

CHAPTER 2

PULSED LASER ABLATION DEPOSITION AND LASER INTERACTION WITH MATERIALS

2.1 Introduction

This chapter aims to review theoretically and experimentally the pulsed laser deposition process, to describe its microscopic and macroscopic mechanisms and to demonstrate its versatility through the equipment involved in the deposition process. Aspects of interest include the initial laser target interactions, by which the solid target material melts and enters the gas phase, the processing and the propagation of material in the plume of ejected species and eventually the accommodation of gas phase species on the substrate that is to be coated. In addition, the importance of film quality, some of the procedures that can affect the quality of the thin films and the major problems of the method, including some of the solutions of those problems, are considered.

2.2 Pulsed laser deposition process

2.2.1 Definitions

Lasers play a very important role in localised melting, laser annealing, surface cleaning by ablation and desorption, surface condensation by rapid cooling, etc. When the beam from a pulsed laser is readily focused onto a solid material, the emitted particles condense on a substrate forming a thin film. The process is called laser ablation, and is now widely used both for the deposition and for patterning of thin films. The lasers normally used have pulse durations in the range 5-50ns.

So, when pulse laser ablation is used for the deposition of thin films, the process is called Pulsed Laser Deposition (PLD) and has been applied to a very wide variety of materials, ranging from simple metals to complex oxide compounds [3, 14, 65, 66]. Today the use of the expression Pulsed Laser Ablation Deposition (PLAD) is more common. When using chemically reactive gases for the

deposition of thin film, the process is called Reactive Pulsed Laser Ablation Deposition (RPLAD) [65-70]. The definition of RPLAD involves the experiments in which metals, oxides, carbides or nitrides are used as targets and in the reaction chamber a dynamic flux of gases (O_2 , CH_4 , N_2 ...) is introduced. The gases react with metal vapour or help to compensate losses of the lighter or volatile elements ablated from the target

2.2.2 Equipment

A typical set-up for PLAD is schematically shown in Fig.2.1. It consists of a target holder and a substrate holder housed in an ultra high vacuum chamber. A high-power laser is used as an external energy source to vaporise materials and grow thin films. A set of optical components (mirrors, lenses, windows) is placed between the laser and the vacuum chamber to focus and raster the laser beam over the target, guiding the laser output pulses. The technique is conceptually simple, in contrast to the different physical phenomena occurring during the process. In an ultrahigh vacuum (UHV) chamber (or reactive gas atmosphere), elementary or alloy targets are struck in general at an angle of 45° by a pulsed and focused laser beam.

Mostly, the substrates are attached with the surface parallel to the target surface at a distance of typically 4-10cm. Generally, the laser source is placed outside the vacuum chamber. In order to obtain a steady ablation rate, the laser beam is scanned by rotation of the target and by additionally sweeping the target or rastering the laser beam over a sufficiently large target area ($\sim$ some cm^2). Under these deposition conditions, in addition to atoms and ions, in most cases some droplets of target material are also deposited on the substrate surface. In most systems, the formation of large droplets can be reduced by using dense and smooth targets [71]. However, the ablation of smaller droplets originating from the formation of a liquid layer at the target surface, due to the pulsed laser illumination, is hardly avoided. The corresponding mechanisms are called hydrodynamic sputtering [72] or subsurface heating [73].

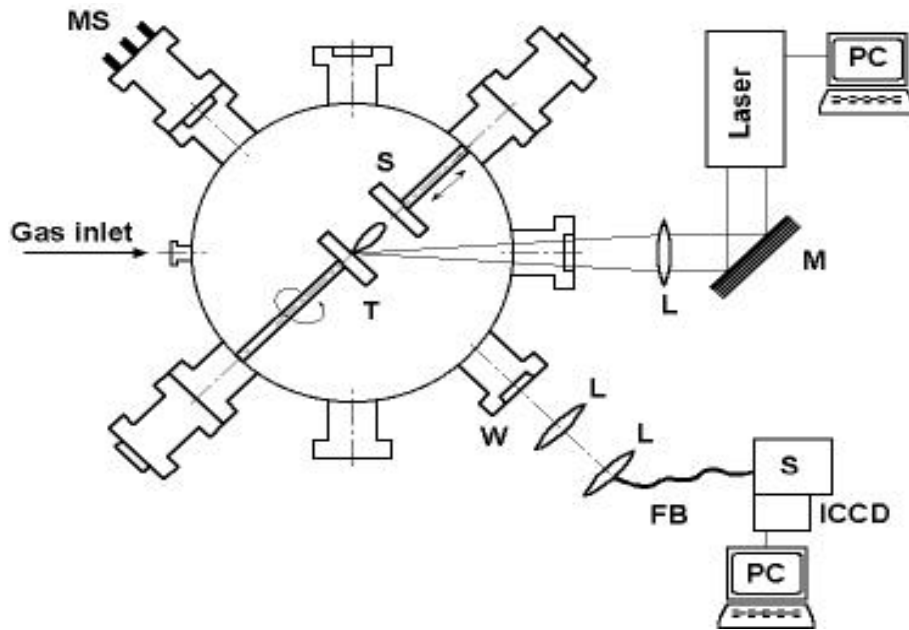


Figure 2.1 Setup of the PLAD system in conventional configuration. MS: mass spectrometer, L: lens; T: target; S: substrate; W: optical window.

These droplets can only be prevented from reaching the substrate surface, by using the so-called off-axis geometry, firstly described by Holzapfel et al. [74] during PLAD of high-temperature superconductors, or by using for instance the cross-beam ablation technique [75], where the substrate is shadowed from the material ablated simultaneously from two targets.

2.2.3 Versatility of the technique

Many experimental parameters during the PLAD process can be varied. The vacuum preparation conditions, including target-substrate distance, substrate temperature, background gas and pressure, may be varied. In addition, laser parameters such as fluence, wavelength, pulse duration and repetition rate can be altered. They thus have a strong influence on film growth and properties.

2.2.4 UHV, gas atmospheres and small target size

The PLAD technique allows preparing films of all kinds of complex material such as oxides, nitrides, carbides, and metallic systems. In Table 2.1, a non-exhaustive list of materials is given.

Table 2.1 List of some materials deposited by PLAD using a reactive atmosphere and references

Materials		Literature
Oxides	SiO ₂	Acquaviva et al.(2000) [30] Fogarassy et al. (1990) [11]
	TiO ₂	Lackner et al. (2004) [35] Narumi et al. (2002) [76] Yamamoto et al. (2002) [77]
	ITO	Baek Choi et al.(2003) [43], Martino et al.(2001) [41], Fotsa-Ngaffo et al. (2005) [78]
Carbides	SiC	Balooch et al. (1990) [79]
Nitrides	TiN	Mihailescu et al. (1993) [67]
Metallic	alloys/multilayers	Krebs et al. (1993) [13]
High-temperature superconductors	YBa ₂ Cu ₃ O ₇	Dijkkamp et al. (1987) [10]
	Ti ₂ Ba ₂ CaCu ₂ O ₈	Foster et al. (1990)[80]

In order to obtain all these various type of materials, an ultrahigh vacuum (UHV) or a reactive gas atmosphere during deposition is needed. Since the energy source is outside the deposition chamber and the laser light does not introduce pollutants, this is done easily. During growth of oxides, the use of oxygen is often inevitable for achieving the correct amount of oxygen in the growing oxide film. For instance, for the formation of silica structures at high substrate temperatures in a one-step process, an oxygen pressure of about 1-5Pa is necessary [30].

