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OCULAR PROTECTION FROM LASER HAZARDS

FINAL, PHASE I REPORT

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NOVEMBER 1990

Supported by

U.S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21702-5012

Contract No. DAMD17-90-C-0083

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Willow Grove, Pennsylvania 19090

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REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this report is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Project Room (0152), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE November 1990		3. REPORT TYPE AND DATES COVERED Final, Phase I
4. TITLE AND SUBTITLE Ocular Protection from Laser Hazards			5. FUNDING NUMBERS DAMD17-90-C-0083 65502A 3P665502M802 CA DA335676	
6. AUTHOR(S) John J. Walls, Jr. Karl H. Guenther				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Evaporated Coatings, Inc. 2365 Maryland Road Willow Grove, Pennsylvania 19090			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Medical Research & Development Command Fort Detrick Frederick, Maryland 21702-5012			10. SPONSORING MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION AVAILABILITY STATEMENT Approved for public release; distribution unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Thin films, today widely used in numerous applications including optics, electronics, and surface protection, are commonly deposited by a variety of physical vapor deposition (PVD) methods. Standard PVD techniques produce films with inherent weakness of their optical and mechanical properties because of their typical columnar microstructure, which is a result of the low mobility of the condensed atoms or molecules on the substrate surface. This is particularly true for coating of plastics, when the substrate temperature needs to be kept low (around ambient). REACTIVE ION PLATING DEPOSITION (RIPD) is an innovative technique which densifies the growing thin film by enhanced surface mobility as well as by continuous ion bombardment, therefore resulting in durable, well adhering thin films at relatively low substrate temperatures. This technique will be used for the fundamental investigation of RIPD as well as for its production-oriented application. The results of the Phase I effort are very encouraging. Several different single layer coatings and hybrid multilayer coatings were successfully deposited on polycarbonate ophthalmics using the RIPD process.				
14. SUBJECT TERMS Thin films; Reactive ion plating deposition; Plasma process; Protective coatings			15. NUMBER OF PAGES	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT	

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INTRODUCTION

The current technologies used to provide "Laser Eye Protection" (LEP) are thin film multilayer reflective rejection filters, absorption filters and holographic filters. Each of these approaches have their good and bad points. The multilayer rejection filters have been used with limited success on polycarbonate surfaces. Their limitation is related to the film structure of the deposited films as well as the uniformity of the coating on curved shapes. This limitation affects both the durability and the optical properties of the deposited multilayer. Their major benefit is the high optical transmittance that can be achieved without any significant absorption characteristics. The absorbing type filters have very limited use because of their broad band rejection properties. This severely affects the scotopic/photopic transmittance as well as the field color neutrality. Absorption type filters can be used for rejecting spectral regions outside of the visible spectrum as long as there is no significant visible absorption properties. The holographic filters have very good optical characteristics, but have high susceptibility to thermal effects and must be protected with a cover plate due to their poor durability.

One key problem associated with the standard Physical Vapor Deposition (PVD) process is the film porosity. Electron microscope investigations of fractured edges of thin films revealed that many metals and most dielectrics form thin films with columnar microstructure. A major research/development thrust in

various areas of thin film applications, including electronics, optics and surface protection, is geared towards the densification and homogenization of the microstructure of thin films, in order to makethem "bulklike". Numerous researchers have spent their efforts in improving abrasion and erosion resistance by way of densifying the thin film microstructure. Most of these efforts had some limited success. In particular, depositing thin films on substrates at relatively low temperatures (room temperature or moderately above) is one of the limitations for many processes, lack of versatility for either the thin material selection or substrate size or shape another.

The technology approach chosen for the Phase I effort is a relatively new process called reactive ion-plating deposition (RIPD). RIPD appeared as a versatile method of producing hard thin film coatings with bulk-like properties for a variety of chemical compounds. These include nitrides and carbides for metallurgical application, and oxides for optical coatings. While ion-plating deposition of metallurgical coatings may still employ substrate temperatures of 400 to 500 degrees C, RIPD of oxide coatings operates at about 100 degrees C. The capability of depositing dense, hard oxide thin or thick films at such a low temperature is advantageous for all applications where the substrate does not allow for the typical temperatures of 300 to 500 degrees C used with other PVD processes. Therefore, RIPD is fully compatible with most optical materials, including classes with a low softening point. One application of RIPD which had not been fully explored to date is the coating of plastics.

The Phase I effort was directed toward demonstrating that this process can be used to deposit reflection rejection coatings on polycarbonate material. The significance of providing multilayer rejection coatings on polycarbonate material, using the RIPD process, is that uniform, durable and optically efficient LEP eyewear will be possible. The hybrid approach of optically efficient polycarbonate IR absorbers with the multilayer coatings will provide ballistic protection and multiline LEP for the visible and NIR spectral region. The significance of using a coating process with ion interaction compared to normal deposition processes is the enhanced durability and optical stability due to bulk-like structural properties of the coating materials.

All of the Technical Objectives stated in the Phase I proposal have been successfully addressed, namely:

1. Demonstrate the capability of using the Reactive Ion Plating Deposition (RIPD) technique for depositing improved thin film oxides on polycarbonate substrates.
2. Determine the optical constants (n , k) of each coating material.
3. Determine the structural properties of each coating material.
4. Deposit a multilayer reflection filter on polycarbonate material.
5. Assess the environmental, physical and optical properties of a multilayer stack deposited on a polycarbonate substrate.
6. Provide to LAIR personnel a sample, using the RIPD process with polycarbonate ophthalmic material.

EXPERIMENTATION/RESULTS

The primary goal of this program is to use "state of the art" technologies and materials to achieve a quantum leap in the performance of LEP hardware. The approach proposed is a combination of the most advanced polycarbonate IR absorbing materials, for a base ophthalmic element and a novel multilayer coating technique that can be used to apply multilayer reflection rejection filters to the polycarbonate materials. Glendale Protective Technologies, Inc. provided the polycarbonate near IR absorbers with specific ophthalmic shapes.

Evaporated Coatings, Inc. and the Center for Research in Electro-Optics and Lasers (CREOL) at the University of Central Florida (UCF) agreed to provide a cooperative effort for studies related to depositing multilayer coatings on polycarbonate materials. CREOL has established a major program in the fundamental and applied research for a substantial improvement of thin film coatings for optical applications. Dr. Karl H. Guenther, Associate Professor (EECS and Physics at UCF, is responsible for this research effort at CREOL. The coating technology proposed is RIPD, which is considered a major breakthrough in thin film deposition technology. This technology can be used to enhance not only the optical properties of multilayer coatings on polycarbonate but also the coating durability and coating uniformity properties.

CREOL STUDIES (SEE ATTACHMENT-CREOL FINAL REPORT)

The coating process (Reactive Low Voltage Ion Plating

Technology (RLVIPT) and system that were used by CREOL is described in detail in their final report (see attachment). Basically, this mode of coating deposition uses a combination of electron beam deposition with a plasma system that ionizes the evaporated atoms/molecules from the electron beam gun. The evaporated ions are then accelerated toward the substrates by a bias voltage. The accelerated ion has increased surface impact energy and surface energy. This provides the densification of the deposited film by increased surface mobility. The films deposited approach "bulk-material" properties compared to a columnar void structure of films formed by standard electron beam deposition technology.

The initial studies performed by CREOL indicated that the process provided too much heat when depositing a multilayer coating on the polycarbonate substrate. The temperature increased enough to start to deform the polycarbonate substrate. It was determined that the source of heat was from both the electron beam gun source and the plasma source.

CREOL personnel designed and built a heat exchange system for the vacuum system. Heat sinks and shields were placed inside the vacuum chamber. A low-cost water chiller system was built to interface with the internal heat sinks. This provided efficient enough to keep the chamber temperature at a significantly lower temperature during the deposition process. Figures 3 and 4 of the CREOL report indicate the temperature rise in the coating chamber with and without the heat exchange system in use during the deposition of hafnium oxide. Much lower deposition

temperatures have been achieved.

