FINAL REPORT ON RESEARCH ON OPTICAL COATINGS

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(Dr. Owen Lewis, DOE, Solid State Program Manager)

by

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FINAL REPORT FOR DEPARTMENT OF ENERGY
Contract Number DE-AI08-79DP40094
OPTICAL COATINGS
W. Haller, D. Sanders, E. Farabaugh

ABSTRACT:

The construction of an apparatus designed to prepare thin films by physical vapor codeposition is described. This apparatus permits the characterization of the substrate prior to deposition using electron spectroscopy for chemical analysis, auger electron spectroscopy, secondary ion mass spectroscopy, and ion scattering spectroscopy. The systems permits deposition of thin films by resistively heated boats and electron beam evaporation sources which can be operated simultaneously. The resulting films can be characterized using the above surface analysis techniques without exposure to the atmosphere using a transfer mechanism described in the report.

KEY WORDS:

Thin Films, High Energy Laser Coatings, Optical Coatings, Codeposition, Surface Analysis of Thin Films.

FINAL REPORT: Project "Optical Coatings"

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INTRODUCTION:

Presently, the weakest elements in high energy laser systems used for both laser fusion research and military applications are the antireflection coatings which must be present on some of the optics. When subjected to high energy laser pulses, these films absorb energy from the laser beam and spall off from the glass surface thereby rendering the underlying optical elements useless. In spite of this difficulty, the basic mechanisms which lead to this failure are not understood. One of the reasons for this lack of understanding is the inability of optical coating manufacturers to produce antireflection coatings with uniformly high laser damage thresholds. This apparent lack of control over the processes used to produce thin films results from incomplete understanding of the basic film forming processes and their ultimate influence on laser damage resistance. Films are normally produced in less than ultra-high vacuum conditions on substrates with poorly characterized surfaces. In addition, the substrates are heated to uncertain temperatures in order to reduce residual stresses to levels which prevent spalling of coatings. As a result, films produced by the same manufacturer have widely varying damage thresholds. If the causes of films having poor performance could be identified it would be possible to substantially increase the reliability of coatings and to find new coatings having

substantially higher resistance to high energy laser damage.

One potential cause of film weakness is the existence of interfaces such as grain boundaries in polycrystalline films. In order to evaluate the effect of these boundaries, an attempt was made to construct an apparatus designed to produce glassy coatings by coevaporation of a glass forming dopant with a normally polycrystalline host. The laser damage resistance would then be evaluated as a function of the amount of the glass forming second phase which would in turn be a function of the extent of crystallinity of the coating. In more distant experiments, gradient index coatings could be produced which would allow the placement of the high energy electric field due to the intense laser light away from the interface between the coating and the underlying optical component. In addition, the system would improve the basic understanding of the processes which lead to thin film formation by permitting in-situ analysis of the glass substrate surface prior to deposition, the thin film surface after deposition, and a depth profile across the interface between the film and its underlying substrate. The deposition subsystem would be designed to achieve greater control over the parameters which determine the ultimate thin film structure. Such parameters include the substrate temperature, the residual gas pressure the deposition rate and the cleanliness of the substrate prior to deposition. Finally, the deposition system would have provision for multiple sources to be operated simultaneously in order to produce the glassy films, the gradient index films and films composed of mixed solid solutions of components having widely varying vapor pressures.

PURPOSE OF PROGRAM:

The purpose of this program was to design and initiate construction of a facility designed to permit the preparation of films by codeposition with subsequent analysis under ultra-high vacuum conditions. At the time of this writing, this goal has been substantially achieved with certain exceptions to be discussed in the course of this report. The work consisted of the following:

1. Design of a deposition/analysis system having the following operational criteria:
 - a. Ability to produce glassy thin films by simultaneous co-deposition from multiple electron beam and resistively heated evaporation sources.
 - b. Provision for introduction of reactive gases such as oxygen during deposition to alter the chemical composition of the film and/or maintain stoichiometry.
 - c. Monitoring of the molecular beams by both mass spectrometer and quartz crystal monitors.
 - d. Ability to bake the system to remove gases adsorbed on the vacuum chamber walls.
 - e. Vacuum pumping designed to provide a combination of high pumping speed, resistance to damage by particulate matter in the chamber, and freedom from backstreaming of vacuum pump oil.
 - f. Heating and measurement equipment to permit the control of substrate temperatures over the range of 100 to 400 °C.
 - g. Ports to permit observation of optical thickness change due to film buildup in both reflected and transmitted light.

