Epitaxial stabilization of SrCu$_3$O$_4$ with infinite Cu$_{3/2}$O$_2$ layers

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Abstract

We report the epitaxial thin film synthesis of SrCu$_3$O$_4$ with infinitely stacked Cu$_3$O$_4$ layers composed of edge-sharing CuO$_4$ square-planes, using molecular beam epitaxy. Experimental and theoretical characterizations showed that this material is a metastable phase that can exist by applying tensile biaxial strain from the (001)-SrTiO$_3$ substrate. SrCu$_3$O$_4$ shows an insulating electrical resistivity in accordance with the Cu$^{2+}$ valence state revealed X-ray photoelectron spectroscopy. First-principles calculations also indicated that the unoccupied $d_{3z^2-r^2}$ band becomes substantially stabilized owing to the absence of apical anions, in contrast to $A_2$Cu$_3$O$_4$Cl$_2$ ($A = $ Sr, Ba) with an $A_2$Cl$_2$ block layer and therefore a trans-CuO$_4$Cl$_2$ octahedron. These results suggest that SrCu$_3$O$_4$ is a suitable parent material for electron-doped superconductivity based on the Cu$_3$O$_4$ plane.
Introduction

The discovery of superconductivity in La$_{2-x}$Ba$_x$CuO$_4$ has led to intensive research to explore layered cupric compounds with high $T_c$’s. They universally possess two-dimensional (2D) CuO$_2$ planes with an apex-linked CuO$_4$ square-planar coordination, sandwiched by blocking layers (e.g., LaO layers in La$_2$CuO$_4$ and BaO layers in YBa$_2$Cu$_3$O$_6$). Superconductivity is observed when appropriate carriers are injected to the ‘parent’ Cu$^{2+}$O$_2$ plane. Carrier doping can usually be done via aliovalent substitution or by creating defects in the blocking layers.

Despite extensive research, most cuprate superconductors are hole-doped, and only a handful electron-doped materials have been reported. In the electron-doped case, the absence of apical anions in the CuO$_2$ plane is considered as essential. ACuO$_2$ ($A$ = alkaline earth metals), which consists of infinitely stacked CuO$_2$ planes, $[\text{CuO}_2]_{\infty}$, separated only by $A$ cations, is therefore the ideal host system. High-pressure synthesis and thin film growth techniques allow the expansion of accessible compositional range. For example, thin film studies show superconductivity upon electron doping, namely in the infinite layer (IL) Sr$_{1-x}$Ln$_x$CuO$_2$ ($Ln$ = La, Nd) with $T_c \sim 40$ K. More recently, the isoelectric nickel oxide film has been shown to exhibit superconductivity at about 10 K.

In parallel with compounds having CuO$_2$ planes, different structural motifs have been explored. In particular, the Cu$_{3/2}$O$_2$ (or Cu$_3$O$_4$) plane in $A_2$Cu$_3$O$_4$Cl$_2$ ($A$ = Sr, Ba), characterized by a periodic insertion of 1/2 Cu in the CuO$_2$ plane (Figure 1b, right), has attracted attention since the Cu arrangement in the Cu$_3$O$_4$ plane is reminiscent of a line-centered square lattice known as the Lieb lattice and electron-doped superconductivity is suggested. Unfortunately, the blocking $A_2$Cl$_2$ layer in $A_2$Cu$_3$O$_4$Cl$_2$ provides apical (Cl) anions to Cu(1), resulting in trans-CuO$_4$Cl$_2$ octahedra (Figure 1a), which is thus unsuitable for electron-doped superconductivity. In fact, the absence of superconductivity in hole-doped Ba$_2$Cu$_3$O$_4$Cl$_2$ has been discussed in terms of hole localization at the apical ligand. It is thus crucial to explore materials with the Cu$_3$O$_4$ plane without apical anions.
This paper reports on the thin film growth of SrCu$_3$O$_4$, using molecular beam epitaxy (MBE). In contrast to A$_2$Cu$_3$O$_4$Cl$_2$, this compound epitaxially grown on a SrTiO$_3$ substrate is composed of infinite layers of Cu$_{3/2}$O$_2$ (Cu$_3$O$_4$) separated only by Sr cations. First-principles calculations verify that the biaxial tensile strain from the substrate stabilize SrCu$_3$O$_4$ against competing phases of “SrCu$_2$O$_3$ + CuO”. Furthermore, the $d_{3z^2-r^2}$ orbitals become substantially stabilized, making SrCu$_3$O$_4$ a unique candidate for electron-doped superconductor based on the Cu$_3$O$_4$ lattice.

