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Ceramics International 39 (2013) 9305–9308

CERAMICS INTERNATIONAL

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The structures and positive magnetoresistance of metallic Sr_2CrWO_6 epitaxial thin film

Wei-jing Ji[a], Jie Xu[a], Long Jiao[a], Jin-Feng Wang[a], Zheng-Bin Gu[a], Y.B. Chen[b], Jian Zhou[a], Shu-Hua Yao[a], Shan-Tao Zhang[a,*]

[a]National Laboratory of Solid State Microstructure and Department of Materials Science and Engineering, Nanjing University, Nanjing 210093, China

[b]National Laboratory of Solid State Microstructure and Department of Physics, Nanjing University, Nanjing 210093, China

Received 11 April 2013; received in revised form 13 May 2013; accepted 15 May 2013
Available online 21 May 2013

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

*Corresponding author. Tel.: +86 25 83594317; fax: +86 25 83595535.
E-mail address: stzhang@nju.edu.cn (S.-T. Zhang).

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http://dx.doi.org/10.1016/j.ceramint.2013.05.045

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 *Fm3m* with lattice parameter of $a=b=c=0.782$ nm [6], whereas STO has the space group of *Pm3m* 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).

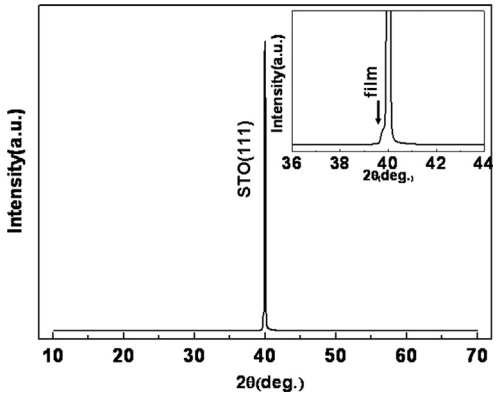

Fig. 1. X-ray diffraction pattern of the Sr_2CrWO_6 film grown on (111) $SrTiO_3$ substrate.

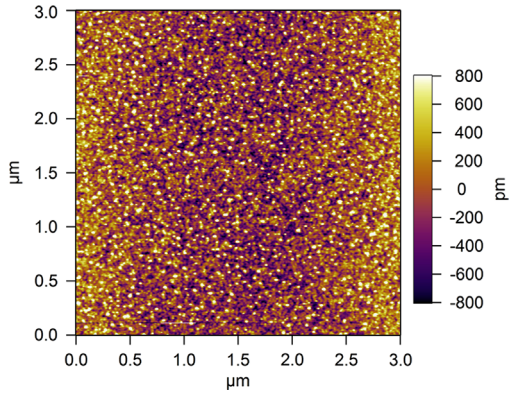

Fig. 2. Typical atomic force microscope image of the Sr_2CrWO_6 film grown on (111) $SrTiO_3$ substrate.

The (111) superlattice diffraction spots arising from Cr/W ordering cannot be observed, consistent with the XRD results.

Magnetization–magnetic field (*M–H*) hysteresis loops for the films at 10 K and room temperature (300 K) are presented in Fig. 4. The locally enlarged *M–H* curves are shown as the inset. The hysteresis of the curves indicates the ferrimagnetic nature of the SCWO films. The saturation magnetization (*Ms*) and the remnant magnetization (*Mr*) are 1.2 μ_B/f.u. and 0.30 μ_B/f.u., respectively, at 10 K. This value is comparable with other metallic SCWO films grown under Ar/O_2 mixed gases or pure Ar gas [5,7].

It is noted the saturation magnetization value (1.2 μ_B/f.u.) is lower than the theoretical value (2.0 μ_B/f.u.). We believe this may be resulted from the oxygen vacancy which is formed during the growing process in a high vacuum, as well as the absence of Cr/W ordering, as explained as follows: on the one hand, the significantly detrimental effects of oxygen vacancy on macroscopic properties have already been confirmed and well studied [18–20]. As the bridge for the magnetic exchange interactions, oxygen plays an important role in the magnetic behaviors. So it is generally believed that the oxygen vacancy is one of the major factors for the reduction of the *Ms* since it can directly weaken the exchange interactions between B and B′ cations by breaking the bridge. Additionally, oxygen vacancy can also lead to lattice distortion, so that the bond length and bond angle change from the ideal settings, this may further weaken the magnetic interaction and thus reduce the saturation magnetization and the Curie temperature. On the other hand, the absence of Cr/W ordering may also suppress the ferromagnetism by forming antiferromagnetic patches [5]. However, in SCWO films, the B-site ordering effects on ferromagnetism may not be as clear as that in SFMO films, actually contrary observations are reported [5,14].

