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Self-Directed Control of Pulsed Laser Deposition

E.F. Stark and S.J.P. Laube

Implementation of self-directed control of pulsed laser deposition (PLD) requires actuators, sensors, and a materials and processing knowledge base. Improvements in quality and reproducibility of material deposits are achieved by driving the process toward desired operating regions. Empirical relationships are determined experimentally to describe the complex dynamical interactions of laser parameters. Feedback control based on this description can then be implemented to reduce process disorder and effectively produce consistent coatings with desired properties.

Keywords

Laser ablation, observer-based control, pulsed laser deposition, qualitative control, qualitative process automation, solid lubricants, tribology

1. Introduction

PULSED laser deposition (PLD) shows great promise as a relatively new coating process for depositing stoichiometric thin films. Some key potential applications for PLD films are high-temperature solid lubricants, machine tool coatings, and coatings for high-precision molds. Using PLD, thin-film solid lubricants recently have been applied to critical components of space-based systems, particularly satellite mechanism bearings, gears, and splines. JPL engineers theorize partial sticking of the high gain antenna of the Galileo space probe was due to loss of coating in transit.[1] The high-energy PLD process produces coating with superior substrate adhesion, which may have prevented the failure. Another major application for solid lubricants is computer disk drives. Outgassing and poor adhesion in computer disk drive bearings can lead to loss of data. High-speed disk drives of the future will require solid lubricants with good adhesion on the face of the disk to counteract centrifugal force of the spinning drive. In another example, the harsh environment found in future turbine engines will require innovative solid thin-film lubricants to meet the Department of Defense (DoD) Integrated High Performance Turbine Engine Technology Program capabilities.[2] In manufacturing tools and high-precision parts, tightly specified end items benefit from using ultraviolet lasers in PLD depositions. Film thicknesses on the order of 100 to 10,000 Å can be achieved at room temperature.[3] By depositing films at room temperature, precision machining tolerances are preserved.

A PLD system (Fig. 1) consists of a high-energy laser, beam handling optics, and a vacuum chamber. The laser pulse impinges on a surface of the target material. This material is ablated and deposits on the surface to be coated. To date, PLD has been shown to be an excellent technique to deposit adherent, crystalline thin films of a number of important materials. It is clear that PLD is a complex, highly energetic process that is not completely understood.[4] To gain control of the PLD process, sensors must be developed for *in situ* measurements of essential state variables of the deposition process. This sensor information will allow a more fundamental understanding of film growth characteristics. The primary goal of self-directed control of PLD is to significantly improve the consistency and quality of the films.

Efficient and effective control of PLD relies on changing the laser parameters in real time. The high-energy laser is the main actuator for ablation. Cavity voltage of the laser is varied during operation, proving real-time actuation of energy density.[5] Similarly, the frequency of pulses is also varied in real time. Excimer lasers are constrained to fixed pulse lengths during operation. Empirical PLD relationships are found by varying laser energy density and pulse repetition rate and recording sensor data. Molybdenum disulfide (MoS_2) is the target material selected for the initial baseline study.

Two main sensors provide feedback information to drive the deposition process. First, a quartz crystal microbalance (QCM) provides an indication of the amount and rate of deposition of ablated material. Systematic variations of laser parameters provide information to empirically model their relationship with deposited material thickness. Second, a high-speed photomultiplier tube (PMT) is used to examine the plume of ablated material. PMT waveform digitization during deposition provides real-time information that pertains to Mo I plume constituent ions. The waveform indicates ion velocity and relative density. Spectroscopy of the PLD plume has been performed for a variety of materials by other researchers.[6] It is reported to be a valid method of detecting ionized plume constituents of the pulsed laser ablation process. A known cluster of spectral lines for molybdenum that occurs near 3900 Å is chosen for sensing due to their uniqueness.[7] As with the QCM data, the material velocity and relative density of the specific ion species determined using a PMT can be empirically modeled with respect to variations in laser parameters.

A matrix set of actuator values is used to map the relationships between actuator values and sensor readings. The prime operating regions can be identified for rate of deposition, relative density, and velocity measurements. These relationships are not linear. Changes in laser parameters can drastically affect final film thickness, relative material density, and material velocity. By including the information about the prime operating regions in the knowledge base, self-directed control can be achieved.

