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PULSED LASER DEPOSITION IMPROVEMENTS BY SELF-DIRECTED CONTROL

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13. ABSTRACT

Improvements in material thin coatings for the year 2000 and beyond require a radical new approach to deposition processes. Pulsed Laser Deposition (PLD) is one such deposition process which offers deposition of complex materials currently not possible with other deposition methods. Unfortunately, it is not enough to control thin film material composition, but thin film stoichiometry, micro and macro stress and strain, and thickness as well. It is also desirable to have a deposition process that is easy to use and is repeatable.

In order to propel the current thin film deposition culture into accepting PLD as a manufacturing process, the automation of PLD is inevitable. The inception, development, and implementation of PLD automation methods is the aim of this document.

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List of Symbols, Abbreviations and Acronyms

Unit symbols:

sec. - Time in seconds.
Hz. - Cyclical frequency. (1/sec.)
kV - Potential EMF in 1000 volts.
mj/cm^2 - Incident electromagnetic Poynting energy density in 10^{-3} joules per square centimeter.
mb - Pressure in 10^{-3} Bars.
Å - Distance in angstroms.
GPa - Pressure in Pa x10^9

Acronyms and Abbreviations:

WPAFB - Wright Patterson Air Force Base.
MLIM - Materials and Process Design Group.
PLD - Pulsed Laser Deposition.
IPM - Integrated Process Manufacturing.
HTSC - High Temperature Superconductor.
XPS - X-ray Photon Spectroscopy.
TEM - Tunneling Electron Microscopy.
ASCII - American Standard for Computer Information Interchange.
GPIB - General Purpose Interface Bus. (1978 IEEE 488 and modifications.)
RS-232 - Remote control Radio Standard 232. (1932 IRE 232 and modifications.)

Summary

Higher performance to cost ratios, combined with IPM demands require new advances in materials and the processes that produce them. Pulsed laser Deposition (PLD) is a new promising deposition process that is capable of surpassing existing methods of thin film deposition. It is possible to deposit material with unique characteristics that do not exist in other deposition methods. Unfortunately, PLD is primarily used by researchers and government laboratories to make superior thin films for high demand and experimental use, such as aerospace coatings. There is very limited customer demand, due to implementation and manufacturing difficulties with current processing techniques.

Currently, PLD process design is based on research philosophy. PLD systems are designed by basic research scientists, who are interested in acquiring the most scientific measurements for proof of a scientific hypothesis. Consequentially, process construction is biased to reflect first principle research instead of film production. In order to utilize PLD as a manufacturing process, a change in view of PLD processing is necessary. Process automation and integrated manufacturing techniques such as process hierarchical control and sensor development are needed. PLD must be viewed as a viable manufacturing process, instead of a laboratory curiosity.

PLD is suitable for growth of thin films having complex stoichiometries.[1] Materials currently deposited by PLD range from tribological materials to superconductors. Unfortunately, implementation complexities and uncertainty of theoretical understanding has restricted wide spread use of PLD. Overcoming these barriers by feedback control enables PLD to produce superior materials. Development of a control design methodology specific to PLD is necessary so reduced uncertainty can be realized, ultimately improving thin film quality.

A novel process control design and implementation methodology has been developed [2,3] to make PLD predictable and reliable enough for industrial production of tribological thin films. Sensors and actuators are selected that affect material chemistry, and reduce deposition time. A hierarchical control scheme is designed so that process variability can be contained and stabilized in real time.

PLD process system identification, intelligent feedback control architecture, and implementation for ultraviolet pulsed laser deposition processes have been demonstrated. Many possible applications of this new coating process need to be investigated. An immediate direct application of PLD is dry machining mill end coatings. An investigation methodology and results are given in the form of a technical approach.

1.0 INTRODUCTION

PLD is a process for depositing thin films (100-1000 Å) of many different materials, ranging from superconductors to solid lubricants. A PLD system typically consists of a high energy excimer laser (248nm), beam handling optics, and an ultrahigh vacuum (UHV) chamber. The vacuum chamber contains the part to be coated, as well as a source of coating material called a target. Laser pulses are focused on the target surface. Target material is ablated and deposits in a thin film on the part surface. An excellent overview of PLD is contained in Hubler. [4, 5]

PLD has been shown to be an excellent technique to deposit adherent, crystalline thin films of complex chemistry and morphology. Its primary strength is stoichiometric transfer of material. PLD is a complex, highly photo-energetic process, the physics of which are not completely understood. [6] Several methods are available to improve the understanding of the PLD process. One method is to improve the observation technique of the process in real time. Another is to reduce process uncertainty, through the application of feedback control. [7]

To gain control of the PLD process, suitable sensors must be identified and developed for in situ measurements of essential state variables of the deposition process. Sensor information will generate further understanding of basic film growth characteristics. The primary goal of self-directed control of PLD is to significantly improve the consistency and quality of the films, while simultaneously increasing process knowledge. [8]

Effective control of PLD also requires the identification of actuation parameters. The high energy laser is the main source of ablation energy, and a suitable choice for the actuator. Since cavity voltage of the laser can be varied per pulse, real-time actuation of energy density can be directly changed during a deposition. Similarly, the pulse frequency can be varied in real time to affect the instantaneous energy on the target. The excimer lasers used for PLD are typically constrained to fixed pulse lengths during operation, so varying the pulse length is not currently possible. Nor is it possible to change the laser wavelength in real time at the high energy densities needed for PLD. Thus, any real time control of PLD will be by adjusting the excimer laser energy density and pulse repetition rate.

2.0 TECHNICAL APPROACH

2.1 Desired Film Characteristics And Motivation

In this particular study, the application of diamond like carbon (DLC) thin films produced by PLD was investigated, with DLC end mill tool coatings as the goal application. Ceramic tool insert coatings of DLC have been found to extend tool life by up to two times in lathe operations. Current methods of producing DLC coatings utilize either microwave plasma chemical vapor deposition (CVD), plasma torch, or cathodic arc as the deposition process.

Unfortunately, these deposition methods require heating of the substrate to temperatures of 500°C to 900°C. Temperatures in this range exceed the maximum allowable temperature for common tool steels used in end mills. An alternative to microwave CVD, plasma torch, or cathodic arc is PLD. PLD can be used to make DLC thin films of comparable hardness and young's modulus and superior wear life with substrate temperatures approaching room temperature.

