Molecular beam epitaxial growth of SrCu$_2$O$_3$: Metastable structures and the role of epitaxy

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Within the study of oxide materials, high pressure bulk growth has generated a number of new and interesting materials. More recently, attention has been paid to using epitaxy to stabilize these high pressure oxide materials as thin films. In this article we report on the molecular beam epitaxial growth of SrCu$_2$O$_3$; a high pressure, highly correlated, model oxide. We find that the choice of substrate can significantly alter not only the structure but also the chemistry of the resulting film. For growth on SrTiO$_3$ substrates the epitaxially stabilized structure for single phase films with a SrCu$_2$O$_3$ composition is based on a tetragonal unit cell. For identical growth conditions, but on a LaAlO$_3$ substrate, a single phase film with the composition and structure of the infinite layer material (SrCuO$_2$) is formed. We also review the literature for the successes and failures of epitaxy to stabilize high pressure structures. © *2002 American Institute of Physics.*
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I. INTRODUCTION

The addition of high pressure as one of the variables during the growth of bulk materials, particularly high pressure oxygen, has led to the discovery of a number of new and interesting materials, and the promise of many more.[1–4] The growth of epitaxial thin films has been considered as another way to stabilize these high pressure oxides in a technologically useful form. However, the literature only shows success for a very limited class of materials, and there seems to be a belief that the reason for the failure to grow other high pressure oxides is related to an inability to fully oxidize the growing film.

In this article, we present our results on the epitaxial growth of SrCu$_2$O$_3$ using a high flux atomic oxygen source that is more than sufficient to ensure the necessary oxidation of the films. We find that films of the correct stoichiometry can be grown on SrTiO$_3$ substrates, however, these films do not have the orthorhombic structure found in the high pressure bulk form of SrCu$_2$O$_3$. Instead, we find an epitaxially stabilized structure based on a tetragonal unit cell. Growth on LaAlO$_3$ substrates, under identical deposition conditions, results in the formation of the related compound SrCuO$_2$.

As discussed in the main section of this article, these results serve to demonstrate that epitaxy can strongly influence the critical and delicate interplay between the chemistry and the structure of these oxide films. The results also demonstrate the necessity of powerful *in situ* (and ideally real-time) characterization of these oxide thin films if the film's structure and chemistry is to be effectively determined. The article will end with a discussion of the published accomplishments and failures in using epitaxy to stabilize high pressure phases.

II. BACKGROUND

In order to make progress with the concept of growing high pressure materials with thin-film-type processes, it is useful to separate the effect of pressure into two components. The first is the ability to drive the oxidation reaction to a product with a higher oxidation state, via the thermodynamic argument relating oxidant activity to the oxygen partial pressure. The second is the role of pressure in stabilizing a particular structure—in this case, a high pressure structure. Using this separation of oxidation and structure stabilization, three separate classes of materials can be defined within the category of high pressure oxide materials. *Oxidation high pressure materials* are those in which the high pressure acts to provide full oxidation, but does nothing to affect the structure. There is generally no low pressure structure with the same stoichiometry, and the structure that forms is stable with nonstoichiometric amounts of oxygen (i.e., oxygen deficiencies). *Structural high pressure materials* are materials that undergo a structural phase transition as a function of pressure, with no change in oxidation level or stoichiometry. A low and a high pressure phase therefore exist for the same stoichiometry. Many materials fall into this class. Finally, *combination high pressure materials* are those in which the high pressure oxygen both fully oxidizes the material and allows a high pressure structure to be stabilized. These tend to be line compounds with no similar stoichiometric low pressure phase.

By dividing the effect of pressure into these two components and using the three classes defined earlier, we can better understand the limiting step, either oxidation or structure stabilization, in growing high pressure materials via thin film deposition processes. To grow materials from either the *oxidation high pressure materials* or the *combination high pressure materials* classes, the oxidation reaction must be driven to generate products of higher oxidation state than can be obtained with molecular oxygen under molecular beam epi-

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taxy (MBE)-type growth pressures. Hence, to drive the needed oxidation reaction, the activity of the oxidant must be increased. Changing the chemistry of the oxidant will accomplish this while maintaining a low pressure. In Ingle *et al.*[5] we describe, in detail, a method to produce and measure very large fluxes of atomic oxygen. We have also shown that the previously inaccessible highest levels of oxidation for the group VIB elements are well within reach with this high flux atomic oxygen source.[6]

Growing materials in the structural high pressure materials and the *combination high pressure materials* classes requires a means to stabilize the alternative, high pressure structure. This article deals with the use of epitaxy on a suitable substrate to stabilize the high pressure structure in lieu of high pressure. Experimentally, the growth of $SrCu_2O_3$, a material within the class of *combination high pressure materials,* will be studied on several substrates both as an interesting case study and because it is a potential model system for the study of highly correlated, low dimensional materials.

