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Thin films development by pulsed laser-assisted deposition

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Abstract

The method of pulsed laser deposition (PLD) is intensively used in material research, as well as the industry, for developing thin films and coatings of special materials, such as: ferroelectrics, superconductors, oxides, polymers, complex hybrid metal-organics, etc. This simple, yet versatile thin film deposition method can be applied to such materials that are not suitable to process by other techniques. In this paper we describe the phenomenology of PLD and other related laser assisted procedures, and consider some of their advantages vs. disadvantages.

Keywords: thin films, laser assisted deposition, PLD, RF-PLD, MAPLE.

1 Introduction

In 1917, *Albert Einstein* first theorized about the process which makes lasers possible, called "stimulated emission". The name LASER is an acronym for Light Amplification by the Stimulated Emission of Radiation. *Gordon Gould* was the first person to use the word "laser". There is good reason to believe that *Gordon Gould* made the first light laser. *Gould* was a doctoral student at Columbia University under Charles Townes, the inventor of the maser. In 1954, *Charles Townes* and *Arthur Schawlow* invented the maser (microwave amplification by stimulated emission of radiation), using ammonia gas and microwave radiation – the maser was invented before the (optical) laser. The technology is very close but does not use visible light. *Gould* was inspired to build his optical laser starting in 1958, the same year that Charles Townes and Arthur Schawlow theorized and published papers about a visible laser, an invention that would use infrared and/or visible spectrum light. However, they did not proceed with any research at the time.

Theodore Maiman made the first laser to operate on May 16^{th} in 1960, at the Hughes Research Laboratory in California, by shining a high-power flash lamp on a ruby rod with silver-coated surfaces. He promptly submitted a short report of the work to the journal Physical Review Letters, but the editors turned it down. Some have thought this was because the Physical Review had announced that it was receiving too many papers on masers – the longer-wavelength predecessors of the laser – and had announced that any further papers would be turned down; another paper of his on a similar matter was already on its way to be published [1]. Eager to get his work quickly into publication, *Maiman* then turned to Nature, usually even more selective than Physical Review Letters, where

the paper was better received and published on 6 August. At that time, the laser were described as "a solution looking for a problem" [2]. Since then, it has been developed into a powerful tool in many applications.

In 1965, lasers have been used for the first time in thin film deposition experiments when *H.M Smith* and *A.F Turner* ablated material from a target in a low pressure chamber, by usind a ruby laser, but the thin films were not perfectly uniform in thickness and did not adhere to the substrate [3]. During the next two decades, however, laser ablation was mainly used for the analysis of various materials and further development of PLD was slow. The turning point in PLD applications was the development of YBCO superconductor thin films by *Dijkkamp* et al. in 1987 [4], such that from that point on, and also due to the development of high power, pulsed laser sources that give nano-, pico- and femto-second pulses, the laser ablation technique was improved and other laser-assisted techniques were developed, such that nowadays there is an impressive number of applications that include: mass spectrometry, UV lithography, production of free atoms for laser spectroscopy, and inertial confinement fusion research in the future. A significant amount of papers are present in literature: more than 17000 articles, reviews and proceeding papers that deal with pulsed laser deposition (PLD), radiofrequency-assisted pulsed laser deposition (RF-PLD) and/or matrix assisted pulsed laser evaporation (MAPLE). These techniques can be used in developing thin films of almost any known material, using the appropriate laser wavelength [4] - [25].

2 Experimental: the laser-assisted techniques and involved fenomena

2.1 *The PLD and the RF-PLD technique*

The principle of laser ablation is illustrated in Figure (1). The basic idea of the technique is to exploit high-power laser pulses, e.g., from an excimer, a Nd:YAG or another similar laser, in order to evaporate a small amount of matter from a solid target.

The focused laser pulses are absorbed at the target surface in a small volume. The absorbed energy density is sufficient to break any chemical bonds of the molecules within that volume. What essentially happens is that high-pressure gas is produced in the surface layer. As a result of the pressure gradient, a supersonic jet of particles is ejected normal to the target surface. In practice, the process is far more complicated than the idealized model discussed above. The particle cloud absorbs a large amount of energy from the laser beam producing an expansion of hot plasma (plume) through the deposition chamber. The ablated species condense on the substrate placed opposite to the target forming a thin film after some hundreds or thousands of laser pulses. Laser-pulse energy density, fluence [J/cm^2], on the target surface is one of the most important ablation parameters. When the fluence is sufficiently high, rapid evaporation of material occurs in a thin surface layer, which is necessary for stoichiometric transfer of material from a multicomponent target. PLD can take place both in vacuum and in the presence of some dilute background gas which is used to influence the composition of the film.

