7 Pulsed Laser Deposition of ZnO-Based Thin Films

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Pulsed laser deposition (PLD) is a growth method for thin films by condensation of a laser plasma ablated from a single target, excited by the high-energy laser pulses far from equilibrium. First, the PLD technique is briefly described beginning with the history and the fundamental processes. In the main part, the suitability of PLD as a fast and flexible exploratory research technique for high-quality ZnO-based thin film heterostructures is demonstrated by reviewing recent results. Finally, the innovative potential inherent to PLD will be demonstrated by mentioning advanced PLD techniques, including a high-pressure PLD process for free-standing ZnO-based nanowire arrays.

7.1 Brief History and Basics

Pulsed laser deposition (PLD) [1–3] uses high-power laser pulses with an energy density of more than $10^8 \text{W cm}^{-2}$ to melt, evaporate, excite, and ionize material from a single target. This laser ablation produces a transient, highly luminous plasma plume that expands rapidly away from the target surface. The ablated material is collected on an appropriately placed substrate surface upon which it condenses and a thin film nucleates and grows.

The first demonstration of PLD by Smith and Turner in 1965 was induced by the development of the ruby lasers [1]. The technique remained dormant for the next 20 years, and only about 100 PLD papers were published until 1986. The breakthrough of PLD as an accepted growth technique was made possible by the development of high-power lasers with sufficiently high pulse energy and short pulse length, i.e., gas lasers with high-power thyatron switches or Q-switched solid state lasers [4]. In addition, with the discovery of the high-$T_c$ oxide superconductors a complex oxide material of a high technological relevance was found [5, 6], which was very well suited for PLD. Concerning this, Dijkamp and Venkatesan demonstrated in 1987 the superior quality of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ films grown by PLD compared to those previously grown by other deposition methods [1]. The considerable research efforts concentrated in the 1990s on the high-$T_c$ superconductor thin films pushed the development of the PLD in terms of reproducibility [2, 7, 8], scaling to larger substrate areas [9, 10], and deposition of heterostructures and multilayers [11]. Present day, PLD is an established growth technique for a variety of
Advantages of PLD compared to other established techniques are as follows [2, 5]:

- The capability for stoichiometric transfer of multielement compounds from a single target to the substrate, i.e., the chemical composition of complex materials such as YBa$_2$Cu$_3$O$_{7-\delta}$ can be reproduced nearly unchanged in the deposited films. However, as will be shown later, exceptions from this general rule exist.

- PLD is a reliable, versatile, and fast process. The deposition rate is in the order of tens of nm min$^{-1}$ on small substrate areas of 1 cm$^2$. The film thickness can be easily controlled by the number of applied laser pulses.

- The laser as the external energy source for materials vaporization and the deposition chamber are spatially separated, resulting in an extremely clean process. The PLD process requires no filament or plasma gas inside the growth chamber as in contradiction thermal evaporation and sputtering do. Thus, an inert or reactive background gas can be applied during PLD growth with nearly no limitation of pressure, which can be controlled over orders of magnitude from the $10^{-5}$ mbar up to the 1 mbar range.

- The synthesis of metastable materials and the formation of films from species appearing only in the laser plasma are possible by PLD [2].

In spite of these advantages, industrial use of PLD has been slow [13] and nowadays there are only a few examples of smaller start-up companies using PLD for highly specialized applications [14–16]. Most PLD work up to now has been focused on the research field and the reasons for that are listed here:

- The volume deposition rate of PLD is only about $10^{-5}$ cm$^3$ s$^{-1}$, that is much lower than that of other physical vapor deposition techniques as electron beam evaporation, magnetron sputtering, and vacuum arc deposition [17]. Furthermore, the energetical efficiency of high power lasers is only a few percent, which means that the overall efficiency of PLD is also low [18]. Consequently, upscaling of PLD to larger substrate areas is limited to about 5 in. diameter [9] due to the highly forward directed plasma plume [19]. Therefore, without additional lateral scanning of the substrate, a sufficiently good thickness and composition homogeneity of the deposited films is limited to an area of about 1 cm$^2$.

- Depending on target density and material and on the deposition parameters, particulates and globules of molten material, the so-called droplets, can be found on the deposited films [20]. The size of the droplets is typically in the 1 µm range. The droplets are detrimental for some film applications at the microscale, especially if lateral structuring in the micrometer range is required. For reduction or even suppression of the droplets, velocity filters, parallel off-axis configurations of plasma plume and substrate, and PLD setups with two colliding plasma plumes [21] have been used successfully. These additional precautions are based on