2002

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Recommended Citation

McKinnon, J; Ionescu, Mihail; Shi, Dongqi; and Dou, S. X.: On the growth mechanisms of thin films produced by pulsed laser deposition 2002, 547-554.
<https://ro.uow.edu.au/engpapers/564>

ON THE GROWTH MECHANISMS OF THIN FILMS PRODUCED BY PULSED LASER DEPOSITION

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ABSTRACT

For more than ten years Pulsed Laser Deposition (PLD) has been used to produce $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7.8}$ (YBCO) thin films. Most groups have reported their capacity to produce films with roughly optimum characteristics. Unfortunately, the deposition parameters used by the individual groups vary within broad limits [1-5]. Each group develops a similar but unique recipe of deposition parameters, which, combined with other system specific characteristics, optimises their film properties. The implication of this is that the set of parameters being reported is not the whole story. In this paper we put forward a set of generally accepted facts about the PLD process and we list the necessary implications of these facts. To account for the facts we suggest a model based upon the evolution of a collisional layer at the surface of the film and the selective retention of impinging species.

INTRODUCTION

The fact that no universally accepted set of parameters has been established, no model that provides predicting power developed, and that high quality films can be produced over a wide range of parameter values is indicative of a shortcoming in the current approach. It is necessary that any assumptions underlying the current approach be re-examined and that universally accepted facts be stated and a new paradigm postulated.

There are many parameters that affect the quality of films produced by PLD [1] and for more than a decade investigators have endeavoured to isolate and quantify the nature of their dependencies. At this time it seems that the degree of interconnectedness and non-linearity of the dependence of the film quality on these variables has limited progress to the development of a plethora of process parameter recipes [1-5].

Characteristics of the pulsed laser deposition process, such as the ability to produce stoichiometric films from stoichiometric targets without compensation, point to the underlying mechanisms being fundamentally different from those of other thin film techniques. Compensation here refers to the use of off-stoichiometric targets or sources, to compensate for differences in the saturated vapour pressure of the constituent species of the desired final film, at the temperature of the substrate. Consideration of this and other facts about the process make it increasingly

CP614, *Advances in Cryogenic Engineering:*
Proceedings of the International Cryogenic Materials Conference - ICMC, Vol. 48,
edited by B. Balachandran et al.
© 2002 American Institute of Physics 0-7354-0060-1/02/\$19.00

apparent that the film growth mechanisms cannot be separated from the process that delivers the species to be incorporated in the growing film.

In the more traditional techniques, the species that one wishes to deposit are evaporated into a low pressure ambient, typically 10^{-8} Torr [6], so that the ratio of evaporated atoms to residual gas atoms favours the condensation of the evaporated species. The substrate is chosen to encourage epitaxy and its temperature is chosen to maximise adatom mobility. Most theories of film growth include the stages of nucleation, growth and coalescence. Commentators tend to limit their discussion to what occurs after an adatom is located on the surface and it is usually assumed that the sticking coefficient, the ratio of the number of atoms that remain on the surface to the number of atoms that impinge on the surface, is close to unity. This assumption is based on kinetic and thermodynamic arguments on nucleation [6,7], which although arguable as to their application when the number of species is small, do produce qualitative agreement with experiment. The significant factor is that for these techniques the consequences of the assumption being not quite correct are minimal.

EXPERIMENTAL PROCEDURE

Experiments were conducted to see if the correlation of outgrowths with film surface features and with substrate features would be verified. YBCO films were prepared on YSZ <100> by PLD using a Compex 301 KrF excimer laser with a wavelength of 248nm and an energy of 600mJ per pulse. The substrates were attached to a resistive heater with silver paste and brought to a temperature of 800°C. The target – substrate separation was 70mm. The laser beam was focussed onto an area of approximately 2mm x 10mm of a 25mm diameter stoichiometric YBCO target. The fluence was approx. 3 Jcm^{-2} . The target was rotating at 10 rpm. The base pressure of the chamber was approx. 1×10^{-6} Torr and the deposition pressure was 150mTorr of Oxygen. The YBCO target was polished then pre-ablated for 10 minutes at the deposition frequency of 3Hz. After 20 minutes deposition, the chamber was brought to 750Torr and the heater switched off. The films were patterned using a positive photolithographic technique. After AFM examination of the YSZ/YBCO step edge and individual surfaces, CeO_2 was deposited over the patterned YBCO films to allow for subsequent removal of the YBCO with H_3PO_4 . This left patterned CeO_2 (in the absence of an etchant for CeO_2 this technique has been found to work well). The CeO_2 films were deposited for 10 minutes at 5Hz at 790°C and 750°C in 200mTorr Oxygen and Argon/10%Hydrogen respectively. The YSZ/ CeO_2 step edge and individual surfaces were examined using an AFM. All films were examined using XRD. As well as the aforementioned experiments, data was extracted from the literature to find a set of statements that would be generally consistent with all investigators' experience.

