Correlation between plasma dynamics and thin film properties in pulsed laser deposition

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Abstract

The pressure–distance scaling law for pulsed laser deposition is examined for several thin film systems. This scaling law is due to the plasma dynamics occurring within the laser plasma plume near the location of the substrate. Time-of-flight studies of both ions and neutrals confirm the existence of an optimal velocity distribution for optimal film deposition. Fast ions play a major role in determining the quality of the films deposited. They may provide surface activation of the film or induce damage to the film depending on their kinetic energies.

1. Introduction

Pulsed laser deposition (PLD) is now an established method for thin film deposition. Its advantages have been amply demonstrated in many instances where PLD films compare favorably to films made by other methods (see for example Ref. [1]). This includes the much heralded high temperature superconducting films, ferroelectric ceramic films, semiconducting films of all combinations, and transparent conducting films [2–4]. Obviously, many studies have been devoted to the understanding of the fundamental mechanisms of the thin film deposition process, especially the correlation between the quality of the thin film and the deposition parameters [5–9].

One difficult problem with such studies is the complex nature of the laser plasma plume. This plasma plume is extremely dynamic in characteristics, especially for reactive deposition where an ambient reactive gas is present. There are many studies of the plasma plume generated by the excimer laser pulse. Methods ranging from optical spectroscopy to ion mass spectroscopy have been employed [5–7]. The properties of the plasma have been measured as a function of time, distance and for specific ionic and atomic species. Temporal resolutions ranging from nanoseconds to milliseconds have been used in an attempt to extract different types of information on the plasma.

However, many studies are aimed at examining the physics of the laser generated plasma without considering the thin film formation process itself. Hence considerable plasma studies were carried out at conditions not appropriate for good film deposition. While there are plenty of interesting physics to

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be learnt, however, it is ultimately the properties of the thin film deposited that count. Some films may be easy to make, while some are more sensitive to the plasma conditions. Therefore it is important that plasma dynamics be correlated to thin film properties.

In this study, we attempt to correlate the properties of the film and the laser generated plasma. Time-of-flight characterization of the laser plume for both ionic and atomic species were performed. Ion probe and emission spectroscopy were both employed. We also monitor simultaneously the properties of the thin films deposited as a function of the plasma parameters. It was found that the most important plasma parameter is the velocity of the various ionic and atomic species at the location of the substrate. This is manifested as a target distance–background pressure correlation law in PLD. We shall call it the *PD* scaling law [10]. This *PD* scaling law was found to be present for superconducting films as well as semiconducting film deposition [11].

2. Pressure–distance scaling law

There are a few important parameters that can be varied in PLD: the substrate temperature T_s, the ambient pressure P, the ambient gas flow rate, the target–substrate distance D, and the laser fluence J. While it is generally true that the deposition parameters can be varied independently to optimize the quality of the thin films, some of these parameters are related. The most obvious is the correlation between P and T_s. It is well-known from thermodynamic considerations that for each substrate temperature, the ambient pressure has to have an optimal value in order for the deposited film to achieve stoichiometry [12,13]. This is particularly true for reactive deposition of oxides and nitrides where a background oxygen or nitrogen is necessary. A less obvious correlation is that between P and D. We found that in general, for good quality thin films, PD^γ has to be a constant for some positive exponent γ, i.e. if P is reduced, D has to be increased correspondingly, and vice versa. We shall delay the discussion of the physical origin of this *PD* scaling effect to the later sections. Here we describe the manner in which this scaling law is arrived at.

There are many measures for 'good quality' films against which we can obtain the *PD* scaling law. We shall show 2 examples. Fig. 1 is an example for the case of high temperature superconducting yttrium barium copper oxide (YBCO). Here we use the superconducting transition temperature as a measure of the quality of the deposited film. Fig. 1 plots T_c versus P for various fixed values of D. It can be seen that for a fixed D, T_c is maximized for a particular optimal value of P. It is interesting to note that this optimal value of P is not the same for the various values of D. For the YBCO system discussed here, we can plot the optimal values of P for each value of D. The result is shown in Fig. 2. The data points can be fitted well with the scaling law of $PD^2 = $ constant [10].