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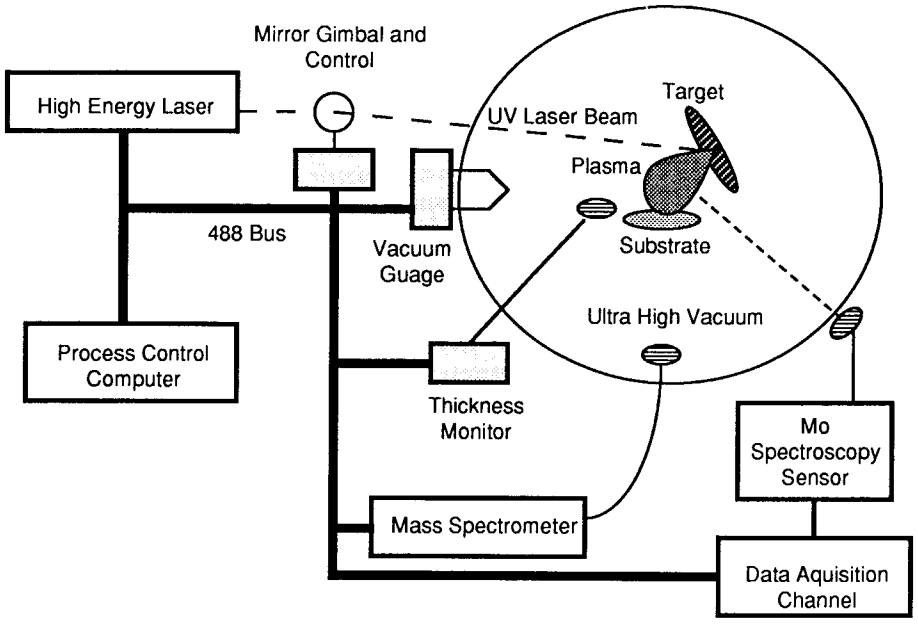

Fig. 1 PLD self-directed control system.

2. Background

Examination of PLD modeling research reveals laser ablation and plume dynamics as two basic phenomena that have been investigated.[8] Efforts of PLD modeling are aimed at identifying the fundamental physics of PLD by exploring possible effects of a single laser pulse. Because usable coating requires from 10^4 to 10^6 pulses, these idealized models do not take into account several other factors affecting thin-film growth.

Many theories are used to describe laser ablation. Ready[9] provides a purely thermal description for energy transfer due to use of comparatively long wavelength YAG lasers. Thermodifferential equations can be solved for material evaporation rates. Expulsion patterns and densities of the material were experimentally verified in air. The Richardson-Smith[10] equation can be used to find the plume current density if purely thermionic emission is assumed as the mechanism for material evaporation. Because the particular material threshold of evaporation is known, material evaporation rates can be found. The Garrison-Srinivasan[11] model is microscopic model that addresses the nonthermal photochemical aspect of PLD. In particular, the attraction force between the particles is determined by the charge potential difference between the particles. These models do not take into account nonthermal effects and particle interactions, although these phenomena are evident.

Work on PLD plume dynamics is more useful to self-directed control. Two primary areas are species ratio and plume distribution. Langmuir-Saha[12] have done work with species ratios that have generated a description of thermodynamic equilibrium in the plume with spectroscopic analysis. Singh[13] has developed a description of the material expulsion partial pressures of the plume distribution following a single laser pulse with respect to time. Neither model takes into consideration changes in nonthermal phenomena or the target condition, which can have a dramatic effect on ionized states and ablated target density.

This summary of work in fundamental understanding PLD phenomena is not intended to be a complete review, but to highlight relevant aspects. Existing models provide useful insight for process control, but no relationships currently exist for connecting laser parameters to deposited material properties. For more precise control, accurate relations are needed between particle species liberation rates and laser wavelengths of known energy density profile and temporal design. This article advocates the need for material process models that describe the effects of molecular quantum mechanics on molecular bond resonance.

3. Method

3.1 *Theory*

Self-directed control is a particular intelligent processing of materials (IPM) approach that involves adjusting process variables with respect to predicted or *in situ* measured changes in the material state. The limitations of existing material process models that sufficiently represent PLD prohibit the development of a complete analytical dynamic system description. Hence, a self-directed control knowledge base combines available elements of analytic information and empirical information about the process.

The method for development of self-directed control involves four steps:

1. Identification of appropriate sensors and actuators that determine process behavior

2. Establishment of empirical relationships by experimentation because analytical models do not exist
3. Correlation of testing results with experimental results to establish qualitative relationships, particularly stoichiometry
4. Incorporation of this information into the process knowledge base, which will direct the system into the desired operating regions

The general approach to designing a self-directed control algorithm can be illustrated by a feedback loop, where the actual process is mirrored by a process model. This model incorporates a knowledge base as well as error norms, which provide a more realistic mapping of the process model to the actual process. The compensator error is then minimized as the process model is linearized about a point and as the process model mimics the actual process.