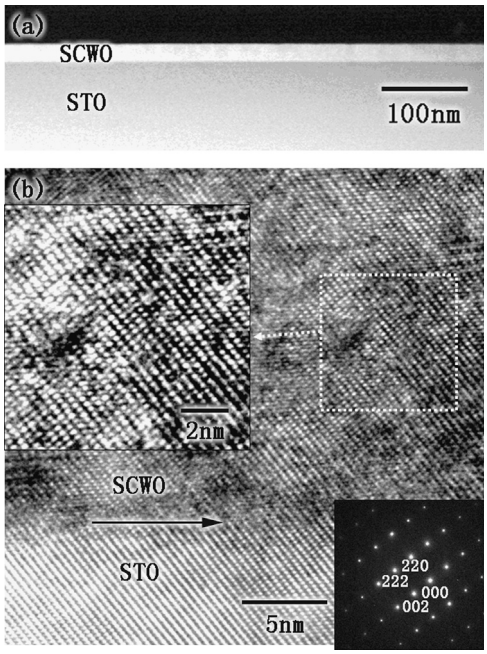

Fig. 3. (a) Low magnification scanning transmission electron microscopy image and high resolution transmission electron microscopy image of the Sr_2CrWO_6 films. The corresponding enlargement of the image and the selected area electron diffraction pattern are shown as the insets of (b).

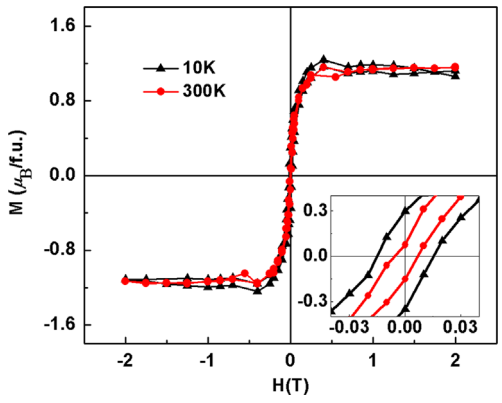

Fig. 4. Magnetization hysteresis loops measured both at 10 K and room temperature.

Fig. 5(a) shows the temperature dependent resistivity of the films. In the whole measuring temperature range, the resistivity increases with increasing temperature, indicating a typical metallic behavior. The inset shows a linear relationship between the resistivity and the temperature in the temperature range from 200 K to 400 K, which further illuminates the metallic nature. It is noted that the metallic SCWO films can also be obtained under Ar/O_2 mixed gases or pure Ar gas [5,7].

Fig. 5(b) plots the temperature dependent magnetoresistance (MR), which is defined as $MR(\%) = [R(H) - R(0)]/R(0) \times 100\%$,

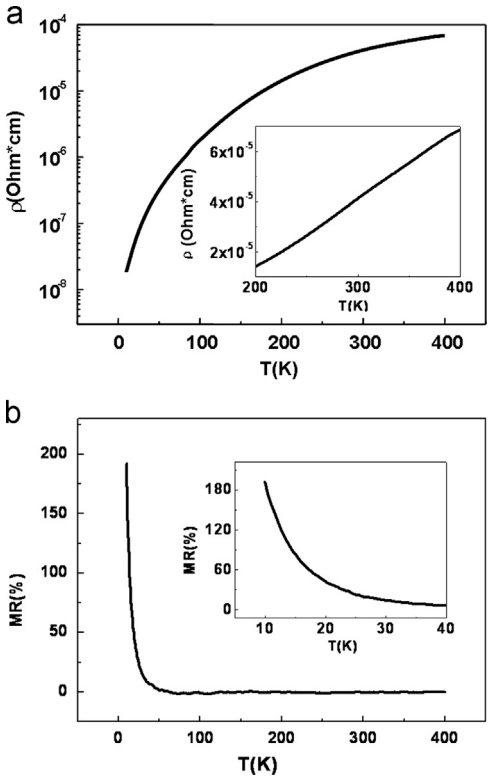

Fig. 5. (a) The temperature dependent resistivity of the film, the inset shows the partially enlarged figure within a temperature range from 200 K to 400 K. (b) The temperature dependent MR, the partially enlarged figure is shown as the inset.

where $R(H)$ and $R(0)$ are the measured resistance with an applied magnetic field of 2 T and without field, respectively. As can be seen, the films exhibit positive MR in the whole measured temperature range, which is the results of metallic behavior of the films and consistent with other reports on metallic SCWO thin films [7]. Especially, at low temperature, the positive MR is extremely large. For example, the MR reaches the value of ~180% at 10 K, as shown in the inset of Fig. 5(b). Such value is considerably larger than that in other reported metallic SCWO films [7] and metallic Sr_2FeMoO_6 thin films [21]. We believe the metallic conductive mechanism, indicated by the low resistivity, should be responsible for the large positive MR.

4. Conclusions

(111)-epitaxial SCWO thin films have been prepared on (111) STO substrates by PLD under high vacuum (10^{-5} Pa). Structure measurements by XRD, AFM and TEM show the films are well strained with smooth surface and sharp, coherent interface. The metallic behavior, magnetic property and extremely large positive magnetoresistance of the films are related with the oxygen vacancy. Oxygen vacancy can decrease magnetization by directly weakening the exchange interactions between Cr and W cations and by changing the bonding lengths and bonding angles.

Acknowledgment

This work was supported by the State Key Program for Basic Research of China (2013CB632900 and 2013CB632702), the National Nature Science Foundation of China (11174127, 11134006, and 51032003), the Doctoral Fund of Ministry of Education of China (20110091110014).

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