Under proper process parameters (e.g., the background gas pressure, the substrate temperature, and the laser fluence), the film grows epitaxially and the stoichiometry of the film is a replica of that of the target. Process parameters have also an effect on the

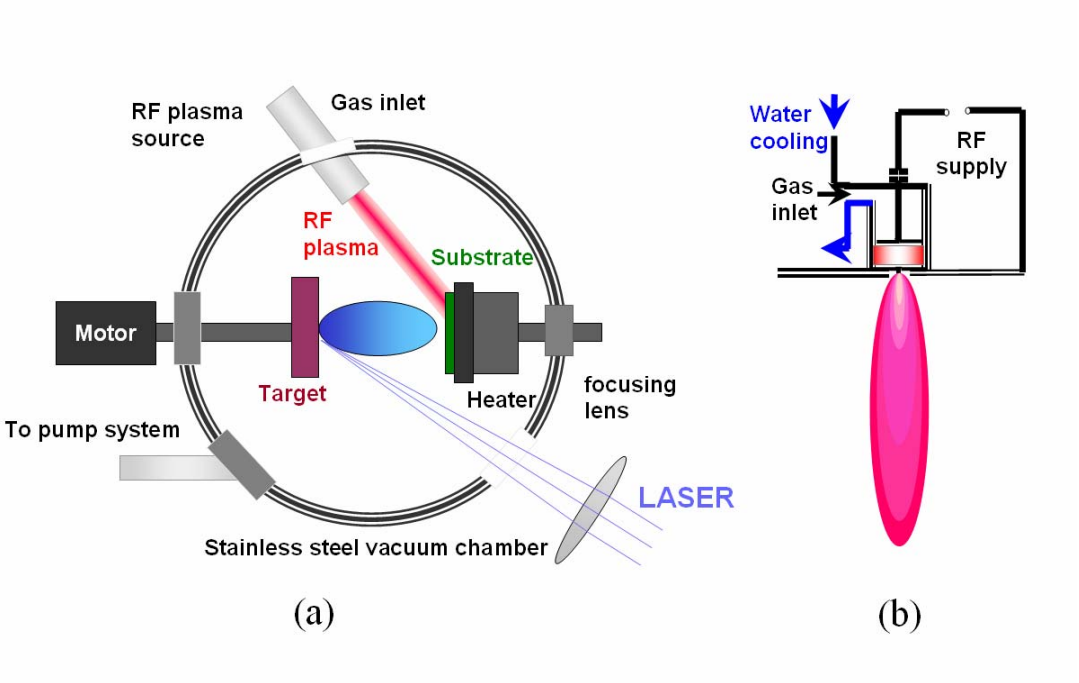

Figure 1: Schematic of the laser ablation technique: the RF assisted PLD vacuum chamber (a) and detail of the RF plasma source (b).

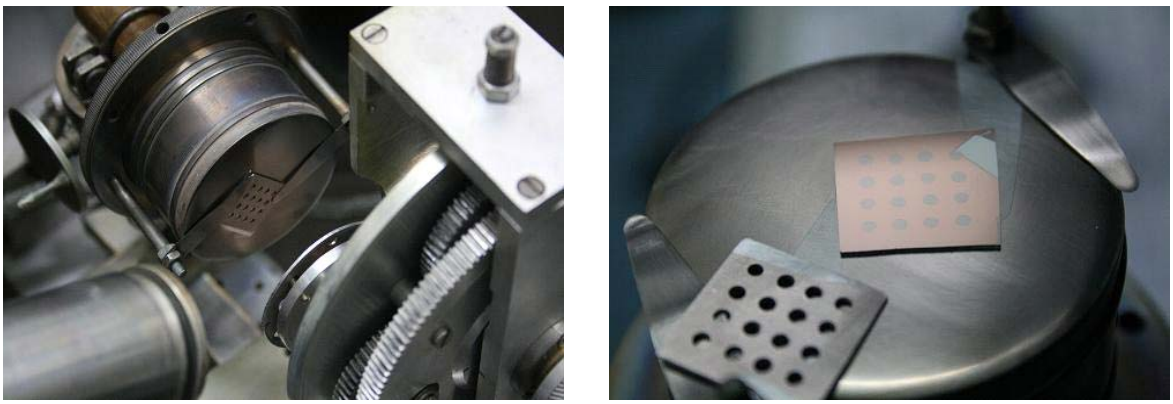

Figure 2: Photographs of the RF-PLD setup: the target holder carousel, the heated substrate holder and the RF plasma gun can be observed (a) and detail of the heated substrate holder: the substrate and mask (b)

growth rate of the film but when the fluence and the target-substrate distance have been optimized, the rate remains nearly constant (approximately 1 Å/pulse for oxides).

A tipical deposition setup is presented in Figure (2), and consists of a target holder (a carousel, if it is a multi-target system), a substrate holder (sometimes rigurously heated, as in some experiments a high temperature is needed when depositing thin films) and an RF-plasma gun for the RF-PLD experiments, where needed; usualy, oxygen and nitrogen are the most common used gases (sometimes mixed together), but also argon and the other noble gases or even hydrogen are sometimes used. In the following paragraphs, the three phases of a pulsed laser-deposition process are discussed in detail: laser-target interaction, plume formation, and film condensation on the substrate.