Material studies for silicon dioxide and zirconium oxide were then performed for coatings deposited with just electron beam deposition and the RLVIPT process. The ion plated (IP) coatings had refractive indices higher than the electron beam (EB) deposited coatings. For example, the value for IP zirconium oxide was 2.2 and the EB coating was 2.15. This difference in refractive index is significant since less layers are required with IP coatings to yield the same optical density compared to EB coatings.

The intrinsic stress of each of these coating materials deposited with the IP process, was determined. It is important that the intrinsic stress is not too high. If it is too high the film tends to delaminate from the substrate since the self-induced bending force exceeds the adhesion of the film to the substrate surface. The stresses measured were basically compressive and practical for a multilayer deposit.

CREOL deposited several single layer coatings of ZrO_2 and SiO_2 using the RLVIPD process. The coatings were deposited on polycarbonate samples provided by Glendale Protective Technologies, Inc. Samples with and without an organic protective overcoat for the polycarbonate were used for the coating studies. The single layer coatings were evaluated for their cosmetic properties under a 200X microscope. The best samples obtained were for both the ZrO_2 and SiO_2 films deposited on the polycarbonate samples with the protective overcoat. They looked clear and defect free. The samples without the protective overcoat appeared cloudy and

had some large and small stress fracture patterns on the coated surface. This was consistent for all of the samples evaluated.

CREOL also provided samples with a multilayer coating on samples with/without a protective overcoated polycarbonate material. The multilayer was constructed of the first two layers coated with the IP process followed by the next sixteen layers coated with the EB process and the final two layers coated with the IP process. It was reasoned that the initial and final layers would provide environmental and durability properties and the multilayer stack "sandwiched" between these layers would provide a less stressed coating and be more compatible with the higher expansion coefficient properties of the polycarbonate substrate. These samples were also evaluated cosmetically. Again, the samples coated without the protective overcoat were of poor quality and indications of a high stress were evident. The samples with the protective overcoat were very clear. There was some evidence of fine stress marks under higher magnification but the overall quality was good. The spectral curve for this multilayer is indicated in figure A. The optical density achieved for this twenty layer coating was about 2.5.

ECI STUDIES

Several multilayer samples were prepared at ECI using normal EB deposition techniques. The series of samples prepared utilized both CREOL and ECI single base layer coated samples that were then coated with a multilayer coating designed to reject the 1.06 micron region. There was an equal distribution

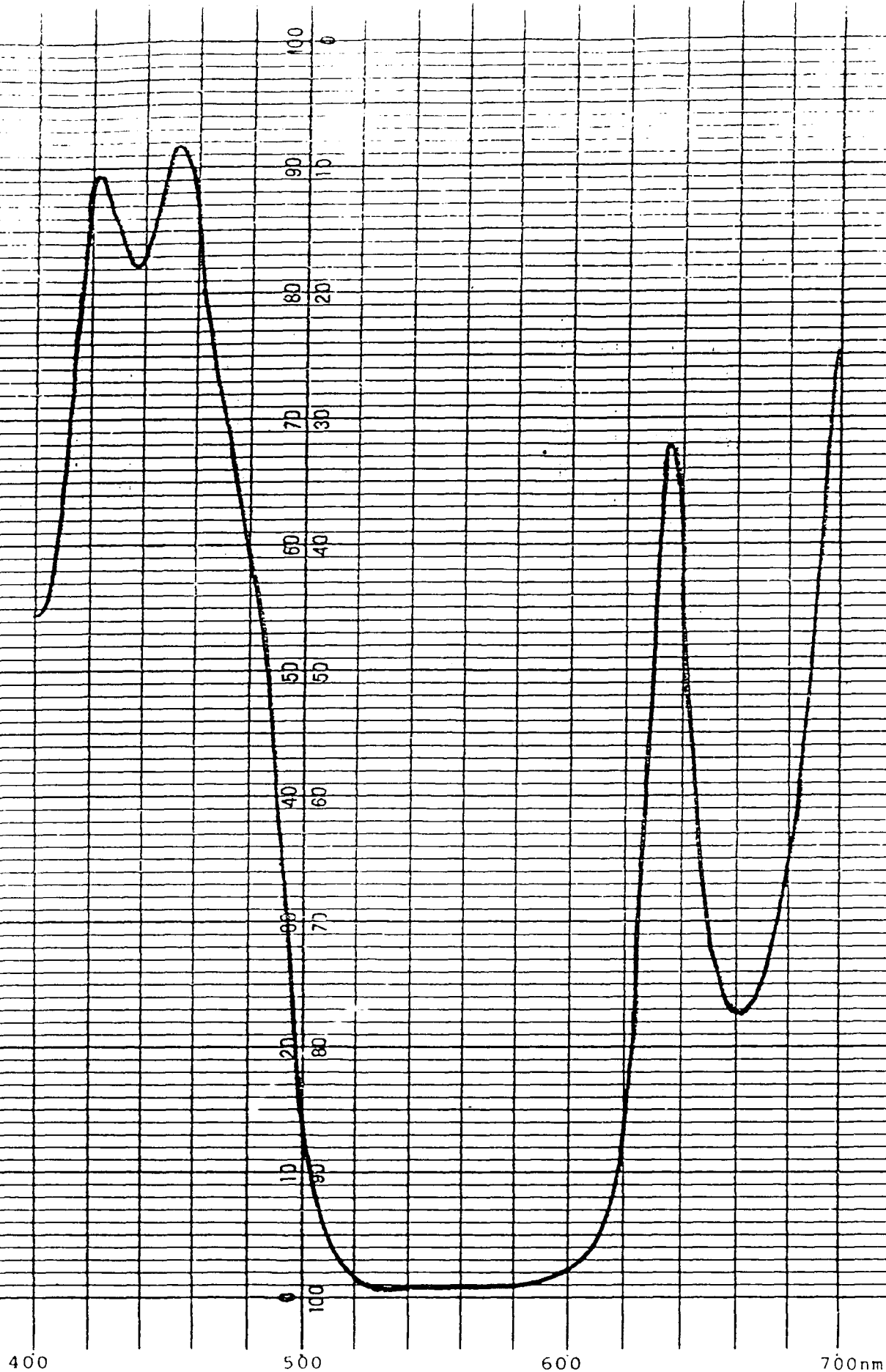


Fig. A Spectral Transmittance of Multilayer Coating
"confidential proprietary information"

of these samples with/without the protective organic coating on the polycarbonate material. The single layer samples prepared at ECI utilized a rf sputtered process to form a high refractive index film on the polycarbonate surface. Also part of this matrix of parts were uncoated polycarbonate samples with/without the protective overcoat. All of these samples were then cleaned and coated with the EB multilayer coating.

