A Review of the Segmented-Target Approach to Combinatorial Material Synthesis by Pulsed-Laser Deposition

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Combinatorial material synthesis has led to a significant acceleration in the optimization of multinary compounds and a more efficient usage of source and substrate materials. Various growth methods, including physical vapor deposition, can be adopted to realize material libraries. Herein, two approaches to combinatorial material synthesis based on ablation of segmented targets during pulsed-laser deposition are reviewed. For these two processes, either laterally or radially segmented targets are utilized and allow the creation of lateral and vertical composition spreads, respectively. Radially segmented targets can additionally be used to synthesize a discrete binary material library. Both approaches are introduced by calculating the expected material distribution with a simple geometric plasma expansion model. Then, experimentally determined elemental distributions and growth rates are compared to predictions and it is demonstrated that differences between calculated and experimental data contain vital information on the influence of, for example, thermodynamic processes on the growth mechanism.

1. Introduction

Approaches to combinatorial material science have become more and more common in solid-state physics since the 1990s, even though first attempts date back to the 1960s. At that time, Kennedy et al. introduced the simultaneous evaporation of metals from three different sources that were arranged at the corners of an equilateral triangle. The co-evaporation of three different metals yielded their ternary-phase diagram determined by spatially resolved X-ray diffraction measurements. In the next few years, co-sputtering of two targets was used for instance to systematically study the impact of noble metal concentration on properties of cermet films and to investigate the critical temperature in binary superconducting thin films with lateral composition spread, respectively. In 1970, Hanak used a single but segmented target in a sputtering process to obtain a systematic lateral variation of the chemical composition in thin films. Twofold and threefold segmented-target configuration were suggested resulting in a binary or ternary-phase diagram, respectively. They referred to the method as “Multiple-Sample Concept” and applied it to determine the transition temperature $T_C$ of Mg–Mo mixtures as a function of composition. Hanak estimated the output rate of experimental results of the Multiple-Sample Concept and the conventional one-by-one sample approach. The output rate was about 30 and 750 times higher for binary and ternary-phase diagrams, respectively. However, it took until the 1990s for combinatorial material science to seriously enter solid-state physics. Czapla and Kusior followed Hanak’s segmented-target sputtering approach and grew Al$_2$O$_3$–TiO$_2$ thin films with continuously changing refractive index for gradient-index optical filter applications. In 1995, Xiang et al. developed a physical mask-based procedure to realize discrete solid-state compound libraries for material discovery. In a discrete material library, there exist distinguishable regions/samples with homogeneous composition, whereas in a continuous composition spread (CCS) library, the material composition exhibits a continuous systematic variation along a gradient direction. Xiang et al. used masks to control condensation of the incoming particle flux on predefined substrate sites with lateral dimensions down to 200 μm × 200 μm. Combinations of different masks and sputter targets results in different compositions on different sites and with that a spatially addressable thin film library. A thermal annealing step of the room-temperature sputtered layers leads to a homogenization of the individual compounds. This approach was successfully used to seek new magneto-resistive and superconducting material combinations. These studies triggered adaptations of other physical-deposition techniques including electron beam evaporation, molecular beam epitaxy, and more.

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and pulsed-laser deposition (PLD). The advances in the determination of material properties with high spatial resolution since the 1990s made the multiple-sample concept of Hanak and coworkers easier to handle and growth of thin films with CCS for the investigation of phase diagrams of ternary or quaternary alloys became highly efficient. Concerning PLD, this was demonstrated first by construction of the phase diagram of the doped Mott insulator La$_{1-x}$Sr$_x$MnO$_3$. The exchange of ceramic LaMnO$_3$ and SrMnO$_3$ targets was synchronized with the movement of a mask partially shadowing one of the sides of a heated substrate enabling a continuous change of thin film composition. PLD with segmented targets was reported for growth of laterally homogeneous layers. In 2013, a facile CCS–PLD approach was introduced that is based on a synchronized rotation of target and substrate, the ablation of segmented PLD targets, and off-axis PLD. If these conditions are fulfilled, CCS–PLD does not require any changes in existing PLD chambers and presents a simple approach to combinatorial material science. The segmented-target method can be adapted such that a material gradient in growth direction and discrete combinatorial synthesis (DCS) is feasible. In the following, we will introduce and describe these two variants in detail and will discuss numerical and selected experimental results on group-II sesquioxides and (Mg,Zn)O alloy semiconductors.

2. The Segmented-Target PLD Approaches Developed at the University of Leipzig

In this section, the two segmented-target PLD processes that were developed within the Collaborative Research Center 762 are introduced by simulations of the respective process. Both methods, to which we refer to as CCS–PLD and the vertical CCS–PLD (VCCS–PLD), are by now standard processes in our laboratories and significantly helped to reduce target as well as substrate consumption.

