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The structures and positive magnetoresistance of metallic Sr_2CrWO_6 epitaxial thin film

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Abstract

Double perovskite Sr_2CrWO_6 films have been prepared on $SrTiO_3$ (111) substrates by pulsed laser deposition in high vacuum (10^{-5} Pa). X-ray diffraction patterns indicate that the films are (111)-oriented. Both atomic force microscopy (AFM) and cross-section transmission electron microscopy (TEM) images prove that the films have very smooth surfaces. Detailed microstructures given by high resolution transmission electron microscopy (HRTEM) further confirm that the films are epitaxial with sharp and coherent substrate/film interface. Well saturated magnetization–magnetic field hysteresis loop is observed with the saturation magnetization of 1.2 μ_B/formula unit at 10 K. The films show metallic transport behavior and large positive magnetoresistance (~180% at 10 K). The structure–property relationship is discussed in detail.

Keywords: A. Films; Double perovskite; Microstructure; Metallic; Positive magnetoresistance

1. Introduction

Double perovskites show rich physics and potential applications in spintronics. Sr_2FeMoO_6 (SFMO), which is a typical example of double perovskite with extremely high Curie temperature of 415 K, has half-metallic nature and low field magnetoresistive (LFMR) effect even at room temperature, and has been well studied [1]. In SFMO, the Fe^{3+} ($3d^5$, $S=5/2$) antiferromagnetically couples with Mo^{5+} ($4d^1$, $S=1/2$), resulting in an ideal net magnetization of 4 μ_B/formula unit (f.u.). Beside Fe-based double perovskites, Cr-based double perovskites also exhibit half-metallic nature [2–4], and generally have relatively higher Curie temperature [4–10]. A key difference between Cr-based and Fe-based double perovskites is that in Fe (3d t_{2g}, e_g) the majority spin band is fully occupied whereas in Cr (3d, t_{2g}) it is partially filled. Therefore, Cr-based double perovskites are also of particular interests and importance from both science and applications and are worthy of investigating. As an example of Cr-based double perovskites, ferrimagnetic Sr_2CrWO_6 (SCWO) has high Curie temperature about 460 K. The antiferromagnetical coupling between Cr^{3+} ($3d^3$, $S=3/2$) and W^{5+} ($5d^1$, $S=1/2$) leads to an ideal net magnetization of 2 μ_B/f.u. [2–4]. Compared with wide investigations on Fe-based SFMO, reports on SCWO are relatively rare.

In addition, high quality epitaxial thin films are important for investigating the intrinsic properties and even tune properties of materials. As we know, it is relatively difficult to prepare high quality metallic SFMO thin films, actually, atomically flat metallic SFMO films can only be fabricated under reducing atmosphere at higher temperature (>850 °C) [11], otherwise, if SFMO films are prepared under high vacuum or other partial gases like N_2 or O_2, bad film surfaces, semiconductor behaviors, and second phases are generally formed [12,13]. However, SCWO films have considerably easier preparation process. For example, atomically flat epitaxial films can be grown at a relatively lower deposition temperature under inert atmosphere or even mixed gases of Ar and O_2 [5,7,14]. Although SCWO films can be prepared under Ar/O_2 mixed gases and other inert gases, such process

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must be precisely controlled in a very limited window, as critical growing requirements for SFMO films [15]. To further optimize the preparation process of SCWO films, it is interesting to investigate the structure and properties of SCWO films under high vacuum. On the other hand, it is noted for double perovskite materials, if pseudocubic/cubic structure is adopted, the B and B′ cations show a natural superlattice structure along $[111]_c$, that means investigations on (111) SCWO thin films are interesting. However, very few literatures focus on (111)-oriented or epitaxial SCWO thin films.

Based on the above descriptions, in this paper, we prepared SCWO films on (111) $SrTiO_3$ (STO) substrates by pulsed laser deposition (PLD) under high vacuum (10^{-5} Pa). The films show atomically flat surface, sharp and coherent substrate/film interface, and especially, metallic electric behavior and large positive magnetoresistance.

2. Experimental

The stoichiometric SCWO ceramics used as PLD target was synthesized by solid state reaction with starting materials of $SrCO_3$, Cr_2O_3, and WO_3, the details can be found elsewhere [16]. In our experiments, the PLD processes were performed by using a 248 nm KrF excimer laser, the substrate temperature was 800 °C, the laser repetition rate was 2 Hz, the laser energy density was 1.2 J/cm^2, and the pressure was 10^{-5} Pa. After deposition, the films were *in situ* annealed in chamber for 10 min.