2.2 *The MAPLE technique*

Laser processing of complex materials represent a solution for obtaining smooth, continuous and chemically intact thin films: conventional pulsed laser deposition (PLD) using UV laser sources has become a successful, widespread technique for fabricating inorganic thin films of well-controlled thickness and composition. Unfortunately, this technique cannot be applied to most organic and/or soft materials, since irradiation by UV light induces substantial decomposition of the target molecules. Complex and coordinative compounds, hybrid metal-organics, polymers and biomaterial films can be produced by an alternative technique, known as matrix assisted pulsed laser evaporation (MAPLE), which has the potential to create thin films of controlled thickness at nanometer scale (10-500 nm) on surfaces of various substrates. Such studies upon organic thin films, including metal-organic complex compounds, are reported in literature [15] - [30]. A schematic of the MAPLE experimental setup is presented in Figure (3).MAPLE is a thin film depo-

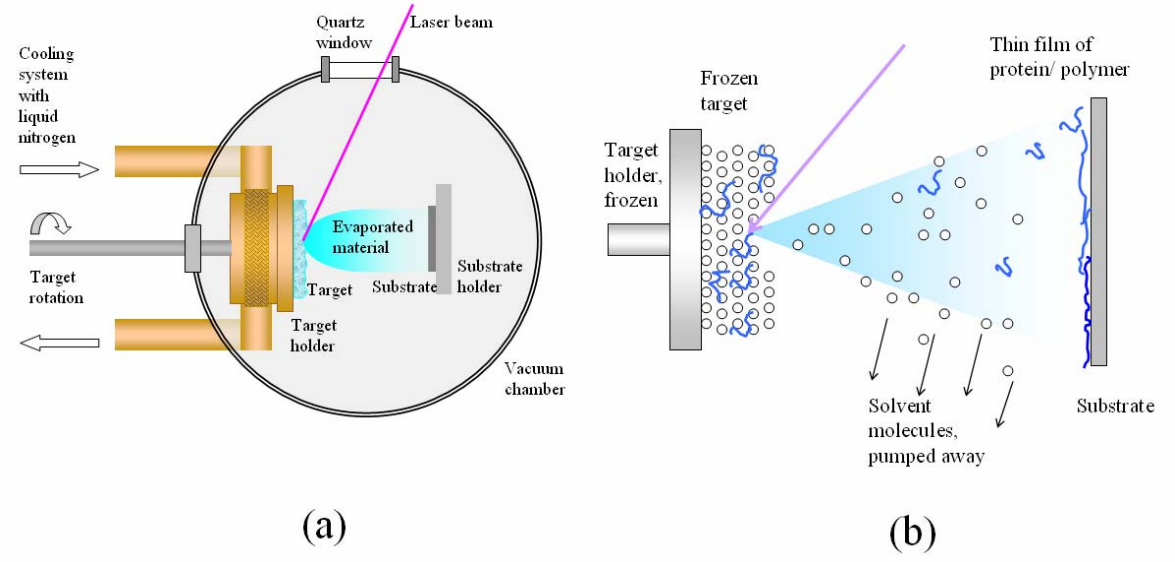

Figure 3: Schematic of the MAPLE technique: the vacuum chamber (a) and detail of the target, evaporation and deposition process (b).

sition technique, that involves dissolving or suspending the biological, sensitive and/or complex material in a volatile solvent, freezing the mixture to create a solid target, as

Figure 4: Photographs of a MAPLE target holder during the cryogenic procedure (in liquid nitrogen, 77K): freezing a solution of $Cu(DAB)_2$, a complex metal-organic hybrid compound, dissolved in toluene (a) and while freezing a solution of lactoferrin (a protein) dissolved in deionized water (b).

seen in Figure (4), and using a low fluence pulsed laser to evaporate the target for deposition of the solute inside a vacuum system. In MAPLE, a guest molecule, usually with a concentration of 0.1–4 wt %, is dissolved and subsequently frozen into a light absorbing matrix. When the matrix is irradiated by laser light the solvent evaporates, whereas the guest molecules are collected on a substrate.

A successful film deposition with MAPLE requires a matrix with an absorption band in the range of the working wavelength of the laser and a relatively low absorption by the guest material. It is also important to consider that possible photochemical reactions between the matrix and guest materials should be avoided or considerably reduced, but these requirements are usually difficult to fulfill completely.

As the film is not in contact with any solvents during and after the deposition, the MAPLE technique can be used for combinations with film layers, when no common solvent exists. Thus, this technique is of interest in the area of multilayered thin films for various applications, such as: optical coatings, preparation of sensitive layers on sensors, biocompatible coating of medical implants, etc [15] - [27].

2.3 *The laser-target interaction*

The interaction between the laser pulses and the target depends strongly on the intensity of the incoming laser beam. In PLD, the intensity is on the order of 108 - 109 W/cm^2 corresponding to a pulse duration of a few nanoseconds (such as those from a Nd:YAG laser). Therefore, there is enough time for the pulses to absorb, heat the target surface, and, finally, lead to the removal of matter. There are many different mechanisms through which energy can be transferred to the target and the most important ones will be briefly discussed in the next pages. In this context, the term sputtering is used to describe the different phenomena. More information on the laser-beam interaction with materials can be found in [8]. In *collisional sputtering*, the momentum of the incident beam is transferred to the target, which results in an ejection of particles from the surface. The mechanism is of great importance if the incoming beam consists of massive particles, such as ions. In the case of photons, the maximum transfer of energy (E_2) is negligible as one can see from the following equation [6]:

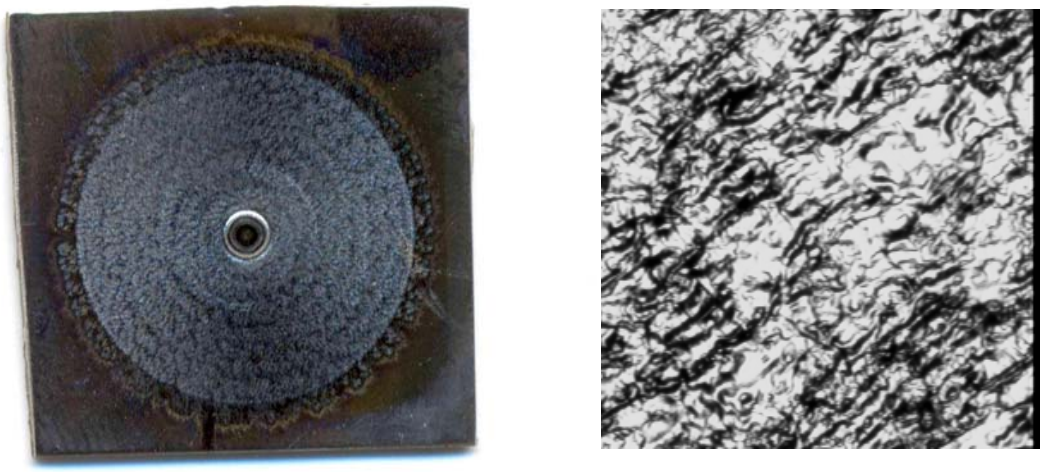

Figure 5: Photograph of a laser ablated permalloy target surface (a) and details on it seen through an optical microscope at 10X magnification (b), after 40.000 laser pulses

$$E_2 = \frac{E_1^2 \times 2.147 \times 10^{-9}}{M_2} + \frac{4 M_1 M_2 E_1}{(M_1 + M_2)^2}$$

where E_1 is the energy of the incoming particles, and M_1 and M_2 are the masses of the incoming and the target particles, respectively. In *thermal sputtering*, the absorbed laser beam melts and finally vaporizes a small area of the target material. The surface temperature of the target is typically above the boiling point of the ablated material but the observed material removal rates typically require even higher temperatures [6].

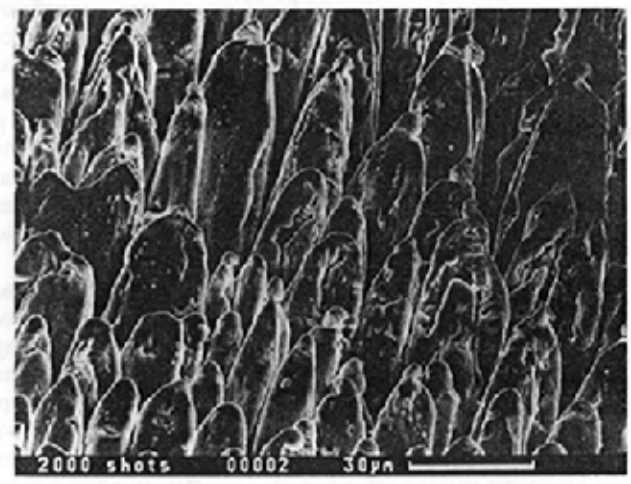

Figure 6: Scanning electron microscope image of a target surface after 2000 pulses, from [5].

Therefore, the mechanism can only partly explain the formation of the ablation cloud. *Electronic sputtering* is consired to be the principal interaction mechanism of a laser pulse with the target. The mechanism is not a single process but rather a group of processes, all of which have the common feature of involving some form of excitations and ionizations. The incident photons strike the target, producing electron-hole pairs and electronic excitations in a femtosecond timescale. After a few picoseconds, the energy is

transferred to the crystal lattice, and during the laser pulse, within a few ns, a thermal equilibrium between the electrons and the lattice is reached. This leads to a strong heating of the lattice and, with continued irradiation, to a massive particle emission from the surface [6]. At the microscopic level, the explanation for the emission is the increasing number of crystal defects and weakly bound atoms in the damaged surface, which results in the desorption of particles [5]. At the same time, the heating of the material may lead to thermal sputtering, i.e., the melting and vaporization discussed above. The electronic sputtering model is able to predict not only the observed emission rates and the direction of the ablated particles but also the high temperature (larger than 1000 K) of the ejected species. Furthermore, the existence of a threshold fluence for particle emission is another feature that is best explained with the help of this model.

Examples of other sputtering mechanisms include *exfoliational* and *hydrodynamic* sputtering. Hydrodynamic sputtering refers to the processes in which the target surface melts forming small droplets of material which are finally expelled from the surface [6]. Exfoliational sputtering, on the other hand, takes place when the fluence on the target is sufficiently high. Owing to repeatedly occurring thermal shocks and intense laser irradiation, the surface begins to crack since thermal stresses do not have time to relieve by melting, as it can be seen in Figure (5) b and Figure 6. As a consequence of this kind of behaviour, an uneven surface with cone-shaped features is formed [6]. These cones are considered to be partly responsible for the particulates frequently observed on the film surface [31]. In addition to particulates, cone formation can also change the direction of the plume towards the incoming beam and decrease the deposition rate from 1 Å/pulse to approximately 0.2 Å/pulse after a few hundred pulses [6], [11], [32]. However, the reflectivity of the target is decreased, which enhances the absorption and thereby ablation. The stoichiometry of the cones is different from that of the surrounding material, which may disturb stoichiometric ablation.