For many other oxide or nitride films, a larger amount of oxygen or nitrogen must be added in the reaction chamber [10, 11, 13, 35, 41, 43, 67, 76-79]. The PLD technique is flexible, because the spot size of the focused laser beam is small and the target area may even be less than 1cm^2 . This allows preparing complex samples with enrichments of isotopic markers within the deposited film. Being able to easily prepare samples for research purposes or application tests is interesting especially if the sample is extremely expensive or impossible to prepare with other techniques. Here, the flexibility of the PLAD technique pays off, due to the possibility of easily exchanging and adjusting the targets.

2.2.5 Stoichiometry transfer

Laser ablation of material from bulk target is a highly non-equilibrium process, which allows stoichiometric transfer and delivery of the target composition to the substrate. This aspect is crucial for metal oxide where material systems of interest are often comprised of multiples component with different vapour pressure. Therefore, it is possible to prepare stoichiometric thin films from a single alloy bulk target. This so-called stoichiometry transfer between target and substrate has made the PLAD technique interesting for the growth of complex systems for technical applications. Stoichiometry is difficult to obtain with evaporation or sputtering by using a single target, because in general the partial vapour pressures and sputtering yields of the components are different from each other, which give rise to a different concentration of the thin film growing on the substrate.

In the case of PLAD, with most materials a stoichiometry transfer between target and substrate is obtained. The material transfer between target and substrate occurs in a material package, where the separation of the species is small. The expansion of the whole package can be well described by a shifted Maxwell-Boltzmann centre-of-mass velocity distribution [81].

As regards all the factors above described, one conclude that the technique is

- **conceptually simple:** it is only necessary to have rotating target and substrate-holder placed in an irradiation chamber. In addition, a laser

beam vaporises a target surface, producing a film with the same composition as the target;

- **versatile**: many materials can be deposited in a wide variety of gases pressure. The reactive conditions can be easily controlled mainly by adjusting the substrate temperature and the laser fluence;
- **fast**: as high quality samples can be grown reliably in 15-30 minutes;
- **scalable and cost effective**: as complex oxides move toward the volume production; one laser can serve many vacuum systems.

The following section is consecrated to the description of different mechanisms occurring in a PLD or PLAD process, from the laser light interaction with the target to the nucleation and film growth on the substrate.

2.3 Mechanisms

In general, when a nanosecond laser pulse of ultra violet radiation is incident on the surface of a solid target, it will be absorbed. Absorption of laser light induces an extremely rapid heating of significant volume of target material. This may cause phase transition, and introduce high amplitude stress waves in the solid target. Material will start to boil off and expand into the gas phase. The evaporated materials consist of highly excited and ionised species [82]. Therefore, the study of the basic mechanisms of PLAD is a great challenge because laser ablation depends not only on the target thermo-physical properties but also on the laser beam parameters.

The physics of the different processes is quite complex, given that it involves laser-material interactions, plasma plume formation with high energetic species and expansion of the ablated material to the substrate surface, with its associated atomic physics and hydrodynamics features. As described in the previous section, the most important feature of PLAD is that the stoichiometry of the target can be retained in the films. This is the result of the extremely high heating rate of the target surface (10^{10} K/s) due to pulsed laser irradiation [83]. It leads to the congruent evaporation of the target irrespective of the evaporating point of the

constituent elements or compounds of the target. Thus, the thin film formation process in PLAD can be globally divided into the following five stages as illustrated in Fig.2.2. Each stage is critical to the formation of high quality, stoichiometric, uniform thickness thin film.

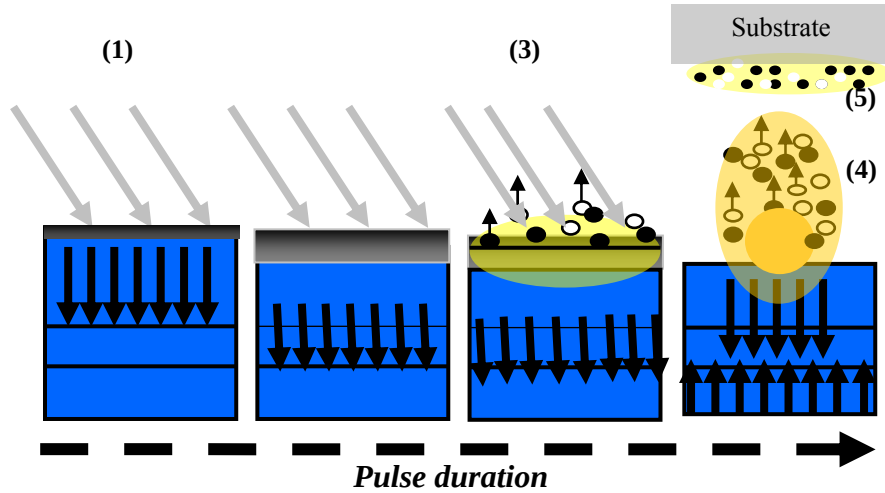


Figure 2.2 Laser ablation mechanism occurring during a pulse duration: 1. Initial absorption of laser radiation (long arrows), melting and evaporation begin (melted area is indicated by the black surface area while motion of the solid-liquid interface is indicated by short arrows). 2. The melt front propagates into the target, the vaporisation and the laser-plume interaction grow continue. 3. Absorption of the incident laser radiation by the plume and plasma formation. 4. The laser pulse ends; plasma expansion. 5. Condensation of species on the substrate.

2.3.1 Laser melting and interaction with material

The interaction of laser light with materials and the properties of the plasma produced have been investigated for many years [3, 71, 84, 85]. Still the effect of stresses of the melting processes, the generation of high-density and high-temperature plasma is a growing field in basic science and material processing [84-86]. When the laser beam is focused on the surface of the solid target, all elements in the target are rapidly heated up to their evaporation temperature at sufficiently high flux densities and short pulse duration. The melting starts most likely on the surface of the target material. Upon melting of a particular volume of

the solid, a part of its thermal energy goes to the latent heat of melting that in turn decreases temperature of the surrounding region. Such local temperature decrease along the solid-liquid interface may lead to variation of the velocity of melting front propagation and development of the melting front instabilities.

Thus the question of the melting mechanism is still open, and it is of a great practical and scientific significance to understand the very nature of such solid liquid transition phase. Intensive theoretical, numerical and experimental investigations are still in progress in order to obtain accurate knowledge of all the physical processes involved in the phenomenon. The most popular of them is the two temperature model, which will be summarised in the following section.

