

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Pulsed Laser Deposition of Large-Area Thin Films and Coatings

Armen S. Kuzanyan and Astghik A. Kuzanyan

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/64978>

Abstract

Simple and inexpensive methods of obtaining large-area uniform in thickness and composition thin films on rotating substrates and moving ribbons through pulsed laser deposition have been proposed. Thin films of different compositions were prepared using these methods. The thickness uniformity of obtained films was preserved within the limits of $\pm 3\%$ on up to 300 mm diameter substrates. Also, a method of creating a laser spot with a certain configuration on the target is proposed allowing almost full utilization of the target material.

Keywords: pulsed laser deposition, large-area films

1. Introduction

The wide application of thin films in newest technologies has revealed the need of developing simple methods of obtaining large-area thin films. One of these methods is provided by pulsed laser deposition (PLD). It equally provides high speed of deposition, correspondence of the film composition to that of the target, and possibilities to vary the gas pressure in the deposition chamber in a wide range.

PLD started developing rapidly after the discovery of high-temperature superconductivity. Scientists needed samples of new multicomponent materials, superior in their characteristic to the ceramic ones, for identification of their physical properties and disclosure of high-temperature superconductivity mechanism. For solution of these issues, the Laboratory of High-Temperature Superconductivity was founded in the Institute for Physical Research NAS of Armenia in September 1987. Here, we present the research conducted in this laboratory to

develop new approaches and solutions for the preparation of large-area homogeneous in composition and thickness thin films and coatings of complex compounds. PLD turned out to be a very convenient tool to obtain thin films of high-temperature superconductors.

PLD is used to grow thin films of metals, oxides, polymers, biocompatible materials, and so on. It allows the fabrication of ultra-thin epitaxial single-crystalline, polycrystalline and amorphous films, heterostructures and nanocrystalline coatings [1, 2]. PLD is simple in application and, therefore, is widely used in research laboratories. However, it is also promising for various commercial applications, in particular, growth of large-area films. Films of uniform thickness on large-diameter substrates are necessary for many applications in microelectronics, optical industry, and other modern technologies.

Wide use of PLD in the growth of large-area films is impeded by the following circumstance: the angular distribution of the mass-transfer rate in the plasma plume formed by laser radiation is nonuniform. Therefore, using conventional laser deposition, one cannot obtain films of uniform thickness on substrates larger than 10 mm in diameter. In this chapter, we describe some main solutions to this problem and propose a new technique for depositing thin films of uniform thickness on large-area substrates the size of which is limited by the deposition chamber dimensions only.

All versions of PLD of large-area films are based on the fact that the angular distribution of the mass-transfer rate in a plasma plume is set by the function $F(\theta) = A \cos^m \theta$ [1], where θ is the angle of deviation from the perpendicular to the target plane. The plasma plume axis, that is, the direction in which the mass-transfer rate is maximal, is perpendicular to the target surface in a wide range of variation in the angle of incidence of laser beam on the target. Knowing the angular distribution of the mass-transfer rate of the material evaporated from the target, one can arrange the mutual position and motion of the target and substrate to provide identical amount of evaporated material per substrate unit area over the substrate surface and thus grow films uniform in thickness.

2. Main solutions for depositing large-area films

Let us briefly consider the main existing ways for large area films deposition [1]. In one of them, a laser beam is incident on a rotating target, before which a rotating substrate is located parallel to the target. The substrate axis is shifted with respect to the plasma plume axis by some distance (**Figure 1a**). This distance is determined by the width of the gap between the target and the substrate, the substrate diameter, and the angular distribution of evaporated particles in the plasma plume. Thus, the part of the plasma plume that is characterized by a higher mass transfer of evaporated material arrives at the substrate edge, where a larger area must be coated for the same time; as a result, a film of uniform thickness grows. A modification of this technique is the version shown in **Figure 1b**. Here, the substrate simultaneously rotates and moves in the horizontal plane. A computer controls the horizontal displacement velocity of the substrate in such a way that the plasma plume axis is directed toward the substrate edge for a longer period as compared to the center.

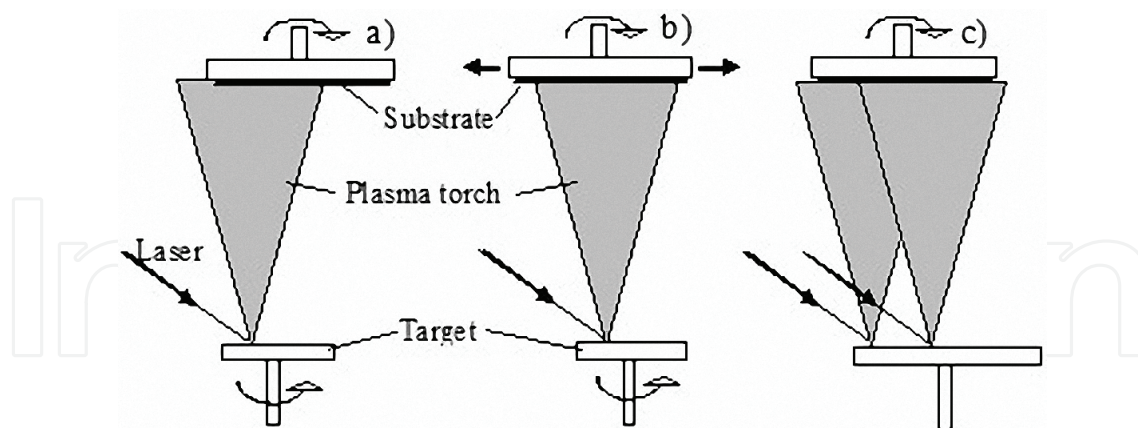


Figure 1. Schematics of the main techniques for depositing large-area films: (a) “off-axis” deposition, (b) deposition on substrate that simultaneously rotates and moves in the horizontal direction, and (c) scanning the laser beam on the surface of a large target.

The drawback of the first version (**Figure 1a**) is the spatial confinement of the ablation plasma plume. Substrates whose diameter exceeds some limiting size are not overlapped completely by the plume region where the mass-transfer velocity is sufficiently high. This drawback can be compensated for by mounting the substrate at a larger distance from the target; however, the larger the substrate, target distance, the lower the deposition rate. In addition, the stoichiometry of multicomponent films can be preserved only in certain range of variation in the substrate—target distance.

The drawback of the second version (**Figure 1b**) is the necessity of preliminary analysis of the angular distribution of the mass-transfer rate in the plasma plume in specific geometry and under specific deposition conditions. In turn, the angular distribution of the mass transfer may vary during deposition, because it depends on several parameters, which may also vary during long-term deposition. There are many modifications of the above-described techniques. Some achievements in growing large area films by PLD were described in the study of Eason [2]. As previously, the main technique is based on scanning the laser beam on the surface of a large target (**Figure 1c**). However, the manufacture of a large target for some of the compounds can be very expensive.

3. Proposed methods of deposition on rotating substrate

Three relatively simple methods of laser deposition of large area thin films are proposed [3, 4]. The first method is based on the target tilt control relative to the laser beam and its focal spot while the substrate is maintained in the same position. Specifics of other two methods include the deposition of a compound on a substrate through a mask with consideration of various slits on it. In one of the options, the mask has a slit in the form of a sector symmetrical to the substrate radius and with variation of angular sizes at different values of the radius. Another option uses a mask with two bent sector-shaped slits located symmetrically relative to the line of equal velocity of the compound mass transfer path.

Conditions of films deposition at experimental verification of the proposed methods were the following. The deposition was performed using the third harmonic of an Nd³⁺:YAG laser ($\lambda = 355$ nm) with the pulse characteristics: energy, 15 mJ; width, 10 ns; and repetition rate, 20 Hz. The target and substrate rotation speeds were 37 and 2 rpm, respectively. AMBIOS XP-1 profiler was used to control the thickness of the obtained films.

