An improved continuous compositional-spread technique based on pulsed-laser deposition and applicable to large substrate areas

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The Emergence of Nanoscale Cooperative Phenomena (ERKCS49)

Motivation:

In recent years, numerous combinatorial materials synthesis methods and high throughput evaluation techniques have been developed to accelerate the process of materials discovery and optimization.

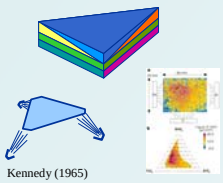
In order to successfully integrate such an approach into our thin-film physics efforts, the method must meet the following criteria:

- Applicability to non-equilibrium synthesis
- Precise control over composition (uniform profiles)
- Constant deposition parameters as function of position
- Applicability to large sample size (sufficient for traditional characterization)
- Capability of producing uniform samples in the same apparatus under identical conditions

Despite the large amount of on-going work in this area, **no approach satisfying all of these requirements** has previously been introduced.

Continuous Compositional-Spread (CCS)

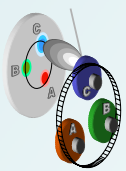
Previous approaches:



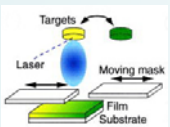
Kennedy (1965)

Schneemeyer (1998)

Schenck, Kaiser, *et al.*



Christen *et al.* (2001)



Fukumura *et al.* (2000)

Precursor approaches:

Using moving masks, precursors are first deposited, and the alloy is formed in a subsequent heat treatment process. (LBNL, Symyx)

Advantage: Precise control over composition

Disadvantage: Limited to equilibrium-route synthesis only; heterostructures not possible.

Co-deposition approaches:

Sputter approaches were first introduced in the 1960s and "revived" by Schneemeyer *et al.*, Ginley *et al.*

Overlapping *pulsed laser deposition (PLD)* plumes (Schenck *et al.*) can also be used.

Advantage: No masks needed, in-situ reaction; applicable to metastable alloys and to heterostructures.

Disadvantage: Thickness and deposition energetics vary as function of position on the substrate, thus several parameters are convoluted with the composition. Composition is a non-trivial function of position.

Sequential deposition of sub-monolayer amounts:

The pulsed nature of PLD allows the repeated deposition of sub-monolayer amounts of the constituents. Our earlier implementation (Christen *et al.* (2001) *Rev. Sci. Instrum.*) uses the flexibility of PLD to facilitate ternary phase spreads and easy "zoom-in" to a portion of the phase diagram.

Advantage: No masks needed, in-situ reaction; applicable to metastable alloys and to heterostructures. Zoom-in capability.

Disadvantage: Thickness and deposition energetics vary as function of position on the substrate, thus several values are convoluted with the composition. Composition is a non-trivial function of position.

A mask-based approach (Tokyo Inst. of Technol., Univ. of Maryland) eliminates the above-mentioned disadvantages for small substrates (i.e. if the substrate is small as compared to the length scale on which natural variations in deposition rate and energetics are observed in a PLD plume).

Their technique is thus particularly suited for experiments involving scanning measurement techniques / rapid screening approaches.

Basic principles of the new approach:

"Wedge"-type deposition profiles are obtained by translating the substrate behind a slit through which deposition occurs. The laser is fired when the substrate passes predefined positions.

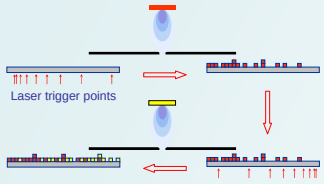
For a linear wedge profile with thickness $t = t_0 + ax$, where x is the distance measured along the substrate surface, two successive pulses are spaced by δx_i given by

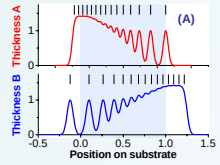
$$\delta x_i = \sqrt{\left[\sum_{n=1}^{i-1} \delta x_n + \frac{t_0}{a}\right]^2 + 2\delta x_1 \frac{t_0}{a} + \delta x_1^2} - \sum_{n=1}^{i-1} \delta x_n - \frac{t_0}{a}$$

