

# Thin Film Synthesis of Solids

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## Glossary

**Thin films:** coatings that have thicknesses ranging from a single crystal unit-cell to several microns

**Laser ablation:** light-driven nonequilibrium evaporation of a solid

## Abbreviations

PLD = pulsed laser ablation and deposition;  $T_c$  = superconducting transition temperature; RBS = Rutherford backscattering spectrometry; RHEED = reflection high-energy electron diffraction.

## 1 INTRODUCTION

Inorganic thin films play a central role in many areas of technology and basic research.<sup>1,2</sup> Thin film coatings are essential to the function of numerous mechanical devices. Electronically active thin films have also been central to the discovery of new physical phenomena such as the quantum Hall effect. In general, it is possible to categorize the wide spectrum of inorganic thin films into two categories, passive or active, based simply on their function in a structure or device. Passive thin films are coatings that may be used for cosmetic purposes or to protect a surface from wear or deleterious chemical reactions; however, passive films do not serve a specific electronic or catalytic role. Examples of technologically important passive thin films include: (1) metal nitrides (e.g. TiN) and carbides, which are used as hard, wear-resistant coatings; (2) oxides such as  $Al_2O_3$  and  $SiO_2$ , which are used as diffusion barriers and insulators; and (3) metal coatings (e.g. Au), which are used to provide chemically inert, decorative finishes.<sup>1-3</sup> In addition, electronically and chemically active thin films are of great importance to microelectronic devices, sensors, and other key technological areas. For example, alternating thin layers of GaAs and AlGaAs form the basis for optical detectors and semiconductor lasers. On the other hand,  $ZrO_2$  thin films represent the key chemically selective component of oxygen sensors used in many automobile engines.

Central to thin film technology and research are the synthetic methods used to fabricate coatings and new thin film materials. These synthetic methods, which differ significantly from familiar inorganic preparative techniques, can be classified as either chemical or physical in nature. Chemical techniques include *Chemical Vapor Deposition* (CVD),<sup>1</sup> sol-gel techniques (see *Descent in Symmetry*),<sup>2</sup> and electrochemical plating. In general, chemical techniques rely on the decomposition of molecular precursors (see *Metallic Materials Deposition: Metal-Organic Precursors*), where the quality of a resulting thin film depends critically on excluding ligands and other contaminants. Inorganic chemists have made an impact in designing molecular precursors for film growth.

In contrast, physical techniques of thin film synthesis are based upon evaporation or sputtering of elemental or multicomponent sources and subsequent deposition of this material onto a target;<sup>3,4</sup> molecular precursors do not play a significant role in thin film synthesis via these techniques. Examples of physical techniques used to prepare thin films include: (1) *Molecular Beam Epitaxy* (MBE);<sup>4</sup> (2) sputtering,<sup>4</sup> and (3) pulsed laser ablation and deposition (PLD).<sup>6</sup> Physical techniques can be extremely powerful methods for fabricating new materials since they allow atomic level control of growth. For example, MBE has revolutionized the fabrication of complex semiconductor superlattices (e.g. GaAs/AlGaAs) that have abrupt variations in composition on an atomic scale. A major limitation of MBE is that it relies on thermal evaporation to generate the elemental components of a film. Equilibrium evaporation will yield films that have a stoichiometry which differs from the bulk starting material when the starting materials melts incongruently. Because most chemically interesting complex inorganic materials, such as metal oxides and metal nitrides, melt incongruently, it is not clear whether MBE can contribute greatly to the synthesis of interesting inorganic oxides and nitrides.

On the other hand, we believe there is an emerging body of results which indicate that PLD may revolutionize the synthesis of complex inorganic thin film materials. A unique feature of PLD is that the source material is evaporated (ablated) in a nonequilibrium process such that material is evaporated at the stoichiometry of the bulk. Hence, it is possible to prepare thin films of incongruently melting solids that have a stoichiometry characteristic of the solid phase prior to melting. For example, PLD has been the most effective method for preparation of crystalline  $YBa_2Cu_3O_7$  superconductor thin films for both research and commercial applications. Since  $YBa_2Cu_3O_7$  melts incongruently, it is difficult to prepare films via conventional thermal evaporation. Furthermore, the PLD technique is a general one for thin film synthesis, and has been used to prepare materials with metallic, insulating, ferroelectric, piezoelectric, magnetic, and superconducting properties.<sup>6</sup> Because PLD can in principle be used to deposit widely varying types of materials and arbitrarily complex stoichiometries, we believe that it is a uniquely powerful approach to the synthesis of inorganic thin films. The remainder of this article will focus on the PLD technique of thin film synthesis, including the fundamental principles of laser ablation and applications of PLD to the synthesis of novel inorganic materials.

