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Review Paper

Thin Film Growth by Pulsed Laser Deposition

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Abstract: The application of Pulsed Laser Deposition (PLD) to grow advanced inorganic films and coatings is described. The underlying principles governing the laser–target interaction and subsequent removal of material from the irradiated surface, together with the current understanding of the controlling mechanisms, are briefly reviewed. Characteristic advantages and drawbacks of the technique are outlined, present results in thin film growth are reported and the prospects for future uses discussed. © 1996 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Considerable attention has been extended to the application of photons to initiate or enhance thin film growth and coating methodologies over the past decade.[1] Ceramic, dielectric, semiconducting, metallic and superconducting layers have been grown by a variety of processing modes involving laser- or lamp-assisted reactions. One technique currently attracting enormous interest is Pulsed Laser Deposition (PLD), particularly for multicomponent thin film growth. Although first reported in 1965,[2] significant attention in PLD only surfaced towards the late 1980s when it was repeatedly shown to be readily applied to forming thin films of layered cuprate superconductors. Some of the best quality and indeed most unique superconducting structures reported to date have been prepared by PLD.

The history and background of PLD will be briefly reviewed here. The numerous and unique advantages, as well as the few drawbacks associated with the technique, will be particularly highlighted. Emphasis on versatility will provide the main theme of the paper, by describing applications towards the growth of buffer interface layers, as well as active and passive coatings. Finally, the future potential for PLD applications will be summarised.

2 BACKGROUND AND THEORY

PLD is a conceptually simple technique involving the collection, on a nearby substrate, of material ejected from a pulsed laser-irradiated target. It offers many attractions. Material transfer from target to substrate is congruent (i.e. stoichiometry is preserved). Atomic flux is easily regulated through geometric considerations and application of digital control of the laser radiation. Novel layers and multilayers may be readily grown by irradiation of consecutive targets of different materials. Additionally, it generally does not require an ultra-high vacuum environment and is relatively inexpensive to apply. Over the years a wide variety of descriptive terms have been associated with PLD. It has been referred to as laser evaporation,[2–6] laser assisted deposition and annealing (LADA),[7] laser flash evaporation,[8] laser assisted sputtering,[9] laser MBE,[10] hydrodynamic sputtering,[11] laser ablation,[12–14] laser ablation deposition (LAD)[15] and laser evaporation deposition (LED).[16] Figure 1 gives a schematic representation of a typical PLD set-up for film growth.

To make the process as efficient as possible, such that energy is not lost due to carrier or thermal diffusion during absorption, short laser pulses should be used at a wavelength strongly absorbed by the target material. Lasers operable in the Q-switched mode, therefore, the Nd:YAG (1.064 mm, 532 nm, 355 nm, 266 nm), ruby (694 nm), and excimers (XeCl at 308 nm, KrF at 248 nm, and ArF at 193 nm), can deposit large amounts of energy efficiently into a thin surface region of the target. With the recent improvements in performance, e.g. reliability, uniformity and stability, the excimer and Nd:YAG lasers have been particularly widely used in PLD. The typical beam fluences involved in PLD are quite close to those required to heat the target materials well beyond their

