Excimer laser annealing of *p*-type perovskite thin films

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The ability of excimer laser irradiation to anneal and to crystallize amorphous films of the *p*-type perovskite $SrFe_yCo_{1-y}O_{2.5+x}$ ($y=0.5$) has been investigated. The films were prepared by the pulsed laser deposition technique on Si and sapphire substrates held at room temperature or 240 °C. Both film deposition and film annealing were carried out using a KrF excimer laser ($\lambda=248$ nm). Films of $SrFe_{0.5}Co_{0.5}O_{2.5+x}$ deposited at room temperature on sapphire substrates have been crystallized with 160 laser pulses at 50 mJ/cm^2, while irradiation of a film deposited at room temperature on a Si substrate has resulted in its crystallization following 40 pulses at 100 mJ/cm^2. Films deposited at 240 °C have been crystallized with 480 and 320 pulses at 50 and 60 mJ/cm^2, respectively. The application of the excimer laser annealing technique permits the modification of film crystallinity after deposition, and because this can be achieved with a high degree of control of irradiation energy, this facilitates the integration of crystalline films of high melting temperature perovskites with substrates which have a low melting point.
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I. INTRODUCTION

Strontium iron cobalt oxide perovskite $SrFe_yCo_{1-y}O_{2.5+x}$ films have been demonstrated to be promising gas sensor materials of the conductometric family.[1,2] These compounds are *p*-type semiconductors and are nonstoichiometric in oxygen. For these materials, the oxygen nonstoichiometry range can be as high as $0.0\leqslant x\leqslant 0.5$, depending on y, and for $T>350$ °C reversible uptake of oxygen can readily occur.[1] The end member phases for these compounds are the orthorhombic brownmillerite form at $x\sim 0$ and cubic or pseudocubic perovskite at $x>0.4$.

The electrical and gas sensing properties of the films are strongly dependent on cation and oxygen stoichiometries and on morphological structure.[2] However, both the structure and the morphology of the films are dependent upon deposition temperature. Previous studies have also shown that films deposited at different temperatures have varying degrees of crystallinity and preferential orientation.[3] Films prepared on single-crystal $(1\bar{1}02)$ sapphire at 630 °C are preferentially oriented (200), whereas those grown above 730 °C are preferentially oriented (110) as shown by x-ray diffraction. Films grown below 470 °C show no evidence of any type of preferred texture or crystallinity. Films which exhibit no crystallinity or texture show limited sensor functionality and cannot easily reversibly change from the brownmillerite to the cubic perovskite structures.[4] Thus, depositions at high temperatures ($T>700$ °C) favor the formation of textured films which possess the desired sensor qualities of functionality. However, the high deposition temperature is a condition which is particularly unfavorable when attempting growth and integration of such perovskites upon low melting point materials, such as plastics or silicon-based substrates with integrated complementary metal oxide semiconductor (CMOS) electronics and photoresists.

Hence, low-temperature deposition of these films is beneficial for applications where specific device microstructure or properties of substrates prohibit high-temperature treatment. Recently, it was shown that it was possible to grow crystallized $SrFeO_{2.5+x}$ films at room temperature by pulsed laser deposition using an off-axis geometry and through careful control of the Ar gas pressure.[5] Alternately, excimer laser annealing has the potential to crystallize amorphous films,[6–8] thus it offers another solution to this problem. Other recent studies show that an excimer laser can be used to modify the morphology of bulk high-temperature oxides[6] and $SrFe_{0.5}Co_{0.5}O_{2.5+x}$ films,[9] and recrystallize crystalline films.[10,11] This study reports the use of excimer laser annealing for crystallizing amorphous films of $SrFe_{0.5}Co_{0.5}O_{2.5+x}$ grown on single-crystal sapphire $(1\bar{1}02)$ or single-crystal Si (111) substrates.