EXPERIMENTAL RESULTS

The θ -2 θ XRD scans showed that the YBCO had only (00l) peaks and the CeO_2 was higher 95% pure c-axis oriented. As shown in the AFM images (FIG 1A) and (FIG 1B) there is a clear correlation between the substrate features and film surface features for YBCO on YSZ and for CeO_2 on YSZ respectively. Outgrowths associated with these features indicated in (FIG 1B) are shown in (FIG 1 C, D). This correlation had been noticed when in some earlier work film

thicknesses were being determined using an atomic force microscope. The scans had been done across the step edge of patterned films, and some of the polishing scratches, that were evident in the surface of the YSZ <100> substrate, appeared to continue across the film surface. This didn't seem to be what one would expect with the substrate scratches being made up of features essentially the same as the background and having a surface roughness R_a of about 5nm. The films were up to 200nm thick with typical $10\text{nm} < R_s < 30\text{nm}$. Similarly the film surface features, consistent with the continuation of the scratches, were made primarily of patterns of the general background features. Outgrowths of up to 70nm were seen to be associated with these features.

THE FACTS AND THEIR IMPLICATIONS

The facts stated below are derived primarily from the literature and also from our own experimental results stated above. Where there may be some differing points of view, it is thought that the differences do not affect the overall argument presented.

1) There is no requirement for compensation to produce multi-element films with PLD in contrast to continuous, steady state deposition techniques. The rate of evaporation (V_E) or growth (V_G) of a film surface is typically described using the equilibrium expression [7,8]:

FIGURE 1. Atomic force microscope images of step edges showing feature correlation: (A) YBCO on YSZ and (B) CeO_2 on YSZ. Detail of the correlation of outgrowths with these features on films with: (C) contact image and (D) deflection image of the area indicated in (B).

$$V_G \text{ or } V_E = \frac{P - P_o}{(2\pi M k_B T)^2}$$

Here P is the vapour pressure and P_o is the saturation vapour pressure for species with mass M at temperature T , and the other symbols have their usual meaning; $(P - P_o)$ is called the supersaturation and is the driving force for deposition or evaporation. For complex systems it is clear that the value of this expression will be different for each species. If for instance the substance consisted of A and B components with atomic weights M_A and M_B and saturated vapour pressures of P_A and P_B respectively, the ratio of deposited particles may be calculated [6]:

$$\frac{N_A}{N_B} = \frac{C_A}{C_B} \cdot \frac{P_A}{P_B} \sqrt{\frac{M_B}{M_A}} \quad (2)$$

Here C_A and C_B are the fractions of the components in the evaporation source. The equilibrium expression (1) is comprised of two components, an absolutely general expression [7] for the impingement rate:

$$I = \frac{P}{(2\pi M k_B T)^2} \quad (3)$$

and an expression for the desorption rate, which is derived from the equilibrium condition where the net evaporation or growth is zero:

$$D = \frac{P_o}{(2\pi M k_B T)^2} \quad (4)$$

For conditions that vary slightly from equilibrium, the expression is useful but it is clear that for PLD where the pressure is transient in both space and time and conditions are clearly far from equilibrium, its efficacy is minimal. What may be said is, that the net rate of growth is still determined by the difference between the impingement and desorption rates and as the pressure goes up the impingement rate goes up.

2) There exist a multiplicity of system specific recipes for the production of similar PLD films [1-5]. The inescapable implication of this is that the deposition parameters monitored and reported do not provide sufficient information to reproduce the film characteristics in different systems. Further to this, we can say that results are reproducible within the same deposition system and this means that it is not that the process can't be controlled but that we are not directly controlling the ultimate process determining parameters.

3) 2D (mesa type) and 3D (spiral type) features exist [9,10], which means that the net result of the retention of impinging species is non random. The impingement itself, is random, therefore

certain locations on the surface of the growing film are more likely than others to retain adatoms. Now this means that adatoms must either move to these favoured sites from their site of impingement or only those adatoms that impinge on favoured sites are retained or possibly some combination of the two.

