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Controlled deposition of wedge-shaped profiles for thin (~10Å) layers by pulsed laser deposition

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ABSTRACT

A method yielding precisely controlled thickness profiles in thin-film growth is necessary for continuous compositional spread techniques. While multiple approaches have been introduced and successfully tested, some specific applications require the use of very thin "wedge"-type profiles (~10 Å at the thickest point), while at the same time yielding lateral sample sizes of several centimeters. Here we introduce the basic principles of a pulsed-laser deposition based approach utilizing the translation of the substrate behind a slit-shaped aperture and demonstrate by simple calculations that this method can satisfy these requirements.

INTRODUCTION

Recent advances in data analysis, data acquisition, and robotic techniques have led to intensive efforts to develop combinatorial and compositional-spread techniques, i.e. approaches in which a multitude of samples are prepared in one fabrication run. The clear advantage over the conventional "single-sample approach" is that all fabrication parameters are kept identical by design, while the effect of chosen variables (such as composition, film deposition temperature, or film thickness) can be studied in much detail.

In continuous compositional-spread (CCS) methods, a continuous variation of the composition across the sample is obtained either by sputtering, evaporation, or pulsed laser deposition (PLD). Fundamentally, all of these techniques rely on an intentional spatial variation of the deposition rate, i.e. the deposition of wedge-shaped thickness profiles of thin films. Two wedges having opposite orientations and corresponding to different composition can either be deposited simultaneously [1-5] or sequentially [6-11].

The deposition of controlled "wedges" is thus the foundation of all of these approaches, and three basic techniques can be used (see Fig. 1).

The simplest and oldest approach relies on the naturally occurring variation in growth rate across a substrate, as shown in Fig. 1a. The inherent simplicity of this approach is its main advantage, and the technique has found applications in sputter-based [1-4] and PLD-based [5-7] studies. However, the resulting thickness profile is non-uniform and difficult to adjust.

The approach illustrated in Fig. 1b relies on the gradual motion of a shield during the deposition. If the deposition rate is uniform across the substrate (and in time), then a simple linear motion of the shield will result in a linear deposition variation [8-10]. In PLD, where the deposition profile usually varies significantly in space, this approach is limited to small sample sizes.

As an alternative to moving the shield, the sample can be translated parallel and behind a slit-shaped aperture, as shown in Fig. 1c [11]. However, careful synchronization between translation and deposition rate is required.

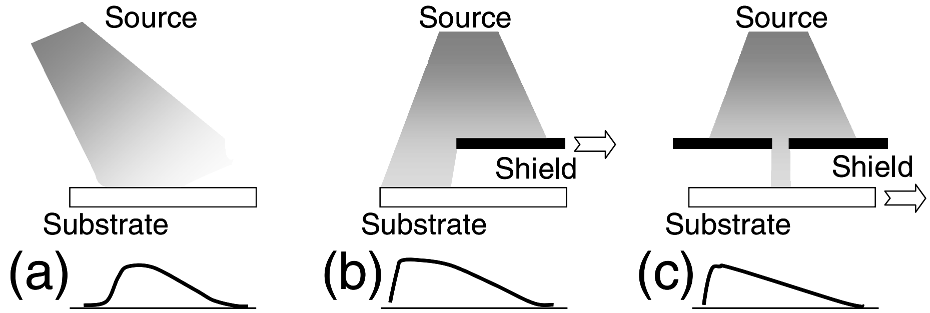

Figure 1. Basic approaches for the deposition of wedge profiles. In (a), the natural variation of the growth rate from a deposition source is utilized. In (b), a moving shield is used to deposit controlled wedges (limited only by the uniformity of the deposition source). In (c), a shield is used to select a uniform portion of the deposition zone, and the substrate is moved.

For many applications, the total amount of material to be deposited is small. For example, for the subsequent formation of nanoparticles, or in the study of catalysis, the largest amount of deposited material may only be a few Angstroms. Therefore, for verification of the growth rate after the process, the approach must be capable of depositing (in the same run) a reference layer of much larger thickness. This requires a large spatial range over which deposition can occur uniformly, and thus implementations (a) and (b) are not suitable.

Here, we present the basic principles of an approach satisfying these criteria, based on the translation of the substrate behind a slit-shaped aperture (case (c)).