II. EXPERIMENTAL DETAILS

The $SrFe_{0.5}Co_{0.5}O_{2.5+x}$ target was prepared by conventional ceramic preparation techniques. $SrCO_3$, Fe_2O_3, and Co_3O_4 powders (>99.9% pure on a metal basis) were mixed and ground together in the required quantity, followed by

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heat treatment at 1100 °C under oxygen atmosphere. The sample was ground up again and characterized by x-ray diffraction (XRD). Once the single-phase product was obtained in powdered form, the powder was pelletized and sintered at 1150 °C in oxygen. After XRD analysis confirmed the pellet to be single phase, the pellet was used as the target material for the deposition of $SrFe_{0.5}Co_{0.5}O_{2.5+x}$ films by pulsed laser deposition (PLD).

The $SrFe_{0.5}Co_{0.5}O_{2.5+x}$ films were deposited by the PLD technique on $(1\bar{1}02)$ sapphire and (111) Si substrates using a Lambda-Physik LPX305i excimer laser operating with Kr/F at 248 nm and a PLD setup described earlier.[3] The pulse duration was about 25 ns. A series of three films was prepared. Films 1 and 2 were fabricated on sapphire and film 3 on Si substrates. The substrates were held at either room temperature (films 1 and 3) or 240 °C (film 2). For comparison purposes, a crystalline film was also deposited onto a sapphire substrate at $T=650$ °C. All depositions were carried out under a background oxygen pressure of 100 mTorr. The films, typically 200 nm thick, were fabricated by ablating a $SrFe_{0.5}Co_{0.5}O_{2.5+x}$ target with the laser operating at 8 Hz and delivering pulses with an energy fluence of 1.5 J/cm^2. The average deposition rate was 10 nm/min.

Laser annealing was carried out with the same KrF excimer laser operating at 4 Hz. An area of 7×7 mm^2 of the sample was irradiated with a fly-eye homogenized beam delivered through a Microlas optics system. The irradiation was carried out in an ambient atmospheric environment with up to $N=960$ pulses, each delivering a fluence of 50–100 mJ/cm^2. The crystallinity and grain properties of $SrFe_{0.5}Co_{0.5}O_{2.5+x}$ films before and after annealing were characterized by both XRD and transmission electron microscopy (TEM). All XRD measurements were performed on a Bruker D8 diffractometer equipped for parallel beam geometry with primary and secondary double Göbel mirrors using a step size of $2\Theta=0.04°$ with a dwell time of 2 s/step. The TEM image and diffraction were obtained using a Philips CM20 electron microscope equipped with an Oxford Instruments Energy Dispersive x-ray spectrometer (Link exl II) and a Gatan UltraScan 1000 CCD camera.

III. RESULTS AND DISCUSSION

Figure 1 shows a series of XRD spectra obtained for as-grown film 1, and for the same film following its irradiation with a different number of pulses at the fluence of 50 mJ/cm^2. The progress of crystallization is indicated by the development of a diffraction peak at $2\Theta=32.4°$ [reflection (110) based on the cubic perovskite lattice] which has been observed for the film irradiated with 160 pulses. However, for $N\geqslant480$, the film material starts to decompose; at 560 pulses, the film was ablated from the substrate surface. At a higher fluence of 60 mJ/cm^2, film 1 was ablated after 80 pulses.

Figure 2 shows a series of XRD spectra obtained for as-grown film 2 and after annealing at 50 mJ/cm^2 with a different number of pulses. The film starts crystallizing at 480 pulses and the evidence of its improved crystallinity has been observed for up to 800 pulses. The position of the (110) reflection which developed in this film is $2\Theta\sim32.8°$, which is slightly higher than that for the room-temperature grown film (compare Fig. 1 and Fig. 2). A shift to higher 2Θ is due to a decrease in the unit-cell volume, which for nonstoichiometric perovskites such as $SrFe_{0.5}Co_{0.5}O_{2.5+x}$ is caused by the increasing oxygen content.[2]

Figure 3 shows a series of the XRD spectra obtained for film 2, which was irradiated with pulses at 60 mJ/cm^2. It can be seen that the film has partially crystallized following irradiation with 320 pulses. At 800 pulses, the crystal quality of the film appears to be maximized. Some decomposition