2.3.2 Two Temperature Model (TTM)

TTM is a widely used computational model for the analysis of the short pulse laser interaction with metals. In this section, the basic assumptions of the model and its applicability shall be briefly reviewed. The temperature dependence of the parameters, the electronic heat conduction, the electron-phonon coupling, and some of the limitations of TTM are discussed. Upon laser light absorption by the conduction band electrons, the deposited energy is equilibrated within femtosecond among the electrons and, more slowly, is transferred to the atomic vibrations. When the laser pulse duration is comparable to the time needed for thermal equilibrium between the electrons and phonons, a non-thermal equilibrium is created by laser irradiation. Based on the energy balance, Anisimov et al. [85] suggested that at the continuum level, the time evolution of the lattice and electron temperatures, T_l and T_e , respectively, can be described within a so-called two temperature model (TTM) by two coupled nonlinear differential equations:

$$\begin{cases} C_e(T_e) \frac{\partial T_e}{\partial t} = \frac{\partial T_e}{\partial z} \left(K(T_e) \frac{\partial T_e}{\partial z} \right) - G(T_e - T_l) + S(z, t) \\ C_l(T_l) \frac{\partial T_l}{\partial t} = \frac{\partial T_l}{\partial z} \left(K(T_l) \frac{\partial T_l}{\partial z} \right) + G(T_e - T_l) \end{cases} \quad (2.1)$$

where C and K are the heat capacities and thermal conductivities of the electrons and lattice, G is the electron-phonon coupling constant. The source term $S(z, t)$ is used to describe the local laser energy deposition per unit area and unit time during the laser pulse duration. The phonon heat conduction is negligible as compared to the electron heat conduction in metals. The system of differential Eqs (2.1) can be solved by a finite difference method and the spatial and time evolution of the electron and lattice temperatures can be obtained.

TTM is based on a number of assumptions like the instantaneous thermalisation of the excited electrons and the absence of surface charging and repulsive charge interactions. Approximations for the temperature dependence of the electron thermal conductivity and coupling parameter are also important. Calculations assume that electron thermalisation takes place instantaneously upon the laser pulse irradiation. This is justified by the calculations presented in [86]. Another important assumption of the TTM is that charging of the surface due to the electron emission can be neglected. If positive charge can be accumulated at the surface, this would result in strong electrostatic ion repulsion forces that could cause the break-up of the surface.

The processes that contribute to the surface charging have been considered by Bulgakova et al. [87]. The results of the calculations suggest that surface charging may indeed play an important role for dielectric materials, whereas for metals, the high electron mobility and the high density of available free electrons ensure an effective screening of the irradiated metal target.

In addition to the diffusive electron energy transport assumed in TTM, the ballistic motion of the excited electrons can significantly alter the initial energy deposition depth. It has been suggested [88] that the effect of ballistic electrons can be incorporated into TTM by substituting the optical penetration depth L_p in the source term by an effective laser energy deposition depth defined by both optical absorption and ballistic energy transport, $L_p + L_b$, where L_b is the ballistic range. The source term can be written as:

$$S(z, t) = I(t)(1 - R_{\text{ref}})e^{-z/(L_p + L_b)} / (L_p + L_b) \quad (2.2)$$

where R_{ref} is the reflectivity of the target and $I(t)$ is the laser intensity. An additional correction should be introduced in the source term for systems with size comparable to the effective energy deposition depth [88]. The source term representing laser pulse irradiation in TTM calculations is described in details in the following section.

2.3.3 Source term description

A Gaussian temporal profile is used in the simulations to describe the laser energy deposition according to the following equation:

$$S(z, t) = I_0(1 - R_{\text{ref}})(L_p + L_b)^{-1} \exp(-z/L_p) \frac{\exp[-(t - t_0)^2 / 2\sigma^2]}{(1 - \exp[-d/(L_p + L_b)])} \quad (2.3)$$

here I_0 is the peak intensity, d is the thickness of a film, and σ is the standard deviation of the Gaussian profile, related to the pulse duration as $\tau_L = \text{FWHM} = \sigma\sqrt{8\ln(2)}$. Laser fluence F is related to the peak intensity I_0 as $F = \sqrt{\pi/4\ln(2)}\tau_L I_0 \approx 1.0645\tau_L I_0$. The absorbed laser fluence, related to the incident fluence as $F_{\text{abs}} = F(1 - R)$, is also used in the discussion of the simulation. The laser pulse initialisation time t_0 is usually taken 2.5 times of the pulse duration τ_L . The finite size d of a target was accounted for in the source term by means of its additional scaling by factor of $(1 - \exp[-d/(L_p + L_b)])$. The latter becomes important when the range of laser energy deposition $L_p + L_b$ is comparable with the thickness d of the target

2.3.4 Limitation of the TTM

The TTM model has been used to predict the threshold fluences of laser melting [89], the laser induced desorption of species from metal surfaces [90], and to explain the dynamics of ion ejection in laser ablation [91]. Despite the successful

applications and popularity of TTM, the model has a number of inherent limitations which can be overcome by adding “more physics” [84] within the framework provided by TTM. In particular, recent developments include incorporation, through the parameters of TTM, of the description of the surface and grain boundary scattering [92], as well as the energy transfer by ballistic electrons [88, 93], combining TTM with the hot electron blast model [94] and thermo-elasticity equations to investigate the conditions for non-thermal damage to thin metal films [95].

Other limitations are harder to overcome within a continuum model. In particular, the description of phase transformations occurring under highly non-equilibrium conditions induced in the target material by short-pulse laser irradiation is difficult at the continuum level and typically involves a number of assumptions and simplifications. Even the basic questions on the microscopic mechanisms of melting under strong overheating continue to remain the subjects of active scientific debates. A computational method that is suitable for simulation of fast non-equilibrium processes and therefore can provide insights into the mechanisms of laser matter interactions is the Molecular Dynamics (MD) method.

The advantage of the MD method is that only details of the interatomic interaction need to be specified, and no assumptions are made about the character of the processes under study. In particular, MD has been demonstrated to be an efficient tool for a microscopic analysis of the melting mechanisms under conditions of overheating in both the bulk of a crystal [96-97]. Generation and propagation of laser induced pressure waves [98], and laser ablation [99-100] have been also reported. The classical MD method, however, is not directly applicable for simulation of laser interactions with metals. Since the electronic contribution to the thermal conductivity of a metal is dominant, the conventional MD method significantly underestimates the total thermal conductivity.

A model aiming at overcoming these limitations and combining the advantages of TTM and MD for a realistic description of the diverse range of processes induced

by short-pulse laser irradiation of a metal target is called the combined TTM – MD model and has been investigated by Zhigilei and al [84, 101]. The model allows a realistic description of the diverse range of processes induced by short-pulse laser irradiation of a metal target. Details description of the model is beyond the scope of this current work.