The structures of the films were investigated by X-ray diffraction (XRD, Rigaku Ultima III), atomic force microscopy (AFM, Cypher), and transmission electron microscopy (TEM, FEI Tecnai F20). The cross-section sample for TEM was prepared by ion milling with 3.2–4.5 keV Ar^+ ions for a few hours after mechanical thinning. The magnetic and transport properties were measured by using a superconductor quantum interference device (SQUID, Quantum Design, MPMS XL-7) and a physical property measurement system (PPMS Quantum Design, 2001NUGC).

3. Results and discussion

In bulk form, SCWO has the space group of *Fm*3*m* with lattice parameter of $a=b=c=0.782$ nm [6], whereas STO has the space group of *Pm*3*m* with lattice parameter of $a=b=c=0.390$ nm [17]. The lattice mismatch is 0.26%. However, according to the XRD pattern shown in Fig. 1, it is clear that the diffraction peak from SCWO $(222)_{pc}$, shown as the shoulder indexed by the arrow, is almost emerged into that from STO (111). This observation indicates that the SCWO films are well strained and the films have high quality. The strain films can be attributed to the substrate effect, which produces pressure strain in SCWO films, and such strain cannot be relaxed within 30 nm thickness. Additionally, it should be emphasized that no superstructure peak can be detected in the XRD pattern, this means the disorder of Cr/W, which is attributable to that the very close ionic radii of Cr and W cations can result in a very small gain of structural energy by ionic order [14].

Fig. 2 shows the typical surface morphology recorded by AFM. Clearly, the films have very smooth surface without any observable cracks or voids in the scanned range (3 μm × 3 μm). The smooth surface is comparative to that of other reported high quality SCWO films [14].

The cross-sectional morphology of the films is measured by scanning transmission electron microscopy (STEM), the typical low magnification STEM image is shown in Fig. 3(a). Again, as can see, the films have very flat surfaces with the thickness of 30 nm. From this high angle annular dark filed image, which provides *Z* (atomic number) contrast, the sharp and coherent interface between the SCWO films and the STO substrates can be seen clearly, again indicating the high quality of the films. Fig. 3(b) shows the high resolution transmission electron microscopy (HRTEM) image of the films taken from $[1\bar{1}0]$axis. The sharp substrate/film interface in atomic scale is indicated by the black arrow. The atoms are coherently arranged across the interface, indicating that the film is not only well epitaxially fabricated on the substrate, but also well strained, which is consistent with the XRD data. Some scattered defects like dislocations are observed as the black holes (the absent of cations) in the enlarged top-left inset. The selected area electron diffraction (SAED) pattern taken from $[1\bar{1}0]$ axis is shown in the bottom-right inset of Fig. 3(b).

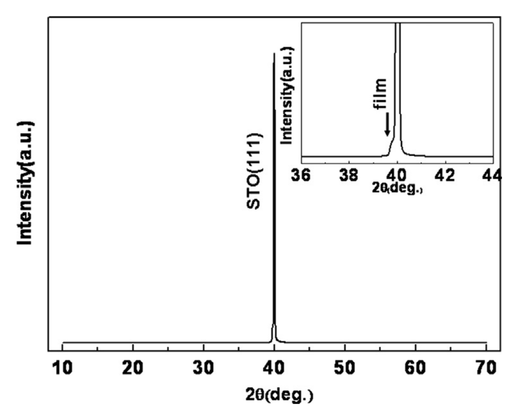

Fig. 1. X-ray diffraction pattern of the Sr_2CrWO_6 film grown on (111) $SrTiO_3$ substrate.

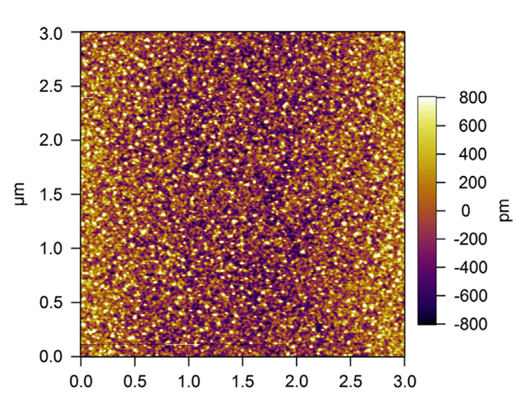

Fig. 2. Typical atomic force microscope image of the Sr_2CrWO_6 film grown on (111) $SrTiO_3$ substrate.