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High-Throughput Multi-Plume Pulsed-Laser Deposition for Materials Exploration and Optimization

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ABSTRACT A high-throughput multi-plume pulsed-laser deposition (MPPLD) system has been demonstrated and compared to previous techniques. Whereas most combinatorial pulsed-laser deposition (PLD) systems have focused on achieving thickness uniformity using sequential multilayer deposition and masking followed by post-deposition annealing, MPPLD directly deposits a compositionally varied library of compounds using the directionality of PLD plumes and the resulting spatial variations of deposition rate. This system is more suitable for high-throughput compound thin-film fabrication.

KEYWORDS pulsed-laser deposition, high-throughput

1 Introduction

Modern advanced materials with novel properties require increasingly complex compositions. Although materials development once focused on limited ranges of composition that were amenable to sequential optimization in an "Edisonian" approach, new applications require the synthesis of ternary, quaternary, or even higher-order mixtures of elements. Examples of advanced materials of particular interest include solar absorbers (e.g., $CuIn_xGa_{1-x}Se_2$ [1, 2] and $CuIn_{1-x}Ga_xSe_{2-y}S_y$ [3]) and high-temperature superconductors (e.g., $Ca(Fe_{1-x}Co_x)_2As_2$ [4] and $HgBa_2Ca_{m-1}Cu_mO_{2m+2+\delta}$ [5]). The properties of these compounds are closely dependent not only on composition, but potentially also on the morphology and surface texture of the compounds. Studying and optimizing such materials via series of samples, which have varying composition and are grown one sample at a time, is extremely time-consuming. It is therefore of great importance to devise an efficient and systematic way to search through libraries of such compounds so that materials research, especially studies on ternary and quaternary materials that have not been explored, can be accelerated.

In the mid-1900s, Merrifield developed the combinatorial synthesis of peptide chains [6]. In the 1990s, the synthesis technique was extended to commercial applications for the discovery of new pharmaceutical compounds [7]. In combinatorial chemistry, molecules are attached to a solid support such as a small bead and synthesized step-by-step in a series of reactant solutions. The molecular building blocks are initially protected by blocking moieties at all reactive sites. A desired reaction between reactants in the solution and the substrate on the bead can then be controlled by de-protecting the relevant sites in the correct order. By sequentially separating and dividing a distribution of beads into a matrix of reactant solutions, it is possible to synthesize a large library of structurally-related molecules in a relatively short time. In concept, this is a relatively simple process since the aim is only to synthesize the correct chemical structure. Combinatorial materials development is potentially a far more complex challenge.

In 1995, Xiang et al. published a combinatorial method for making compounds such as high-transition-temperature superconductors and novel blue phosphors, using a series of aligned masks in front of a substrate while sputtering from precursor targets [8–10]. Figure 1(a) shows a typical series of masks. The deposited film was separated by the masks into a library of segment samples on the substrate, as shown in Figure 1(b). Using a series of steps of changing masks and targets, Xiang et al. successfully controlled the deposition of precursors onto these segments and obtained a different precursor amount at each segment. The precursors at each

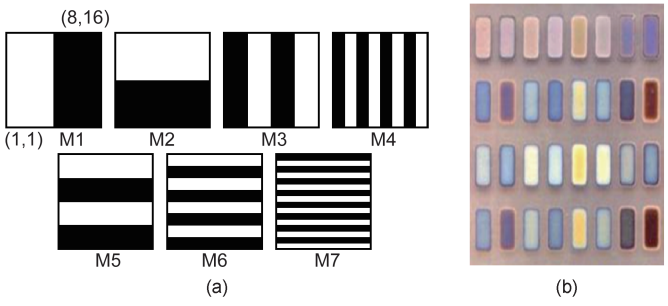

Figure 1. (a) Binary masks used for combinatorial synthesis [8]; (b) an image of a materials library prior to sintering [8].

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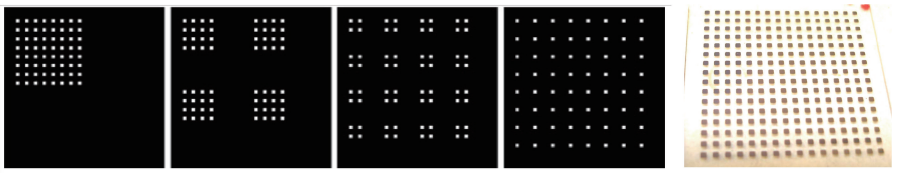
segment were then mixed into one compound via a post-annealing process. Since amounts of deposited precursors are different for different segments, compositions of the compounds after annealing are different and a diverse library of compounds is generated.