III. $SrCu_2O_3$

$SrCu_2O_3$ is a low dimensional quantum magnet which can currently be grown only as a bulk material under high pressures of oxygen, and falls within the class of combination high pressure materials. It is a model system for studying low dimensional quantum magnets in a regime between the one-dimensional chains (in materials such as Sr_2CuO_3) and the two-dimensional planar configuration of the high-T_c parent compound $SrCuO_2$ (see, for example, Refs. 7–14). However, as a bulk material it is hard to probe experimentally the many questions that need to be answered about the electronic properties of the material due to the difficulty of chemically doping the material and the difficulty in generating clean surfaces for photoemission spectroscopy studies. Both of these problems could potentially be solved by the growth of a thin film. Additionally, several well-matched substrates can be used to study the effects of epitaxy on the growth of $SrCu_2O_3$.

$SrCu_2O_3$ is the first member of the homologous series of compounds with a stoichiometry of $Sr_{n-1}Cu_{n+1}O_{2n}$, where $n= 3, 5, ... \infty$, as was determined by Hiroi *et al.*[1] This series is defined by the layered structure of Cu–O planes, with CuO_4 squares defining the planar geometry, and by oxygen-free Sr planes. The last member of this series ($n=\infty$) is $SrCuO_2$, the so-called infinite layer material upon which most of the high temperature superconductors are based. As n steps down in the series the Cu–O/Sr/Cu–O layering is maintained, while the arrangement of the CuO_4 squares changes, from all corner-sharing in the $n=\infty$ case ($SrCuO_2$) to half corner-sharing and half edge-sharing in the $n=3$ case of $SrCu_2O_3$. $SrCu_2O_3$ has the *Cmmm* space group with $a=3.934$ Å, $b=11.573$ Å, $c=3.495$ Å [Sr $(\frac{1}{2},0\frac{1}{2})$, $Cu(0,\frac{1}{6},0),O1(0,0,0),O2(6\frac{1}{2},\frac{1}{6},0)]$. The b unit cell length is just less than three times the a unit cell length. This is required for the half corner-sharing, half edge-sharing motif to generate a translationally symmetric unit.

TABLE I. Possible Sr–Cu–O phases with unit cell sizes.

Phase	a (Å)	b (Å)	c (Å)	Ref.
Sr_2CuO_3	12.68	3.90	3.49	50
$SrCuO_2$	3.92	3.92	3.43	51
$Sr_{14}Cu_{24}O_{41}$	11.46	13.39	3.94	52
$SrCu_2O_2$	5.47	5.47	9.83	53
$SrCu_2O_3$	**3.93**	**11.57**	**3.49**	**1**
$Sr_2Cu_3O_5$	3.93	19.41	3.46	1

IV. EXPERIMENTAL CONSIDERATIONS

Ideally the substrate should be a very close match to the crystal structure of the material that is to be grown, not only in the unit cell size, but also in terms of the space group. The structure of $SrCu_2O_3$ is quite unusual and therefore there has yet to be found a substrate with a direct space group and lattice parameter match. The next best alternative is to choose a substrate with similar point group symmetries at the important atomic positions, normally the position of the close-packed atoms. In $SrCu_2O_3$, the structure is constrained by the close-packed oxygen sublattice in the $a–b$ plane. With this in mind, the $a–b$ plane of the $SrCu_2O_3$ structure closely resembles that of the $a–b$ plane of the perovskite structure $SrTiO_3$. In both materials, the oxygen-to-oxygen spacing is 2.79 Å.

Considering $LaAlO_3$ and MgO as possible substrates can help shed light on the influences of epitaxy. $LaAlO_3$ is also a perovskite structure, but with a smaller lattice parameter, making the oxygen-to-oxygen distance in the $a–b$ plane 2.67 Å. MgO, on the other hand, has the structure of simple rock salt (NaCl). In this case, the similarity in the structure to $SrCu_2O_3$ is solely through the oxygen sublattice in the $a–b$ plane, with a larger oxygen-to-oxygen spacing of 2.97 Å.

The family of Sr–Cu–O compounds is summarized in Table I. Ideally the desired ratio of Cu to Sr in our film should be 2:1, this ratio is controlled in the electron-beam MBE chamber by maintaining the ratio of fluxes (also called the deposition ratio) of Cu to Sr at 2:1 using atomic absorption rate control. However, there is no guarantee that the ratio of atoms that ends up being incorporated in the film will be the same as the ratio of fluxes generated, so the ratio must be checked after the film is grown.

To this end, *in situ* core-level x-ray photoelectron spectroscopy (XPS) was used to determine the composition of the film. Since the core-level peak area is directly related (via the photoemission cross section) to the number of atoms present, the ratio of the cross-section corrected core-level peak areas allows one to determine the stoichiometry of the film without the need for models or fitting parameters. The XPS spectra were measured in an *in situ* VG ESCALAB Mark 2 spectrometer equipped with a twin anode x-ray source. All XPS data shown in this work were collected with Mg x rays and have had the spectral components associated with the $K\alpha_{3,4}$ x-ray satellites subtracted and then a Shirley-style[15] background removed. No contaminants (e.g., carbon) were seen in the spectra.