The wavelength of the laser has a significant effect on the yield of the ablated particles. Usually, lasers with short wavelength (UV region) are preferred because at shorter wavelengths the reflectivity of most materials is much lower than at long infrared wavelengths [8]. When the reflectivity decreases, a larger part of a laser pulse is absorbed, which increases the number of sputtered particles. Another advantage is that also the absorption coefficient is larger in the UV region such that the beam energy is absorbed in a thin surface layer and the ablation occurs more efficiently.

The fluence of a laser pulse has to be larger than a certain threshold value so that all the species can be stoichiometrically removed from the target. Typically, values of about 2-7 J/cm^2 for PLD or RF-PLD, and 0.05-1 J/cm^2 for MAPLE, are used in order to reduce the number of particulates on the deposited film. On the other hand, a higher fluence may result in the ejection of large target fragments which increases the number of droplets on the film surface [14]. Background gas pressure usually is as low as 10^{-5}-10^{-8} mbar in PLD, 10^{-1}-10^{-3} in RF-PLD experiments and 10^{-3}-10^{-5} mbar in MAPLE.

2.4 *The plume formation*

The material that is ablated from the target is hot and, therefore, part of the atoms in the vapour are ionized. In addition, the particle cloud absorbs energy from the laser beam and becomes more ionized. Finally, a fully ionized plasma is formed in the vicinity ($\sim 50\mu m$) of the target. The plasma expands away from the target, much like the rocket exhaust from jet nozzles, with a strongly forward-directed supersonic velocity distribution. The visible part of the particle jet is referred to as an *ablation plume*. The plume consists of several

types of particles: neutral atoms, electrons, and ions. Furthermore, clusters of different compounds of the target elements are observed near the target surface. The visible light of the plume is due to fluorescence and recombination processes in the plasma. Although atomic transitions have typical lifetimes of a few nanoseconds, collisions can re-excite atoms such that the emission lines are observed many microseconds after the initial laser pulse [6]. The dynamics of the plume is discussed in [6], [33]. Photographs of different plumes are presented in Figure (7).

The plume behaves in a different manner in vacuum and in the presence of an ambient background gas. In vacuum, the plume does not expand unidirectionally but backward velocity components appear as well because of the high density of the plasma [11], [12], [13]. The ejected species diffuse in the plume and collide with each other, which leads to a rapid thermalization of the particle cloud. Moreover, the plume in vacuum is visible to the eye only in the immediate vicinity of the target. Ambient gas scatters and attenuates the plume, changing its spatial distribution, the deposition rate, and the kinetic energy distribution of the different species. In addition, reactive scattering results in the formation of molecules or clusters which are essential for the proper stoichiometry and content of the film. This so-called secondary sputtering has a significant role when the gas pressure increases: for example, at a typical oxide material deposition pressure (0.2-0.3 mbar oxygen), only 20 % of the initially ablated material condenses on the substrate. The velocity distribution of the particles changes from unidirectional to isotropic in an equilibrium sheet called a *Knudsen layer*. The Knudsen layer is formed near the target surface after the plume has expanded a few micrometers. The next step is the formation of a shock-wave front between the Knudsen layer and the surrounding gas. In this layer, the plasma becomes more reactive and the structure of the plume is changed: it is no more a diffuse particle cloud with a dense core but rather a bubble with higher density in the outer region. A raising in the gas pressure results in an increase of the fluorescence, sharpening of the plume boundary and the shock front, slowing of the plume relative to the propagation in vacuum, and a higher spatial confinement of the plume [6]. The properties of the plume, such as colour, shape, and size, depend on several parameters. If the laser spot size on the target is reduced keeping the fluence constant, less material is removed from the target and the plume becomes wider and shorter [6]. On the other hand, if the fluence is increased a longer plume is produced because the initial velocity of the particles is higher. Gas pressure has also an influence on the length of the plume and it is often the easiest parameter that can be slightly modified during the deposition. Process parameters have to be adjusted in such a way that the plume tip touches the substrate. A plume that is too short does not provide enough material to the substrate, while in the case of a too long plume, the interaction of different elements is insufficient and adhesion to the substrate weak.

