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EVALUATION OF LSCO ELECTRODES FOR SENSOR PROTECTION DEVICES

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ABSTRACT

We have evaluated lanthanum strontium cobalt oxide ($\text{La}_{0.50}\text{Sr}_{0.50}\text{CoO}_x$; LSCO 50/50) as a candidate “transparent” electrode for use in an electrostatic shutter-based infrared sensor protection device. The device requires that the electrode be transparent (80% transmission) and have moderate sheet resistance (300 – 500 $\Omega/\text{sq.}$). To meet these needs, the effects of post-deposition annealing on the resistivity and optical absorption characteristics of sputter deposited LSCO thin films were studied. The as-deposited films were characterized by an absorption coefficient of $\sim 12,500 \text{ cm}^{-1}$ and resistivities of ~ 0.08 to $0.5 \Omega\text{-cm}$. With annealing at 800°C , the resistivity decreased to $350 \mu\Omega\text{-cm}$, while the absorption coefficient increased to $\sim 155,000 \text{ cm}^{-1}$. By using a post-deposition annealing step at 800°C and controlling film thickness, it appears that a standard LSCO 50/50 material may possess the requisite conductivity and optical transmission properties for this sensor protection device.

INTRODUCTION

“Optical” information, whether obtained by electronic sensors or the vision of an individual soldier or aircraft pilot, is becoming of greater importance in a range of battlefield management scenarios. Because of the increased reliance on optical information, protection of sensor systems is, therefore, also becoming ever more important. At the same time, the threat of damage to these sensors by antagonistic forces is also increasing. While the U.S. and other governments have agreed to prohibit the use of weapons that are designed to cause blinding, the use of tunable lasers by terrorist organizations still poses a significant threat [1]. Thus, devices that provide optical limiting and serve to protect sensor systems are of great importance to the U.S. Military because of the increasing threat of optical “warfare” and the critical need for battlefield intelligence information that is obtained by human sources and electronic sensors.

One sensor protection approach is an electrostatic shutter [2] that can be operated at frequencies approaching 100 kHz. A schematic of this shutter, which is currently under development at MCNC [3], is illustrated in Fig. 1. The device is being designed for utilization with sensors that operate in the 3 – 5 and 8 – 12 μm bands. In the “on” state, the shutter is open (curled) and the underlying sensor device is utilized to gather information. When an optical threat is sensed, through an associated photodiode or similar device, a signal is sent to close the shutter, thus protecting the sensor. The shutter is actuated via an electrostatic mechanism.

For the operation of the device, stringent material requirements are placed on the shutter itself as well as the supporting substrate, electrode, and insulating layers. In general, the substrate, electrode and insulator should be as transparent as possible to limit the reduction in the sensitivity of the device, but the electrode must also possess an adequate conductivity to close

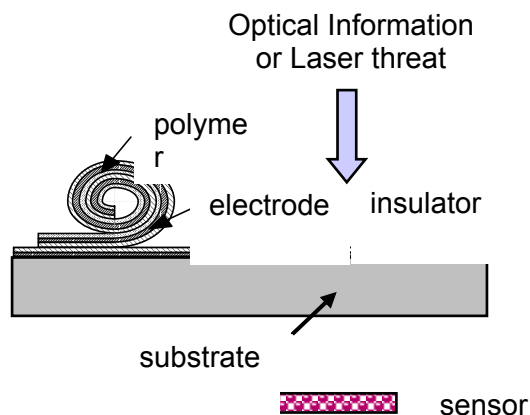


Fig. 1. Electrostatic shutter for the protection of optical sensor systems [2,3].

the shutter electrostatically. Target goals for the transparency and resistance of the electrode are 80% transmission and a sheet resistance of 300 to 500 Ω /sq.

The focus of the present research is to evaluate lanthanum strontium cobalt oxide (LSCO) for use as the lower electrode. While a variety of materials may be considered for this layer, the moderate resistance and high transparency demanded place fairly stringent requirements on material performance. Since LSCO demonstrates a “free carrier” conduction mechanism, it is expected that increases in the conductivity of the material will be accompanied by a decrease in transparency. For the design of new materials, the optimal approach is to achieve high conductivity through enhancement of the carrier mobility, rather than an increase in carrier concentration. This method improves conductivity without degrading the transmission characteristics of the material as extensively. However, due to previous experience with LSCO, and preliminary results that indicated that resistivity was strongly dependent on post-deposition annealing conditions [4], we have evaluated the suitability of LSCO for this application.