Experiments and Calculations

Target films were grown on (001)-SrTiO$_3$ single crystalline substrates using a custom-made reactive MBE system (EGL-1420-E2, Biemtron). Elemental Sr and Cu fluxes were simultaneously provided from conventional Knudsen cells typically with flux rates of 0.05 Å/s for Sr and 0.02 Å/s for Cu, as determined by an INFICON quartz crystal microbalance system before the growth. These rates approximately correspond to the nominal composition of Sr:Cu = 1:2. Ozone gas was supplied using a commercial ozonizer with a background pressure of $4 \times 10^{-6}$ Torr. After annealing the substrates at about 700 °C for 2–4 hours in vacuum, the temperature, monitored by an optical pyrometer with the wavelength of $\lambda = 8–13$ µm (IR-CAI3TS, CHINO), was set at 472 °C. The surface structure of the film and the substrate was monitored \textit{in-situ} by reflection high-energy electron diffraction (RHEED) with an acceleration voltage of 20 keV.

X-ray diffraction (XRD) measurements after the growth were carried out at room temperature (RT) using a Rigaku SmartLab diffractometer equipped with a Cu K$\alpha_1$ monochromator. The scanning transmission electron microscopy (STEM) observation and chemical composition analysis were conducted using a JEOL transmission electron microscope (JEM-ARM200F) at an operating voltage of 200 kV equipped with an energy dispersive X-ray spectrometer (JED-2300T SDD). Incident electron beam along the stacking direction of the
film was transmitted through a hole made by removing the substrate by Ar-ion beam milling. The valence state of copper was investigated by means of X-ray photoelectron spectroscopy (XPS) with Mg Kα radiation \( (hν = 1253.6 \text{ eV}; \text{Ulvac-Phi Model5500}) \). The binding energies \( (E_B) \) of each XPS spectrum with potential extrinsic \( E_B \) shifts caused by the charging effect were calibrated with the adventitious C 1s peak at 284.5 eV. As a reference of divalent copper, XPS spectra for powder samples of SrCuO₂ and SrCu₂O₃ prepared under the reported conditions⁹,¹⁴ were collected. The electrical resistivity \( \rho \) was measured by using a standard four-probe method. Magnetization measurements were performed with a commercial superconducting quantum interference device (SQUID) magnetometer (magnetic property measurement system (MPMS), Quantum Design).

To examine structural stability and electronic properties, we performed first-principles calculations using the projector augmented wave method¹⁸ as implemented in the Vienna \textit{ab initio} simulation package (VASP).¹⁹–²² We used the Perdew-Burke-Ernzerhof parametrization of the generalized gradient approximation (PBE-GGA)²³ without the spin-orbit coupling. For calculations of the total energy and the phonon dispersion, we optimized the crystal structure until the Hellmann-Feynman force acting on each atom becomes less than 0.01 eV Å⁻¹. The plane-wave cutoff energy was 550 eV, and \( 10 \times 4 \times 10, 10 \times 14 \times 10, \) and \( 10 \times 10 \times 10 \) \( k \)-meshes were used for CuO, SrCu₂O₃, and SrCu₃O₄, respectively. To calculate the phonon dispersion, we assumed for simplicity a non-magnetic state using a \( 3 \times 3 \times 3 \) \( q \)-mesh, using the experimental lattice constants of the thin film \( (a = 5.42 \text{ Å} \) and \( c = 3.53 \text{ Å}) \). The finite displacement method, as implemented in the Phonopy software,²⁴ was used. The (non-magnetic) electronic band dispersion of SrCu₃O₄ was obtained using the structural parameters obtained by our experiments.
Result and discussion

We initially investigated the crystal structure of the obtained film on the SrTiO$_3$ substrate using high-resolution XRD. The out-of-plane $\theta$–$2\theta$ pattern shows peaks around $2\theta = 25^\circ$ and $52^\circ$, suggesting the growth of well-oriented epitaxial films (Supporting Information, Figure S1). The out-of-plane lattice constant was estimated to be 3.53 Å, slightly larger than the bulk samples of IL-SrCuO$_2$ (3.432 Å) and spin-ladder SrCu$_2$O$_3$ (3.495 Å), both composed of Cu$^{2+}$–O layers with Sr$^{2+}$ cations in between. Distinct fringes in the XRD profile (Figure S1) indicate the atomic scale smoothness of the interface between the substrate and the film. The spacing of fringes gave a film thickness of about 30 nm, in agreement with that estimated from the growth rate. The rocking curve of the peak around $25^\circ$ gave a full width at half-maximum (FWHM) value of $\Delta\omega = 0.09^\circ$, indicating excellent film quality. No target phase was observed when KTaO$_3$ and DyScO$_3$ substrates with larger strain (vs. SrTiO$_3$) were used under the same growth conditions (Supporting Information, Figure S2).