2.1. CCS–PLD: Creation of Lateral Continuous Composition Spreads

Within the Multiple-Sample Concept of Hanak, segmented targets enabled the deposition of thin films with lateral variation of the composition with a single sputter source. In the sputtering process, the whole target area is ablated and if target and substrate are fixed, a lateral variation of the thin film composition is obtained in a straightforward manner. Concerning PLD, for which a schematic of the deposition geometry is shown in Figure 1, the spot size of the laser on the target defines the ablation area which is typically smaller compared with the target surface. Therefore, PLD targets are rotated during deposition to assure an uniform ablation of the target material. Typically, the substrate is rotated as well and enables deposition on larger substrates if an off-axis PLD configuration, for which a certain lateral distance (offset) between the projection of the laser spot on target and the substrate center as shown in Figure 1b exists, is used. This offset is referred to $\varepsilon$ from now on and is, in addition to target segmentation, one of the crucial requirements of our CCS-PLD process. We will explain the method for a two-fold segmented target as shown in Figure 2. The two semicircular target segments shall consist of material A and B, respectively. At the start of the process, the laser is incident on segment A and the ablated material condensates around position 1 on the substrate as shown in Figure 2a. Target and substrate rotation are synchronized and after both have rotated 180° as shown in Figure 2b the laser ablates material B condensing in the vicinity of position 2 (being on the opposite substrate side of position 1, around which material A condensed). This process is now repeated until the desired film thickness is deposited. Since this approach does
Differences in the sputter yield of material A and B are considered on the elemental distribution is expressed by the exponent \( \gamma \). The thin film composition \( x \) and thickness \( t \) (or alternatively the growth rate \( \gamma \)) at a position \( r \) is

\[
x(r) = \frac{f_B(r)}{f_A(r) + f_B(r)}
\]

\[
t(r) = (f_A(r) + f_B(r)) \cdot k
\]

The offset \( \epsilon \) is considered in the angle \( \theta = (r \pm \epsilon)/z_s \), where \( r \) represents the distance from the substrate center. For a single composition gradient \( r \) corresponds to the radial distance from the substrate center along the gradient line. The distribution of A and B on the substrate is with that

\[
f_A(r) = \gamma_A \cos \left( \frac{r + \epsilon}{z_s} \right)^n
\]

\[
f_B(r) = \gamma_B \cos \left( \frac{r - \epsilon}{z_s} \right)^n
\]

The offset \( \epsilon \) is visualized. For \( \epsilon = 0 \) mm, the positions 1 and 2 of the previous explanation are located both at the substrate center and hence material A and B are deposited equally across the entire substrate—the composition of the film is \( A_{0.5}B_{0.5} \) as shown in Figure 3a. The film thickness is maximal at the substrate center and decreases according to the \( \cos(\theta)^n \) distribution with increasing distance from the center as shown in Figure 3a. For \( \epsilon > 0 \) mm, a material gradient establishes. The lateral composition change is virtually linear along the gradient direction for \( \epsilon \leq 15 \) mm and the composition range is considerably smaller than the entire binary phase diagram. For higher offset, the variation becomes more and more S-shaped. Furthermore, the maximal span of compositions increases strongly with \( \epsilon \) for \( \epsilon \leq 30 \) mm. For larger values of \( \epsilon \), the composition at the endpoints of the gradient line approaches A and B, respectively. The lateral variation of film thickness decreases for \( \epsilon > 0 \) and is minimal for \( 30 \text{ mm} < \epsilon < 35 \text{ mm} \). For even higher \( \epsilon \), the film thickness inhomogeneity increases again and \( t \) has a minimum at the substrate center. The offset can be used to determine the spatial dependence of the composition change, the span of accessible mixtures, and to control the variation of film thickness. The influence of the target-to-substrate distance \( z_s \) is shown in Figure 3b. Smaller values of \( z_s \) result in a strong S-shaped change in composition with comparatively high gradient around the substrate center. Such configuration is beneficial for deposition on smaller substrates. With increasing \( z_s \), the curvature decreases and the range with approximately linear spatial composition change increases. In general, the mixing of material A and B increases with increasing target-to-substrate distance, the effect...
Figure 3. Composition $x(r)$ along the gradient direction on a 70 mm in diameter substrate with its center at $r = 0$ mm. The lateral variation of $x$ is calculated as function of a) the offset $\varepsilon$, b) the target-to-substrate distance $z_s$, c) the exponent of the cos-function $n$ being related to the background pressure, and d) the transfer coefficient ratio $\gamma_B/\gamma_A$. The values of the parameters are provided in the legends; in case of (a) and (b), they are given in dimensions of mm.

