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# VACANCY RELATED DEFECTS IN $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ THIN FILMS

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## ABSTRACT

Laser ablated $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ thin films have been studied by Doppler-broadening-detected positron annihilation using a variable-energy positron beam. The oxygen partial pressure during cooling from the growth temperature was altered through the range 760 torr to $10^{-5}$ torr to change the oxygen non-stoichiometry of the films.

The measured Doppler broadened lineshape parameter S was found to increase with increasing oxygen nonstoichiometry.For films cooled with an oxygen partial pressure of $\leq 10^{-4}$ Torr positron trapping to monovacancy type defects is infered. For the film cooled in $10^{-5}$ torr oxygen the magnitude of the increase in S, with respect to that measured from the film cooled in 760 Torr oxygen, showed positron trapping to vacancy cluster defects was occuring.

## INTRODUCTION

The metallic pervoskite oxide $La_{0.5}Sr_{0.5}CoO_{3-d}$ is finding application in metal-oxide-based electronic device technologies. The material properties are sensitive to oxygen non-stoichiometry. The resistivity can be increased from metallic, <100 $\mu\Omega$cm, to insulating as $\delta$ increases from the intrinsic value, 0.06 [1]. The nature and role of vacancy related defects induced by increased oxygen non-stoichiometry is consequently of interest.

The doping of $LaCoO_3$ with Sr results in a significant increase in electrical conductivity with the maxiumum value occurring in the region x = 0.4-0.5 [2]. Substitution of $La^{3+}$ by $Sr^{2+}$ requires charge compensation. This can take place either by an increase in the valence of an appropriate proportion of Co from 3+ to 4+ with the generation of holes and/or by the formation of oxygen vacancies. Hole formation is exclusively found for $x < 0.3$; for larger values d increases to 0.06 and both forms of compensation occur, but with hole formation still very dominant [1]. These findings are consistent with lattice defect simulation studies [3]. For reduced oxygen partial pressures, compensation by creation of oxygen vacancies increases.

With the generation of an oxygen vacancy, two holes are consumed, and so the film conductivities transform from metallic to insulating with increased oxygen nonstoichiometry. Changing the Sr content or changing the oxygen nonstoichiometry have been shown to have a similar effect on the oxygen chemical potential in the films [4].

Positron annihilation is sensitive to open volume defects of neutral or negative local charge. Positrons implanted into solids thermalize within 10 ps and enter a Bloch state from which they can annihilate directly or they can be trapped into a localized state from which annihilation can take place on a timescale typically in the range 100 to 500 ps. A thermal positron annihilating with an electron in a solid will do so predominately via a two-$\gamma$ process. The resultant 511 keV annihilation $\gamma$-rays, when viewed in the laboratory frame, are Doppler broadened by the longitudinal component of the annihilation pair momentum. The pair momentum is dominated by that of the electron. The Doppler broadened $\gamma$-ray energy spectrum provides a measure of the momentum distribution of the electrons with which the positron is annihilating. Vacancy defects, due to the missing ion core, represent an attractive potential to positrons. Annihilation from such a site is more likely to occur with low momentum valence electrons resulting in a narrowing of the Doppler-broadened spectrum. The electron density at the vacancy is reduced, which results in an increase in the positron lifetime over that for bulk annihilations. The S-parameter is defined to be sensitive to low-momentum events. An increase in S-parameter results from an increase in trapping to vacancy defects and/or to the formation of larger open volume defects. The S-parameter for saturation trapping to monovacancy type defects in GaAs results in an 2% increase, while for small vacancy clusters this rises to 3.5-5%.

## EXPERIMENTAL DETAILS

Thin films of $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ were deposited on $LaAlO_3$ substrates by pulsed excimer laser deposition from a solid stoichiometric ceramic target of the same composition. The substrate temperature of 650 °C and an oxygen partial pressure of 100 mTorr were maintained during deposition. The films were cooled in a predetermined oxygen ambient at 5 °C/min to room temperature. The partial pressure of oxygen present during cooling was varied between $10^{-5}$ and 760 Torr. X-ray diffraction confirmed the phase purity and structural quality of the films. Epitaxial (001) oriented films with a thickness of approximately 250 nm, as determined by RBS, were produced.

Electrical transport measurements were performed by a standard DC four probe measurement technique. Four indium silver contact pads were deposited on the sample and connected by thin gold wire. The resistance was measured through the temperature range 4-350 K. Positron annihlation measurements were performed on a horizontal magnetically guided variable energy, 0-80 keV, positron beam. The Doppler broadening of the 511 keV annihilation $\gamma$-ray was measured with a high purity Ge detector. The energy spectrum lineshape was

## DISCLAIMER

characterized by the S-parameter defined as the ratio of counts in a window ranging from 510.25 to 511.75 keV to the total counts in the 511 keV line.

## RESULTS

The room temperature resistivity of the films cooled in 760 Torr oxygen was found to be $5x10^{-5}$ Ωcm. The resistivity increased with decreasing oxygen partial pressure during cooling. The room temperature resistvity of the film cooled in $10^{-5}$ Torr oxygen was $2x10^{4}$ Ωcm. The temperature dependence of the resistivity showed a transition from metallic behaviour to semiconducting behaviour as the cooling oxygen partial pressure was reduced from 1 to $10^{-2}$ Torr.

The positron annihilation results are shown in Figure 2. Positrons implanted into the thin film annihilate predominantly in the film for implantation energies up to approximately 7 keV. For higher energies an increasing proportion of the positrons are annihilating in the $LaAlO_3$ substrate. For very low implantation energies (< 1 keV) annihilation from surface states is of importance.

