Surface topography and electrical properties in Sr_2FeMoO_6 films studied at cryogenic temperatures

IOP Conf. Series: Journal of Physics: Conf. Series **969** (2018) 012107 doi:10.1088/1742-6596/969/1/012107

Surface topography and electrical properties in Sr_2FeMoO_6 films studied at cryogenic temperatures

I. Angervo[1,2], M. Saloaro[1], J. Mäkelä[2,3], J. -P. Lehtiö[3], H. Huhtinen[1] and P. Paturi[1]

[1] Wihuri Physical Laboratory, Department of Physics and Astronomy, FI-20014 University of Turku, Finland
[2] University of Turku Graduate School (UTUGS), University of Turku, FI-20014 Turku, Finland
[3] Materials Research Laboratory, Department of Physics and Astronomy, FI-20014 University of Turku, Finland

E-mail: ijange@utu.fi

Abstract. Pulsed laser deposited Sr_2FeMoO_6 thin films were investigated for the first time with scanning tunneling microscopy and spectroscopy. The results confirm atomic scale layer growth, with step-terrace structure corresponding to a single lattice cell scale. The spectroscopy research reveals a distribution of local electrical properties linked to structural deformation in the initial thin film layers at the film substrate interface. Significant hole structure giving rise to electrically distinctive regions in thinner film also seems to set a thickness limit for the thinnest films to be used in applications.

1. Introduction

Complex magnetic oxide material candidates, including magnetoresistive double perovskite Sr_2FeMoO_6 (SFMO), have risen to challenge the dominance of semiconductor based electronics, which is already close to its physical limits in size. In order to understand the physical phenomena in these substances enthusiastic research has taken place. Investigations of electrical properties have been previously conducted mainly by using techniques, which give a result over the entire sample, without local information. Scanning tunneling microscopy (STM) enables, not only examination of surface structure with outstanding sub-nanometer resolution, but also the electrical structure, a method known as scanning tunneling spectroscopy (STS) [1,2]. Ideally these methods provide a way to map the sample surface with atomic scale resolution and with information of the local density of states.

Magnetic and resistive properties in SFMO thin films have shown to be greatly affected for example by the substrate and film thickness, since the lattice mismatch between the film and the substrate distorts the initial layers of the film close to the film substrate interface [3–6]. Resistivity measurements have revealed a low temperature upturn, indicating semiconductive behaviour, which seems to be connected with the band structure [3, 4, 6–8]. Alterations in the band structure can be caused by lattice deformation like anti-site disorder (ASD), oxygen vacancies and strain [9–12]. In addition structural defects like dislocations could affect the transport properties [12]. In this study, we investigate the link between the surface microstructure and the local electronic structure of SFMO thin films.

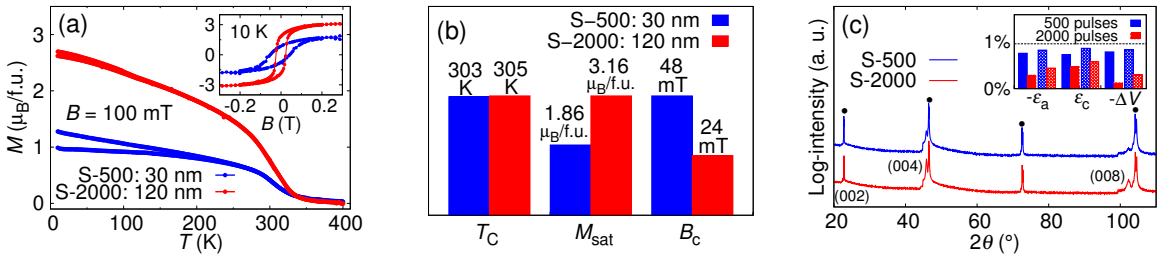

Figure 1. (a) ZFC/FC magnetization curves in 100 mT field for the 30 nm and 120 nm thick SFMO films. The inset shows the hysteresis loops at 10 K for the same samples. (b) The comparison of the main magnetic properties between the 30 nm and 120 nm thick SFMO films. (c) $\theta - 2\theta$-scans of the SFMO films with different thicknesses. The SFMO peaks are indexed and peaks arising from the substrate are marked with black dots. The inset shows our earlier results of in-plane strain, ε_a, out-of-plane strain, ε_c, and the change in the unit cell volume, ΔV, for similar SFMO films deposited with 500 and 2000 pulses. The results from [15] are presented with solid bars and the results from [14] are presented with patterned bars.

