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FINAL REPORT ON GLASSY THIN FILMS

by

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National Bureau of Standards
Washington, D.C. 20234

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ABSTRACT:

This report describes the initial results of a long term program to study order-disorder phenomena in dielectric thin films. To achieve this overall goal, an apparatus was constructed to permit the co-deposition of a glass-forming additive such as SiO_2 in a polycrystalline matrix film such as MgO . The extent of crystallinity of mixture films in the MgO-SiO_2 system was determined using techniques developed for X-ray powder diffraction. With this approach, it was determined that the addition of SiO_2 in concentrations less than 20 mass % has a relatively small influence on crystallinity. On the other hand, at concentrations greater than 25 % SiO_2 causes the mixture film to become completely disordered.

Key Words: Thin Films, Order-Disorder, MgO-SiO₂, Co-deposition,
Mixture Films.

FINAL REPORT: Project "Glassy Thin Films"

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INTRODUCTION:

Optical antireflection coatings used in high energy laser systems represent the limiting factor determining overall system performance. The exact mechanism leading to destruction of such coatings by the high electric fields produced by high energy laser pulses is not yet well understood. It is not yet clear, for instance if such damage results from defects at interfaces between the coatings and their underlying optical element surfaces, absorption and/or scattering at grain boundaries in polycrystalline high index components, or from intrinsic defects in the optical coatings themselves. The last effect also leads to their higher optical absorption in comparison to glass fiber optical waveguides.

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The purpose of the present study was to initiate a research program to determine if amorphous thin films have inherently greater laser damage thresholds than their polycrystalline counterparts. In order to produce these films under well characterized deposition conditions, it was necessary to design and construct an apparatus which permits codeposition of thin films from multiple sources. In the simplest case, one source would supply the polycrystalline base composition, while another would permit the simultaneous evaporation of a second glass-forming dopant. The description of the apparatus is discussed in detail in the final report for contract # DE-AI08-79DP⁴/0094. In this report, some preliminary results are described for the system MgO-SiO_2 , which were carried out to determine the amount of glass forming dopant that would be necessary to produce an amorphous film. In addition, it was necessary to establish a technique to evaluate the extent of disorder of optical coatings prior to laser damage evaluation. The latter procedure is also described in this report.

THE GLASSY FILM FACILITY:

The system used to carry out this study is pictured in Fig.

1. It consists of four interconnected but separately pumped vacuum chambers. Substrates for deposition are first mounted in stainless steel substrate holders, positioned on a carousel in the loadlock chamber (Fig. 1-B) and cleaned by oxygen glow discharge. This procedure can be done while chamber B is isolated from both the deposition chamber (Fig. 1-A) and the surface analysis chamber (Fig. 1-C). Once the substrates are cleaned and a good vacuum achieved in chamber B, valve 17 between chambers A and B is opened, the central magnetic linear manipulator 11 is moved into chamber B, and one substrate can be transferred onto the manipulator. At this point the substrate can be analyzed for possible surface contamination by opening valve 17 between B and C and transferring the substrate to the analysis position (#34 in Fig. 1). Once the substrate surface is characterized, it is transferred to the deposition chamber B and heated by conduction using a copper block heater. (As discussed in the final report entitled "Optical Coatings," the block heater was not capable of producing substrate temperatures over 135 C. The current heater design therefore uses a quartz lamp heater directly over the sample and is able to produce temperatures in excess of 500 C.) The results reported here, however, were obtained using the copper block heater.

The analysis of the films for cleanliness was accomplished by transferring them in their freshly prepared state to the surface analysis system for ESCA measurement without leaving the vacuum. Films to be evaluated for extent of crystallinity were transferred to the loadlock for storage until an X-ray analysis could be made using the procedure to be described shortly.