To clarify the in-plane structure of the film, we conducted STEM experiments. Figure 2a shows a high-angle annular dark-field (HAADF) STEM image for a 30 nm thickness sample, highlighting the atomic position of Sr and Cu corresponding, respectively, to bright and dark spots. The line scans in Figure 2b demonstrate the change in intensity $I$ at Sr and Cu positions. Since $I$ is proportional to the average atomic number $Z$ of the projected atomic column and scales as $I \sim Z^n$ ($n = 1.6$–$1.9$), these scans can distinguish between Sr and Cu atoms. The observed pattern is different from those expected from the CuO$_2$ plane (Figure 1b, left) and the BaCu$_3$O$_4$-type structure, but instead suggests the formation of Cu$_3$O$_4$ (Cu$_{3/2}$O$_2$) planes (Figure 1b, right), as found in $A_2$Cu$_3$O$_4$Cl$_2$, leading to SrCu$_3$O$_4$. Annular bright-field scanning transmission electron microscopy (ABF-STEM) is also consistent with the formation of Cu$_3$O$_4$ (Cu$_{3/2}$O$_2$) planes (Figure 2c). Note that EDX analysis exhibited a slightly smaller atomic ratio of Cu/Sr $\simeq$ 2.5, probably due to the influence of surface impurity phases, as will be shown later. The corresponding electron diffraction along the $c$ axis (i.e., perpendicular to the substrate) shows a four-fold symmetry with an in-plane lattice
constant of \(a = 5.42\, \text{Å}\) (Supporting Information, Figure S3), which is consistent with the STEM image. The right panel of Figure 1b shows the most plausible structure of SrCu\(_3\)O\(_4\) with the \(P4/mmm\) space group (No. 123), where Sr is at the 1b site, Cu at the 1c and 2f sites, and O at the 4j site (Supporting Information, Table S1). The in-plane cell is related to the substrate (SrTiO\(_3\) perovskite) by \(\sqrt{2}a \times \sqrt{2}a\), as depicted in Figure 2c.

The X-ray reciprocal space mapping (RSM) in Figure 3a shows a peak around \(2\theta = 30.2^\circ\) and \(\chi = 33.1^\circ\), corresponding to the 101 reflection of SrCu\(_3\)O\(_4\). Known Sr-Cu-O compounds including Sr\(_2\)CuO\(_3\),\(^{26}\) SrCuO\(_2\),\(^{27}\) Sr\(_{14}\)Cu\(_{24}\)O\(_{41}\),\(^{27}\) SrCu\(_2\)O\(_2\),\(^{28}\) and Sr\(_{n-1}\)Cu\(_{n+1}\)O\(_{2n}\) (\(n = 3, 5\))\(^{14}\) exhibit no reflection at this \(2\theta\) angle. The azimuthal \(\phi\) scan for the 101 reflection showing four peaks separated by 45° from the 101 peaks of the SrTiO\(_3\) substrate (Figures 3c and 3e) is consistent with the STEM image (Figures 2a and 2c). Coherent growth of the film on the substrate is confirmed by the RSM around the 113 reflection (Figure 3b), and such coherent growth is reproduced in other films (Supporting Information, Figure S4). The in-plane lattice constant estimated from RSM measurements, \(a = \sqrt{2} \times 3.90 = 5.52\, \text{Å}\), was found to be 2% more tensile-strained than that estimated from ED measurements (\(a = 5.42\, \text{Å}\), Supporting Information, Table S2), as a consequence of the removal of the SrTiO\(_3\) substrate to observe the in-plane structure for ED measurements. Other reflections, such as 111, 131, and 202, are also compatible with the crystal symmetry of the SrCu\(_3\)O\(_4\) structure (Figure 3d). SrCu\(_3\)O\(_4\) is the first experimental realization of Cu\(_3\)O\(_4\) infinite layers (Figure 1a and 1b, right). We note that the orthorhombic BaCu\(_3\)O\(_4\) also has a layer of the Cu\(_3\)O\(_4\) composition, but is composed of diamond chains (or diagonal ladders).\(^{25,29}\)

Using the lattice constants of \(a = 5.42\, \text{Å}\) and \(c = 3.53\, \text{Å}\) determined by XRD and STEM observations, we performed bond valence sum calculations and obtained +2.13 for Sr and +1.94 for Cu, in accordance with the formal valences of Sr\(^{2+}\) and Cu\(^{2+}\). Figure 4a shows the 2p-core-level XPS spectrum of Cu in a SrCu\(_3\)O\(_4\) film (5 nm thickness), plotted with SrCuO\(_2\), SrCu\(_2\)O\(_3\), Cu\(_2\)O, and CuO.\(^{6}\) The spectrum has distinct satellite peaks separated by \(\sim 9\, \text{eV}\), thus being reasonably ascribed to the divalent copper state.
Figure 4b shows the temperature dependence of the in-plane electrical resistivity $\rho$ of the SrCu$_3$O$_4$ film with 30 nm thickness. It shows an insulating behavior in the temperature range from 400 to 270 K, but $\rho$ was too large to measure at lower temperatures. Impurity scattering from defects and impurities will have a negligible effect on the resistivity in the temperature range currently measured. The $\rho$–$T$ curve can thus be fitted well by a variable range hopping in 2D ($d = 2$), $\rho(T) = \rho_0 \exp(T_0/T)^{1/(d+1)}$, implying carrier hopping in the Cu$_3$O$_4$ plane. $A_2$Cu$_3$O$_4$Cl$_2$ with the Cu$_3$O$_4$ plane exhibits a canted antiferromagnetic phase transition of Cu(1) spins at $T_N = 380$ K ($A = $ Sr) and 332 K ($A = $ Ba). No sign of antiferromagnetic phase transition is seen in the resistivity and magnetization data collected at 270 K $< T < 400$ K and 5 K $< T < 400$ K, respectively, although SrCu$_3$O$_4$ is expected to be a Mott insulator. This is because it is difficult to probe antiferromagnetic order using thin films.