2. Experimental details

A set of SFMO thin films was deposited on niobium doped $SrTiO_3$ (STO) single crystal substrates with pulsed laser deposition (PLD). The conductive niobium doped STO with small lattice mismatch was chosen to ensure the tunneling conductivity in the STM system along with expected good structural film quality. The deposition was carried out at 1050 °C temperature in 9 Pa Ar-atmosphere, the first film with 500 laser pulses and the second with 2000 pulses. The films fabricated with 500 and 2000 pulses are to be called S-500 and S-2000, respectively. Based on our recent analysis, 500 PLD laser pulses correspond to thin film thickness of 30 nm [13, 14]. Assuming linear growth rate, S-2000 has a thickness of 120 nm.

Phase purity and texture of the films was confirmed with $\theta-2\theta$-scans X-ray diffraction (XRD) measurements between 20° and 110° as well as with the SFMO (204)-peak ($2\theta = 57.106°$), $SrMoO_4$ (112)-peak ($2\theta = 27.68°$) and Fe 110-peak ($2\theta = 44.98°$) $\phi - \psi$-scans. XRD measurements were performed with a Philips X'Pert Pro MPD diffractometer with a Schulz goniometer. Zero field cooled (ZFC) and field cooled (FC) magnetizations were measured as a function of temperature between 10 K and 400 K, with a Quantum Design MPMS SQUID magnetometer. The FC results were used to determine the Curie temperature (T_C). Magnetic hysteresis was measured between ±500 mT, at temperatures of 10 K and 400 K.

Thin film surface topography was investigated using OMICRON Fermi SPM ultra high vacuum scanning probe microscope. The equipment was also used for tunneling spectroscopy imaging. In order to enhance the thermal stability of the system and the resolution of the results, the system was cooled using liquid nitrogen. During the STM and STS measurements the sample temperature was 84 K.

3. Sample quality monitoring

The ZFC/FC magnetization curves and the hysteresis loops of both SFMO thin films are presented in figure 1 (a). Diamagnetic background arising from the substrate and the sample holder has been removed from the hysteresis loops. The results show clear ferro−paramagnetic phase transition with T_C around 300 K. The Curie temperature was determined from the minimum of the first order derivative in FC measurement. Compared to our earlier results, the T_C is decreased around 50 K [13, 14]. Even though the Curie temperature is decreased from

our earlier samples, due to the different Ar gas flow and temperature during the deposition, the saturation magnetization obtained from the hysteresis loop of S-2000 sample is rather high. Since our previous results have shown that ASD and oxygen vacancies affect the magnetic properties of SFMO films, the observed results suggest that we have been able to reduce the amount of structural defects by using a new sample holder [15].

In addition to the saturation magnetizations, M_{sat}, the coercivity fields, B_{c}, were also determined from the hysteresis loops shown in the inset of figure 1 (a). These values are presented together with the T_{C} in figure 1 (b), which illustrates the differences in the magnetic properties between 30 nm and 120 nm thick SFMO films. Only a small difference is observed in the Curie temperature, which can be explained with the different level of substrate induced strain [15]. However, the saturation magnetization is clearly lower and the coercivity field clearly higher in the thinner S-500 film. The obvious difference in the low temperature part of the ZFC/FC curves between films shows larger magnetization deviation in S-500. These all suggest that there are more structural defects in the thinner S-500 film, which cause the domain wall formation and pinning. All in all, the values for T_{C} and M_{sat} presented here are comparable with our previous results, but still showing slightly higher M_{sat} and lower T_{C} than in general [3, 5, 6, 13].