It is currently not possible to completely understand the PLD process and how it produces the resulting DLC carbon films. In fact, the nature of DLC formation and structure is not well understood, but it is believed that a ratio of sp^2 and sp^3 bonds exist between the carbon atoms, forming a matrix that has the physical properties of diamond. There are many theories of how graphite, with sp^2 bonding, can be combined with the strictly sp^3 bonding found in diamond. One possible structure is by Wong[9], and is shown in Figure 2.1-1.

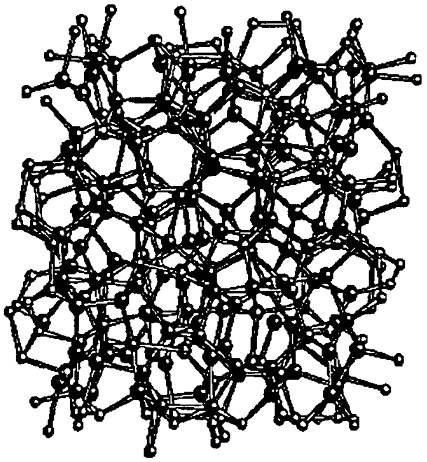

Figure 2.1-1. One theory of a possible diamond like carbon (DLC) structure.

Unfortunately, this is not quite the structure of natural diamond. Diamond consists of only sp^3 bonds, and is configured in a tetrahedron shape, that is, it consists of the same bond lengths throughout. This structure is a four faced three dimensional shape that has an isosceles triangle on each face. A view of the unit cell is shown in Figure 2.1-2, with one tetrahedron completed:

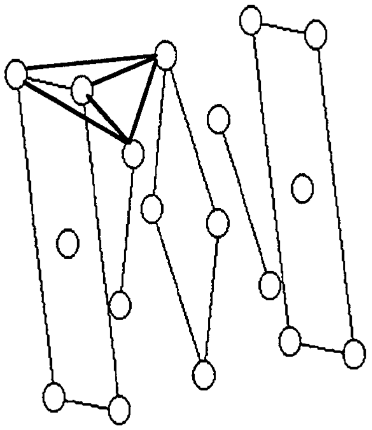

Figure 2.1-2. Theoretical diamond unit cell structure (A. Jackson).

It is suspected that the DLC material produced by PLD is some combination of sp^2 and sp^3 bonds, having both carbon and diamond properties. An increase in sp^3 bonds usually causes more diamond like tribological properties, while an increase in sp^2 bonds causes more graphitic properties. Films produced with few sp^2 and sp^3 bonds are amorphous carbon, with the least attractive tribological properties of all. The DLC films produced by PLD are typically a dark gray color, while those produced by CVD are more a silver-gray, possibly indicating higher sp^3.

As the film is produced, *in situ* sensors may provide some indication of the sp^3 to sp^2 bond ratio, and thus the film structure that is produced. *Ex situ* analysis can verify the type of DLC material that was made during a particular deposition. A correlation between indicated process *in situ* data and *ex situ* film studies can provide a method of determining the film quality while the deposition is occurring. In this way, it is also possible to actually control the film sp^3/sp^2 ratio during a deposition by manipulating *in situ* parameters.

Typically, DLC films have been made with either amorphous carbon targets of high purity (superconductor grade), or polycarbon ($[C_{13}H_{10}O3]_n$: "LEXAN") targets. Typically, the amorphous carbon targets yield amorphous carbon films (a-C), and with higher fluence, DLC films. The polycarbon targets yield hydrogenated carbon films (a-C:H), due possibly to the breakdown of the complex polycarbon molecule that yields hydrogen. Both target materials are capable of generating DLC films, although the DLC film generated with an amorphous carbon target yield superior tribological performance.[10]

3.0 *IN SITU* FILM ANALYSIS

3.1 Optical Emission Spectroscopy

The optical emission spectroscope, or laser induced florescence spectroscope, can indicate an ionized species velocity in the plume. The spectroscope provides real time data on ionized plume photon emitters, as they race away from the target. The apparatus used here is the same as the one used on the MoS_2 studies,[11,12] although the optical filter is different· Theoretical models by Laughlin of carbon ablation indicate that the most plentiful species are C^{2+} and C^{3+} instead of C^+. [13] The spectroscopic filter utilizes the 455 nm line from C^{2+}, after initial trials using the 193 nm line for C^+ did not yield any appreciable spectroscopic signal. This lack of detected C^+ and large detected signals for C^{2+} adds credence to the Laughlin model.

The spectroscopic data were collected for 1024 sample points for 0.5 microseconds after an external trigger pulse was detected by a high speed photo diode. The external triggering was necessary, due to the largest pulse to pulse trigger jitter present on the LPX 110i external trigger digital line. Each curve was averaged for 3 minutes, to remove any signal variations due to laser target rastering, target inhomogeneities, and laser pulse to pulse variation. As can be seen, the results for an amorphous graphite target shows two distinct peaks. The peaks increase with increasing laser fluence, indicating a denser ion constituency. There is also a subtle shift of the peak maxim with fluence, with the lower velocity peaks increasing from 100 to 140 km s^{-1} and the faster peak velocity decreasing from 400 to 350 km s^{-1} with an increase in laser fluence. These curves are shown in Figure 3.1-1.