4) The incidence of edge and screw dislocations correlates with the incidence of non-stoichiometric nucleation sites and, at least over certain dislocation densities, not with the release of misfit strain or with the number of dislocations in the substrate [11]. The latter two may indeed induce the formation of dislocations in the film but the number so induced could only be a lower limit as other causes, such as the incidence of the aforementioned non-stoichiometric nucleation sites dominates. It is concluded by Dam et al. [11] that the dislocations are formed as a result of the merging of misaligned growth fronts, when overgrowing precipitates.

5) Film surface features correlate with substrate features. Features, with dimensions of the order of 5nm and consistent with the overall background surface roughness (R_a), that exist on the surface of yttrium stabilized zirconia <100> substrates, correlate with features in the surface of thick films of YBCO and CeO_2 up to at least 200nm thick with R_a of <20nm. Growth mechanisms and hence which sites are favoured may be modified by underlying structures.

6) The incidence of 2D and 3D growth features is altered by the deposition conditions [10,11] which means that although underlying features can affect subsequent layers the extent to which they do so is moderated by the growth conditions.

7) Outgrowths exist on the surface of PLD YBCO and CeO_2 films, and at least some of them are associated with substrate features. Growth conditions control the extent to which underlying influences propagate from layer to layer, and more specifically the growth rate is different in certain areas of the film.

8) Investigations of plumes developed by pulsed laser on $\text{Y}_1\text{B}_2\text{C}_3\text{O}_{7.5}$ have revealed the presence of ions, neutral atoms and oxides of all species [12]. The trend, as you increase the distance from the target, is for a decrease in intensity of emissions from ions and excited neutrals and for an increase in oxides [12]. Time of flight studies, for species originating from the target, show a broadening of the intensity/time profile as you increase the distance from the target [12,14]. These results are consistent with a decrease in the energy of the highest energy species and a general decrease and equilibration of the energies of all plume species. The energy of the species, in a plume produced by pulsed laser, range from 10eV - 100eV, an order of magnitude higher than other evaporative techniques [13]. It is not clear what the average energy is at a typical substrate distance of 60mm. Many studies on plume dynamics have been done without a substrate or heater assembly in place so that the plume expands into a space empty except for the ambient gas. Work done by Biggers [1] with the substrate heater assembly in place, shows that the presence of such an obstruction causes variations in the time of flight data. This is evidence of an increase in pressure at the substrate surface whose effects feed back through the plume like a reflected pulse [1,14]. The localised and time dependent increase in pressure combined with the higher average energies suggest a possible origin for the observed differences in thin film production techniques.

FIGURE 2. Terrace ledge kink model of a singular surface showing various sites

THE SELECTIVE RETENTION MODEL

For films grown by pulsed laser deposition, we suggest that the fundamental characteristic of the process is precisely that the sticking coefficient is far from unity. Films produced by PLD also pass through the stages of nucleation, growth and coalescence but rather than rely on the mobility of adatoms and the extent of their surface diffusion to explain how this is done, if we invoke a model of selective retention we can not only explain these stages, but can understand all of the aforementioned facts. In this model most interactions between the impinging species and the surface do not result in the addition of an atom to the surface. Most atoms will have multiple interactions with the surface and in so doing will, due to significant variations in the relative sticking coefficients for different species and for different sites, selectively build the most preferred phase.

The selective retention model incorporates two basic ideas: the first of these is that a substrate surface presents to any impinging species a range of possible occupation sites. For various reasons these sites have a greater or lesser capacity to accommodate species over a range of energies and chemical potentials. The second idea is that if the distribution of energies of the impinging species overlaps the range of capacities for accommodation on the substrate, then sites will selectively retain particular species, typically as a result of multiple interactions.

Representing a singular surface using the terrace, ledge, kink model [8] gives a very clear idea of how the selective retention model would operate. (FIG 2) shows various stages in the growth of {001} crystal surfaces of a simple cubic system. The capacity of a site to retain an atom would depend on the number of bonds that could be formed. Surface atoms could form a maximum of five bonds at a surface vacancy, four at a ledge vacancy, three at a kink site, two at a ledge site and one on a terrace. The number of interactions per site, per unit time, in accordance with (3), is a function of the pressure and, while the pressure is maintained and an atom has not been retained a site will continue to have interactions with impinging atoms. If we postulate a system where all of the impinging atoms have the same energy and the energy remains constant

and further that we have the capacity to set the energy at any level we choose, then various scenarios can be envisaged. Firstly, for the extreme cases, if the energy is set such that even one bond would retain an atom then every impingement would result in an atom being added to the surface and the growth would be stochastic. If the energy is set very high where five bonds was not sufficient then no growth would take place. If five bonds were required then surface vacancies would fill up and growth would stop. If two bonds were sufficient then terraces would grow to the edge of the substrate and growth would stop.

