IOP Publishing Journal of Physics: Conference Series **59** (2007) 50–53
doi:10.1088/1742-6596/59/1/011 Eighth International Conference on Laser Ablation

Excimer laser annealing of perovskite thin films: morphology and gas-sensor properties

X Du[1], J Tunney[1], M Post[1] and J J Dubowski[2]

[1] National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada
[2] Université de Sherbrooke, Sherbrooke, Québec J1K 2R1, Canada

E-mail: xiaomei.du@nrc-cnrc.gc.ca

Abstract. Pulsed laser annealing was used to modify surface morphology and to enhance crystallization of amorphous films of the *p*-type perovskite $SrFe_yCo_{1-y}O_{2.5+x}$ (y=0.5). The films were prepared by the pulsed laser deposition technique on sapphire substrates. Both film deposition and film annealing was done using a KrF excimer laser (wavelength = 248 nm). The effects of laser energy and pulse number on film morphology, structure and gas-sensing properties were investigated. An amorphous film did not show any sensor response to oxygen composition changes, while the same film after 80 pulses of annealing at 100mJ/cm^2 showed a fast response at 300°C and 400°C. In comparison to a dense crystalline film deposited at 700°C, the annealed film showed a faster response to oxygen composition changes at 300°C.

1. Introduction

The family of non-stoichiometric, substitutional perovskites, $SrFe_yCo_{1-y}O_{2.5+x}$, are *p*-type semiconductors which have been shown to exhibit promising conductometric gas sensor properties *[1, 2]*. In such sensors, changes in electrical resistance are exploited as sensor transduction signals when the sensor materials are exposed to analyte gases. The sensing properties of thin films of these materials are strongly dependent on the film chemical structure, the microstructure and morphology. When prepared by pulsed excimer laser deposition, (PLD), the film structure depends on preparation temperature, with optimum sensor functionality being found for films grown at elevated temperatures, $T > 600^{o}C$, where high levels of crystallinity and texturing are common. Low substrate temperature deposition, particularly at ambient temperature, of these films using PLD would be attractive for applications where specific device microstructure or properties of the substrate prohibit high temperature treatment. However, films deposited by PLD at these lower temperatures are amorphous and with poor sensor functionality. It has been shown *[3]* that increased crystallinity enhances sensor response characteristics. Recent studies showed that pulsed laser annealing (PLA) is an attractive tool to crystallize amorphous films *[4-8]*. With this approach, the localised and rapid heating of the film surface and sub-surface regions facilitates fabrication of films with structural and chemical characteristics that otherwise would require their deposition at temperatures exceeding 600 ^{o}C. A previous study has demonstrated that laser annealing can be used to crystallize amorphous $SrFe_yCo_{1-y}O_{2.5+x}$ films *[8]*. In the present work, the effects of PLA on the morphology, structure and gas sensing properties of amorphous thin films of $SrFe_{0.5}Co_{0.5}O_{2.5+x}$ are presented.

2. Experimental

The $SrFe_{0.5}Co_{0.5}O_{2.5+x}$ thin films were deposited by the PLD technique on $(1\bar{1}02)$ sapphire using a Lambda-Physik LPX305i excimer KrF laser operating at 248nm and with a pulse duration of about 25ns. The experimental setup has been described elsewhere *[9]*. The films were fabricated on sapphire substrates at ambient temperature, and for comparison purposes a film was also deposited onto a sapphire substrate at $T = 700^{o}C$. All depositions were carried out under an oxygen partial pressure of

100 mTorr. The films, typically 200 nm thick, were fabricated by ablating the $SrFe_{0.5}Co_{0.5}O_{2.5+x}$ target with the laser operating at 8 Hz and at an energy fluence of 1.5 J/cm^2. The average deposition rate was 10nm/min.

Laser annealing was carried out with the same KrF excimer laser operating at 2 Hz. An area of 7 x 7 mm^2 of the sample was irradiated with a flat-top beam produced by a Microlas fly-eye homogenizer. The irradiation was carried out in an ambient atmospheric environment with up to N = 160 pulses, each delivering a fluence selected within the range 5 to 100 mJ/cm^2.