- h. Ability to transfer samples from the deposition chamber to the analysis chamber without disturbing the vacuum in either.
 - i. Analysis chamber having facilities to analyze formed films by Secondary Ion Mass Spectrometry (SIMS), Auger Electron Spectroscopy (AES), Electron Spectroscopy for Chemical Analysis (ESCA), and Ion Scattering Spectroscopy (ISS).
 - j. Rapid Energy Loadlock to permit up to six samples to be introduced into the vacuum system without disturbing the vacuum in either the deposition chamber or the analytical chamber.
 - k. Provision in the loadlock for glow discharge or sputtering etching of substrates prior to deposition of thin films.
 - l. Computer automation of both surface analysis system and deposition source rates.
2. Technical specification writing based on information obtained from literature and vendors.
 3. Writing of orders, sole source specifications and other papers required by government procurement process.
 4. Review of bids.
 5. Preparation of room (power connections, floor covering, recirculated cooling water)
 6. Construction of subsystems and interconnection to permit transfer of thin films between the loadlock carousel and the surface analysis and deposition chambers.
 7. Evaluation of the ability of the overall system to produce amorphous thin films.

In the status report for this contract dated Sept. 6, 1979, a detailed description of the difficulties encountered in construction of this facility was given. Because of these difficulties, the anticipated completion of the facility was delayed by roughly one year, so that even at the time of this writing, the facility does not yet have its complete design capability. In spite of this, we have been able to produce mixed oxide coatings by coevaporation from either resistively heated boat sources or from electron beam evaporation sources. This report will be restricted to a description of facility which has thus far been completed. Specific experiments on the MgO-SiO_2 system will be discussed in the final report for contract number DE-AI08-79DP40095.

DESCRIPTION OF THE GLASSY FILMS FACILITY

As expected, work during this contract period was largely devoted to the design and construction of an experimental facility which will ultimately have the capability described earlier. This apparatus consists of a surface analysis system purchased from Inficon Leybold Heraeus, Inc. coupled to a NBS designed deposition chamber by a carrousel load lock chamber. The configuration of this facility is pictured in Fig. 1. It consists of three subsystems which will be described individually in more detail:

1. The Deposition Subsystem
2. The Carrousel Loadlock, Cleaning and Environmental Treatment Chamber
3. The Surface Analysis Subsystem

The Deposition Subsystem

The deposition chamber consists of a stainless steel vacuum chamber with copper seal flanges to permit an ultimate vacuum after baking to 250 °C of 1×10^{-10} mbar. The chamber is pumped by two helium cycle cryopumps, each having pumping speeds of 1600 liter/sec for nitrogen. These pumps are of a special design to permit the required ultimate vacuum. They are oil-free and are not damaged by particulate matter produced during the deposition process. Currently, the deposition chamber contains a triple source evaporation module which permits simultaneous evaporation of materials having widely different vapor pressures. The chamber contains a water-cooled baffle directly over the source compartment to protect the upper vacuum chamber from contamination and excessive heating during the evaporation process. A liquid nitrogen shroud is suspended directly under the deposition position (see Fig. 1) to trap material which rebounds from the substrate. Individual shutters have been placed directly over each source and, in addition, a shutter wheel has been constructed directly under the substrate position to shield various combinations of the substrate and the deposition monitors.

Initial attempts were made to control the rate of deposition using a quadrupole mass filter positioned at the plane of the substrate. These efforts were successful when metal films (iron and aluminum) were deposited using resistively heated boat sources. We experienced difficulties however, in monitoring dielectric coatings, presumably due to charging of the ionization stage of the mass filter. Currently, we are using quartz crystal monitors which are narrowly shielded so that each faces a single evaporation source. These monitors produce a control signal which is proportional to the condensation rate of the source the crystal faces and have been used in

conjunction with process controllers to apply servo control to the deposition rate of each individual source.