Following the same principle of multiple depositions through shadow masks, other groups developed pulsed-laser deposition (PLD) systems for combinatorial growth. PLD has been widely used in materials research since its successful growth of $YBa_2Cu_3O_{7-\delta}$ thin films for high-temperature superconductor applications in 1987 [11]. Compared with other techniques such as chemical-vapor deposition and sputtering, PLD has several advantages. The composition of thin films deposited by PLD is almost the same as that of the target material. It is relatively easy for PLD to grow stoichiometric materials, which is very important for the growth of compound materials, such as high-temperature superconductive oxides and semiconductor compounds. Note that the material deposited in the center of the PLD plume is sometimes different from that at the edge of the plume. In addition, PLD is a very versatile technology. Most materials in nature can be ablated by high-energy ultraviolet (UV) laser. PLD can therefore be used to grow many kinds of materials, including metals, semiconductors, superconductors, and insulators. The precursor material is just a small pellet, and is much easier to obtain than the sources of other techniques. With these advantages, PLD has been widely used in new materials research and exploration. It has been adopted for the sequential fabrication of combinatorial libraries for the study of semiconductors [12, 13] and high-temperature superconductors [14], among other materials. Figure 2(a) shows a typical series of quaternary masks and Figure 2(b) shows the semiconductor thin-film materials library fabricated into a 16 × 16 array.

However, the industrial application of PLD has been limited by the well-known disadvantage of its spatial non-uniformity. The film thickness deposited on a substrate at a lateral distance x can be described by $\cos^n(x)$ with a shape



(a) (b)

Figure 2. (a) Quaternary masks used for combinatorial synthesis [13]; (b) an image of a 256-member semiconductor material library grown on a quartz substrate [13].

similar to a Gaussian curve [15]. Indeed, the growth rate of PLD films can decrease by more than 50 times at a distance of 60 mm from the center. There is also potentially a spatial non-uniformity in the energetics of the PLD plume. If both the film thickness and the deposition energetics vary as a function of the position on the substrate, several variables may be convoluted within the compositional library, making meaningful analysis impossible. Work on combinatorial libraries based on PLD-grown films has therefore paid particular attention to eliminating the natural non-uniformity of the deposition process. Examples include using a moving-slit masking technique to grow oxide libraries [16, 17] and a programmed temporal sequence of laser pulses to grow transparent conducting oxides [18].

Notwithstanding these successes, however, a combinatorial approach that combines thin-film deposition and physical masking techniques is usually a mixing-after-deposition process requiring one or more post-deposition annealing steps. If the precursors are deposited sequentially as thin-film multilayers, nucleation could occur at each interface between the precursors at elevated temperatures. Indeed, Fister and Johnson have shown that it is possible to modify the reaction path of a solid-state reaction by adjusting the layer thickness of the initial composite, in some cases yielding stoichiometries that are not amenable to bulk synthesis [19]. In most cases, therefore, synthesis using multi-step masking techniques requires either a complex series of low-temperature annealing steps [8] or a sub-monolayer coverage of the precursor species [18] to eliminate the need for post-annealing, either of which is time-consuming. The potential for mask misalignment, particularly in libraries grown on small substrates, is a further potential limitation of this technique.

As an alternative to serial, multilayer fabrication techniques, it is possible to conceive of a continuous thin-film co-deposition system in which the natural non-uniformity of a deposition technique is used to generate compositional variation across a substrate. In this parallel-deposition case, interfaces between different precursor compositions where undesirable nucleation can occur are entirely eliminated. Indeed, Kennedy et al. demonstrated a very early implementation of combinatorial thin-film deposition using just such a technique with e-beam evaporation sources to generate a complete metal alloy phase diagram in a single experiment [20]. Hanak subsequently generated a binary compositional gradient using radio-frequency sputtering from a target consisting of two half-disks of different materials [21]. Co-sputtering with overlapping plasmas from separately controlled targets gave better control for the deposition of libraries of transparent conductive oxides [22], dielectrics [23–25], and metal alloys [26]. Results from parallel deposition using PLD, however, are relatively sparse, possibly due to the concerns about non-uniform energetics expressed above.

In this study, a high-throughput multi-plume pulsed-laser deposition (MPPLD) system is proposed and discussed in detail. This mixing-during-deposition system, which is more uniform and more suitable than normal PLD systems for the growth of compound films, can greatly facilitate compound optimization and new materials exploration.