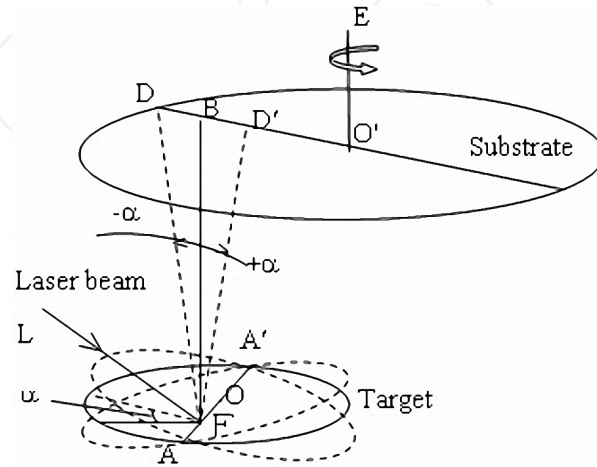


Figure 2. Geometry of tilting target method.

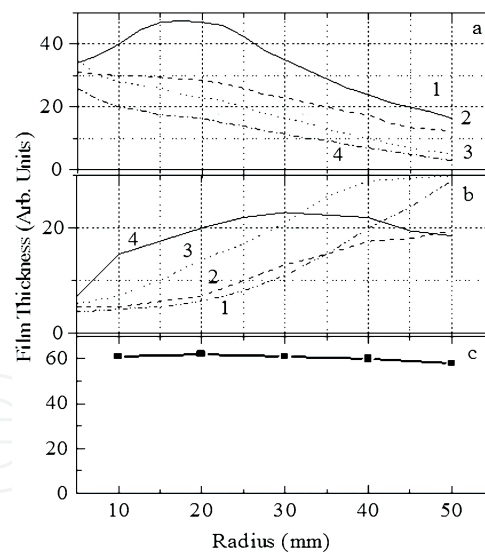


Figure 3. Dependence of film thickness on substrate radius. (a) $\alpha = +18^\circ$: $d = 0.8$ mm (1), 0.65 mm (2), 0.45 mm (3), 0.3 mm (4); (b) $\alpha = -30^\circ$: $d = 1.05$ mm (1), $\alpha = -24^\circ$: $d = 1.05$ mm (2), $\alpha = -30^\circ$: $d = 0.8$ mm (3), $\alpha = -24^\circ$: $d = 0.65$ mm (4); and (c) $\alpha = -24^\circ$: $d = 1.05$ mm and $\alpha = +18^\circ$: $d = 0.45$ mm.

3.1. The method of tilting target

The first method directing the plume flux to various substrate areas is illustrated in **Figure 2**. Here, the target with a center in point O is tilted around the axis passing through the center

and perpendicular to the laser beam. This AOA' axis is parallel to the substrate plane rotating around O'E. In original substrate position, the plume axis coinciding orthogonal to the target plane is crossing the substrate at point B. With tilted substrate, this intersection point is traveling from point D to point D' as it is marked by the dashed lines.

Angular distribution of the material ablated by the laser beam has a number of parameters it depends on. We have narrowed the variability to the slant angle (α) and the laser beam diameter (d). **Figure 3** shows the dependence of deposited film thickness on mentioned parameters as a function of substrate radius. It is clear from the charts in **Figure 3** that the proposed target tilting method allows achievement of a thicker deposition on the center and edges of the substrate. So it is possible to obtain uniform film thickness by superposing two tilts as it is shown in **Figure 3c**. Variation of the thickness of the film deposited by such a technique did not exceed $\pm 3.3\%$.

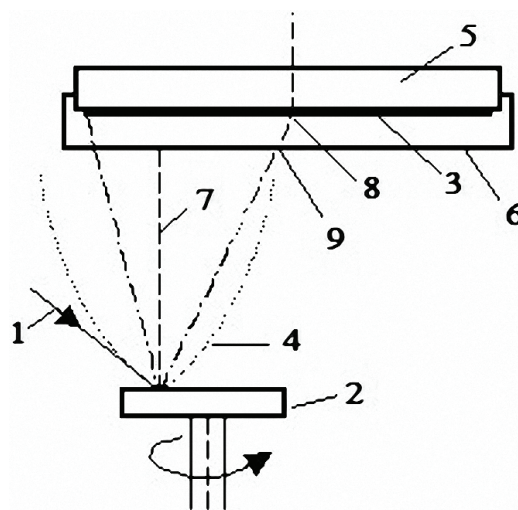


Figure 4. Geometry of mask method of deposition on a rotating substrate. 1, laser beam; 2, target; 3, substrate; 4, plasma torch; 5, substrate holder; 6, mask; 7, axis of the plasma plume; 8, center of rotation of the substrate; 9, point of intersection of the line connecting the focal spot and the center of rotation of the substrate with the mask plane.

3.2. Mask method of deposition

We have proposed two essentially different solutions of the problem of obtaining large-size films on a rotating substrate. The first method is based on the use of a mask with a slit in the form of a sector of different angular sizes at different distances from the substrate rotation axis. The slit configuration is determined on the basis of the angular dependence of the mass-transfer rate so that the thickness uniformity of the deposited film is provided. The second method uses the slits in the form of a sector with a curved symmetry axis coinciding with the equal thickness line of the film deposited on a stationary substrate. **Figure 4** shows schematically the geometry of film deposition on a rotating substrate. It is seen that it differs from the conventional off-axis deposition (**Figure 1a**), in that the deposition is performed through a mask placed in the immediate vicinity of the substrate.

3.2.1. Sectorial slit with varying angular sizes

This technique supposes deposition through a mask with a slit in the form of a sector symmetric with respect to the substrate radius and having different angular sizes at different distances from the axis of substrate rotation. The sector vertex must be in the point of intersection of the straight line connecting the focal spot and the center of the rotation of the substrate with the mask plane. **Figure 5a** shows the variation of the thickness of films along the substrate radius in different deposition processes. Curve 1 presents the process with no mask and rotating substrate. Curve 2 corresponds to deposition on the rotating substrate through a mask with a slit in the form of a sector. As expected, in this case, we obtain films of nonuniform thickness. However, curve 2 indicates where the sector should be narrowed and where broadened. Performing several depositions with different masks, we succeeded to reveal a mask configuration (**Figure 5b**) providing the thickness uniformity of the films (curve 3).

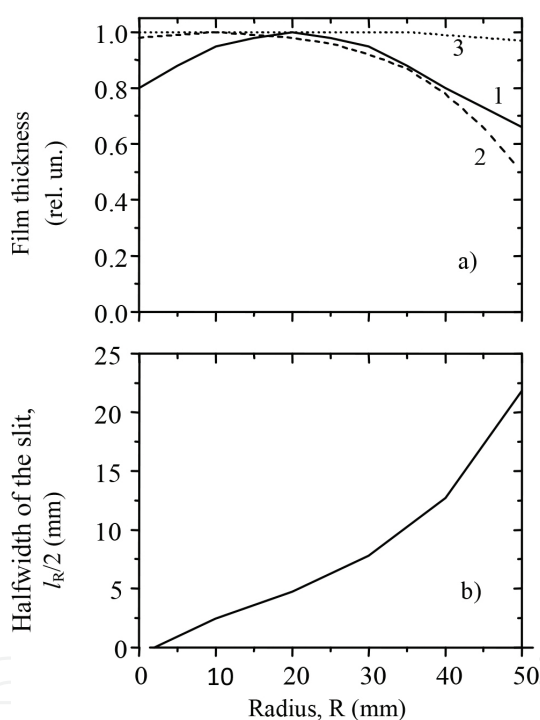


Figure 5. Radial distribution of film thickness (a) slit configuration which provided film thickness uniformity (b).

3.2.2. Calculation of the configuration of slit in the mask

In order to exclude experimental optimization of the mask-slit configuration, a method has been designed to calculate the slit form based on the data from one deposition process onto a stationary substrate. With this purpose, the deposition is performed onto a non-rotating substrate without a mask. **Figure 6** shows the relative thickness of a CuO film obtained under indicated conditions. After choosing the position of the plume axis with respect to the axis of rotation of the substrate and taking the center of rotation for the origin, we determine the

variation of the film thickness along an arc of circumference for different values of R inside a sector with an angle δ .