2.5 *Thin film condensation on the substrate*

The conventional theory of film growth during the deposition separates the nucleation into three different modes: three-dimensional island growth, two-dimensional monolayer formation, and the growth of separate islands on top of a full monolayer [6]. In three-dimensional growth, the formation of film-atom clusters involves several processes that a particle can undergo after arriving on the substrate. These processes are illustrated in Figure (8). The balance between growth and dissociation of a cluster is governed by the total free energy of the system. Either a decrease in the surface energy between the arriving atoms and the cluster or an increase in the magnitude of the negative volume

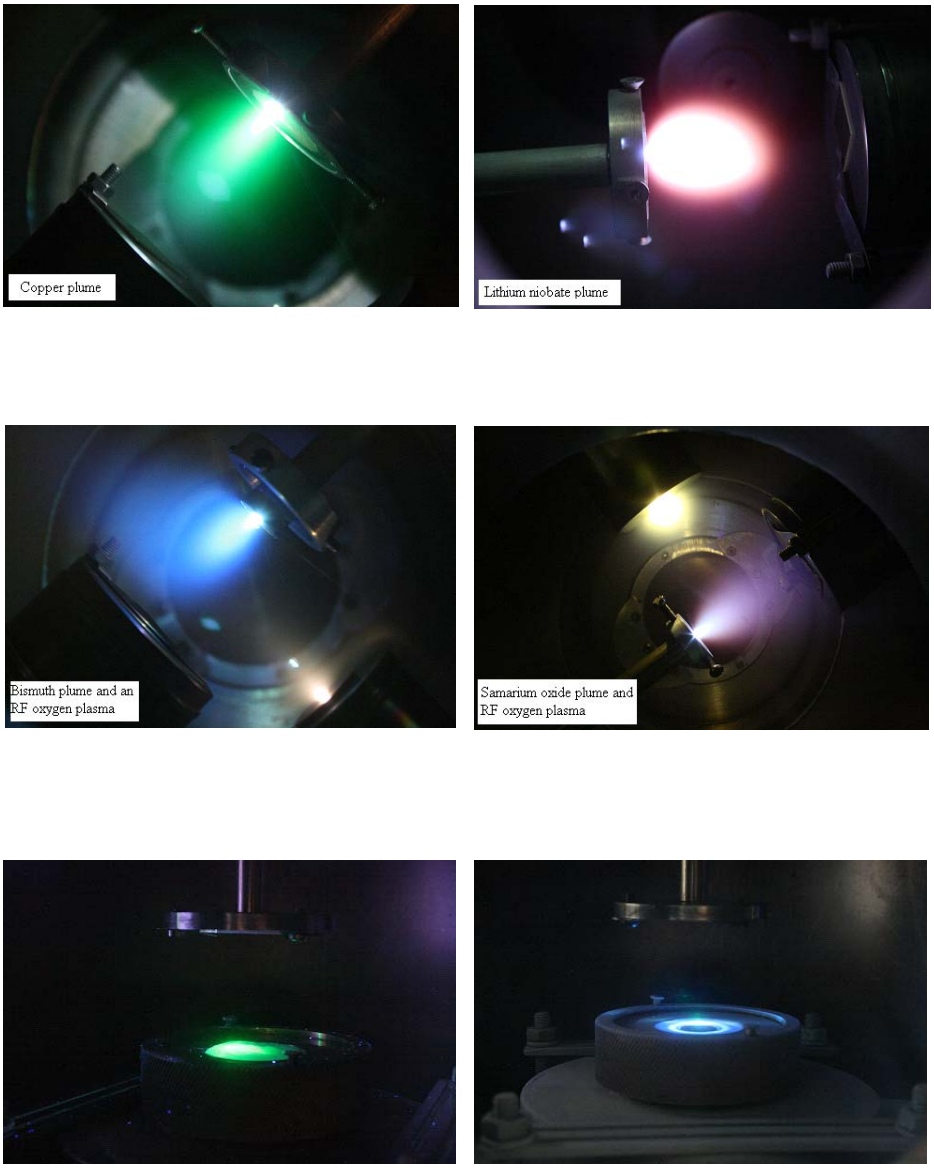

Figure 7: Examples of plasma plumes produced during PLD (a), RF-PLD (b) and MAPLE (c) procedures.

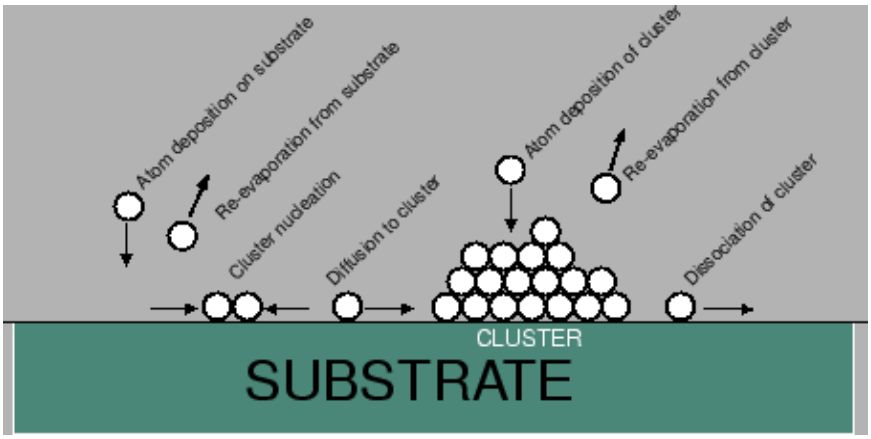

Figure 8: Illustration of thin film growth on a substrate

free energy decreases the size of a stable cluster [6]. As a result, the nucleation rate of the cluster increases. In practice, the free energy can be changed by lowering the temperature or increasing the deposition rate. A typical example is the change from the growth of a crystalline phase to the growth of an amorphous phase at low temperatures (hence sometimes the use of a heated substrate holder).