The stoichiometry of $SrCu_2O_3$ implies that because Sr is oxidized to $+2$, which is the only option for this strongly
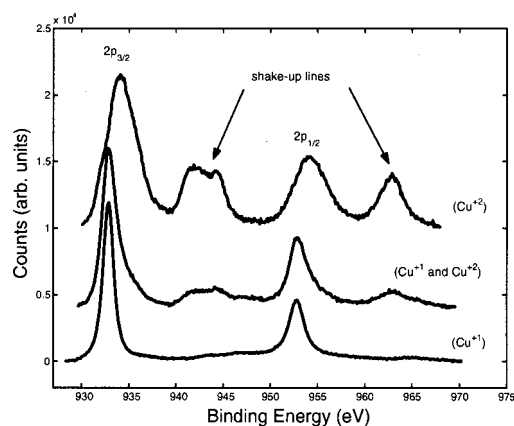
FIG. 1. The oxidation state of Cu as determined via XPS of the Cu $2p$ core level for films grown under varying oxidation conditions.

ionic group II metal, Cu must be in the $+2$ oxidation state (the highest oxidation state for Cu). In this work the oxidant used is atomic oxygen, generated from a high flux atomic oxygen source (see Ref. 5). This allows the product of the oxidation reaction to be driven to a higher oxidation state than would be possible using molecular oxygen as the oxidant, while still maintaining MBE-type growth pressures. To determine the oxidation level of the film, we can concentrate solely on the oxidation level of Cu because Sr is limited to a single oxidation state ($+2$). A change in the oxidation state of an atom will cause both a spatial rearrangement of the valence charges of that particular atom and a different potential due to the change in the surrounding nuclei and electrons. These changes show up as a shift in the binding energy and the satellite structure of the core-level peaks in XPS. The oxidation state of Cu is therefore obtained by studying the binding energy and satellite structure of the Cu $2p$ core level. Figure 1 shows the $2p$ core level of Cu for several films when the oxidation state is changed by varying the flux of atomic oxygen. As shown in previous works (see, for example, Refs. 16 and 17), the appearance of extra satellite peaks around 942.5 and 962.5 eV and a shift of the $2p\frac{3}{2}$ core level from 932.4 to 933.6 eV, which are clearly discernible, indicate the presence of Cu in the $+2$ oxidation state.

Reflection high-energy electron diffraction (RHEED) was digitally recorded and analyzed during growth and was primarily used to determine the long range ordering of the structure. Beyond the qualitative knowledge gained by simple visual inspection of the obtained images, this technique is useful for the information it provides regarding the in-plane symmetry, and the rough estimates of the in-plane lattice parameters.

X-ray diffractometry (XRD) was done *ex situ* on a Phillips Materials Research diffractometer using Cu K_α radiation with a four-axis goniometer. The c-axis lattice parameter of a thin film is easily determinable with XRD, but as can be seen from Table I this will not uniquely determine which phase has formed. However, judicious examination of specific off-axis peaks can distinguish between all the unit cells listed in Table I. Therefore, off-axis XRD was done as well, with the

aid of a collimator and parallel beam detector setup to maximize count rates.

V. RESULTS

A. On (001) SrTiO₃ substrates

The exact surface that $SrTiO_3$ presents for epitaxial growth is a matter of some debate. Although recent articles have proposed methods for chemical and thermal surface treatments to obtain either SrO or TiO_2 termination,[18–20] typical core level XPS results always find the ratio of Sr to Ti to be 1.6:1 instead of 1:1 (seen, for example, by correcting with cross sections the XPS core level ratios published by Gonda *et al.*).[21] Time-of-flight ion scattering and recoil spectroscopy also shows more Sr on the surface than expected.[22] The reason for the incorrect ratios of Sr to Ti is not clear, but it is commonly thought to be related to the layered nature of the $SrTiO_3$ structure, possibly influenced by the lack of oxygen at the surface,[23] or by the formation of another member of the $Sr_{n+1}Ti_nO_{3n+1}$ Ruddlesden–Popper homologous series within the top several surface layers.

In this work all substrates were cleaned *in situ* by heating to 600 °C under a flow of atomic oxygen. XPS on the $SrTiO_3$ substrates showed core level peaks for Sr, Ti, and O only, and the cross-section corrected core level peak areas of Sr and Ti consistently produced a ratio of 1.6:1. The 1.6:1 ratio was also seen for substrates treated with the chemical and thermal procedure described in Koster *et al.*[18] to generate a TiO_2 terminated surface.

Separate calibration of the Cu and Sr atomic absorption rate monitors via quartz crystal monitors allows the determination of the number of Cu and Sr atoms hitting the substrate. Empirically it was determined that a deposition ratio of 2.5 Cu atoms for every Sr atom hitting a $SrTiO_3$ substrate at 550 °C, as controlled by atomic absorption, led to a film with a Cu:Sr ratio of 2:1, or a composition of $SrCu_2O_x$, as determined by cross-section corrected *in situ* XPS core level peak area ratios. In addition, an atomic oxygen flux of at least 5×10^{16} atoms/cm^2 s was needed in order to fully oxidize the Cu (i.e., to produce the correct binding energy shift and satellite structure as shown in Fig. 1) under these deposition conditions. From this point on, all films discussed in this article showed an oxidation state of $+2$ for the Cu as determined by the binding energy and satellite structure of the Cu $2p$ XPS core level.