Let us discuss why the present MBE method has enabled the stabilization of SrCu$_3$O$_4$. In general, MBE growth provides near thermal equilibrium conditions, with much smaller kinetic energy than other growth techniques such as pulsed laser deposition and sputtering. For this reason, the synthesis of SrCu$_3$O$_4$ cannot be explained in terms of kinetic trapping. On the other hand, epitaxial strain from the substrate is the most likely source for the SrCu$_3$O$_4$ phase formation. This scenario is consistent with the observation that SrCu$_3$O$_4$ is formed only when the film thickness is less than 30 nm. For thicker films, impurity phases such as SrCu$_2$O$_3$ and CuO were observed in the STEM and RHEED images (Figure S5) and in the XPS data for the 30 nm film (Figure S6). In addition, finely tuned conditions are required (Supporting Information, Table S3); SrCu$_3$O$_4$ can be prepared with a narrow growth window of temperature ($T = 472 \pm 1$ °C) and Cu/Sr ratio (nominal ratio of Cu/Sr = 2$\pm 0.3$).

First-principles calculations were conducted to theoretically address the stability of SrCu$_3$O$_4$, in comparison with competing phases of SrCu$_2$O$_3$ and CuO. In an early stage of calculations, it was found that SrCu$_3$O$_4$ does not have an imaginary mode in the phonon dispersion when
calculated using experimental lattice constants (Figure S7). However, the total energy of SrCu$_3$O$_4$ is higher than that of “SrCu$_2$O$_3$ + CuO” by 0.19 eV per formula unit (here all the structural parameters were optimized), meaning that SrCu$_3$O$_4$ is dynamically stable (or structurally stable as one of the possible structures in the Sr-Cu-O composition) but not the most thermodynamically stable. In other words, this material cannot form in bulk owing to competing phases found in the Sr-Cu-O phase diagram.\textsuperscript{3,5,41} It is interesting to compare the stability between SrCu$_3$O$_4$ and the competing SrCu$_2$O$_3$ from the structural perspective. SrCu$_3$O$_4$ consists only of edge-sharing CuO$_4$ square planes, whereas SrCu$_2$O$_3$ has both edge- and corner-sharing CuO$_4$ square planes.\textsuperscript{44} Thus, the former structure appears to be more energetically unfavorable according to Pauling’s third rule.\textsuperscript{42} However, when tensile strain is applied to SrCu$_3$O$_4$, the Cu$_3$O$_4$ layer is stretched and the Cu-Cu repulsion between the edge-sharing CuO$_4$ square planes is relaxed.

We further compared the total energies of “SrCu$_3$O$_4$” and “SrCu$_2$O$_3$ + CuO” in the presence of epitaxial biaxial strain. To do this, in-plane lattice constants were fixed to the ‘normalized’ substrate lattice constant $a_0$ (where $a = b = \sqrt{2}a_0$ for SrCu$_3$O$_4$ and $a = c = a_0$ for SrCu$_2$O$_3$), and other structural parameters were optimized. The strain effect for CuO was not taken into account since CuO was found as an island on the film surface (Figure S5a). When biaxial strain is turned on (i.e., $a_0$ is varied), the relative energy of SrCu$_3$O$_4$, $E$(SrCu$_3$O$_4$) − $E$(SrCu$_2$O$_3$) − $E$(CuO), shows a parabolic shape with negative values for 3.91 Å < $a_0$ < 3.96 Å (Figure 5). The minimum is found at around 3.93 Å, which is close to the lattice constant of SrTiO$_3$ (3.905 Å) used as the substrate, suggesting that adequate tensile strain can stabilize the metastable phase of SrCu$_3$O$_4$. The appearance of SrCu$_2$O$_3$ and CuO impurities for thicker films (> 30 nm) would be due to some relaxation of the SrCu$_3$O$_4$ film from the substrate strain, as the film thickness increases. It is naturally considered that multiple domain formation can reduce the stress from the substrate.\textsuperscript{7,8} In this case, when the film thickness exceeds the critical value, the epitaxially stable phase and bulk stable phase grow simultaneously.\textsuperscript{7} This is another strain relaxation mechanism.
different from the misfit dislocations that appear in the film-substrate interface.\textsuperscript{9,10} Cross-sectional TEM images will provide detailed features of the domain formations and other possible dislocations along the growth direction, which will be left for future studies.

