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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

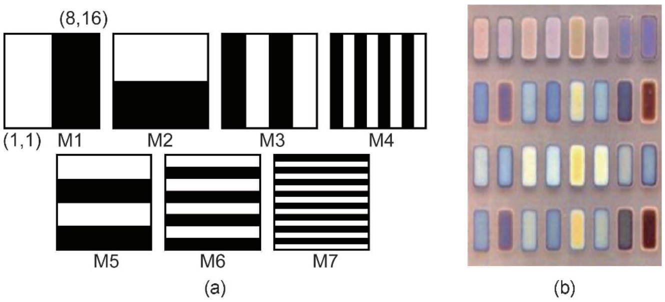

Figure 1. (a) Binary masks used for combinatorial synthesis [8]; (b) an image of a materials library prior to sintering [8].

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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 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].

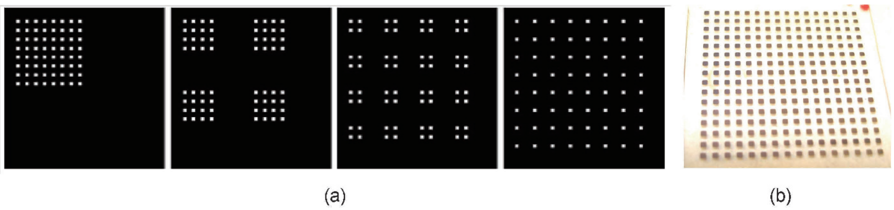
(a)
(b)

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].

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