Figure 4. Thickness $t(r)$ along the gradient direction on a 70 mm in diameter substrate with its center at $r = 0$ mm. The lateral variation of $x$ is calculated as function of a) the offset $\varepsilon$, b) the target-to-substrate distance $z_s$, c) the exponent of the cos-function $n$ being related to the background pressure, and d) the transfer coefficient ratio $\gamma_B/\gamma_A$. The values of the parameters are provided in the legends; in case of (a) and (b), they are given in dimensions of mm.
is similar to the reduction of the offset parameter \( \epsilon \). The variation of film thickness, depicted in Figure 4b, illustrates this clearly. For \( z_s = 90 \) mm, a rather homogeneous thickness is achieved which is similar to that of Figure 4a for \( \epsilon = 30 \) mm. The change in the thickness distribution for lower (higher) values of \( z_s \) is alike to the change for higher (lower) \( \epsilon \). The impact of the background pressure is shown in Figure 3c by a variation of \( \gamma \). For high \( \gamma \) values (low pressure), the plasma plume is highly directional and hence the mixing of material A and B is lowest. The spatial compositional variation is S-shaped, similar to the case for high \( \gamma \) values or lower target-to-substrate distances. For increasing background pressure (decreasing \( \gamma \)), the plasma plume broadens, which means that materials A and B are distributed over a larger substrate area, implying that a stronger mixing of the two occurs. This translates to smaller range of compositional variation and a more and more linear change in composition along the gradient line. Again, similar effect is seen as shown in Figure 4a,b for decreasing \( \epsilon \) and increasing \( z_s \), respectively.

In general, different materials have different sputter yield and growth rate. This can be considered by the transfer coefficient \( \gamma \). The ratio of transfer coefficients can be obtained from the midpoint composition ratio \( \gamma_B/\gamma_A = \gamma_{MP} = x/(1-x) \) at \( r = 0 \) mm. In Figure 3d, gradient profiles are shown as a function of \( \gamma_B \) and \( \gamma_A = 1 \). As \( \gamma_B \) and the share of material B decreases \( \gamma_{MP} \) systematically decreases and the gradient profile is strongly bent at the material A side of the substrate \( r < 0 \) mm), whereas the bending decreases on the opposite substrate side. Different transfer coefficients lead to an asymmetric thickness distribution. The film thickness will be higher at the substrate side where the material with higher transfer coefficient \( \gamma \) is deposited as shown in Figure 4d.

In conclusion, CCS–PLD allows to control the spatial variation of thin film composition by adequate choice of the offset \( \epsilon \), the background pressure, and the target-to-substrate distance \( z_s \). The influence of these parameters on the elemental distribution can be summarized as follows: steep gradient around the substrate center and strong bending are obtained in tendency for 1) high \( \epsilon \) values, 2) small target-to-substrate distance \( z_s \), and 3) low background pressure. Smaller \( \epsilon \), higher pressure, and higher \( z_s \) yield a nearly linear change in composition. Hence, if one of these three parameters has to be fixed, the other two parameters can be adjusted such that, for example, a nearly linear gradient across a predefined substrate area is achieved. Furthermore, the CCS–PLD growth rate is similar to conventional PLD, as neither a shadowing by (movable) masks nor a target exchange is required. Furthermore, the segmented-target PLD approach can easily be extended to create multinary phase diagrams. For that, three or more target segments are required. In Figure 5, we show examples of possible target segmentations and the expected composition spread in false colours.

### 2.2. VCCS–PLD Process: Discrete Combinatorial Synthesis and Creation of Vertical Composition Gradients

Composition gradients in the direction of thin film growth enable bandgap or doping profiles as well as strain engineering in device structures such as high electron-mobility transistors, quantum well light-emitting diodes (LEDs) or laser diodes as well as photodetectors. Such vertical composition gradients require the exact control of the particle flux offered at the substrate. This is established for deposition methods such as molecular beam epitaxy or metal–organic chemical vapor deposition. However, for PLD, the particle flux composition is directly correlated to the target stoichiometry. Therefore, a variation of the particle flux composition typically requires a change in the target such that rather complicated multi-beam or movable-mirror setups emerged. In 2018, we introduced a straightforward approach to gain control over the particle flux that requires only a single radially segmented target and the control over the radial position of the laser spot on the target surface.

We demonstrated this technique using elliptically segmented targets, where the inner segment of the ellipse features a different composition than the outer segment. We shall denote the composition of the inner segment as A\(_1\)B\(_{1-x}\)O, the one of the outer segment as A\(_2\)B\(_{1-y}\)O, respectively. In our standard PLD approach for single-composition targets, the target would be rotated and the radial position \( R \) of the laser spot on the target surface would be changed continuously to ensure a homogeneous ablation of the target surface. We will use the capital \( R \) to describe the radial distance of the laser spot from the target center and will continue to use \( r \) for a radial distance from the substrate center. In our VCCS–PLD approach, we fix this radial laser spot position to a certain value of \( R \) and rotate the target similar to the standard approach, such that the laser ablates a circular track on the target surface as shown in **Figure 6a**.