Finally, we discuss the difference in electronic structures between SrCu$_3$O$_4$ and A$_2$Cu$_3$O$_4$Cl$_2$. Here, the main purpose of the band structure calculation is to see the band width of the $d_{x^2-y^2}$ orbital between Cu(1) and Cu(2), and the energy difference between $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals. We thus performed the calculation assuming a non-magnetic and metallic state because otherwise the band width and the energy difference are strongly affected by the size of exchange splitting and become spin-dependent. The calculated band dispersion for “non-magnetic” SrCu$_3$O$_4$ near the Fermi energy (Figure 6a, 6b) show that the wide band from Cu(1) $d_{x^2-y^2}$ orbitals and the narrow band from Cu(2) $d_{x^2-y^2}$ orbitals are nearly decoupled, as found in A$_2$Cu$_3$O$_4$Cl$_2$.\textsuperscript{45} Furthermore, the $d_{3z^2-r^2}$ bands of SrCu$_3$O$_4$ are substantially stabilized (Figure 6c, 6d) owing to the square-planar coordination, in contrast to A$_2$Cu$_3$O$_4$Cl$_2$ containing chloride anions at the apical Cu(1) site. This means that SrCu$_3$O$_4$ is an ideal 2D system with half-filled $d_{x^2-y^2}$ orbitals on the Cu$_3$O$_4$ lattice, where electron-doped superconductivity may occur because the absence of apical anions is known to be crucial for electron-doped superconductivity in the CuO$_2$ case.\textsuperscript{2,5} If electron doping is possible in SrCu$_3$O$_4$, the absence of apical anions at the Cu(1) site is expected to prevent carrier localization, as observed in the CuO$_2$ system.\textsuperscript{16,17} The “inserted” Cu(2) may bring about an exotic superconducting state or magnetic ground state, for example, by ferromagnetic fluctuations introduced through 90°-type Cu(1)–O–Cu(2) interaction. Electron doping by chemical substitution, as demonstrated in La- or Nd-substituted IL-SrCuO$_2$\textsuperscript{2,10,11} and electric field gating\textsuperscript{46} in SrCu$_3$O$_4$ films, would be an interesting subject in the future.
Conclusion

We have succeeded in synthesizing SrCu$_3$O$_4$ thin films on a SrTiO$_3$ substrate using molecular beam epitaxy. SrCu$_3$O$_4$ consists of infinitely stacked Cu$_{3/2}$O$_2$ (Cu$_3$O$_4$) planes separated only by Sr cations, in contrast to $A$$_2$Cu$_3$O$_4$Cl$_2$ ($A$ = Sr, Ba) with the $A$$_2$Cl$_2$ block layer. Experimental and theoretical investigations revealed that this material is a metastable phase that can exist by applying suitable tensile biaxial strain from the substrate. Thus stabilized SrCu$_3$O$_4$ shows an insulating behavior, as expected from the formal Cu$^{2+}$ valence. The band structure with substantially stabilized (unoccupied) $d_{3z^2-r^2}$ orbitals (vs $A$$_2$Cu$_3$O$_4$Cl$_2$) owing to the absence of apical anions suggests that this material is a suitable parent material for electron-doped superconductivity based on the Cu$_3$O$_4$ lattice.

Associated content

Supporting Information Available

Additional information on results of X-ray diffraction, electron diffraction, HAADF-STEM, XPS, and calculations of phonon dispersion of SrCu$_3$O$_4$.