2 Multi-plume pulsed laser deposition (MPPLD)

Figure 3 shows the MPPLD system schematically. An excimer laser (Lambda

Physic LPX 210i) produces a high-energy UV laser beam at a wavelength of 248 nm. Using two beam splitters (the first one having 30% reflectance and 70% transmittance and the second one having 50% reflectance and 50% transmittance) and one mirror, the laser beam is split into three beams. The beam splitters are mounted on flippers so that the setup is also compatible with two-plume deposition. Before entering the vacuum chamber, each of the three beams is focused by a spherical lens onto one of three targets, respectively (targets A, B, and C). A substrate wafer (with a diameter of 4 inches or larger) is positioned facing the targets. The substrate is heated by a resistance block and covered with a mask. Gas (either inert or reactive) is introduced into the chamber and controlled by a mass flow controller. The system includes a programmable laser shutter that is mounted on a stage and controlled by a linear actuator. Using the laser shutter, the ablation of each target can be controlled sequentially.

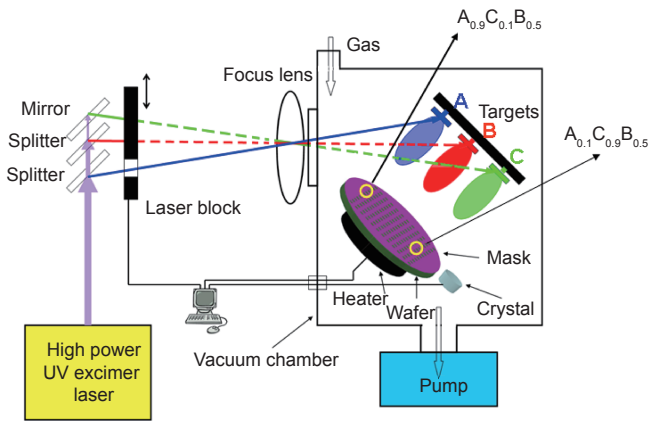


Figure 3. A schematic of the MPPLD system.

The deposited species pass through holes in the mask and form a library of small films on the substrate. Since the three plumes are physically separated and thicknesses of PLD films are not uniform on the substrate, the deposition rate of each target material at each film segment is different. Therefore for each sample segment, the ratio of the three precursors is different. If the laser shutter is open, the three materials will be deposited and mixed simultaneously. It is optional to use the shutter to control the timing of each target ablation. The linear actuator is controlled by a programmed recipe. A crystal monitor measuring film thickness may be used and connected to a computer as a feedback for control.

We use the thickness non-uniformity of the PLD plume, which is usually a problem for the practical application of thin-film deposition, to enable the generation of a combinatorial library. According to modeling by Tyunina et al. and Anisimov et al., the normalized thickness can be expressed as follows [27–29]:

$$H(x,y)=\left(1+ax^2+by^2\right)^{-3/2} \quad (1)$$

where H is the thickness, normalized to unity at the plume center on the substrate; x and y are the distances to the center along orthogonal x and y axes, respectively. Also,

$$a=\frac{k_\zeta}{Z_s^2} \quad \text{and} \quad b=\frac{k_\zeta}{k_\eta^2 Z_s^2} \quad (2)$$

where Z_s is the distance between the target and the substrate; k_ζ and k_η are values determined by the plume characteristics. These latter values can be changed by adjusting the ambient gas pressure, laser pulse energy, and so forth. Details about these parameters are discussed by Anisimov et al. [28].

Neglecting any interaction between the plumes and assuming the same molar volume and plume center deposition rate, the composition of the compound at each segment is simply illustrated in Figure 4 using typical values of Z_s, k_ζ, and k_η (Z_s = 55 mm, k_ζ = 4, and k_η = 1). The other two parameters used in the model are l and d. Parameter l is the distance between laser spots assuming that the three spots form an equilateral-triangle shape, as illustrated in Figure 5. This distance is equal to the distance between the plume centers on the substrate. Parameter d is the distance between two neighboring segment film centers on the substrate. As analyzed in Ref. [28], in the simulation of Figure 4, the values 60 mm and 12.5 mm are used for l and d, respectively. It is easy to see three areas on the substrate: an A-rich area, a B-rich area, and a C-rich area. Different distributions can be obtained by changing the parameters described above.