CONCEPT OF THE APPROACH

As mentioned above, in an approach utilizing a moving shield, a simple constant-velocity translation of that shield in combination with a constant deposition rate suffices to yield a linearly-varying thickness profile. In the approach based on a moving substrate (as required for large deposition areas), either the translation velocity or the deposition rate must be adjusted during each pass. Pulsed laser deposition is particularly suited for this approach because the deposition in "quantized" and can be precisely controlled using simple automation techniques (laser firing controlled from motion control software). With an aperture in the shape of a slit, each laser pulse will deposit a rectangular-shaped "line" across the substrate, having a width w. The sample is then moved in finite steps by a distance s. Note that the use of simple laser beam scanning in the direction parallel to this slit-shaped aperture yields good uniformity along the profile.

ADVANTAGES AND DISADVANTAGES OF DIFFERENT OPTIONS

In Fig. 2 we show the two basic possibilities: (a) illustrates the case where the substrate is moved in steps that are equal in size to the width of the deposition profile (i.e. $w = s$), and at each point, an incrementally larger amount is deposited. (b) illustrates the case where the slit is wide as compared to the step size ($w = 3s$). These curves are obtained under the assumption of an ideally sharp profile. However, due to the physical distance between the shield and the substrate, the deposition lines will be broadened. In Fig. 2c and 2d, the solid lines are the profiles correspond-

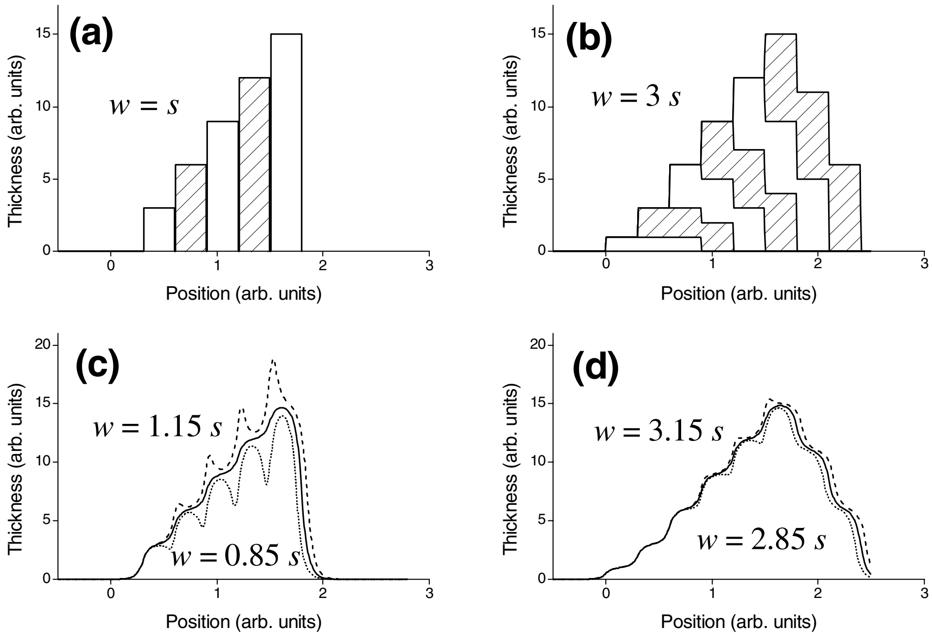

Figure 2. Illustration of the approach (a) in which to the width of the line-shaped profile deposited on the substrate is equal the step size ($w = s$) and (b) in which $w = 3s$; for ideally sharp lines. Broadening of the deposited lines yields the profiles indicated by solid lines in (c) and (d). Also shown in (c) and (d) are profiles calculated for erroneous values of w.

ing to those in (a) and (b), re-calculated with the assumption of a broadening ("smearing-out") of the lines by an amount of $0.15s$.

The most significant difference between the two approaches is the slight non-linearity for the case of $w > s$. In fact, it is readily seen that the profile is non-linear for the first distance L_{NL}, given by the overlap between successive deposition lines:

$$L_{NL} = w - s \,. \tag{1}$$

In addition to broadening of lines, in real experiments the actual line width may be slightly different from the ideal value. An error of $0.15s$ was assumed for some of the calculations in Figs. 2c and 2d. The dotted lines correspond to an underestimate, the dashed lines to an overestimate.

Here, distinct differences between the two approaches are observed: clearly, a method where the line width is large as compared to the step size is much more "robust" than the case of $s = w$.

The effect of line broadening and asymmetry is illustrated by the calculations presented in Fig. 3. Cases (a) and (b) correspond to the ideal and slightly broadened examples of Fig. 2. Despite the small non-linearity near the beginning and the end of the wedge, the overall quality of the profile is excellent. Further broadening (case (c)) yields an even smoother variation of the thickness; however, there's an additional deviation from the desired profile near its beginning and its end.