It is important to quote that all the methods agree that after the melting, target materials are dissociated from the target surface and ablated out with the same stoichiometry as the target. The ensuing plume will thus be irradiated by the later part of the incident laser radiation. Some of this radiation will be absorbed by the plume, leading to an attenuation of the light intensity on the target, and excitation and ionisation of species in the plume. Plasma formation and subsequent optical emission will result. Interests have been increased in this field because of both fundamental aspects of laser solid interaction and consequent plasma generation [102, 103].

In addition to the melting process, the ablation mechanisms involve many other complex physical phenomena such as collisional, thermal and electronic excitation, exfoliation and hydrodynamics. This first process can be divided schematically into two different regimes: the regime at low laser fluences and the regime at high laser fluences. Several authors [104-107] have analysed the laser-ablation process in the regime at low fluence regime and have found that the vapour produced by the leading edge of the laser pulse behaves like a thin medium and the laser beam passes nearly non-attenuated through the vapour. The main physical processes involving heat conduction, melting and vaporisation of the target [108-110] are not described in the framework of this dissertation as phenomena occurring when the laser energy is higher than the threshold fluence are important

2.3.5 Regime at high laser fluence

The vapour temperature is high enough to cause appreciable atomic excitation and ionisation. Detailed analysis [106, 111] of the different vaporisation mechanisms

active in nanosecond laser-solid interaction show that for sufficiently high laser fluences, phase explosion occur involving homogeneous nucleation when the target temperature reaches a value close to the material thermodynamic critical temperature T_c . As a result, the hot region near the target surface undergoes in a very short time a rapid transition from a superheated liquid to a mixture of vapour and liquid droplets. For the ultra-short laser pulses irradiation of targets, detailed analysis of the heat flow demonstrate that thermal conduction into the target can be neglected, so the target temperature at the end of the laser pulse is given by:

$$T(z, \tau_p) \approx \alpha A F \times \exp(-\alpha z) / \rho c \quad (2.4)$$

where α , ρ , c and A are, respectively, the absorption coefficient, the mass density, the specific heat and the surface absorbance. Significant target vaporisation takes place when $\rho c T(z)$ becomes larger than the latent heat of evaporation per unit volume ρL_v , where L_v is the latent heat per unit mass. Using Eq (2.4), the condition for vaporisation, and the ablation depth per pulse, respectively, can be written in the forms:

$$F \geq F_{th} \exp(\alpha z) \quad (2.5)$$

$$\Delta z_v \approx \alpha^{-1} \ln(F_i / F_{th}) \quad (2.6)$$

where F_{th} is the threshold laser fluence for vaporisation, given by

$$F_{th} = \rho L_v / \alpha A \quad (2.7)$$

For nanosecond laser pulses and metallic targets the condition $L_{th} \geq \alpha^{-1}$ is usually fulfilled, L_{th} being the heat penetration depth given by $L_{th} \approx (2D\tau_p)^{1/2}$, where D is the heat diffusion coefficient ($D = \kappa / \rho c$). In such a case, there is enough time for thermal wave propagation into the target and the absorbed energy is stored in a layer with a thickness of the order of L_{th} . Since metals need much more energy to

vaporise than to melt, evaporation occurs when the energy (per unit volume) absorbed into the vaporised layer becomes larger than the latent heat of evaporation per unit volume, namely

$$\Delta z_v \approx A(F_1 - F_{th})/\rho L_v \quad (2.8)$$

In Eq (2.6) the laser fluence threshold F_{th} represents the minimum energy above which appreciable evaporation occurs. Since in this case the evaporation takes place from liquid metals, F_{th} is given approximately by the energy needed to melt a surface layer of the order of L_{th} :

$$F_{th} \approx \rho c \Delta T_m L_{th} / A \quad (2.9)$$

$\Delta T_m = T_m - T_0$, where T_m and T_0 are the melting and initial target temperature, respectively. The fluence threshold grows as $\tau_p^{1/2}$ and depends on the thermal and optical properties of the target, being for most metals of the order of $1\text{-}2\text{J.cm}^{-2}$ [112, 113]. If the material parameters are supposed constant, Eq (2.6) predicts a linear increase of the ablation depth per pulse as a function of the laser fluence. Such behaviour is typically observed at low laser fluences [114]. However, a nonlinear behaviour, especially at high laser fluence, could be observed due to changes in material parameters with the target temperature and to laser beam absorption by the vapour cloud formed above the target surface [115, 116].

The vapour absorbs the incident laser radiation leading to vapour breakdown and plasma formation. The temperature of the laser produced plasma is so high that an efficient shielding of the target occurs during the laser pulse. The properties of the laser-ablation process are strongly influenced by both laser-plasma coupling and plasma kinetics. In nanosecond laser ablation of metals in vacuum, for fluences higher than the fluence threshold ($F > 2\text{Jcm}^{-2}$), a plasma is always produced above the target surface. A review of existing data and models [113, 117-119]

reveals that at laser pulse durations of $10^{-8} < \tau_p < 10^{-3} \text{ s}$, the intensity I_p at which plasma ignition occurs verifies the relation $I_p \tau_p^{1/2} \approx B_p$, with $B_p \approx 4.5 \times 10^4 \text{ W cm}^{-2} \text{ s}^{1/2}$ for an aluminium target, for example [120].

In the analysis of the laser ablation process it is useful to consider the adiabatic limiting case description of the process, i.e. that laser light absorption and the resulting simultaneous target heating, vaporisation and plasma formation take place much faster than the expansion of the ablated material. Under these assumptions, the laser ablation process can be divided schematically into two stages: evaporation of the solid target and formation of the laser plasma and expansion of the ablated vapour cloud in the chamber.

Heating and expansion take place almost simultaneously leading to a complicated interaction of the expanding cloud with laser light. However, the adiabatic approximation is equivalent to the simplification that the energy deposited by the laser pulse is first converted to internal energy of the target and vapour cloud, and, subsequently, it partially decays to the kinetic energy of the ablated particles. If one uses the assumption, simple numerical approaches can be used to model the plasma formation and expansion.

2.4 Dynamic of the ablation materials

2.4.1 Plasma formation and laser-plasma interaction

In this section, the microscopic mechanism of ablation is mostly analysed. This later has been investigated by several authors [116, 121, 122] and particularly by theoretical models based on plasma self-regulating absorption via inverse bremsstrahlung (IB) processes [118, 123, 124]. A numerical model based on thermal evaporation and IB absorption [118] explains the mass ablation rate observed in UV laser ablation of brass targets. Some authors [125-127] have drawn attention to the importance of photo ionisation (PI) of the excited neutrals present in the plasma and numerical models including laser absorption, excitation and ionisation in the laser-induced plasma have been reported. It results that the

main dominant mechanisms active in laser-induced plasma formation and interaction are Inverse Bremsstrahlung (IB) absorption and Photo Ionisation (PI). The IB process involves the absorption of photons by free electrons. Nevertheless, the electron-neutral interaction can be of importance in weakly ionised vapour. However, in this last case the vapour behaves like a thin medium and the absorption is very low.