In this paper, we report on the effects of post deposition annealing on the resistivity and IR transmission characteristics of sputter deposited LSCO. A composition of $(\text{La}_{0.50}\text{Sr}_{0.50}\text{CoO}_x)$ was utilized since it was previously reported to have the lowest resistivity [5-8]. We have attempted to meet the device requirements of 80% transmission and 300 Ω /sq. sheet resistance, which may be considered as engineering parameters, through control of intrinsic material properties (extinction coefficient and resistivity) and tailoring of film thickness. In the present study, these properties are manipulated through control of crystalline quality via post-deposition annealing at different temperatures. To maximize the transparency of the electrode layer, it may be anticipated that thin layers will be required. Therefore, we also discuss our preliminary results on the effects of film thickness on the resistivity of the LSCO layers.

EXPERIMENTAL

The LSCO films were deposited by rf-magnetron sputtering with two different systems: (i) a Unifilm Technology, Inc. PVD-300 with a 3” diameter target that utilizes substrate rotation and scanning (lateral motion of the substrate under the source) to provide a high degree of film uniformity [4]; and (ii) a fairly standard Kurt J. Lesker system with a 3” sputter gun. Films were deposited onto (100) LaAlO_3 , BaF_2 , and (100) MgO , and thickness was varied from 15 to 150 nm through control of deposition time. Both systems were evacuated to a background pressure in the range of 10^{-7} torr prior to deposition. Table I provides a summary of the deposition conditions utilized. Following deposition, the films were annealed in air at temperatures ranging from 300 to 850°C for times of either 30 or 60 minutes.

Table I. Experimental conditions for the sputter deposition of LSCO 50/50 thin films.

Deposition Parameter	Unifilm Technology, Inc. PVD-300 [4]	Lesker Sputtering System
O ₂ :Ar sputter gas ratio	0:100 – 50:50 (sccm)	0:100 – 50:50 (sccm)
Deposition Pressure	10 mtorr	10 – 40 mtorr
RF power density	1.5 w/cm ²	4.4 w/cm ²
Target to substrate distance	3.5 cm	3 – 5 cm
Substrate scanning mode	97% uniformity; 4" diameter	NA
Deposition temperature	Ambient	Ambient

Resistivities of the films were characterized using a standard 4-point probe resistance measurement technique. Infrared transmission properties were studied with a Nicolet Magna550 spectrometer and subtracting the substrate transmission characteristics as the background. Thicknesses of the films were determined either by cross-sectional SEM method or by using the SEM results to calculate the sputtering rate, and then specifying a particular sputter deposition time. Absorption coefficients of the films were estimated using a simple Beer's Law approximation; reflection losses were neglected. While the estimate is not as accurate as actual measurements of refractive index and absorption coefficient, it at least gives a general feeling regarding the absorptivity of the films. Film composition was not investigated in this study, but previous studies have shown that the composition of the films may vary during deposition [4].

RESULTS AND DISCUSSION

Fig. 2 shows the effects of post-deposition annealing on the resistivity of the LSCO films. The films prepared previously by Raymond [4] were approximately 150 nm in thickness while those shown for the current study were 50 nm, except for the 850°C film that is 145 nm thick. In the as-deposited state, the resistivity of the film deposited by Raymond [4] is approximately 0.3 Ω-cm. Similar resistivity values (0.08 to 0.5 Ω-cm) were obtained for the as-deposited films of the present study prepared with a different sputtering system. Atomic force microscopy investigations suggest that the as-deposited films are at least partially crystallized, although we have not verified this with x-ray diffraction at this time. With annealing at 800 – 850°C, the resistivity of both sets of films decreased by about 3 orders of magnitude to ~ 350 – 750 μΩ-cm. The lower value compares favorably with the best reported values for this material [5-8].

The resistivity of the films also varied systematically as a function of post-deposition annealing temperature. For the films prepared by Raymond, annealing at lower temperatures appears to initially increase the resistivity (note the measured value for the 400°C anneal), followed by a strong decrease in resistivity with annealing temperature. In contrast, while the results of the present study also suggest a strong relationship between annealing temperature and resistivity, no increase in resistivity is observed for lower annealing temperatures, at least for the 50 nm films. Further, the dependence of resistivity on annealing temperature does not appear to be as strong as for the samples prepared earlier by Raymond [4]. The results do indicate, however, that for both thicknesses (50 and 150 nm), it is possible to “tune” the resistivity of the films by the choice of the post-deposition annealing temperature.