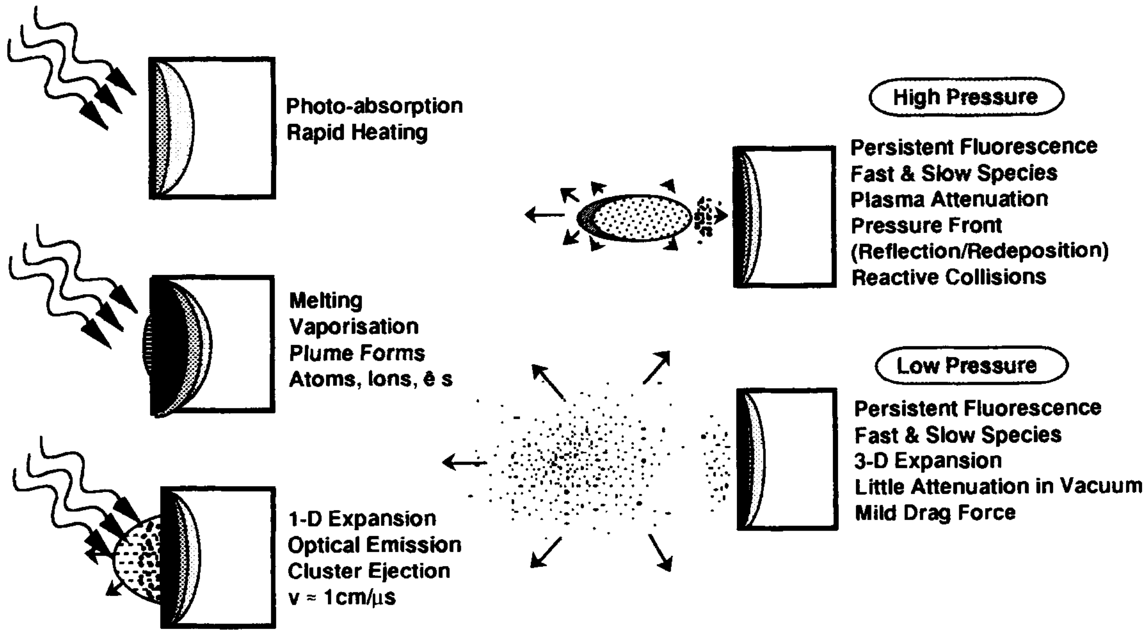

Fig. 1. (Left) Summary of absorption and ejection processes and (right) pressure effects of PLD.

melting temperatures and initiate significant evaporation. Material ejection is accompanied by an easily recognisable snapping sound as the velocity of some of the species exceeds the speed of sound in the immediate environment, as a bright-coloured plasma (or plume) of emitted particles is formed just above the target surface. Although a very large number of thin films have been produced by PLD, it is the multi-component systems that can benefit from this technique, such as the new families of high temperature superconductors and various ferroelectric, magnetic and sensor layers.

The underlying non-equilibrium mechanisms involved in this removal process are extremely difficult to model. Several recent papers have nevertheless addressed this complicated subject.[17,18] It is instructive to model the energy balance of the system as a conventional laser heating problem. By taking temperature averaged values of the usual optical and thermal constants one can obtain reasonable values of the fluences required to melt a range of materials. For example, for 248nm and 1064 nm light, these are calculated to be at least 70 mJ/cm^2 and 260 mJ/cm^2, respectively, for YBaCuO, and fluences of 140 and 560 mJ/cm^2 are found to be the minimum values to induce thermal removal,[19] in good agreement with the reported observations.[20–23] A more complete model clearly must take into account the non-linear behaviour of the optical and thermal properties with temperature, as well as the spatial and temporal extent of the beam but nonetheless these are already good estimates for the process.

Interactions between the photons and the ablated plasma must also be considered. For example, electrons present near the surface will strongly couple the electromagnetic radiation, accelerate and collide with any plasma ions or any nearby solid or gas phase atoms (inverse bremsstrahlung). The electron population can then be increased and excited further, causing extremely rapid cascade ionisation. The collective properties of the plasma can thus strongly determine what happens to the remainder of the incident light. The energy absorbed in the plasma will be rapidly shared amongst the individual particles, raising their kinetic energy, i.e. temperature, and shielding the surface from further exposure to the laser beam. If the optical absorption of the plasma falls, its increased transparency will enable further surface exposure to re-populate the plasma and again increase absorption and surface shielding. Thus, it could be deduced[24] that an instantaneous equilibrium plasma density, once formed, would try to self-regulate against any changes in density, temperature or irradiance. The plasma temperature can be as much as 20,000 K, whilst the surface temperature of the underlying solid will only reach a modest amount above the evaporation point ($\sim$2000–3000 K). Clearly, the mechanisms by which material leaves the surface, and their subsequent interactions and behaviour, are much more complex than can be predicted using thermal evaporation.

