Supplementary Material Available: Analytical data including ^{1}H NMR, ^{13}C NMR, IR, $[\alpha]_D$, HRMS, and combustion data for the key compounds, 4-α, 4-β, 8, and 1 (3 pages). Ordering information is given on any current masthead page.

Low-Temperature Growth of the Infinite Layer Phase of SrCuO2 by Pulsed Laser Deposition

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The products obtained from conventional solid-state synthetic reactions are often limited to the high-temperature thermodynamic ones,[1,2] and thus there has been considerable interest in developing new low-temperature approaches that might provide access to novel phases and materials. For example, several groups have described the use of low-temperature reactive fluxes to prepare new metal–chalcogenide phases,[3,4] and other researchers have investigated the low-temperature synthesis of inorganic solids via the controlled decomposition of molecular precursors.[5] Herein, we report a strikingly different approach for low-temperature solid-state synthesis based on pulsed laser deposition (PLD), and we use this method to prepare the tetragonal infinite layer phase of $SrCuO_2$. The tetragonal phase of $SrCuO_2$ is an important target since it represents the parent structure of the high-temperature copper oxide superconductors; however, it is inaccessible by conventional high-temperature synthetic routes.

PLD is a well-established technique for the preparation of thin film materials.[6-9] It involves ablation of a target material with a high-energy pulsed laser, and deposition of the evaporated target material onto a substrate to yield a thin film product. There are several features of the ablation and deposition processes that make PLD ideally suited for the synthesis of new materials, including the following: (1) material is congruently evaporated from the target during rapid laser heating; (2) growth of a crystalline product can be carried out at temperatures significantly lower than

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Figure 1. Schematic view of the PLD chamber. Major components: (1) target rotation feedthrough, (2) turbomolecular pump, (3) quartz window, (4) focus lens, (5) excimer laser, (6) substrate manipulator, (7) gas inlet, (8) substrate shutter, (9) target, (10) substrate, (11) substrate heater, (12) quartz crystal thickness monitor.

Figure 2. Experimental X-ray diffraction patterns for (A) the orthorhombic $SrCuO_2$ target and (B) a 5000-Å $SrCuO_2$ film prepared by PLD. A simulated diffraction pattern for c-axis oriented tetragonal $SrCuO_2$ is shown in part C.

those of conventional solid-state reactions; (3) the substrate can be chosen to enforce the growth of a specific structural phase; and (4) sequential multitarget evaporation can be used to prepare complex layered structures with atomic-level control.[6-8] An indication of the potential of PLD for materials synthesis has been the growth of high-quality, epitaxial films of copper oxide superconductors, because these materials are compositionally complex and melt incongruently.[7,8] There are few studies, however, that have utilized the unique characteristics of PLD for new materials synthesis.[9]

Our PLD experiments were carried out in a stainless steel vacuum chamber that is evacuated with a turbomolecular pump (Figure 1). The $SrCuO_2$ target material was prepared by conventional high-temperature methods from a 1:1 mixture of $SrCO_3$ and CuO.[10] This preparative route yields an orthorhombic phase

(10) Stoichiometric amounts of CuO (99.999%, Johnson Matthey) and $SrCO_3$ (99.999%, Johnson Matthey) were ground, heated at 800 °C for 12 h, reground, and heated at 900 °C for 24 h. Finally, the resulting polycrystalline powder was pressed into a pellet and sintered at 950 °C.

with a = 3.57 Å, b = 16.34 Å, and c = 3.91 Å (Figure 2A).[11] Notably, ablation of orthorhombic $SrCuO_2$ targets using a KrF excimer laser (248 nm) and deposition of the ablated material onto <100> oriented $SrTiO_3$ substrates at 500 °C yields a new structural phase with a 1:1 Sr:Cu stoichiometry.[12] X-ray diffraction patterns (θ–2θ scans) of the new $SrCuO_2$ films can be indexed as a tetragonal $SrCuO_2$ layered phase with the c-axis oriented perpendicular to the substrate surface (Figure 2B). The c-axis lattice parameter calculated from these experimental data is 3.35 Å. To support our structural assignment of the product, we have simulated the diffraction pattern for tetragonal $SrCuO_2$ (Figure 2C). The excellent agreement between the experimental and simulated patterns shows that the product obtained by PLD is the infinite layer phase. Small impurity peaks that can be indexed as the (111) and (061) peaks of the orthorhombic phase are also observed in the experimental diffraction scans at 2θ = 34.4° and 40.3°. Since this impurity represents <10% of the product, we conclude that the major phase produced in our low-temperature PLD studies is tetragonal $SrCuO_2$.