Finally, cases (d) and (e) illustrate the situation for asymmetric lines. Such lines occur, for example, in PLD when the plume and the aperture are strongly misaligned. As these calculations indicate, even in this case, the overall linearity of the profile is preserved. This shows the inherent robustness of this approach.

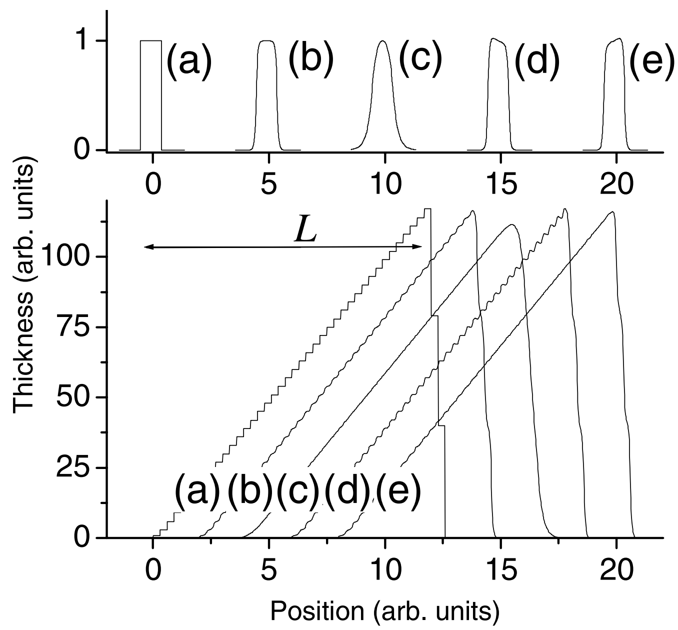

Figure 3. Effect of line shape on the resulting “wedges”. Cases (a), (b), and (c) are symmetric profiles with varying degrees of broadening. (d) and (e) are broadened to the same extent as (b), but are asymmetric. In all cases, the overall linearity of the wedge is preserved.

PRACTICAL CONSIDERATIONS

In a typical experimental configuration, the width of the line (w), the growth rate per pulse (d), the thickness D at the thickest point, and the distance L (see Fig. 3) over which the entire wedge should be deposited, are the external parameters that are imposed. The step size (s) and the number of steps (N) are then to be determined. The pulsed nature of the process obviously limits the use of s to values for which $w = k\,s$, where k is an integer, and therefore not all combinations of w, d, D, and L are possible.

Therefore, for a typical experiment, it is useful to first determine an initial (“desired”) value D_d, for which the parameters s and N are then determined. Because some combinations of s and N are incompatible with the experimental w, the value of s must be adjusted. The actual value of D_a is then re-calculated. For $N >> w/s$, we will find that $D_a \approx D_d$.

For these calculations, we first note that for values of N such that $N >> w/s$, the total thickness can be approximated as

$$D_d \approx d\,N\,w\,/\,s. \tag{2}$$

Obviously, the total length of the profile is given by

$$L = N\,s. \tag{3}$$

Combining equations (2) and (3), one finds

$$s \approx \sqrt{\frac{d}{D_d} L w}\,. \tag{4}$$

Using the result of equation (4), the ratio w / s will in general not be an integer. For sufficiently small growth rates d per pulse, w/s will be quite large (typical values in our experimental configuration range from 10 – 100), and can easily be rounded to the nearest integer.

With the value of s now determined, N is calculated from equation (3), and the correct value of D_a is obtained from

$$D_a = d\left[\left(N - \frac{w-s}{s}\right)\frac{w}{s} + \sum_{n=1}^{w/s-1} n\right]. \tag{5}$$

Once again, it is readily seen that for $N >> w/s$, equation (5) reduces to equation (2).

Finally, it is worthwhile to note that for a sufficiently broadened profile, the requirement of $w = k\,s$, where k is an integer, can be lifted, and the determination of the parameters becomes trivial.

CONCLUSIONS

The results presented here clearly indicate that an approach based on the translation of a substrate behind a slit-shaped aperture can be used to deposit linearly-varying thickness profiles as required for continuous compositional-spread (CCS) approaches. Calculation of the parameters is straight-forward using the equations presented in this paper. Applications of the approach include a variety of CCS experiments. In particular, the method is particularly suited to the deposition of thin wedge-shaped profiles, as used, for example, in studies of catalysts.

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