![Figure 5. Exemplary target segmentations and the resulting modeled thin film composition.](image-url)
The resulting thin film composition is now changing constantly over time either being \( A\text{B}_{1-x}\text{O} \) or \( A\text{B}_{1-y}\text{O} \), depending on whether we are ablating in the inner or outer segment of the target and assuming stoichiometric ablation of the segments. The resulting thin film composition for this particular value of \( R \) is then given by the time average of the particle flux composition \( \chi(R) \). This time average is directly correlated to the ratio of path lengths of the laser spot in the outer and inner segment of the target. The path length ratio is given by the angle \( \varphi(R) \), which is the intersection angle of the circular path of the laser spot and the elliptical boundary of the inner target segment. In the upper panel of Figure 6a, a radial position of \( R \) corresponds to an intersection angle \( \varphi_1(R_1) \) and, if a stoichiometric material transfer is assumed, a resulting thin film composition of \( \chi_1(\chi(R_1)) \). If the radial position \( R \) is now increased to a value \( R_2 \), the intersection angle decreases to \( \varphi_2(R_2)<\varphi_1(R_1) \). This corresponds to an increased path length ratio as is shown in the lower panel of Figure 6a that directly correlates to a different average composition of the flux of particles and therefore also a different thin film composition \( \chi(R_2) \). Under the assumption of an ideal point-like laser spot on the target as well as a stoichiometric transfer from the target segments to the substrate, we can give an analytical expression for the expected thin film composition based on simple geometrical considerations. The intersection angle \( \varphi(R) \) is directly given in the known equation for an ellipse

\[
R(\varphi) = \frac{b}{\sqrt{1 - e^2 \cos^2 \varphi}}, \quad e = \frac{\sqrt{a^2 - b^2}}{a}
\]

where \( a \) is the longer side of the ellipse and \( b \) the shorter side; see also the inset in Figure 6b. The path length in the inner segment can be expressed as \( 4\varphi R \) and in the outer segment by \( 2\pi R - 4\varphi R \) consequently. The resulting average particle flux as well as thin film composition \( \chi(R) \) is simply the sum of the composition-weighted ratio of these path lengths to the total circumference \( 2\pi R \) of the circle of the laser path

\[
\chi(R) = \left( \frac{4\varphi R}{2\pi R} \right) x + \left( \frac{2\pi R - 4\varphi R}{2\pi R} \right) y
\]

We now only need to solve Equation (5) for \( \varphi \) and plug the result in Equation (6) to obtain an analytical result for the expected thin film composition

\[
\chi(R) = y - (y - x) \frac{2}{\pi} \arccos \left[ \frac{1}{e} \sqrt{1 - \left( \frac{b}{R} \right)^2} \right]
\]

The result is plotted in Figure 6b. If we choose the laser spot position \( R \) smaller than the shorter axis of the ellipse \( b \), the composition \( x \) of the inner segment is reproduced, and consequently, we obtain the composition \( y \) of the outer segment for \( R > a \). A smooth variation of composition between \( x \) and \( y \) can be realized for values of \( R \) between these two extremes. One can therefore control the thin film composition in a well-defined way by a simple geometric change in the radial position \( R \) of the laser spot on the target surface. If \( R \) is changed in situ and stepwise during ablation, one can deposit a thin film with a (quasi-)continuously in growth direction. The smoothness of the gradient is of course then determined by the exact number of steps and the respective step size as well as the thickness of each layer. With this, one has a powerful tool that allows the control over the particle flux composition of the PLD plasma that can be utilized to realize any possible bandgap or dopant profile as well as to perform strain engineering. Moreover, this method can be used to deposit homogeneous thin films with any desired composition between...
x and y and enables DCS for any alloy system or dopant in a material. In analogy to the segmented-target approach for lateral CCS presented in the previous section, we call this method vertical (quasi-)continuous composition spread (VCCS). Thin film quality regarding crystal structure, surface morphology and optical properties, as well as deposition rates and phase stabilization limits were shown to be similar to a standard PLD process.\[18\]

It should be noted that not only an elliptical segmentation may be used to create composition gradients or to generally vary the particle flux in a well-defined way. Also other radial segmentations are possible as long as the path length ratio varies with \( R \), such as rectangular shapes, star-like shapes, or even heart-shaped segments. In the inset of Figure 7a, heart-shaped inner segment is shown. The borderline of each half resembles an Archimedean spiral for angles of rotation between \( 0 \leq \phi \leq \pi \). These segments are adjoined mirror-symmetrically leading to the heart-shaped inner segment. The resulting linear dependence of the thin film composition (stoichiometric transfer assumed) on the radial laser spot position is shown in Figure 7.

The aforementioned analytical model can be refined to account for different shapes of the segments as well as the exact size of the PLD laser spot as parameters that can practically vary for a specific PLD setup or during target fabrication. For this, Monte-Carlo simulations were performed where the shape of the target segmentation and laser spot size can be defined. The size of the PLD laser spot is considered by defining an annulus on the target surface with given inner and outer radii \( R_i \) and \( R_o \), respectively. The laser spot position is set to \( R_o \) and the size of the laser spot by \( R_o/C_0 \). A large number of random positions confined inside the area of the annulus is then created and the number of those positions that are within the inner segment are counted as well as the total number of created positions. The ratio of the number of positions inside the inner segment of the target compared with the total number of incidents can then be evaluated similar to the path length ratio in the analytical model.