The crystallinity of the $SrFe_{0.5}Co_{0.5}O_{2.5+x}$ films before and after annealing was characterized by X-Ray diffraction (XRD). All XRD measurements were performed on a Bruker D8 diffractometer using Cu-K$_\alpha$ radiation. The diffractometer was equipped for parallel beam geometry with primary and secondary double Göbel mirrors. Data was collected using a scan step size of $2\Theta = 0.02°$ with dwell time of 2 sec/step. The film morphology was characterized by scanning electron microscopy (SEM) using a Philips XL 30S FEG-SEM at an acceleration voltage of 5kV.

Gas sensor functionality was determined by *in-situ* measurement of the electrical conductivity of the films in a custom fabricated chamber and gas flow system *[1]*. The conductivity measurements of the films were taken using a two-wire method in a controlled environment where the temperature could be varied from 20°C to 500˚C and the composition of the flowing gas changed as required. The gas mixtures used were dry air (zero grade; nominally 21%O_2 in balance N_2) and a 6%O_2 mixture in balance N_2.

3 Results and discussion

3.1 Pulsed laser annealing

Figure 1 shows a series of SEM images obtained for the as-grown (20˚C) film and for the same film following irradiation with 20 pulses at different fluences increasing from 40mJ/cm^2 to 100mJ/cm^2. The surface of the as-grown film (Figure1a) is smooth and featureless; this, together with XRD data, is in concordance with a previous TEM study suggesting that films deposited at room temperature have an amorphous structure with a domain size of ~10 nm *[8]*. Following 20 pulses of irradiation at 40mJ/cm^2, the film morphology is observed to change substantially. Initially the irradiated film develops a high density of pores. With an increase in fluence, the porosity decreases, and after irradiation at100mJ/cm^2 a crystallized film was produced.

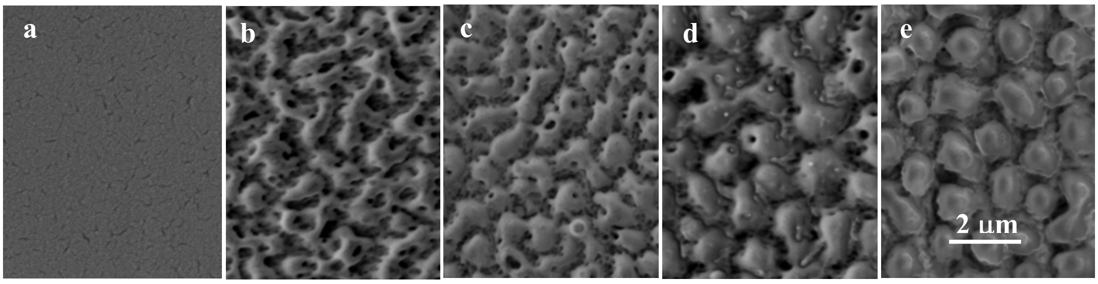

Figure 1. SEM images of the as-grown film (a) and the same film following 20 pulses irradiation at (b) 40 mJ/cm^2, (c) 60 mJ/cm^2, (d) 80mJ/cm^2 and (e) 100mJ/cm^2 at 2Hz.

In order to optimize the experimental parameters of annealing $SrFe_{0.5}Co_{0.5}O_{2.5+x}$ films, another series of measurements were conducted at a constant energy fluence of 100mJ/ cm^2 with a varying number of pulses. Figure 2 shows a series of SEM images for the same film following irradiation with the number of pulses increasing from 5 to 160. Following only 5 pulses of laser irradiation the film morphology starts to change, and after about 40 pulses the film shows pores. The previous TEM study showed that this treatment produces films with grain size of up to 30-40nm *[8]*. Generally, with an increasing number of irradiation pulses, the grain size increases and the overall film porosity decreases.

