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Supersonic cluster beam deposition of nanostructured thin films with uniform thickness via continuously graded exposure control

C. Chiappini and P. Piseri
Dipartimento di Fisica and CIMAINA, Universitá di Milano, Via Celoria 16, 20133 Milano, Italy

S. Vinati
Tethis srl, Via Russoli 3, 20151 Milano, Italy

P. Milani
Dipartimento di Fisica and CIMAINA, Universitá di Milano, Via Celoria 16, 20133 Milano, Italy

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Supersonic cluster beam deposition is a powerful technique for the production of nanostructured thin films and the microfabrication with stencil masks of patterns with very good lateral resolution. The high focusing of cluster beam typical of supersonic expansions causes the deposition of films with strong thickness variation over a small area. To overcome this problem we have designed and tested a rotating screen allowing a continuously graded exposure of the substrate during cluster beam deposition. This allows the production of nanostructured films with uniform thickness over a large area while keeping all the features typical of supersonic beams. © *2007 American Institute of Physics.* [DOI: 10.1063/1.2746824]

Among different gas phase approaches to nanofabrication, supersonic cluster beam deposition (SCBD) is gaining increasing attention for its wide variety of applications.[1] SCBD offers considerable advantages for neutral cluster manipulation compared to other techniques based on effusive beams making the seeded supersonic beam approach very powerful for the deposition of nanostructured films and, in particular, for the coupling with microfabrication techniques.[2,3] Cluster-assembled films with tailored structural and functional properties can be obtained by exploiting aerodynamic focusing in seeded supersonic beams.[4,5] In particular, the use of aerodynamic lenses[4,6] allows an unprecedented control on nanoparticle spatial and mass distribution while keeping very high fluxes and deposition rates.[4] Highly focused cluster beams allow the production of patterned microstructures[3] and the deposition in batch of nanostructured materials on microfabricated arrays by combining SCBD with stencil masks.[7]

One drawback of the use of highly focused cluster beams is the strong intensity gradient that can be both radial and angular, which causes the deposition of nanostructured films with a very strong thickness variation over a small area (typically on the millimeter scale for a source-to-substrate distance in the range of 1 m).[4] This makes impractical the production of films with uniform thickness over large substrates or arrays [Fig. 1(a)]. This problem, which is the molecular beam analog of thickness gradients experienced in conventional evaporation or sputtering coating,[8] can be circumvented by rastering the substrate perpendicularly to the cluster beam during the deposition; however, this very simple solution makes partially ineffective the high level of definition of the particle velocities, typical of supersonic beams,[4] an issue which is totally irrelevant in the evaporation or sputtering source analog. The accuracy to which a mask pattern is reproduced in SCBD deposited material is dominated by the penumbra effects whose extension is controlled by the size of the virtual source (effective nozzle) from which the nanoparticles appear to emerge.[4,9] By rastering the substrate, the equivalent effect of having a virtual source as wide as the collimated beam at the deposition point is obtained, causing a considerably lower lateral resolution obtainable by stencil mask patterning. Rastering the substrates is thus a good way to obtain uniform nanostructured films over a large area, but it is not compatible with high resolution patterning.

In order to solve this problem we have developed a deposition technique not requiring substrate rastering and capable of producing films with uniform thickness over a large area. A cancellation of the angular intensity gradient can be obtained simply by rotating the substrate around an axis coincident with the supersonic beam axis. Figure 1(b) shows a nanostructured TiO_2 film obtained with this method: the radial gradient is still present whereas no angular gradient is evident. We have measured, by atomic force microscopy, the film thickness sampled at different distances from the rotation axis, obtaining thus a thickness profile, as shown in Fig. 2: we used this information to reduce the radial thickness gradient by selectively varying the beam exposure time in different regions, using the same concept introduced by Hanfmann in 1975.[10] The idea is to cover with a screen every point of the substrate at a given distance from the beam axis for a fraction of the total exposure time corresponding to 1 minus the ratio between the lowest measured thickness (corresponding to the target uniform flux) and the thickness at that point. To obtain this selective screening, similarly with Ohji *et al.*,[8] we produced a rotating screen where, for each distance from the center, a given fraction of a full angle is opaque; this fraction corresponding to 1 minus the ratio between the lowest thickness measured and the thickness at the corresponding radial distance from the beam axis is described by

