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Phase stability and orientation of $SrCu_2O_2$ films grown by pulsed laser deposition

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Abstract

The formation of $SrCu_2O_2$ thin films using pulsed laser deposition is discussed. The $SrCu_2O_2$ phase is observed for growth condition outside those observed from thermodynamic bulk studies. The structure and properties of epitaxial $SrCu_2O_2$ films on (100) $SrTiO_3$ are described. The epitaxial films grow with the tetragonal *a*-axis oriented perpendicular to the substrate surface. The in-plane orientation is $SrCu_2O_2$ (001)‖$SrTiO_3$ {011}.
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1. Introduction

$SrCu_2O_2$ is a semiconducting oxide of potential interest for wide bandgap electronics, photonics, and sensors [1–4]. It is a p-type material, with polycrystalline films exhibiting a Hall mobility on the order of 0.5 cm^2/V s and a carrier density in the mid-$10^{17}/cm^3$ range when doped with K. $SrCu_2O_2$ exhibits a tetragonal crystal structure with bulk lattice constants of $a = 5.48$ Å and $c = 9.82$ Å. In describing the $SrCu_2O_2$ crystal structure, Sr atoms are at the center of a distorted octahedron formed by O atoms. It possesses a dumbbell O–Cu–O unit that is similar to that of Cu_2O. In fact, $SrCu_2O_2$ can be conceptually derived from Cu_2O, where one Cu atom is removed for each unit of distorted Cu_2O, with the addition of an inter-penetrating body-centered tetragonal Sr sublattice. Unlike the three-dimensional dumbbell structure in Cu_2O, the O–Cu–O dumbbells in $SrCu_2O_2$ are connected to form one-dimensional zigzag chains along [100] and [010] directions, respectively. The angle between them is $\theta = 96.3°$. This value is smaller than the tetrahedral angle of $\theta = 109.5°$ in Cu_2O. However, the Cu–O bond length of 1.84 Å in $SrCu_2O_2$ remains nearly the same as in Cu_2O [1,5,6]. The origin of the p-type behavior appears to reside in the +1 valence of the Cu cation. Band structure calculations for $SrCu_2O_2$ indicate that it is a direct bandgap material with a band edge at the zone center (Γ). An experimental bandgap of 3.3 eV for $SrCu_2O_2$ has been measured [5,6]. The band structure around the energy gap region is similar to that of Cu_2O, except for a considerably larger energy gap for $SrCu_2O_2$ compared with that of Cu_2O (2.17 eV).

With the described bandgap and transport properties, significant effort has focused on exploiting this material as a p-type wide bandgap semiconducting oxide in transparent thin film electronics [7–10]. These activities have included epitaxial thin film materials, yielding the possibility of developing epitaxial oxide electronics [11]. In this paper, we describe the phase formation, crystallinity, and orientation of $SrCu_2O_2$ thin films grown using pulsed laser deposition. This work includes analysis of phase pure epitaxial $SrCu_2O_2$ film growth. While the availability of epitaxial $SrCu_2O_2$ materials is of interest for fundamental studies, the primary motivation is to develop this material for device applications. The focus includes delineating how the epitaxial

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growth of this tetragonal material proceeds on a common perovskite template typically used for oxide epitaxy.

2. Experimental details

Pulsed laser deposition was used as the deposition technique. Growth was carried out in a pulsed laser deposition system with a base pressure of 10^{-6} torr. The ablation targets were polycrystalline ceramics with a Sr/Cu ratio of 1:2. The targets were synthesized from $SrCO_3$ (99.99%) and CuO (99.995%) via 1 atm sintering in air. In most cases, the targets did not assume the $SrCu_2O_2$ phase, consisting of a mixture of $SrCuO_2$ and CuO. Growth experiments were performed over a temperature range of 200–600 °C. A key to achieving the $SrCu_2O_2$ phase in thin films is to realize a +1 valence state for the Cu. The introduction of hydrogen into the growth process was explored as a possible means of reactively controlling the valence state of the Cu cations. The experiments reported here include both O_2 and H_2 as reactants during growth. The hydrogen source was 2% H_2/98% Ar mixture. A KrF (248 nm) excimer laser was used as the ablation source. Laser energy densities on the order of 2–3 J/cm^2 were utilized. The laser repetition rate was 1 Hz. Target to substrate distance was on the order of 4 cm. The structure of the films was characterized using 2- and 4-circle X-ray diffraction with Cu Kα radiation. The latter was needed to determination of in-plane orientation of the material. Scanning electron microscopy was used to determine the surface morphology using a JEOL JSM-6335F. The transport properties of the films were determined via van der Pauw four point resistivity measurements. The measurements were performed at room temperature.