For laser ablation using visible or UV wavelengths it has been shown[25] that within a cone of acceptance the angle of incidence of the incident laser beam does not affect the trajectory of the ejected material, which is virtually always perpendicular to the irradiated surface. The spatial density of the plume is affected by many factors, the most important of which include beam fluence and spot-size, and ambient gas content and pressure. Analysis of the deposits obtained by short wavelength laser ablation often reveals two components to the thickness contour.[25,26] The expected broad cos ϕ profile due to thermal evaporation is usually present, but superimposed upon this is a highly peaked deposit whose profile can be fitted by a $\cos^n \phi$ curve, where $4 < n < 15$ (depending especially upon gas pressure), is superimposed.[19,26–28] For shorter wavelengths at fluences near the threshold for material removal only the pure cos ϕ form is found, while a $\cos^{10}\phi$ deposition is found only at higher fluences.[25] The irradiation geometry can be altered to modify the deposited profile. One way, amongst many, to homogenise the deposit is to tilt the rotating target during ablation in order to "spray" the deposit across the substrate. An angle of wobble of about 30° can produce a uniform film over a few square centimetres.[29] Other tilting approaches can also be applied, and positioning the substrate edge-on inside the plume instead of directly perpendicular to it has also been shown to produce more homogeneous films. However, Rutherford back-scattering studies have shown that while the centres of the peaked areas grown by PLD are essentially stoichiometric, the outer edges (containing the cos ϕ component only) are not,[25] an observation which may limit some approaches to homogenisation.

The ablation mechanism, as well as the confinement of the ejectant, has been described in terms of hydrodynamic sputtering,[11] whilst the effects of shock waves, surface superheating, and sub-surface explosions[30–33] have also been proposed. Singh *et al.* [17,33] have modelled a plasma expanding isotropically into the vacuum and have been able to obtain similar atomic profiles to those mentioned above.

The most spectacular accompaniment to the ablation growth of films is the colourful plume that forms between target and substrate. It occupies a volume containing high densities of electrons, excited and ionised atoms, and molecular clusters, all moving at very high velocities away from the surface. Its formation and content are subject to intense investigation using, for example, Laser Ion Mass Spectroscopy[34] and optical emission spectroscopy.[35] The phenomena are reminiscent of dielectric breakdown, caused by the highly localised electric field strengths at the surface.

Many neutral species are also known to form, apparently more so when longer wavelength lasers are used (i.e. 1064 nm rather than 193 nm).[22] This is most likely due to the restricted variety of interactions available to the less energetic photons, thus eliminating, for example, the possibility of photoionisation of the species in the plasma. Electron impact ionisation or cascade ionisation will also be less and so generally the plasmas associated with the shorter wavelength ablation will be the most energetic and reactive. With CO_2 laser ablation, very efficient inverse bremsstrahlung photon-coupling can be achieved in the plasma. Particle velocities can thus be much higher than for 248 nm ablation,[36] though it is not clear why stoichiometric ablation can only be achieved at 10.6 μm for low and not high fluences.[37]

Because of the usual irradiation geometries used, the plasma, consisting of ions, electrons, atoms, neutrals, molecules, and clusters and particulates of varying sizes, will initially be thin and flat, spreading above the surface exposed to the laser beam. Soon after its formation and until the end of the laser pulse it can be considered isothermal, with temperatures exceeding 10^3 K ($\approx$7.5 eV). Immediately after irradiation, the amount of material augmenting the plasma will drop considerably. It will then expand preferentially away from the target, this being the direction of the greatest density gradients, into the surrounding gas or vacuum, accelerating the species to speeds approaching cm/μs (up to 10^3 times the usual velocities encountered during thermal evaporation). This expansion can push any existing gases away from the target, setting up a pressure wave. As the particles slow down and lose energy, they give rise to characteristic UV and visible emission patterns that can be studied *in situ*. Such spectroscopic studies have revealed the predominance of excited elemental and monoxide species, agreeing with the mass spectrometry results, although collisions within the plasma may lead to the formation of more intricate structures. Time-resolved photography has recently been applied to the expanding plume *in vacuo* and moderate pressures,[38] and evidence of particulate back-reflection leading to redeposition on the target at high pressures has been found.[39] Figure 1 summarises the general scheme of the ablation processes.