In order to produce strain-free thin films it is necessary to heat the substrates upon which the films are to be deposited. The first design for heating the substrate involved bringing a copper block heater in contact with the backside of the glass substrates. A thermocouple was attached to the side facing the sources in order to measure the film temperature. Another thermocouple was imbedded in the block and the readings of the two thermocouples were correlated for any given heater setting. Using this design, we were only able to obtain a maximum temperature of 135 °C. Currently, radiant quartz lamp heaters have been installed which irradiate the front surface of the substrate. This increases the substrate heating capability to 400 °C. Direct measurement of the thin film surface will be accomplished using a narrow spectral range infrared thermometer. A control signal from this monitor can also be used to control the substrate temperature via a process controller.

While optical thickness monitors have yet to be constructed, the fixturing for mirrors and windows have already been installed as part of the deposition chamber design. Currently, the optical thickness is estimated from the actual thickness measured using the quartz crystal monitors.

The bakeout system for the deposition chamber has been 85% completed at the time of this report. Without bakeout the base pressure of the system is 1×10^{-8} mbar. This pressure increases to 5×10^{-6} mbar during deposition due to source material dissociation.

The Carrousel Loadlock, Cleaning and Environmental Treatment Chamber

A carrousel based loadlock has been designed and constructed in order to permit introduction of up to six samples into the deposition or analysis chamber without disturbing the vacuum of either. This is an important design feature because of the time involved in baking those larger systems to produce ultra-high vacuum conditions. In addition, it is useful to be able to keep the source material under vacuum at a temperature slightly below the point where significant vaporization occurs. This tends to outgas dissolved gases and inhibit source contamination. The configuration described here permits such preheating of the source material because the deposition chamber is under vacuum while the substrates are being introduced into the carrousel loadlock. The loadlock assembly is carefully designed to prevent oil contamination from its pumping system. A molecular-sieve oil-trap, for instance, is positioned between the turbo pump and its backing pump in order to prevent any possible chance of oil backstreaming. Ordinarily, the action of the turbomolecular pump alone should be sufficient, but the sieve provides additional protection.

Once the loadlock has been evacuated, oxygen is introduced into the chamber and a glow discharge is established in order to clean the substrates. The chamber is then re-evacuated to ultra-high vacuum conditions and the valve to the deposition chamber opened to permit the positioning of the 120 cm linear manipulator to the transfer position. One substrate holder is then transferred unto the central manipulator using a smaller linear manipulator. At this point, the substrate can be transferred into the analysis chamber for evaluation of its cleanliness. Once the substrate is evaluated, the central manipulator is repositioned to the deposition stage and rotated for the deposition process. While deposition is taking place, the loadlock is valved off to prevent possible particulate intrusion into the turbomolecular pump of the loadlock.

The Surface Analysis Subsystem

Due to favorable circumstances, the National Bureau of Standards was able to acquire a surface analysis system having other analytical techniques in addition to ESCA. This system is pictured as part of the overall facility in Fig. 1. The surface analysis subsystem consists of two interconnected but separately pumped vacuum chambers. The preparation chamber on the far right is part of a rapid entry loadlock (different than the carrousel loadlock) for introduction of samples for analysis independent of the thin film effort. It allows deposition of metal films for ESCA standard work using either direct current sputtering or thermal evaporation. The preparation chamber is pumped using a 450 liter/sec turbomolecular pump and achieves an ultimate base vacuum of 1×10^{-9} mbar after baking to 250 °C.

To the left of the preparation chamber is the main analytical chamber. This is pumped by a 450 liter/sec turbomolecular pump, a liquid nitrogen baffle, and a titanium sublimation pump. It typically reaches an ultimate base pressure of 5×10^{-11} mbar. Provision is made in this chamber for all of the experimental techniques listed in Table 1, in addition to the ability to carry out rastered sputtering for depth profiling. These available techniques include ESCA, angle resolved ESCA for improved surface sensitivity, Secondary Ion Mass Spectroscopy (SIMS), Ion Scattering Spectroscopy (ISS), and Auger Electron Spectroscopy (AES). The three added techniques should prove extremely useful in the interpretation of the ESCA spectra because they provide complimentary information about the same area of the sample surface. The ISS technique, for instance, permits quantitative analysis of the first atomic layer of the sample surface. This layer would be the most susceptible

to changes in composition during possible reactions between the thin film and its environment. The ISS technique involves measuring the energy of inelastically backscattered primary sputtering ions using the same hemispherical electrostatic energy analyser as is used for electrons when carrying out AES and ESCA, but electrically biased in the opposite sense.