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## 2 FUNDAMENTALS OF PLD

The utility of PLD for thin film synthesis is due in large part to the unique characteristics of the laser ablation process. As indicated above, laser ablation is a nonequilibrium process that enables stoichiometric evaporation of elements from a target source. In addition, it is also possible to control the energy of evaporated species in PLD, and thus control film growth on the substrate surface. The underlying basis for these features of laser ablation and their utility in thin film synthesis are described below.

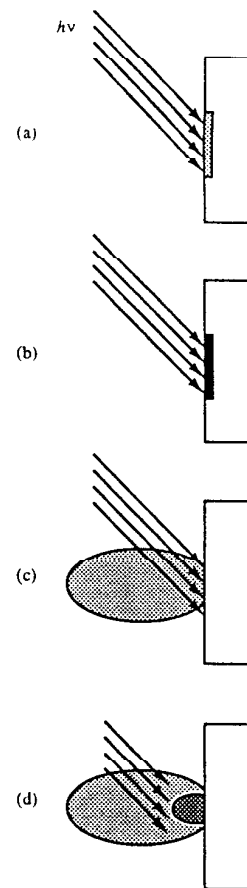
### 2.1 Laser–Solid Interaction

The interaction of intense laser light with solid surfaces is a complex physical process. This section does not focus on the physics underlying this interaction, but rather reviews the factors that directly influence thin film growth. More detailed explanations of the laser–solid interaction can be found in several reviews of this subject.<sup>7–9</sup>

The interaction of pulsed laser light with a solid surface is shown schematically in Figure 1. Typically, lasers with pulse lengths  $<50$  ns and energies on the order of  $1 \text{ J cm}^{-2}$  are used for thin film synthesis. Initially, laser light is absorbed by the solid and heats and melts the near-surface region of a target. The depth of the melted region depends upon the power density and rate of thermal diffusion.<sup>7–9</sup> At high power densities, the surface melts during the initial part of the laser pulse, and is then vaporized. In the intense electromagnetic field of the laser light, the vapor is ionized to form a plasma that contains ions, electrons, neutral atoms, and small clusters. The plasma, which is self-regulating,<sup>7–9</sup> is directed perpendicularly away from the target or source surface; this directional vaporization is termed laser ablation. The ions and neutral elements in the plasma can be readily deposited on a substrate located diametrically opposite to the target. During laser ablation it is important to recognize that temperatures in excess of 4000 K are readily achieved, and thus virtually any material can be evaporated. Furthermore, since the target material acts as its own crucible, contamination from a reaction crucible, which is common in conventional solid-state synthesis, is not a problem in PLD synthesis.

### 2.2 Important Laser Parameters

Central to the application of laser ablation in synthesis is the ability to control the rate, energies, and neutral:ion ratio of the evaporated elements through systematic variations in the wavelength, pulse-width, and power density of the laser light. The absorption depth of light by a solid is wavelength dependent, and thus the efficiency of target heating and evaporation will depend on the wavelength of irradiation. The target temperature increase during laser irradiation is inversely proportional to the optical penetration depth for a fixed energy input, where the penetration depth is directly proportional to wavelength.<sup>10,11</sup> Hence, the surface temperature of a target irradiated with short and long wavelength lasers of equal energy and pulse length will be higher for the former. In addition, the rate of energy input, which is governed by the laser pulse width, is directly related to the temperature increase of the target; i.e. for a shorter pulse length a smaller amount of heat will be



**Figure 1** Schematic view of the interaction of laser light with a solid. Initial irradiation heats (a) and then melts (b) the surface. The liquid is then vaporized (c) and ionized (d) to form a plasma that is ejected away from the target surface. The time from (a) to (d) is approximately 30 ns

transported into the bulk by thermal diffusion. Short wavelength and short pulse length lasers will thus ablate material from a small near-surface volume without segregation of elements from the bulk. That is, regardless of the nature of the equilibrium phase diagram, the evaporated species have the average stoichiometry of the bulk target. Therefore, laser sources that emit short UV pulses (e.g. the excimer laser) are ideal for complex thin film synthesis using PLD.

