Pulsed laser deposition - today and tomorrow

S.M. Kaczmarek

Institute of Optoelectronics, Military University of Technology, 2 Kaliski Str., 01-489 Warsaw, Poland

ABSTRACT

An analysis of actual state of a view about pulsed laser deposition method, its applications and perspectives and also physical phenomena during laser deposition processing were presented.

Keywords: pulsed laser deposition processing, vaporization, ablation, thin-film and multilayer growth, precipitates, particulates, cuprate superconductor substrates.
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1. INTRODUCTION

Pulsed laser deposition (PLD) has been regarded as a versatile method to grow ceramic thin films such as cuprate superconductor films[1, 2], semiconductor films[3] and ferroelectric films[4]. In case of high-T_c superconducting films, excellent electrical properties such as a high T_c and J_c, low microwave surface resistance and good crystallinity have been reported[1]. Most often $YBa_2Cu_3O_{7-\delta}$ superconducting films (YBCO) are deposited with this method. Also $BaTiO_3$ and $SrTiO_3$ films are obtained. They are used as pyroelectric detectors, thin film capacitors, nonvolatile memory, displays, surface-acoustic wave devices, and electro-optic devices due to their ferroelectricity, high dielectric constant and large electro-optic coefficients. Recently, strong second harmonic generation from poled $BaTiO_3$ thin films has also been reported [5]. It has also been shown that $BaTiO_3$ works as an excellent buffer layer for YBCO high-T_c superconductor on various substrates, in particular Si and Al_2O_3 [6]. Since MgO has a lower index of refraction than $BaTiO_3$ (small optical loss), $BaTiO_3$/MgO structure is favorable for use in waveguide applications. Moreover, MgO has previously been deposited on both Si and GaAs substrates[7]. The use of MgO as a buffer layer reduces problems related to interdiffusion and oxidation which are prevalent for these semiconductor substrates. Large quadratic electro-optic effect from high quality pulsed laser deposited $BaTiO_3$ thin films on (001) MgO substrates was observed in [8].

2. EXPERIMENTAL EQUIPMENT

Conventional arrangement for PLD for the synthesis of thin solid films is characterised by the following features:

1. A focused laser beam is directed at the target surface to induce material ablation. For example, quartz lens of 500 mm focal length focuses the beam to a spot of roughly 1×1 mm^2 leading to fluences from 0.5 to 10 J cm^{-2} and intensities from 25 to 500 MW cm^{-2}.
2. A planar target is rotated or (x, y) - scanned in the focal plane of the laser beam to achieve a stationary ablation rate. Carousel with the target can rotate at a speed up to 600 rpm with a positioning accuracy of 0.36^o. Target is placed in a stainless steel vacuum chamber and fixed on a cooper target holder. Chamber is evacuated down to 10^{-6} mbar with the aid of a turbomolecular pump. During laser irradiation of e.g. Ti target, the chamber is filled with nitrogen at pressures typically between 10^{-3} and 1 mbar.
3. A planar substrate located at a typical separation from the target is held stationary or is rotated for homogenization of the deposition rate; for particular film growth regimes the temperature of the substrate may be selected between room temperature and typically 1000 ^{o}C,
4. A processing gas supply is often provided for the inlet of selected gases to produce desired chemical reactions during film growth.

Thin films and multilayers can be prepared using different types of lasers. The working parameters typically applied are given in Table 1.

Conventional experimental setup for PLD method is presented in Fig. 1. For example an ArF excimer laser at a wavelength 193 nm, focused onto a sintered $BaTiO_3$ target with a fluence of 1.5 J cm^{-2} at various repetition rates (2-20 Hz) is used for evaporation. The distance between the target and the substrates is fixed at about 6 cm. While actual depositions are performed in an ambient pressure of 140 mTor of oxygen, the deposition chamber is pumped to $<10^{-5}$ Tor prior to the