A similar scaling law exists for the case of CdS deposition [11]. This is an interesting case because intuitively, no background gas should be required, other than perhaps sulfur, for the deposition of this material. Reactive deposition with a background gas during deposition should be needed only for the cases of oxides or nitrides. For CdS, one might think that the deposition chamber should be a total vacuum. Actually, it turns out that a certain amount of inert gas is needed in the background for good quality film deposition. The most common inert gas used is argon. The reason is not to replenish the lost
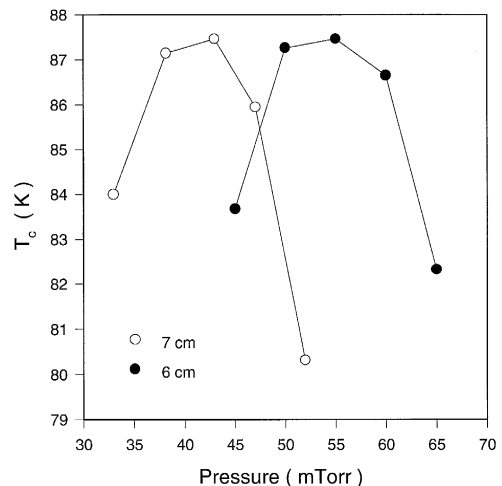

Fig. 1. Superconducting transition temperature for films deposited at various O_2 pressures at $D = 6$ cm (open circles) and $D = 7$ cm (closed circles).
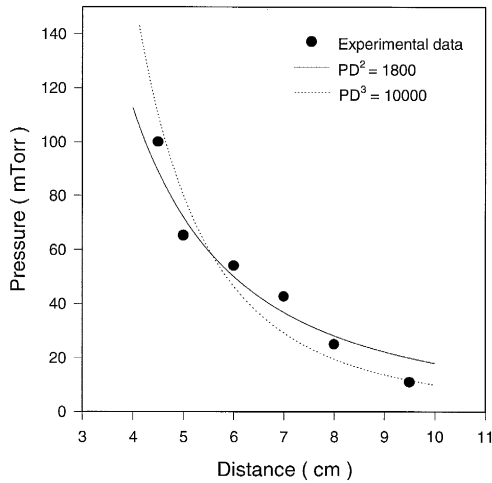
Fig. 2. Optimal pressure for depositing YBCO films as a function of target–substrate distance.

Fig. 4. Optimal Ar pressure as a function of target–substrate distance for CdS deposition. Note that zero pressure is never a good operating condition.

cations as in the case of oxides and nitrides. Rather, the reason is due to plasma dynamics. A background gas is needed to slow down the energetic ions, which otherwise will cause damage to the film deposited.

Fig. 3 shows the full-width-half-maximum of the X-ray rocking curve of the (100) peak of the CdS film as a function of D, for various fixed P. In this case, the X-ray peak is a good measure of the 'goodness' of the film. It can be seen that for each P, there is an optimal value of D, just like the case of YBCO. In fact, the obvious condition of a vacuum for the deposition of CdS is not an optimal condition.
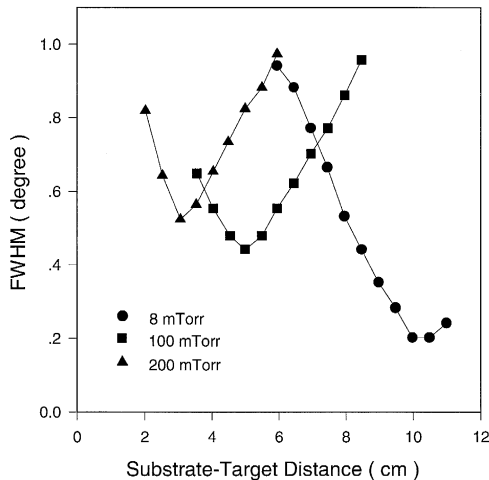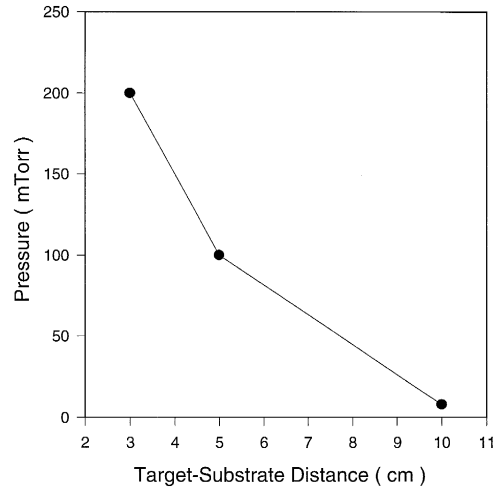