The IB absorption coefficient α_{IB} of an electron gas with a Maxwellian velocity distribution and a kinetic temperature T_e due to electron-ion collisions is expressed as [111, 128]:

$$\alpha_{IB} = \sigma_{IB} N_e = \frac{4}{3} \left(\frac{2\pi}{3\kappa_B T_e} \right)^{\frac{1}{2}} \frac{Z^2 e^6}{h c m_e^{\frac{3}{2}} v^3} N_i g_{ff} \left(1 - \exp \left(- \frac{h\nu}{\kappa_B T_e} \right) \right) N_e \quad (2.10)$$

where σ_{IB} is the IB cross section, N_i and N_e the number density of ions and electrons, ν the laser frequency, m_e and e the electron mass and charge, Z the ionic charge, h the Planck's constant and κ_B , the Boltzmann's constant, respectively. The Gaunt factor g_{ff} is introduced in a more exact theory of the absorption coefficient and is always assumed to be 1 by Kramer's rule [129].

Eq (2.10) shows that the IB process is less efficient in the UV than in the visible and in the Infrared (IR) part of the light spectrum. Nevertheless, the IB absorption coefficient depends both on the plasma degree of ionisation and on the effectiveness of the vaporisation process. Thus, the actual effectiveness of the IB absorption process involve the target thermo-physical properties and the interaction of the laser beam with the evaporated species i.e. the ionisation potential and electronic structure of the evaporated atoms. In IR laser-ablation processes, primary electrons coming from vaporisation are able to absorb laser photons by IB even at very low electron density. This leads to strong electron heating and breakdown ionisation. Due to this high absorption of infrared radiation, the energy can not be efficiently couple to the target and the ablated

vapour density, so the ablation depth remains low [130]. In visible and UV laser-ablation processes, IB absorption is less efficient, but direct PI of excited atoms in the vapour can play a significant role. In fact, the absorption coefficient α_{PI} (in cm^{-1}) of this process is given approximately by [111]:

$$\alpha_{PI} = \sigma_{PI} N_n \approx \sum_n N_n 2.9 \times 10^{-17} \epsilon_n^{\frac{5}{2}} / (h\nu)^3 \quad (2.11)$$

where σ_{PI} is the cross section, $h\nu$ the photon energy (in eV), ϵ_n (in eV) and N_n (in cm^{-3}) are the Ionisation Energy (EI) and the number density of the excited state n . The summation is performed over the energy levels which satisfy the condition $h\nu > \epsilon_n$. The photon energy is comparable to the typical ionisation energy of excited atoms, making σ_{PI} of the order of 10^{-17}cm^2 in most cases. Excitation and ionisation time constants are much shorter than the laser pulse duration τ_p [125, 126] producing an effective enhancement of the excited/ionised species. Detailed of analysis of the various excitations, ionisation and relaxation processes influencing the laser-produced plasma kinetics are given in [117].

On the other hand, recombination processes can counterbalance the electron generation by EI and PI thus reducing the charged particles number densities in the plasma. The rate of recombination can be estimated by considering the relaxation times of Three-Body Recombination (TBR) and Photo-Recombination (PHR) Processes [113], respectively, given by:

$$\tau_{TBR} \approx 1.1 \times 10^{26} Z^{-3} T_e^{\frac{9}{2}} N_e^{-2} \quad \text{and} \quad \tau_{PHR} \approx 3.7 \times 10^{12} Z^{-2} T_e^{\frac{3}{4}} N_e^{-1} \quad (2.12)$$

T_e is given in eV while N_e is in cm^{-3} . For plasma electron density in the range (10^{18} – 10^{20}cm^{-3}) and electron temperature of several eV, τ_{TBR} is comparable to the excitation and ionisation time constants, influencing significantly the laser plasma dynamics during the laser pulse, whereas τ_{PHR} is much longer than the laser pulse

in typical experimental conditions [81]. As the plume expands out, τ_{TBR} becomes so long that the degree of ionisation of the plume remains practically ‘unchanged’. This state of the plume is typically observed at distances of a few cm from the target by charge collection techniques, whereas at larger distances and times photo-recombination takes place, producing a further partial re-equilibration in the expanding plume [131].

The effective degree of ionisation of the laser-produced plasma results from the balance between all the ionisation and recombination mechanisms discussed above. These, in turn, depend on the vapour temperature, which is governed by the energy electron transfer to massive particles by collisions. In particular, for a degree of ionisation larger than 5×10^{-3} , the heat transfer relaxation time τ_{HT} is determined by electron-ion collisions, and can be approximated by [113]:

$$\tau_{\text{HT}} \approx 3 \times 10^8 \Lambda T_e^{\frac{3}{2}} / Z^2 N_e \ln \Lambda \quad (2.13)$$

where Λ is a plasma parameter given by $\Lambda = 1.55 \times 10^{10} T_e^{\frac{3}{2}} N_e^{-\frac{1}{2}}$ if T_e is in eV and N_e in cm^{-3} . With $N_e \approx 10^{18} - 10^{20}$ and $T_e = 1 - 5 \text{ eV}$, the relaxation time τ_{HT} is almost always less than 1ns, and the electron and heavy particles temperatures can be assumed to be approximately equal.

Experimental studies involving ablation of metallic targets with visible and UV laser light have shown that under moderate irradiation intensities ($10^8 - 10^{10} \text{ W.cm}^{-2}$), the laser-produced plasma has elevated electron temperatures [132-135] and a degree of ionisation of 1-10% after electron-ion recombination. A higher ionisation fraction is present in the plasma before recombination processes take place. Moreover, the effectiveness of the PI absorption mechanism in UV laser ablation of metals and the PI of excited atoms in nanosecond pulse UV and visible laser ablation of metallic targets has been clearly demonstrated [103, 124-126].

2.4.2 Plasma expansion

A number of studies have been devoted to the problem of a gas cloud created by transient evaporation from a solid surface. These include both numerical simulation (Monte Carlo simulations) studies [136-139] and analytical approaches [91, 140] with the common agreement that, during laser ablation of solid targets in vacuum, low laser intensities and very low material vaporisation rates typically result in the formation of a collisionless low-density vapour in front of the target surface.

The emitted materials move towards the substrate according to the laws of gas-dynamic and show the forward peaking phenomenon [141]. In such a case, the angular and velocity distributions of the expanding vapour atoms are described by a thermal $\cos\beta$ law, β being the angle with respect to the normal of the target surface [142]. The theory agrees quite well with Singh experiments [73]. He reported that the thickness of the deposited layer vary as a function of $\cos^n \beta$, where $n \gg 1$ and β being the angle with respect to the normal of the target surface.

As the laser intensity increases, the vapour density rises and collisions occur in a zone near the surface. The fast and strong heating of the target surface by the intense laser beam (temperatures of 5000K or more within a few ns, corresponding to a heating rate of about 10^{12} K/s) ensures that all target components evaporate at the same time. When the ablation rate is sufficiently high (at laser fluences well above the ablation threshold), a so-called Knudsen layer is formed [73] above the target surface and further heated forming a high-temperature plasma [121], which then adiabatically expands in a direction perpendicular to the target surface.