Figure 8a shows the expected thin film composition as function of \( R \) when the laser spot size is varied between 0.5 and 5 mm in comparison with the analytical model. As can be seen, a controllable variation of the composition is given for all spot sizes. For low spot sizes, the shape of the analytical model can be reproduced quite well, whereas the characteristic S-shape smears out for larger spot sizes and the variation of the composition takes place in a larger range of radial positions as the laser still ablates in the inner segment for radial positions larger than the longer axis of the ellipse. The effect of the variation of the shape of the elliptical segment on the evolution of the particle flux

![Figure 7](image-url)  
**Figure 7.** Linear variation of thin film composition as function of the normalized radial PLD spot position \( R/R_{tot} \) enabled by a heart-shaped inner target segment depicted in the inset. Its borderline resembles an Archimedean spiral for rotation angle \( 0 \leq \phi \leq \pi \) mirrored at the vertical center line. Dashed white lines indicate point-like laser spot race tracks for normalized radial positions of 0.2, 0.4, 0.6, and 0.8.

![Figure 8](image-url)  
**Figure 8.** Monte-Carlo simulations of the expected particle flux composition ratio \( |x(R) - x|/|y - x| \) for elliptically segmented targets. a) Target with shorter axis \( b \) and longer axis \( a \) of the inner elliptical segment and a variation of the PLD laser spot size as indicated, respectively. The green curve is the analytical model for an ideal point-like shaped laser spot. b) Simulation for a fixed laser spot size of 2 mm and shorter axis of the ellipse of 3.5 mm and a variation of the ratio \( a/b \) as indicated. Bold lines represent typical conditions in our laboratories.
composition is shown in Figure 8b. Here, the ratio a/b of longer to shorter axis of the ellipse was varied from a value of 1 (corresponding to a circular inner segment) to 2.29. A controllable particle flux composition is given here as well for a large range of target geometries. For larger values of the ratio, the characteristic S-shape of the analytical model is reproduced again. When the inner segment is circular, the composition varies almost linearly, but only in a limited range of radial positions such that the target area cannot be utilized completely.

3. Growth of Ternary Semiconducting Oxides by CCS–PLD and VCCS–PLD

In the following, we will discuss the lateral elemental distribution of ternary group-III sesquioxides grown by CCS–PLD. Experimental and calculated gradient profiles will be compared not only to elucidate the strength but also the limitations of the basic geometrical CCS model described earlier. After that, we will discuss (Mg,Zn)O thin films with composition gradient in growth direction obtained by VCCS–PLD. Furthermore, VCCS–PLD is used for DCS of a (Mg,Zn)O material library. Finally, selected fundamental material properties of CCS–PLD as well as VCCS–PLD thin films will be discussed as a function of the alloy composition.

3.1. Target Preparation

The segmented PLD targets were fabricated in-house using Al2O3 (purity 99.97%), Ga2O3 (99.999%), In2O3 (99.995%), MgO (99.99%), ZnO (99.999%) as source powders. In our standard process, the source powders are presintered at 1150 °C for 10 h in air. Subsequently, the powders are ball-milled. For ternary target pieces, adequate amounts of presintered source powders are mixed and homogenized. For laterally and radially segmented targets, semicircular or elliptical molds are used to define the shape target segments. The molds are filled with the respective powder, then they are removed and the powders are cold-pressed. The cold-pressed targets are finally sintered at about 1150 °C (1350 °C) for 12 h (72 h) in the case of ZnO and MgZnO (Al2O3, Ga2O3, and In2O3). Figure 9 shows a photographic image of a laterally and a radially segmented target right after sintering.

Initially, laterally segmented targets were realized by simple sawing of entire targets into semicircular pieces and by assembling two pieces into one target.[17]

3.2. CCS–PLD of Group-III Sesquioxides

The group-III sesquioxides and particularly Ga2O3 have gained significant research interest in the last years, which was triggered by the demonstration of a power transistor by Higashiwaki et al. in 2012.[23] The advantages of Ga2O3 with respect to SiC and GaN are the availability of large-area native substrates, high bandgap of about 4.9 eV combined with high electrical conductivity and large electric breakdown field of about 8 MV cm−1.[24–27] Ga2O3 appears in five different polymorphs, among which the so-called β-Ga2O3 modification, crystallizing in monoclinic beta-gallia crystal structure (C2/m), is most stable at ambient conditions. For high-power device applications but also for exploitation as deep-UV photo detectors bandgap engineering is needed and can be achieved by alloying with indium and aluminium resulting in a decrease and increase of the fundamental bandgap, respectively. The ground-state crystal structure of In2O3 and Al2O3 are the cubic bixbyte and the rhombohedral corundum structure and hence phase separation is expected in ternary (In,Ga)2O3 and (Al,Ga)2O3 layers.