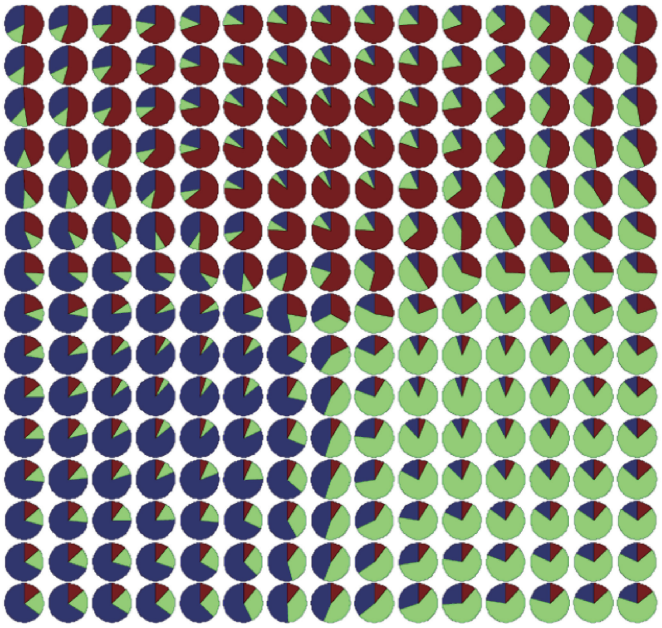


Figure 4. Compound compositions of deposited films on a substrate. Each cycle shows, by sector areas, compositions of three precursors (red: material A; blue: material B; and green: material C) for each corresponding segment sample on the substrate.

Therefore, because of the directionality of PLD plumes and the thickness non-uniformity of PLD films, this system is able to grow hundreds of thin films with different compositions on one substrate in a single batch. We now investigate whether useful compositional information can be extracted from such a system in the presence of non-uniformity in the total film thickness and potentially also in the deposition energetics at different points on the plume profile.

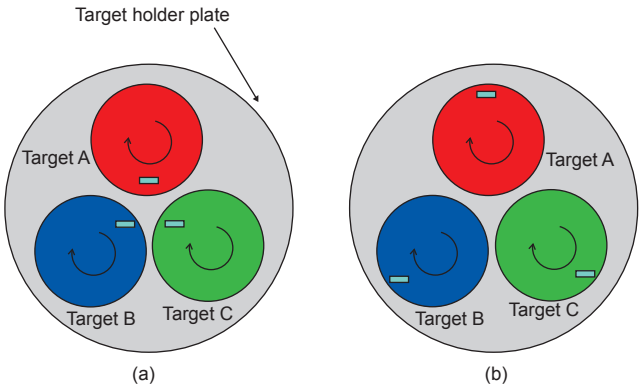


Figure 5. A schematic of the target holder showing different spot positions. (a) Spots are close; (b) spots are far away. Rectangles represent focused laser spots.

The MPPLD system has many potential advantages.

(1) As with sequential combinatorial methods, this system can fabricate compounds with different compositions at the same time instead of one-by-one fabrication. It can be used to fabricate more than 200 samples in a single deposition.

(2) By using a simple automatic scan or programmable switch circuits, the measurement process can be automated to run at speeds that are compatible with combinatorial library synthesis. For example, in order to fabricate hundreds of solar cells on a substrate wafer, electrodes can be deposited first using the mask. Absorber materials with various compositions or doping can then be grown using this MPPLD technique. After the fabrication of an array of heterostructured solar-cell devices on the wafer, it is then possible to measure them by mounting the wafer onto a programmed motor stage or connecting the electrodes to programmed switches. The output data can be collected and compared automatically for the efficient optimization of composition or doping.

(3) Instead of depositing precursor materials layer by layer, precursor materials grow simultaneously, thus avoiding the slow and problematic post-annealing process.

(4) The technique is amenable to depositing thick films by simply extending the deposition time.

(5) This system minimizes mask-misalignment problems. In sequential combinatorial processes, the distribution of precursors is controlled by masks that are changed and aligned during deposition. It is also simple to heat the substrate. *In situ* heating is essential for the deposition of most materials. However, in combinatorial process, the mechanical alignment of masks has been proved to be very difficult while heating the substrate. Use of a single mask also improves the system flexibility with respect to substrate size, sample size, and so forth.

(6) The composition change of segment samples grown by MPPLD is ordered and continuous, which is good for measurement and fast screening. In order to save time and find good samples quickly, measurement of each sample is therefore not necessary. One sample can be picked out from every four or nine neighboring samples. Detailed measurement can be done later after interesting properties have been found.