In order to demonstrate the performance of this system, ESCA spectra were measured on freshly deposited films which were prepared using the electron beam module and subsequently transferred under vacuum into the surface analysis facility. Fig. shows spectra of SiO₂, MgO, and a MgO-SiO₂ mixture film. In these broad scans, the carbon peak at 970 eV kinetic energy is negligible, indicating the films are free from carbon contamination. In addition, the absence of Si peaks in the MgO films and vice versa demonstrates the absence of cross contamination between e-beam sources.

THE GLASSY FILM EXPERIMENT:

Magnesium oxide and MgO-SiO₂ mixed films of varying composition were evaporated in vacuums ranging in value

from 7×10^{-6} to 2×10^{-5} mbar using electron beam heated sources. The total deposition rate was 7 angstroms/sec, the value determined by summing the readings of two quartz crystal monitors each shielded to view its own source. The desired film composition was achieved by controlling the deposition rate of each source independently. The substrates were cut from microscope slides, washed in ethyl alcohol, and loaded onto the carousel in the loadlock chamber. Substrates were next transferred to the deposition chamber, and heated to 135 C prior to deposition of films of 4500 angstroms thickness. After the films were deposited, the substrates were transferred to the surface analysis system for ESCA analysis and then to the carousel for storage prior to X-ray evaluation of crystallinity.

For the latter, monochromatized Cu radiation from a fine focus (0.4 mm x 12 mm) tube irradiated a 15mm x 17 mm area of the thin film. The resulting diffraction pattern was recorded at 1/4 deg. 2 theta/min using a theta compensation lithium drifted silicon detector. Fig. 1 is a typical diffraction pattern from a 4500 angstrom thick 100% MgO film. Swanson and Tatge (1) give the (200), (220) and (420) as the three strongest lines. The 100% MgO diffraction patterns reproducibly show the (111) to be the strongest reflection followed by the (220) and (220), demonstrating that the 100% MgO films have a decided (111) preferred orientation. Mixed MgO-SiO₂ films also show the same (111) preferred orientation effect. Adding up to 20% SiO₂ to the MgO results in a film whose diffraction pattern has a strong (111) peak and vanishingly small (200) and (220) peaks. Addition of 20 % or more of SiO₂ results in an apparently "glassy" film whose diffraction pattern has no features other than a wide diffuse hump around 25 Deg. 2 theta.

The effect of addition of SiO₂ to the MgO film was investigated by comparing the integrated intensity of the (111) peak as a function of the added SiO₂. The integrated intensities were obtained from the area under the various (111) diffraction peaks. The areas were measured from the diffraction pattern itself by: (1) weighing the cut area under the curve from the diffraction pattern or by numerical integration. Fig. 3 shows the results of these measurements. They reflect the effect of addition of glass forming SiO₂ on the crystallinity of the MgO films as indicated by the areas under the (111) peaks. The plotted values are the average of measurements on

several films of each composition. It can be seen from this plot that the crystallinity decreases sharply with very small additions of SiO₂, forms a plateau indicating constant crystallinity till 20% is reached, and then drops sharply to an apparently completely amorphous structure with silica additions greater than 25 %. While these results are still in a preliminary stage, we believe that the initial change represents a chemical disruption similar to that which causes the sharp drop in liquidus temperature of MgO-SiO₂ solutions. The plateau suggests that the effect of such a chemical disruption on crystallinity is constant until 20 % silica is reached. At that point geometric effects are expected (2) which destroy the overall long range order in the films. This speculation is based on preliminary ESCA scans of the oxygen 1S peak which is seen to shift with small additions of less than 5% SiO₂ and subsequently remain constant for as much as 50% SiO₂ even though there is an obviously significant structural change occurring at 20% SiO₂ as evidenced by the X-ray results. Problems with reproducibility of ESCA results will require repetition of the measurements using system design modifications which permit better control of the substrate temperature during deposition.

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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 bakable isolation valves; (18) carousel 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) load lock 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.

Fig. 2 Broad scan ESCA spectra for freshly prepared thin films of:
a) 100 % SiO₂; b) 50% SiO₂, 50% MgO; c) 100% MgO

Fig. 3 Plot of area under (111) diffraction peak as function of concentration of SiO₂.

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