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The effect of deposition parameters on the properties of $SrCu_2O_2$ films fabricated by pulsed laser deposition

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Abstract

$SrCu_2O_2$ (SCO) thin films have been fabricated by pulsed laser deposition at oxygen partial pressures between 5×10^{-5}–5×10^{-2} mbar and substrate temperatures from 300 °C to 500 °C. All films were single-phase $SrCu_2O_2$, p-type materials. Films deposited at a substrate temperature of 300 °C and oxygen pressure 5×10^{-4} mbar exhibited the highest transparency (~80%), having conductivity 10^{-3} S/cm and carrier concentration around 10^{13} cm^{-3}. Films deposited at oxygen partial pressure higher than 10^{-3} mbar exhibited higher conductivity and carrier concentration but lower transmittance. Depositions at substrate temperatures higher than 300 °C gave films of high crystallinity and transmittance even for films as thick as 800 nm. The energy gap of $SrCu_2O_2$ thin films was found to be around 3.3 eV.

Keywords: Laser ablation; Depositon process; Strontium

1. Introduction

During the past years the interest for p-type transparent conducting oxides (TCOs) has grown rapidly, due to their potential technological applications [1,2]. TCOs are wide band gap materials that have the uniquely combined properties of high optical transparency in the visible region, along with high electrical conductivity. The wide band gap is a prerequisite for transparent materials, so that there is no absorption in the visible spectrum. However, up to now only n-type TCOs have exhibited such physical properties and thus have been extensively used as optical materials. Research in p-type materials appeared as late as 1997 when the first p-type, transparent, $CuAlO_2$ films were reported [3]. Since then, one of the materials that has attracted a lot of attention is $SrCu_2O_2$ [4]. The main advantage of $SrCu_2O_2$ over delafossites (such as $CuAlO_2$) is that it can be deposited at low temperatures (<400 °C), making it a good candidate for large scale technological use.

From structural point of view, $SrCu_2O_2$ belongs to the $I4_1/a\,m\,d$ space group 4 and is constructed by one-dimensional, zig zag, O–Cu–O chains along the [100] and [010] directions, at an angle $\theta=96.3°$. The Sr atoms are situated at the centre of the distorted octahedral formed by the O atoms [5]. This geometry results in the widening of the energy gap, which reaches a value greater than 3 eV.

Various deposition techniques have been reported recently for fabricating of $SrCu_2O_2$ thin films, such as pulsed laser deposition (PLD) [4,6], e-beam evaporation [7], and spray deposition [8]. According to these reports, the formation of single phased materials with good optical and electrical properties has not been straight forward.

In this work, PLD has been employed for the fabrication of $SrCu_2O_2$ thin films and their optical and electrical properties have been studied, at various partial O_2 pressures and substrate temperatures during deposition. The films are studied structurally, electrically and optically, revealing p-type, single phased $SrCu_2O_2$ films, with high transparency reaching 85% and conductivity as high as 10^{-2} S/cm.

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2. Experimental

Polycrystalline $SrCu_2O_2$ films were grown by the conventional PLD method in a flowing oxygen environment. The target used was supplied by Umicore. A KrF excimer laser (Lambda Physik, $\lambda = 248$ nm, $\tau = 34$ ns pulse duration, 600 mJ/pulse maximum) was used for the ablation, delivering pulses at a repetition rate of 10 Hz. The beam was incident on a rotating target at an angle of 45° with respect to the target normal and was focused by a spherical lens to yield an energy fluence of 0.5 J/cm^2 per pulse. The base pressure prior to deposition was better than 10^{-6} mbar, while the partial pressure of the O_2 was in the range 5×10^{-5}–5×10^{-2} mbar. The ablated material was collected on Corning Glass 7059 substrates placed parallel to the target at a distance of 4 cm and heated up to 300 °C–500 °C using a resistive heater. The sample was cooled to room temperature at the same oxidized environment as during deposition.

The crystallographic structure of the films was determined by X-ray-diffraction measurements using a Rigaku D/MAX-2000H rotating anode (12 kW) Cu K_α monochromated diffractometer. For the surface analysis Atomic Force Microscopy (AFM) was engaged. The UV–VIS optical properties of the films were monitored by a Cary 50 spectrophotometer.

Transport measurements were also performed for the determination of the electrical properties of the films. The electrical resistivity, ρ, was measured by the standard two-probe technique, in the temperature range of $120 < T < 300$ K. Hall measurements were done by the van der Paw configuration. Finally, the thermoelectric power at room temperature was measured for determining the Seebeck coefficient, the sign of which is regulated by the type of carriers.

The thickness of the films was determined by a Stylus profilometer (alpha-step 100 Tencor).