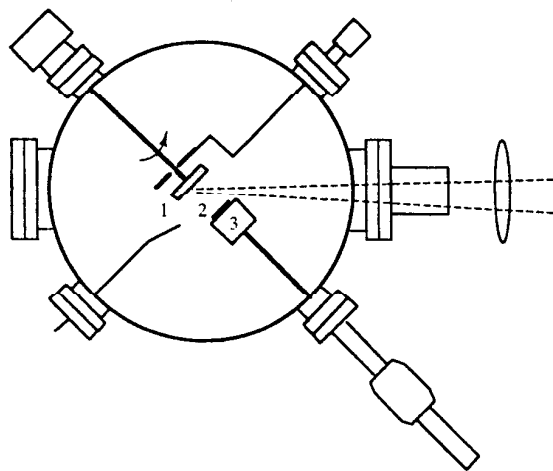
The laser power density also plays an important role in the evaporation process. First, at very low power densities (not employed typically for PLD) evaporation is nearly an equilibrium thermal process. As the power density increases, however, the process becomes nonequilibrium since heating and evaporation occur more rapidly than thermal and atomic diffusion. Furthermore, as the power density increases, the fraction of ionic to neutral species in the plasma and the kinetic energy of these species increases. Explicit measurement of these dependencies is possible using mass spectroscopy.<sup>12–18</sup> Time of

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flight mass spectroscopy measurements have shown that the energy of neutral species can be varied between 3 and 30 eV, while the energy of ions produced in the plasma may have energies from 0.1 to >100 eV. These relatively high kinetic energies enhance the chemical reactivity and surface diffusion of the ablated species. Diffusion and reactivity are both important parameters for controlling film growth. Because it is straightforward to change the power density through simply focusing or defocusing of the laser, the synthetic chemist has a powerful variable for controlling thin film growth. Lastly, it is important to reiterate that high power density laser ablation in nearly all cases results in congruent (i.e. stoichiometric) evaporation of the source target. Congruent evaporation has been demonstrated in many important systems which cannot be prepared using conventional thermal evaporation, including ternary semiconductors such as HgCdTe and  $\text{Pb}_{1-x}\text{Cd}_x\text{Se}$ ,<sup>19,20</sup> electronic ceramics,<sup>21,22</sup> and high-temperature copper oxide superconductors.<sup>23</sup> Of even greater importance to the synthesis of new inorganic thin films is the fact that congruent evaporation is also observed for multiphase targets.<sup>24</sup> That is, a thin film of virtually any stoichiometry can be prepared by laser ablation of a target that simply contains elements mixed in the desired stoichiometry.

### 3 EXPERIMENTAL APPARATUS FOR PLD

A general experimental apparatus for preparing thin films by PLD is shown in Figure 2. The PLD apparatus consists of a vacuum chamber containing a target holder, substrate heater positioned diametrically opposite to the target, optical window, and other components (Figure 2), together with a pulsed laser. Key features and considerations for the deposition apparatus are discussed below.



**Figure 2** Schematic view of the PLD synthetic chamber. The target (1) is attached to a feedthrough that is rotated during laser irradiation. The growth substrate (2) is attached to a heater (3) that controls the growth temperature between 25 and 900 °C. The dashed lines represent the laser beam (laser not shown); the beam is focused on to the target

Deposition chambers are typically constructed of stainless steel in order to obtain a clean vacuum. Glass chambers can also be used for PLD, although they are generally less versatile than metal chambers. In either case, it is important to minimize the build-up of deposits on the optical window in the chamber since this effectively attenuates the laser power density at the target surface. The build-up of deposits on the optical window can be reduced by locating this window as far away from the target as is possible.

The synthesis of oxide and nitride materials is often carried out with a background pressure in the PLD chamber of 10 to 500 mTorr. This pressure regime can be readily achieved using inexpensive mechanical pumps. However, it is good synthetic procedure to use a turbomolecular pump to establish a high vacuum in the chamber initially, and then to increase the pressure using purified oxygen or nitrogen.

Another key element in the PLD apparatus is the substrate heater. Thin film synthesis of oxide materials may be carried out at temperatures as high as 800 °C in oxygen. These highly oxidizing conditions place severe demands on heating elements, although two general types of heaters, radiant and resistive, have been used successfully. Radiant heaters utilize lamps as a heat source. A simpler solution to this problem is to utilize simple resistance heaters. Resistance heaters are easily fabricated; however, the metal alloy utilized for the heater element must be chosen with care to ensure reliable heater operation at high temperature in oxygen.

Lastly, it is important to irradiate the target uniformly. If the laser is focused on a stationary target, the ablation process will create a localized depression in the surface. The formation of surface depressions or craters is deleterious to synthesis since it leads to incongruent target evaporation. One method to avoid the formation of localized craters is to rotate the target asynchronously with the laser pulses. Alternatively, when target rotation is not possible, the laser beam itself should be scanned over the surface of the target. Target rotation and beam scanning both lead to uniform (and stoichiometric) removal of material from the target.

