P-02

Extended Abstract

LEEM and XPEEM studies of electroforming process in Fe-doped $SrTiO_3$ epitaxial films

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Keywords: $SrTiO_3$, Fe doping, thin film, LEEM, XPEEM, valence band

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In the last decade the resistive switching effect occurring mainly in oxide materials was intensively study [1]. The strontium titanate (STO) is a potential candidate for future applications in random access memories due to the interesting properties related to resistive switching [2].

The electrical properties of STO can be tuned by doping. It was found that doping with iron or niobium influences the STO resistive switching properties [3].

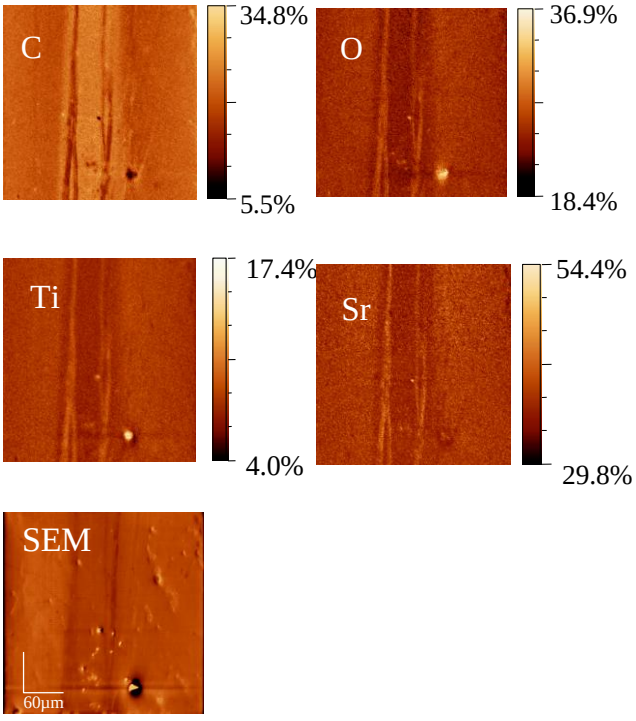

Figure 1. The AES chemical distribution maps for carbon, oxygen, titanium and strontium of the contact area with the electrode for the Fe doped STO film. The SEM image of the analysed area was added.

In our earlier work the ultra thin epitaxial films of strontium titanate doped with 1%, 2% and 5% (STO:Fe) iron were studied with the use of synchrotron radiation. X-ray absorption spectroscopy (XAS) results indicate existence of two Fe oxidation states 2+ and 3+ in the films independent of Fe concentration. Moreover, Fe 2+ appeared to be situated mostly on the surface of films [4]. The Fe 2+ and 3+ ions in STO:Fe films were found to give different contributions (the partial density of states - PDOS) to the structure of valence band through the resonant photoemission (RESPE) study [5]. An increased density of states in the energy-gap region for iron doped films was found in all performed PES studies [5].

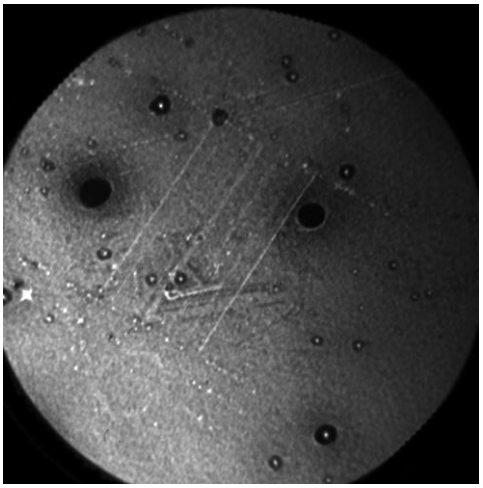

Figure 2. The LEEM image of 2% Fe doped STO film recorded from the area with the diameter of 20 micrometers. The white parallel lines are the effect of earlier contact with the biased AFM tip.

The electroforming process is usually necessary prior to attain stable switching. However, the origin of this behaviour is not clear. In order to get insight to this phenomenon we tested modification of the Fe:STO thin films surface properties after treatment with the biased electrode. Two kinds of experiment were performed – both took place in the UHV chambers.

First was realised by application of aluminium foil electrode with a positive bias of +10 V to Fe:STO film. The electro-modified surface was examined in-situ by RESPE and XAS methods. The results showed a slight decrease of the density of states in the band-gap region originating from the +2 Fe ions [6]. A similar effect was observed from the XAS studies during heating of films at elevated temperature [4]. It was found that the electroforming process does not influence the shape of the Fe PDOS for 3+ state but changes the Fe PDOS +2 contribution. The influence of the atmosphere on the electroformed sites was studied by the AES method. The maps, presented in Figure 1 show the chemical distribution of carbon, oxygen, titanium and strontium in the region which was treated by the biased aluminum foil electrode. The maps show strong chemical modification of the film surface as the effect of contact with the positively biased electrode. The effect was stable despite the stay of the sample in air for a few days. It shows that electroformation is not only related with the forced depletion of oxygen but leads to chemical modification of the surface region.

To verify the results obtained in our previous studies, the LEEM (Low-energy Electron Microscopy) [7] and XPEEM (X-ray Photoemission Electron Microscopy) [7] investigations of the 2% Fe doped STO film were performed. The sample was electroformed in UHV by the conducting AFM tip biased with the voltage up to 10 V. Then it was transferred in air to the LEEM chamber. The scanned modified area was 8x8 micrometers.