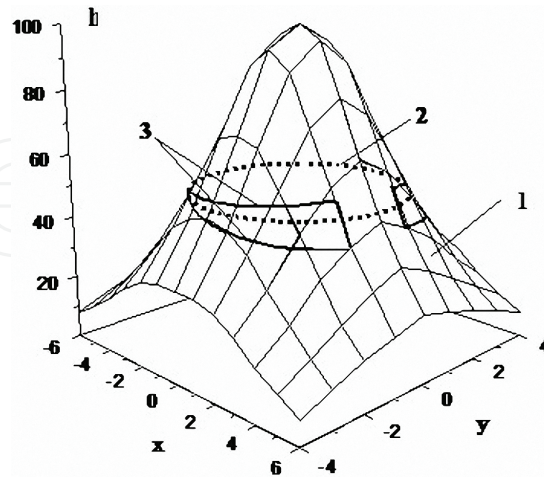


Figure 6. Relative thickness of the film deposited from CuO target on a resting substrate (1), ellipse of equal thickness (2), and the part of the plasma plume passing through the mask (3).

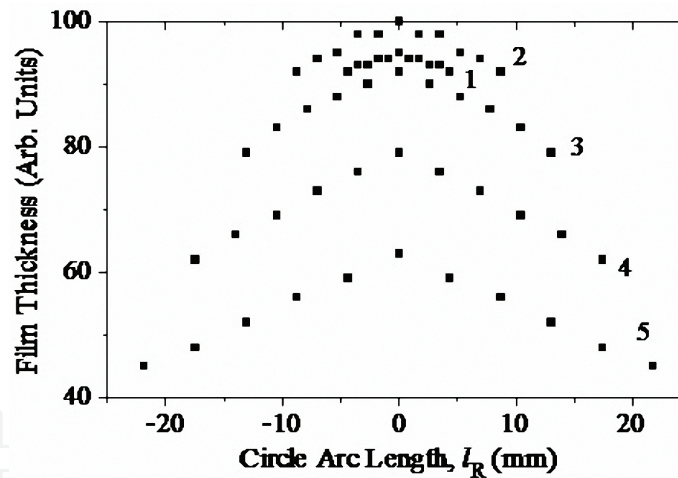


Figure 7. Distribution of film thickness along the arc at different radii R : 1, 10 mm; 2, 20 mm; 3, 30 mm; 4, 40 mm; and 5, 50 mm. The pattern is symmetric and the maximal thickness is associated with the origin of the l_R coordinate.

For given (parallel) position of substrate and target rotation axes, the film thickness on various R from the center of substrate inside the sector with δ angle is determined. **Figure 7** shows the case corresponding to $\delta = 50^\circ$ (the distance between two rotation axes is 2 cm). Using these data, the average film thickness $\bar{h}_R$ on various R is calculated in the first approximation. Then, the optimal length of the circle arc l_R is determined (i.e., the slit width on various R). This provides obtaining films with the same thickness on various R , equal to the average thickness $\bar{h}_{Rm}$ on the maximal radius R_m , according to the formula $l_R = \bar{h}_{Rm} l_R(\delta) / \bar{h}_R$. Here, $l_R(\delta) = \pi R \delta / 180^\circ$ is the

length of the arc of the radius R in the sector with an angle δ . More accurate values, l_R^2 , may be obtained if we repeat the calculation using the average values of the film thickness $\bar{h}_R^2$ for the slit corrected in the first approximation. After this step, a test of the obtained results is performed.

Both the calculation data and the experiments have shown that the described computation methodology provides the necessary precision for obtaining films with excellent thickness uniformity.

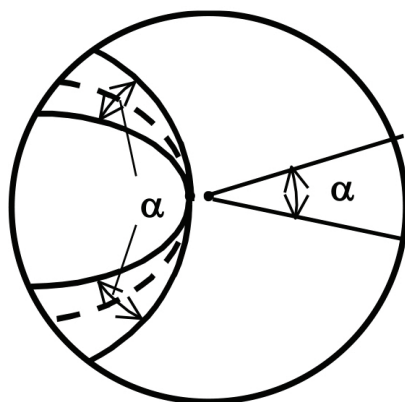


Figure 8. Distortion of sectorial slit. The mask slit curved along the uniform thickness ellipse (dashed line) provides both thickness and composition uniformity of deposited films.

3.2.3. Slit in the form of a sector with the curved symmetry axis

The method of the mask with a slit in the form of a sector with the curved symmetry axis is realized also with the use of geometry presented in **Figure 4**. This possibility to obtain thickness-uniform large-area films is due to the following circumstances. For obtaining a thickness-uniform film on rotating substrate, the slit in the mask must be a sector with the vertex coinciding with the rotation axis of the substrate. This is valid for the case of uniform flow of deposited substrate. Consider now the realistic pattern shown in **Figure 6**. If we intersect the three-dimensional surface outlining the thickness of the film, by a plane parallel to the xy -plane, we obtain the line of equal thickness of the film. This line is usually an ellipse. Intersecting the surface above by planes parallel to the xy -plane at different heights, we obtain a set of concentric ellipses. **Figure 8** shows the ellipse passing through point 9 in **Figure 4**. In every point of this ellipse, we have the same thickness of the film. The reason for this is the spatial uniformity of the flow of deposited material along this line. Hence, the slit in the mask in the form of a curved sector having the middle line coinciding with equal thickness ellipse (**Figure 8**) should provide the uniformity of the film thickness. The choice of the ellipse is caused by striving to obtain a uniform film over the entire surface of the substrate. Symmetry of the pattern with respect to the substrate radius causes the possibility to use two slits which doubles the deposition rate. The deposition rate depends as well on the value of angle α .

Figure 6 shows the domain corresponding to the part of the plasma torch passing through the mask. It is obvious that if in this domain the three-dimensional surface outlining the film thickness has no abrupt changes in curvature, inside this domain the average thickness of the film along the radius of substrate rotation will be the same for different radii and equal to the thickness corresponding to the chosen ellipse. The smaller the angle α , the better this condition is met. On the other hand, the smaller is the angle α , the lower is the rate of film deposition. Hence, it is necessary to choose α in each case depending on the specific problem.

Implementation of both mask methods of deposition onto a rotating substrate has revealed a possibility of providing for thickness uniformity for both CuO and YBa₂Cu₃O_{7- δ} films within $\pm 3.3\%$ on substrates with the diameter of 100 mm. The YBa₂Cu₃O_{7- δ} films had a high value of temperature of a superconducting transition ($T_c = 90$ K) independent of the distance between the chosen domain and the center of substrate rotation which indicates radial uniformity of the composition of deposited films. This refers more to especially the method of mask in the form of a sector with curved symmetry axis, since the rate of mass transfer for components of complex compound may vary depending on the solid angle inside the plasma torch. Another advantage of such a mask is that the central part of the plasma torch is cut off. Thereby, the density of micron-size particles inherent to laser deposition decreases.

We also point out the possibility to combine the principles underlying the two different types of slit configurations, when requirements to the film quality are especially rigid. This may be done if we employ a mask with slits having curved symmetry axis and different angular sizes at different distances from the axis of rotation of the substrate.

3.3. Deposition of large-size films

Figure 9 shows schematically the deposition geometry for large-area thin uniform films, whose transverse sizes are limited by only the deposition chamber dimensions [4]. Its distinctive features are as follows:

- the presence of a diaphragm, partially transmitting the evaporated material, between the target and the substrate.
- the translatory motion of the rotating substrate with respect to the target at a certain velocity and selecting beams with identical and maximum mass-transfer rate from the plasma torch.

It can be seen in **Figure 9** that the substrate undergoes translatory motion with respect to the target. Obviously, in this geometry the substrate motion can be replaced by the joint motion of the target and the diaphragm.

To grow a film of uniform thickness over the entire substrate surface, it is necessary to determine the motion law for the substrate. The calculation results for substrate transferred velocity V were experimentally checked by depositing thin CuO films on silicon substrates 30 mm long, located over the radius of a disk 300 mm in diameter. The angles between the target plane, laser beam axis, and diaphragm plane were chosen so as to make the diaphragm select a particle beam oriented perpendicular to the target from the plasma plume. At any changes in the deposition parameters during a long-term process in the chosen geometry, the mass

transfer rate of the target material to the substrate will be maximum and the deposition time of a film of specified thickness will be minimum.