The formation of the Knudsen layer transforms the half-Maxwellian velocity distribution function of the nascent atoms into a full-range Maxwellian with a centre of-mass velocity in the direction perpendicular to the target surface [91, 140, 143]. The target-substrate distance is an important parameter that governs the

angular spread of the ablated materials. Hanabusa [144] also found that a mask placed close to the substrate could reduce the spreading.

2.4.3 Hydrodynamic models

This model was introduced by Vertes et al. [122] in 1989 and has been investigated by many authors [73,139, 145-153]. The formation of a Knudsen layer, in which the half-Maxwellian velocity distribution of the particles at the surface is transformed into an equilibrium thermal distribution, is considered. For a sufficiently high material yield, the flow is found to evolve into an unsteady adiabatic expansion. This alternative approach considers the solutions of the hydrodynamic equations for an unsteady adiabatic expansion with the correct boundary conditions.

Since it was found that the necessary number of collisions is surprisingly low (3-5 collisions per particle for equilibration) [146], it is appropriate to follow this approach for all cases where quantities of more than one monolayer vaporise on a time scale of tens of nanoseconds. Both numerical solutions of hydrodynamic equations and experimental findings show that the velocity distribution of particles formed as a result of collisions in laser-generated plumes can be well described by the so-called elliptical velocity distribution which in spherical coordinates in the velocity space (v, β, φ) is given by [81, 113]:

$$f(v, \beta, \varphi) \propto v^2 \exp \left[-\frac{mv^2 \sin^2 \beta}{2\kappa_B T_{xy}} - \frac{m(v \cos \beta - u_{CM})^2}{2\kappa_B T_z} \right] \quad (2.14)$$

where,

$$T_{xy}^{-1} = \frac{\sin^2 \varphi}{T_x} + \frac{\cos^2 \varphi}{T_y} \quad (2.15)$$

In Eqs. (2.14) and (2.15), m is the particle mass, κ_B the Boltzmann's constant, u_{CM} the macroscopic drift velocity of the gas cloud, and $T_z(T_{xy})$ the kinetic temperature in the direction of the jet axis, (the target surface normal in a coordinate system flowing with velocity u_{CM}). The elliptical kinetic temperatures T_x , T_y and T_z are related to the variances of the velocity distributions along the x, y and z axes [147, 148].

In the hydrodynamic approach, the features of the vapour cloud expansion are related to the average temperature and dimension of the gas cloud at the end of the laser pulse. Moreover, results of the hydrodynamic approach show that an ellipsoidal vapour cloud goes faster along the axis that initially was shorter. This explains the experimentally observed apparent rotation of the laser-ablated particles cloud during its expansion [149, 150]. The theoretical predictions show that the angular distribution of the ejected particles can be approximated by:

$$Y(\beta) = A \cos^p(\beta) \quad (2.16)$$

where A is a constant depending on the laser fluence, and the exponent p depends on the aspect ratio of the plasma cloud. Many experimental data have been fitted to Eq (2.16), with good agreement for most of the IR, visible and UV laser-ablation experiments [81, 132, 150-152].

Geohegan [153] described the vapour expansion in the presence of an ambient gas by taking into consideration the shock waves and the viscosity force models. We note that Kools [154] predicted that a shock wave cannot be initiated in a gas having a pressure below 100Pa. Also, the model based on the introduction of viscosity force fails to provide an accurate description of the plume expansion, mainly because it does not take into account neither the inelastic collisions nor the eventual development of chemical reactions in the gas phase.

The physical phenomena involved in plasma expansion cannot adequately account for by the exclusive application of either of the two mentioned models under consideration (i.e. shock-wave propagation or viscosity force models). Neither a simple combination of the two models [155], is good enough to overcome these difficulties. Indeed, according to Kools [154], a shock wave can only be initiated during the initial one dimension (1D) plasma expansion phase, which contradicts the approach of Gonzola [155].

It could be therefore concluded that a more precise plasma jet modelling, under conditions characteristic of RPLAD experiments, requires the consideration of the local phenomena developing around the individual collisions processes. Monte Carlo simulations can best handle this analysis. The model can be applied to any gas combination. Information about the thickness and profile of the films deposited on different collectors can be obtained when working in a low-pressure chemically active gas [156, 157].

2.4.4 Monte Carlo Simulations

Monte Carlo (MC) simulations have been performed as an alternative approach to the problem of laser ablated particles expansion in vacuum. The simulations show that for a collision-free flux the angle dependence is only via $\cos(\beta)$. Eq (2.16) gives excellent fits of the flux distribution along the normal, as obtained in MC simulations [103]. MC simulation results also show that the values of the elliptical temperatures can be significantly different, depending on the initial gas cloud aspect ratio [153], as already observed in hydrodynamic models. Nevertheless, important features of the flow, such as the angular distribution and the mean energy per particle angular dependence are fairly well represented by the elliptical distribution of Eq (2.16).

The effect of the plasma contribution to pulsed laser-ablated particle expansion has been studied with direct MC simulations [133, 155]. Their results show that the distribution of both hot (corresponding to the ions) and cold particles (i.e. neutral) is strongly peaked in the forward direction, but angular and energy

distributions of ablated particles are strongly influenced by the presence of hot particles. Particularly, it is demonstrated that a delayed redistribution of internal energy transported by ionised and excited species can lead to the presence of the high kinetic particles observed experimentally [157].

Several other numerical studies have been performed on the modelling of the expansion of the ablated particles as well as the clusters condensation and nanoparticles formation in pulsed laser ablation in a background gas [137, 138, 155, 157- 161]. Other mechanisms involved plasma plume characterisation giving more details of the thin films properties. Optical spectroscopy and interferometry are suited for the analysis of the neutral and excited species in the plume. On the other hand, mass spectrometry is particularly useful for plume composition characterisation.

In particular, due to its peculiar capability of recording a complete mass spectrum at each laser shot, time-of-flight mass spectrometry allows one to follow plasma kinetics and to elucidate the reaction dynamics of the different species present in the plume. This is particularly useful in the case of ablation of complex materials and for thin-film deposition monitoring. These techniques provide a tool for elucidating the mechanism of energy coupling to the target and to the laser-produced plasma, and to investigate its dependence on laser parameters and processing environment. Full details and studies of such investigations are far beyond the scope of this research work

2.5 Deposition of the ablation materials, nucleation and growth of a thin film on the substrate

After the evaporation process, the ejected high-energy species impinge on the substrate surface. These energetic species sputter some of the surface atoms and a collision region is formed between the incident flow and the sputtered atoms. Film grows after a thermalised region is formed. The region serves as a source for condensation of particles. When the condensation rate is higher than the rate of particles removed by the sputtering, thermal equilibrium condition can be reached

quickly. Nucleation growth and thin films quality are dependent on fundamental parameters such as the energy density, ionisation degree, the deposition rate, as well as the substrate temperature [14]. Background gas, laser spot size and plasma temperature have significant effects on the deposited film uniformity and can thus be included as a fundamental parameter. The importance of some of these parameters will be discussed in the following sections.