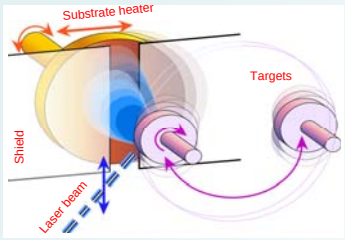
where δx_1 is chosen such that the total scan distance L is given by $L = x_N + \frac{\delta x_N}{2}$

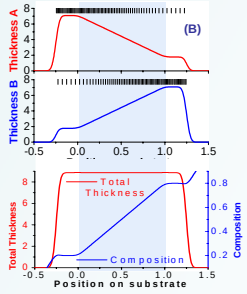
For a given slit width and travel range, a sufficient number of positions x_i must be used in order to obtain a uniform profile (see figure on right), and the profile is typically extended beyond the useful sample area.

For alloying, each pass must deposit less than a monolayer of each material; the software therefore uses several passes across the substrate to deposit on all predefined positions.









Simulations: **(A)** An insufficiently small number of deposition pulses per pass leads to thickness "ripples". However, smooth profiles **(B)** can be obtained if a sufficient number of deposition pulses are used.

Apparatus:

Target Exchange:

Fully automated, 4-target carrousel. Target exchange in < 0.5 sec.; or continuous rotation of carrousel. Target rotation; target exchange mechanism additionally allows for target rastering.

Substrate Heater:

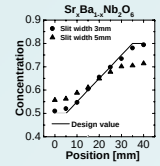
>800ºC in oxygen, 50mm diameter hot area; Translation: 70mm travel, <0.5 sec. for full travel; Rotation: <0.5 sec. to reach any angle.

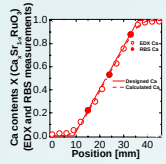
Excimer Laser:

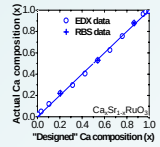
Lambda Physik LPX 325i, ≤250Hz, KrF. External triggering fully synchronized with target/substrate manipulation

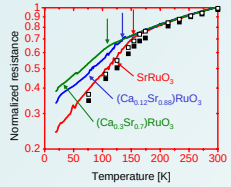
Proof of concept:

The "sharpness" of the compositional profile depends strongly on the width of the slit-shaped aperture. As shown in these figures, a well-defined, linear composition profile can be obtained, and the actual composition (as measured by EDX and RBS) agrees extremely well with the desired values.

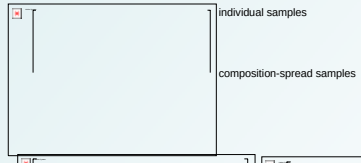






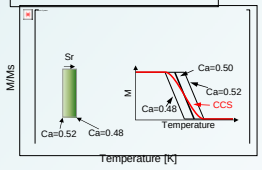


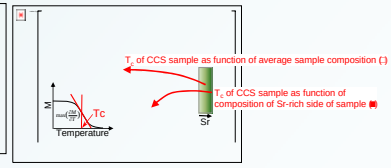
On $Ca_xSr_{1-x}RuO_3$ samples obtained by this technique, R(T) and SQUID magnetometer measurements were performed, and the data are in excellent agreement with those for individual samples and literature values. The composition varies by 3~5% across each sample if the entire range ($0 \le x \le 1$) is studied in a single spread. M-T curves of composition-spread thin films are therefore broader than those of individual thin films due to the composition inhomogeneity. Curie temperatures of composition spread thin films determined by SQUID magnetometry are in good agreement with those of individual thin films and literature values of bulk samples



Note: the composition varies by 3~5% across a composition-spread sample.

This must be considered for data interpretation. Our analysis shows good agreement between individual samples and CCS-samples in T_c determination from SQUID data





Summary:

This work demonstrates a compositional-spread approach **for the rapid discovery of materials**, combining the following criteria:

- precise composition control
- non-equilibrium route synthesis
- applicability to superlattices and heterostructures
- zoom-in capability
- uniform deposition energetics and film thickness

with a sample size that allows us to use standard characterization techniques, such as SQUID magnetometry, X-ray diffraction, R(T) measurements, and ellipsometry.

Significance and impact :

Integration of a compositional-spread approach into a complete thin film physics research effort provides significant time-savings and facilitates the systematic investigation of compositional-dependencies.

The apparatus and method developed here will thus lead to increased productivity and discoveries of interesting new materials in a number of projects.