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Figure 1: (a) Crystal structures of $A_2Cu_3O_4Cl_2$ ($A = \text{Sr, Ba}$) (left) and SrCu$_3$O$_4$ (right) with Cu$_3$O$_4$ (Cu$_{3/2}$O$_2$) planes. (b) The pristine CuO$_2$ plane with apex-linked CuO$_4$ units (left) and the Cu$_3$O$_4$ plane with edge-linked CuO$_4$ units (right) showing interpenetrating square lattices by Cu(1) and Cu(2) (dashed lines).
Figure 2: (a) High resolution HAADF-STEM image of the film with 30 nm thickness taken at RT. (b) Line scans along lines a-i \((i = 1, 2, 3)\) (top) and those along lines b-i \((i = 1, 2, 3)\) (bottom) shown in (a). (c) ABF-STEM image.
Figure 3: (a)–(b) X-ray reciprocal space mappings around 101 and 113 of the SrCu$_3$O$_4$ film. (c)–(e) φ scans of the 101 reflection of the SrTiO$_3$ substrate and representative peaks of the film.
Figure 4: (a) XPS Cu 2p core-level spectra of the SrCu$_3$O$_4$ film and several copper oxides. (b) Temperature dependence of electrical resistivity $\rho$ of the SrCu$_3$O$_4$ film. The solid line represents the variable range hopping model for 2D (see text).
Figure 5: Energy difference between the calculated total energy of SrCu$_3$O$_4$ and that of SrCu$_2$O$_3$ + CuO under the epitaxial strain, where $a_0$ is the in-plane lattice constant of the substrate. We assumed the fixed in-plane lattice constants $a = b = \sqrt{2}a_0$ for SrCu$_3$O$_4$ and $a = c = a_0$ for SrCu$_2$O$_3$. This line is the guide to the eye.
Figure 6: Calculated electronic band structure of SrCu$_3$O$_4$ with (a) Cu(1) $d_{x^2−y^2}$, (b) Cu(2) $d_{x^2−y^2}$, (c) Cu(1) $d_{3z^2−r^2}$, and (d) Cu(2) $d_{3z^2−r^2}$ orbitals highlighted in blue. The Fermi energy is set at zero. Note that the notation of $d_{x^2−y^2}$ is used here in accordance with the usual manner of cuprates, while $d_{xy}$ is a more suitable notation to the present case since the $ab$ axes of SrCu$_3$O$_4$ are rotated by 45° from the $xy$ axes used in the calculations; i.e., the in-plane structure of SrCu$_3$O$_4$ is expanded to $\sqrt{2}a \times \sqrt{2}a$ with respect to IL-SrCuO$_2$. 
**TOC graphic and synopsis**

We prepared epitaxial SrCu$_3$O$_4$ thin films with infinitely stacked Cu$_3$O$_4$ layers composed of edge-sharing CuO$_4$ square-planes, using molecular beam epitaxy. Experimental and theoretical characterizations revealed that SrCu$_3$O$_4$ can exist under tensile biaxial strain from the (001)-SrTiO$_3$ substrate. This material is a suitable system for electron doped superconductivity based on the Cu$_3$O$_4$ plane.

![Diagram of SrCu$_3$O$_4$ structure](image)

For Table of Contents Only
Supporting Information of “Epitaxial stabilization of SrCu$_3$O$_4$ with infinite Cu$_{3/2}$O$_2$ layers”

Abstract

In this supporting information, we present X-ray diffraction (XRD), experimental and calculation results of electron diffraction (ED) for SrCu$_3$O$_4$ films grown on the (001)-SrTiO$_3$ substrate. We also show results of high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) for thick (30 nm) films, and X-ray photoelectron spectroscopy (XPS) for the thin (5 nm) and thick (30 nm) films. In addition, we present the first principles calculation of the phonon dispersion of SrCu$_3$O$_4$ with the experimental lattice constants ($a = 5.42$ Å and $c = 3.53$ Å).

XRD analysis of the SrCu$_3$O$_4$ film on the SrTiO$_3$ substrate

Figure S1 shows the out-of-plane $\theta$–$2\theta$ XRD pattern for the film on the (001)-oriented SrTiO$_3$ substrate grown in the present optimal growth condition ($T = 472$°C, nominal ratio of Cu/Sr = 2, and O$_3$ gas flow with a background pressure of $4 \times 10^{-6}$ Torr). Sharp peaks with distinct fringes were observed around $2\theta = 25^\circ$ and $52^\circ$, suggesting the successful growth of a well-oriented and excellent quality film, although a tiny unknown peak is present at around $42^\circ$. A film thickness is estimated from the spacing of fringes to be about 30 nm, which agrees with the estimation from the growth rate. The inset shows the rocking curve of the peak around $25^\circ$, showing a full width at half-maximum of $\Delta \omega = 0.09^\circ$. In Table II we summarized structural parameters of SrCu$_3$O$_4$. 
Figure S1: Out-of-plane $\theta$–2$\theta$ XRD patterns of films with a 30 nm thickness. SrTiO$_3$ substrate peaks are marked with asterisks. Inset shows rocking curve of the peak around 25°.

Growth of films on other substrates

We also performed experiments using other substrates than SrTiO$_3$, such as the (001)-oriented KTaO$_3$ and (110)-oriented DyScO$_3$ substrates under the present optimal growth condition for the growth of SrCu$_3$O$_4$ films on the SrTiO$_3$ substrate. For these KTaO$_3$ and DyScO$_3$ substrates, one can expect larger tensile strain than the SrTiO$_3$ substrate for SrCu$_3$O$_4$ (see the inset of Figure S2). However, we did not obtain the single phase of SrCu$_3$O$_4$ on these substrates, respectively. Using the KTaO$_3$ substrate, we obtained a film containing three phases such as $c$-axis oriented SrCu$_2$O$_3$, $a$-axis oriented Sr$_{14}$Cu$_{24}$O$_{41}$, and possibly $c$-axis oriented SrCu$_3$O$_4$ (Figure S2). On the other hand, using the DyScO$_3$ substrate, we obtained a film containing two phases such as $c$-axis oriented SrCu$_2$O$_3$, and $a$-axis oriented Sr$_{14}$Cu$_{24}$O$_{41}$, although XRD intensities of these phases are very small (Figure S2). Since DyScO$_3$ has a pseudo-cubic structure, it is also possible that SrCu$_3$O$_4$ could not be obtained due to anisotropic strain. The obtained phases here are determined by XRD peak
Table 1: Structural parameters for the thin film of SrCu$_3$O$_4$. The space group: $P4/mmm$ (No. 123); lattice constants: $a = 5.42$ Å, and $c = 3.53$ Å.