2.5.1 Substrate temperature

The substrate temperature is a highly important process parameter influencing the film morphology and structural properties. In the initial stages of the film growth, the particle flux deposited on the substrate might re-evaporate from the surface, nucleate into a cluster, be consumed by the existing clusters or be trapped onto a surface defect site. These enumerated processes are dependent upon mobility of the deposited atoms on the surface and their activation energies. Such surface rearrangements are possible at higher temperatures, while at low temperature they might be inhibited. For the large nuclei, a characteristic of small supersaturation, island (Volmer-Weber) growth results in the formation of isolated islands on the surface, which subsequently grow and coalesce together.

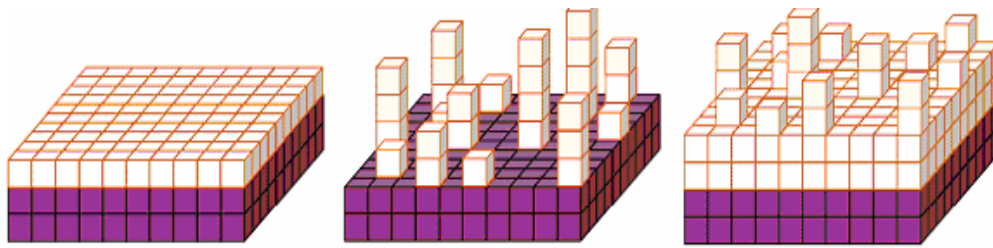


Figure 2.3 Different growth modes in thin film deposition, (a) Frank - van der Merwe growth, (b) Volmer-Weber growth and (c) mixed layer plus island growth.

This occurs when the cohesive energy of the atoms within the film is greater than that between the film and atoms on the surface. As the supersaturation increases, the critical nucleus shrinks until its height reaches on atomic diameter and its

shape is that of a two-dimensional layer. The nucleation process depends on the interfacial energies between the substrate, the condensing material and the vapour. The minimum-energy shape of a nucleus is like a cap. The critical size of the nucleus depends on the driving force, i.e. the deposition rate and the substrate temperature.

Three modes of initial film growth [160] can be distinguished as can be illustrated in Fig.2.3. For large supersaturation, the layer-by-layer (Frank-van der Merwe) nucleation will happen for incompletely wetted foreign substrate. The growth involves a deposition of one monolayer at the time and results in a very smooth epitaxial film. It occurs when the cohesive energy between the film and the surface atoms is greater than the cohesive energy of the film atoms. The cohesive energy will decrease monotonically as each film layer is added.

Mixed growth involves growth of islands after the first monolayer has formed successfully. In general growth at 0 K is characterised as a Volmer-Weber growth, while film growth at higher temperatures follows the Frank-van der Merwe growth model [161]. The substrate temperature can also have a profound influence on the film thickening [162]. The closer the temperature of the substrate to the melting temperature (T_m) of the film, the more film relaxation channels are energetically accessible. At lower substrate temperatures ($< 0.2T_m$), film growth proceeds via an athermal process, enabling metastable structures formation.

Clearly, the microstructural morphology of the film is highly dependent on the growth temperature. Indeed, the temperature can be used as a process parameter to induce different structures. Metastable structures are grown preferentially at lower substrate temperatures, while the growth of crystalline materials will require higher ($> 0.3T_m$) substrate temperatures to induce reconstruction and surface relaxation. The crystalline film growth depends on the surface mobility of the adatom (vapour atoms). The adatom diffuses through several atomic distances before sticking to a stable position within the newly formed film. The surface temperature of the substrate determines the adatom's surface diffusion ability.

High temperature favours rapid and defect free crystal growth, whereas low temperature or large supersaturation crystal growth may be overwhelmed by energetic particle impingement, resulting in disorder or even amorphous structures.

2.5.2 Energy of the deposition flux

Growing films from species impinging at higher kinetic energies generally improves the film quality; this fact has been first recognised by Mattox [163]. The effects of high kinetic energy ion bombardment of the substrate include ballistic collisions, ion mixing and thermally stimulated exchange mixing. These effects produce similar effects to raising the substrate temperature and govern film properties like the film stress and crystal structure. The effects of a high kinetic energy deposition flux have been investigated via MD simulations of Ag deposition on Ag at 300 K, as a function of incident particle kinetic energy [164].

The calculation showed that the film grows in islands at low kinetic energies ($<10\text{eV}$), but that layer-by-layer growth dominates at higher kinetic energies. Ion mixing was also noticeable at higher kinetic energies. Some of the substrate atoms are located in the film and vice versa. This effect scales with impact energy and is associated with vibrational relaxation of the interface. The above mechanism is distinctly different from ion mixing during high-energy ion bombardment in which the ballistic collisions induce direct displacements of substrate atoms. Assuming that the surface displacement energy sets a window for the ‘ideal’ deposition conditions, surface modification considered beneficial for film growth is allowed, while bulk displacement and ion mixing are minimised. Such purely ballistic collision effects are also dependent on the substrate atom mass, and the mass of the incoming atoms. A detailed study of the influence of the different parameters has been reported by Brice et al [165].

A second mechanism, in which high incident kinetic energies are important but where energy plays a contrary role to temperature, is during the growth of metastable films. The mechanism describing such film growth is the sub-

plantation model [166], which finds extensive use in discussions of the growth of diamond like carbon (DLC) films. A deposition flux at lower energy induces to less compaction, while a deposition flux at higher energy gives rise to sputtering. In contrast, increased temperature would expect to induce thermodynamically favoured growth of the stable structure, i.e. graphite. A consequence of this high kinetic energy is a large degree of ion mixing during deposition of these films.

2.5.3 Deposition rate, vacuum quality and background gas

The rate at which material sticks on the surface (henceforth 'the deposition rate') is highly dependent on the material that is to be deposited and has to be considered on a case by case basis. Nevertheless, too high a deposition rate will cause film deterioration because of the reduced film relaxation. Too small a deposition rate, on the other hand, will result in unacceptably long deposition runs. The deposition rate is also correlated to the quality of the available vacuum, since high deposition rates tend to put fewer demands on the vacuum quality. The lower the deposition rate, the more chance the film will incorporate unwanted gaseous impurities.

When depositing films from multi-component targets, the introduction of background gas can enable the production of the multi-component film from a mono-component target and the background gas. Chemical reactions which might aid in the deposition can also arise as a result of introducing background gas. However, introduction of a background gas is not universally advantageous to all deposition techniques. If the deposition flux does not have high kinetic energy and directionality it will be scattered by background gas collisions. In such cases the deposited film thickness drops precipitously as either the source-substrate distance or the pressure is increased.