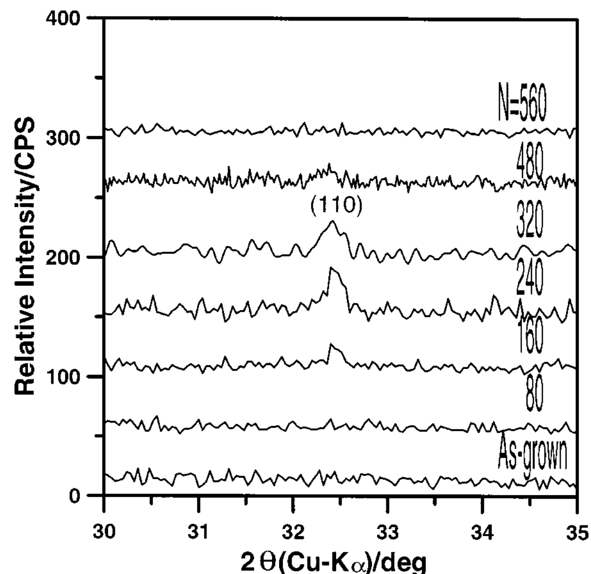

FIG. 1. XRD spectra of a $SrFe_{0.5}Co_{0.5}O_{2.5+x}$ film grown at room temperature on a sapphire substrate (film 1) and annealed at a fluence of 50 mJ/cm^2. N=number of pulses.

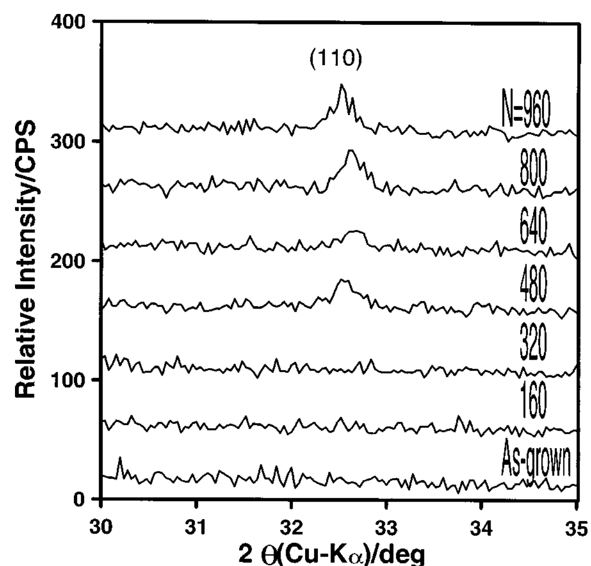

FIG. 2. XRD spectra of a $SrFe_{0.5}Co_{0.5}O_{2.5+x}$ film grown at 240 °C on a sapphire substrate (film 2) and annealed at a fluence of 50 mJ/cm^2. N=number of pulses.

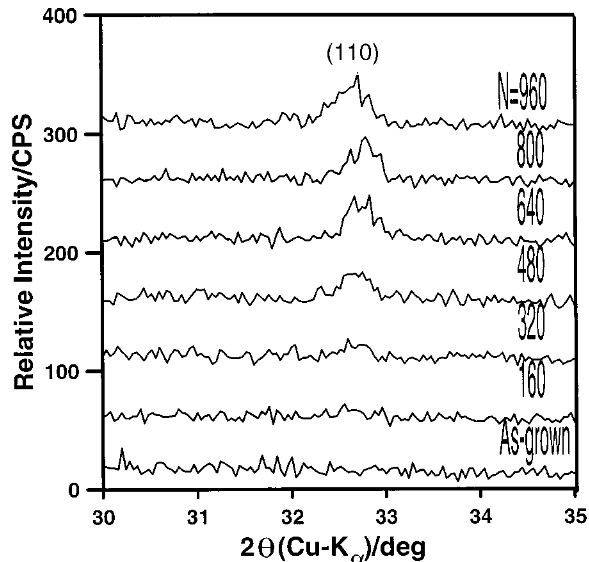

FIG. 3. XRD spectra of a $SrFe_{0.5}Co_{0.5}O_{2.5+x}$ film grown at 240 °C on a sapphire substrate (film 2) annealed at a fluence of 60 mJ/cm^2. N=number of pulses.

probably took place for a higher number ($N>800$) of irradiating pulses, as evidenced by a weaker (110) XRD peak. Also, the position of that peak appears shifted to near $2\Theta \sim 32.5°$.