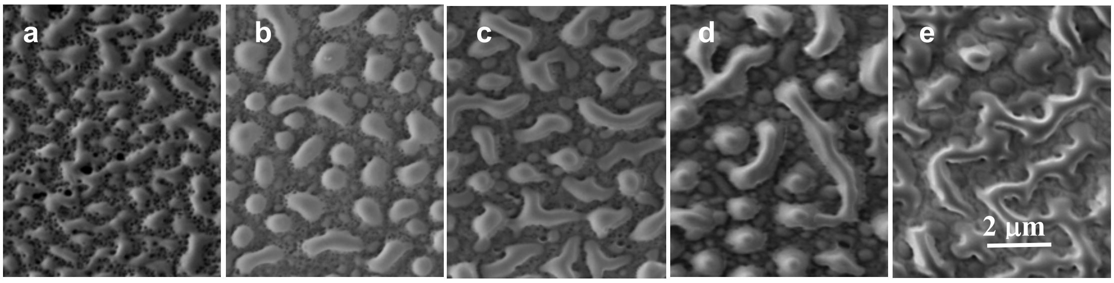

Figure 2. SEM images of a $SrFe_{0.5}Co_{0.5}O_{2.5+x}$ film deposited at ambient temperature after (a) 5, (b) 10, (c) 40, (d) 80 and (e) 160 pulses irradiation at $100mJ/cm^2$.

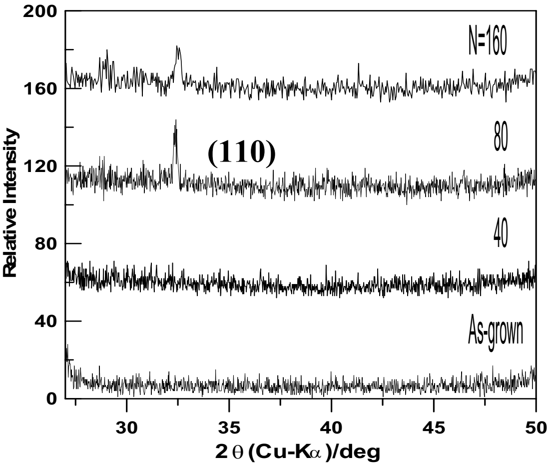

Figure 3. XRD spectra of a $SrFe_{0.5}Co_{0.5}O_{2.5+x}$ film grown at room temperature and annealed at $100mJ/cm^2$. N = number of laser pulses.

Figure 3 shows XRD patterns obtained from samples discussed in Figure 2. It can be seen that the progress of crystallization is indicated by the development of a diffraction peak at $2\Theta = 32.4^o$, {reflection (110) based on the cubic perovskite lattice which is the same as for 700˚C deposited films *[2]*} which begins to appear at around 80 pulses. However, for a higher number ($N \geq 160$) of irradiating pulses, although the crystallization is still evident with the presence of the (110) reflection, there is also a weaker XRD peak at $2\Theta \sim 28^o$. This is due to an unidentified phase, and is indicative that some decomposition or phase separation has taken place.

3.2 Sensor functionality

Measurement of sensor functionality by monitoring conductivity changes occurring on gas exposure was carried out for the as-grown film and with the same film after PLA with 80 pulses at $100mJ/cm^2$. Sensor response data (Figures 4 and 5) is presented in the form of Relative Response as defined by the ratio R(gas)/R(0): where in this case R(gas) is the resistance as measured in 6% O_2 and R(0) is the "baseline" resistance as measured in zero air (21% O_2). The as-grown film showed no gas sensing response, whereas after annealing the film displayed some degree of sensitivity to changes in oxygen composition as shown in Figure 4. Two test temperatures (300°C and 400°C) were used, and a similar response of between 7%-8% increase in resistance was observed each time for a change in oxygen composition of 21% to 6% in nitrogen. To compare the sensing ability at 300°C of the laser annealed film to a higher temperature deposited film, a 700˚C deposited film was tested with the same gas compositions, and the film response is shown in Figure 5.

This data demonstrates that at the lower test temperature of 300°C, the annealed film has a more rapid response to changing oxygen concentration than the denser film deposited at 700°C. At 300°C the latter film clearly did not reach a stable condition of conductance over the time period of the measurement. It is proposed that the faster reaction time for the annealed film is due to the higher porosity of the film surface in comparison to the 700°C film which has higher density. Among the potential mechanisms influencing the sensor response is gas diffusion into the film bulk, and the annealed film provides a high degree of porosity to enhance this process. Therefore the annealed film has better sensing properties than a high temperature deposited film. Hence, annealing amorphous films into a porous and, at least partially, crystallized form offers interesting advantages for the fabrication of a $SrFe_{0.5}Co_{0.5}O_{2.5+x}$ based oxygen sensor and its integration with substrates that do not allow the high-temperature processing.