3. Results and discussion

The behavior of phase formation and texture for $SrCu_2O_2$ films grown on $SrTiO_3$ substrates was examined. Fig. 1 shows the $\theta-2\theta$ X-ray diffraction scans for $SrCu_2O_2$ films deposited at temperatures ranging from 200 to 600 °C on $SrTiO_3$. The substrate peaks were deleted from the displayed data. The $SrCu_2O_2$ phase was observed for films deposited in the temperature range of 400–600 °C. The films were deposited at an oxygen partial pressure of 0.1 mtorr with no hydrogen. Films grown at 500 °C were nearly phase-pure. Interestingly, the $SrCu_2O_2$ films grown at 400 °C and 500 °C exhibit uniaxial texture with the *a*-axis perpendicular to the substrate. This is in contrast to many other tetragonal oxides, such as $YBa_2Cu_3O_6$, in which growth tends to be *c*-axis oriented. At 600 °C, the films are not phase pure, but consist of $SrCu_2O_2$ and Cu_2O. It is interesting to compare the phase behavior in thin films with the bulk phase stability as reported by Suzuki [12]. In bulk, the phase stability line for $SrCu_2O_2$ at an oxygen pressure of 10^{-4} torr lies at approximately 560 °C. At 400 °C and 500 °C, the stable phase assemblage in bulk is $SrCuO_2$+CuO. Yet, thin films grown under these conditions yield $SrCu_2O_2$. This behavior is attributed to the $SrCu_2O_2$ phase being kinetically trapped in thin-film form, growing with a preferred texture. Interestingly, the film grown at 600 °C shows a weak $SrCu_2O_2$ peak with Cu_2O as a secondary phase. This is more consistent with the bulk behavior as the Cu_2O phase is observed at $P(O_2)=10^{-4}$ torr and 570 °C.

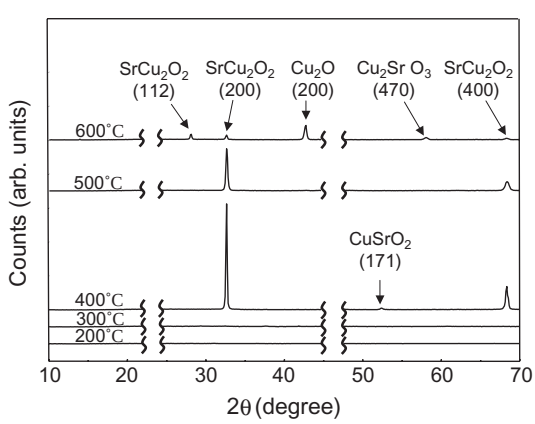

Fig. 1. $\theta-2\theta$ vs. temperature XRD data plotted for $SrCu_2O_2$ thin films grown at various temperatures with 0.1 mtorr of oxygen gas pressure.

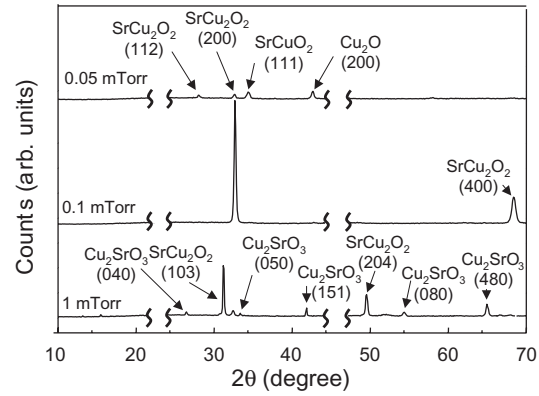

Fig. 2. $\theta-2\theta$ vs. O_2 partial pressure plot for $SrCu_2O_2$ thin films grown at 500 °C with various O_2 gas pressures.