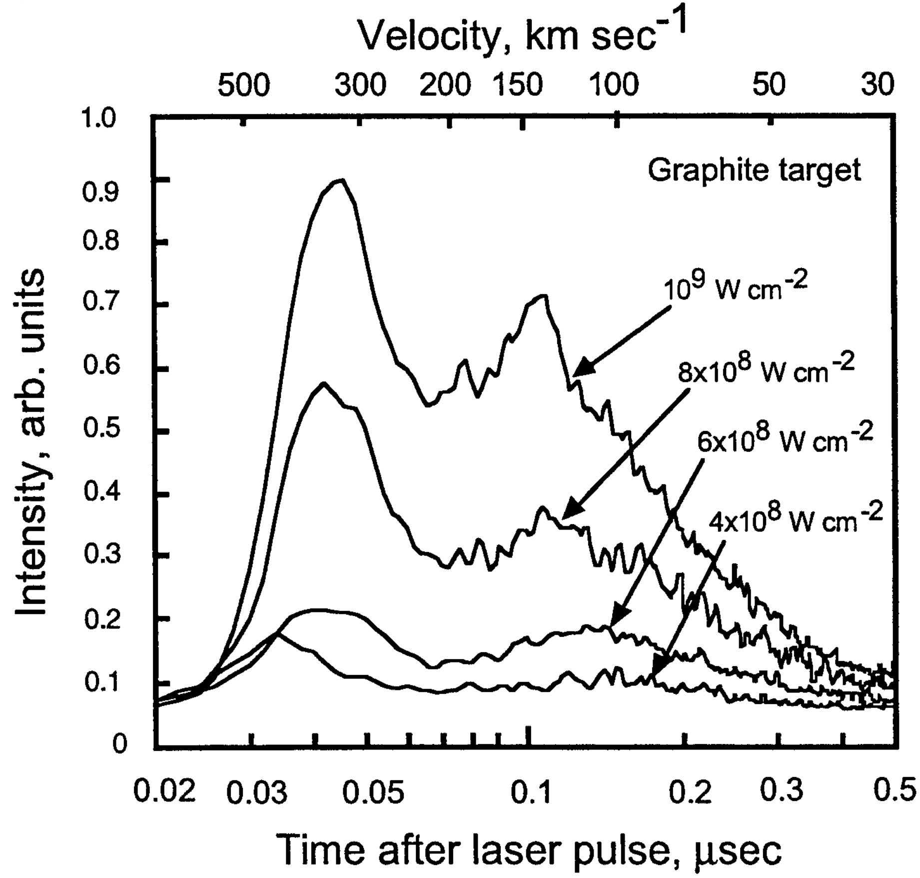

Figure 3.1-1. Emission spectroscopy waveforms for different laser fluences at 20 Hz pulse rate.

As can be seen, the maximum achievable laser energy density with the LPX110I and 0.25 meter short focus lens was 10^9 w cm^{-2}. This intensity cannot be measured directly, because these intensities will ablate the energy sensor detector surface, and permanently damage it. An approximate method had to be used. The intensity was approximately measured by first measuring the laser output intensity at the cavity aperture. Then optical losses were approximated by placing the energy sensor inside the chamber and operating the laser unfocused. Once approximate mirror and path losses were found, a magnification factor had to be estimated from optical handbooks and data sheets. This lens magnification factor was used to approximate intensity at focus, with some rough verification also done by melting a graphite and stainless steel target, which indicates greater than $1\text{x}10^8$ W cm^{-2}. The average pulse power is then calculated by:

$$p = \frac{e}{T} = \frac{20\text{J}}{20\text{x}10^{-9}\,\text{sec.}} = 10^9\,\frac{\text{J}}{\text{sec.}} = 10^9\,\text{watts}$$

This assumes a 0.2J cm^{-2} beam (after losses) is magnified 100 times to get 20 J cm^{-2} at focus. The 0.25 meter short focus lens used in these experiments can provide this magnification, because of the shorter focal length combined with less of the focus path being outside the vacuum system. These experiments were originally tried with the 0.5 meter focus lens, with no appreciable ablation of the graphite or stainless target. This is to be expected, due to a magnification factor of 10, greater path losses and divergence for a 0.5 meter focal length lens.

Calculation of species velocity measured by the spectroscope was done with a 1.5 cm. path distance between the target and the center of the spectroscope collimating tube. The speed was then calculated by:

$$v = \frac{\Delta s}{\Delta t} = \frac{0.015\text{cm.}}{0.5\text{x}10^{-6}\,\text{sec.}} = 30\,\frac{\text{km}}{\text{sec.}}$$

We can also assume that only carbon atoms are ionized, although this may not be true, as in the case of clusters or other ionized molecules that contain C^{2+} carbon. At any rate, making this assumption, we can calculate species energies by the kinetic energy equation of a particle of mass m, traveling at velocity, v:

$$e = \frac{1}{2}mv^2, \left[1.6\text{x}10^{-19}\,{}^{\text{J}}\!/_{\text{ev}}\right] = \tfrac{1}{2}[\text{kg}]\left[\frac{\text{m}}{\text{sec.}}\right]^2$$

The atomic mas number of carbon ,C^0, is 12 grams per mole, so the mass of a single carbon atom is:

$$m = \frac{12\,{}^{\text{g}}\!/_{\text{mole}}}{6.02\text{x}10^{23}\,\text{atoms}/_{\text{mole}}} = \left[\frac{1\text{kg}}{1000\text{g}}\right]\left[\frac{\text{g}}{\text{atoms}}\right]$$

So, if the 30 km/sec. measured was carbon, then the kinetic energy in electron volts would be:

$$e = \frac{1}{2}\left[\frac{12}{6.02\text{x}10^{23}}\right]\left[\frac{1}{1000}\right][30{,}000]^2\left[\frac{1}{1.6\text{x}10^{-19}}\right] = 56\text{eV}$$

The spectroscope data showed C^{+2} species with kinetic energies ranging from 50 eV to 35,000 eV for ablated carbon species.

Next, the target material was changed from graphite to polycarbon, and spectroscopic data were collected. The two distinct bumps present with the graphite target were not as pronounced when polycarbon targets are used. The overall species velocities were reduced as well. There also was a subtle shift in the measured species velocity maxim of about 100 km s^{-1} for $4\text{x}10^8$ W cm^{-2} to 70 km s^{-1} for 10^9 W cm^{-2} laser fluence. This may be due to melting of the polycarbon target, and subsequent degradation of local vacuum around the plasma plume. The resulting species curves are shown in Figure 3.1-2 for a polycarbon target:

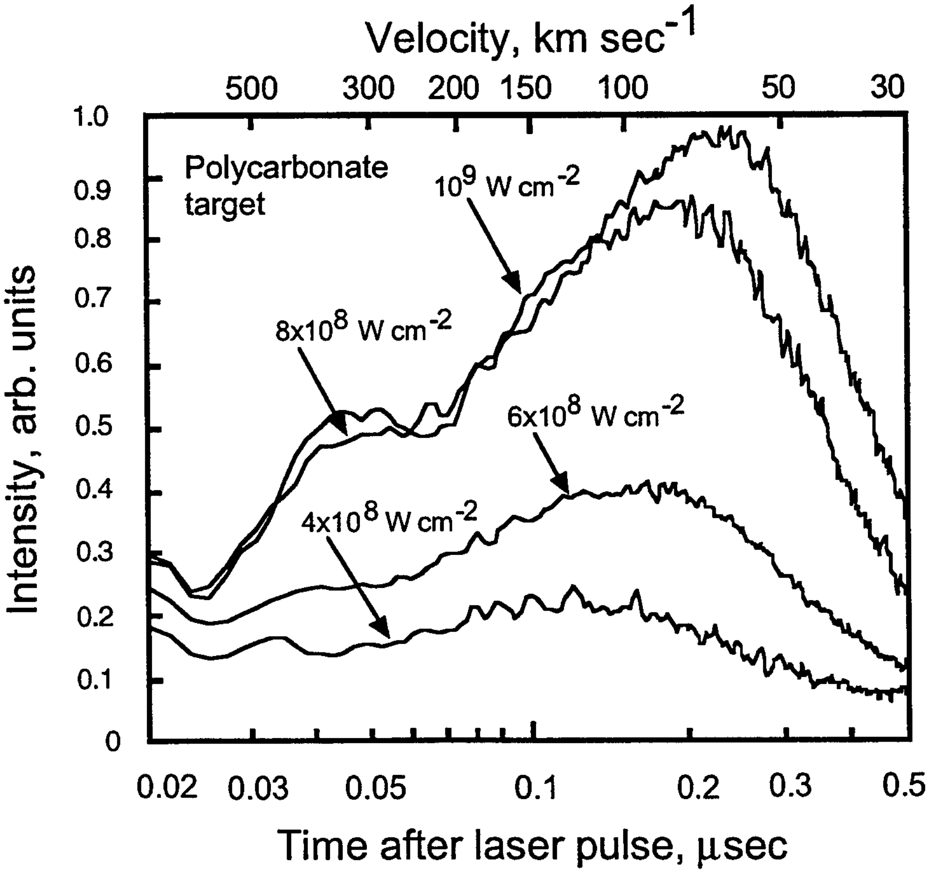

Figure 3.1-2. Emission spectroscopy waveforms for different laser fluences at 20 Hz pulse rate.

The graphite target intensities increased more dramatically with higher fluences. The opposite seemed to be the case for polycarbon targets. As laser fluence was increased from $8\text{x}10^8$ to 10^9 W cm^{-2}, the change in intensities was relatively minor for the polycarbon target, while for the graphite, it was most significant.

3.2 Plume Ion Density

Further experiments were performed with the ion probe to detect total plume ionization density. The ion probe was the same as described in the references. No modifications were done to the previous design. Data were collected simultaneously with spectroscopic curves. Several depositions were performed for both polycarbon and graphite targets. The integrated ion current is shown with respect to fluence in Figure 3.2-1.

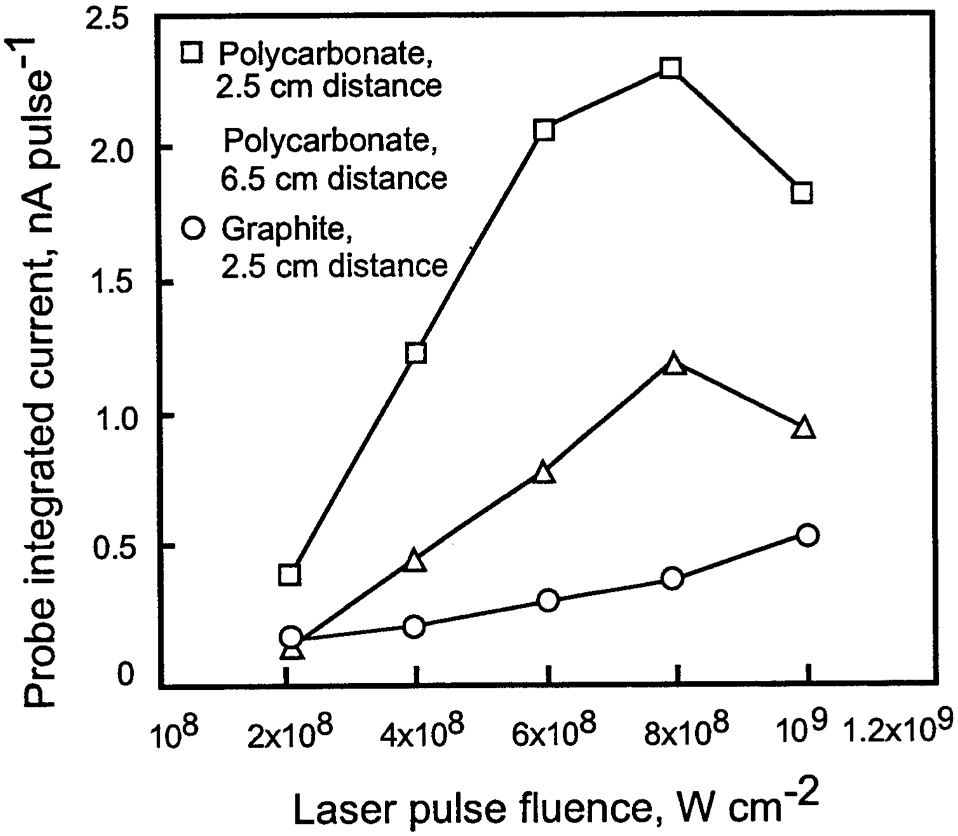

Figure 3.2-1. Plume relative ion intensity for different laser fluences and target materials.

As to be expected, ionization current increased with increasing fluence, although for polycarbon targets, a decrease was observed for laser intensities greater than 8×10^8 W cm^{-2}. The graphite target had a much lower plume ion current than the polycarbon target, with a factor of three difference. The graphite target did not appear to exhibit any saturation with increasing fluence. This saturation effect for polycarbon targets would coincide with the reduction in species as seen in the spectroscope data. It also follows that the graphite ion probe data increase most dramatically at the highest fluence.

3.3 Quartz Crystal Microbalance

As alluded to in the spectroscopic data, there seems to be a saturation effect occurring with the polycarbon target ablation at higher fluences. The total ion probe current also indicates this. Thickness data were also collected simultaneously during the depositions for polycarbon targets and is shown in Figure 3.3-1. Calculating a backward difference shows approximate thickness derivative, or growth rate. The growth rate for polycarbon increased exponentially up to 8x10^8 W cm^{-2}. Laser intensities greater than this showed a reduction effect as well, indicating either a reduction in ablation rate, a major change in quartz crystal temperature, or a discrete change in the mass and density of the film. Thickness changes such as this are attributable to the way the quartz crystal microbalance calculates thickness information, and are discussed extensively in Laube's Dissertation.