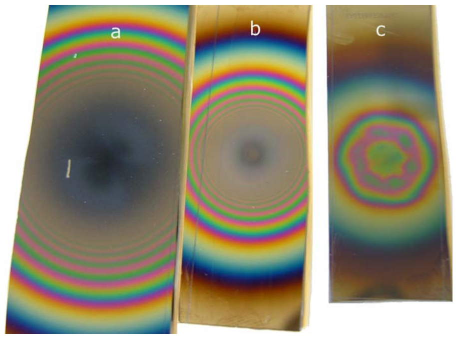

FIG. 1. (Color online) Nanostructured TiO_2 thin film deposited on polished silicon wafers by SCBD. The picture shows the Fizeau fringe pattern due to the angular and radial thickness gradients. A rough estimation of the thickness can be done considering that the thickness variation corresponding to the transition of one dark fringe to the next one is in the range of 100 nm. (A) Film deposited by simple exposure to the cluster beam. (B) Film deposited on a rotating substrate with the rotation axis parallel to the cluster beam axis. Angular uniformity is achieved while the radial gradient is still present. (C) Film deposited on a rotating substrate and with a rotating mask for continuously graded exposure control. The slight angular gradient is due to a small misalignment of the three axes of the cluster beam, rotating screen, and rotating substrate system.

$$s(r) = 1 - t_{\min}/t(r), \tag{1}$$

where $s(r)$ is the screening fraction of the full angle at distance r from the beam axis, $t(r)$ is the film thickness at that point, and $t_{\min}$ is the minimum thickness (measured at distance $r_{t\_\min}$). Equation (1) determines the shape of the screen needed to produce uniform thickness over the full circle centered at the beam axis and with a radius corresponding to the point where $t_{\min}$ was measured. In this way every point at distance r will be exposed to the beam for a fraction of the total exposure time corresponding to $1-s(r)$. If $I_0(r)$ is the mean unscreened beam intensity over a full angle rotation at distance r from the beam axis, the mean (averaged over the whole deposition time) screened beam intensity $I(r)$ will be

$$I(r) = I_0(r)[1 - s(r)]. \tag{2}$$

Since film thickness can be defined as $I(r)T$, where T is the exposure time, the screened thickness will be

$$t_s(r) = I(r)T = I_0(r)T[1 - s(r)] = t(r)t_{\min}/t(r) = t_{\min}. \tag{3}$$

With this kind of graded screening, the film thickness at any distance r from the center smaller than $r_{t\_\min}$ will be the same as $t_{\min}$.

No special restrictions are present in general on the rotating speeds of both mask and substrate, but a simple rational relationship between the two should be avoided in order to get better averaging conditions by preventing the recurrence of mask-substrate configurations. Also, a general good practice should be to make the period of rotations considerably smaller than the deposition time in order to reduce the errors introduced by incomplete shading cycles. In the presence of source intensity fluctuations versus time, better results are obtained when the period of rotation is significantly smaller than the typical correlation time scale of intensity modulations. A different situation occurs with pulsed sources where periodic intensity modulations are present on a fast time scale as compared to the mask rotational speed. In this latter case the best results should be obtained again by adjusting the repetition frequency of the source and the rotation frequencies in order to avoid simple rational relationships.

The screen is fabricated as a metal disk etched in a clamshell-like pattern, as shown in Fig. 3. The etching pattern was computed and drawn by a specifically written numerical code according to the formulas reported above; the actual screen was then obtained by a photoetching technique. In detail, after removing the oxide surface layer from a 100 μm thick foil of copper-zinc alloy, we sprayed both faces with photoresist. The foil thickness was selected to show the best agreement against foil stiffness and etching simplicity and resolution; the low stress accumulation characteristics of nanostructured materials grown by cluster assembling[11] allow us to use very thin foil for mask fabrication (no mask deformation was observed even after several microns of deposited material). We printed the clamshell pattern on a transparent vinyl acetate sheet. We then exposed the metallic foil to UV light with the acetate sheet interposed between the UV source and the foil, thus transferring the pattern on the photosensible layer sprayed on the metallic foil. We then developed the photoresist pattern by immersion in NaOH. The final etching step was conducted in $FeCl_3$