If the surface energy of the cluster is low and that of the substrate is high, it is energetically more favourable for the film to form as full monolayers. A higher temperature and a lower deposition rate promote the formation of larger islands, instead of numerous small clusters [6]. The third way for the film to condensate is that, initially, two-dimensional layers are formed but later the growth mode changes to three-dimensional nucleation. One obvious reason for this change is the increase in stress due to mismatched lattice spacings with increasing thickness of the film. Another possibility is that strong chemical bondings between the substrate and the film alter the surface energy and the whole system is driven into a new steady state.

The quality of the deposited film is, above all, determined by the crystallinity of the lattice and the surface smoothness. The generation of particulates during the PLD process is one of the most important factors affecting the smoothness of the resulting film. These particulates can be classified into small droplets (typical size: $0.2-3\mu m$) and large irregularly-shaped outgrowths (diameters up to more than $10\mu m$) [31]. The number density of all kinds of particulates increases with the number of laser pulses. The largest outgrowths are believed to originate directly from the target. Breaking of protruding surface features or splashing of a molten surface layer are typical explanations for the occurrence of large target fragments on the substrate. Droplets, on the other hand, are resolidified molten drops resulting from hydrodynamic sputtering of the target [31]. Furthermore, the loss of epitaxy in thicker films generates many types of differently shaped outgrowths. Droplets can be totally eliminated from the film surface by properly adjusting PLD conditions but, simultaneously, the number of so-called precipitates increases. Precipitates are particles whose stoichiometry is different from that of the surrounding film. The crystallinity and surface structure of the thin film is improved when precipitates are formed since the film is separated into two phases: the precipitates and the crystal matrix. The photograph in Figure (9) gives an example of how wrong PLD deposition parameters, such as the fluence, the laser wavelength and/or the background gas pressure influence the procedure: large, luminous clusters (drops) are expelled from the target under laser irradiation. Such situations can easily be avoided by simply adjusting laser energy, laser spot area, laser wavelength or background pressure.

Despite the fact that PLD has provided an excellent tool for producing high-quality multicomponent films, it has not yet fully emerged as a reproducible process for commercial thin-film applications. This is mainly because the deposited films have only a small area of structural and thickness uniformity. Especially, microwave device applications of HTS materials and special or complex oxides for fuel cell devices would greatly benefit from the usage of large-area (>1 cm^2) films. Several papers in this matter have been published to date [6], [11], [13]. During the past few years, several suggestions have been made to scale up the PLD process to coat substrates with diameters of 50 mm or larger. Two of these techniques - off-axis PLD and rotational-translational PLD - are so-called static-beam approaches, i.e., the optical path of the laser beam is fixed. A compatible alternative to these techniques takes advantage of laser-beam rastering across a rotating target. These three approaches are illustrated in Figure (10).

In off-axis PLD, the target is positioned such that the center of the ablation plume has a certain offset from the center of the rotating substrate. In the second static-beam

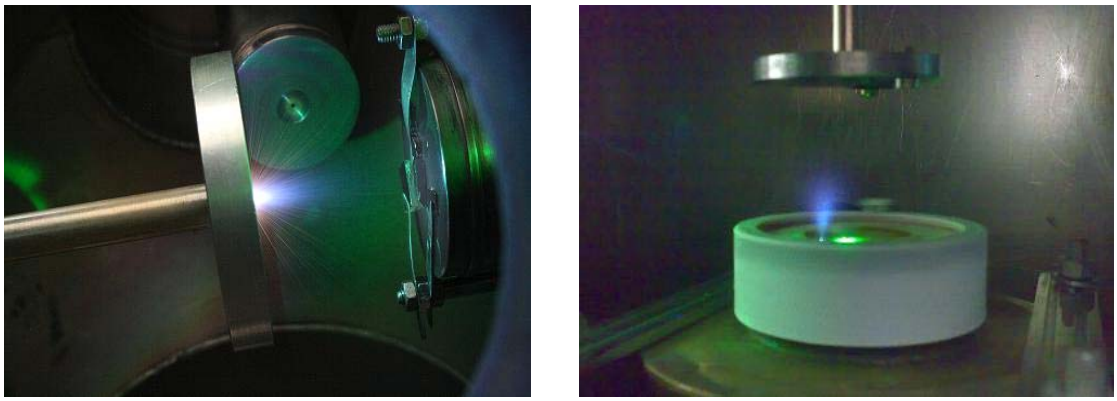

Figure 9: Photographs of laser ablation with an unsuited fluence (usually to be avoided) on: an AlNiCo target, revealing that large, luminous clusters are thrown away under laser irradiation (subplot a), and on a frozen matrix of $Cu(DAB)_2$ in toluene revealing that a luminous plasma forms during MAPLE (subplot b)