The explosive velocity distributions associated with the particles leaving the ablated surface have been measured directly using time-of-flight (TOF) measurements[40] to be about 2 km/s in 100 mTorr pressures,[40–42] while speeds up to 2×10^6 cm/s for particles some 7 cm away from the target have been measured using an ion probe.[41] The velocity distributions compare well with the formation of supersonic molecular beams in chemical studies, where the velocities can be described by:[14]

$$f(v) = Av^3 \exp(m(v - v_o)^2/2kT_S) \qquad (1)$$

A major problem that often arises during the application of PLD is the presence of particulates (from 100s of nm to 10s of μm in size) on the film surface. Many of these, known also as droplets or blobs, are associated with particles ejected from the target, which travel behind the plume at velocities of typically 50–200 m/s.[12] In general, more droplets are formed at higher fluences, for picosecond rather than nanosecond pulses, and where less dense or porous targets are used. Several techniques can minimise droplet formation. The most successful involves target rotation. This ensures that the remnants of previous ablation events, often resolidified off-stoichiometric mixtures, are not re-irradiated and ejected from the surface. Barr[43] and others have used a 10,000 rpm rotating deflector that selectively deflects slow particles and transmits faster moving species. Gaponov *et al.*[44] used two colliding beams to generate a high pressure zone which expanded towards the substrate, encouraging heavier lumps to miss the surface altogether. A negative substrate bias of several hundred volts can also considerably reduce heavy clusters that are similarly charged, and this significantly improved the growth of Ge by PLD.[45] Koren *et al.*[46] and Chiba *et al.*[47] have also used a second laser beam to excite and dissociate the larger particles within the plasma. Sankur *et al.*[48] found that using molten target sources virtually eliminated droplet formation with Ge, and for limited fluences, B_2O_3. Alternative geometries, such as the edge-on placement of substrates inside the plume, have also been shown to be varyingly successful.

In summary, the ablation process (see Fig. 2) may be considered as follows. Under intense absorption of optical energy, all the component atoms are ejected in a violent rupture of an ultrathin surface layer. This ensures stoichiometric transfer. Once formed, the plasma, containing ions, electrons, neutrals, and clusters, may absorb the remaining light in the incident laser pulse and attain a very high temperature. The species speed away from the surface, the dynamics of the plasma expansion and subsequent emission being delicately related to the background gas type and pressure. After collisions with themselves and with any background gas they lose kinetic energy, and particles may form in the gas phase. If they are intercepted by a solid, a thin film can grow. Thus, the substrate position with respect to the plume is critical to film quality. This is because, in some cases, the parameters that minimise droplet formation on the surface may not necessarily be identical to those necessary for optimum film quality.

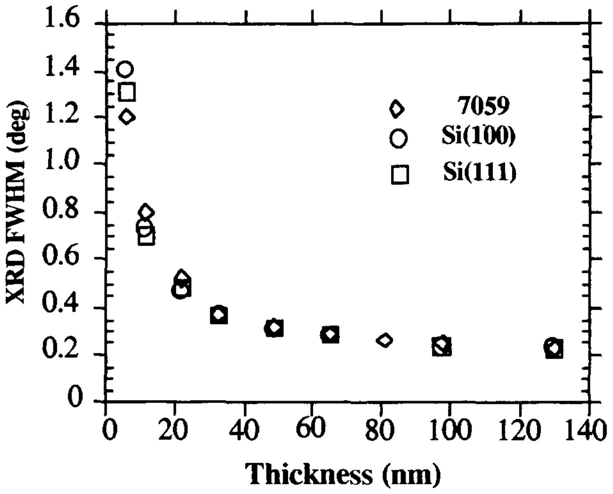

Fig. 2. Evolution of the FWHM values of the 111 peaks of CeO_2 films grown on Si and glass.