Table 1. Typical parameters of lasers applied in PLD method

Laser type[Ref]	Wavelength [nm]	Pulse energy [J]	Pulse repetition [Hz]	Pulse length [μs]
CO_2:TEA[11]	10600	7.0	10	2-3
Nd:YAG[11]	1064	1.0	20	$(7\text{-}9)\times10^{-3}$
2nd harmonics[11]	532	0.5	20	$(5\text{-}7)\times10^{-3}$
3rd harmonics[11]	355	0.24	20	$(4\text{-}6)\times10^{-3}$
XeCl - excimer[10]	308	2.3	20	40×10^{-3}
ArF - excimer[9, 10]	193	1	50	$(1\text{-}4)\times10^{-2}$
KrF - excimer[14]	248	1	50	$(1\text{-}4)\times10^{-2}$

deposition. The substrate temperature (e.g. in case of (001) MgO substrate) is maintained at constant temperature 720°C. The deposition rate is equal to about ~0.08 Å/pulse. For preparation of high-quality films, i.e. specimens of good physical perfection and high chemical purity, not only the film morfology but also the film composition has to be optimized. Thus, for deposition rates of the order of 0.1 mm s^{-1}, which is equivalent to the condensation of typically 3×10^{14} atoms cm^{-2} s^{-1}, if the residual gas contribution is to remain distinctly below 0.1%, a base pressure of typically $p\approx10^{-10}$ mbar has to be guaranted.

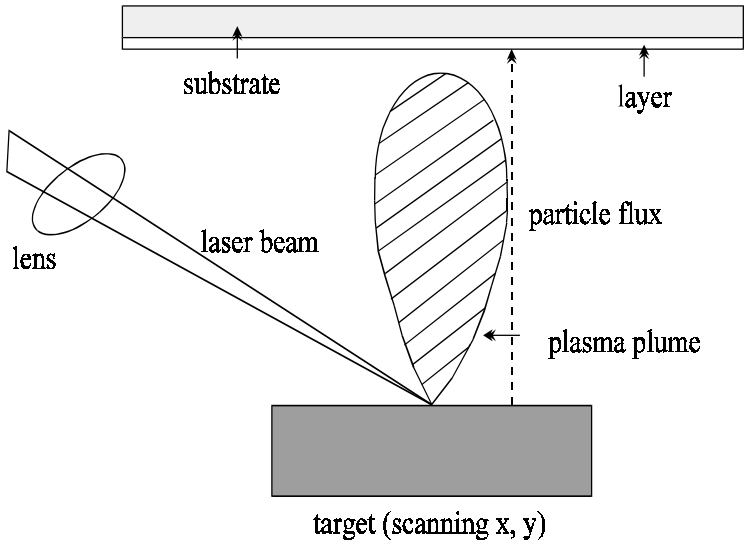

Fig. 1 Conventional experimental setup used in PLD method [11].

Epitaxial thin films with smooth surfaces are necessary for optical waveguide electro-optic devices, due to the requirement of low propagation loss. It was found[8] that laser deposition rate plays an important role on the surface morfology of the deposited films. Despite local flatness, particulate formation has been observed in some films such as YBCO. Although its origin is complicated and has not yet been fully understood, it is a generally accepted view that particulate formation is affected by the target material, the target surface morfology, the target density, and the laser power density. Two kinds of particles in laser deposited films have been reported: particulates, boulders, or droplets which usually have rounded shapes and the same composition as the film matrix, precipitates or outgrowths which have a composition different from the film matrix[9].

Whether particulates or precipitates are the dominant particles on the film depends on the deposition conditions. The particulates are observed to reduce at a low laser power density, e.g., ~1 J cm^{-2} for YBCO. However, the use of such a low laser densities usually degrades the film stoichiometry, resulting in growth of precipitates or in surface roughness at temperatures which are suitable to obtain good crystallographic and electrical properties. Such precipitates were observed to reduce when lowering the substrate temperature (T_s), which causes a slight degradation of the electrical and crystallograpgic proprties. Indeed, there seems to be a trade-off among the particulate density, the precipitate density, and the electrical and crystallographic properties for a given target material. The success of optimization is material dependent.