Since conductivity is related to the concentration of free carriers, the variation in resistivity with annealing suggests that the optical properties of the films in the infrared region (which are also dependent on carrier concentration) should also strongly depend on the post-deposition annealing conditions. This relationship between transmission and annealing temperature is shown in Fig. 3. It may be seen that the optical transparency decreases concomitantly with the resistivity, shown previously in Fig. 2. The values reported in this figure are for a wavelength of

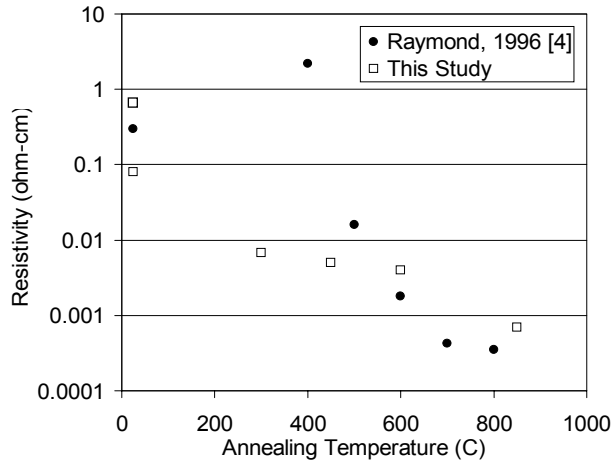


Fig. 2. Resistivity of LSCO electrodes as a function of post-deposition annealing conditions.

8.3 μm , which is just above the cut-off of the LaAlO_3 substrate. The percent transmission for the unannealed 150 nm film is $\sim 82\%$ while the corresponding film annealed at 800°C displays a transmission of only $\sim 9\%$. This suggests that as the post-deposition annealing temperature is increased, the concentration of free carriers is increased, which promotes more intense absorption. The transmission results for the as-deposited film explain our interest in this material as a “transparent oxide conductor.” In the unannealed state, the transmission is high but the resistivity is still relatively low ($< 1 \Omega\text{-cm}$).

We have also calculated the effective absorption coefficients of the films as a function of annealing temperature using Beer’s law and the results are shown in Fig. 4. In these calculations we have neglected reflection losses. As expected from the measured transmission characteristics of the films, an increase in annealing temperature causes a significant increase in the absorption coefficient of the film. Values of the absorption coefficient range from $\sim 12,500 \text{ cm}^{-1}$ for the as-deposited film to $\sim 155,000 \text{ cm}^{-1}$ for the film annealed at 800°C . While these values are only rough estimates they suggest that the optical absorption of the materials is not as strong a function of annealing temperature as resistivity. While the resistivity varied by nearly three orders of magnitude over the annealing temperature range studied, the absorption coefficients varied by slightly more than one order of magnitude. We also note that by studying the

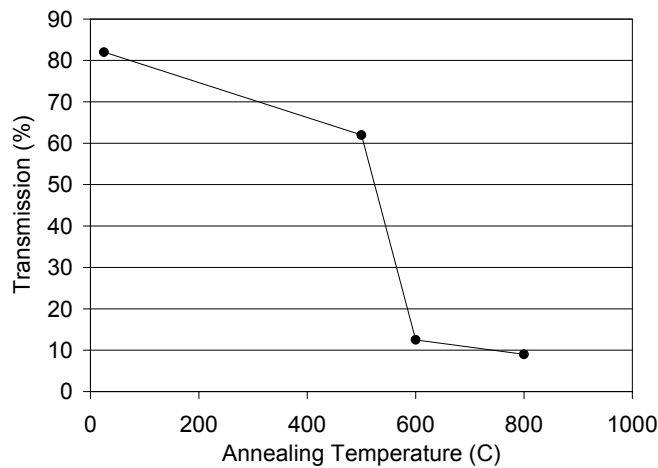


Fig. 3. Transmission of 150 nm thick LSCO 50/50 films at $8.3 \mu\text{m}$ as a function of post-deposition annealing temperature.

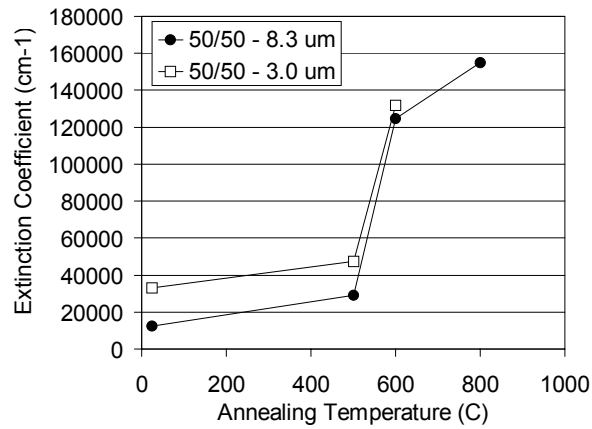


Fig. 4. Calculated absorption coefficients of LSCO 50/50 thin films as a function of annealing temperature.

transmission characteristics of films with different thicknesses, an estimate of the reproducibility of the calculated absorption coefficients is possible. Calculated absorption coefficients were within 5% for films that varied in thickness from 50 to 150 nm; i.e., similar absorption coefficients were obtained for the 50 nm films prepared on BaF₂ and MgO as for the 150 nm films prepared on LaAlO₃. These results imply that for the annealing temperatures investigated, no chemical interaction occurred between the BaF₂ or MgO substrates and the LSCO films.