3.2.1. Lateral Composition Spread in (InxGa1–x)2O3 and (AlxGa1–x)2O3 Thin Films—Comparison of Experiment and Geometrical Model

Two-fold segmented PLD targets were fabricated and consisted of semicircular segments of 1) binary In2O3 and binary Ga2O3 or 2) binary Al2O3 and binary Ga2O3.[28–30] Ternary thin films were grown on 2 in. in diameter (100)MgO substrates at T G ~ 650 °C and oxygen-rich conditions (pressure P2O = 0.08 mbar) by CCS-PLD. The target-to-substrate distance is zs = 100 mm and the offset is ε =26 mm.

Energy-dispersive X-ray (EDX) spectroscopy was used to map the composition of the thin films with high spatial resolution. In Figure 10, the lateral variation of the cation composition is depicted along the gradient direction. In perpendicular directions, the composition of the thin films is essentially constant. For both alloys, the spatial dependence of composition has a slight S-shape only, indicating that the experimental conditions resemble calculation corresponding to 1) intermediate values of ε, 2) intermediate to higher values of n and zs. Indeed, the geometric parameters are with ε = 26 mm and zs = 100 mm in the respective range. For both ternary systems, the midpoint (r = 0 mm) ratio of composition YMP is not 50/50, implying that different transfer factors γ have to be considered. As for both cases γMP < 1, and as for (AlxGa1–x)2O3, γMP is smaller than for (InxGa1–x)2O3, the following relation for the transfer coefficients must hold: γGa2O3 > γIn2O3 > γAl2O3. We have modeled the gradient profiles for the two ternary thin films and plotted the data in Figure 11. The transfer coefficient of Ga2O3 is fixed at γGa2O3 = 1. The transfer factor of the Al2O3 and In2O3 are then obtained from the respective midpoint (r = 0 mm) ratio of...
composition $\gamma_{MP}$. For (Al,Ga)$_2$O$_3$, $\gamma_{MP} = x/(1-x) = 1/3 = 0.5$, and for (In,Ga)$_2$O$_3$, $\gamma_{MP} = 0.425/0.575 = 0.74$. Despite the similar growth conditions, slightly different values of $n = 12$ and $n = 13$ reproduce the experimental data of (Al$_{1-x}$Ga$_x$)$_2$O$_3$ and (In$_{1-x}$Ga$_x$)$_2$O$_3$, respectively, best. The calculated gradient profiles for these $n$-values are highlighted in the Figure. A careful look on the experimental data (cf. Figure 10) reveals a somewhat stronger bending and stronger S-shape for (In$_{1-x}$Ga$_x$)$_2$O$_3$, which requires (cf. Figure 3) a higher value of $n$ in the model. Overall, the experimentally determined composition gradients of ternary group-III sesquioxides grown under oxygen-rich conditions can be well described by the simple geometrical model.

The model also yields the spatial dependence of the growth rate and with that lateral variation of thin film thickness. Experimentally, the thin film thickness was deduced at selected sample positions from spectroscopic ellipsometry measurements [31,32]. The experimental and calculated data are compared in Figure 12 for various $n$-values. For the calculations, the same input parameters as in the calculation mentioned earlier were used. As different transfer coefficients were required to model the EDX-data, a lateral variation of the thickness is expected. As can be seen in Figure 12a, the thin film thickness of (Al$_{1-x}$Ga$_x$)$_2$O$_3$ decreases toward the Al-rich side, which is well reproduced by the model with the same parameters used for calculating the composition gradient. The higher transfer coefficient of Ga$_2$O$_3$ results in a higher thin film thickness on the Ga-rich side. For (In$_{1-x}$Ga$_x$)$_2$O$_3$, the difference of the binary transfer coefficients is smaller and hence the model predicts a smaller relative variation of the thickness than for (Al$_{1-x}$Ga$_x$)$_2$O$_3$. Furthermore, it predicts a maximum shifting toward the Ga-rich side for increasing $n$-values as shown in Figure 12b. Experimentally, a systematic increase in the sample thickness with increasing In-content is observed in contrary to the model. As the composition gradient was reproduced well by the model with the same parameters as used for thickness calculation, the binary growth rate of both In$_2$O$_3$ and Ga$_2$O$_3$ must increase similarly with increasing In-content. Otherwise, the compositional gradient would be distorted and not have the point-symmetric S-shape. For (In$_{1-x}$Ga$_x$)$_2$O$_3$ thin films, grown by molecular beam epitaxy, an increase in the growth rate of binary Ga$_2$O$_3$ was observed in the presence of In$_{33,34}$. The oxidation of In occurs at higher rate than the oxidation of Ga and leads to the formation of In$_2$O$_3$ at the surface. Subsequently, Indium can be exchanged by Ga as the Ga–O bond strength is higher than that of In–O. The remaining In is either desorbed or is fully reoxidized and then incorporated or again subjected to cation exchange. As for low $r$, the Ga-flux is much higher than the In flux, gallium atoms will be oxidized as well. Some of these atoms will form volatile Ga$_2$O and will be desorbed. The rates of these processes change with increasing amount of In in the particle flux, particularly the share of In taking part in the exchange reaction and the share of Ga being lost due to desorption of volatile Ga$_2$O will both decrease leading to
However, these thermodynamically driven processes cannot be in addition to the kinematic plasma expansion. if thermodynamics plays a decisive role during sample growth.