For a very large range of stoichiometry on the Cu rich side (Cu:Sr deposition ratios from 2.5:1 to 20:1), the first 10–15 Å deposited on $SrTiO_3$ substrates always show an epitaxial RHEED pattern. Moreover, XPS measurements on these samples show a small Ti peak which is due to the substrate (and expected for such a thin film), and a cross-section corrected Cu to Sr XPS core level peak ratio that is independent of the deposition ration. The ability to grow a 10–15-Å-thick film with a range of Cu to Sr deposition ratios from 2.5:1 to 20:1 and yet always generate an epitaxial thin film with a fixed Cu to Sr ratio demonstrates that the substrate can have a huge influence on the local chemistry. For films thicker than 10–15 Å, the cross-section corrected XPS core level peak ratio increases as the Cu to Sr deposi-

tion ratio is increased and the epitaxial RHEED pattern is lost for deposition ratios greater than 3:1. All of the XPS results were robust as a function of position on the sample, suggesting that phase separation or precipitate formation did not occur.

We note on passing that depositing a Cu to Sr ratio of 2.5:1 on a MgO substrate at 550 °C generates an amorphous film with a cross-section corrected XPS core level peak ratio of 1.5:1. And as we will discuss later, deposition under identical conditions and LaAlO$_3$ substrates generates a cross-section corrected XPS core level peak ratio of 1:1—further demonstrating that the substrates play a large role in determine what ratio of Cu to Sr will stick, and therefore which phases can be grown.

For growth up to 500 °C on SrTiO$_3$ with a wide variety of Cu to Sr deposition ratios, the films grown were polycrystalline. Starting at 600 °C, and with a set deposition ratio of Cu to Sr, there was a decrease in the ratio of Cu to Sr measured by the cross-section corrected XPS core levels as the temperature was increased. At growth temperatures of 800 °C and above there was no Cu in the resulting film, as determined by XPS. This would suggest that the Cu is highly mobile (or volatile).

RHEED patterns obtained throughout the growth of a 1000-Å-thick film on SrTiO$_3$ substrates at 550 °C (with a deposition ratio of 2.5:1, a cross-section corrected core level XPS peak area ratio of 2:1, and the correct XPS core level binding energy and satellite structure to indicate a +2 Cu oxidation state) show three different patterns: A, B, and C, with spacings of 3.9, 5.6, and 8.8 Å, respectively, depending on the orientation of the substrate with respect to the RHEED beam. As the film is rotated around its normal, the patterns are seen in the sequence A–C–B–C–A, which is repeated four times within each 360° rotation. Assuming a homogeneous film, this four-fold symmetry implies square planar symmetry in the plane of the sample (i.e., the unit cell must be either tetragonal or cubic), which allows pattern A to be indexed as 100, pattern B as 110, and pattern C as 210, making the a and b unit cell dimensions 3.9 Å. These RHEED patterns then require the unit cell of the film to be either cubic or tetragonal, not the orthorhombic unit cell listed for SrCu$_2$O$_3$ in Table I. No three-dimensional transmission spots were seen throughout the growth of these films, suggesting that a second phase, or precipitate, did not form.

XRD is the easiest method for obtaining the unit cell size in the direction normal to the sample. Figure 2 shows a standard 2θ–ω XRD scan. Two peaks are shown that, if indexed as (001) and (002), give a c-axis spacing of 3.49 Å. From Table I we see that the tetragonal unit cell size of $a=b$ $=3.9$ Å and $c=3.49$ Å is more like that of SrCuO$_2$ than SrCu$_2$O$_3$. On the other hand, the cation stoichiometry determined by XPS is clearly 2:1.

With a basic unit cell in hand, off-axis XRD can be done to further enhance the certainty with which the structure can be identified. A peak was found at the correct 2θ and ψ angles for the (101) peak and at those locations a ϕ scan showed four peaks, as expected for a tetragonal unit cell. The (121) peak was found at the correct 2θ and ψ angles for this tetragonal unit cell and a ϕ scan indicated the expected eight

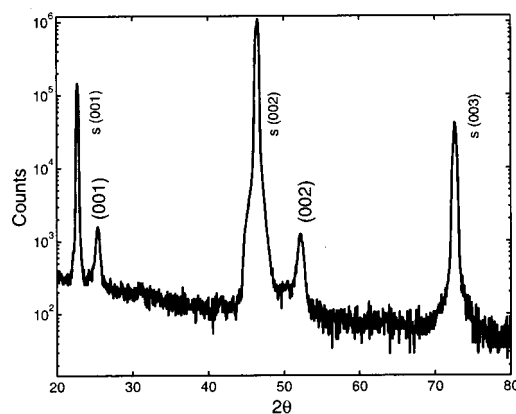FIG. 2. A 2θ–ω x-ray scan of a film grown at 550 °C on SrTiO$_3$, indexed.