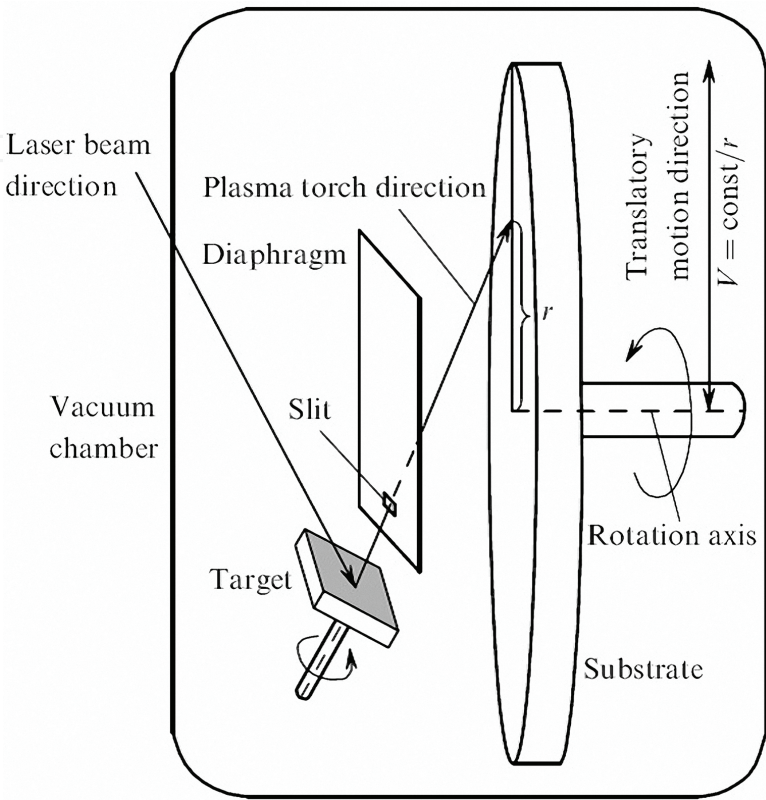


Figure 9. Schematic of the new technique for depositing thin films of arbitrary sizes.

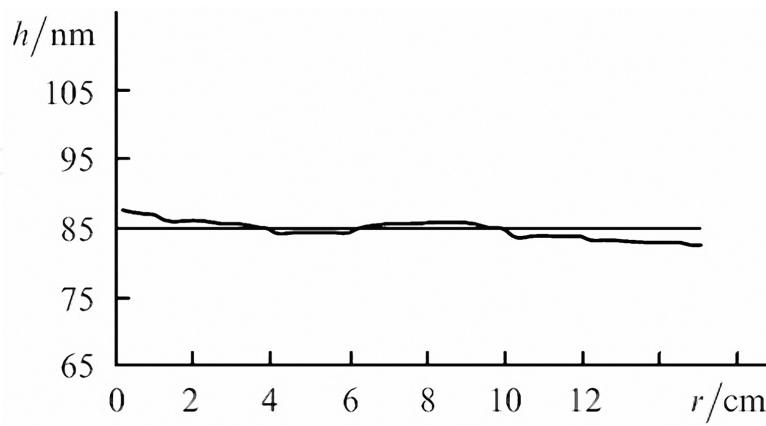


Figure 10. Surface profile of a CuO film deposited on a substrate transferred at a velocity $V = \text{const}/r$.

The surface profile of a CuO film deposited on a substrate transferred with a velocity $V = \text{const}/r$ is shown in **Figure 10**. The average film thickness is 85 nm. The thickness deviation from the average value did not exceed $\pm 3\%$ over the entire substrate surface. The method proposed

makes it possible to obtain thin films of uniform thickness on substrates with sizes limited by only the deposition chamber size.

4. Effective utilization of the target material

A commercial of PLD is hindered by its few drawbacks, main among those are a nonuniform thickness of the deposited film and a low coefficient of effective utilization of the target material. Consider the second drawback in more detail. In this method, the films are deposited due to ablation of the target material by a laser beam. Obviously, if both the target and the laser beam are immovable, then a crater arises on the target in a certain time interval. The crater affects the angular distribution of the evaporated material, that is, the thickness of the film deposited per unit time on a certain area of the substrate.

One more undesirable result is overheating of the target and distortion of its composition. The target is also overheated in the case when the laser beam is focused onto the entire surface of the target. In this geometry, no crater is formed in the target; however, the target undergoes overheating. Thus, in the case of PLD with both immovable target and the laser beam, the thickness and composition of the film deposited would vary in time. There is a simple solution to the problem—rotation of the target, which substantially facilitates the situation preventing the target from overheating and prolonging the duration of deposition without disturbing the film composition and angular distribution of the evaporated material.

However, such geometry does not solve the problem yet. A groove arises in the rotating target (**Figure 11**) and the angular distribution of the evaporated material changes with time. After several deposition cycles with a variation in the distance of the laser beam from the target center, concentric grooves arise on the surface of the target and the latter becomes unsuitable for further employment. In the conventional geometry, utilization efficiency of PLD (the fraction of its evaporated volume) is very poor (0.01–0.02). It is not important if the target material is cheap. However, if the films of rare metals and its alloys are deposited or the target is made of very high purity chemicals or isotopes, then such a low efficiency is inappropriate.

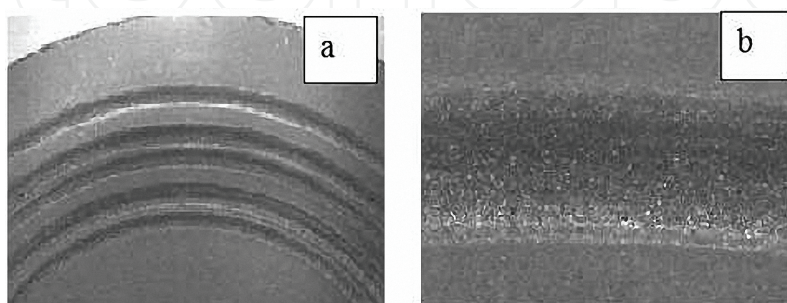


Figure 11. Target made of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ of diameter 50 mm after five deposition cycles performed by the conventional PLD method at magnification (a) 10× and (b) 60×.

4.1. Ways of increasing the target utilization efficiency

There are several known solutions to the problem for improving the target utilization efficiency in PLD of thin films. The targets employed for deposition may have polished surfaces. In this case, up to 75% of the target material may be lost [5]. There are cardinal approaches, which, however, substantially complicate the deposition installation suggesting the computer-controlled scanning of the large target surface by a laser beam (**Figure 12a**) or moving the target in two perpendicular directions relative to the fixed laser beam (**Figure 12b**). In this case, the material ablation occurs from 90% of the target surface providing in this way a noticeable improvement in the utilization efficiency.

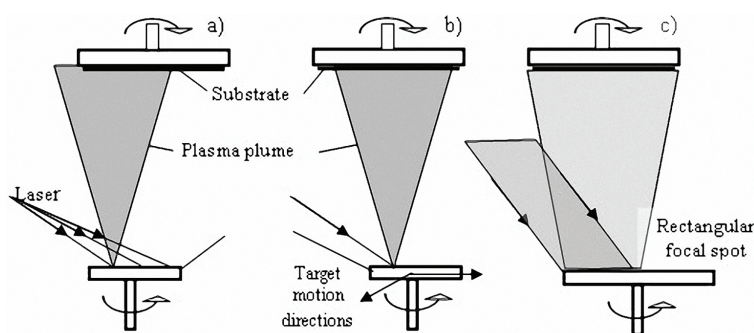


Figure 12. Geometry of the PLD method with: (a) laser beam screening the surface of target; (b) target motion relative to the laser beam, (c) rectangular focal spot along the radius of the target.

The suggestion in [6] is simple to realize: it is assumed that the laser beam is split into four parts, each of them performing material ablation from a certain area of the rotating target. Thus, a wider plasma jet of the evaporated material is formed (which facilitates the uniformity of the film thickness) and ablation occurs from a larger surface of the target. From the viewpoint of enhancing the target utilization efficiency, this approach is simply an increase in the focal spot dimensions. However, the grooves on the rotating target will still be produced with the following negative consequences. A more reasonable suggestion was patented [7, 8]. The authors complicated the mechanism of target rotation in such a way that the target rotates around two parallel axes. In this case, the laser beam circumscribes a cycloid rather than a circle over the target surface, which will increase the target utilization efficiency. Unfortunately, this approach has also a serious disadvantage (see below), which hinders obtaining high values of target utilization.