Phase formation was examined as a function of oxygen partial pressure. Fig. 2 shows the X-ray diffraction data for $SrCu_2O_2$ films deposited on $SrTiO_3$ at various O_2 partial pressures. For these experiments, the deposition temperature was fixed at 500 °C. Clearly, the formation of $SrCu_2O_2$ thin films as the dominant phase requires significant control over oxygen pressure as it relates to the Cu valence. At the O_2 pressures of 1 mtorr or higher, the film consists of mixed phases of $SrCu_2O_2$ and $SrCu_2O_3$. The latter phase possesses the same cation stoichiometry as the desired phase, but with Cu in the +2 valence state. The bulk phase diagram predicts $SrCuO_2$+CuO for these conditions. For an oxygen pressure of 0.05 mtorr, the film consists of $SrCu_2O_2$ as well as $SrCuO_2$ and Cu_2O. The latter represents a decomposition product of the desired phase as predicted in the bulk phase

diagram. The oxygen conditions for achieving phase-pure $SrCu_2O_2$ thin films is rather narrow, realized at an oxygen pressure of 0.1 mtorr.

As pointed out earlier, realization of Cu in the +1 valence state is a prerequisite to forming the $SrCu_2O_2$ phase. One approach to controlling the valence state of Cu is to create a chemically-reducing environment during film growth by employing hydrogen as part of the background gas. In order to examine this, the growth of $SrCu_2O_2$ films with a hydrogen background was examined. Fig. 3 shows the X-ray diffraction data for films deposited at 500 °C in 0.1 mtorr oxygen and two different pressures of a 2% H_2/98% Ar mixture. Again, the $SrTiO_3$ substrate peaks are not shown. For the ablation target used in these experiments, the film grown in an Ar/H_2 pressure of 0.5 mtorr yielded a mixture of $SrCu_2O_2$ and $CuSrO_2$, with the latter possessing the Cu +2 valence state. However, at $P(Ar/H_2)=5$ mtorr, the dominant phase in the film was *a*-axis oriented $SrCu_2O_2$. Clearly, the use of a reducing environment impacted the valence state in the deposited film, yielding the desired phase. Films grown at various hydrogen partial pressures are consistent with this trend.

The $\theta-2\theta$ X-ray diffraction data for films grown at 400 °C and 500 °C in an oxygen ambient of 0.1 mtorr is shown with a log intensity scale in Fig. 4. In both cases, *a*-axis oriented $SrCu_2O_2$ growth is observed. For the films grown at 400 °C, the dominant peaks are associated with (l00)-oriented $SrCu_2O_2$, although (110) oriented $SrCuO_2$ is clearly evident as well. At a film-growth temperature of 500 °C, (100)-oriented $SrCu_2O_2$ is more predominant. Also shown in the pattern are minor peaks from unidentified impurity phases in the film. From high-resolution scans of in-plane and out-of-plane reflections, the lattice spacing for the $SrCu_2O_2$ film grown at 500 °C is determined to be $a=b=5.486$ Å and $c=9.79$ Å. The *a*-axis oriented epitaxial growth does not coincide with the smallest possible lattice mismatch. With $a=b=5.486$ Å, a 45° rotation of the $SrCu_2O_2$ $a-b$ plane yields a lattice mismatch with $SrTiO_3$

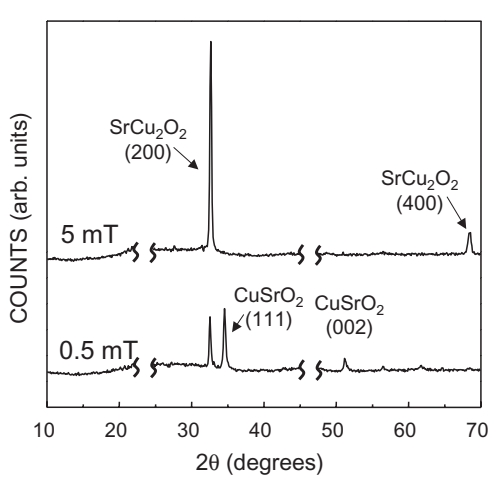

Fig. 3. XRD data for $SrCu_2O_2$ thin films grown at 500 °C having 0.1 mtorr of oxygen at 0.5 and 5 mtorr H_2 partial pressure.