In the PLAD process, due to the short laser pulse duration ($\sim 10\text{ns}$) and hence the small temporal spread ($\leq 10\text{ns}$) of the ablated materials, the deposition rate can be enormous ($\sim 10\text{mm/s}$). Consequently, a layer-by-layer nucleation is favored and ultra-thin and smooth film can be produced. In addition, the rapid deposition of

the energetic ablation species helps to raise the substrate surface temperature. In this respect, PLAD tends to demand lower substrate temperature for crystalline film growth. For this reason, the semiconductor and integrated circuit can refrain from thermal degradation.

2.6 Advantages and drawbacks of the PLAD and RPLAD techniques

2.6.1 Advantages

It has been shown that PLAD is an extremely versatile technique for preparing a wide range of thin films and multi-layered structures for any kind of materials by using appropriate lasers parameters. The PLAD and reactive PLAD techniques have been successfully employed in the last 15 years to deposit high quality thin films. The advantages of this technique over conventional film growth methods are:

- the non-equilibrium evaporation process produces an intense plasma and transfers the composition of the sputtered target on the film;
- the cleanliness of the method and the use of small target;
- the high control on the growth rate by adjusting the laser fluence;
- the precise control of thickness;
- the possibility of in-situ processing of multilayer hetero-structures by using a multiple target carousel;
- the possibility to use non toxic gases as the reactive atmosphere during the growth;
- the cost advantage over many other vacuum techniques; it costs 10 times less than Molecular Beam Epitaxy (MBE) system but is capable of producing similar high quality films.

Additionally, laser ablation may be used as a low temperature thin film process because the energy of the species in the laser induced plasma plume is considerably high, which makes it possible to grow crystalline films at a low substrate temperature. With these techniques, great varieties of compounds have

been deposited. It is generally easier to obtain the desired film stoichiometry for multi elements material using PLAD than with other deposition technologies.

PLAD as a method to synthesise thin layers [14, 103, 167] presents the following advantages:

- high uniformity and adherence of deposited structures
- low impurity concentration in deposited structures
- possibility to use any material as substrate
- coating of materials at room temperature with excellent adhesion strength due to the high ionised vapour ablated from the target
- high potential for producing rough surfaces films.

This process has been widely acclaimed not only for its efficiency, but even more importantly for the uniformity of film depth and the high quality of the samples produced. The technique has many advantages because the reactive conditions can be controlled easily by adjusting the gas partial pressure and the substrate temperature or other laser parameters. PLAD is now recognised as one of the most promising techniques for in-situ preparation of thin films. These peculiarities are very interesting, compared to those of other deposition techniques. However, there are also some intrinsic limitations, which prevent PLAD and RPLAD from emerging as a technology for industrial applications.

2.6.2 Drawbacks

The main shortcoming for the applications in technological fields of the thin films synthesised and deposited by PLAD/RPLAD is related to the presence of various types of particulates, both on the surface of the films as well as embedded into the bulk. For the technological applications, particulate-free, smooth surfaces are required. The micrometer and sub-micrometer sized particulates present on the surfaces of thin films can be:

- droplets, expelled in liquid phase from the target surface
- irregular shaped solid target material fragments

- clusters, which condensate during the transit of the ablated material from the target to the collector surface [10, 14, 81, 160, 168].

The origin of these particulates may be attributed to different processes, such as:

- explosive dislocation of the substance caused by the subsurface boiling of the target
- gas phase condensation (clustering) of the ablated substance
- liquid phase expulsion, under the action of the laser generated plasma recoil pressure
- blast-wave explosion at the liquid-solid interface, and/or hydrodynamic instabilities evolving across the molten target's surface (Kelvin-Helholtz, Rayleigh-Taylor, capillary waves).

Several techniques have been applied for eliminating the particles formation. These include incorporation in the PLAD apparatus of an eclipse, the use of the second laser pulse to vaporise particulate in the laser-induced plasma heating, the application of polarised electrodes and special geometric configurations... However, in most cases, the deposition efficiency is decreased significantly. Formation mechanisms of most of these particulates imply the presence of liquid/molten material inside craters. These later are formed on targets under the action of micro- or nanosecond multipulse laser irradiation [167, 169].

Implementation of PLAD by using picosecond or sub-picosecond laser has been predicted to be more precise and expected to lead to a better morphology, in comparison to experiments performed with nanosecond laser pulses [110, 170-172]. Material processing by ultrafast lasers may give rise to several advantages, such as:

- lower energy exposure (lower ablation threshold)
- possibility of lower temperature thin film growth (ejection of directional energetic particles in ablation), and more importantly
- reduction of undesirable thermal and photochemical effects due to the minimisation of energy diffusion.

Clean ablation of solid targets is achieved without the evidence of the molten phase, due to the insignificant thermal conduction inside the irradiated material during the sub-ps and fs laser pulse action. Accordingly, ablation with sub-ps laser pulses is expected to produce much smoother film surfaces than those obtained by ns laser pulses [84].

2.7 Conclusion

Pulsed laser ablation deposition has raised enormous interest in the last few years, as demonstrated by the large number of experimental and theoretical studies carried out on the subject. In fact, it provides a powerful and flexible tool in a wide class of research applications spanning from material science to the field of medicine. For example, thin films of almost all materials grown by PLAD present unique properties. The stoichiometry transfer between target and substrate and the possibility of working in UHV as well as in different reactive and inert gas atmospheres are particularly attractive features of PLAD.

At the same time, many studies also indicate the importance of an accurate knowledge of the various physical processes involved in the phenomenon as well as the in situ monitoring of the process itself. This is accomplished by using various experimental techniques typically employed in atomic and molecular physics, as well as in plasma physics. In this chapter, the equipment involved in the process of PLAD has been reviewed. It was seen that using a reactive gas atmosphere makes this method versatile. The possibility of additionally changing laser features, such as wavelength, repetition rate, pulse length, fluence and target-substrate distance, and the deposition conditions, such as substrate temperature and substrate orientation with respect to the deposited material, further demonstrates the enormous versatility of PLAD.

The numerical, theoretical models and experimental techniques employed in the analysis of the laser-ablation process, as well as its basic microscopic mechanisms were also reviewed. A brief survey of relevant experimental results obtained on the topic over the last 15 years has also been presented. Both the basic physics of

the laser-solid interaction and the experimental results show that short laser pulses offer the advantage of removing material from the target surface without a significant transfer of energy to the surrounding areas.

On the other hand, when nanosecond laser pulses are used, ablation occurs from both the melt and vapour phases and a considerable amount of material can be removed in a single shot. In this case, heat conduction into the solid target is the main source of energy loss. Moreover, the effectiveness of the ablation process and the properties of the emitted particles flux are largely influenced by the generation of plasma, occurring even at low laser fluence. Finally, the theoretical and experimental analyses reviewed in this chapter also demonstrate how the peculiarity of laser evaporation and ablation processes leads to the development of very promising correlated studies and techniques.