Fig. 3. FWHM of the X-ray rocking curve for CdS for various Ar pressures and target–substrate distance.

Fig. 4 shows a plot of the optimal conditions for deposition. In this particular case, since there were only 3 sets of optimal (P, D) values, it is not accurate to obtain the exponent γ. Nevertheless, for vacuum deposition, it can be seen that a large target–substrate separation of over 10 cm is needed for achieving good films. Actually, the optimal pressure as a function of D drops off much faster for CdS than for the case of YBCO. Also, unlike the case of YBCO, where all the optimal conditions of (P, D) produce similar quality films, the optimal conditions for CdS are not equivalent. The condition of lower pressure and longer distance results in better quality films.

Similar PD scaling law can be found in the case of indium–tin–oxide deposition and GaN deposition. So the obvious question to ask is, what is the underlying fundamental mechanism responsible for such scaling laws, and whether there is any universality and predictability for the optimal (P, D) conditions. We answer these questions by examining the plasma dynamics.

3. Optical time-of-flight spectroscopy

The optical emission time-of-flight measurement arrangement is similar to our earlier publication [7].

Basically, the emission from the laser plume was measured as a function of time and wavelength. The spatial resolution was achieved with an imaging lens in combination with a slit at the entrance to the spectrometer. It is usually about 0.5 mm along the propagation direction of the plume, and much longer in the transverse direction. The wavelength resolution is needed to identify emissions from individual atomic and ionic species.

In our earlier study we showed that the time-of-flight velocity distribution can be fitted well by a shifted center of mass Maxwell–Boltzmann function (SCMMB) [7]:

$$f(v) = Av^3 \exp\left[-M(v - v_0)/2kT_{\text{eff}}\right] \qquad (1)$$

where M and v_0 are mass and center of mass velocity of the atom or ion, and is T_{eff} the effective temperature of the velocity distribution. The original study was performed in a vacuum. We later on extended that study to an O_2 ambient and found that the O atoms are also 'pushed' to the same velocity distributions by the plasma [14]. We recently measured the velocity distribution of the constituent atoms more systematically as a function of O_2 pressure and distance. Fig. 5 shows a typical time-of-

Fig. 6. Optical TOF spectra for Ba and Ba^+ at 15 mTorr of O_2 and at $D = 5$ cm. It can be seen that there are more Ba^+ than Ba, but the velocities are the same.

flight spectrum for Cu atoms at a distance of 6 cm from the target under various background pressures. At intermediate pressures, a bimodal distribution of velocities can clearly be seen. Similar results have been reported by us earlier [13]. This observation was also made by Geohegan who found by absorption spectroscopy that the velocity distributions sometimes became bimodal (see for example Ref. [1]). Fig. 5 clearly shows the systematic trend for the velocity distributions. The dotted lines are theoretical fits using the SCMMB function in Eq. (1) with 2 centers of mass velocity. The velocities peak at 2×10^5 cm/s and 8×10^5 cm/s respectively for the slow and fast components, respectively.