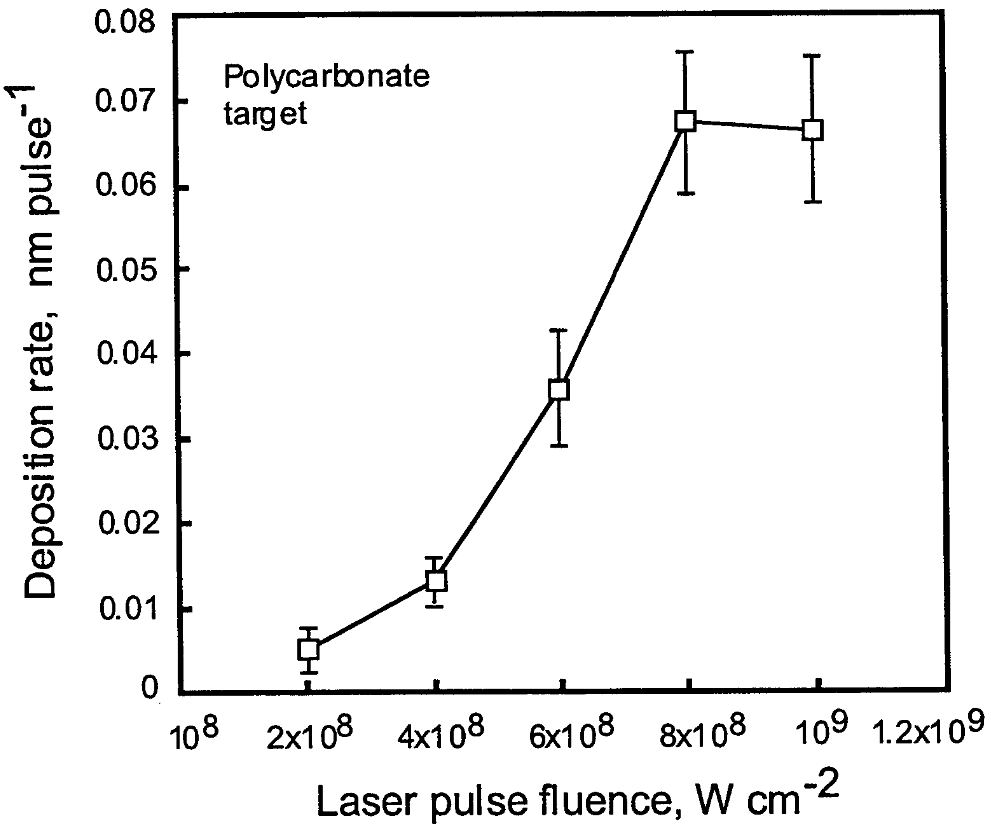

Figure 3.3-1. QCM deposition rate for different laser fluences at 20 Hz pulse rate.

4.0 *EX SITU* FILM ANALYSIS

4.1 Electron Energy Loss Spectroscopy

Ex situ analysis was performed on the resulting films. The data shown here is only representative of the work done in the references. Analysis was done by A. A. Voevodin that included Raman spectroscopy and micro hardness tests. Electron energy loss spectroscopy (EELS) was performed by J. Solomon of UDRI. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) was performed by S. Walck of SYSTRAN. This information was also presented in complete form in the references, which are attached to this document. The most significant detected result was the tribological data, combined with the EELS spectrum. EELS spectra are highly correlated to bond energies, and thus the material type.

As can be seen in Figure 4.1-1, a reduction in the p electron peak is noted for an increase in laser fluence for a polycarbon target. There is also a broad peak at around 27 eV, which has been associated to the presence of graphite in the thin film. When depositions are made with a graphite target instead of a polycarbon target, the p electron peak is also no longer present. There is also a shift in the broad peak from 27 to 36 eV, indicating a greater presence of sp^3 bonds.

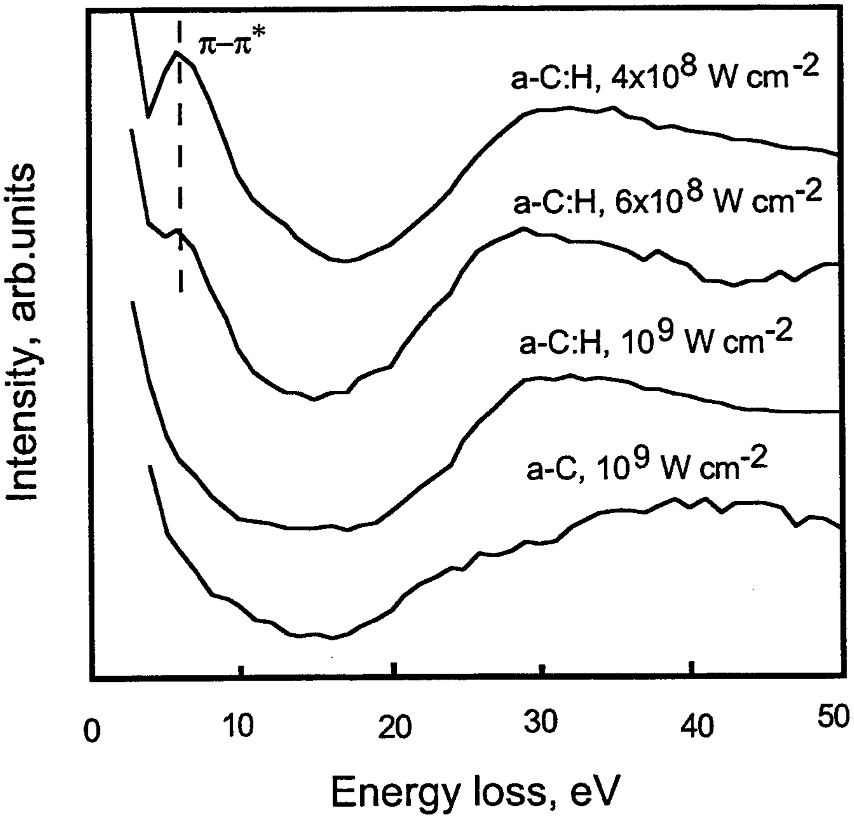

Figure 4.1-1. Electron energy loss for films produced with different laser fluences (J Solomon) .

From these results, it appears that films produced with high fluences and graphite targets yield films that have a high percentage of sp^3 bonds.

4.2 Raman Spectroscopy

Raman spectroscopy of carbon materials has become a common method of determining DLC film quality, due to the relative ease in which a Raman spectra can be obtained, combined with the distinct differences between the resulting Raman spectra of graphite, diamond and amorphous carbon. Recently, there has been extensive research in rationalizing possible relationships between Raman spectra and film structure of DLC films.