An environmental and durability test and evaluation was performed on all of the samples described above. The testing and evaluation was performed in the following sequence:

1. Cosmetic evaluation per MIL-C-48497
2. Adhesion test per MIL-M-13508
3. Abrasion test per MIL-C-48497
4. Humidity (40 hours per MIL-C-48497)
5. Water solubility (3 days per MIL-C-48497)
6. Adhesion test per MIL-M-13508
7. Cosmetic evaluation per MIL-C-48497

Illustrated in Table I are the results of this testing. A weighting factor was assigned to rate the results of each test. The weight factors are as follows:

1. No damage
2. Some damage
3. Severe damage

The results of the single layer coatings supplied by CREOL indicated that both the ZrO_2 and SiO_2 coatings deposited on the polycarbonate substrates without the organic protective layer had a cloudy appearance. The samples with the organic overcoat

Sample		Cosmetic	Adhesion	Abrasion	Humidity (40 hrs.)	Water Solubility (3 days)	Adhesion	Total
CREOL w/o overcoat (ZrO ₂)	A	2-Cloudy	1	3	1	1	1	9
CREOL w/overcoat (ZrO ₂)	B	1	1	3	1	1	1	8
CREOL w/o overcoat (SiO ₂)	C	2-Cloudy	3	3	3	3 Badly crazed	3	17
CREOL w/overcoat (SiO ₂)	D	1	2	1	1	1	3	9
CREOL w/o overcoat (Multilayer)	E	2 Stress cracks	1	1	1	3 crazed	1	9
CREOL w/overcoat (Multilayer)	F	2 Stress cracks	2	1	1	3 crazed	3	12
ECI w/o overcoat rf film & (Multilayer)	G	1	1	1	1	1	1	6
ECI-w/overcoat rf film & (Multilayer)	H	1	1	1	Small 2 edge area	1	1	7
Polyc w/o overcoat & ECI Multilayer	I	2 Cloudy	1	1	1	1	1	7
Polyc w/overcoat & ECI Multilayer	J	1	1	1	Small 2 edge area	3 Coating removed	3	11
CREOL w/overcoat & SiO ₂ & ECI Multilayer	K	1	3	1	Small 2 edge area	Small 2 area removed	3	12
CREOL w/overcoat & ZrO ₂ & ECI Multilayer	L	3	1	1	Small 2 edge area	2 crazed	3	12

Table.I. Sequential Testing

were very clear. After the sequential testing the SiO₂ samples showed very poor adhesion on both the polycarbonate samples with/without the organic protective layer. The major defect with the ZrO₂ samples was their poor abrasion characteristics. However, their appearance after all the testing was quite good. Their abrasion characteristics could be significantly improved by ending with a quartz like layer. The important conclusion from the single layer analysis is to use a polycarbonate substrate with the organic overcoat, start with a high index material, e.g. ZrO₂ and end with a quartz-like material, e.g. SiO₂. This should provide good cosmetic, abrasion and adhesion properties when subjected to a series of sequential physical and environmental testing. The benefit of the organic coating appears to be that it seals the polycarbonate surface from absorbing water and thereby stops water vapor being emitted during the coating process. Also, it may function as more of a compatible layer that can adjust for the expansion coefficients of the substrate and deposited thin film.

The two CREOL multilayer samples that were processed with a hybrid EP and EB deposition process were slightly crazed prior to testing. The samples looked very well after adhesion, abrasion and humidity testing, but showed significant deterioration after the three day water solubility test. It is believed that the initial stress cracks were the weak areas that precipitated the further damage during the water solubility test. Despite the severe damage after this test, one sample was still able to pass the adhesion test. The initial and final IP layers did provide additional protection.

Two single layer CREOL samples (SiO_2 and ZrO_2) that were coated with an ECI multilayer (EB) were subjected to the same sequence of tests. Again, the sample (K) that had the SiO_2 base layer did not pass the adhesion test. The other sample (ZrO_2) had some initial stress cracks. It also failed as the testing progressed. This points out the significance of starting out with a multilayer that does not have any initial stress cracks.

The final samples that were evaluated consisted of two samples (with/without organic overcoat) that had a high index material rf sputtered on the surface. The other two samples were polycarbonate substrates with and without the organic overcoat. Each of these four samples were then coated with an ECI multilayer (see figure B) using EB technology. The results of the sequential testing indicated that the best samples obtained were the ones with the initial high index film formed by the rf sputtering process. There was one of these samples (G) that passed all the testing without any degradation. The other sample (H) had a small mark on the edge of the part. Sample (I) which is polycarbonate with the multilayer had some initial cloudiness but also passed all of the tests. Sample (J), the polycarbonate with the organic overcoat and the ECI multilayer, started to show coating removal and poor adhesion after the water solubility test. The necessity of using some ion enhanced coatings to achieve better durability properties is evident from the results of these last two samples.

Figure B. Spectral Transmittance
of ECI Multilayer Coating

Evaporated Coatings, Inc.

Customer LAIR

Date 10/29/90

PC

Scale 0-100%T

Chart Format 50mm/cu

Angle 0°

Medium AIR

Wavelength Range 4-12μ

Analyst J. Cygan

* With protective coating

CONCLUSIONS/RECOMMENDATIONS

Conclusions:

1. The initial high temperature problem associated with the RIPD process can be controlled with the use of shielding and thermally controlled heatsinks located in the vacuum process chamber.

2. Additional modifications on the thermal and heat shield system designed and fabricated in the Phase I effort can be made to further improve the process to make it fully compatible with coating polycarbonate ophthalmics.

3. The coating uniformity on curved ophthalmic polycarbonate elements is excellent with the RIPD process.

4. The deposition rates for the coating materials studied using the RIPD process are practical and similar to the conventional electron beam deposition process.

5. The use of some type of protective organic layer on the polycarbonate material does provide benefits in the form of cosmetic properties as well a compatibility of the multilayer with the polycarbonate substrate.

6. The use of films deposited with some form of ion deposition process and conventional EB deposition does provide practical mechanism for the enhancement of the physical and optical properties of LEP polycarbonate elements.

7. The Phase I effort clearly demonstrated that the primary objective of depositing multilayer reflection rejection filters on polycarbonate curved surfaces is feasible with the RIPD process.

Recommendations:

There is no question that a Phase II effort will yield a practical, cost effective and property enhanced multiline LEP polycarbonate ophthalmic element. The tasks to be performed for this Phase II effort include:

a. Further refine the heat exchange system and chamber shields, for the RIPD process, to ensure a minimum substrate temperature increase during coating processing.

There are additional changes to the heat exchange system that can be done to improve the overall heat exchange efficiency. Better thermal contact of the water lines with the shield is but one example. Additional shields can be added to reduce the process heatload. It is very important to keep the temperature low and stable because a resulting temperature increase of the plastic substrate would endanger it if going beyond 80°-100°C.

b. Study the properties of a transition layer(s) that will enhance the adhesion between the multilayer coating and the polycarbonate substrate as well as accommodate the expansion coefficient differences.

The results achieved in Phase I show clearly that the dielectric hybrid multilayers adhered better to the polycarbonate lenses which already had a hard coating as compared to those lenses consisting of plain polycarbonate.

The studies to be performed will basically consist of evaluating organic/inorganic film structures between the polycarbonate multilayer interface to enhance adhesion and "blend" the expansion coefficients for the plastic and multilayer. Additional studies will also be focused on the structure of the

multilayer. Composite structures of ion enhanced coatings with e-gun deposited films are also expected to accommodate expansion coefficient differences.

c. Evaluation of hybrid ion enhanced coatings with e-gun deposition coatings to achieve optimal physical and optical properties. The Phase I results indicated that enhanced properties are feasible. The studies will be used to determine the optimal hybrid technique.

d. A multilayer/polycarbonate absorber hybrid will be designed to provide visible/near IR LEP.

e. In order to demonstrate the enhanced properties, cost and practical considerations associated with this process, several ophthalmic sets with LEP and ballistic protection and associated process time data will be provided for evaluation.