### 4 THIN FILM SYNTHESIS USING PLD

In the remainder of this article specific examples of thin film synthesis using PLD are described. These examples are chosen to illustrate the unique characteristics of PLD that make it a powerful technique for the preparation of complex multicomponent solids and for exploratory synthesis of new materials.

#### 4.1 Preparation of Known Materials

The discovery of high-temperature superconductivity in copper oxide based materials has been a remarkable triumph of inorganic solid-state chemistry (see *Superconductivity* and *Oxides: Solid State Chemistry*). A number of families of copper oxide superconductors are now known, and the transition temperatures ( $T_c$ ) in many of these solids exceed the boiling point of liquid nitrogen ( $\text{LN}_2$ ). The observation of  $T_c$ s above the boiling point of  $\text{LN}_2$  has renewed interest in developing superconductor thin films for a variety of electronics devices. For the fabrication of thin film devices it is essential that thin film material (1) is homogeneous and crystalline, (2) has a high

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critical current density, and (3) does not react with the substrate on which it is grown. PLD has been by far the most widely used technique for the preparation of these high- $T_c$  thin films.<sup>24-26</sup> These films have been shown to preserve the structure and composition of bulk  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . Thin films prepared by PLD also exhibit the high critical current densities required for technological applications. In addition, it is possible to grow crystalline, superconducting films of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  at temperatures significantly lower than those used to form the bulk phase (700 vs. >900 °C). Low-temperature growth minimizes, and in some cases eliminates, interdiffusion and reaction at the superconductor-substrate interface.

The successful preparation of high-quality  $\text{YBa}_2\text{Cu}_3\text{O}_7$  films shows that PLD can readily deposit complex stoichiometry materials in crystalline form at temperatures significantly lower than those required in bulk syntheses. Furthermore, high-quality films have been routinely prepared in many laboratories worldwide. Hence, it is indeed reasonable to consider PLD as a general technique for the synthesis of complex inorganic films.

Another general class of solids that has been prepared as thin films using PLD is ferroelectric materials. A potentially useful characteristic of ferroelectric materials is that they can be polarized by an electric field and retain this polarization when the field is removed. In ferroelectric thin films it may be possible to exploit this polarization phenomena to make sensors, displays, and memory devices.<sup>27</sup> A number of techniques have been used to prepare ferroelectric thin films. However, it has been difficult to control the stoichiometry (and correspondingly the properties) of these materials using thermal and sputtering techniques. In part, the difficulty in maintaining correct stoichiometry is due to the volatility of a component in the material (e.g. Pb in  $\text{PbTiO}_3$ ).

The success of PLD in preparing high-quality superconductor thin films has led to considerable interest in applying this technique to the ferroelectrics. PLD is particularly attractive for the synthesis of ferroelectric materials since it can deposit stoichiometric and crystalline materials at low temperature. Deposition at low temperature (e.g. 300–500 °C) prevents the loss of volatile components from the film. However, simply preparing a film at low temperature using thermal sources would not yield a crystalline thin film since there is insufficient energy for elements to diffuse to the proper crystallographic sites. Laser ablation produces high kinetic energy particles (see Section 2) that can diffuse to the correct crystal sites after deposition and yield highly crystalline thin films at low growth temperatures.

PLD of crystalline and stoichiometric ferroelectric materials has been successful for a number of materials. For example, crystalline  $\text{PbTiO}_3$  thin films have been deposited at only 350 °C using a KrF excimer laser ( $\lambda = 248$  nm).<sup>28</sup> The low deposition temperature makes this a potentially attractive method for directly fabricating ferroelectric/semiconductor hybrid devices. A related solid that is more difficult to prepare in thin film form is  $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ . To maintain the Pb stoichiometry and ensure random mixing of Ti and Zr requires careful control of film synthesis conditions.<sup>29,30</sup>

Another recent application of PLD thin film synthesis has been in the area of magnetic ferrites. Thin film ferrites are of great technological interest since they could play a key role in high-density magnetic recording devices and in monolithic microwave integrated circuitry. It has been difficult to prepare thin films of ferrites due to their structural and compositional

complexity. Attempts to prepare ferrite using sputtering and plasma spraying have not yet achieved high quality thin films.