(7) It is easy to change the distribution of precursors on the substrate wafer by controlling the process. Sharp composition change might sometimes be needed for fast screening. Finer scale variations might be needed for detailed characterization. The precursor distribution can easily be changed by adjusting the substrate-to-target distance, ambient gas pressure, or the distance between the plumes. More gradual change of compositions is expected at a larger substrate-to-target distance [27]. The distribution can also be changed by adjusting the ambient gas pressure during deposition. In addition, it is also easy to change the distance between laser spots by adjusting the positions of beam splitters and the mirror. Laser-spot positions on targets can be changed, and as a result, the positions of the plumes can be changed, which will affect precursor distribution on the substrate.

Balancing these advantages is an overall non-uniform film thickness that must be backed out of any thickness-dependent analysis, and the potential for non-uniform energetics in the various plumes.

3 Ternary semiconductor combinatorial library

We tested whether useful information can be extracted from the MPPLD system by depositing and measuring a composition-spread library of the ternary semiconductor $Ga_xAg_yTe_{1-x-y}$.

Detectors for high-energy photons currently use cadmium zinc telluride (CZT), which directly converts X-ray or gamma-ray photons into electrons. Unlike silicon and germanium detectors, CZT can operate at room temperature and has a higher resolution than commercially available scintillators. It is, however, difficult to produce high-quality crystalline CZT that has the desired carrier-transport properties due to, for example, large size differences of the constituent atoms. A useful replacement material must have an appropriate band gap to ensure low radiation-detector leakage current. Furthermore, the product of the carrier mobility and charge carrier lifetime must be high to allow efficient charge collection. Finally, elements with high atomic number (high Z) or large neutron absorption cross-section are desired. We previously examined $Ga_xAg_yTe_{1-x-y}$ as a possible CZT replacement using a sequential combinatorial system [12].

We used Ag_2Te and Ga_2Te_3 as targets. A mask defining 100 element samples was placed in front of the substrate, producing the film pattern shown in Figure 6. Using the automatic scanning function of the FilmTek 3000PAR SE ellipsometer (transmission and reflection mode), the optical transmittance and reflectance spectra of the sample were obtained. The compositions were measured by X-ray fluorescence (XRF). Optical bandgaps were extrapolated using the method mentioned previously [12]. Thin films with different Ag or Ga compositions have been obtained in a batch-growth method, with measured bandgaps ranging from 1.89 to 2.38 eV. Detailed analyses of these results are underway.

4 Conclusions

A high-throughput MPPLD system has been developed and compared to the previous combinatorial approach method. With the directionality of PLD plumes and the resulting spatial non-uniformity of PLD films, this new system has many advantages over the combinatorial method, such as low cost,

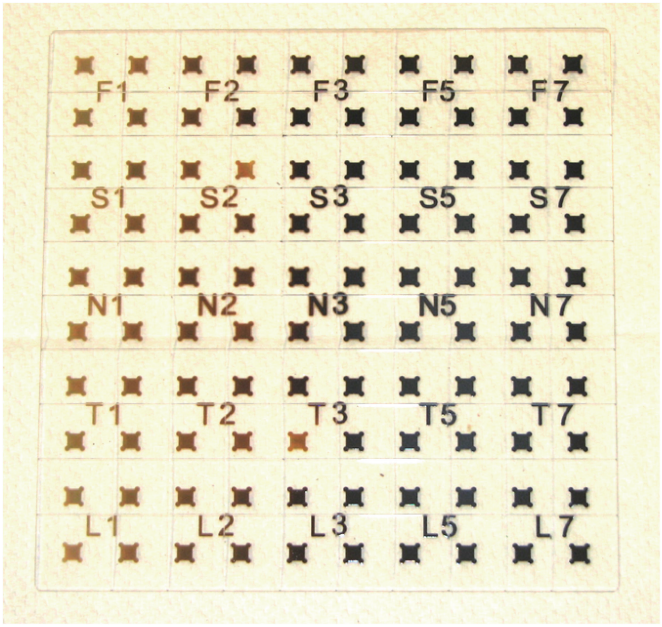


Figure 6. A picture of a fused quartz substrate with 10 × 10 samples and labels.

high throughput, simplicity, flexibility, and so forth. It is suitable for the high-throughput compound thin-film fabrication of materials systems that are only amenable to PLD.

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Compliance with ethics guidelines

Samuel S. Mao and Xiaojun Zhang declare that they have no conflict of interest or financial conflicts to disclose.

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