Final Report

***Exploration of
Reactive Low Voltage Ion Plating for the
Deposition of Stable Multilayer Coatings for
Laser Eye Protection on Polycarbonate Substrates***

Work Performed Under Subcontract by
Evaporated Coatings, Incorporated
for an SBIR - Phase I Contract

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Period of Performance:

April 2 - October 2, 1990

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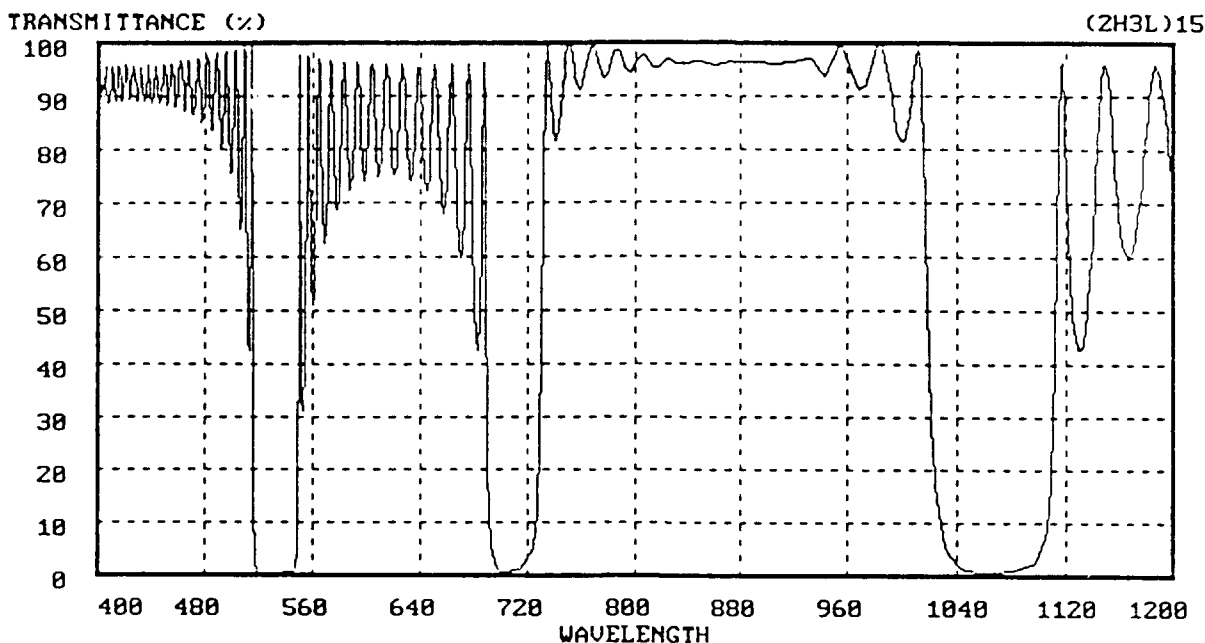
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Summary

The reactive low voltage ion plating (RLVIP) process implemented in our state-of-the-art high vacuum deposition system Balzers BAP 800 has shown to make dense, durable and non-shifting dielectric multilayer coatings on unheated substrates. The heating of the substrates customary in conventional electron beam deposition for obtaining hard, durable coatings is not necessary for RLVIP. The task of this effort was to investigate the microstructure of ion plated dielectric thin films deposited on substrates kept at room temperature or slightly above, and to evaluate the compatibility of the expected dense dielectric (ceramic) thin films with polycarbonate substrates. Although the process does not require substrate heating *per se* from a fundamental point of view, the temperature in the coating chamber increases more than encountered with standard electron beam evaporation because of the plasma discharge involved in the reactive low voltage ion plating process. Therefore, a major portion of our effort was directed toward the installation of additional heat sinks inside the coating chamber with stainless steel shields welded to appropriate stainless steel water piping. This work was performed completely by a young engineer in our thin film group who graduated in May with a B.S. in Engineering Technology. He built also a low-cost water chiller which proved efficient enough to keep the chamber temperature at the required low levels during deposition. After the completion of this engineering task, we were able to coat several plastic lenses, both with a lacquer hard coat and without, with different designs of multilayer coatings, consisting of zirconia and silica. In order to keep the chamber temperature low, we used hybrid designs, where the first and/or last few layers were deposited by reactive low voltage ion plating and the remaining layers necessary to achieve the desired spectral performance were deposited by conventional electron beam evaporation, carried out in the same coating run without breaking the vacuum. Electron microscope investigations of these hybrid coatings show a clear difference in microstructure of ion plated and electron beam deposited layers. The ion plated thin films are more dense than those deposited by electron beam evaporation.

Introduction

Laser eye protection for military personnel has been a topic of research and development interest ever since laser range finders, target designators, and other laser equipment for field use became available.¹ Various schemes for obtaining efficient laser eye protection have been suggested, including dyes for plastic lenses and visors, holographic reflectors, and dielectric multilayer coatings. Evaporated Coatings, Inc., (ECI) is pursuing a hybrid approach of combining all 3 of the aforementioned elements in one device. While it is possible, in principle, to reject laser lines in the Visible and Near Infrared with a single stack or multiple stacks of thin film coatings (Figure 1), this solution becomes impracticable for plastic substrates because of the large number of thin films and the resulting physical thickness of the complete coating necessary for the rejection of multiple laser wavelengths. Such coating would become highly stressed and incompatible with the soft plastic (polycarbonate) substrates, particularly under additional thermal or mechanical stress, as might be expected in field use from the exposure to the environment or ballistic impact. Therefore, the solution proposed by ECI takes advantage of laser rejection provided by dyed polycarbonate in the Near Infrared, and a holographic grating taking care of short wavelength laser line rejection. For a steep cutoff at the longer wavelength end of the visible spectrum ($\lambda = 690 \text{ nm}$), the combination of the dyed polycarbonate (for rejection of the 1054 and 1064 nm laser lines) with a multilayer dielectric as a short wave pass filter has been envisioned. The task of this effort was to explore the compatibility of dense, non-shifting dielectric multilayer coatings deposited by reactive low voltage ion plating with the polycarbonate substrates intended for use with the laser eye protection gear. The P. I.'s previous experience in coating of ophthalmic lenses,² in particular plastics,³ proved useful in successfully meeting this challenge, with the active support of several members of the Thin Film Group at CREOL. The results achieved in this Phase 1 feasibility study lay the grounds for the further development of the hybrid concept proposed by ECI for a practical device, suitable for economic mass production.



Wave (nm)	% Refl	% Trns	O.D.	% Abs
520.0000	99.87056	.12944	2.88795	.00000
525.0000	99.98091	.01909	3.71910	.00000
530.0000	99.99102	.00898	4.04695	.00000
535.0000	99.98970	.01030	3.98708	.00000
540.0000	99.96968	.03032	3.51826	.00000
545.0000	99.64188	.35812	2.44597	.00000
695.0000	98.28251	1.71749	1.76511	.00000
700.0000	99.35975	.64025	2.19365	.00000
705.0000	99.55986	.44014	2.35641	.00000
710.0000	99.51960	.48040	2.31840	.00000
715.0000	99.20707	.79293	2.10077	.00000
720.0000	98.00457	1.99543	1.69996	.00000
725.0000	91.82939	8.17061	1.08775	.00000
1030.0000	94.86092	5.13908	1.28911	.00000
1035.0000	97.39494	2.60506	1.58418	.00000
1040.0000	98.49676	1.50324	1.82297	.00000
1045.0000	99.02876	.97124	2.01267	.00000
1050.0000	99.30578	.69422	2.15850	.00000
1055.0000	99.45553	.54447	2.26403	.00000
1060.0000	99.53393	.46607	2.33155	.00000
1065.0000	99.56586	.43414	2.36237	.00000
1070.0000	99.56030	.43970	2.35684	.00000
1075.0000	99.51514	.48486	2.31439	.00000
1080.0000	99.41560	.58440	2.23329	.00000
1085.0000	99.22439	.77561	2.11035	.00000
1090.0000	98.85233	1.14767	1.94018	.00000
1095.0000	98.06725	1.93275	1.71382	.00000
1100.0000	96.16386	3.83614	1.41611	.00000
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Fig. 1. Example of multi-laser line rejection filter consisting of one multilayer stack. The design necessary to cover three different regions with reasonable optical density (OD, tabulated for the stop bands) would have a physical thickness of almost 10 μm !