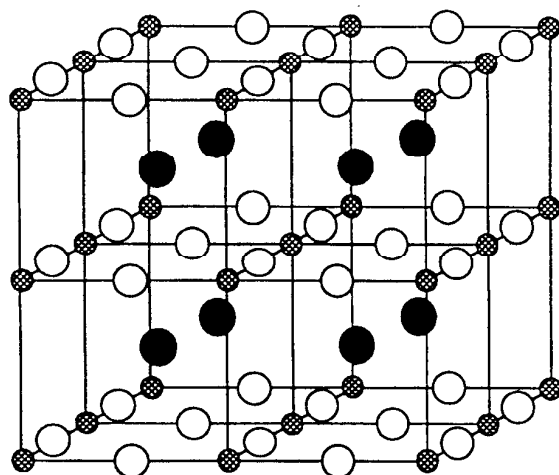
In contrast, synthetic investigations using PLD have been quite promising.<sup>31,32</sup> Recent studies of  $\text{Mn}_2\text{Zn}_{1-x}\text{Fe}_x\text{O}_4$  have shown that crystalline films can be prepared on <100> oriented  $\text{MgO}$  substrates. Because the physical properties (e.g. resistivity and saturation magnetization) of this ferrite depend critically on the Mn:Zn:Fe ratio and the oxygen stoichiometry, PLD can be used to readily tune the properties of the films for specific applications. In addition, PLD has been used to grow high-quality epitaxial thin films of  $\text{BaFe}_{12}\text{O}_{19}$  on <0001> sapphire and  $\text{Y}_3\text{Fe}_5\text{O}_{12}$  on <111> garnet substrates. These results are quite promising and may lead to practical applications for thin film ferrites produced by PLD. More generally, however, they demonstrate the utility of PLD in the synthesis of complex inorganic thin films.

## 4.2 Synthesis of New Materials

Conventional synthetic methods for the preparation of inorganic materials involves the reaction in the solid state. To facilitate diffusion and reaction in the solid state requires high temperature conditions. Hence, the products obtained from conventional solid-state reactions are typically limited to the ones thermodynamically stable at high temperature. In the past most solid-state synthetic studies have focused on high-temperature chemistry, although there is now a growing interest in the development of low-temperature approaches to inorganic solid-state synthesis.<sup>33</sup> Controlled low-temperature synthesis is a particularly attractive goal since it offers the possibility of obtaining new phases and materials with novel properties. PLD is an especially attractive method to explore the low-temperature synthesis of new materials since (1) stoichiometry can be readily controlled (i.e. laser evaporation is congruent irrespective of the equilibrium phase diagram) and (2) crystalline products can be grown at temperatures much lower than is possible with conventional solid-state reactions. Below, specific examples of the synthesis of several new materials by PLD are described.

The tetragonal infinite-layer phase of  $\text{SrCuO}_2$ , which consists of alternating  $\text{Sr}^{2+}$  and  $\text{CuO}_2^{2-}$  sheets, represents the parent structure of high- $T_c$  copper oxide superconductors (Figure 3). In principle, this system is ideally suited for investigating high- $T_c$  superconductivity since it contains only essential copper oxide layers and counterions. It has not been possible, however, to prepare and systematically dope this phase using conventional solid-state methods. Notably, recent studies in our laboratory have shown that it is possible to prepare this phase for a wide range of compositions,  $\text{Sr}_{1-x}\text{M}_x\text{CuO}_2$  ( $\text{M} = \text{Nd, Ca, Ba}$ ) using PLD.<sup>33-35</sup>

$\text{Sr}_{1-x}\text{Ca}_x\text{CuO}_2$  targets can be prepared using conventional solid-state methods at 900 °C. The  $\text{Sr}_{1-x}\text{Ca}_x\text{CuO}_2$  targets are, however, multiphase, except for  $\text{SrCuO}_2$  which has an orthorhombic structure. Laser ablation of these targets using a KrF laser and deposition onto <100>  $\text{SrTiO}_3$  substrates at 500 °C yields single-phase materials for all values of  $x$ . The films can be structurally characterized using X-ray and electron diffraction. X-Ray diffraction scans ( $\theta$ - $2\theta$ ) of  $\text{Sr}_{1-x}\text{Ca}_x\text{CuO}_2$  films prepared by PLD are shown in Figure 4. These relatively simple diffraction patterns can be indexed as the infinite-layer phase (Figure 3), where the  $\text{CuO}_2$  planes are all oriented parallel