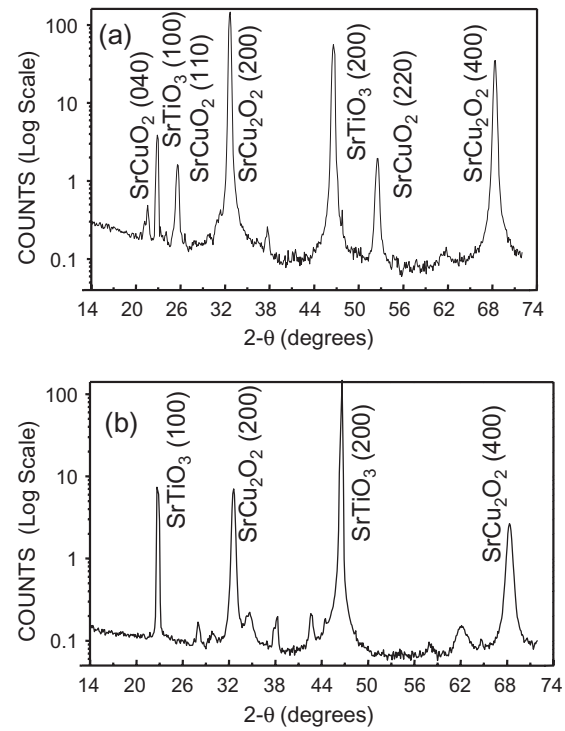

Fig. 4. Low resolution $\theta-2\theta$ plot (in Log Scale) for $SrCu_2O_2$ thin film grown at (a) 500 °C and (b) at 400 °C with $P(O_2)=0.1$ mtorr.

of only −0.7%. Given that the film grown at 500 °C is nearly phase-pure $SrCu_2O_2$ with a singular (100) orientation, the subsequent description of film properties focuses on films grown under these conditions.

Detailed diffraction studies of the films indicate an unusual and interesting epitaxial orientation of the film on the (100) $SrTiO_3$ surface. Fig. 5 shows the θ scan (rocking curve) through the $SrCu_2O_2$ (200) for the film grown at 500 °C. The rocking curves indicate that the film and substrate (100) planes are not exactly aligned. Instead, the rocking curves show double-humped shapes at $\phi=0°$, 90°, 180° and 360°. At $\phi=45°$, a central peak with wings is observed. Fitting the double intensity humps at $\phi=0°$ with two peaks shows that the $SrCu_2O_2$ (100) planes can be considered on average to be tilted ~1.9° towards the in-plane $SrTiO_3$ [0±10] and [00±1] directions. The total $SrCu_2O_2$ (200) full-

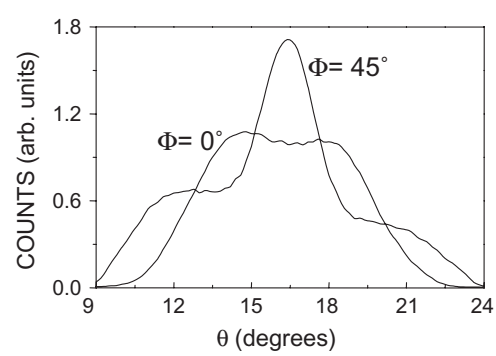

Fig. 5. θ scans through (200) for $SrCu_2O_2$ thin film grown at 500 °C with 0.1 mtorr O_2 partial pressure, at $\phi=0°$ and 45°.

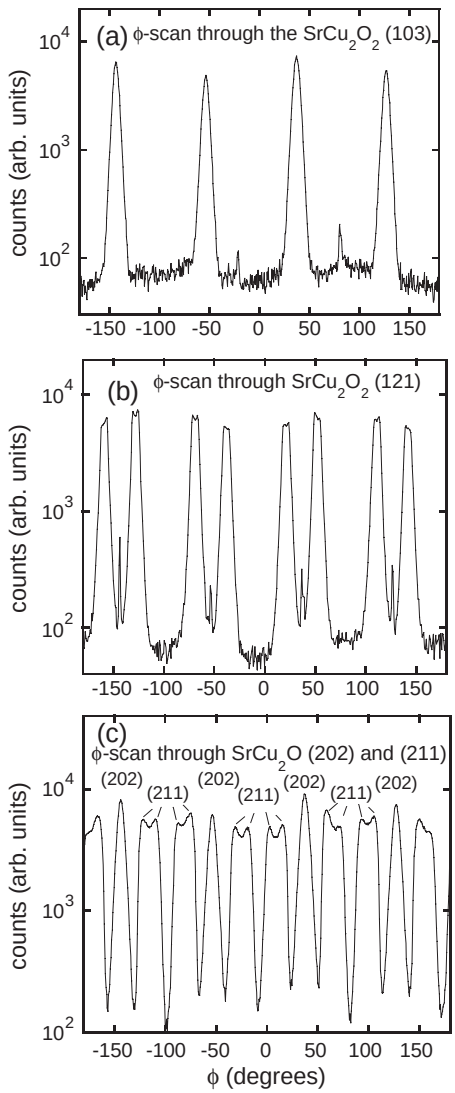

Fig. 6. ϕ scan through a) (103), b) (121), c) (202)+(211) planes for $SrCu_2O_2$ thin film grown at 500 °C with 0.1 mtorr of O_2.

width half-maximum (FWHM) is approximately 7.5°, but is perhaps more accurately described as the sum of multiple peaks, each with FWHM ~4°. Small tilts away from exact alignment have been observed in several film–substrate heteroepitaxial systems and are due to the detailed atomic structure of the interface [13–15].