{121} peaks with a 26° offset from the {101} peaks, as shown in Fig. 3. Furthermore, peaks indexed as {111} were found at the correct 2θ and ψ angles for this tetragonal unit cell and rotated by 45° in ψ from the {101} peaks.

It is worth noting that all of these peaks can also be indexed by an orthorhombic unit cell with dimensions $a=3.905$, $b=11.71$, and $c=3.49$ Å, i.e., like that of SrCu$_2$O$_3$ but with a slightly expanded b axis. However, with the atomic arrangement of SrCu$_2$O$_3$ on this orthorhombic cell, the structure factor indicates that the tetragonally indexed 101 peak should be absent and that the symmetry shown in the ϕ scan (Fig. 3) for the tetragonally indexed 211 peak is incorrect. This therefore rules out such an interpretation.

Nonetheless, there are two problems with assessing the films structure to be a SrCuO$_2$ tetragonal unit cell. The first is that for any body-centered unit cell, such as SrCuO$_2$ (regardless of whether it is cubic, tetragonal or orthorhombic), any plane with $(h+k+l)$ equal to an odd number should generate a systematic absence of the corresponding peak in the x-ray data. Significantly, Fig. 2 clearly shows the strong presence of the 001 peak. The second problem is that the cross-section corrected XPS core level area ratios imply the Cu to Sr ratio of the film is 2:1, not 1:1.

One possible interpretation of the results is that we have formed the SrCuO$_2$-type tetragonal structure but with a ran-
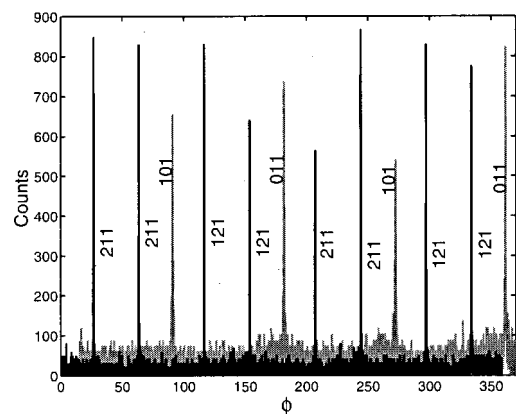

FIG. 3. Two ϕ scans, of the {101} and {121} family of peaks, indexed and overlayed to show the tetragonal nature of unit cell.
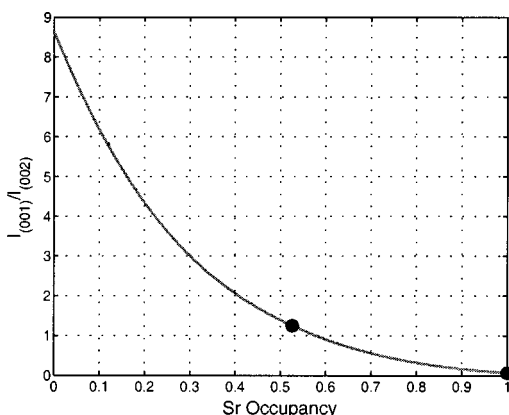
FIG. 4. The ratio of intensities from the (001) and (002) reflections from the SrCuO$_2$ structure as a function of Sr occupancy. Blue line is calculated from the structure factors, the red points are experimental data.

domly distributed Sr atom missing from one out of every two unit cells. This makes the Cu to Sr ratio 2:1, as the XPS results require, and removes the required absence of the 001 peak because half the unit cells no longer are body centered. The line in Fig. 4 shows the calculated ratio of the intensities of the 001 to the 002 XRD peaks as a function of Sr occupancy in SrCuO$_2$. The two points are for experimental data, where the I_{001}/I_{002} is determined from the XRD data and the Sr deficiency is determined by the cross-section corrected XPS core level peak area ratios. The point at the Sr deficiency of 0.52 is for the film discussed in this section, and the point at a Sr deficiency of 0 is for a film with an XPS Cu to Sr ratio of 1:1.

When comparing the ideal infinite layer structure of SrCuO$_2$ to the orthorhombic, high pressure structure of SrCu$_2$O$_3$, it is important to realize that the local environment (the nearest neighbor atoms) for the Sr atom in either structures is identical, and that the overall oxygen sublattice is identical. For this reason, the unit cells are very similar and SrCu$_2$O$_3$ may be considered simply as having a longer range order than SrCuO$_2$. It is the longer range order that is obviously not forming in the grown films. Epitaxy may help maintain the c-axis layering, and the oxygen sublattice as desired, but the Cu and Sr in the grown films do not have the long range order needed to generate the two-leg ladder structure of SrCu$_2$O$_3$. It is interesting to note that one of the important components of the SrCu$_2$O$_3$ structure, the half corner-shared half, edge-shared CuO$_4$ units, is not found in any of the Sr–Cu–O phases that have been prepared as thin films. This arrangement is prominent in the low pressure, orthorhombic version of SrCuO$_2$, but there is no published literature showing its growth as an epitaxial thin film.