Based on these results we also speculate that there is a well-defined relationship between resistivity and absorption coefficient in LSCO, although we have not studied this relationship in detail. The measured absorption coefficients at 3.0 μm are apparently higher but we attribute this difference to an increase in reflection losses at this wavelength which are not accounted for in our simple Beer's law calculation. The increase in reflection is expected due to the higher refractive index at shorter wavelength.

The absorption coefficient and resistivity data were then used to determine the suitability of the LSCO films annealed under different conditions for use in the electrostatic shutter application. The results of these calculations are presented in Table II, in terms of the film maximum thickness that may be used while still retaining 80% transmission, and the minimum film thickness required to obtain a sheet resistance of 300 or 500 Ω/sq. It may be seen in the table that the best opportunity to use LSCO for this application occurs for the highest annealing temperature where crystalline perfection would be expected to be greatest. For LSCO annealed at 800°C, to obtain a sheet resistance of 500 Ω/sq., the film needs to be at least 5 nm thick, while to obtain the desired transparency, the film must be thinner than 14 nm.

Hence, following this preliminary study, LSCO still appears to be a viable candidate electrode for this application. However, this evaluation neglects the fact that as film thickness is decreased, it may no longer be possible to retain bulk material property values. To begin to investigate the effect of thickness on resistivity, films with thicknesses ranging from 15 to 145 nm were prepared, subjected to different annealing conditions, and characterized. The results of

Table II. Opportunities for engineering the resistance and transparency properties of LSCO through the control of annealing conditions.

Post-Deposition Annealing Temp. (°C)	Maximum Thickness for 80% Trans. (nm)	Minimum Thickness for 500 Ω/sq. (nm)	Minimum Thickness for 300 Ω/sq. (nm)
As-Deposited	180	3400	5670
500	74	210	350
600	16	26	43
800	14	5	9

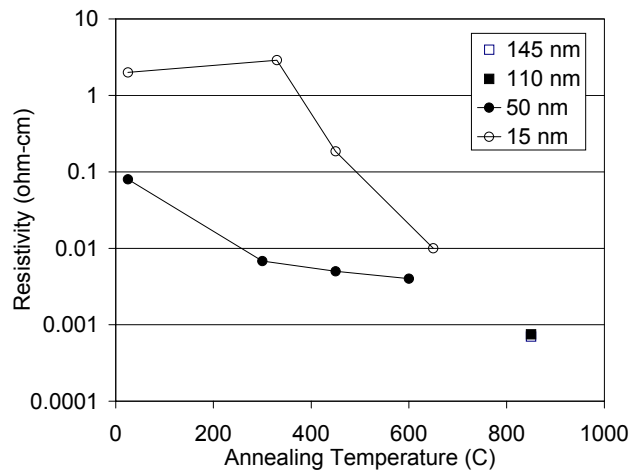


Fig. 5. Effect of film thickness of LSCO 50/50 on the measured resistivity as a function of annealing temperature.

these preliminary studies are shown in Fig. 5. The resistivity of the films seems to be more dependent on thickness at the lower annealing temperatures, while at annealing temperatures above 650°C, this dependence seems less pronounced. However, further studies are still required for films 8 to 15 nm in thickness that are annealed at 800 to 850°C for more conclusive evidence regarding this observation.

CONCLUSIONS

We have studied the effects of post-deposition annealing on the resistivity and infrared transparency of LSCO materials. Higher annealing temperatures resulted in a three order of magnitude decrease in resistivity from $\sim 0.3 \Omega\text{-cm}$ (as-deposited) to $350 \mu\Omega\text{-cm}$ (800°C). Concomitant with the decrease in resistivity was an increase in the optical absorption throughout the infrared spectral region. The calculated absorption coefficients increased by approximately one order of magnitude for the same change in annealing conditions. Despite this increase in absorption, LSCO appears to be a viable electrode for this device, primarily due to the moderate sheet resistance that is required for this application.

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