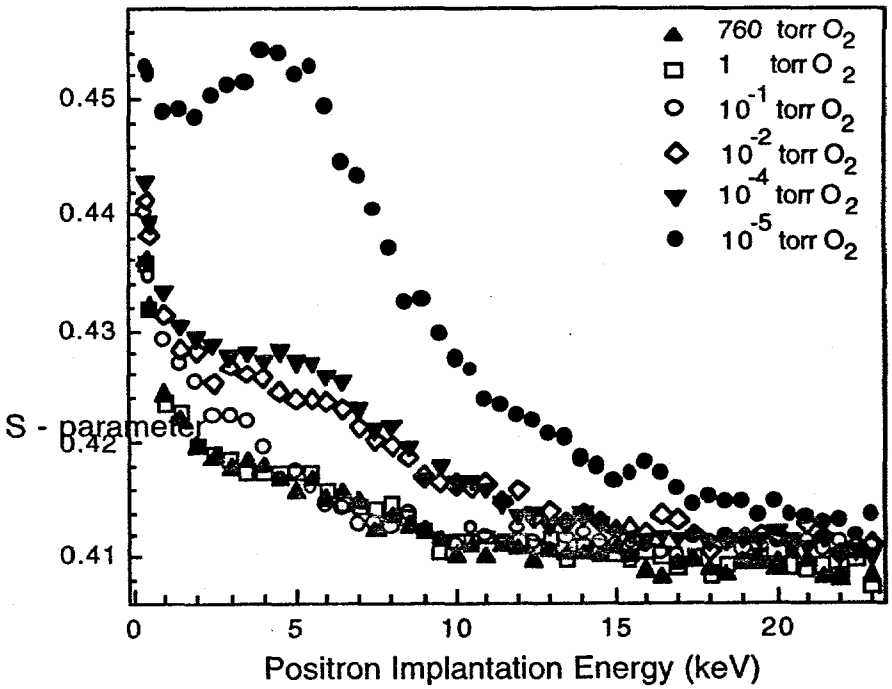

**Figure 2.** The Doppler broadened lineshape parameter, S, as a function of positron implantation energy for the series of $La_{0.5}Sr_{0.5}CoO_{3-d}$ films grown with a cooling oxygen partial pressure from 760 to $10^{-5}$ Torr.

The $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ layer S parameter determined for the implantation energy range 2-6 keV is 0.417(1) for the metallic samples cooled in 760 and 1 Torr oxygen. This value increases to 0.426(2), or $S = 1.022S_{760}$, for the semiconducting samples cooled in $10^{-2}$ and $10^{-4}$ Torr oxygen. The layer S value for the film cooled in $10^{-5}$ Torr oxygen shows a significantly larger value of 0.452(2), or $S = 1.084S_{760}$.

## DISCUSSION

Positron annihilation results for films with increasing Sr contents were also measured show the S-parameter for the layer to be similar for x = 0.15 and 0.30 but to have increased for x = 0.50 by approximately 1.5%. On increasing the oxygen nonstoichiometry by decreasing the partial pressure of oxygen during cooling from the growth temperature, the S-parameter was found to increase. The increase of approximately 2% with respect to the 760 Torr cooled sample for the $10^{-2}$, $10^{-4}$ Torr samples is suggestive of trapping to monovacancy type defects. This is dependent on the 760 Torr film giving an S value for undefected bulk $La_{0.5}Sr_{0.5}CoO_3$. From a simple ionic model oxygen vacancies would present a local charge of 2+, and so would be highly unlikely to trap positrons at room temperature. Lanthanum cobalt oxide is, however, highly covalent so the local charge state may be reduced from this value. The presence of Sr ion oxygen vacancy cluster defects has been proposed and recent Mott-Littleton method simulations have shown this complex to be bound for lanthanum cobalt oxide [2, 5]. An ionic model would predict that a $(Sr_{La}V_OSr_{La})^x$ complex would be neutral. Recent high resolution transmission electron microscopy and selected area electron diffraction studies of $La_{1-x}Sr_xCoO_{3-\delta}$ have shown domain structure with sizes in the range 30-200 nm may occur [6, 7]. Parallel electron energy loss spectroscopy measurements showed the domain regions to have an increased Co/O ratio, and that an increased proportion of $Co^{4+}$ ions exist in the domain. This is consistent with the expectation from ligand field theory that $Co^{4+}$ prefers square pyramidal coordination and so a higher concentration of oxygen vacancies would be expected[6]. Simulation of electron diffraction images suggest segregation of La and Sr into layers can occur with the domains [7]. These experiments provide further evidence for the presence of $(Sr_{La}V_OSr_{La})^x$ complexes. We propose that positron trapping to such complexes is occurring for films cooled in oxygen partial pressures to $10^{-4}$ Torr.

The observed S-parameter for the film cooled in $10^{-5}$ Torr oxygen is approximately 8% greater than that cooled in 760 Torr. This indicates trapping to vacancy cluster defects is occurring.

## CONCLUDING REMARKS

The oxygen nonstoichiometry of laser ablated epitaxial $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ thin films was controlled by controlling the oxygen partial pressure during cooling from the growth temperature. Increasing oxygen nonstoichiometry results in a decrease in the conductivity consistent with the behaviour of ceramic material. A change from metallic-like to semiconductor-like conductivity was observed for films cooled in oxygen partial pressure of $10^{-2}$ Torr.

An decrease in the Doppler broadened $\gamma$-ray linewidth (an increase in S) from positron annihilation within the film was observed with increased oxygen nonstoichiometry. For oxygen partial pressures $\leq 10^{-4}$ Torr positron trapping to monovacancy type defects is inferred. It is proposed that Sr ion oxygen vacancy complexes are the trapping sites. On increasing the nonstoichiometry trapping to vacancy cluster defects is observed.

## ACKNOWLEDGMENT

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