The process will be linearized in the prime operating region determined by the knowledge base. The controller can then direct the process to obtain specific film growth characteristics. Controller parameters may need to be adjusted periodically by updating the linearization point based on available information on the state of the deposited material. Additionally, the controller must be capable of a smooth transition between linearization points. Due to the lack of a complete analytical description of the PLD process, there must be frequent interaction between the controller and a set of process performance measures. Qualitative information about the state of the material guides the process to produce useful coatings. The process knowledge base contains rules based on qualitative descriptions and the definition of prime operating regions.

3.2 *Experimental*

Molybdenum disulfide (MoS_2) films were grown using a Lambda Physik LPX-110i excimer laser* operating at a frequency of 248 or 193 nm. The laser pulse energies were varied between 10 to 220 mJ, and the pulse repetition rate was varied from 10 to 100 Hz. The substrates were 1-in. diameter 440C stainless steel disks that were highly polished. The substrate was held at room temperature during deposition. The deposition took place in an ultrahigh vacuum environment with the base pressure typically at 5×10^{-9} torr. The laser was focused to a spot size of approximately 0.03×0.06 m on a 1-in. MoS_2 cold pressed target.

Molybdenum disulfide has been selected as a baseline material for developing the self-directed control structure for PLD. MoS_2 is a versatile solid lubricant with a wide temperature range for operational use, from −130 to +370°C. The coefficient of friction (μ) of MoS_2 is approximately 0.06 to 0.20 sliding in vacuum.[14] MoS_2 has a long wear life, is readily available, and is radiation stable. All these factors, as well as a long history of use, make MoS_2 an ideal baseline material.

The substrate was rotated, and the laser beam created a raster pattern across the target surface. The raster was controlled using stepper motors connected to an Oriel control interface** controlled by a Macintosh IIfx computer.*** The deposition chamber was fitted with a QCM sensor† and a PMT looking through the plume, both connected to a 488 controller bus linked to a Macintosh IIfx running LabVIEW[15] process control software.††

The QCM provides an indication of ablated material amount and rate. A high-speed PMT provides relative density and velocity measurements of Mo I luminescent species. Real-time sensing of plume constituents yields insights into growth rate and, ultimately, material quality. Narrow UV optical filters combined with a high-speed PMT and 500-MHz amplifier provides real-time digitization signals on a per-shot basis.

3.3 *Knowledge Base*

The prime operating regions are derived from the QCM and PMT sensor readings. During the course of a deposition experiment, several parameters change, most notably the target condition. Using the process identification information, relationships can be derived between the sensor and actuator values as these conditions change. Using a set of rules, the knowledge base can be used to determine event completion, such as target deterioration beyond useful life. Evaluation of the sensor data and the empirical system description in conjunction with qualitative rules comprise the knowledge base. The empirical description may determine one or more prime regions of operation. The knowledge base selects a linearization point within the prime operating region of highest priority. This information is passed to the controller that does error minimization to determine actuator values. The knowledge base continues to monitor the error. When it falls outside predetermined error norms, the knowledge base selects a new linearization point. Self-directed control of PLD relies on the premise that the combination of qualitative rules and empirical system descriptions can maintain the consistency and quality of the film.

4. Results and Discussion

Results of experiments with respect to the variables for laser energy density and laser pulse rate show that the relationships

* Product of Lambda Physik, Goettingen, Germany.
** Product of Oriel Corp., Stratford, CT.
*** Product of Apple Computer, Cupertino, CA.

† Product of Inficon Leybold-Heraeus, Inc., East Syracuse, NY.
†† Product of National Instruments, Austin, TX.

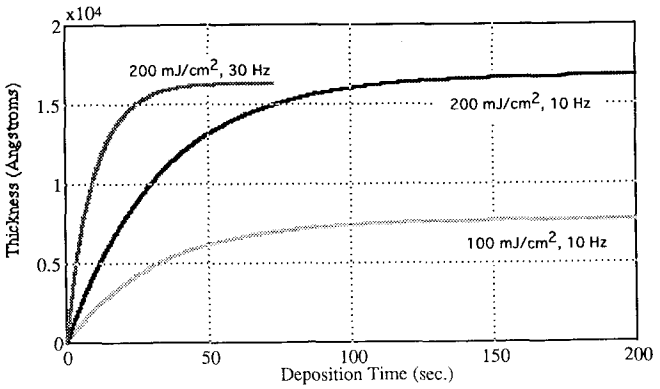

Fig. 2 Typical MoS_2 thicknesses for different laser parameters.