According to the chemical shift in the core level XPS results, the oxidation of Sr and Cu is +2. This would suggest an overall stoichiometry of SrCu$_2$O$_3$ for the films grown with a cross-section corrected XPS core level Cu to Sr ratio of 2:1. In oxides, as discussed in Sec. VI, the local electrostatic forces are very strong; so, if the structure is taken to be the infinite layer unit cell with 50% of the Sr atoms missing from random locations and the oxidation of Cu is +2, the Cu–O

planes can no longer be perfect. Unfortunately, information regarding the location of O and Cu atoms is unobtainable from XRD on thin film due to geometrical issues.

The accumulated results of RHEED, XRD, and XPS suggest that the film is single phase (within our capability to tell) with a stoichiometry of SrCu$_2$O$_x$ (where $x=3$, assuming formal valences) and with a tetragonal unit cell of dimensions $a=b=3.90$ and $c=3.49$. Taking into account the local similarities between SrCu$_2$O$_3$ and SrCuO$_2$, one interpretation is that epitaxy has stabilized an alternative, metastable structure best described as a slightly compressed infinite layer structure with 50% of the Sr atoms missing.

B. On (001) LaAlO$_3$ substrates

The deposition conditions which generated the metastable phase with the nominal composition of SrCu$_2$O$_3$ on SrTiO$_3$ (a deposition ratio of 2.5:1, a temperature of 550 °C) generate a cross-section corrected XPS core level peak ratio of 1:1 on (001) LaAlO$_3$ substrates while maintaining the +2 oxidation state of Cu. RHEED patterns recorded throughout the growth of 1000-Å-thick films on LaAlO$_3$ substrates show similar patterns to those of the films grown on SrTiO$_3$. Again, three different patterns, A, B, and C, were detected in the sequence A–C–B–C–A, but not with spacings of 3.8, 5.4, and 8.5 Å, respectively. Again the four-fold symmetry as the film is rotated around its normal implies a tetragonal or cubic unit cell, but this time one with of a slightly smaller size (that of 3.8 Å a side). This is not surprising, given that the unit cell size of the LaAlO$_3$ substrate is slightly smaller than that of SrTiO$_3$, being $a=b=c=3.78$ Å. However, LaAlO$_3$ is not absolutely cubic because the angles between axes of the unit cell, α, is 90.12°.[24]

When an isotropic, purely elastic unit cell is put under a two-dimensional compression, the lattice parameter of the unit cell perpendicular to the surface will compensate, by increasing in size, such that the overall energy is minimized. Poisson's ratio, ν, is a measure of this response, defined as $\nu=-\epsilon_a/\epsilon_\perp=-\epsilon_b/\epsilon_\perp$, where ϵ_a and ϵ_b are the strains in the plane, and $\epsilon_\perp$ is the strain perpendicular to the two-dimensional compression. For an isotropic and purely elastic medium, $\nu=\frac{1}{3}$. In reality, most materials have a $\nu \approx 0.25$–0.3.

Assuming the original lattice parameter for this film is the same as that for SrCuO$_2$ and assuming a Poisson's ratio for SrCuO$_2$ of 0.25, a decrease in the a and b lattice parameter to 3.78 Å would lead to an expansion in the c axis to 3.91 Å. As shown in Fig. 5 a c-axis spacing of 3.87 Å is seen if the peaks are indexed as (002) and (004). Off-axis XRD shows that the {103} and {112} peaks have the correct ϕ scan symmetries and are in the correct θ and ω angles for a unit cell of dimensions $a=b=3.78$ Å and $c=3.87$ Å, giving a Poisson's ratio of 0.27 for this film.

Beyond the lattice parameters fitting those of a strained SrCuO$_2$ phase, as seen from Fig. 5, the only peak that is visible is the 002, suggesting a systematic absence of the $(h+k+l)=n$ peaks where n is odd. This is to be expected for a body-centered unit cell such as SrCuO$_2$. As already mentioned, the cross-section corrected XPS core level area ratios for Cu to Sr is 1:1, even though the deposition condi-
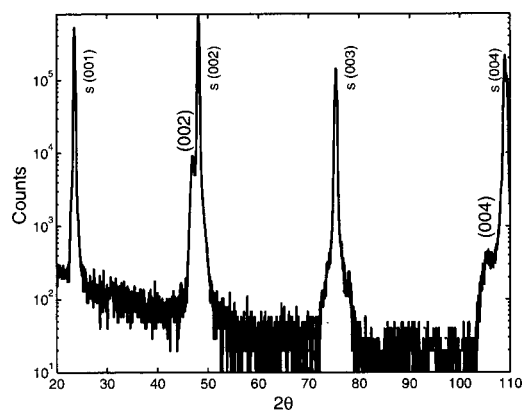
FIG. 5. A $2\theta-\omega$ x-ray scan of a film grown at 550 °C on LaAlO$_3$.

tions were set, similar to the growths on SrTiO$_3$ substrates, to grow a film with a 2:1 Cu to Sr ratio. To within our capability, these films are single phase.