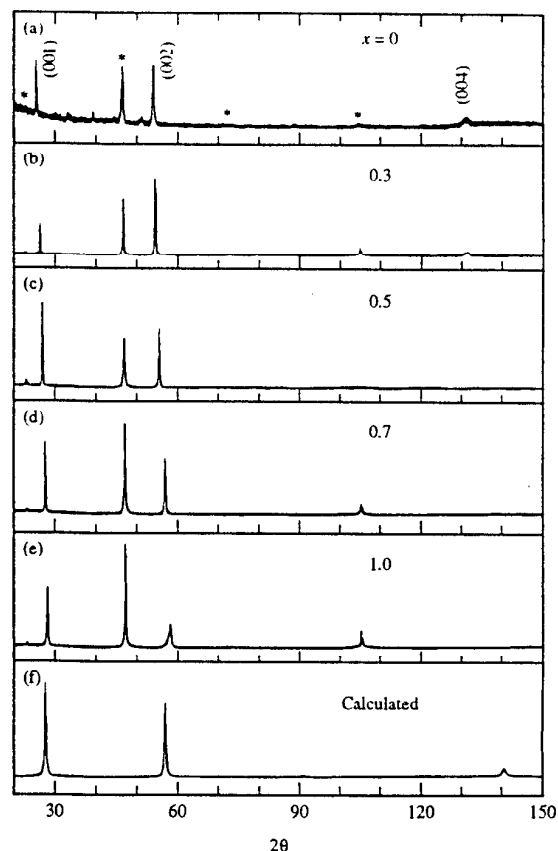
**Figure 3** Structural model of the tetragonal infinite layer phase of  $\text{SrCuO}_2$ . The  $\text{Sr}^{2+}$  ions appear as isolated solid black spheres between the  $\text{CuO}_2^{2-}$  layers. The copper ions are cross-hatched circles and the oxygen ions are open circles

to the surface of the  $\langle 100 \rangle$   $\text{SrTiO}_3$  substrate. A simulation of the diffraction pattern expected for a thin film with this orientation also agrees quite well with the experimental data.

The  $\theta$ - $2\theta$  diffraction scans elucidate the layered structure of the  $\text{Sr}_{1-x}\text{Ca}_x\text{CuO}_2$  materials. Electron diffraction can be used to complete the structural identification of these thin film materials. Electron diffraction patterns recorded along the  $[001]$  plane axis characterize the in-plane structure. An example of an electron diffraction pattern recorded on a  $\text{Sr}_{0.7}\text{Ca}_{0.3}\text{CuO}_2$  sample is shown in Figure 5. The diffraction peaks exhibit a square symmetry, as expected for the in-plane structure of the tetragonal infinite-layer phase. Simulations have been used to confirm this in-plane structure. Thus, the X-ray and electron diffraction measurements provide an unambiguous identification of the structure of these thin film materials.

It is also possible to characterize accurately the composition of new thin film materials using RBS. RBS analysis of the  $\text{Sr}_{1-x}\text{Ca}_x\text{CuO}_2$  materials demonstrates that the single-phase infinite-layer thin films have the same average composition as the multiphase targets from which they were prepared by laser ablation. These compositional analysis results demonstrate that PLD can be used to prepare readily a specific stoichiometry material even when the target is not single phase.

Since it was not possible to prepare the infinite-layer  $\text{Sr}_{1-x}\text{Ca}_x\text{CuO}_2$  materials previously using conventional solid-state methods, it is important to clarify what features of PLD enable the general synthesis of this new phase. Structural studies of the  $\text{Sr}_{1-x}\text{Ca}_x\text{CuO}_2$  products obtained from PLD growth at different temperatures provide key insight into this question. Temperature-dependent growth studies demonstrate that low-temperature growth is a key factor in stabilizing the infinite layer phase.<sup>33-35</sup> X-Ray diffraction patterns obtained from samples grown at temperatures from 500 to 700 °C (Figure 6) show that the concentration of the orthorhombic phase increases