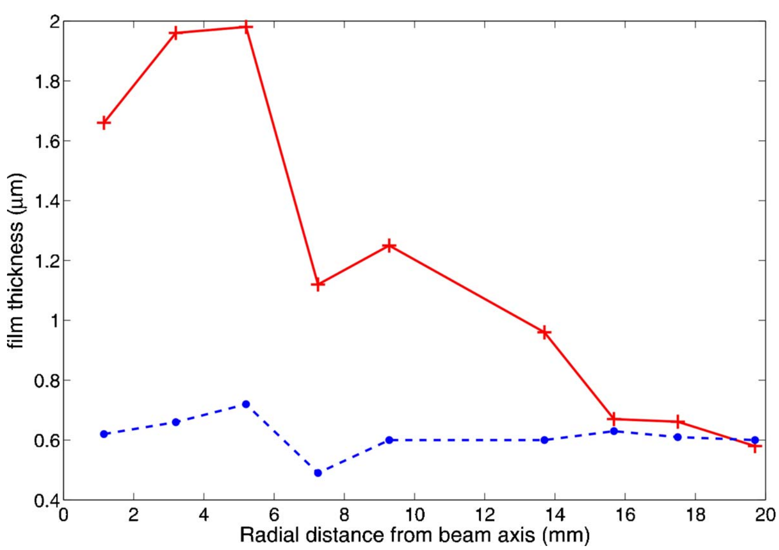

FIG. 2. (Color online) Radial thickness profile of a nanostructured TiO_2 film by atomic force microscopy (AFM) with and without a graded exposure screen for the compensation of radial intensity variation.

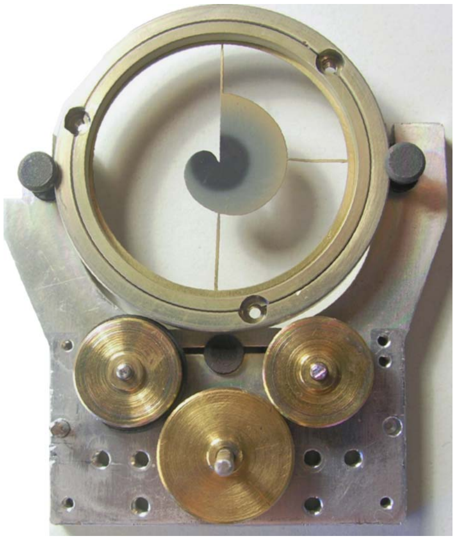

FIG. 3. (Color online) Graded exposure screen holder and rotator with screen mounted.

where the etching solution eroded the exposed part of the metal, resulting in the desired screen form. A resolution of the etched screen in the order of 100 μm could be achieved this way. A high vacuum compatible screen holder and rotator has been realized that allows rotation around a given point in the screen pattern without the need of a physical axis passing through that point (Fig. 3).

We have tested this device for SCBD deposition of nanostructured TiO_2 films with angular thickness uniformity obtained by substrate rotation. The films are deposited on a polished silicon substrate that allows a direct estimation of thickness gradient through the observation of the Fizeau fringe pattern [Fig. 1(c)]. The strong improvement in film thickness uniformity is clearly evident (Fig. 2); only close to the beam axis a residual radial thickness gradient can still be observed. This is due both to the limited photoetching precision and to some imperfect alignment of the cluster beam, rotating screen, and rotating substrate system.

A very critical parameter for the reduction of gradients within this approach is the precise alignment that must be obtained between the cluster beam axis, the substrate rotation axis, and the screen rotation axis. This is quite complex and extremely difficult to achieve with the required precision. The double rotation of the screen and the substrate can also cause, in conjunction with a slight misalignment, the reemergence of the angular gradient and an incomplete obliteration of the radial gradient. These newly generated angular and

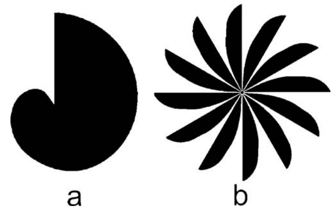

FIG. 4. (A) Single and (B) multiple leaflet radial thickness screens.

residual radial thickness gradients are, nevertheless, much smaller than the original ones.

In order to reduce these residual gradients while simplifying the alignment procedure, we designed a screening disk composed of multiple identical leaflets (Fig. 4), each one shadowing only a fraction of the full angle. The principle described above can be applied indeed to any integer fraction $1/n$ of the full angle by repeating the same shape n times in a daisylike mask pattern. It can be easily seen how in the limit of very large n the screen can be efficient in producing radially uniform deposits even without rotating. Numerical computations suggest that good results should be obtained with a fixed screen if the number of leaflets is larger than 10, i.e., with each leaflet spanning an angle of $2\pi/10$ or less. The production of screens with a large number of leaflets requires though an etching technique with a higher resolution compared to what is used for the results described in this article.

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