C. Previous growth conditions for SrCuO$_2$

Previous thin film work on the growth of SrCuO$_2$ on SrTiO$_3$ has generally been done at about 500 °C and under oxidation conditions which are typically provided by about 1×10^{-5} torr of NO$_2$, or a maximum atomic oxygen flux of roughly 5×10^{15} atoms/cm^2 s. Typical XRD results show that the Sr to Cu ratio is not 1:1, but rather ≈ 0.8:1.[25–29] One group, however, did grow SrCuO$_2$ with an XRD result that suggests a Sr:Cu ratio of 1:1.[30] In this current work, the growth conditions that generated SrCuO$_2$ were different from these previously published works. We have generated SrCuO$_2$ while under a much higher oxidation potential due to the use of the high flux atomic oxygen source.

VI. EPITAXIAL INFLUENCE

The effects of epitaxial influence can range from simply generating a strained version of a stable phase to forcing an alternative, metastable structure to grow. In the case of growing a stable phase under strain, ample reports in the literature indicate that this can be a meaningful way of controlling material properties such as the critical temperature of superconductors.[31] One interesting issue surrounding this is the ability of oxides to maintain a strained structure well beyond the predicted critical thickness at which relaxation occurs. The theoretical work on relaxation thickness is based on the assumption of an energy balance between the strain energy of the film and energy associated with defect nucleation and motion (see, for example, Ref. 32). These models, which predict a critical thickness in the vicinity of 5–50 monolayers for a 1% strain, have little connection to oxides for which examples abound of films in highly strained states (often, as in this work, more than ten times thicker than the models would predict). For example, the work of James and Hibma[33] showed the critical thickness of NiO on MgO to be 600 Å, as compared to the predicted 75 Å value. In this work, about 1000 Å of SrCuO$_2$ maintained a highly strained structure thereby allowing it to grow coherently on LaAlO$_3$.

The main interest of this work is in the stabilization of an alternate, or metastable structure—in this case, a high pressure structure. In 1980, Machlin and Chaudhari[34] published a theory of pseudomorphic stabilization (i.e., stabilizing an alternative and assumed metastable structure), which considers a balance between surface energy, bulk free energy, and strain energy. When trying to deal with the growth of oxides (versus the case of metals and alloys, with which Machlin and Chaudhari dealt), the form of the surface energy term must take into account the electrostatic energy and polarity issues relevant to such highly ionic compounds. The use of Machlin and Chaudhari's underlying equation is difficult, as little data exists for many of the terms. They, however, make headway by assuming there is no difference in the interface energy between the metastable phase and the substrate as compared to the interface energy between the stable phase and the substrate. For metals this is a legitimate assumption as the first atomic layer above the substrate surface is in distinguishable between the metastable and stable phases. For multielement oxides, this is probably an inappropriate assumption, given that there is evidence of unit-cell-by-unit-cell[35] growth which suggests that the electrostatic energy strongly influences even a single monolayer.

Almost all the experimental literature associated with epitaxial stabilization of an alternative, high pressure structure deals with compounds having the formula $(ABO_3)(AO)_n$, where A is a larger cation than B. If the ABO_3 ($n=0$) compounds form a perovskite structure under atmospheric pressure, then it is expected that the other members of the $(ABO_3)(AO)_n$ series can also be formed.[36] SrTiO$_3$(SrO)$_n$ is a prime example of this type of series. The $n=0$ compounds SrTiO$_3$ is easily grown as a thin film, and the $n \neq 0$ series of compounds, $(SrTiO_3)(SrO)_n$, has also been generated as thin films.[37] Kafalas and Longo[36] further suggest that for bulk materials, growing the $n=1$ compounds (A_2BO_4) requires the lowest pressure, and that as n decreases to zero $(n=\frac{1}{2}, \frac{1}{3}, \ldots, 0)$, the pressure required increases—meaning that growing-ABO_3 would require the highest pressure out of the series.

Typically the $n=0$ compounds (ABO_3) belong to the *structural high pressure materials* class with a high pressure perovskite structure and a low pressure hexagonal structure. An example of a successful growth of both the perovskite and hexagonal structures is YMnO$_3$. Salvador et al.[38] grew the perovskite structure on SrTiO$_3$, NdGaO$_3$, and LaAlO$_3$ while Fujimura et al.[39,40] grew the hexagonal structure on MgO. BiMnO$_3$[41] has also been grown with the perovskite structure on SrTiO$_3$, but the hexagonal structure has yet to be grown. A report of the growth of the high pressure structure of LaCuO$_3$[42] as a thin film on SrTO$_3$ is in the literature, although the oxidation of the structure was not complete. The published failures to stabilize the perovskite structure within the class of structural high pressure materials are for BaRuO$_3$[43] and SmCuO$_3$.[44]

When $n \neq 0$, the compounds (i.e., layered perovskite-type materials) fall under the definition of *oxidation high pressure materials*. Ba$_2$CuO$_{4-\delta}$,[45,46] La$_2$CuO$_{4-\delta}$,[47] and Ba$_2$RuO$_{4-\delta}$[48] have all been grown. It is interesting to note

that while $Ba_2RuO_{4-\delta}$, where $n=1$, could be grown, the $n=0$ version, $BaRuO_3$, could not.