A most simple solution is, evidently, a uniform distribution of laser radiation over the entire surface of a fixed target. Such a distribution can be obtained, for example, with raster-focusing systems [9]. Nevertheless, as mentioned above, such a scheme cannot be used for depositing multicomponent compounds, because overheating of the target will affect the composition of the latter. Thus, the known methods of enhancing a PLD process aimed at increasing the target utilization efficiency either noticeably complicate the installation or do not solve the problem completely. In the present work, we suggest a simple solution to the problem for attaining a

maximal utilization of the target material, capable of increasing the utilization efficiency actually to unity.

4.2. Rectangular focal spot arranged along the target radius

One possible solution to the problem for increasing the target utilization efficiency is a rectangular spot of the laser beam arranged along the radius of the rotating target, where the focal spot of width L has the length of at least the target radius (**Figure 12c**). The center of one focal spot side coincides with the target rotation center O , and the axis of symmetry coincides with the target radius (**Figure 13**). At a first glance, it may appear that it is a simple and effective solution, because ablation of the target material will occur from the entire surface. But the quantity of the substance evaporated from a unit area is proportional to the energy passed on it. The sites of focal spot closer to the target center will affect (per single round) a smaller area than those residing far from the center. Consequently, the target material at its center will be consumed faster than at periphery.

Let a laser beam fall onto the rotating target, which has the form of a disk with radius R and thickness h_0 , forming the rectangular focal spot of width L arranged along the target radius. In time t_0 , the target executes N revolutions and the laser burns a hole at the center of the target. How much of target volume is ablated in this case?

According to **Figure 13**, one should consider two domains of the target surface: inside the circle of radius $L/2$ and outside it [10]. When the target rotates at a constant angular velocity ω , all the points inside the circle of radius $OA = L/2$ are exposed to laser radiation during half the process duration ($t_0/2$), because for these points the focal laser spot is a semicircle. In other words, inside the rectangular focal spot of width L the trajectory of any point residing closer than $L/2$ to the center of rotation (point O) is a semicircle. For example, point D on the target surface is subjected to laser radiation as long as it follows semicircle DF (**Figure 13**). Point B residing at a distance longer than $L/2$ is subjected to laser radiation until it reaches point C having passed the arced path BC .

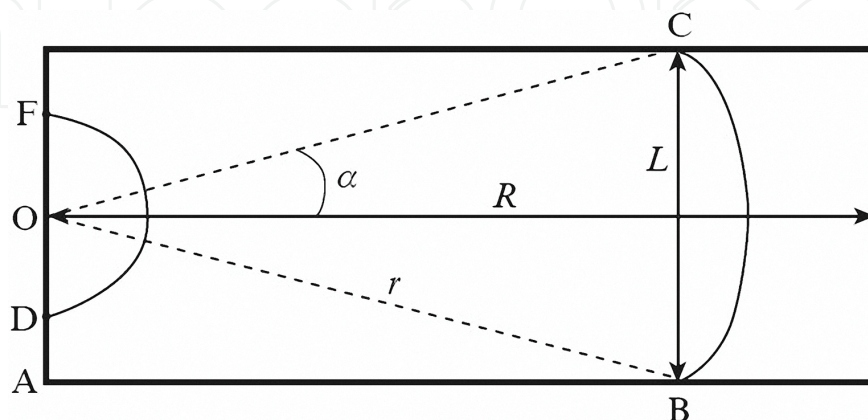


Figure 13. Scheme of the rectangular focal spot directed along the radius of the rotating target [10].

By denoting the rate of target evaporation σ (the thickness evaporated per unit time), from the condition of burning the target to a throughout hole, we may write

$$h_0 = \sigma t_0 / 2, \sigma = 2h_0 / t_0 \quad (1)$$

The points of the target surface outside the circle of radius $L/2$ at a distance r from the center are exposed to laser radiation during the time interval Δt (a single revolution of target) so that after N revolutions the target thickness reduces by the value ,

$$h = \sigma \Delta t N = \sigma N |\widetilde{BC}| / v = \sigma N |\widetilde{BC}| / (\omega r), \quad (2)$$

where v is the linear speed of point B, $|\widetilde{BC}| = 2ra = 2r \times \arcsin(L/2r)$ is the length of arc BC, and $\omega = 2\pi N/t_0$.

Then at $r \geq L/2$, the reduction of the target thickness will be

$$h = \frac{2h_0 \arcsin(L/2r)}{\pi} \quad (3)$$

Dependences of $h(r)$ for various L are given in **Figure 14**. For the points $0 < r \leq L/2$, we obtain $h = h_0$. The volume of the ablated target material is determined by the rotation of curve $h(r)$ around axis h :

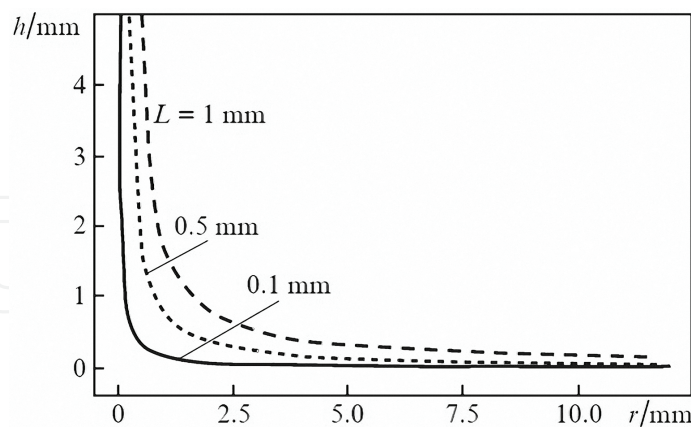


Figure 14. Target thickness h versus radius r under PLD in the rectangular focal spot geometry [10].

$$V = \pi h_1 R^2 + \pi \int_{h_1}^{h_2} \left[\frac{L}{2 \sin(\pi h / 2h_0)} \right]^2 dh, \quad (4)$$

where $h_1 = [2h_0 \arcsin(L/2R)]/\pi$ and $h_2 = h_0$. This entails

$$V = 2h_0 R^2 \arcsin\left(\frac{L}{2R}\right) + h_0 L R \left(1 - \frac{L^2}{4R^2}\right)^{1/2}. \quad (5)$$

One can see that the volume depends on three parameters: the target height h_0 , the target radius R , and the width of the laser beam L . Because the value of the target material utilization efficiency is $\eta = V/V_0$, where $V_0 = \pi h_0 R^2$ is the target volume prior to ablation, in view of Eq. (5), we obtain

$$\eta = \left[2 \arcsin\left(\frac{L}{2R}\right) + L R^{-1} \left(1 - \frac{L^2}{4R^2}\right)^{1/2} \right] \pi^{-1}. \quad (6)$$

The value of η depends only on two parameters L and R . Dependences of $\eta(R)$ for various values of L are shown in **Figure 15**. One can see that at a fixed parameter R , the volume of the ablated part of the target is greater at longer L .

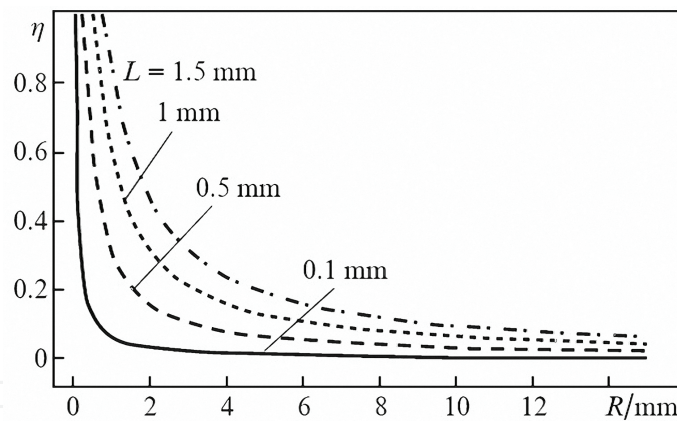


Figure 15. Target utilization efficiency versus target radius at various laser beam spot widths [10].

The expression for the target material utilization efficiency may be simplified. By introducing the parameter $k = L/R$, we may write Eq. (6) in the form

$$\eta = \left[2 \arcsin(k/2) + k \left(1 - k^2/4\right)^{1/2} \right] \pi^{-1} \quad (7)$$

Recall that the calculations are performed for the case $R \geq L/2$. At $0 < R < L/2$, the equality $\eta = 1$. **Figure 16** presents the dependence $\eta(k)$.