Ex situ Raman spectra sensing have been applied to DLC films produced by various deposition processes to diagnose the sp2 /sp3 ratio in deposited films. Some authors have also demonstrated the use of Raman as an *in situ* sensor and process diagnostic [14] by gated detectors. These diagnostic methods are usually based on the ratio of two Raman peaks, the disordered, or "D" peak, at 1360 cm^{-1}, and the graphite, or "G" peak, at 1575 cm^{-1}. These peaks are based on the assumption of a uniform spectral evolution from the diamond Raman spectra, with a combination of peaks, to the synthetic graphite Raman spectra, with a single peak at 1575 cm^{-1}. Unfortunately, other authors have shown that Raman spectra for various carbon based materials vary widely. [15] Consequentially, it becomes specious to assume a certain ratio of sp^2/sp^3 bonds by a Raman spectra.

Raman spectra can yield relative information about the deposited film, though. A distinct Raman fingerprint can be identified that corresponds to the existence of certain material structures that have been verified by other means. The relative information provided by the Raman spectra can be used in process control as an *in situ* sensor to determine if the process controller has achieved the desired film property.

Raman spectra from films produced by a graphite target and a polycarbon target are shown in Figure 4.2-1. The Raman signature from films produced with a polycarbon target (a-C:H) resemble peaks observed in Cuestra for subbituminous coal. Other authors have shown highly similar Raman spectra for physical vapor deposited DLC films [16] that were combined with micro indentation tests, yielding hardness to 20 GPa and Young's modulus of 300 GPa. Thus, the presence of DLC can not be surmised by Raman spectra alone. Other *ex situ* tests are needed, such as hardness and modulus tests. Once a combination of information from various analysis methods can be gathered, a material type can be surmised with greater confidence.

As shown in Figure 4.2-1, there is a decrease in the 1575 cm^{-1} peak in films produced with a graphite target. There is no indication of diamond spectra. The films produced by polycarbon targets have a strong 1575 cm^{-1} peak. There is also no indication of diamond Raman spectra. More analysis must be performed to determine the film composition.

4.3 Tribological Film Results

Other analysis includes applications specific tests of thin films. In the case of DLC applications for Air Force needs, tribological applications are a common goal. Hardness tests combined with Young's modulus tests provide direct indication of film quality as a tribological hard coating. Currently, 440C stainless steel has a hardness of 80 GPa. This steel is seldom used, even though it provides superior hardness and corrosion resistance. This is because the steel is expensive, heave, and brittle, due to the hardness. Natural diamond has a hardness of 100 GPa, and a Young's modulus of 800 GPa. Hardness tests using micro indentation methods are shown in Figure 4.3-1 for various loads.

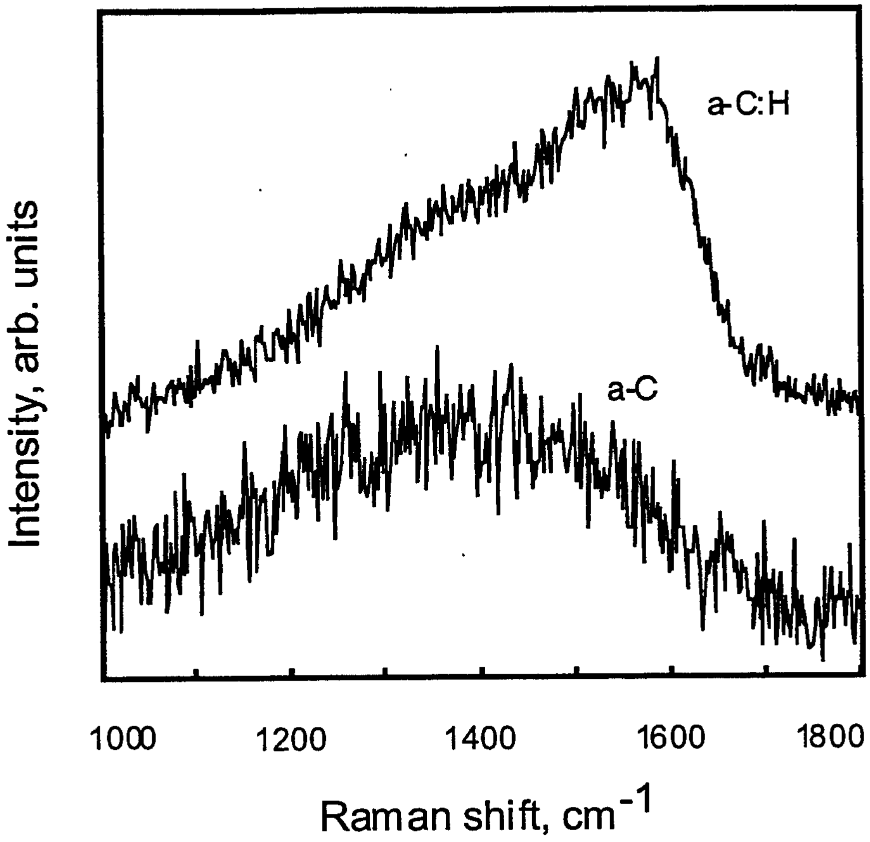

Figure 4.2-1. Raman spectra for films produced from polycarbon and graphite targets (N. McDevitt).

Fused silica was also tested and is shown in Figure 4.3-1 for reference. As can be seen, the hardness of films produced by PLD of an amorphous carbon target yielded hardnesses in excess of 80 GPa for a 1 mN load, exceeding hardnesses of the stainless steel substrate. This film is the same one that was shown in Figure 4.2-1 to have no Raman spectra. Unfortunately, the Raman spectra taken in Figure 4.2-1 was limited to the range of 1000 to 1800 cm^{-1}, precluding the observation of other Raman peaks.

Additional hardness tests were repeated for films generated from polycarbon targets with respect to laser fluence. These results are shown in Figure 4.3-2. Both hardness and Young's (elastic) modulus were measured. The films produced by PLD of the polycarbon target were much softer than the films produced with the carbon target, although an increase in fluence appears to increase film hardness. The Young's modulus also increased with increasing fluence. The saturation effects indicated by Figures 3.1-2, 3.2-1, and 3.3-1 appear not to have affected the film properties, except for deposition rate, even though ion density and plume constituent velocity both decreased when laser fluence exceeded $8x10^8$ W cm^{-2}.

The drastic increase in hardness is most likely due to the relatively fast ion speed observed in Figure 3.1-1 for a graphite target as compared to the slower speeds shown in Figure 3.1-2 for a polycarbon target. Increases in ion speeds detected by the spectroscope indicate resulting increases in film hardness. Thus, to generate hard DLC films, PLD of graphite targets are necessary.