| Atom | Site | x   | y   | z    |
|------|------|-----|-----|------|
| Sr   | 1b   | 0   | 0   | 1/2  |
| Cu   | 1c   | 1/2 | 1/2 | 0    |
| Cu   | 2f   | 0   | 1/2 | 0    |
| O    | 4j   | 0.25| 0.25| 0    |

We discuss more details of the strain effect for the synthesis of SrCu$_3$O$_4$ in the main text of this paper.
Figure S2: Out-of-plane $\theta$–2$\theta$ XRD patterns of films on the SrTiO$_3$, DyScO$_3$, and KTaO$_3$ substrates. The upper inset shows the relation between the substrate lattice constant and the in-plane lattice constant of SrCu$_3$O$_4$ divided by $\sqrt{2}$. The lower inset shows the enlarged XRD data of the film on the DyScO$_3$ substrate. Vertical dot lines indicate peak positions of SrCu$_3$O$_4$.

Experiments and calculations for ED of the SrCu$_3$O$_4$ film

In Figure S3a, we present experimental ED patterns for the same SrCu$_3$O$_4$ film as shown in Figure 2 of the main text. One can clearly see that the in-plane structure has a four-fold symmetry. The in-plane lattice constant is estimated as $a = 5.42$ Å. This observation is in good agreement with the calculation of the ED pattern (Figure S3b), assuming the tetragonal unit cell of the given structure of SrCu$_3$O$_4$ (see the right panel of Figure 1a of the main text and Table [1]). We summarized observed and calculated $d_{hkl}$ parameters in Table 2.
Figure S3: (a) Electron diffraction pattern of the film taken at room temperature along [001]. (b) Calculated pattern of electron diffraction, assuming a tetragonal structure with the in-plane lattice constant of 5.42 Å.

Table 2: Observed and calculated $d_{hkl}$ for representative ED spots. Numbers correspond to spot numbers in Figure S2a.

| No. | measured $d_{hkl}$ (nm) | calculated $d_{hkl}$ (nm) | hkl |
|-----|------------------------|--------------------------|-----|
| 1   | 0.541                  | 0.542                    | 100 |
| 2   | 0.543                  | 0.542                    | 010 |
| 3   | 0.384                  | 0.383                    | 110 |
| 4   | 0.271                  | 0.271                    | 200 |
| 5   | 0.384                  | 0.383                    | 110 |

Growth condition and reproducibility of the SrCu$_3$O$_4$ growth

For the determination of optimal growth conditions, we performed experiments by changing temperature and the flow rate of O$_3$ gas. In Table 3, we summarized the results of the synthesis of SrCu$_3$O$_4$ on the SrTiO$_3$ substrate at various temperatures and background pressures at a Cu/Sr ratio of 2. Here, the quality of the film was checked by XRD peak positions, fringes in the out-of-plane $\theta$–$2\theta$ XRD scan, impurities and multiple phases. In the present study, the optimal growth condition for the SrTiO$_3$ substrate was 472 ± 1°C and 4×10$^{-6}$ Torr at a nominal Cu/Sr ratio of 2. Note that in the same temperature and pressure conditions, the single phase of SrCu$_3$O$_4$ was not obtained at different Cu/Sr ratios such as
Table 3: Summary of the growth conditions (temperature and background pressure) for SrCu$_3$O$_4$ films, with a nominal Cu/Sr ratio of 2. Double circles indicate that the XRD data showed the expected peaks and fringes. A single circle means that the film possesses the expected peaks, but no fringe is present. Triangles indicate the inclusion of multiple phases, including SrCu$_3$O$_4$, and crosses indicate the absence of peaks from SrCu$_3$O$_4$.

| $T$(K)/$P$(Torr) | $3.0 \times 10^{-6}$ | $3.5 \times 10^{-6}$ | $4.0 \times 10^{-6}$ | $5.0 \times 10^{-6}$ |
|------------------|----------------------|----------------------|----------------------|----------------------|
| 440              | -                    | ×                    | -                    | -                    |
| 450              | -                    | ×                    | -                    | -                    |
| 455-458          | -                    | ×                    | ×                    | -                    |
| 460              | -                    | ×                    | ×                    | -                    |
| 461-463          | ×                    | ×                    | ×                    | -                    |
| 465              | -                    | -                    | △                    | -                    |
| 470-471          | -                    | △                    | △                    | -                    |
| 472-473          | -                    | ⊙                    | ⊙                    | ○                    |
| 473-474          | -                    | ○                    | ○                    | -                    |
| 475              | -                    | -                    | △                    | -                    |
| 475-477          | -                    | -                    | △                    | -                    |
| 480-482          | -                    | -                    | ×                    | -                    |

Cu/Sr = 1, 1.5, 1.7 and 2.3.