The high quality of the films was confirmed with the X-ray diffraction measurements. The $\theta - 2\theta$-scans presented in figure 1 (c) together with the pole figures of SFMO 204-, Fe (110)- and $SrMoO_4$ (112) -peaks (not shown here) confirmed the SFMO films to be phase pure, fully textured and c-axis oriented. The inset of the figure 1 (c) is based on our earlier comprehensive XRD analysis of the similar 500 and 2000 pulses films as the S-500 and S-2000 samples in this work [14, 15]. These results are in good agreement with each other and they show that the in-plane strain, ε_{a}, out-of-plane strain, ε_{c}, and the change in the unit cell volume, ΔV, are decreased with the increasing film thickness. Therefore, we can conclude that the thicker S-2000 film is less strained and the SFMO unit cell volume is closer to the literature value compared to the thinner S-500 film.

4. Topography and tunneling spectroscopy

STM measurements were conducted before any additional measurements. The images shown in figure 2 present the STM results for S-500, (a) and (b), and S-2000, (c). Multiple STM scans were taken across the film surface to achieve stable STM signal with the best possible resolution. However, all the images showed height scales very similar with the images presented here. It is evident, according to the STM results for S-500 in figure 2 (a), that SFMO seems to prefer island-like film growth combined with single layer atomic terraces. Island-like film growth seems to give rise to hole-like structures between separate islands. The hole depths are within the limits of image height scale, from approximately 5 nm to 15 nm. As already pointed by Borges *et.al.* [16], holes could oppose a serious obstacle for tunneling type spin valves, since atomically flat surfaces are preferred. Large structural defects at the multilayer interface can for example lead to diminished exchange coupling, which will affect the properties of multilayer spin valves [17]. Since similar holes were not observed in the thicker S-2000 sample (figure 2 (c)), this suggests that thickness is one of the limiting factors considering applications. The absence of hole structures in S-2000 indicates that the growth might be modified from initial island-like growth towards layer-by-layer growth [18].

In figure 2 (b) the results reveal a clear step-terrace structure presented for S-500 and the inset shows height profile from the line indicated in the figure. Steps are divided into two groups, with height of ≈ 0.4 nm and ≈ 0.8 nm. This corresponds well with either single perovskite step or double perovskite c-parameter lattice size [19]. Atomic scale step-terraces were identified also for S-2000 from figure 2 (c). However, steps seem to include more height scales exceeding the ones seen in figure 2 (c) for S-500. Similar results, showing step terrace structure with atomically flat surface, have been reported for epitaxially grown SFMO thin films [20]. More widely, the

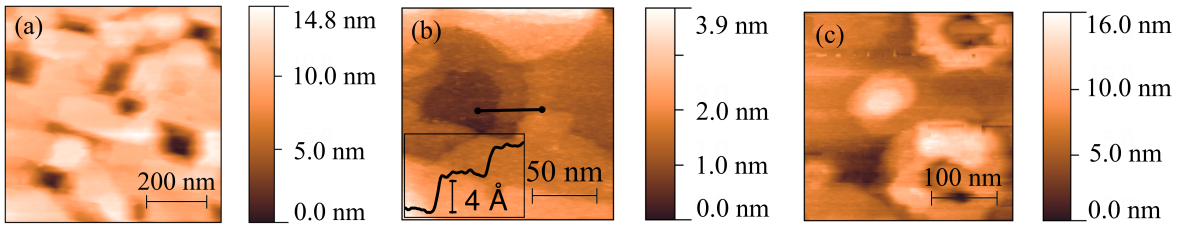

Figure 2. Surface microstructure of S-500, (a) and (b), and S-2000 SFMO thin films, (c), characterized by STM at 84 K temperature. The inset of (b) shows height profile from the region of the surface, which is indicated with black line.

terrace like structure without a clear evidence of atomically flat step size, has also been reported for SFMO thin films by various groups [14, 18, 21–23]. The atomically flat step-terrace structure provides our first evidence of atomic scale thin film growth in SFMO films and gives hope for the fabrication of SFMO spin-valves with atomically flat interface sections in multilayers.

