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

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Received February 4, 1992

The products obtained from conventional solid-state synthetic reactions are often limited to the high-temperature thermodynamic ones, 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, and other researchers have investigated the low-temperature synthesis of inorganic solids via the controlled decomposition of molecular precursors. 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 SrCuO₂. The tetragonal phase of SrCuO₂ 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. 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 those of conventional solid-state reactions; (3) the substrate can be chosen to enforce the growth of a specific structural phase; and (4) sequential multiset target evaporation can be used to prepare complex layered structures with atomic-level control.

Figure 1. Schematic view of the PLD chamber. Major components: (1) target rotation feedthrough, (2) cryogenic 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 SrCuO₂ target and (B) a 5000 Å SrCuO₂ film prepared by PLD. A simulated diffraction pattern for c-axis oriented tetragonal SrCuO₂ is shown in part C.

Our PLD experiments were carried out in a stainless steel vacuum chamber that is evacuated with a turbomolecular pump. A simulated diffraction pattern for c-axis oriented tetragonal SrCuO₂ is shown in part C.
with \( a = 3.57 \, \text{Å}, b = 16.34 \, \text{Å}, \) and \( c = 3.91 \, \text{Å} \) (Figure 2A).\(^{11}\) Notably, ablation of orthorhombic \( \text{SrCuO}_2 \) targets using a KrF excimer laser (248 nm) and deposition of the ablated material onto \(<100>\)-oriented \( \text{SrTiO}_3 \) substrates at 500 °C yields a new structural phase with a 1:1 Sr-Cu stoichiometry.\(^{12}\) X-ray diffract patterns \((θ-2θ)\) scans of the new \( \text{SrCuO}_2 \) films can be indexed as a tetragonal \( \text{SrCuO}_2 \) 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 \( \text{SrCuO}_2 \) (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 the layered phase presents <10% of the product, we conclude that the major phase produced in our low-temperature PLD studies is tetragonal \( \text{SrCuO}_2 \).

The tetragonal phase of \( \text{SrCuO}_2 \) 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 \( \text{Sr}_{1.14}\text{Ca}_{0.68}\text{CuO}_2 \).\(^{13,14}\) Unfortunately, the subtle ionic size effects that stabilize the tetragonal phase for this compound preclude kinetic trapping of the metastable tetragonal phase of \( \text{SrCuO}_2 \). For example, attempts to prepare \( \text{SrCuO}_2 \) by applying very high pressures \((20-65 \, \text{kbar})\) during high-pressure syntheses of \( \text{SrCuO}_2 \) yield only tetragonal-phase product.\(^{15,16}\) These results strongly indicate that low-temperature growth (accessible by PLD) kinetically traps the metastable tetragonal phase of \( \text{SrCuO}_2 \). We also find that 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 thermon-dynamically stable tetragonal compound \( \text{Sr}_{1.14}\text{Ca}_{0.68}\text{CuO}_2 \) 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 \( \text{SrCuO}_2 \).

Since the \( \text{SrCuO}_2 \) 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 \( \text{Sr}_{1.14}\text{Ca}_{0.68}\text{CuO}_2 \) 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 \( \text{SrCuO}_2 \). We also find that there is a decrease in the degree of \( c \)-axis orientation of the tetragonal phase and an increase in the percentage of orthorhombic phase formed for films grown on MgO \((a = 4.2 \, \text{Å})\) versus \( \text{SrTiO}_3 \) \((a = 3.905 \, \text{Å}) \). Since the \( a \)-axis lattice parameter of tetragonal \( \text{SrCuO}_2 \) \((a = 3.92 \, \text{Å}) \) is better matched for epitaxial growth on \( \text{SrTiO}_3 \), 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 \( \text{SrCuO}_2 \). 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\(^{16,17}\) and suggests in general the potential of PLD for new materials synthesis.

Acknowledgment. We thank Dr. E. M. Carnahan for helpful discussions. C.M.L. acknowledges support of this work by the NSF, the David and Lucile Packard Foundation, and a Camille and Henry Dreyfus Teacher-Scholar Award.

Supplementary Material Available: Experimental X-ray diffract patterns for a tetragonal \( \text{Sr}_{1.14}\text{Ca}_{0.68}\text{CuO}_2 \) ceramic target and a \( 5000-Å \) \( \text{Sr}_{0.14}\text{Ca}_{0.86}\text{CuO}_2 \) film prepared by PLD and a simulated diffraction pattern for \( c \)-axis oriented tetragonal \( \text{Sr}_{1.14}\text{Ca}_{0.86}\text{CuO}_2 \) (1 page). Ordering information is given on any current masthead page.

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

\[ W_2\text{(H)}_2(\text{O-i-Pr})_{13} \] An Polynuclear Polyhydride Supported Exclusively by Alkoxide Ligands

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Received November 7, 1991

Complexes of transition metals with metal-hydrogen bonds are of critical importance in many stoichiometric and catalytic reactions.\(^{12}\) Since the initial discovery of \( \text{HCo(CO)}_6 \) and \( \text{H}_2\text{Fe(O)CO}_6 \) 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, cyclopentadienides, 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 \( d \)-orbitals. Within this field a potentially important class of compounds are metal hydrides supported by alkoxide ligands, \( \text{M}_n(\text{H})_m(\text{OR})_n \). The first well-characterized member of this series was \( W_6\text{(H)}_2(\text{O-i-Pr})_{13} \) followed by related \( W_7\text{(H)}_2(\text{OR})_{12} \) and \( \text{NaW}_6\text{(H)}_2(\text{OR})_{12} \) complexes. For tantalum, Wolczanski and co-workers\(^{18} \) reported the synthesis of \( \text{Tal}(\text{H})_2(\text{OR})_{12} \), where \( r = \text{(CH}_2\text{CH})_2 \), and its reactions with carbon monoxide. More recently, Rothwell and co-workers\(^{18} \) have characterized a novel stereochemically rigid seven-coordinated tantalum(V) trihydride supported by attendant aryloxide ligands: \( \text{TaH}_2(\text{O-iPr})_2\text{L}_2 \), where \( \text{L} = \text{PMeq}+\text{Ar} = \text{2,6-R}_2\text{C}_6\text{H}_3 \), and found that these and related niobium complexes provide catalysts for the cis-hydrogenation of fused aromatic rings.\(^{19} \) Hoffman et al.\(^{19} \) reported the reversible formation of...