**3.2.2. Nonstoichiometric Material Transfer**—the Influence of Thermodynamics on Lateral Composition Spread in (In$_x$Ga$_{1-x}$)$_2$O$_3$ and (Al$_x$Ga$_{1-x}$)$_2$O$_3$ Thin Films

The growth of group-III sesquioxides at oxygen-poor conditions is an indicative example for a nonstoichiometric incorporation of cations in ternary thin films. In Figure 13, the lateral distribution of In and Al in (In$_x$Ga$_{1-x}$)$_2$O$_3$ and (Al$_x$Ga$_{1-x}$)$_2$O$_3$ CCS thin films along the gradient, respectively, is shown. Both gradient profiles reveal significant deviations from calculated profiles discussed in Section 2.1. Similar to group-III nitrides,[35] the common feature of ternary samples grown at metal-rich conditions is the preferential incorporation of that metal with stronger bonding strength to the anion. For the three elements involved, the bond dissociation energy $E_{dis}$ to oxygen is: $E_{dis,Al} = 5.22$, $E_{dis,Ga} = 3.90$, and $E_{dis,In} = 3.60$ eV.[36] Several studies addressed the influence of growth temperature $T_C$ and oxygen pressure $p_O_2$ on growth rate and alloy composition of PLD-grown ternary (In$_x$Ga$_{1-x}$)$_2$O$_3$ and (Al$_x$Ga$_{1-x}$)$_2$O$_3$ thin films.[28,37] Furthermore, Wakabayashi et al. demonstrated that the cation composition can be altered significantly if, for given growth conditions, oxygen molecules or oxygen radicals are offered.[38] For a growth temperature of about 800 °C and a growth pressure of $9.3 \times 10^{-5}$ mbar thin films, deposited using a (Al$_{0.06}$Ga$_{0.94}$)$_2$O$_3$ PLD target, had composition of (Al$_{0.06}$Ga$_{0.94}$)$_2$O$_3$ and (Al$_{0.06}$Ga$_{0.94}$)$_2$O$_3$ for growth without and with oxygen radicals, respectively. In Figure 14, EDX line scans of CCS-PLD (In$_x$Ga$_{1-x}$)$_2$O$_3$ thin films grown at various $T_C$ and $p_O_2$ are compared. In red, samples grown at high $T_C = 680$ °C on c-plane Al$_2$O$_3$ are compared. For $p_O_2 = 8 \times 10^{-2}$ mbar, the indium content $x$ increases virtually linear along the gradient direction, whereas a completely different relation is observed for $p_O_2 = 3 \times 10^{-4}$ mbar. For growth at high $p_O_2$, the indium content is (except for the very In-rich side) notably higher than for growth at low $p_O_2$. As discussed earlier, these differences are due to the higher oxidation rate of indium, the cation exchange of indium by gallium, and desorption of Ga$_2$O and In during growth.[33,34] CCS-PLD growth at low $p_O_2 = 3 \times 10^{-4}$ mbar and low growth temperature $T_C = 420$ °C leads to a much higher indium incorporation compared with growth at $T_C = 680$ °C. The spatial dependence of the indium content $x$ is similar to the sample grown at high $T_C$ and high $p_O_2$. The differences observed for $x < 0.3$ and $x > 0.6$ are connected to phase transitions occurring in the sample grown at low $T_C$. 

**Figure 12.** Experimental and calculated lateral variation of sample thickness of a) (Al$_x$Ga$_{1-x}$)$_2$O$_3$ and b) (In$_x$Ga$_{1-x}$)$_2$O$_3$ thin films. The calculated data is shown as function of the exponent $n$ as labeled. Best matching curves are indicated by bolder red-dashed lines. For the calculations, we used for Ga$_2$O$_3$ transfer factor of $\gamma_{Ga_2O_3} = 1$, for In$_2$O$_3$ of $\gamma_{In_2O_3} = 0.74$, and for Al$_2$O$_3$ of $\gamma_{Al_2O_3} = 0.5$. 