Tunneling spectroscopy was used for local electrical characterization. STS measurements lack statistical signifigance, since STS-mapping was obtained from only single location with the best structural resolution. The SFMO film surface was scanned with STM, simultaneously mapping the surface area with scanning tunneling spectroscopy at 84 K. Figure 3 (a) presents the results obtained from STM topography, alike the results already presented in figure 2, along with STS mapping in figure 3 (b). The STS results present the $I(V)$-map corresponding to a threshold voltage of 1.0 V. Green areas, having lower current at 1.0 V, correspond well with the holes seen in STM topography. In order to prevent any of the influences from the tip instability possibly caused by too slow feedback, we analyze the results for two $(dI/dV)/\sqrt{(I/V)^2 + b^2}$ curves shown in figure 3 (c) obtained from the areas indicated in the $I(V)$-map, to see differences in the local density of states (LDOS) which is proportional to normalized conductivity. The normalization method is similar as reported in [24]. The b in $(dI/dV)/\sqrt{(I/V)^2 + b^2}$ corresponds to a small constant, in the main panel of figure 3 (c) $b = 0.003$ nA/V, chosen to diminish noise around small current values. In the inset b was set to 0 nA/V. The results reveal slight changes in normalized conductivity curves. Conductivity near the Fermi level is smaller when comparing green area in the $I(V)$-map to yellow area. The results for S-2000 did not reveal as clear connection with electrical properties and surface structure. It was also more difficult to obtain stable STS for S-2000, when for S-500 this was relatively straight forward.

According to our best knowledge, SFMO has not been studied with STS before, but few reports about STM and STS on manganites with similar properties, have been published [25–28]. Besides the atomically flat step terrace structure [25], intrinsic inhomogeneities have been identified along with alleged evidence of half-metallicity by STM and STS technique [25–27]. Wei *et.al.* concluded the peaks in the conductance data to arise from spin-polarized density of states [25]. Similar evidence of half-metallicity was not observed in our measurements, despite the measurements being conducted at 84 K, well below the Curie temperature (see figure 1 (a)), and despite the good structural data obtained with STM. Other reports show spatial distribution of insulating and conductive regions [26–28]. These results have been used to study the metal−insulator−transition, in the materials where it is observed. In addition lattice strain caused by the substrate material is known to influence the electric properties [28].

SFMO does not exhibit similar first order phase transition between metallic and insulating state as colossal magnetoresistive materials [29, 30]. However, the link between resistive and magnetic phenomena is close and studying local electric properties will reveal valuable information about SFMO thin films. Electric properties in SFMO are known to be influenced

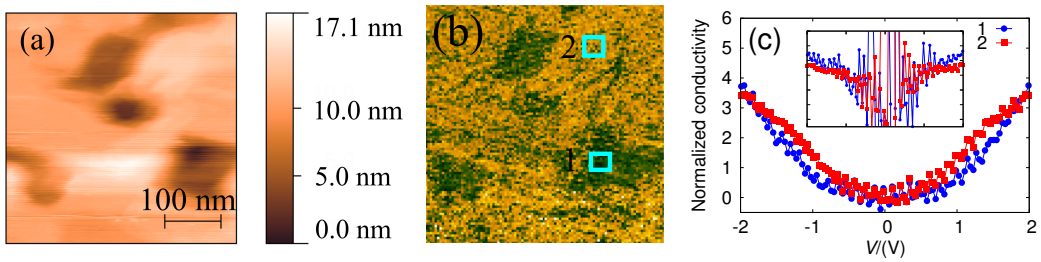

Figure 3. Surface of S-500 characterized by low temperature STM (a) along with STS $I(V)$-map (b). Aquamarine coloured squares illustrate the areas, which have been chosen to demonstrate the difference between yellow region and green region. The main panel of (c) shows an example of normalized $(dI/dV)/\sqrt{(I/V)^2+b^2}$, $b = 0.003$ nA/V (inset $b = 0$ nA/V), curves for the indicated map areas, red curve indicating the yellow region and blue the green region.