Reactive Low Voltage Ion Plating Deposition

The process has been described in sufficient detail by the P. I. in several publications contained in the appendix to this report.⁴⁻⁶ In short, thin films growing from the deposition of electron beam evaporated coating material become very dense when they are concurrently bombarded with high density low energy argon ions, produced in a low voltage high current plasma source operating at about 50 to 60 A, 50 to 70 V, and an argon pressure in the source of 2 to 4 mbar. If the deposited thin films ought to be dielectric (oxide, nitride), the starting material is either the metal or a sub-stoichiometric composition of the desired compound. Backfilling the coating chamber with sufficient supply of the respective reactive gas (oxygen, nitrogen) which gets partially ionized in the argon plasma by electron transfer processes assures fully stoichiometric thin films. The formation of a dense film structure can be explained both with a molecular dynamics computer simulation model⁴ with the numerical evaluation of many impulse transfer processes triggered by the impinging argon ions of 5 to 50 eV energy, and more qualitatively, by the transfer of energy to the growing film.⁷

The Coating Equipment

The state-of-the-art high vacuum deposition system Balzers BAP 800 available at UCF/CREOL consists of an 800 mm (32 inch) stainless steel box with a front loading door, which carries the peculiar low voltage (50 - 60 V) high current (50 - 70 A) argon plasma source in its lower portion (Figure 2). The vacuum chamber is pumped by an oil diffusion pump with liquid nitrogen cooled baffle, backed by a dual stage rotary vane forepump with a roots blower in between. The coating chamber contains 2 electron beam evaporation sources of the type Balzers ESK 110 and 113, with a rotating pot and an indexable four pocket crucible, respectively. The substrates are located on a single rotation dome with four 90° segments which in turn carry 5 trapezoid inserts, holding the optical elements (lenses) to be coated in stainless steel bezels.

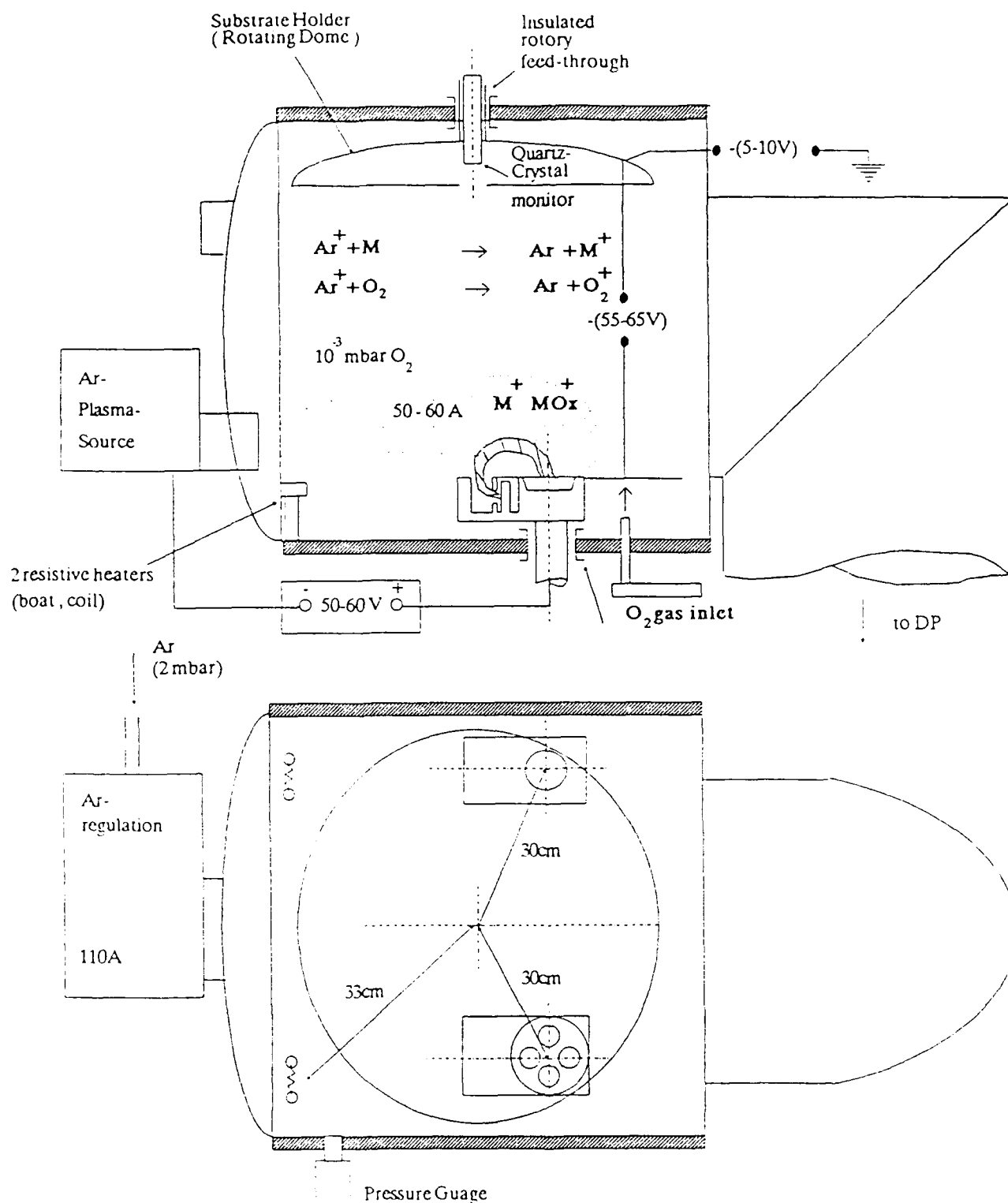


Fig. 2. Schematic of the Balzers BAP 800 equipment for reactive low voltage ion plating (RLVIP). Note the two electron beam evaporation sources in the ground view (bottom) and the low voltage, high current argon plasma source, particularly well seen in the side view (top).

The dome is insulated from ground potential, to allow the build-up of a negative self-bias on the substrate surfaces exposed to the plasma sheath generated by the argon plasma. A quartz crystal monitor located in the center of the rotary dome measures the total film thickness and, at the same time, serves as deposition rate monitor. A residual gas monitor Balzers QMG 064 (quadrupole mass spectrometer for atomic mass units [amu] ranging to 64) is also available.

Custom modifications of the coating equipment for plastic coatings

An obvious problem in the coating of plastics (inclusive of polycarbonate) with durable dielectric thin films is the susceptibility of the substrates to deformation and damage at elevated temperature. In conventional electron beam or thermal evaporation, substrates need to be heated up to 250 - 350 °C to achieve reasonably dense films with acceptable hardness and environmental stability, although even such coatings tend to shift their spectral performance upon exposure to ambient temperature or humidity variations.^{8,9} Ion and plasma assisted vacuum deposition processes avoid, in principle, the deliberate heating of the substrates by providing additional energy to the deposited film species in form of ion impact.⁷ However, the energy dissipation of the ions and neutrals produced and accelerated in an ion gun for co-irradiation of the growing film gives rise to an increase of the substrate temperature in Ion Assisted Deposition (IAD)¹⁰ as well as in plasma assisted processes, such as the Reactive Low Voltage Ion Plating (RLVIP) applied in this study. Here, the energy contained in the plasma discharge (50 - 60 A, 50 - 70 V) adds to the thermal load already generated by the 6 - 10 kW of electron beam energy in the evaporation source(s). Hence, the temperature in the coating chamber as measured with a thermocouple increases about twice as fast when the plasma discharge is on, as compared to standard electron beam evaporation conditions (Figures 3, 4). Therefore, in order to coat plastic (PC) lenses with a stack of thin films sufficient for the required optical density (OD) of about 3, which takes about 2 - 3 hours and would cause the chamber temperature to rise up to 250 °C, we had to introduce custom modifications into our coating equipment as described below.