The SIMS technique, on the other hand, involves the measurement of the ions which are sputtered from the sample surface by an ion beam using a specially designed prefilter quadrupole mass spectrometer arrangement. This technique is extremely sensitive for some ions and is unique in its ability to analyze surface hydrogen ions.

The ESCA technique permits quantitative analysis of all elements except hydrogen and in addition provides information concerning chemical bonding in the form of shifts in peak location. This measurement normally involves sampling X-ray or UV induced photoelectrons from a depth of as much as 30 angstroms from the surface. This surface sensitivity can be increased still more by tilting the sample with respect to the analyzer optics. In this mode the depth of analysis can be reduced to the top few atomic layers.

Computer Automation

The overall performance of the entire Glassy Films Facility will be increased still further with the introduction of computer automation. At the time of this writing, a Hewlett-Packard System 1000 computer system has been purchased and delivered. In addition, the interfaces and software between the Inficon Leybold Heraeus Surface Analysis Subsystem and that

computer have been ordered and await internal procurement procedures. Once the latter has been delivered the entire surface analysis process will come under complete computer control and will result in a greatly improved rate of data acquisition.

Future plans involve the automation of the deposition process to permit computer controlled variations in the index of refraction of the thin films produced across their depth. Such variations should permit tailoring of films having greatly improved resistance to damage by high energy laser pulses.

REPORTED RESULTS:

The series of experimental results which have been thus far obtained are reported in the final report for contract number DE-AI08-79DP40095. In addition, an abbreviated description of the experimental apparatus has been accepted for publication in the Journal of the American Vacuum Society Jan-Feb 1981.

Table 1

Surface Analysis Techniques

Technique	In	Out	by:	Analysis Depth of	Advantages	Disadvantages
Auger Electron Spectroscopy (AES)	Electrons	Electrons	Energy	4-20 Å	High Rate/ Spatial Resolution	Charging of Dielectrics/ Quantitative Analysis Difficult
Ion Scattering Spectroscopy (ISS)	Primary Ions	Primary Backscat. Ions	Energy	1-3 Å	Interferences Minimal/Depth Resolution	Difficult Interpret./ Slower Rate
Secondary Ion Mass Spectroscopy (SIMS)	Primary Ions	Sample Ions	Mass	3-10 Å	High Sensitivity	Strong Interfere.
Normal X-ray Photoelectron Spectroscopy (XPS or ESCA)	X-ray UV	Photo Electrons	Energy	15-30 Å	Quantitative Analysis/ Charge Compensation Possible	Slower Analysis Rate
Angle Resolved XPS	X-ray UV	Photo Electrons	Energy	5-10 Å	Quantitative Analysis/ Charge Compensation	Slower Analysis Rate

FIGURE CAPTIONS

Fig. 1

Schematic of thin film facility. Items numbered are:
(1) titanium sublimation pump; (2) detector for transmitted light; (3) manipulator for stressing films; (4) manipulator for substrate heater; (5) liquid nitrogen-cooled shroud; (6) 1800 liter/sec cryopump (10 inch gate valves not shown); (7) light source; (8) water cooled shroud; (9) three resistively heated evaporation sources; (10) detector for reflected light; (11) 1.2 m magnetic linear manipulator; (16) shutter wheel; (17) all-metal bakeable isolation valves; (18) carrousel rotation manipulator; (19) sample transfer manipulator; (20) 220 liter/sec turbomolecular pump (butterfly throttle valve not shown) (21) sorption pumps for roughing; (22) quadrupole mass spectrometer (SIMS); (23) X-ray source (ESCA); (24) electron multiplier; (25) particle energy analyzer (ESCA, ISS, AES); (26) charged particle optics; (27) electron gun (AES); (28) ion gun (ISS, SIMS); (29) loadlock chamber; (30) gas mixing manifold; (31) liquid nitrogen baffle and titanium sublimation pump; (32) 450 liter/sec turbomolecular pumps; (33) roughing forepumps; (34) sample position for analysis; (34) quadrupole mass spectrometer.

DEPOSITION CHAMBER

ANALYTICAL CHAMBER