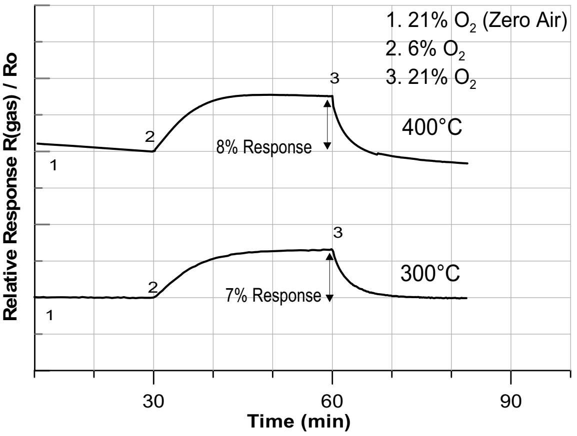

Figure 4. Sensor response of the as-grown film after PLA with 80 pulses at $100 mJ/cm^2$.

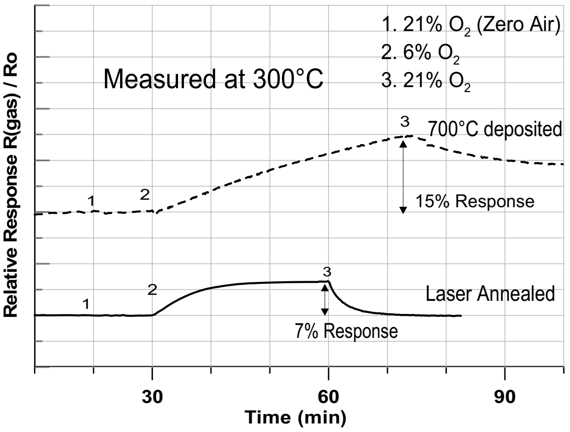

Figure 5. Sensor response of the film deposited at 700˚C and the as-grown film after PLA.

4. Conclusions

$SrFe_{0.5}Co_{0.5}O_{2.5+x}$ thin films deposited at room temperature by PLD have an amorphous structure which has no sensing ability to oxygen composition changes. Pulsed laser annealing (PLA) has been used to modify the morphology, structure and degree of crystallinity of these films. The gas sensing functionality of $SrFe_{0.5}Co_{0.5}O_{2.5+x}$ thin films deposited at room temperature has been induced by processing films at low fluence ($<100 mJ/cm^2$) using the PLA technique. The controlled evolution of the degree of porosity of the film which is possible with PLA offers a means of optimizing sensor response characteristics. The combination of film deposition at ambient temperature by PLD, together with subsequent PLA treatment, provides a route to the integration of functional sensor films with substrates which cannot withstand high temperature processing.

5. Acknowledgements

The authors thank Q. Yang for SEM imaging and M. Kunkel for assistance with sensor response measurements.

6. References

[1] Tunney J, Post M, Du X, and Yang D 2002 *J. Electrochem. Soc.* **149**, H113
[2] Tunney J, Whitfield P, Du X and Post M 2003 *Thin Solid Films* **426**, 221
[3] Sanders B, Yao J and Post M 1994 *Mat. Res. Soc. Proc.*, **343**, 463.
[4] Tomita H, Nimomiya Y, Ito A and Obara M 1995 *IEEE Laser and Electro.-optics Soc. Symp. Proc 8th*, 304
[5] Watakabe H, Sameshima T, Kanno H , Sadoh T and Miyao M 2004 *J. Appl. Phys.* **95 (11)**, 6457 .
[6] Zhu T, Zhou Y, Liu Z 2002 *Mater Sci. & Eng.* B **89**, 390
[7] Benatmane A, Montgomery P, Fogarassy E and Zahorski D 2003 *Appl. Sur. Sci.* **208-209** 189
[8] Du X, Dubowski J, Post M, Wang D and Tunney J 2004 *J. Vac. Sci. Technol. A* **22(3)** 870
[9] Sanders B and Post M 1993 *Mater. Res. Soc. Symp. Proc.,* **285**, 427