3 EXPERIMENTAL APPROACH

In this section, specific examples of PLD will be presented. In fact, a vast number of layers can be grown by this method.[19] A typical experimental set-up, as already shown in Fig. 1, basically consists of an evaporation chamber, with a laser beam and directing optics positioned outside the cell. The target pellet is commonly irradiated at an angle of around 45–60°. The substrate upon which the film grows is usually positioned parallel to the target, although this is not essential, and is often heated to high temperatures to help promote epitaxy. To assist in optimising stoichiometric transfer during irradiation, the target is either rotated, or the impinging beam is scanned across it. Although working pressures around 10^{-6} Torr are common, precise amounts of O_2, N_2O, N_2, or other gases may be pumped through the chamber during deposition. The beam fluences used for ceramic ablation are around 1–4 J/cm^2 (higher values may occasionally be employed), while most of the lasers operate at 10 Hz, although in principle higher rates might be desirable. Typical deposition rates are around 0.5–5 Å/pulse, and in 10–20 min films up to 1 μm in thickness can be grown. Depending on the nature of the target irradiated, and more importantly the thermal and chemical properties of the host substrate and its temperature, the grown films may be amorphous or crystalline. Mismatch in lattice and thermal expansion is important as in any heterogeneous layer growth. Any chemical reactivity at the interface should not be detrimental to the growing film. Substrates of strontium titanate ($SrTiO_3$), magnesium oxide (MgO), and yttrium stabilised zirconia (YSZ) have been host to amongst the best thin film superconductors reported to date.

There is presently a great deal of investigation into the possible use of buffer layers that might in future enable successful combination of superconducting films with c-Si devices. Crucial amongst the criteria to be observed are:

(a) Intermixing and chemical reaction at the superconductor–semiconductor interface.
(b) Thermal mismatch between the two components.
(c) Strain introduced by mismatch in the lattice constants of the two materials.

Buffer layer growth on Si, especially CeO_2 because of its good lattice match and dielectric properties, has been studied in recent years. Both substrate temperature and O_2 pressure are important in determining the crystalline quality of the films. Figure 2 shows that the substrate properties are not crucial for ordered growth, as a narrowing of the FWHM of the (111) peak of the XRD pattern with film thickness occurs independently of whether the substrate was Si(111), Si(100), or 7059 glass. The dense packing of the Ce atoms on the glass substrate or on the native oxide present on the Si, due to their strong affinity for O, leads to preferred growth in this direction. Differently doped buffers can also be grown by PLD to engineer the lattice constant. For example, CeO_2 doped with 40% La_2O_3 can change the lattice constant of PLD-grown buffers by some 2.5%.[49]

The growth of superconducting $Ba_2YCu_3O_7$ films on crystal substrates by PLD is well established. Conditions used by the vast majority of groups are based on the work of Inman *et al.*[50] Although modifications are possible, typical conditions involve the use of fluences of 1.5 J/cm^2 at 248 nm, about 100 mTorr of O_2, and substrate temperatures from 700 to 750°C. High quality films can also be grown on buffer layers, such as CeO_2 or YSZ, deposited by PLD on a variety of substrates, such as c-Si.