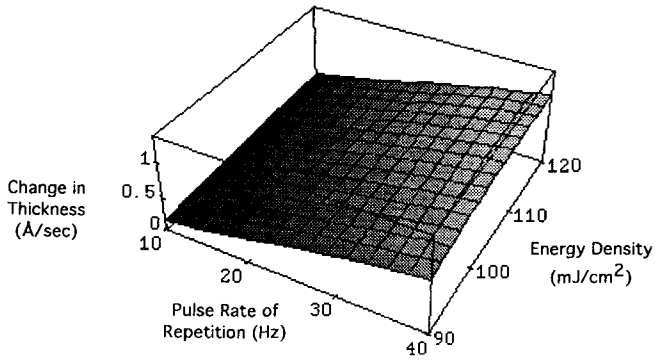

Fig. 3 UV PLD MoS_2 deposition rate fit at $x_0 = 500$ Å.

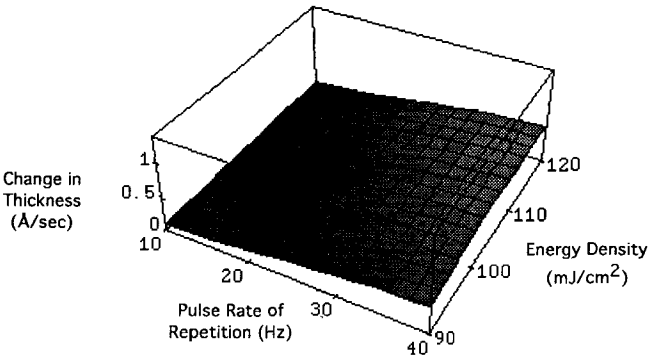

Fig. 4 UV PLD MoS_2 deposition rate fit at $x_0 = 1500$ Å.

between deposited thickness and spectroscopy energy density are not linear. In fact, changes in the laser parameters can cause drastic changes in sensor measurements.

4.1 *Process Behavior: Deposition Thickness*

Effects of laser parameters on deposition final thickness and deposition rates were investigated. Three experiments for MoS_2 are depicted in Fig. 2. Each experiment began with the specified actuator values, and these values remained unchanged throughout. The thickness of the film is recorded with respect to time. Because the laser is capable of operating with pulse repetition rates to 100 Hz and energy densities to 250 mJ/cm^2, these graphs by no means represent the entire range of deposition behavior. Different laser energy density and pulse repetition rates result in variations in deposition rates and final film thickness. Target degradation has been determined to be responsible for reduction in deposition rate. Repeat experiments with the same settings show similar trends as depicted in Fig. 2, but the values can vary by as much as 30% due to process variability.

To determine identifiable trends for the deposition rates with respect to pulse rate of repetition and energy density, 28 experiments were performed. These experiments were conducted to provide a means of determining a mapping of the process parameters with respect to the change in thickness and Mo I relative density. The process parameters are laser pulse

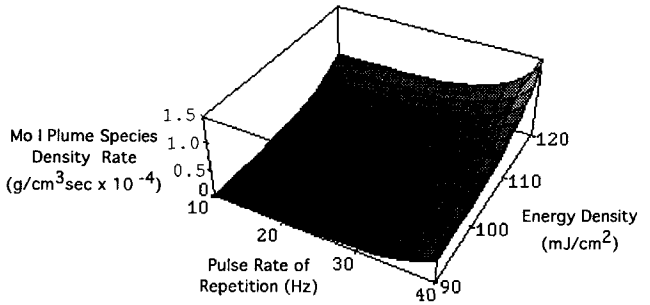

Fig. 5 Mo I species density rate at $a_0 = 0.15 \times 10^{-4}$ g/cm^3 s (uncalibrated).

repetition rate (PRF), energy density (E_d), previous deposited thickness (x), and Mo I species density (a). The deposition rate function is found from least-squares fit analysis of a polynomial function. The function is chosen to have a form that will minimize the root sum square error (RSS), while not extending complexity of the equation to simply follow the data points. Equation 1 is the dynamical model of PLD with respect to laser parameters.

$$\begin{bmatrix} x' \\ a' \end{bmatrix} = \begin{bmatrix} f(x, E_d, PRF) \\ g(a, E_d, PRF) \end{bmatrix} \quad [1]$$

The expression form of Eq 1 was chosen to be a nonlinear first-order differential equation. The accuracy of the polynomial fit is within an average of 4% of the experimental data. Deposition rates can vary from 0 to 2 Å/s, and the Mo I plume species density rate can vary from 0 to 0.00015 (arbitrary units). Other expression forms were evaluated, but this particular representation yields the best compromise between complexity and accuracy.

