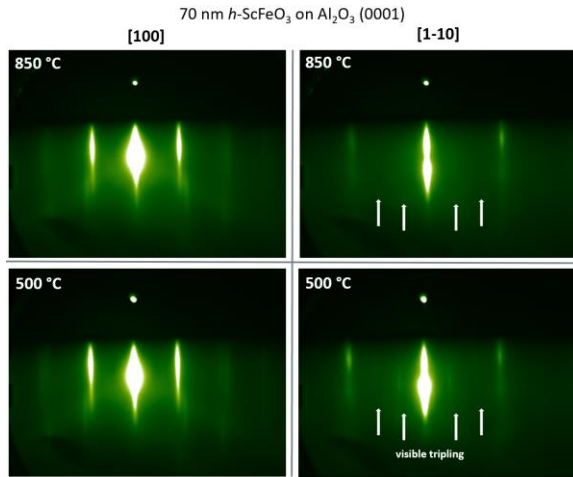
Figure 1. RHEED patterns at the [100] and $[1\bar{1}0]$ azimuths of 70 nm h-ScFeO$_3$ film on Al$_2$O$_3$ (0001) at growth temperature of 850 °C and after cooling to a temperature of 500 °C.

After the samples were fully cooled down and removed from MBE chamber, they were immediately analyzed using XRR and XRD to determine their thickness and phase purity, respectively. Samples that showed promising RHEED patterns displayed XRD patterns with no visible impurity peaks at thicknesses up to 70 nm (Fig. 2). At thicknesses higher than 70 nm, impurity peaks, such as the bixbyite form of ScFeO$_3$ (Fig. 2), were present in the XRD even if they were not visible on the RHEED images.
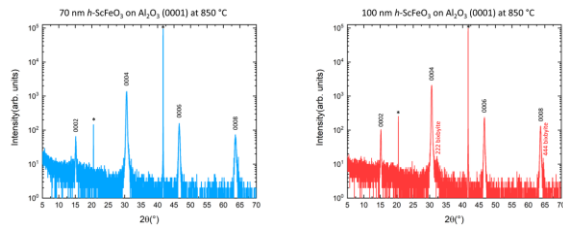
Figure 2. X-ray diffraction of 70 nm (left) and 100 nm (right) h-ScFeO$_3$ films grown at same substrate temperature.

The pure-phase 70 nm h-ScFeO$_3$ was then further analyzed using RSM and rocking curves to determine the overall crystallinity of the film. The compactness of the h-ScFeO$_3$ point on the RSM indicates good crystallinity (Fig. 2a), and the presence of a narrow

inner peak in the rocking curve data provided further support (Fig. 2b).
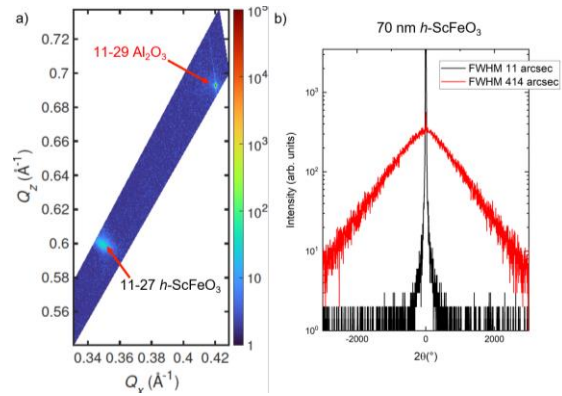
Figure 3. a) Reciprocal space mapping of 70 nm h-ScFeO$_3$ on Al$_2$O$_3$ (0001). b) Rocking curve analysis of 70 nm h-ScFeO$_3$ at (0004) peak.

Lastly, AFM analysis showed that the 70 nm h-ScFeO$_3$ had a relatively smooth surface topography, with a RSM of ~580 pm with no visible surface impurities.

Conclusions

Through MBE, h-ScFeO$_3$ was successfully epitaxially stabilized on Al$_2$O$_3$ (0001). Using both in-situ and ex-situ characterization methods, the films were confirmed to be pure-phase, crystalline, lacking impurities, and smooth. At present, films of up to 70 nm can be deposited before impurities begin to form. To determine if these films exhibit multiferroic properties at Néel temperatures greater than previously reported, further magnetic analysis will be conducted in the future.

Acknowledgements

References

[1] S. M. Disseler, *et al.*, *Physical Review B* **92**, 054435 (2015)
[2] J. A. Moyer, *et al.*, *APL Materials* **2**, 012106 (2014)
[3] K. Sinha, *et al.*, *Physical Review Letters* **121**, 237203 (2018)
[4] Y. Hamasaki, *et al.*, *Crystal Growth and Design* **16** (9), 5214-5222 (2016)