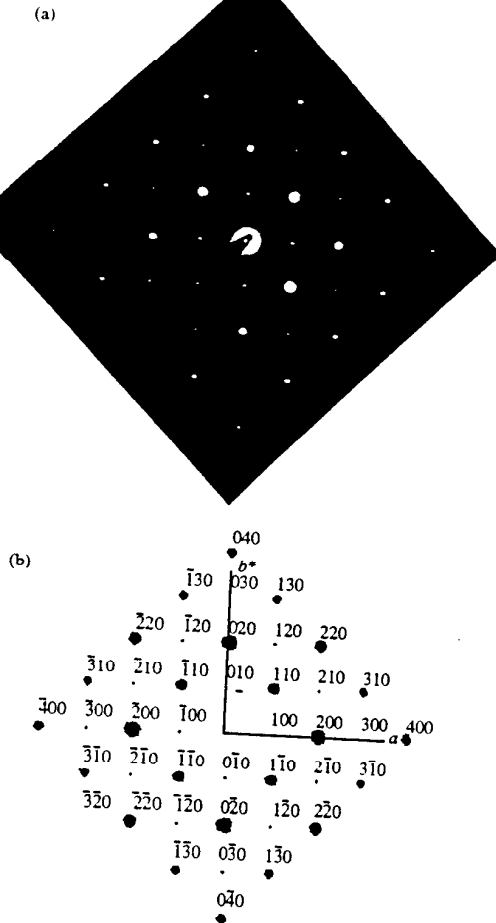
**Figure 4** X-Ray diffraction patterns recorded on (a)  $\text{SrCuO}_2$ , (b)  $\text{Sr}_{0.7}\text{Ca}_{0.3}\text{CuO}_2$ , (c)  $\text{Sr}_{0.5}\text{Ca}_{0.5}\text{CuO}_2$ , (d)  $\text{Sr}_{0.3}\text{Ca}_{0.7}\text{CuO}_2$ , and (e)  $\text{CaCuO}_2$ . A simulation of the diffraction pattern for  $\text{SrCuO}_2$  is shown in (f)

as the growth temperature increases. In the case of  $\text{SrCuO}_2$ , the orthorhombic phase, which is not a layered structure, is the single stable phase at high temperature. These results demonstrate that in the case of  $\text{Sr}_{1-x}\text{Ca}_x\text{CuO}_2$ , PLD can be used to trap a new metastable phase through low-temperature growth. This idea is expected to be generally useful for inorganic thin film synthesis in the future.

A second distinct example of PLD new materials synthesis involves substitutional doping of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .<sup>36-38</sup> It is well known that substitution of Y with other rare earth elements does not affect  $T_c$  significantly unless the rare earth is Pr. Indeed,  $\text{PrBa}_2\text{Cu}_3\text{O}_7$  is not a superconducting material. To explain the disappearance of superconductivity in the Pr-substituted material it has been suggested that either Pr exists as  $\text{Pr}^{4+}$  (vs.  $\text{Y}^{3+}$ ) or that the magnetic moment on Pr suppresses  $T_c$ . An experimental test of this hypothesis would be to prepare another  $\text{M}^{4+}$ -substituted compound and a  $\text{M}^{4+}/\text{M}^{2+}$  solid that would have the same average valence as  $\text{Y}^{3+}$ .

Substitution of  $\text{Ce}^{IV}$  for  $\text{Y}^{III}$  would be one possible choice, although it has not been possible to prepare single-phase Ce-

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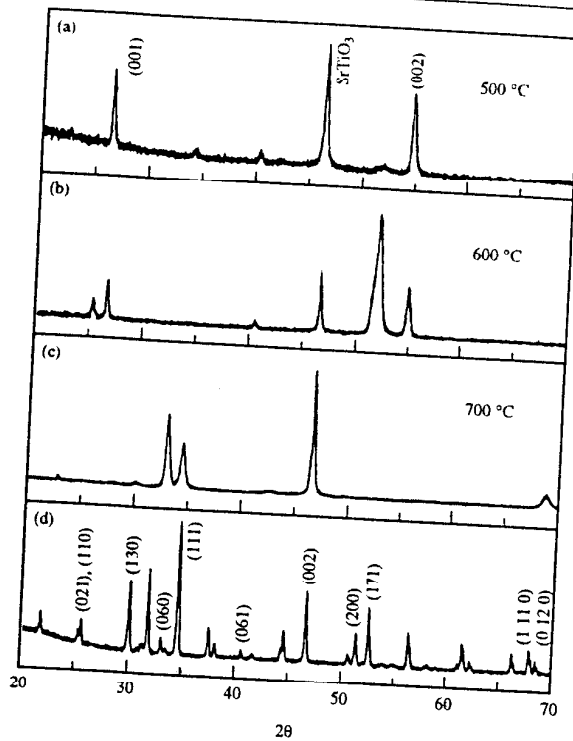
**Figure 5** (a) Electron diffraction pattern recorded along the  $\langle 001 \rangle$  zone axis of a  $\text{Sr}_{0.7}\text{C}_{0.3}\text{CuO}_2$  sample. (b) Simulation of diffraction pattern for the infinite-layer phase

doped solids. Nevertheless, PLD syntheses from multiphase  $\text{Ce}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_7$  targets yield high-quality single-phase materials. Since  $T_c$  is suppressed in the Ce-doped solids, these results indicate that  $\text{M}^{\text{IV}}$  cations may localize or trap carriers in the solid. Similarly, PLD has also been used to synthesize  $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_7$  materials from multiphase targets. Notably, the resulting thin films are single-phase crystalline Pr/Ca solids that exhibit superconductivity. On the basis of the studies of these new materials, which were prepared by PLD, it is apparent that it is the oxidation state of the substituted metal (and not magnetic moment) that is critical to  $T_c$ .