In case of YBCO, it was difficult to reproducibly reduce the particulate density below one per 0.01 mm^2. Contrarily, particulate densities of $(La, Sr)_2CuO_4$ and $BaTiO_3$ films reduced easily and reproducibly well below one per 0.01 mm^2 without degrading their electrical properties. These differences are probably due to difference in the optimum laser density range, where exact stoichiometry and suppression of particulates can be obtained. Since the film stoichiometry is generally known to degrade as the laser density decreases, we need to know the maximum laser density at which the particulate formation is still suppressed[9].

It was stated, that major factor that determines particulates formation is normalized deposition rate, defined as a ratio of the laser density to the material-specific ablation threshold. The results of [9] suggest an approach to eliminate the particulate: namely, the use of a metal or alloy target consisting of metals having a similar T_m (melting temperature) to void the segregation and the decomposition due to gas-element reduction, and use of a low normalized deposition rate to suppress the growth of morphological irregularities on the target surface. Previous studies showed, however, compositional change of target surface over time when laser irradiated at a low laser power density, so that particulates could be suppressed. Simple control of the film composition is achieved only in a narrow range of gas pressure, target-substrate distance and laser power density.

Authors of [10] proposed new method: a rapid sequential pulsed laser deposition (RSPLD). This is a method of pulsed laser codeposition using many targets, multiple pulse lasers and multibeam path by using beam splitters in a single pulse laser system. For deposition of YBCO film they used Ba and YCu_3 or BaCu and YCu. Homogeneous YBCO was deposited onto 1 cm^2 of $SrTiO_3$ (100) and MgO (100) substrates for energy densities of about 0.2 J cm^{-2} for Ba target and about 1.5 J cm^{-2} for YCu_3 target, and the average deposition rate 10-20 Å/min. Fig.2. illustrates an idea of RSPLD method which enables fast deposition by using a scanning laser beam instead of a target holder carousel.

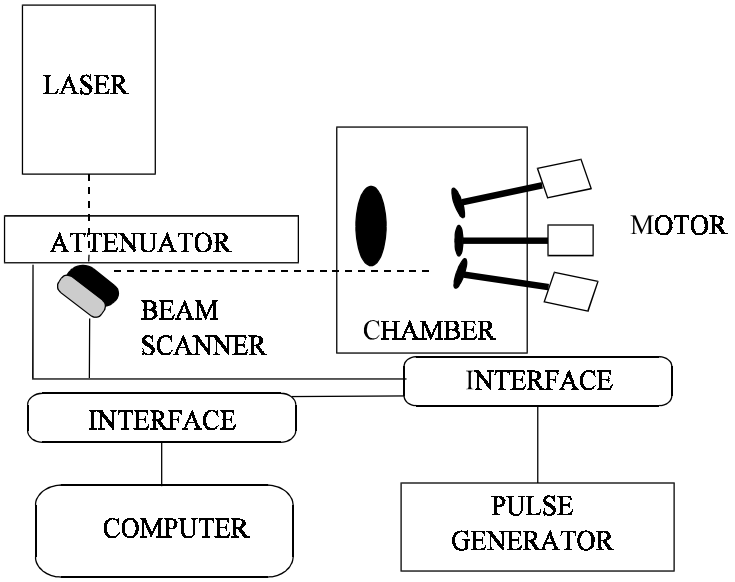

Fig. 2 Schematic diagram of RSPLD setup which enables fast deposition by using a scanning laser beam instead of a target holder carousel [10].

The application of particular techniques of physical vapour deposition of thin solid films (e.g. thermal and electron beam evaporation, Knudsen cell evaporation, ion beam coating, PLD) is often limited when the coating of large-size substrates is required. The conventional thin-film deposition equipment of PLD has been modified in[11] for the preparation of individual thin solid films and nanometer-layer stocks of uniform thickness across 100-mm substrates. The planar target configuration was replaced by a cylindrical one and the target motion regime has been improved to provide precise spatial control of the plasma plume orientation. During thin-film deposition, substrate translation is preferred instead of the usual rotation technique. With this arrangement the emission characteristic of the plasma can be computer controlled and the desired coating can be tailored via a stepper-motor-driven manipulator for the desired layer thicknesss profile across an extended substrate.

Fig.3. illustrates changes in PLD method proposed in[11].