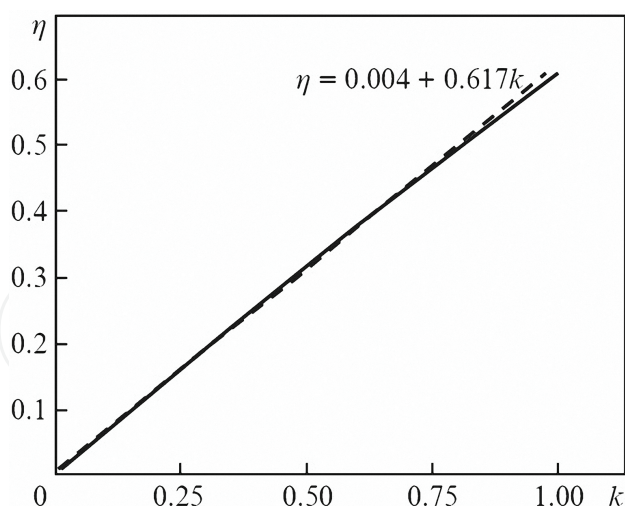


Figure 16. Target utilization efficiency η versus k . The dashed line refers to approximation [10].

One can see that at $k < 1$, it is well approximated by the straight line according to the formula

$$\eta = 0.004 + 0.617k \approx 0.6k \quad (8)$$

Thus, we have the simple expression for target utilization efficiency with a sufficiently good approximation. Obviously, for experimentally actual values of L and R where $k < 1$, the value of η will not be greater than 0.5.

Note that the method suggested in patents [10, 11] has a similar drawback. The cycloidal trajectory described by the focal laser spot on the surface of the target arising due to the rotation around two parallel axes will also result in more intense material evaporation from the central part of the target and reduced utilization efficiency.

4.3. Focal spot in the form of a sector

The consideration of the problem stated above suggests its cardinal solution. In the range $0 < R < L/2$ where the focal spot is a semicircle, the equality $\eta = 1$ holds. But a semicircle is the particular case of a sector with the angle of 180° . The scheme of the modified PLD method is shown in **Figure 17**, which simply and cardinally solves the problem on the maximal utilization of the target material. The laser deposition installation is suggested, which differs from ordinary devices by a simple optical system placed outside the deposition chamber. It comprises two lenses and a diaphragm and provides the focal spot in the form of a sector on the target surface.

If such a focal spot coincides with a sector-shape area on the target surface and the density of energy is uniform over the focal spot, then the surface of the uniformly rotating target will be uniformly irradiated, which will provide a uniform material ablation from the surface.

The device suggested was employed for depositing CuO and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ films from the targets 10 mm in diameter by the pulses of second harmonic radiation of the $\text{Nd}^{3+}:\text{YAG}$ laser with the repetition rate of 20 Hz. The optical system provided the focal spot of laser radiation on the target in the form of the sector with an angle of 60° and the energy density of 4 J cm^{-2} . Variations in the target thickness were within $\pm 2\%$ both before deposition and after five deposition cycles lasting for 45 min. One may assert that the device suggested enhances the target material utilization efficiency up to $\eta = 1$.

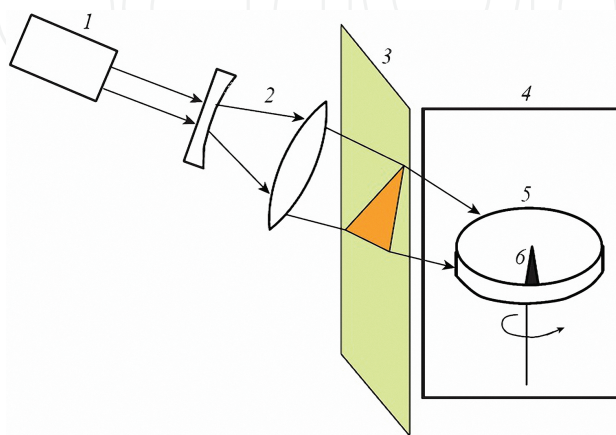


Figure 17. Geometry of the PLD method with the focal spot in the form of a sector: (1) laser, (2) optical system, (3) diaphragm with a hole, (4) deposition chamber, (5) target, and (6) laser focal spot in the form of the sector coinciding with the sector of the rotating target surface [10].

5. Deposition onto ribbon

A method of PLD of thickness- and composition-homogeneous thin films on a translationally moving ribbon of up to 100 mm-width is proposed [11]. The peculiarity of the method is in the matter deposition via a mask placed in vicinity of the substrate. Two configurations of mask slits providing for the thickness homogeneity of films are considered. Exact dimensions of the mask slits are calculated using the data of an angular distribution of mass transfer in a plasma torch.

5.1. The geometry of the proposed technique

The geometry is shown in **Figure 18**. The laser beam (2) is incident at the target (1). The mask (4) and translationally moving substrate (5) are placed perpendicularly to the axis of the plasma torch. The arrow shows the direction of the substrate displacement.

In order to provide an equal thickness of the film deposited onto the uniformly moving substrate, the following condition should be met: equal amounts of the substance must be deposited per unit time on a unit length section placed along the direction of the substrate displacement and this condition should be satisfied over the entire width of the substrate.

Taking into account the peculiarities of angular distribution of the mass-transfer rate in the plasma torch [6], we propose two configurations of the slit in the mask (**Figure 19**). In both cases, the plasma torch axis passes through the geometrical center of the mask. The displacement of substrate occurs in the x -direction. The dashed line in **Figure 19a** indicates the line along which the mass-transfer rate of the deposited matter is constant. A rectangular slit (or slits) curved along dashed line provides, obviously, the uniformity of the film thickness. The second configuration of the mask (**Figure 19b**) takes into account the fact that the angular distribution of the mass-transfer rate in the plasma plume is given by the function $F(\theta) = A \cdot \cos^m(\theta)$ [6], that is, the greater is the angle θ (**Figure 18**), the lower is the mass-transfer rate; thus, in order to provide the uniformity of the film thickness over the substrate width, the greater should be the width of the slit in the mask.

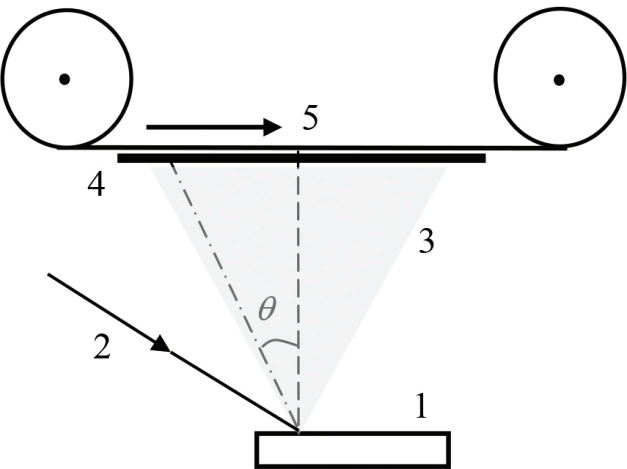


Figure 18. Geometry of deposition onto a moving ribbon.

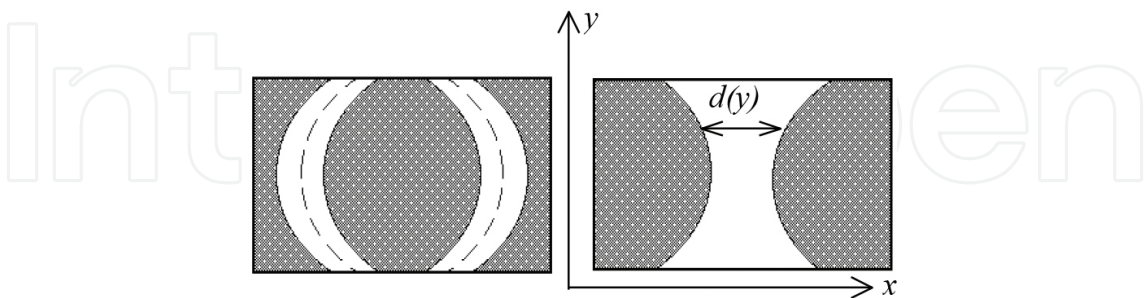


Figure 19. Configurations of slits in the mask.