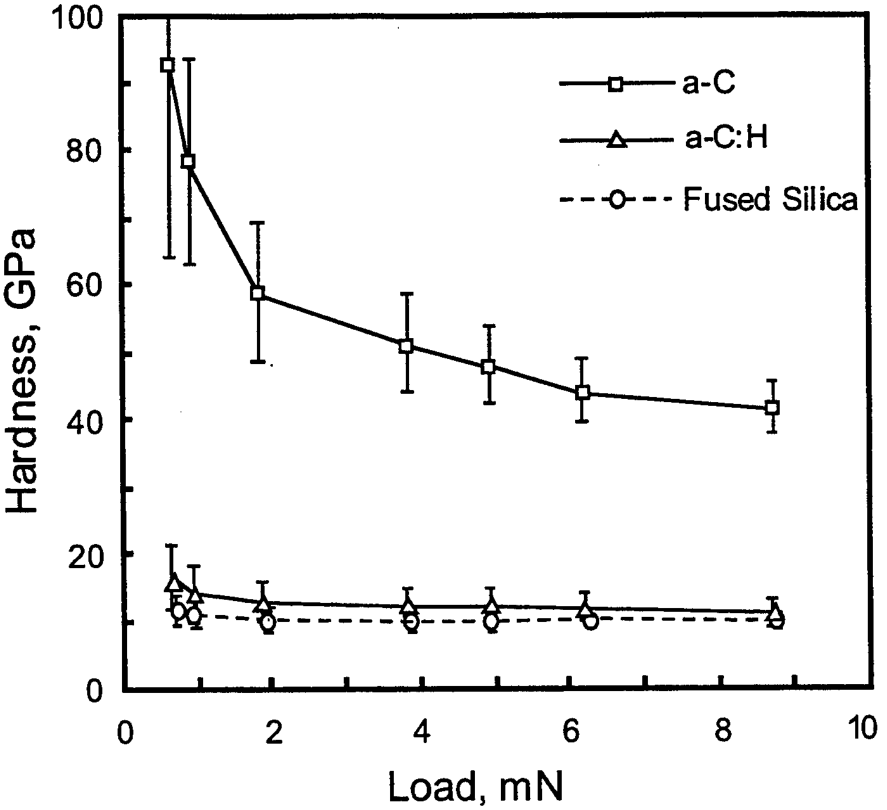

Figure 4.3-1. Hardness for films produced from polycarbon and graphite targets (A. Voevoedin)

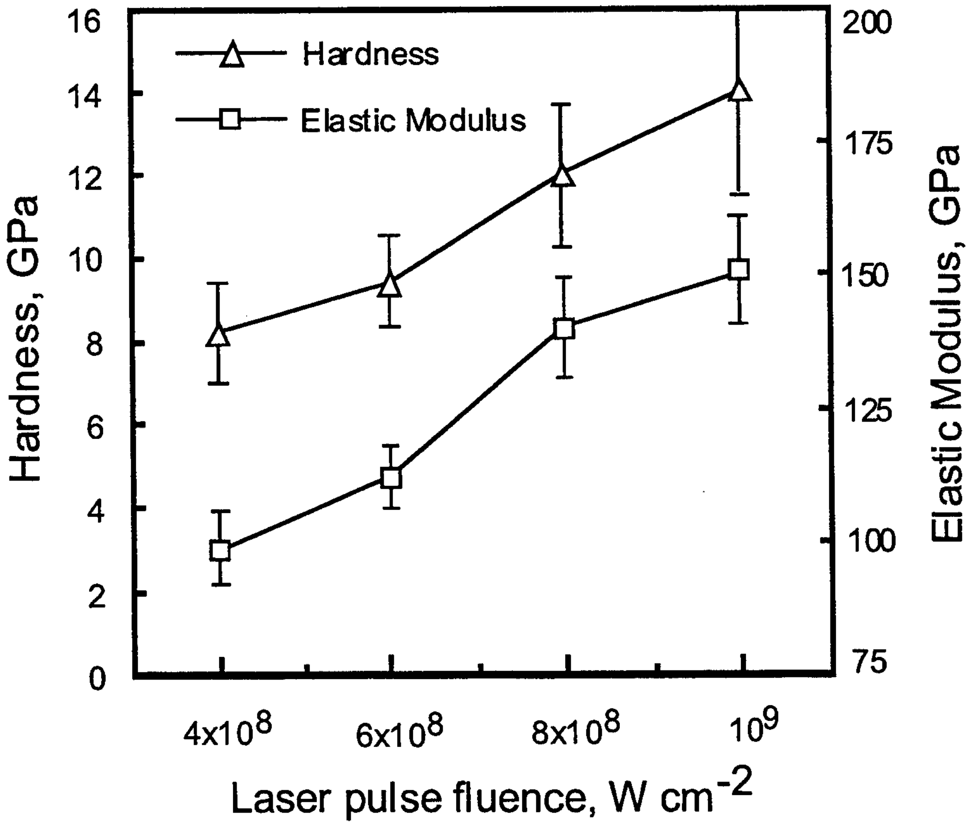

Figure 4.3-2. Hardness for films produced from polycarbon and graphite targets with different laser fluences (A. Voevoedin)

4.4 Technical Approach Conclusions

Data collected for DLC coatings made by PLD indicate that the chosen in situ sensors are capable of indicating the resulting material quality, although indirectly. The optical emission spectroscope shows that species velocity provides a direct indicator of the resulting sp^3 bond fraction in a DLC film. Evidence also indicates that laser fluence determines species velocity. Thus, it becomes possible to determine the sp^3 bond fraction in situ by monitoring the C^{2+} species velocity with the optical emission spectroscope.

There is also an interdependence on laser fluence and deposition rate, total plume ion density, and kinetic energy. These interdependencies strongly affect film composition, structure, and final thickness. A summary of these results is given here:

- LIF optical emission spectroscopy indicate that plume C^{2+} constituent species kinetic energy increases with laser fluence.
- Quartz crystal microbalance data indicate that the bulk deposition rate also increasees with laser fluence.
- Electrostatic ion probe data indicate that total plume ionizatoin levels increase with laser fluence.
- Film composition and structure are improved with increases in plume kinetic energy and total ionization level.
- Carbon targets yield films with superior tribological properties than polycarbon targets.

Based on these results, a closed loop PLD control system is proposed, which allows for adequate control of DLC film properties by *in situ* sensor diagnostics. This closed loop PLD control scheme can control film thickness and film stress by QCM data, species type by LIF spectroscopy, and ionization rate by electrostatic probe data. The in situ sensors can each provide information for a multiple input controller. The process controller can then be programmed with a recipe based on a film design. The film produced in this scenario can be homogeneous, heterogeneous, or a combination. A graphic indicating the general design of this controller is shown in Figure 4.4-1.