The QCM deposition rate and Mo I species density, x' and a' in Eq 1, can be viewed for any set of process parameters (laser actuator values) and deposition rate, and Mo I density can be predicted. A three-dimensional slice of this fit illustrates the general process behavior as the target surface degrades. Figure 3 provides one view of the deposition rate at an initial deposition thickness of 500 Å.

Deposition rate is shown with laser pulse repetition rate from 10 to 40 Hz on the x-axis and energy density from 90 to 120 mJ/cm^2 for the y-axis. The z-axis is the resulting change in thickness. Figure 3 shows a maximum deposition rate at maximum energy density and a PRF of 40 Hz. There is a deposition minimum of 0.1 at the lowest energy density and PRF.

As deposition continues, target damage increases. The deposition rate falls most drastically at lower PRF and energy density, with little change at the maximum values. Continued deposition increases the size of the zero ablation region, as shown in Fig. 4. Target surface is probably severely depleted, over-use of the target may render the deposited thin film useless.

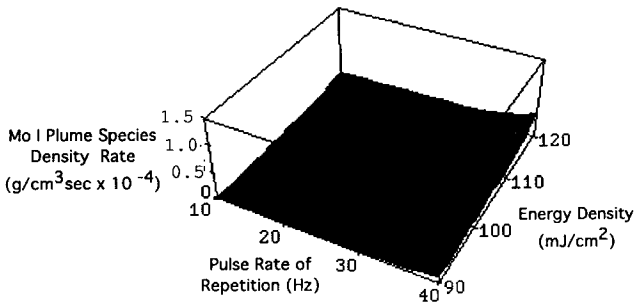

Fig. 6 Mo I species density rate at $a_0 = 0.05 \times 10^{-4}$ g/cm^3 s (uncalibrated).

4.2 *Process Behavior: Spectroscopic*

Measurements of the area under the spectral waveform provide the Mo I density. Variations of the change in Mo I density are fit as a function of laser energy density and pulse repetition rate. A constant Mo I density is desirable so that the thin-film composition can be consistent. By monitoring the density rate of change, a prime operating region can be selected, in which the rate of change is minimal. A multidimensional least-squares fit is used to describe the density rate of Mo I with respect to laser parameters (Fig. 5). This fit is based on 28 experiments, each of 360 s duration; density measurements were recorded simultaneously with thickness rate measurements. Mo I density rates were calculated using a backward difference technique in real time. This approach is combined with linear regression using a least-squares solution over a 360-s period to develop an approximate model of the density rate. The initial density, a_0, is held consistent during this set of experiments.

To make accurate spectroscopic area measurements, the digitization bandwidth must exceed ten times the rise time bandwidth of the spectroscope waveform.[16] High-speed digitization electronics capable of 400 Megasamples/s were used to make accurate spectroscopic waveform measurements.

As shown in Fig. 5, the Mo I density rate is a function of laser parameters and initial density at time of measurement. A changing Mo I rate indicates that the density of excited species in the plume are not constant, but varying. The Mo I density change is slight over the 360-s measurement interval. Increasing laser energy density or pulse repetition rate causes a higher rate of Mo I species.

In comparison to Fig. 5, Fig. 6 illustrates the density rate of change at a lower initial density. Although a reduction in density may indicate a slower growth rate, a reduction in density rate indicates a more consistent composition. A self-directed control scheme provides a method of determining the best balance of high growth rate and low Mo I density rate variation.

5. Summary and Conclusions

Growth regions have been identified in terms of first-order differential equations based on empirical descriptions derived from multiple experiments. This information will be incorporated into a knowledge base as the essential guide for self-directed control of the process. The results of this research have already yielded greater consistency of growth rate for other laboratory tests through direct real-time process measurement. Based on these experiments, an automated system under development is expected to improve consistency and quality of films. Finally, closed-loop control of complex material processes can be achieved, even without availability of all the first principles knowledge and a complete analytical description.

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