The PLD process appears to be an interesting way for the fabrication of thin films of metal nitrides that have a large field of applications. Especially in mechanics and microelectronics due to their hardness, good conductivity, and chemical stability. Typically, laser density applied in PLD processing of e.g. titanium nitride, varies in the range 25-500 $MWcm^{-2}$ [12].

In [13] authors presented results of pulsed laser sputtering of gold with the use of KrF laser providing radiation at 248 nm with 16 ns FWHM pulse duration and surface fluence of ~1.0 J cm^{-2}. Optimization and control of the PLD process requires the understanding of the vaporisation and plasma buildup process. The plasma plays a key role, since it determines the formation of reactive species and high-energy ions.

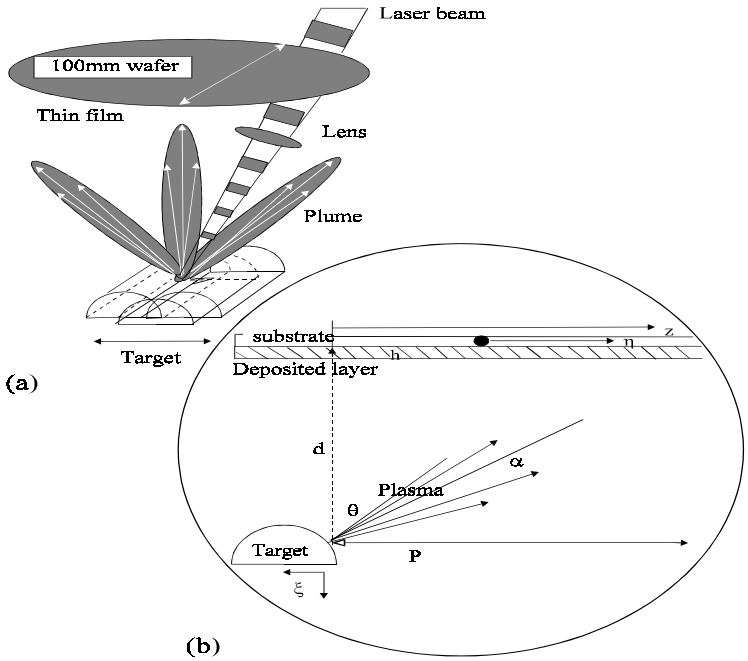

Fig. 3. a). Schematic diagram of PLD target-substrate handling with plume direction control, b). Parameters for process modelling [11].

Experimental studies show that pulsed laser evaporation of metal or semiconductor targets with intensities well above the vaporisation threshold is generally accompanied by plasma formation. Mechanism of this plasma ignition is not yet understood, especially for short wavelength UV lasers. Contrary to infrared lasers (CO_2) the energy coupling to the metal target is much higher. As a consequence, the surface temperature reaches much higher values in the case of UV excimer laser and the ablated material quantity is several orders of magnitude higher than that obtained with a pulsed CO_2 laser beam.

3. DESCRIPTION OF PHYSICAL PHENOMENA DURING PLD PROCESSING

Minimum laser intensity necessary for bulk material evaporation one can compute from equation (1). It is valid for short laser pulses for which the heat diffusion length $\delta_{th} = \sqrt{2\chi t}$ is small compared to the laser spot dimension on the target surface. For a laser pulse with a rectangular temporal shape of duration τ_{las} the vaporisation threshold is[15]:

$$I^*_{vap} = \frac{C_p \rho \sqrt{\pi \chi}\,(T_{vap} - T_0)}{2\,(1-R)\sqrt{\tau_{las}}} \tag{1}$$

where C_p, r and h are, respectively, the heat capacity, specific mass, and the thermal diffusivity of the target material, R - reflectivity of target surface, T_{vap} - vaporization temperature and T_o - ambient temperature. In the case of irradiation of titanium by a XeCl excimer laser, for 20 ns pulse duration, we have: $I^*_{vap} \cong 23$ MW cm^{-2} [12].