### 4.3 Novel Uses of PLD

As science and technology advances, it becomes increasingly important to integrate different materials with different physical properties into monolithic structures. From the perspective of

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**Figure 6** Series of X-ray diffraction patterns recorded on  $\text{SrCuO}_2$  thin films that were deposited at (a) 500 °C, (b) 600 °C, and (c) 700 °C. The diffraction pattern for orthorhombic  $\text{SrCuO}_2$  is shown in (d)

thin film synthesis, integration requires precise control of the deposition, so that multiple layers can be studied.

One method of meeting this challenge is to use PLD to prepare materials a single layer at a time, so-called layer-by-layer growth.<sup>39-42</sup> To achieve layer-by-layer growth requires careful control of deposition. This can be done by calibrating the rate of thin film growth for ablation of specific targets with controlled laser power densities. Alternatively, growth can be monitored in situ using RHEED.

Kawai and co-workers have used *in situ* RHEED to synthesize  $\text{Bi}_2\text{Sr}_2\text{CuO}_6/\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  superlattices and  $\text{Bi}_2\text{Sr}_{2-n}\text{Ca}_n\text{O}_x$  thin films where  $n$  can be as large as 8–10.<sup>39–41</sup> Similar ideas have also been used to carry out band-gap engineering in semiconductor materials. Band-gap engineering is a term coined to describe artificial structures that can be built up atomic layer by atomic layer. For example, Cheung and Shakur have reported the growth of  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  epitaxial layers with any predetermined composition.<sup>42</sup> The volatility of Hg is a problem in conventional film preparation; however, stoichiometric Hg–Cd–Te thin films can be prepared using low-temperature PLD. These examples of synthesis with atomic layer control represent a unique application of PLD, and suggests that it may be possible to build up very complex architectures in inorganic thin films with novel properties in the future.

## 5 SUMMARY

In conclusion, this article has introduced the importance of thin films in basic research and technology, and has reviewed thin film synthesis using PLD. From the standpoint of the synthesis of complex and new inorganic materials, PLD can be seen as a simple yet powerful synthetic tool. PLD has many unique features, including congruent target evaporation and low-temperature growth, that make it unique for thin film preparation. We believe that this technique offers an exciting opportunity for inorganic synthesis in the future.

## 6 RELATED ARTICLES

Metallic Materials Deposition: Metal–Organic Precursors; Oxides: Solid State Chemistry; Thallium: Inorganic Chemistry.

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## Thiocarbonyl

CS, existing as a ligand only and an analog of CO. Often formed in the reactions of CS<sub>2</sub>.

## Thiometalates

Compounds analogous to oxoanions in which S<sup>2-</sup> partially or fully replaces O<sup>2-</sup>. An example is WS<sub>4</sub><sup>2-</sup>.

## Thionitrosyl

NS, existing as a ligand only and an analog of NO.

For References see p.1234

**Thiourea**

$(\text{H}_2\text{N})_2\text{C}=\text{S}$ , a compound which is an excellent ligand, binding via S. In the bound form, the protonated iminothiolate tautomer is favored.

**Tin: Bioinorganic Chemistry** *see* Metal-Based Drugs & Imaging Agents

**Thorium: Inorganic Chemistry** *see* Actinides: Inorganic & Coordination Chemistry

**Thorium: Organometallic Chemistry** *see* Actinides: Organometallic Chemistry

**Three-Center Bond**

Type of bond existing in the equilateral triangular molecule  $\text{H}_3^+$ , in which two electrons are delocalized over three centers (*see Multicenter Two-Electron Bonding*).

**Thulium: Inorganic & Coordination Chemistry** *see* Scandium, Yttrium & the Lanthanides: Inorganic & Coordination Chemistry

**Thulium: Organometallic Chemistry** *see* Scandium, Yttrium & the Lanthanides: Organometallic Chemistry

**Tight-Binding Approximation**

Effectively this is the application of Hückel theory to the generation of the energy bands in solids. Its use is often broadened to include any LCAO type of approach. *See Electronic Structure of Solids; Energy Bands; Semiconductors.*

**Timescale**

The time in which a measurement is taken; differs according to the method used. IR spectroscopy has a much shorter timescale than NMR spectroscopy, for example.

List of General Abbreviations on p.0000