5.2. Calculation of the configuration of slit in the mask

We now give a method for calculation of the configuration of the slit in the mask (**Figure 19b**) providing the thickness homogeneity of the film deposited onto the substrate moving trans-

lationally at a constant velocity. The width of the slit $d(y)$ is determined from the relation $d(y)\bar{A}(y) = \text{const}$, where $\bar{A}(y)$ is the average thickness on the section $d(y)$ of the film deposited on the resting substrate per unit time. The quantities $\bar{A}(y)$ are determined from the experimentally determined function $D(x, y)$. The angular distribution of the ablated material depends on many factors. In our experiments, we tried to change only one parameter, leaving the others unchanged. We chose the laser spot dimensions (S) and the laser fluence (F) as variable parameters. The values of these parameters and the obtained films relative thickness are listed in **Table 1**. The data of films thickness are fitted by the function $D(x, y) = A \cos^{p_x+3}(\theta_x) \cos^{p_y+3}(\theta_y)$. The used designations are clear from **Figure 20**. The obtained values of parameters A , p_x and p_y are presented in **Table 2**. Now, it is possible to initiate calculation of the configuration of the slit.

No.	$F, \text{J/cm}^2$	Spot dimension, mm^2	$D(\theta = 0)^a$, a. u.
1	53	0.205	68
2	76	0.205	83
3	97	0.205	84
4	55	0.361	103
5	18	1.11	157
6	9.9	2.02	127
7	6.2	3.2	76

^aObtained films relative thickness at $\theta = 0$.

Table 1. Variable parameters of a laser deposition.

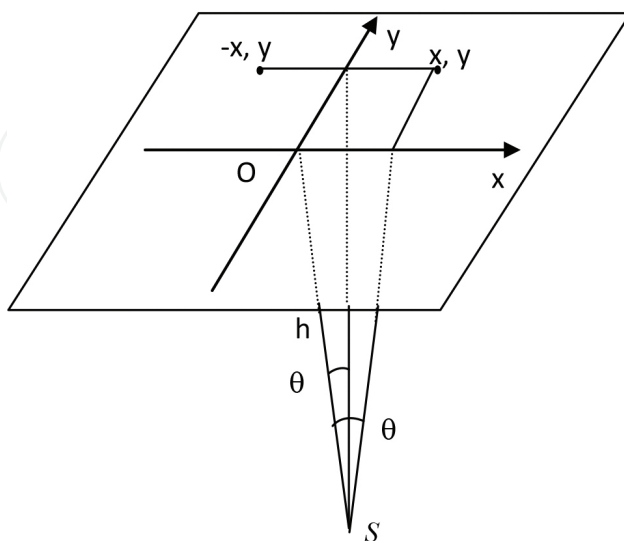


Figure 20. Schematic of deposition geometry. S is the laser spot.

No.	A	$p_x + 3$	$p_y + 3$	χ^{2a}	Area of a slit, cm ²	V ^b , a.u.
1	66.83	8.45	5.8	2.58	24.76	713
2	80.13	8.2	5.3	4.46	26	925
3	80.28	7.09	4.31	5.7	30.39	1220
4	107	7.8	4.5	6.71	28.11	1403
5	147.33	10.03	5.23	6.67	22.24	1219
6	117.51	11.55	7.69	4.99	18.25	700
7	76.22	12.84	6.86	0.96	16.56	340

$$^a\chi^2 = \frac{1}{N} \sum_{i=1}^N (f(x_i, y_i) - z_i)^2.$$

^bVolume of a matter deposited on the ribbon through the mask in a unit time.

Table 2. Parameters of a function $D(x, y)$ and corresponding uniform deposition slit.

If the origin of the coordinates is located at the point that corresponds to $\theta_x = \theta_y = 0$, and a value x_o, y_o is chosen (where y_o stands for the half-width of the ribbon and x_o is determined so that the film thickness is not too small), then the amount of the matter deposited on the segment $[(-x_o, y_o), (x_o, y_o)]$ in a unit time will be given by the expression

$$m = \rho dy \int_{-x_0}^{+x_1} D(x, y) dx \tag{9}$$

where $D(x, y)$ is the thickness profile of the film, ρ is the matter density, and dy is the width of the section. The thickness profile of the film deposited from a point source on a stationary substrate is usually determined by expression $D(\theta) = A \cos^{p+3}(\theta)$ [8]. However, when the focal spot has real sizes that differ in different directions, an asymmetry of function $D(\theta)$ is observed. In this case, the profile of the thickness of the film can be described by the expression

$$D(\theta) = A \cos^{p_x+3}(\theta_x) \cos^{p_y+3}(\theta_y) = A \left(\frac{h}{\sqrt{h^2 + x^2}} \right)^{p_x+3} \left(\frac{h}{\sqrt{h^2 + y^2}} \right)^{p_y+3} \tag{10}$$

Upon substitution of Eq. (10) into Eq. (9), we shall receive an equation for the amount of matter $m(y)$ deposited in unit time on the segment $[(-x, y), (x, y)]$ for any value of y . From the requirement that $m(y)$ is constant for all y from $-y_o$ to y_o and equals m , it is possible to determine the values $x(y)$ at which this condition is fulfilled:

$$m_y = m = \rho dy \int_{-x_0}^{+x_0} \left(\frac{h}{\sqrt{h^2 + x^2}} \right)^{p_x+3} \left(\frac{h}{\sqrt{h^2 + y^2}} \right)^{p_y+3} dx \quad (11)$$

The function $x(y)$ will determine the profile of a slit that provides uniform deposition of matter on the ribbon. At uniform translation of the ribbon with speed v , the thickness of the film D will be determined by the expression

$$D = \frac{A}{2y_0 v} \int_{-y_0-x_0}^{+y_0+x_0} \int_{-x_0}^{+x_0} \left(\frac{h}{\sqrt{h^2 + x^2}} \right)^{p_x+3} \left(\frac{h}{\sqrt{h^2 + y^2}} \right)^{p_y+3} dx dy \quad (12)$$

The computer calculation of the configuration of the slit has been performed. The results are presented in **Figure 21**.

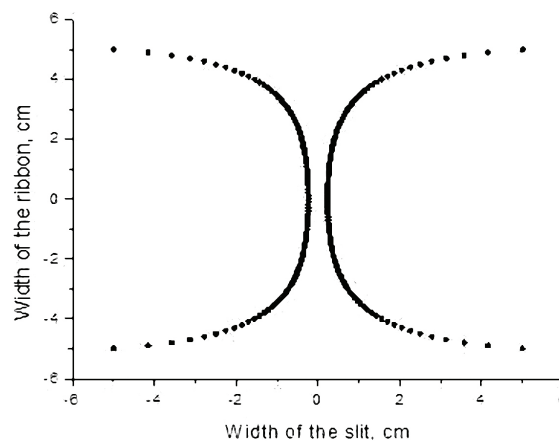


Figure 21. The calculated slit configuration for deposition No 5.

6. Deposition of very large-size films

We have developed special techniques for depositing thin films on rotating disks and translationally moving ribbons. In this paragraph, we propose new solutions, which imply more than one target for deposition, allowing in case of a rotating substrate to shorten the deposition duration and in case of a ribbon to increase the ribbon width or the speed of depositing a film of the same thickness [12].

To reduce the deposition time for films on substrates of very large size, one can modify the above-described way (see paragraph 2.3.) as follows: use several targets instead of one and scan a laser beam over them, applying target after target for deposition. If the laser pulse repetition rate increases in correspondence with the number of targets, the deposition from

each target will be performed at the same frequency as in the case of one target. Each target must have its own diaphragm, moving simultaneously with the target at a velocity $V = \text{const}/r$. Suppose we are going to use N targets to deposit a film on a substrate with a radius R . Obviously, the targets must be located with respect to each other and with respect to the substrate in such a way as, having started deposition from all targets simultaneously and moving each target at a velocity $V = \text{const}/r$, to deposit a film on the entire substrate surface and finish deposition from all targets simultaneously. It can be shown that, to deposit a film of uniform thickness on a substrate of radius R , the N targets must be initially located so as to provide a distance $X_l(t_0) = R(l-1)^{1/2}(N)^{-1/2}$ from the substrate center (Figure 22) to the point of intersection of the perpendicular dropped from the first target with the substrate plane.