We observed the generation of non-crystalline phases and/or Sr$_{14}$Cu$_{24}$O$_{41}$ with some impurity phases when growth conditions are deviated from the optimal condition. For example, in the case of Cu/Sr = 1, SrCuO$_2$ with the infinite CuO$_2$ layer structure was obtained. The excess Sr condition for the growth of SrCu$_3$O$_4$ implies that the initially formed SrCu$_2$O$_3$ may be reconstructed to SrCu$_3$O$_4$ owing to the substrate strain as discussed in the main text, or re-evaporation of Sr from the film surface may take place.

The synthesis of SrCu$_3$O$_4$ is highly reproducible; using the present optimal growth condition and the (001)-SrTiO$_3$ substrate, we have succeeded in synthesizing SrCu$_3$O$_4$ in more than 10 times. It is noted that, to maintain the stability of temperature and monitoring condition, we synthesized the films at a fixed position without rotating the substrates. Al-
Figure S4: X-ray reciprocal space mappings around (a), (c), (e) 101 and (b), (d), (f) 113 for three different films of SrCu$_3$O$_4$. The thicknesses of these films is almost the same (∼30 nm). The coherent and reproducible growth of these films is confirmed.

most the same coherent feature of obtained films was confirmed in reciprocal space mapping of XRD measurements (Figure S4).

Multiple domain formation in thick films of SrCu$_3$O$_4$

A small portion of competing phases of SrCu$_2$O$_3$ and CuO was found in HAADF-STEM data for thicker films (> 30 nm), as shown in Figures S5a and S5b. Competing impurity phases were also detected as spot-like features in the RHEED pattern. A typical RHEED image for the film with a 5 nm thickness shows streaky patterns (Figure S5c), suggesting an extremely flat surface of the SrCu$_3$O$_4$ film. However, further growth under the same condition resulted in spot-like features along with the original streaks (Figure S5d), suggesting the formation of islands of extra phases that coexist with the epitaxially grown phase.
Figure S5: (a) HAADF-STEM image of an island of secondary phases in a thick film with 30 nm. Secondary phases were identified as b-axis oriented SrCu$_2$O$_3$ and CuO. (b) Magnified view for the white square region in (a). (c) RHEED images along the [100] direction of the SrTiO$_3$ substrate for the samples with 5 nm thickness and (d) 30 nm thickness.

Figure S6 shows the 2$p$ core level of Cu for SrCu$_3$O$_4$ films on the (001)-SrTiO$_3$ substrate. The film with 5 nm thickness is the same sample as shown in Figure 4a of the main text. Here we also show the result of a thicker film with 30 nm. For the thin film with 5 nm, we observed distinct satellite peaks, separated by $\sim 9$ eV, which are ascribed to the divalent copper state.$^{88}$ However, intensities of the satellites decreased in the thicker film with 30 nm. This result is probably due to impurity phases in the surface state, which appear in thicker films than 30 nm.

A phase mixture of SrCu$_3$O$_4$ and other phases can be understood as a consequence of multiple domain formation that reduces the stress from the substrate.$^{87,88}$ This result implies
Figure S6: Cu 2p core level XPS spectra of SrCu$_3$O$_4$ films with 5 nm and 30 nm thickness.

that the epitaxially stable phase (SrCu$_3$O$_4$) and secondary phases (SrCu$_2$O$_3$ and CuO) are both thermodynamically stable,\textsuperscript{S7} however, the former phase cannot appear in bulk owing to competing secondary phases that are more stable in bulk. The multiple domain formation is another strain relaxation mechanism different from misfit dislocation.\textsuperscript{S9, S10}
Calculated phonon dispersion of $\text{SrCu}_3\text{O}_4$

The phonon dispersion of $\text{SrCu}_3\text{O}_4$ calculated using the experimentally observed lattice constants of $a = 5.42$ Å and $c = 3.53$ Å is shown in Figure S7. No imaginary modes are present, suggesting that $\text{SrCu}_3\text{O}_4$ is dynamically stable. This result is consistent with the experimental observation of the multiple domain formation for thick films of $\text{SrCu}_3\text{O}_4$ (Figures S5 and S6); that is, $\text{SrCu}_3\text{O}_4$ is considered thermodynamically stable.

![Phonon dispersion of SrCu3O4](image)

Figure S7: Phonon dispersion of $\text{SrCu}_3\text{O}_4$ obtained by first-principles calculation using the lattice constants of the thin film ($a = 5.42$ Å and $c = 3.53$ Å).

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