In Ref. [10], we argued that the optimal (P, D) combination has to do with the compromise between surface activation and impact damage by high energy particles. At any distance D, if the pressure is too low, the velocity of the various species will be too high and cause damage to the film. But if the pressure is too high, the velocities of the atoms and ions will become too slow and there will not be enough surface activation for good film formation. From the above measurements, the kinetic energies for the atoms are about 1 eV, which should not be strong enough to cause surface damage. So it is doubtful that the neutrals are responsible for the PD scaling law. We shall show below that the ions play
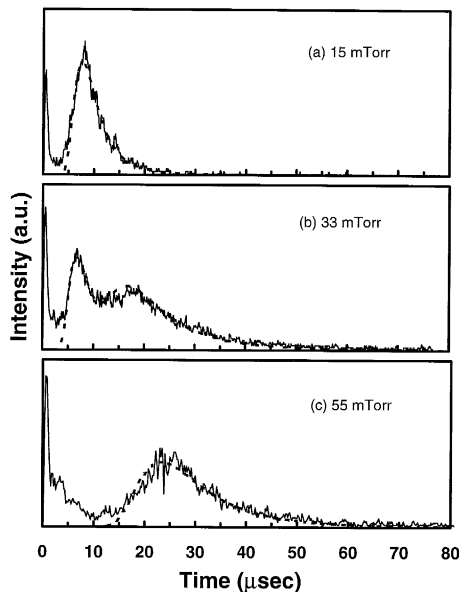

Fig. 5. Optical time-of-flight spectra of Y atoms at various background O_2 pressures at $D = 6$ cm. Dotted curves are best theoretical fits using SCMMB velocity distributions.
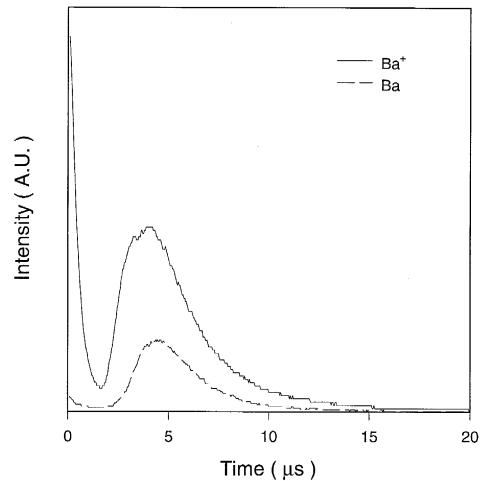
a more important role in PLD in determining the *PD* scaling law.

As mentioned earlier by Geohegan, transmission spectroscopy showed that there are 5 times more Ba ions in the plume than neutrals [15]. Optical time-of-flight spectroscopy can also be performed on ionic species as well to confirm this result. Fig. 6 shows a comparison of the TOF spectra for Ba and Ba^+. The emission lines used were 5777.62 Å for Ba and 6141.72 Å for Ba^+, respectively. It can be seen that the velocity distributions are nearly the same, with the peak of the ions perhaps faster by 10%. From the known oscillator strengths for the 2 lines monitored, the concentrations of the ions is about 5 times higher than the neutrals at this pressure and for the particular excited states monitored, in agreement with Ref. [15]. However, this cannot be construed as the ratio of ions to atoms in the plasma plume since all lines should be measured to get that result.

4. Ion time-of-flight spectroscopy

Ions can be detected easily by electrical probes. It is easier to perform this measurement than optical TOF. But the data is more difficult to interpret because of the disrupting nature of the probe. There are space charge effects and capacitive coupling problems. Moreover the extraction voltage interferes with the plasma. Nevertheless, despite these problems, ion probe measurements are very useful and essential for plasma diagnostics.

Fig. 7 shows typical ion probe signals as seen by an unbiased charge collector placed at 6 cm from the target. The ambient pressure was varied form 0.05 mTorr to 70 mTorr. It was found that the 0.05 mTorr curve was very different from the rest of the curves. In general, for $P < 1$ mTorr, time-of-flight peaks corresponding to different masses can be identified. At $P > 10$ mTorr, only a broad peak can be observed. Different species can no longer be distinguished. Since the mean free path for oxygen is about 0.5 cm at 10 mTorr, it is believed that at higher pressures, the constant collisions among the various species tend to equalize their velocities [12,13]. The broad peak in Fig. 7 encompasses all the different ionic species. The ion TOF spectra are also broadened by the strong Coulomb interaction with the background electrons and ions.
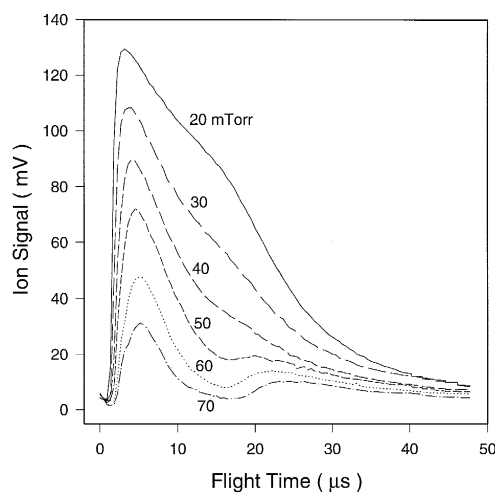
Fig. 7. Ion TOF signal at various ambient O_2 pressures. A bimodal distribution is clearly seen.