by structural deformation. This deformation is more dominant in thinner SFMO films [6, 15]. Our STM results have shown clear evidence of more significant structural deformity, in a form of hole structures. The results obtained in STS represent most likely evidence of locally diminished electrical properties, which give rise to more impaired properties measured from the entire sample. Lower conductivity around the Fermi level might suggest that energy gap in majority spin band is increased within the hole structures. This result would possibly contradict previous studies [3, 6, 11]. Therefore we believe that lower conductivity most likely arises, not from increased band gap in majority band, but from overall perishment of the density of states in both bands. Considering the height scale in STM images for S-500, the atomic layers within the hole structures are likely to be substitued with more deformed layers under more significant structural distortion and lattice strain, resulting with deviation in conductivity and in density of states. XRD measurements along with magnetic measurements support the conclusion of structural deformation in thinner film. The previous XRD results presented in the inset of figure 1 (c) for our other films, suggest that significant structural deformation is always present and the effect is more dominant in thinner films. Also dimished saturation magnetization suggests higher concentration of lattice defects, including ASD and oxygen vacancies.

Due to the samples' exposure to ambient air, the possibility of surface contamination cannot be totally excluded in our results. However, films' uniform surface quality suggests the samples having no major contamination. The measurements were repeated after storing the samples for approximately a week in ultra high vacuum at room temperature. An interesting result was that, compared to the initial results, the surface of both SFMO thin films appeared highly irregular and similar surface structures, like in the initial low temperature measurements, were not observed. This could mean that the long term exposure to the ultra high vacuum modifies the initial atomic layers, possibly by deoxidation. This could explain why stable STS for S-2000 was more difficult to obtain at the beginning of the measurements. Previous investigation has shown that vacuum annealing at 650 °C increases T_C by reducing the oxygen content in the SFMO [15]. Sample contamination is insignificant considering the whole sample, based on sample quality monitoring, but could disturb the STM and STS measurements on the surface. Diminished tip quality could also play a role with worse results and possible sample contamination requires further investigation, but should be considered as a possibility [27].

Despite the sub-nanometer resolution in out-of-plane surface structure revealing atomic step-terrace structure, we have yet to demonstrate atomic-scale in-plane resolution. This proceeding would enable us to directly identify structural lattice defects, including strain, ASD and oxygen vacancies, combined with electrical analysis. Therefore, we will focus our following research,

regarding the SFMO thin film investigation with scanning tunneling spectroscopy, to obtain greater stability in our system.

5. Conclusions

High quality SFMO films were fabricated using PLD and studied for the first time with low temperature scanning tunneling spectroscopy to obtain local information on electric properties accompanied by structural surface characters. The results reveal clear step-terrace structure on thin film surface indicating atomic level thin level film growth, which give hope for the fabrication atomically flat interface sections in multilayer structures. In addition, it was observed that thinner films had significant hole structure accompanied by the atomic steps. The holes could also be identified with STS from the rest of the film due to their electrical properties. The similar hole structure was not observed in thicker film, which indicates a limit for the minimum thickness for thin film, if used in spin-valves.

6. Acknowledgements

Jenny and Antti Wihuri foundation and University of Turku Graduate School are acknowledged for financial support.