Temperature rise during IP and e-beam coatings

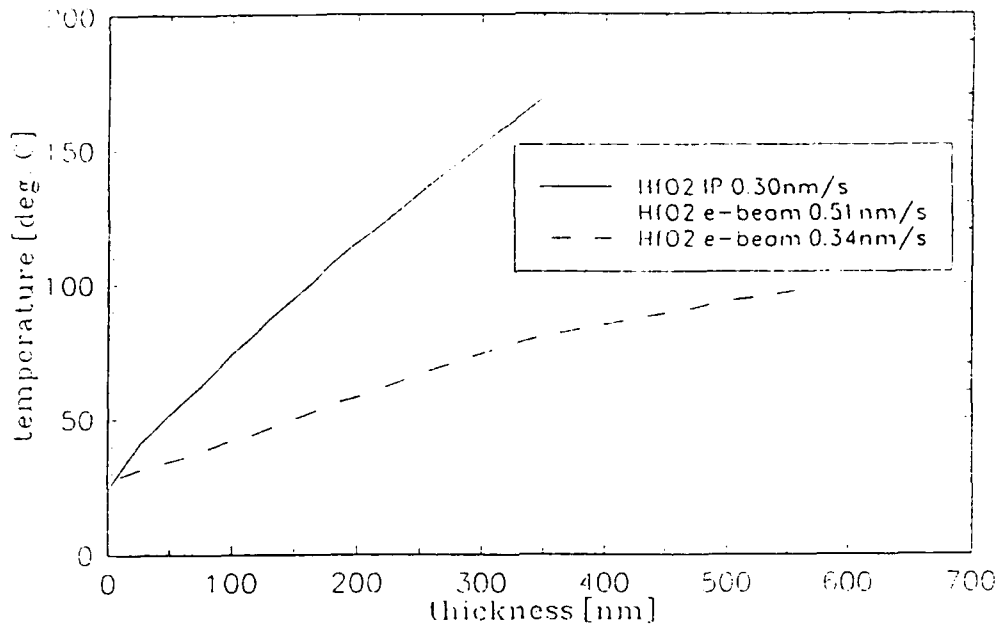


Fig. 3. Temperature rise in the coating chamber of the BAP 800 equipment during ion plating and electron beam deposition of HfO₂, as a function of deposition time.

Temperature rise during IP and e-beam coatings

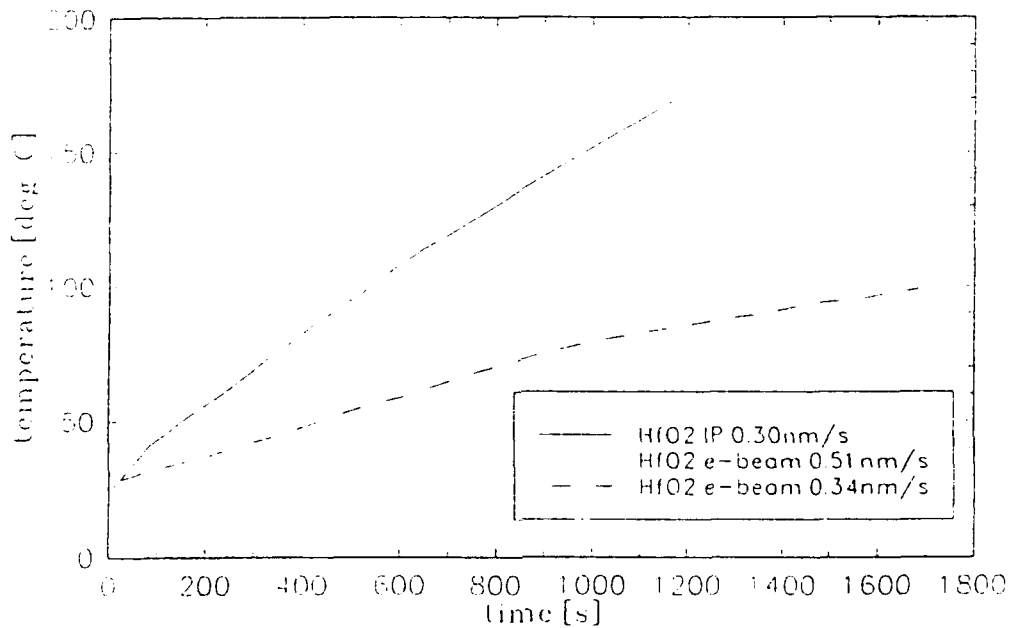


Fig. 4. Temperature rise in the coating chamber of the BAP 800 equipment during RLVIP and EB-evaporation, as a function of deposited film thickness.

Experiments

Thin film deposition

All depositions were carried out in the Balzers BAP 800 equipment described in the previous section. We deposited single layers of zirconia and silica with low voltage reactive ion plating on 2x2" square glass samples and 3" diameter polycarbonate lenses (two per run, 1 each with and without an organic hard coat). The temperature during deposition was monitored with a thermo couple and an Eurotherm control instrument. We deposited also 2 different multilayer coatings of the following hybrid design:

SAMPLE # 900915(HL)_{IP}(HL)_{EB}⁸H_{IP}

SAMPLE # 901001(HL)_{EB}⁸(HLH)_{IP}

where H indicates a quarter-wave layer of high index material (ZrO₂) and L a quarter-wave layer of low index material (SiO₂). The subscript IP denotes the layers deposited by reactive low voltage ion plating, and the subscript EB the layers deposited by conventional electron beam evaporation. The following Table 1 summarizes the starting materials and evaporation condition for each material.

Table 1. Deposition Parameters					
Thin Film	Starting Material	P _{O2} [mbar]	Rate [nm/sec]	T _s [°C]	t [nm] @ QWOT
SiO ₂	SiO ₂	7.x10 ⁻⁴	0.50	44-45	135
SiO ₂	Si	9.x10 ⁻⁴	0.20	25-61	130
ZrO ₂	ZrO ₂	2.x10 ⁻⁴	0.50	45-46	89.4
ZrO ₂	ZrO ₂	9.x10 ⁻⁴	0.20	24-38	88.0
ZrO ₂	Zr	9.x10 ⁻⁴	0.25	24-45	88.0

Determination of optical properties of deposited thin films

From the single layer coatings on the glass witness samples, the refractive index was determined from spectral reflectance and transmittance measurements, using a Perkin-Elmer 330 spectrophotometer. Table 2 below gives the values obtained for both the ion plated and the electron beam deposited thin films. Similarly, the spectral transmission of the two hybrid multilayer coatings was measured from the flat glass witness samples. The measurements are shown in Figures 6 and 7.

Table 2. Optical Properties (Refractive index data)				
Thin Film	Refractive index (n) at			
	400 nm	500 nm	600 nm	700 nm
SiO ₂ - EB	1.450	1.449	1.447	1.446
SiO ₂ - IP	1.500	1.490	1.492	1.480
ZrO ₂ - EB	2.150	2.145	2.131	2.120
ZrO ₂ - IP	2.200	2.170	2.170	2.165