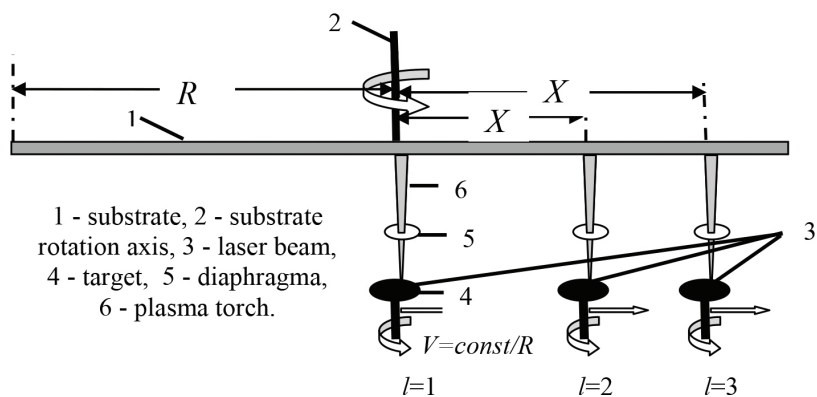


Figure 22. Moving N targets.

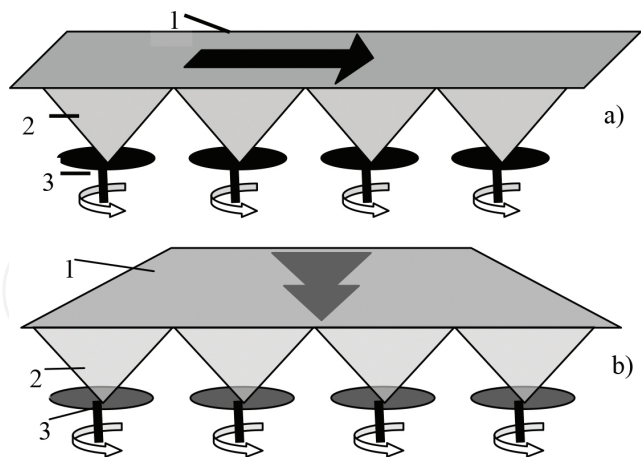


Figure 23. Moving ribbon, N targets: 1, ribbon; 2, plasma torch; 3, target. (a) N times acceleration of sputtering process, (b) deposition on N times wider tape.

We can use more than one target also in the mask method (paragraph 3.2.3). Certainly, we can use more than one target as described in paragraph 5 designs for deposition on a moving ribbon. Using N targets, we can accelerate sputtering process N times (Figure 23a), or obtain a film on the tape which is N times wider (Figure 23b).

7. Conclusions

We believe that the main result of the present work is the proposal and realization of a simple and reliable method of obtaining thickness- and composition-uniform thin films on large areas, with the use of laser deposition. The mask method of deposition on a rotating substrate can be used at any standard arrangement. The size of the obtained films and achieved degree of the thickness uniformity are not limiting. In any specific case where the permissible degree of the thickness nonuniformity is given, one may calculate the slit configuration providing the maximal rate of the deposition.

The new device for laser deposition of thin films is suggested, substantiated, and experimentally tested, which simply and cardinally overcomes the main drawback of the PLD method, namely a low coefficient of the target material utilization efficiency. Taking into account the advantages of laser deposition as compared to other methods of the manufacture of thin films, we hope that the proposed methods will be used in elaboration of new technologies in microelectronics and optical industry.

A more detailed description of the proposed methods can be found in patents [13–20]. Apart from PLD, the proposed methods are applicable to all methods of deposition from a point source.

Acknowledgements

The authors wish to thank all those who have contributed to this area of research, the members of the High Temperature Superconductivity laboratory at the Institute for Physical Research, Armenian National Academy of Sciences. This work was made possible in part by a research grant from the Armenian National Science and Education Fund (ANSEF) based in New York, USA, and was supported by the RA MES State Committee of Science and Russian Foundation for Basic Research (RF) in the frames of the joint research projects SCS 15RF-018 and RFBR 15-53-05047 accordingly.

Author details

Armen S. Kuzanyan* and Astghik A. Kuzanyan

*Address all correspondence to: akuzanyan@yahoo.com

Institute for Physical Research, Ashtarak, Republic of Armenia

References

- [1] Chrisey D, Hubler G, editors. Pulsed Laser Deposition of Thin Films, NY: Wiley; 1994. 613 p.
- [2] Eason R., editor. Pulsed Laser Deposition of Thin Films: Applications-Led Growth of Functional Materials, New Jersey: Wiley; 2006. 682 p. DOI: 10.1002/0470052120.
- [3] Kuzanyan A, Badalyan G, Karapetyan V, Gyulamiryan A, Gulian A. three simple methods to obtain large area thin films by pulsed laser deposition. IEEE Trans. Appl. Supercond. 2001; 11(1), 3852–3855. DOI: 10.1109/77.919905.
- [4] Kuzanyan AS, Petrosyan VA, Pilosyan S.Kh, Nesterov VM. Laser deposition of large-area thin films. Quantum Electron. 2011, 41(3), 253–256. DOI: 10.1070/QE2011v041n03ABEH014417.
- [5] Greer JA. Commercial scale-up of pulsed laser deposition. In Chrisey D, Hubler G, editors. Pulsed Laser Deposition of Thin Films, NY: Wiley; 1994. p. 293–311.
- [6] Nagaishi R. Formation of large surface area thin film by laser deposition method and device therefore. Japanese paten JP83333674 (A), 12.17 (1996).
- [7] Takano S. Film forming device by laser vapor deposition. Japanese paten JP2305957 (A), 12.19 (1990).
- [8] Iwamoto D, Nagao M. Laser ablation mechanism. Japanese paten JP2006124821(A), 05.18 (2006).
- [9] Grasyuk AZ, Zubarev IG, Efimkov VF, Smirnov VG. High-power SRS lasers – coherent summators (the way it was). Quantum Electron. 2012; 42(12): 1064–1072. DOI: 10.1070/QE2012v042n12ABEH015060.
- [10] Kuzanyan AS, Kuzanyan AA, Petrosyan VA, Pilosyan S.Kh, Grasiuk AZ. A simple solution to the problem of effective utilization of the target material for pulsed laser deposition of thin films. Quantum Electron. 2013;43(12):1170–1174. DOI: 10.1070/QE2013v043n12ABEH015194.
- [11] Kuzanyan AS. PLD of large area films onto substrate undergoing translational motion by mask method. IEEE Trans. Appl. Supercond. 2003; 13(2): 2868–2870. DOI: 10.1109/TASC.2003.812027A.A.
- [12] Kuzanyan VA, Petrosyan AS, Kuzanyan. Methods for pulsed laserdeposition of large-area films using more than one target. Int. J. Mod. Phys. Conf. Ser. 2012;15:170–178. DOI: 10.1142/S2010194512007118.
- [13] Kuzanyan A, Karapetyan V, Gyulamiryan A, Badalyan G. Film production method. Patent of Armenia No. 692, 15. 12. 1999.

- [14] Kuzanyan A, Karapetyan V, Gulian A, Badalyan G. Film production method. Patent of Armenia No. 962, 10. 06. 2001.
- [15] Kuzanyan A, Karapetyan V, Gyulamiryan A, Badalyan G. Apparatus for films production. Patent of Armenia No. 963, 10. 06. 2001.
- [16] Kuzanyan A. Method for producing of thin films. Patent of Armenia No. 1432, 21.04.2003.
- [17] Petrosyan V, Kuzanyan A. Method for producing of thin films. Patent of Armenia No. 2048, 17. 12. 2007.
- [18] Petrosyan V, Kuzanyan A. Method of thin films production. Patent of Armenia No. 2530, 27. 06. 2011.
- [19] Kuzanyan AS, Petrosyan VA, Kuzanyan AA. Device to produce thin films. Patent of Armenia No. 2531, 27. 06. 2011.
- [20] Kuzanyan A, Kuzanyan A, Petrosyan V. System for production of thin films. Patent of Armenia No. 2737, 26. 11. 2012.