To get high quality thin layers, one has to avoid particle formation. Two main cases for particle formation during laser evaporation are the breakaway of surface defects under thermal shock and splashing of liquid material due to superheating of subsurface layers. The last phenomenon appears for fast heating rates. To avoid superheating, the laser intensity must be lower than that needed to evaporate a mass volume of depth $\delta_{th}/2$. This gives an upper limit for laser intensity to be applied in a PLD process. The superheating threshold is given by [12]:

$$I^*_{th} = \frac{\rho \Delta H_{vap}}{\alpha t_r} \tag{2}$$

where α - the absorption coefficient, t_r - the relaxation time of hot electrons on the surface, ΔH_{vap} - the enthalpy change per mass unit including latent heat for fusion and vaporisation and heating from ambient temperature to the vaporization point. In the case of titanium exposed to 308 nm radiation the superheating threshold is equal to about 500 MW cm^{-2} (10 J cm^{-2}).

For laser intensities slightly lower than the vaporization threshold, very low material sputtering rates in vacuum result in a collisionless low density vapor in front of the target surface. Evaporation appears to be a thermal process. When the laser intensity increases (a range near 50 MW cm^{-2} for titanium target exposed to 308 nm radiation), the vapor density rises and collisions occur in a zone onto the surface. This is so-colled Knudsen layer. Increasing the laser intensity leads to an increase of atom density and temperature in the Knudsen layer. The ionization degree rises. When increasing the laser intensity above

the plasma ignition threshold, a fully ionized vapor plasma can be identified. Highly ionized plasma for Ti target and 308 nm radiation was observed at $I_{las} \geq 100$ MW cm^{-2} [12].

It seems, that the plasma state is reached by thermal ionization. Heating of electrons by inverse Bremsstrahlung is not necessary for plasma ignition (contrary to CO_2 lasers); neverthelless, it contributes to further plasma heating and high-density plasma formation.

Laser heating of metals can be modelled by three basic processes: the deposition of radiation energy on free electrons, the energy exchange between electrons and lattice, and the propagation of energy through media by free electron motion[16] . In the course of high power laser heating, where the metal is looked upon as a two-temperature system, the free electrons are heated to an effective temperature much higher than that of the lattice. As the result, large local temperature differences arise between the electrons and lattice. Subsequently, the transport of energy from the electrons to the lattice takes place by means of a relaxation mechanism and a heat transfer coupling coefficient between electron and phonon subsystem is considered [17].

4. CONCLUSIONS

Advantages of PLD method over other deposition techniques such as molecular beam epitaxy and metallorganic vapor phase epitaxy include the unique process of source material transfer which limits the amount of heated material virtually only to that which is liberated; its pulsed nature, which affords high controllability of the deposition thickness, plus the potential of synchronizing the high flux/short duration pulses with pulsed reactive gas sources; the high kinetic energy of the ablation plume, which promotes surface mobility on the growing film; and the ease of source material replacement [18].

With respect to other processes such as chemical-vapour deposition or ion implantation, PLD allows for easy handling, since the laser source is placed outside the reaction chamber. Furthermore, the emission of energetic ions during laser-target-vapor interaction has an important influence on the layer formation, i.e., it enables growth of adherent and epitaxial films at lower substrate temperatures than other methods. This is especially important for the deposition on doped semiconductor materials for microelectronics, because heating can alter the depth composition and the physical properties of the crystals.

There appear to be, however, certain drawbacks associated with PLD. Foremost of these are the production of laser droplets, inhomogeneities of deposition rates resulting from the $\cos^n\Theta$ profile of the ablation plume ($2 \leq n \leq 6$); pulse-to-pulse fluctuations in the laser intensity; and possible nonstoichiometric material transfer of multi-elemental targets such as in the case of ceramic high-temperature superconductors. These problems arise not only from material specific properties, but also from technological limitations and an incomplete understanding of the control parameter space. This is defined, among others, the laser fluence, pulse duration, and wavelength [19], the laser pulse's spatial profile, the ablation target absorption properties, target geometry, and the erosion characteristics of the target material.

Laser intensities have reached 10^{19} Wcm^{-2} so far and are projected to reach 10^{24} Wcm^{-2}, which is 20 times larger than the radiation intensity at the surface of the sun. The laser pulse width also has decreased dramatically in the last few decades and has reached to 6 femtoseconds in duration.

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