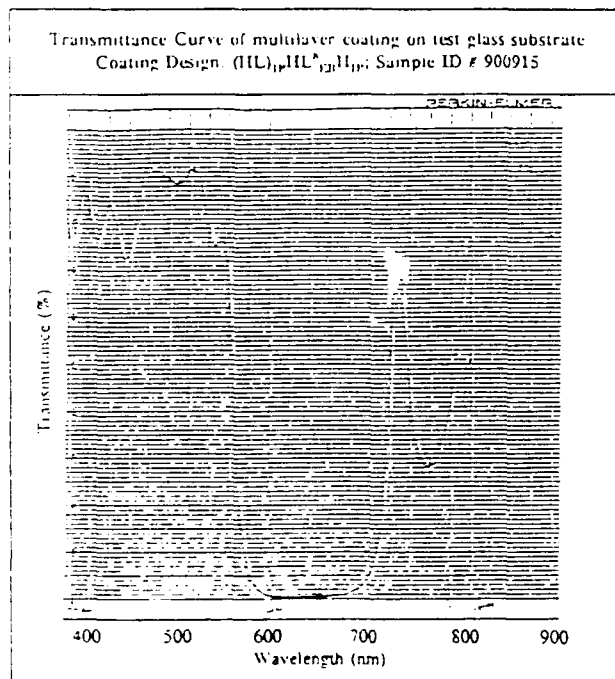


Fig. 6. Spectral transmittance of sample # 900915

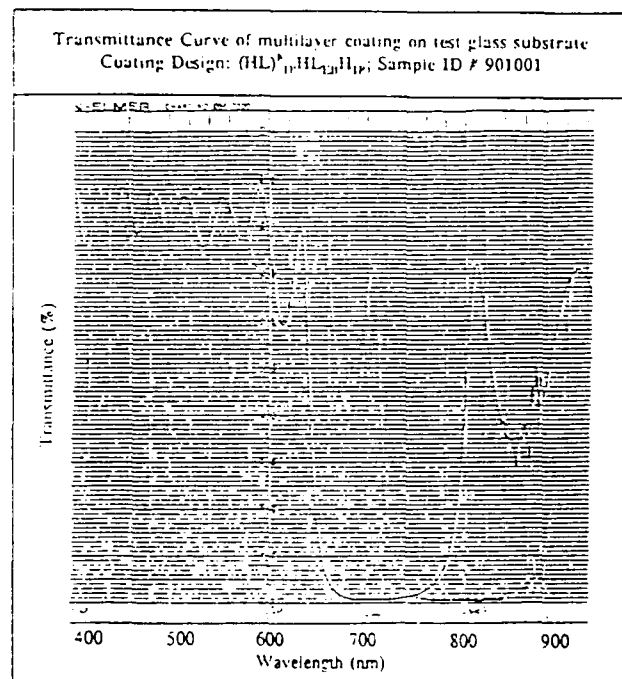


Fig. 7. Spectral transmittance of sample # 901001

Polycarbonate lens samples

Table 3 lists those samples sent to Evaporated Coatings Inc. for further evaluation:

Table 3. Coated samples delivered to Mr. Jack Walls, Evaporated Coatings Inc.				
Item	Sample ID #	Substrate	Coating Description	Starting Material
1	900908	Polycarbonate lens with hard coating	SiO ₂ RIPD QWOT at 750nm	Si metal
2	900908	Polycarbonate lens without hard coating	SiO ₂ RIPD QWOT at 750nm	Si metal
3	900909	Polycarbonate lens with hard coating	ZrO ₂ RIPD QWOT at 750nm	ZrO ₂
4	900909	Polycarbonate lens without hard coating	ZrO ₂ RIPD QWOT at 750nm	ZrO ₂
5	900910	Polycarbonate lens with hard coating	ZrO ₂ RIPD QWOT at 750nm	ZrO ₂
6	900910	Polycarbonate lens without hard coating	ZrO ₂ RIPD QWOT at 750nm	ZrO ₂
7	900911	Polycarbonate lens with hard coating	SiO ₂ RIPD QWOT at 750nm	Si metal
8	900911	Polycarbonate lens without hard coating	SiO ₂ RIPD QWOT at 750nm	Si metal
9	900914	Polycarbonate lens with hard coating	ZrO ₂ RIPD QWOT at 750nm	ZrO ₂
10	900914	Polycarbonate lens without hard coating	ZrO ₂ RIPD QWOT at 750nm	ZrO ₂
11	900915	Polycarbonate lens with hard coating	(HL) _{IP} (HL) ⁸ _{EB} H _{IP} H, L are QWOT at 750nm	ZrO ₂ Si metal SiO ₂
12	900915	Polycarbonate lens without hard coating	(HL) _{IP} (HL) ⁸ _{EB} H _{IP} H, L are QWOT at 750nm	ZrO ₂ Si metal SiO ₂
13	901001	Polycarbonate lens with hard coating	(HL) ⁸ _{EB} (HL) _{IP} H _{IP} H, L are QWOT at 750nm	ZrO ₂ Si metal SiO ₂
14	901001	Polycarbonate lens without hard coating	(HL) ⁸ _{EB} (HL) _{IP} H _{IP} H, L are QWOT at 750nm	ZrO ₂ Si metal SiO ₂

Measurement of intrinsic thin film stress

The intrinsic stress of a thin film is a determining factor for its durability. Conventional thin films, deposited by thermal or electron beam evaporation, have a columnar microstructure which in general causes tensile stress in the films, when the coating material tries to fill the gaps between the columns. Ion and plasma assisted thin film deposition causes a high packing density and typically compressive stress. If this intrinsic stress is too high, the film tends to delaminate from the substrate if the stress-induced bending force exceeds the adhesion of the film to the substrate surface. If the adhesion is strong enough to withstand the delamination tendency, the intrinsic film stress can deform the substrate if its not rigid enough.

Our approach to measurement of thin film stress is based on the measurement of the deformation of thin fused silica monitor plates of 1 inch diameter and 10 mil thickness. The compressive stress in the film deforms the initially plane plate into a slight bell shape which can be approximated by a sphere. The illumination of the coating stress monitor plates placed on an optical flat with monochromatic light from a krypton lamp ($\lambda = 547 \text{ nm}$) causes interference fringes due to the air gap between the deformed plate and the optical flat. We took photographs of these fringes with the macro-lens of a 35 mm SLR camera. An example of such a photograph is shown in Figure 8. The stress evaluation is summarized in Table 4.

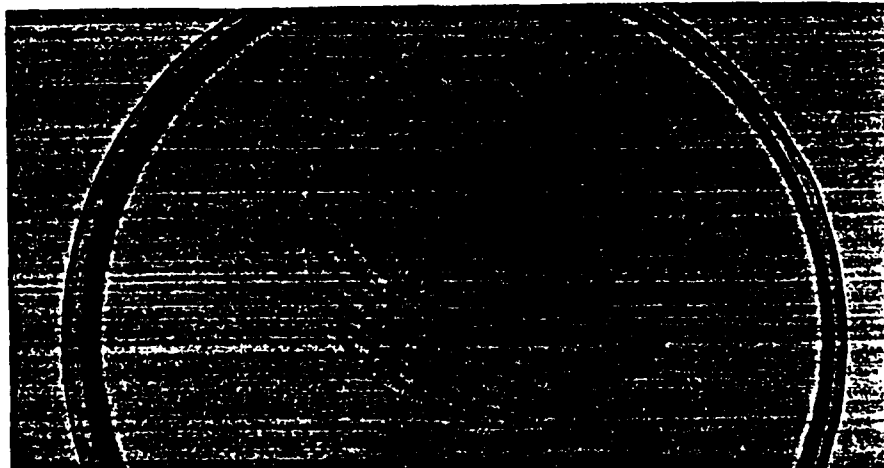


Fig. 8. Photograph of interference fringes caused by the air gap between an optical flat and a thin fused silica monitor plate deformed by intrinsic film stress into a bell shape.

Table 4. Estimation of stresses of RIPD coatings on Fused Silica substrates

- | | | |
|----|-------------------------------------|--|
| 1. | Sample # 900908
Estimated stress | SiO ₂ single layer QWOT at 750 nm
48 N/mm ² (Compressive) |
| 2. | Sample # 900909
Estimated stress | ZrO ₂ single layer QWOT at 750 nm
Negligible |

Comparative stress of MgF₂ and ZnS coatings of approximately same thickness, coated at comparable rates reported in the literature (Ref. 1,2)

- | | | |
|----|------------------|---------------------------------------|
| 1. | MgF ₂ | 170 - 280 N/mm ² (tensile) |
| 2. | ZnS | 5 - 7 N/mm ² (compressive) |

Formula for calculation of stress from plate curvature (derived from interference fringes):

$$\sigma = \frac{Ed^2}{6rt} \quad [N/mm^2]$$

where

E is Young's Modulus = 81×10^3 N/mm² for Fused Silica

d is thickness of substrate = 0.01" = 0.254 mm

t is film thickness = QWOT at 750 nm

r is radius of curvature = 48261.52 mm

Note: The stress values calculated here should be taken only as rough estimates; accurate determinations require more detailed investigations and measurements.