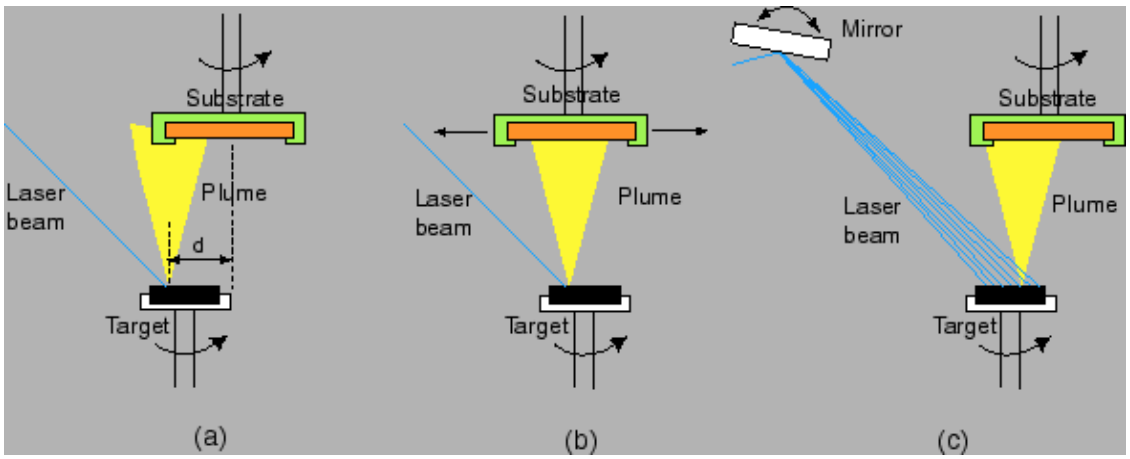

Figure 10: Illustration of the three different large-area PLD techniques: off-axis PLD (a), rotational-translational PLD (b) and laser-beam rastering (c), from [6].

approach, rotational-translational PLD, the substrate both rotates and moves back and forth in one direction. In the beam-rastering approach, a focused laser beam moves linearly across the surface of a rotating target such that the whole target material is efficiently used. The rastering is realized by using, e.g., a mirror held in a motorized kinematic mount. By properly adjusting the raster velocity as a function of position, the center of the ablation plume stays for longer times near the edges of the rotating substrate, which improves the homogeneity of the film. This method has been utilized for the deposition of thin films on up to 125-mm-diameter substrates. There are a few aspects that make coating of large-area substrates difficult, although deposition on smaller substrates is a straightforward process. One reason is, of course, that more material needs to be deposited on, e.g., a 50-mm-diameter substrate than on a square 1-cm2 substrate. Another problem is that at a typical deposition pressure, the ablation plume has a forward-scattered, inhomogeneous, and narrow flux distribution. An epitaxial film is grown only in the region that the center of the plume touches (typically the before-mentioned 1 cm^2). Therefore, all large-area approaches make use of the central part of the plume, which sweeps across the whole substrate. The situation can be further improved if the target-substrate distance is increased since the plume becomes wider when expanding away from the target. Uniform heating of the substrate is another challenge one has to take into account: it is difficult to obtain a proper thermal contact over large areas. One approach is to heat the substrates radiatively. However, unidirectional heating may be difficult since certain substrates (e.g. sapphire) do not absorb strongly in the infrared region of the electromagnetic spectrum. One appropriate solution is the use of a vacuum oven based on blackbody radiation in a cavity [6].

3 Experimental results of the laser-assisted techniques: pros and cons

Pulsed laser-assisted deposition techniques are simple, non-conventional, modern and versatile thin film production methods that can be applied to most know materials, when other techniques fail. Some of the advantages are:

- the energy source is well confined at the surface of the target, and by that it contributes to the eficiency, the flexibility and the control of the processes;
- the enery source is external to the deposition chamber, and can be adjusted in energy and wavelength to meet almost each experimental demand;
- complex stoichiometries, soft metal-organic hybrids, biological materials and even live cells can be developed in thin films by at least one of these methods;
- the thin film properties can be controlled in terms of crystalline structure (poly-crystals, monocrystals, amorphous, etc), thickness, stoichiometry and composition (e.g. starting from a metal, a succesion of several layers with different composition can be grown: metallic, oxidic, nitridic or mixtures of such compounds) thus multilayered or even concentration gradient structures may be obtained.
- these procedures can be used to develop thin films from solid or liquid targets: ablation in liquids is also used, although it is a less common procedure than ablation of solid or frozen targets.

These laser-assisted techniques also have a series of disadvantages, such as:

- only a small area of the substrate can be covered, typically about 1 cm^2;
- droplets and clusters may appear at the surface of the films, that leads to higher roughness, that further leads to bad optical, electrical, magnetical and even crystalline

properties; although large clusters can be avoided, small ones and droplets sometimes represent a problem that is difficult to deal with or can not be fully avoided.

4 Conclusions

Pulsed laser-assisted deposition techniques are clean, simple yet versatile methods that allow good control in thin films and/or multilayer-structured samples. When compared to other thin film techniques (e.g. chemical vapour deposition, sol-gel, magnetron sputtering, etc), PLD does not need expensive or corrosive precursors, large area or large volume targets, very high temperature and/or pressure, and does not need complex prior and/or subsequent treatments, but it can be applied virtually on any sort of complex stoichiometry and/or soft materials. The mechanisms of ablation and thin film growth are mostly related to the laser properties, the target and background gas, and in some cases to substrate temperature.

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