Figure 4 compares the XRD spectra for a $SrFe_{0.5}Co_{0.5}O_{2.5+x}$ film deposited at 650 °C and the film deposited at 240 °C (film 2) after irradiation with 800 pulses. This shows that the (110) cubic perovskite reflections are present in both films and are not significantly shifted, indicating that the same cubic perovskite phase has been induced in the low-temperature grown film by annealing it with the excimer laser.

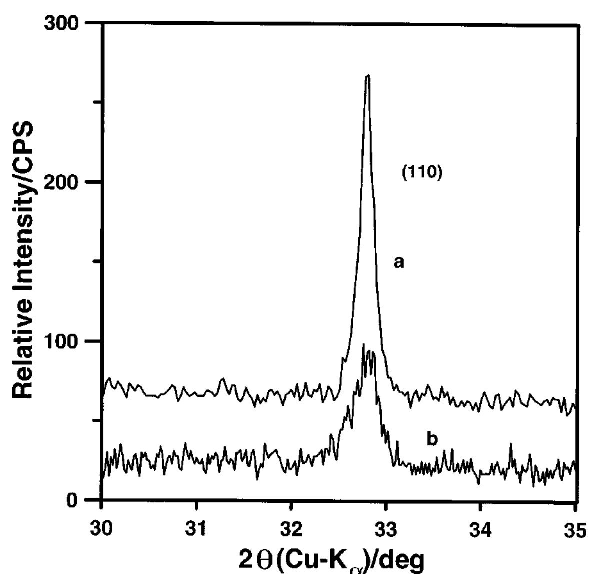

FIG. 4. XRD spectra of a $SrFe_{0.5}Co_{0.5}O_{2.5+x}$ film (a) deposited at 650 °C and (b) deposited at 240 °C and irradiated with 800 pulses at a fluence of 60 mJ/cm^2.

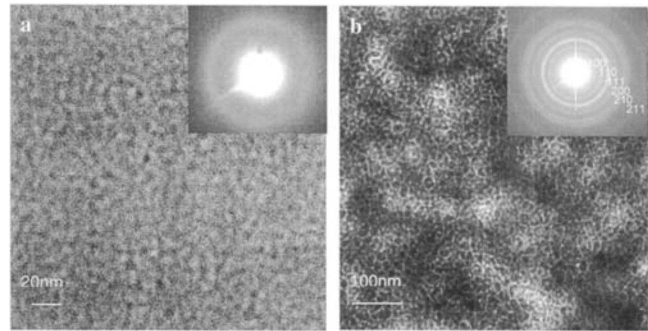

FIG. 5. TEM image and selected area electron diffraction patterns of a $SrFe_{0.5}Co_{0.5}O_{2.5+x}$ film (a) deposited at room temperature on a Si substrate, and (b) the same film following a 40-pulse irradiation at 100 mJ/cm^2.

The full widths at half maximum of the (110) peaks shown in Fig. 4 were 0.16 degrees 2Θ for the film deposited at 650 °C (a) and 0.33 degrees 2Θ for the film deposited at 240 °C and irradiated with 800 pulses at a fluence of 60 mJ/cm^2(b). This line broadening is caused mainly by decreased crystallite size. Since reduced crystallite size and/or nanostructuring of metal oxide films can greatly enhance the sensitivity of gas sensor materials,[12–14] this suggests that laser annealing offers an attractive method to tailor the crystallite size and nano/microstructure of metal oxide films for improved performance.

Figure 5 shows TEM bright field (BF) micrographs with diffraction patterns of film 3 as-grown on Si (111) at room temperature and the same film following irradiation with 40 pulses at 100 mJ/cm^2. It can be seen that the as-grown film possesses amorphous structure with a domain size ~10 nm [Fig. 5(a)]. After laser annealing, the film was crystallized as illustrated by the selected area electron-diffraction pattern [Fig. 5(b)]. According to the indexed pattern the crystallized film has the same crystal structure as $SrFe_{0.5}Co_{0.5}O_3$ (Powder Diffraction File, card 46-0335, Joint Committee on Powder Diffraction Standards) with a cubic unit-cell parameter of $a = 0.385\,74$ nm and a grain size of $30 \leqslant d \leqslant 40$ nm. This result indicated that the film could be crystallized by a small number of pulses with a higher fluence, and without evidence of damage due to ablation.