The BiSrCaCuO system is much more difficult to prepare and process. This homologous series $Bi_2Sr_2Ca_nCu_{n+1}O_x$ contains three members at n = 0, 1 and 2, with superconducting transitions of 20 K, 80 K and 110 K. These are structurally interrelated and differ only by the insertion of the $CaCuO_2$ accommodated by extra layers and are often described by the number of Cu–O planes, i.e. 1 ($n = 0$), 2 ($n = 1$), or 3 ($n = 2$). The chemistry of these phases is very complex and isolation of pure single phase ceramic samples, particularly of the $n = 3$ member, has proven to be a major challenge. This 2223 ($n = 2$, $T_c = 110$ K) phase, for example, is only stable over a 10 K range near its melting point. In general, the thermodynamically stable 2212 ($n = 1$, $T_c = 80$ K) phase is formed preferentially and the 110 K phase is then produced by decomposition.

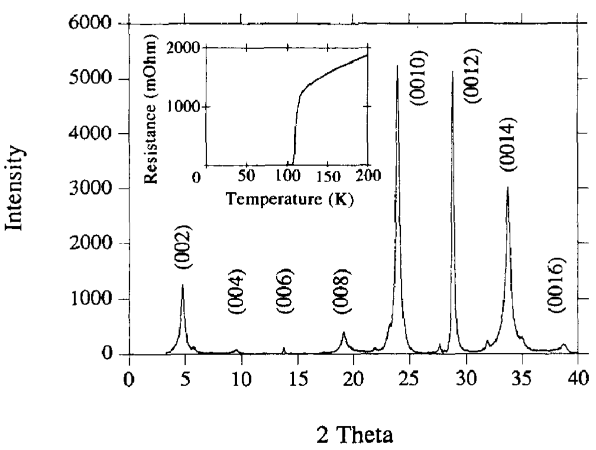

Fig. 3. XRD and resistivity of multilayer-grown Bi(Pb)-SrCaCuO films.

Many attempts to grow films of BiSrCaCuO have been reported, although the level of activity is substantially lower than that for $Ba_2YCu_3O_7$. The incorporation of lead (Pb) on to the bismuth site promotes the formation of the 2223 phase over 2212, and nearly single phase material can be produced by very long annealing times (~ 100 h) in the presence of a Pb vapour. Alternate PLD of BiSrCaCuO and PbO layers in sandwich structures has been shown to promote the 2223 phase.[51] Figure 3 shows the X-ray diffraction pattern and electrical resistivity of such a multilayered film, annealed for 15 h at 854°C. This method has the advantage that it enables independent control over the Pb content in the film and the temperature cycling. A similar approach has been adopted to grow the first films of PbSrYCaCuO by making sandwiches of PbO and semi-conducting SrYCaCuO.[52] The ability to fabricate novel materials by PLD thus opens up a vast new area of exciting research. The methods of sandwiching and reactive growth in O_2 shown here are only a few of the myriad of possibilities available with PLD.

A further example of reactive PLD is the growth of TiN, obtained by ablating pure Ti metal in N_2. Approaches using less dense and more porous TiN targets often report undesirable incorporation of oxygen impurities. The pure Ti method produces crystalline films at 450°C with a much reduced O content and have smooth mirror-like surfaces.[53]

In terms of simple oxide layers, optimised PLD can compare extremely favourably with conventional deposition techniques. For example, ZnO films have been grown at 350°C by ablating ZnO targets in O_2 pressures of 1–4 × 10^{-3} Torr, with a refractive index of 1.97, a bandgap of 3.26 eV, and optical transmission of 85% in the visible, which are *c*-axis oriented with the FWHM value of their

(002) XRD reflection being less than 0.15°. These are amongst the best properties ever reported for thin ZnO films.[54]

In summary, the process of PLD has been described. An outline of the controlling mechanisms has been presented in terms of absorption, particle ejection, and plume dynamics. PLD has very exciting prospects and offers advantages over some traditional deposition technologies. It is clear, however, that PLD will not displace any of these, but will introduce increased scope for new film growth. PLD still retains disadvantages; film uniformity is not optimum and particle formation can be difficult to completely eliminate. These most likely remain a mischief rather than a fundamentally insurmountable problem. Probably the biggest challenge to PLD is the film area that can be currently produced, limited by the beam sizes available with present-day laser technology.

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