When considering these successes and failures it is worth noting the substrate choice and lattice mismatch. The most naive approach to deciding which substrate to use is to pick one that will induce a compressive pressure in the film. In general, most high pressure materials are grown under about 5–7 GPa, and since most oxides have an elastic modulus between 30 and 70 GPa, it is necessary to choose a substrate with an identical space group and a 10% smaller lattice in order to induce a 3–7 GPa compressive-type stress in the film. The listed successes above grew on substrates with related space groups that have a range of mismatch from 6% larger to 2% smaller than the desired film. Unfortunately, data do not yet exist for all these materials with which one could compare the minimum pressure needed for bulk growth and the permissible lattice mismatch for thin film growth. Also, the complied data are not big enough yet to tell much about what is needed from the symmetry of the substrate. Is an identical space group match needed, or is the stacking sequence of the largest element in the substrate and film (normally oxygen) the most important to match?

$SrCuO_2$, $SrCu_2O_3$, and CrO_2 (another notable high pressure material for which MBE-like thin film growth would be advantageous) do not fit into the $(ABO)_3(AO)_n$ formula. $SrCu_2O_3$ and CrO_2 are cases of *combination high pressure materials,* while $SrCuO_2$ is a *structural high pressure material* (although the low pressure structure has not been grown as a thin film). The high pressure structure of $SrCu_2O_3$ cannot be grown, as is shown in this work, even when the stoichiometry of Cu to Sr is set to 2:1 and oxidation of the Cu is maintained at $+2$. Instead, an alternative, metastable structure is grown, consistent with that of $SrCuO_2$ but with 50% of the Sr missing. The lattice mismatch is basically zero for $SrCu_2O_3$ and $SrCuO_2$ on $SrTiO_3$.

The growth of CrO_2 thin films is a special case, as there is currently one method to grow thin film without high pressure. This method makes use of an intermediate chemical reaction to facilitate the growth,[5,49] and so should not be considered within the framework of this discussion. The attempted growth of CrO_2 films without high pressure and without the intermediate chemical reaction has not been successful.[5] In this case, the substrate mismatch was very large because the substrate (TiO_2) unit cell is almost 10% larger than the CrO_2 unit cell. It is worth pointing out that the level of oxidation was not an issue with the attempted growth of CrO_2 as CrO_3, which has the highest oxidation state available for Cr, was successfully grown.

VII. CONCLUSION

With the use of a high flux atomic oxygen source and *in situ* x-ray photoemission spectroscopy, we have achieved the growth of a single phase thin film with a Cu to Sr ratio of 2:1 while maintaining full oxidation, enabling us to obtain the formal $SrCu_2O_3$ stoichiometry. However, an alternative, metastable structure is stabilized on $SrTiO_3$ substrates. This structure can best be described as being based on the tetragonal infinite layer material $SrCuO_2$ with 50% of the Sr atoms

missing, not the bulk high pressure orthorhombic structure expected for $SrCu_2O_3$. Growth under the same conditions on $LaAlO_3$ structures leads to a highly strained $SrCuO_2$ structure with a Cu to Sr ratio of 1:1. This indicates that both the chemistry and the structure can be highly influenced by substrate choice. It also suggests that the Cu is either very mobile or quite volatile. The presence of Cu is also strongly influenced by the substrate temperature, on both $SrTiO_3$ and $LaAlO_3$ substrates. We believe the failure to stabilize the orthorhombic, high pressure bulk structure of $SrCu_2O_3$ is not due to an inability to fully oxidize the materials during growth, but rather the failure of epitaxy to stabilize the required long range order of the desired structure.

The current literature shows only a handful of successes and several failures when trying to use epitaxy to stabilize high pressure structures. All of the successes have been with compounds that are part of the series described by $(ABO_3)(AO)_n$ and which have the layered perovskite type structure. No clear picture emerges from these results as to whether the use of epitaxial influence is a robust means of stabilizing high pressure structures, or whether it only works for a few very select cases. Further systematic work on the bulk growth as a function of pressure, and on thin film growth as a function of substrate symmetry and unit cell size is needed.

Note added in proof. After submission of this paper, an article by Schoen *et al.*[54] claimed field effect-induced modulation of transport properties in thin films of the spin ladder compound $[CaCu_2O_3]_4$, which they claim has an identical structure to $SrCu_2O_3$. The work of Cavellin *et al.*[55] regarding the structure and chemical nature of the $[CaCu_2O_3]_4$ films referenced by Schoen *et al.* does not show an unambiguous analysis of the films structure or chemistry. A technical comment by Ingle *et al.*[56] was recently published on this point.

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