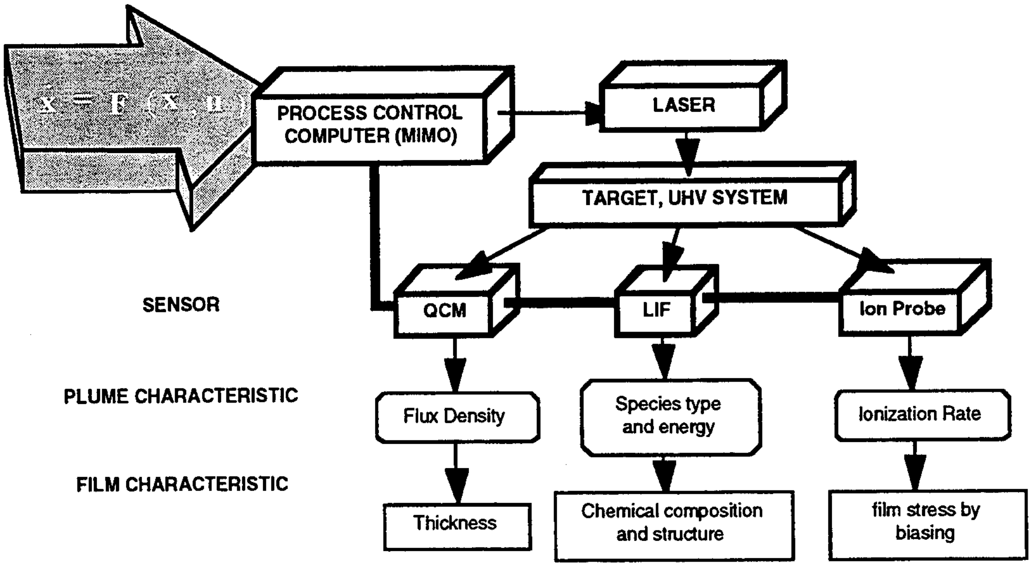

Figure 4.4-1. Proposed DLC process design controller.

This method of control is called "process design," due to the process having the ability of designing the film while the film is being created. A dynamica model of the proces is contained in the process control computer. This model has the form of:

$$\dot{x} = F(x,u) \text{ and } y = x$$

where:

$$x = \begin{bmatrix} t \\ v \\ d \end{bmatrix} \text{ and } u = e$$

where:

t - Bulk flux density from QCM sensor.
v - Carbon C^{2+} plume constituent velocity from LIF spectroscope.
d - Plume ionizatoin rate from electrostatic probe.
e - Laser energy density.

As data are collected in time, several points must be made in order that the process is modelled acurately. These are:

1.) The data must be sampled

Often, an assumption is made that the nonlinearities that exist in the actual process can be approximated by a linear product-sum of nonlinear functions. The matrix expression for PLD of DLC would then be:

$$\begin{aligned}
\dot{x} &= \begin{bmatrix} f_{11}(t,v,d) & f_{12}(t,v,d) & f_{13}(t,v,d) \\ f_{21}(t,v,d) & f_{22}(t,v,d) & f_{23}(t,v,d) \\ f_{31}(t,v,d) & f_{32}(t,v,d) & f_{33}(t,v,d) \end{bmatrix} \begin{bmatrix} t \\ v \\ d \end{bmatrix} + g(e) \\
&= f_{11}(t,v,d)t + f_{12}(t,v,d)v + f_{13}(t,v,d)d \\
&+ f_{21}(t,v,d)t + f_{22}(t,v,d)v + f_{23}(t,v,d)d \\
&+ f_{31}(t,v,d)t + f_{32}(t,v,d)v + f_{33}(t,v,d)d + g(e)
\end{aligned}$$

but there is no reasoning as to why this type of product-sum construction would be any more a better model for the PLD process than any other construction. A more general method would be to maintain the nonlinear function, and then approximate it by series expansion. Another technique would be to realize that the data was sampled in descrete time, and then model the process as a discrete approximation, like:

$$x_{k+1} = G(x_k, u_k)$$

This method would consist of a summation of weighted past values, or functions of weighted past values:

$$x_{k+1} = G(x_k, u_k) = a_1 t_k + a_2 v_k + a_3 d_k e_k + a_4 \sin(d_k) + \text{others...}$$

Unfortunately, it is difficult to choose the functions of weighted past values. A method of defining functions is needed. This method would use the data sets as methods of choosing the functions. There are numerous mathematical methods that exist for finding weights, but no methods of choosing functions of values. This area needs to be explored more completely.

5.0 RESULTS AND DISCUSSIONS

The establishment of a controller for PLD of DLC films was experimentally investigated. Additional findings indicate that there is a relationship between material characteristics and process parameters that greatly determine the quality of DLC films. New applications of DLC PLD thin films would benefit greatly from hard coatings with hardnesses greater than 80 GPa. The results of this research were also presented in two publications.

Conclusion

Transitioning PLD from the laboratory to the production environment will require implementation of novel process improvements. These improvements so far have been implementations of IPM hierarchical control, inexpensive sensor development, improved actuators, and complete process control. These areas of PLD improvement are driven by customer needs. Unfortunately, the current manufacturing culture is not willing to make the transition to PLD. A concerted effort to develop new PLD apparatus that can coat larger areas with superior materials is necessary.

Efforts exerted so far have been directed in identifying a specific niche that only PLD can fill. A niche such as DLC hard coatings on end mills will develop better manufacturing confidence in PLD. End mill machining applications, as well as other applications such as rain erosion resistant coatings, are not currently filled by any other deposition method. New applications that encompass a broader range of uses, such as optical thin films, show the most near-term promise of PLD use in civilian as well as military customer needs.

6.0 RECOMMENDATION

Pursuit of PLD as the deposition process for the year 2000 will require improved processing techniques, control and system design, combined with a more complete understanding of dominant first principles in laser ablation. A reduction in subprocess disorder by process automation and control has already been shown to be one way of modifying molecular structures in tribological thin films. Future efforts have been directed at defining target applications immediately beneficial to the Air Force. Improvements in processing, based on material molecular structure, form the foundation that ultimately will be molecular structure control with PLD.

Likewise, PLD implementation in manufacturing will only come about by a consistent push to identify a niche application of PLD, combined with a continuous effort in making the process a manufacturing entity, and not a laboratory curiosity. In order to bring this about, the real improvements in PLD deposition need to be founded in manufacturing environment needs and problems. Continued process development, combined with applications research is recommended as the best plan to accomplish PLD transition.

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