Additionally, it can be seen in Fig. 7 that the ion velocity distributions show a bimodal behavior as well. Two broad peaks can be seen at any $P > 20$ mTorr. The separation of the 2 peaks is more visible at higher pressures. This behavior is similar to the case of the atoms and ions measured by optical TOF, except that in the latter case, the peaks are sharper. It is a direct confirmation that the results of ion TOF measured by optical spectroscopy and ion probing are in agreement, except that the ion probe signals are broadened by Coulomb interactions. The velocities of the slow and fast components of the ions are in general agreement with the optical TOF results.

From the previous section, it was shown that at the optimal (P, D) conditions for deposition, the atoms are mostly slow ones, with the fast atoms being damped away. However, the results in Fig. 7 indicate that there are still a considerable amount of fast ions at a high pressure of 60 mTorr, which is the optimal operating point for deposition at this target distance. As a comparison, the fast neutrals are unobservable at this pressure. It is therefore concluded that fast ions are more important than fast neutrals in PLD.

From the ion TOF data, it is possible to obtain the peak velocities of the ions for the various optimal deposition conditions depicted in Fig. 2. Very interestingly, it was found that in all cases, the fast peak of the ions always corresponds to a speed of $1.2 \times$

10^6 cm/s. This speed implies kinetic energies of 47 eV, 65 eV and 100 eV for Cu^+, Y^+ and Ba^+ ions, respectively. These are much higher energies than the neutrals. It is believed that it is the fast ions that are responsible for activating the surface of the film during deposition. And it is precisely these fast ions that are responsible for the *PD* scaling law.

Actually the peaks in the ion TOF are rather broad and it is not possible to precisely define the velocities of the ions at the optimal deposition conditions. The peak velocities quoted above can only be regarded as a reference. The important physical interpretation is that fast ions are needed in PLD. However they are detrimental to the deposited film if the kinetic energies are higher than 100 eV. Hence a sufficiently high background gas is needed to slow them down and to reduce their abundance. This is the reason why argon is needed for the deposition of CdS. There is a certain optimal ratio of fast ions to slow neutrals and ions for good PLD. However, the slowing down of the ions should not be overdone or surface activation will not be sufficient for good quality film deposition.

5. Summary

In summary, we have presented some results on characterizing the properties of the laser plasma plume. At the same time we also monitored the properties of the thin films. A strong correlation was observed between the ambient pressure during deposition and the velocity of the neutral atoms and the ions. It was found that there is always a bimodal velocity distribution for both atoms and ions. While the fast atoms are damped away rapidly, the fast ions still survive at the substrate surface under the optimal deposition pressure. The fast ions are very energetic and are believed to be responsible for surface activation during film formation.

The *PD* scaling is universal in PLD. There is a general inverse relationship between the 2 parameters. The *PD* scaling arises from the fact that the velocity of the ions are in general a decreasing function of *P* and *D*. Hence, if *P* is increased, in order to achieve the same peak velocity, *D* has to be decreased, and vice versa. The exact *PD* scaling

depends on the function $v(P, D)$ for the ions and atoms.

Finally, it was observed that there was a bimodal velocity distribution for both the atoms and ions. It should be interesting to find out why there is a bimodal velocity distribution rather than a continuous one. Extensive hydrodynamic modeling should be carried out to obtain the velocity distributions of the various atomic and ionic species. That discussion will be the subject of a separate investigation and publication.

Acknowledgements

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