3.2.2. Nonstoichiometric Material Transfer— the Influence of Thermodynamics on Lateral Composition Spread in (In$_x$Ga$_{1-x}$)$_2$O$_3$ and (Al$_x$Ga$_{1-x}$)$_2$O$_3$ Thin Films

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**Figure 13.** Experimental composition spread of (Al$_x$Ga$_{1-x}$)$_2$O$_3$ and (In$_x$Ga$_{1-x}$)$_2$O$_3$ thin films grown at low oxygen pressure of $p_O_2 = 3 \times 10^{-4}$ mbar clearly showing a nonstoichiometric cation transfer.
3.3. VCCS-PLD of (Mg,Zn)O

3.3.1. Discrete Combinatorial Synthesis by VCCS-PLD

To introduce and benchmark our VCCS-PLD method, a set of homogeneous (Mg,Zn)O thin films were realized by discrete composition synthesis (DCS). For that, a radially segmented target, consisting of ZnO in the inner segment and Mg$_{0.4}$Zn$_{0.6}$O in the outer segment, was used. The thin films were deposited on a-plane sapphire with a ZnO:Al buffer layer at $T_G = 670 \degree C$ and $p_{O_2} = 0.02$ mbar. In Figure 15, the composition of films obtained for $2 \, mm \leq R \leq 8 \, mm$ is compared with the composition calculated with the analytic model according to Equation (7) and the Monte-Carlo simulations. For $R \geq 4 \, mm$, both models reproduce the experimental data well, whereas for smaller $R$ deviations are observed for the analytic model. If the size of the laser spot is considered as in the MC-simulation, the entire data set is matched by the calculations.

Low-temperature photoluminescence (PL) spectra of the DCS sample set are shown in Figure 16a. The near-band edge excitonic emission $E_{PL}$ systematically shifts toward higher energy with increasing $R$ and with increasing Mg-content $x$ as $E_{PL}(x) [eV] = 3.38 + 1.35 x + 2.4 x^2$. Low-intensity PL features in the gray shaded box are due to emissions from the ZnO:Al buffer layer. For lower Mg-content, several phonon replica with an energetic separation of about 70 meV, corresponding to the LO phonon energy in ZnO, are visible. For higher Mg-content, the phonon replica vanish and the full width at half maximum (FWHM) increases due to alloy broadening, which can be well described by a cluster broadening model with an average number of three to four Mg atoms per cluster being in line with results of
(Mg,Zn)O thin films grown by conventional PLD (c-PLD).\cite{18} In Figure 16b, we directly compare the near-band edge emission of Mg$_{0.4}$Zn$_{0.6}$O thin films grown by conventional and VCCS-PLD, respectively. The Mg-content is about $x \approx 0.19$ in both cases. The two spectra are nearly the same concerning peak position, line shape, and broadening, suggesting that the homogeneity of VCCS-PLD thin films grown with fixed $R$ is similar to that of c-PLD films.

3.3.2. Compositional Material Gradient in Growth Direction by VCCS-PLD

For the demonstration of thin films with compositional gradient in growth direction, a radially segmented target consisting of ZnO in the inner segment and Mg$_{0.4}$Zn$_{0.6}$O in the outer segment was used. The thin films were deposited on a-plane sapphire with a ZnO:Al buffer layer\cite{18} at $T_C = 670^\circ \text{C}$ and $p_{0_2} = 0.02 \text{ mbar}$. We will compare samples that have an increasing and decreasing Mg-content in growth direction, respectively. The radial position of the laser spot on the segmented target was varied between $R = 2 \text{ mm}$ and $R = 8 \text{ mm}$ with steps of $\Delta R = 1 \text{ mm}$. Furthermore, a sample with a more uniform gradient and increasing Mg-content was realized with $\Delta R = 0.5 \text{ mm}$ for $1.5 \text{ mm} \leq R \leq 5 \text{ mm}$. The individual layer thickness was about 20 nm for each sample. The respective sample design is shown schematically in Figure 17. Furthermore, low-temperature PL spectra exited by the 325 nm-line of a HeCd laser are shown. For each sample, separated peaks that originate from the various Mg$_{0.4}$Zn$_{0.6}$O layers are visible. For higher Mg-content (larger $R$-values) alloy broadening, as described earlier, causes overlap of individual peaks. For the sample with decreasing Mg-content, these higher energy peaks have weak intensity due to absorption in the layers with lower Mg-content. Even for layers with $\Delta R = 0.5 \text{ mm}$, individual peaks are observed, indicating that intermixing of neighboring layers is negligible for (Mg,Zn)O and the growth parameters chosen. This is substantiated by the very similar peak emission energy of peaks with same $R$ (indicated by the dashed lines in the Figure). This underlines the high reproducibility of layer composition within the VCCS-PLD, rendering this novel method highly suited for growth of, e.g., ternary heterostructures, graded index layers or Bragg mirrors, graded quantum well structures, or strain accommodating within functional layers.

4. Conclusions

Two facile PLD approaches to combinatorial material synthesis were reviewed. Both methods do not require movable shadow masks nor a target exchange and, hence, closely resemble a conventional PLD process; particularly the temperature distribution and growth rates are not altered. The methods reviewed rely on the ablation of laterally or radially segmented targets that enable a lateral composition spread or a variation of composition in growth direction. Furthermore, PLD with radially segmented targets facilitates discrete material synthesis. For both approaches, simple models were presented that allow prediction of the elemental and thickness distribution as long as thermodynamic processes are negligible.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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