The tetragonal phase of $SrCuO_2$ represents the parent structure of the layered copper oxide superconducting materials and has thus been an important synthetic target of solid-state chemists. The tetragonal phase is, however, inaccessible to conventional high-temperature approaches, except for the specific stoichiometry $Sr_{0.14}Ca_{0.86}CuO_2$.[13,14] Unfortunately, the subtle ionic size effects that stabilize the tetragonal phase for this compound preclude systematic investigations of doping. Several groups have also reported that tetragonal $SrCuO_2$ can be prepared at high temperatures by applying very high pressures (20–65 kbar) during reaction.[16,17] These studies offer a general approach to the tetragonal phase (as does PLD), although the instrumentation needed to achieve ultrahigh pressure is available in relatively few laboratories compared to laser deposition systems. The highly-oriented crystalline samples obtained by PLD are also ideal for detailed physical measurements, in contrast to ceramic samples obtained from high-pressure syntheses.

We have carried out a number of studies to elucidate the factors that control the growth of the layered phase. First, we find that as the $SrCuO_2$ growth temperature is increased from 500 to 700 °C, there is a decrease in the degree of c-axis orientation of the tetragonal phase, and there is an increase in the percentage of orthorhombic phase formed. In addition, PLD of the thermodynamically stable tetragonal compound $Sr_{0.14}Ca_{0.86}CuO_2$ between 500 and 700 °C yields only tetragonal-phase product.[14,15] These results strongly indicate that low-temperature growth (accessible by PLD) kinetically traps the metastable tetragonal phase of $SrCuO_2$. We also find that there are a decrease in the degree of c-axis orientation of the tetragonal phase and an increase in the percentage of orthorhombic impurity phase for films grown on MgO (a = 4.2 Å) versus $SrTiO_3$ (a = 3.905 Å). Since the a-axis lattice parameter of tetragonal $SrCuO_2$ (a = 3.92 Å) is better matched for epitaxial growth on $SrTiO_3$, we suggest that

the substrate also helps to stabilize the desired tetragonal phase.

In summary, we have utilized the unique characteristics of PLD to prepare highly oriented films of tetragonal $SrCuO_2$. The ready accessibility of high-quality crystalline samples of this material offers an outstanding opportunity to study electronic and magnetic consequences of doping in this model system[18] and suggests in general the potential of PLD for new materials synthesis.

Supplementary Material Available: Experimental X-ray diffraction patterns for a tetragonal $Sr_{0.14}Ca_{0.86}CuO_2$ ceramic target and a 5000-Å $Sr_{0.14}Ca_{0.86}CuO_2$ film prepared by PLD and a simulated diffraction pattern for c-axis oriented tetragonal $Sr_{0.14}Ca_{0.86}CuO_2$ (1 page). Ordering information is given on any current masthead page.

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(18) Niu, C. M.; Lieber, C. M. In preparation.

$W_6(H)_5(O\text{-}i\text{-}Pr)_{13}$. A Polynuclear Polyhydride Supported Exclusively by Alkoxide Ligands

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Complexes of transition metals with metal–hydrogen bonds are of critical importance in many stoichiometric and catalytic reactions.[1,2] Since the initial discovery of $HCo(CO)_4$ and $H_2Fe(CO)_3$ in the 1930s, the chemistry of metal hydrides and metal polyhydrides has been developed with the now classical ligands of organometallic chemistry, namely, carbon monoxide, tertiary phosphines, cyclopentadienes, and related soft π-acceptor ligands. It has been our belief that hard π-donor ligands such as alkoxides (siloxides and aryloxides) should also support an extensive organometallic chemistry for the early transition metals in their higher oxidation states where there are vacant d_π orbitals.[3] Within this field a potentially important class of compounds are metal hydrides supported by alkoxide ligands, $M_x(H)_y(OR)_z$. The first well-characterized member of this series was $W_4(H)_2(O\text{-}i\text{-}Pr)_{14}$[4] followed by related $W_2(H)(OR)_7L^5$ and $NaW_2(H)(OR)_8$[6] complexes. For tantalum, Wolczanski and co-workers[7] reported the synthesis of $[(silox)_2Ta(H)_2]_2$, where silox = $(t\text{-}Bu)_3SiO$, and its reactions with carbon monoxide. More recently, Rothwell and co-workers[8] have characterized a novel stereochemically rigid seven-coordinated tantalum(V) trihydride supported by attendant aryloxide ligands: $TaH_3(OAr')_2L_2$, where L = PMe_2Ph and Ar' = $2,6\text{-}R_2C_6H_3$, and found that these and related niobium complexes provide catalysts for the cis-hydrogenation of fused aromatic rings.[8] Hoffman et al.[9] reported the reversible formation of

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