3. Results and discussion

Fig. 1 shows the XRD spectra for $SrCu_2O_2$ films prepared keeping the substrate temperature stable at 300 °C during deposition, while varying the oxygen partial pressure. The thickness of these films is between 220 nm and 300 nm. For O_2 partial pressures smaller than 10^{-3} mbar, the films were crystalline and each peak in the diffraction pattern was identified as arising from the $SrCu_2O_2$ phase (PCPDF file #48-1514). Films prepared at partial oxygen pressures higher than of 10^{-3} mbar were amorphous. AFM analysis (not shown here) revealed that all films had a smooth surface with average roughness of approximately 3 nm.

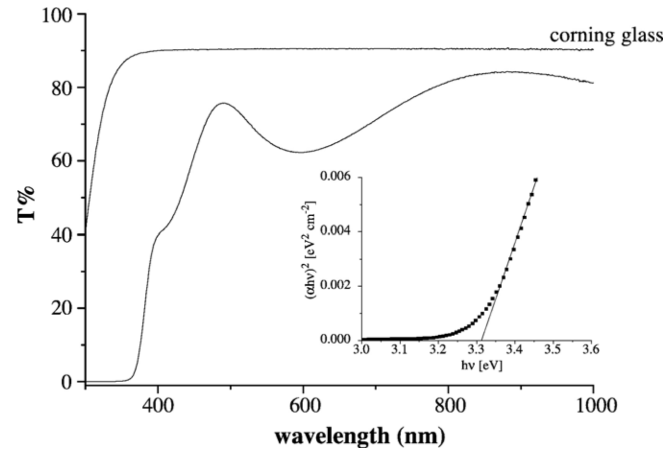

Fig. 2. Transmittance spectrum for $SrCu_2O_2$ film deposited at 5×10^{-4} mbar and 300 °C. In the inset, the absorption coefficient, α, is plotted against the photon energy, hv, for the estimation of the energy gap. The transmittance of the substrate is also shown for reference.

The best transmittance, shown in Fig. 2, was obtained for the sample prepared with partial oxygen pressure of 5×10^{-4} mbar. It is seen that the film is highly transparent in the visible region, with the transparency reaching approximately 80%. In the inset, the plot of $(\alpha h\nu)^2$, where α is the absorption coefficient as calculated from the optical data, is shown against the photon energy, hv, for the estimation of the direct energy gap [9,10]. From the graph, the energy gap is estimated to be around 3.3 eV, a value that agrees with the theoretical predictions for this

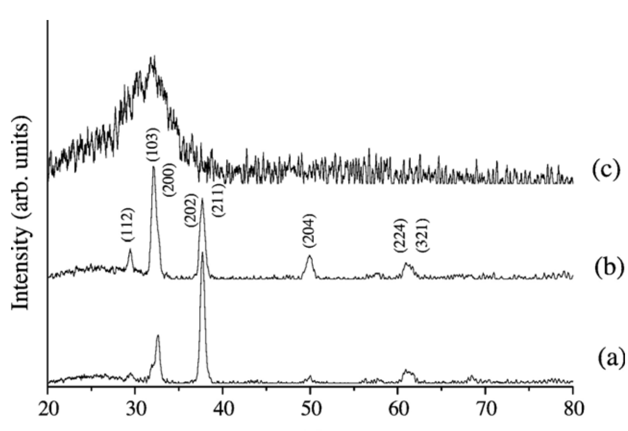

Fig. 1. XRD spectra for $SrCu_2O_2$ films prepared at $T_{dep} = 300$ °C and different O_2 partial pressures (a) 5×10^{-5} mbar, (b) 5×10^{-4} mbar and (c) 2×10^{-3} mbar. The spectra were obtained at incident angle of 2°.

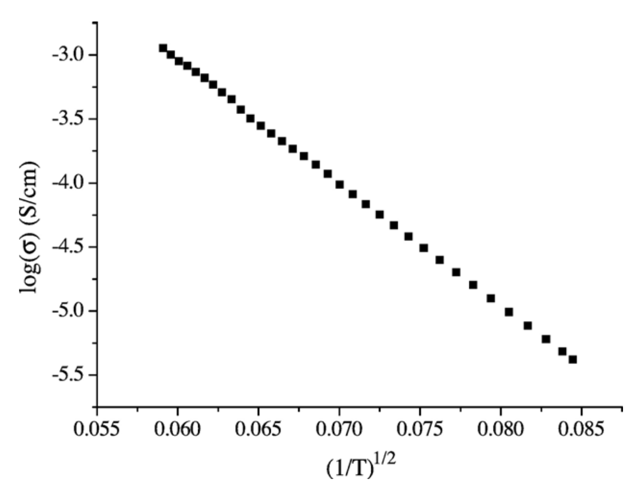

Fig. 3. The temperature dependence of the conductivity for the film prepared at 300 K, 5×10^{-4} mbar O_2 partial pressure.