References

[1] Binnig G and Rohrer H 1983 *Surf. Sci* **126** 236
[2] Feenstra R M 1994 *Surf. Sci* **299** 965
[3] Saloaro M, Majumdar S, Huhtinen H and Paturi P 2012 *J. Phys. Cond. Mat.* **24** 366003
[4] Saloaro M, Majumdar S, Huhtinen H and Paturi P 2013 *EPJ Web of Conferences* **40** 15012
[5] Saloaro M, Deniz H, Huhtinen H, Palonen H, Majumdar S and Paturi P 2015 *J. Phys. Cond. Mat.* **27** 386001
[6] Angervo I, Saloaro M, Palonen H, Majumdar S, Huhtinen H and Paturi P 2015 *20th International Conference on Magnetism* **75** 1011
[7] Venimadhav A, Sher F, Attfield J P and Blamire M G 2004 *J. Magn. and Magn. Mater.* **269** 101
[8] Westerburg W, Reisinger D and Jakob G 2000 *Phys. Rev. B* **62** R767
[9] Stoeffler D and Colis S 2005 *J. Phys. Cond. Mat.* **17** 6415
[10] Stoeffler D and Colis S 2005 *J. Magn. and Magn. Mater.* **290-291** 400
[11] Hoffmann M, Antonov V N, Bekenov L V, Kokko K, Hergert W and Ernst A 2015 *arXiv:1504.02629*
[12] Fix T, Stoeffler D, Colis S, Ullhaq C, Versini G, Vola J P, Huber F and Dinia A 2005 *J. Appl. Phys.* **98** 023712
[13] Angervo I, Saloaro M, Tikkanen J, Huhtinen H and Paturi P 2017 *Appl. Surf. Sci.* **396** 754
[14] Angervo I, Saloaro M, , Huhtinen H and Paturi P 2017 *Appl. Surf. Sci.* **422** 682
[15] Saloaro M, Hoffmann M, Adeagbo W A, Granroth S, Deniz H, Palonen H, Huhtinen H, Majumdar S, Laukkanen P, Hergert W, Ernst A and Paturi P 2016 *ACS Appl. Mater. Interfaces* **8** 20440
[16] Borges R P, Lhostis S, Bari M A, Versluijs J J, Lunney J G, Coey J M D, Besse M and Contour J P 2003 *Thin Solid Films* **429** 5
[17] Coey J M D 2010 *Magnetism and magnetic materials* (Cambridge University Press)
[18] Jalili H, Heinig N F and Leung K T 2010 *J. Chem. Phys* **132** 204701
[19] Nakamura S and Oikawa K 2003 *J. Phys. Soc. Jpn.* **72** 3123
[20] Manako T, Izumi M, Konishi Y, Kobayashi K I, Kawasaki M and Tokura Y 1999 *Appl. Phys. Lett.* **74** 2215
[21] Song J H, Park J H and Jeong Y H 2005 *J. Appl. Phys.* **97** 46105–1
[22] Venimadhav A, Vickers M E and Blamire M G 2004 *Solid State Commun.* **130** 631
[23] Deniz H, Preziosi D, Alexe M, Hesse D, Eisenschmidt C, Schmidt G and Pintilie L 2015 *J. Mater. Sci.* **50** 3131
[24] Prietsch M, Samsavar A and Ludeke R 1991 *Phys. Rev. B* **43** 850
[25] Wei J Y T, Yeh N C and Vasquez R P 1997 *Phys. Rev. Lett.* **79** 5150
[26] Fäth M, Freisem S, Menovsky A A, Tomioka Y, Aarts J and Mydosh J A 1999 *Science* **285** 1540
[27] Becker T, Streng C, Luo Y, Moshnyaga V, Damaschke B, Shannon N and Samwer K 2002 *Phys. Rev. Lett.* **89** 23
[28] Okawa N, Tanaka H, Akiyama R, Matsumoto T and Kawai T 2000 *Solid.. State. Commun.* **114** 601
[29] Salamon M B and Jaime M 2001 *Rev. Mod. Phys* **73** 583
[30] Dagotto E, Hotta T and Moreo A 2001 *Phys. Rep.* **344** 1