The in-plane orientation of the $SrCu_2O_2$ films was examined using four-circle X-ray diffraction. An in-plane ϕ-scan through the $SrCu_2O_2$ (103) reflections is shown in Fig. 6a. The in-plane alignment is essentially a 45° rotated rectangle on the $SrTiO_3$ (100) square-planar surface. In particular, the orientation of the $SrCu_2O_2$ film on the $SrTiO_3$ (100) surface can be described as out-of-plane $SrCu_2O_2$ (100)∥$SrTiO_3$ (100), in-plane $SrCu_2O_2$ (001)∥$SrTiO_3$ {011}, which includes the 90° rotated domains $SrCu_2O_2$ (010)∥$SrTiO_3$ {011}. Fig 6b and c show the in-plane ϕ scans through other reflections and are consistent with the average orientation deduced from Fig 6a. However, the peaks show splitting similar to that observed above for the rocking curves, again indicating that tilts away from the average epitaxial orientation are present. The lattice mismatch for the a-and c-axis of the $SrCu_2O_2$ on $SrTiO_3$ is −0.6% and −11%, respectively in this orientation. Clearly, the *a*-axis perpendicular orientation is driven by surface and interfacial energy and not simply lattice-matching. The effect of lattice miscut from vicinal surfaces is a candidate for causing the observed orientation as has been recently seen for other oxides [16]. Further studies on well-characterized miscut substrates would be needed to delineate this relationship.

The surface microstructure of the $SrCu_2O_2$ film on $SrTiO_3$ was examined using scanning electron microscopy (SEM) and atomic force microscopy. Fig. 7 shows the SEM micrographs of a film grown at 500 °C in 0.1 mtorr O_2. The film is relatively smooth with oriented voids. Atomic force microscopy scans were also taken for the film grown at 500 °C. The root-mean-square roughness was approximately 6.7 nm. In addition to microstructure and morphology, the transport properties of the films were also examined. In most cases, the films were insulating, which is not unexpected given that no K doping was attempted. The highest conductivity was realized for films grown at 500 °C and 0.1 mtorr of O_2 partial pressure. In this case, a resistivity of 140 Ω cm was observed. The film was somewhat opaque in the visible region, indicating a high density of defects in the film, but was relatively transparent in the near-infrared region. Additional work is needed to optimize the optical and transport properties.

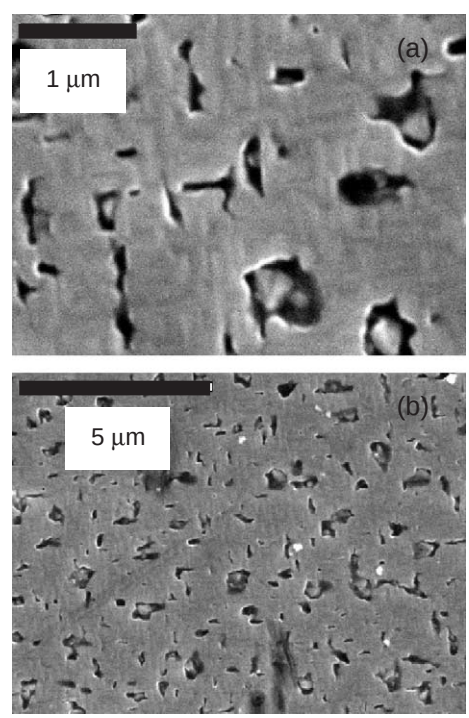

Fig. 7. (a) High resolution and (b) low resolution SEM images of $SrCu_2O_2$ thin films grown at 500 °C with 0.1 mtorr of O_2.

4. Summary

In summary, the phase formation of $SrCu_2O_2$ thin films was examined. At relatively low growth temperatures, the $SrCu_2O_2$ phase in epitaxial thin films appears to be kinetically stabilized. This research was sponsored by the Army Research Laboratory and the Army Research Office under grant no. DAAD19-01-1-0603. The authors would also like to acknowledge the Major Analytical Instrumentation Center, Department of Materials Science and Engineering, University of Florida.

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