If the requirement that the impinging atoms all have the same energy is replaced by an energy distribution such that equal numbers of atoms require 1, 2, 3, 4 or 5 bonds the idea of selective retention via differing sticking coefficients emerges. A site that could accommodate an impinging atom that required only 1 bond could be said to have a sticking coefficient of 0.2 since 80% of the interactions would be with atoms that were too energetic and these atoms would not be retained.

More and more complexity can be added back into the basic model provided the actual conditions of deposition, are still reflected by the model. Real features such as spiral growths can be seen as the predictable outcomes of high energies and substrate surface temperatures. The ledge that tapers back to where the screw dislocation emerges from the surface, provides ongoing preferential growth sites as the ledge winds around the point of emergence producing the spiral growth.

Analogous to the scenarios of suggested conditions, for a given energy profile of the impinging species, there will be an upper limit to the substrate temperature which when approached will limit the capacity of all sites to accommodate any species and in this way tend to result in the growth of high temperature phases. Similarly, as the lower temperature limit is approached increasing disorder is locked into the growing structure, poorer and poorer crystallinity results and eventually a completely amorphous film is formed. Between these extremes, variations in the substrate temperature will modify the differences in the sticking coefficients of various sites and hence the growth mode that is manifest. For a given substrate temperature, energy profiles that have increasingly high average energies will decrease the average sticking coefficient once again to a point where stoichiometric films are not formed. Decreasing the average energy will increase the sticking coefficient probably resulting in the formation of an amorphous film. The low end of this energy range, consistent with a very large separation of target and substrate compared to the plume length, would more than likely result in the failure to form a collisional layer at the surface of the plume and a general breakdown of the model. The model, as stated, requires multiple interactions between the growing surface and a high collisional layer adjacent to the surface.

CONCLUSION

The use of a diffusion mechanism and a sticking coefficient close to unity to explain the formation of observed features such as outgrowths and spiral growth requires that atoms diffuse over significant distances past equivalent sites. Not only do the arguments become strained but a model that relies only on surface diffusion doesn't lead to any greater understanding of the PLD process in general. The implication of the surface retention model is that, for a given substrate, instead of many variables that have a direct influence on the film growth we have two. One of these is the substrate temperature which is easily controlled and the other is the pressure profile of

the ablated species established at the surface of the substrate. Admittedly, the latter of these is derived in a very complex way from many of the normally quoted parameters, but if a suitable monitoring system can be established for the pressure profile, then we suspect that what had hitherto been a multitude of different recipes for optimising film properties will be shown to be differing pathways to the same condition.

REFERENCES

1. Biggers.R.R., Jones.J.G., et al. *Engineering applications of artificial intelligence*.**11**, pp.627 – 635, (1998).
2. Marre.D., Diaspro.A., et al. *Superconducting Science and Technology*,**11**, pp.737 – 743, (1998).
3. Morimoto.A., Takezawa.K., et al. *Applied surface science*.**127 -129**, pp.963 –967, (1998).
4. Pinto.R., Kumar.D., et al. *Superconducting Science Technology*,**7**, pp.95 – 98, (1993).
5. Proyer.S. *Applied Surface Science*,**96-98**, pp.668-671, (1996).
6. Eckertova,L. *Physics of Thin Films*, Plenum,Prague, 1977, pp.28-33.
7. Hudson,J.B. *Surface Science, An Introduction*, Butterworth-Heinemann, Boston, 1992
8. Howe,J.M. *Interfaces in Materials*, John Wiley & Sons, New York, 1997.
9. Dam, B., J. H. Rector, et al. *Physica C*.**296**, pp.179-187, (1998).
10. Yeadon, M. and M. Aindow *Journal of Crystal Growth*.**172**, pp.145-155, (1997).
11. Dam,B. et.al. *Physica C*.**341-348**, pp.2327 – 2330, (2000).
12. Allegrini.M., Fuso.F., et al. *Applied Surface Science*.**106**, pp.438-446, (1996).
13. Singh, R. K. and J. Narayan *Physical review B*.**41**, pp.8843-8859, (1990).
14. Nakata.Y. *Applied Physics Letters*.**66**, pp.3206-3208, (1995).