Comparing the annealing results of film 1 and film 2 using different laser fluences, it is apparent that the film deposition temperature has an influence on post-laser-annealing effects. A film deposited at 240 °C is more stable than one deposited at room temperature. At the same fluence of 50 mJ/cm^2, the 240 °C deposited film needs more pulses to be crystallized. However, when the fluence was increased from 50 to 60 mJ/cm^2, the film deposited at room temperature was ablated after only 80 pulses, while the film deposited at 240 °C was stable. As shown by comparing Fig. 2 and Fig. 3, it is clear that film 2 was crystallized with fewer pulses at a fluence of 60 mJ/cm^2 than at 50 mJ/cm^2.

IV. CONCLUSIONS

It is demonstrated that radiation from a KrF excimer laser can be used to produce a crystalline product by annealing

amorphous $SrFe_{0.5}Co_{0.5}O_{2.5+x}$ films. Room-temperature deposited $SrFe_{0.5}Co_{0.5}O_{2.5+x}$ films on sapphire have been crystallized with 160 pulses at 50 mJ/cm^2. The irradiation at 60 mJ/cm^2 with $N=80$ pulses resulted in ablation of such a film. However, a film deposited at room temperature on a Si substrate has been crystallized with 40 pulses at 100 mJ/cm^2. The film deposited at 240 °C has been crystallized with 480 and 320 pulses at 50 and 60 mJ/cm^2, respectively. For a larger number of pulses ($N>800$), the XRD data indicate that some deterioration of the film crystal structure takes place. These results demonstrate the potential of the excimer laser-induced crystallization of amorphous $SrFe_{0.5}Co_{0.5}O_x$ films grown at temperatures compatible with fragile microstructures, such as plastics or silicon-based substrates integrated with CMOS electronics and photo resists.

[1]J. J. Tunney, M. L. Post, X. Du, and D. Yang, J. Electrochem. Soc. **149**, H113 (2002).
[2]J. J. Tunney, P. Whitfield, X. Du, and M. L. Post, Thin Solid Films **42**, 221 (2003).
[3]B. W. Sanders and M. L. Post, Mater. Res. Soc. Symp. Proc. **285**, 427 (1993).
[4]B. W. Sanders, J. Yao, and M. L. Post, Mater. Res. Soc. Symp. Proc. **343**, 463 (1994).
[5]Z. Wang, T. Sasaki, N. Koshizaki, J. J. Tunney, and M. L. Post, Thin Solid Films **437**, 95 (2003).
[6]H. Azuma, A. Takeuchi, T. Ito, H. Fukushima, T. Motohiro, and M. Yamaguchi, Sol. Energy Mater. Sol. Cells **74**, 289 (2002).
[7]H. Tomita, Y. Nimomiya, A. Ito, and M. Obara, *Proceedings of the 8th IEEE Laser and Electro-optics Society Symposium, 1995* (IEEE, New York, 1995), Vol. 1, 304–305.
[8]T. Zhu, Y. P. Zhou, and Z. G. Liu, Mater. Sci. Eng., B **89**, 390 (2002).
[9]X. Du, J. J. Dubowski, M. L. Post, and J. Tunney, Opto Canada, SPIE Regional Meeting on Optoelectronic, Photonics, and Imaging, Ottawa, Ontario, May, 2002, unpublished results.
[10]A. Ishii, Y. Takano, S. Arisawa, and T. Hatano, Physica C **372–376**, 600 (2002).
[11]D. Shye, B. Chiou, C. Hwang, C. Jaing, H. Hsu, J. Chen, and H. Cheng, Jpn. J. Appl. Phys., Part 1 **42**, 1680 (2003).
[12]C. Xu, J. Tamaki, N. Miura, and N. Yamazoe, Sens. Actuators B **3**, 147 (1991).
[13]N. Yamazoe, Sens. Actuators B **5**, 7 (1991).
[14]N. Barsan and U. Weimer, J. Electroceram. **7**, 143 (2001).