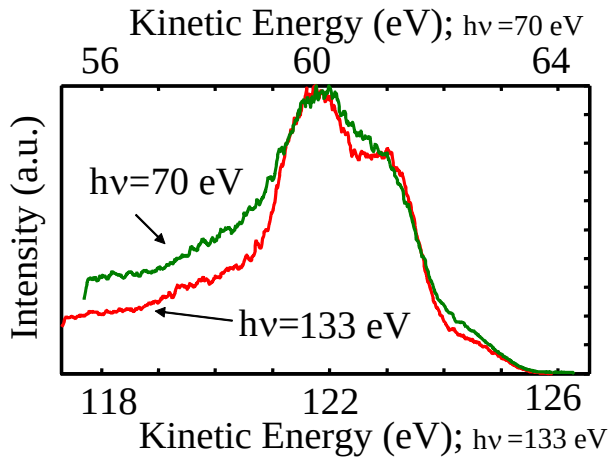

Figure 3. The photoemission spectra obtained with two various photon energy from electro-modified by AFM tip area.

The LEEM study presented in Figure 2 showed clear changes in contrast within the modified area. The lighter parallel lines originate from the contact with the biased AFM tip. The lines consisted of many small dots, which probably can be assigned to the edges of dislocations. It was found that density of dislocations in the STO films deposited by the PLD method is much higher than in the single crystals of STO, for which equals about 10^9 per cm^2 [2]. On the other hand, the electron diffraction (LEED) images showed no structural difference between the virgin and electroformed area. The origin of the contrast visible in LEEM is probably related with the local changes of the work function, and consequently various adsorption of contaminations from air mainly those containing carbon.

The XPEEM spectra from the electroformed area obtained at photon energy of 133 eV and 70 eV and showing the valence band region are presented in Figure 3. The general shape of the valence band is in agreement with the spectra obtained for the macroscopic area including the in-gap region [8].

The various shape of the spectra obtained for two photon energies can be explained by different photoionization cross-section coefficients.

After heating the sample in situ to about 120 ^{0}C the LEEM contrast disappeared but no changes in the XPEEM images were detected.

In Figure 4 the valence band spectra recorded from the electroformed and virgin area are shown. Additionally, the spectrum obtained after annealing was added. A slightly lower intensity of photoemission was found at binding energy of about 2 eV for the not modified area. A small increase of photoemission was found at about 3 eV after heating.

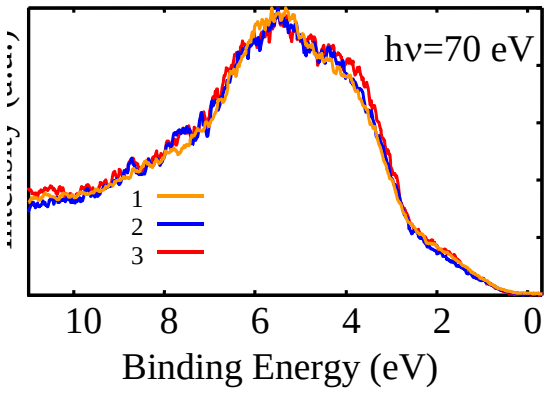

Figure 4. The valence band spectra recorded for: 1 – area electroformed by the biased AFM tip, 2 – outside electroformed area, 3 – after annealing at 120 °C.

Our studies showed that electroforming leads to a significant modification of the surface region of the STO films doped with Fe. The positive bias applied to the surface causes the movement of oxygen ions along dislocations towards to the surface. The chemical change is stable even after reoxidation of the films in air.

Acknowledgments: This work was supported by the NCBiR within the project NCBiR/ERA-NET-MATERA/3/2009.

[1] R. Waser, R. Dittmann, G. Staikov, K. Szot, *Adv. Mater.* **21** (2009) 2632.
[2] K. Szot, W. Speier, G. Bihlmayer and R. Waser, *Nature Materials* **5** (2006) 312.
[3] T. Menke, R. Dittmann, P. Meuffels, K. Szot, and R. Waser, *J. Appl. Phys.* **106** (2009) 114507; R. Muenstermann, R. Dittmann, K. Szot, Sh. Mi, Ch. L. Jia, P. Meuffels and R.Waser *Appl. Phys. Let.* **93** (2008) 023110.
[4] A. Köhl, D. Kajewski, J. Kubacki, C. Lenser, R. Dittmann, P. Meuffels, K. Szot, R. Waser, and J. Szade *Phys. Chem. Chem. Phys.* **15** (2013) 8311.
[5] J. Szade, K. Szot, M. Kulpa, J. Kubacki, Ch. Lenser, R. Dittman, R. Waser, *PhaseTransitions* **84** (2011) 489; J. Szade, D. Kajewski, J. Kubacki submitted to *Phys. Chem. Chem. Phys.*
[6] J. Kubacki, D. Kajewski, A. Koehl, Ch. Lenser, R. Dittmann and J. Szade, *X- Ray Spectr.* **44** (2015) 339.
[7] L. H. Veneklasen *Rev. Sci. Instrum.* **63** (1992) 5513.
[8] J. Kubacki, D. Kajewski, A. Koehl, Ch. Lenser, R. Ditmann and J. Szade, *Syn. Rad. Nat. Sci.* **14** (2015) 23.