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Electron microscope investigation of thin film microstructure

The properties of thin films are, to a great extent, determined by their microstructure¹¹ which, in turn, is strongly influenced by the deposition process.¹² Thus, the study of thin film microstructure supposedly gives some insight of how to modify a deposition process for the improvement of thin film coatings. We used both the direct observation of fractured multilayer coatings in a scanning electron microscope (SEM) and the indirect imaging of the cross-section of fractured multilayers with a carbon replica, investigated in a transmission electron microscope (TEM).

a.) SEM investigations

The P. I. conducted initial investigations employing the SEM at the College of Engineering at UCF, a JEOL JSM 300 T. This instrument is already about 10 years old and does not have the necessary resolution for imaging ultimate details of thin film coatings. However, it proved useful enough to show at least the significant difference in the density of RLVIP and EB thin films, by way of the greatly enhanced secondary electron emission of the former, indicating the presence of more solid state material (i. e., higher density). Figures 9 and 10 show representative pictures taken from the hybrid multilayer samples. For improved resolution, the same samples were investigated with a new SEM (JEOL JSM-6400) at the Major Analytical Instrumentation Center (MAIC) at the University of Florida (UF) in Gainesville, FL, under the P. I.'s supervision. Representative pictures are shown in Figures 11 and 12.

b.) TEM investigations

For the imaging of a solid surface such as the cross-section of a multilayer coating in a transmission electron microscope, it is necessary to prepare an electron transparent specimen of that sample. This could be a thin section, such as widely used in biology and pathology with microtome sectioning of (frozen) tissue. While this technique of microtoming is, in principle, also

applicable to material science specimens, it is difficult to perform and requires a special diamond knife, which we did not have available. Thus, we resorted to the well established technique of preparing a high resolution replica of the fractured cross-section, by first evaporating a minute amount of platinum along with carbon at an oblique angel of incidence (for contrast enhancement by shadowing effects), and then evaporating a plain carbon film covering both the fractured cross-section and the film surface.¹³ This carbon film, along with the previously deposited Pt-C pre-shadowing film, is stripped from the sample by immersing it very shallowly into diluted hydrofluoric acid (about 4%). Leaving it here floating for at least 24 hours (in our case actually 72 and 36 hours) removes any actual coating material which might got stuck to the carbon film, and would show as dark (because nontransparent) areas in the transmission electron microscope picture. The floating carbon replica is finally transferred on copper grids (3 mm o.d., 400 mesh) which are widely used in electron microscopy. Representative TEM micrographs are shown in Figures 13 and 14.

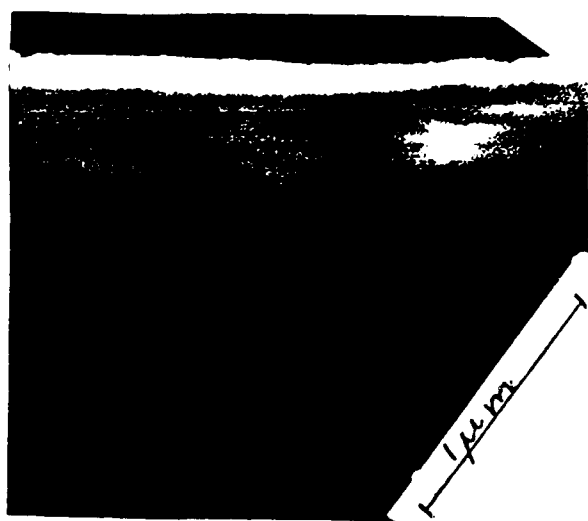
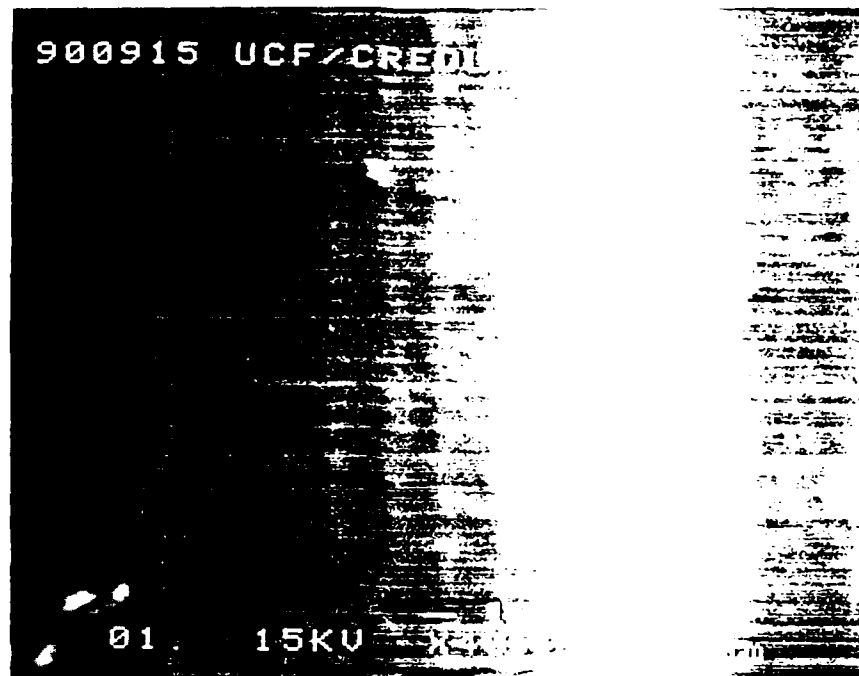


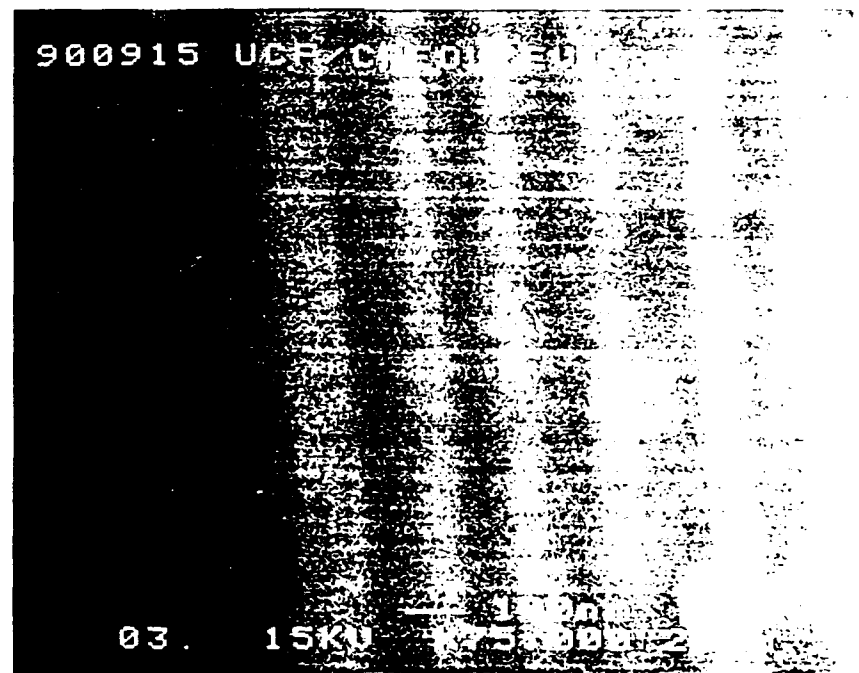
Fig. 9. SEM cross-section of sample # 900915
(JEOL JSM 300 T, UCF/COE)



Fig. 10. SEM cross-section of sample # 901001
(JEOL JSM 300 T, UCF/COE)



Glass



Glass

ZrO₂ SiO₂

Fig.11.(top)
 (bottom)

Cross-section of sample # 900915 (JSM-6400 at MAIC/UF).
 Detail of layers next to the substrate, showing the first two (IP) layers
 (bright = ZrO₂, dark = SiO₂) denser than the following (EB) ones.

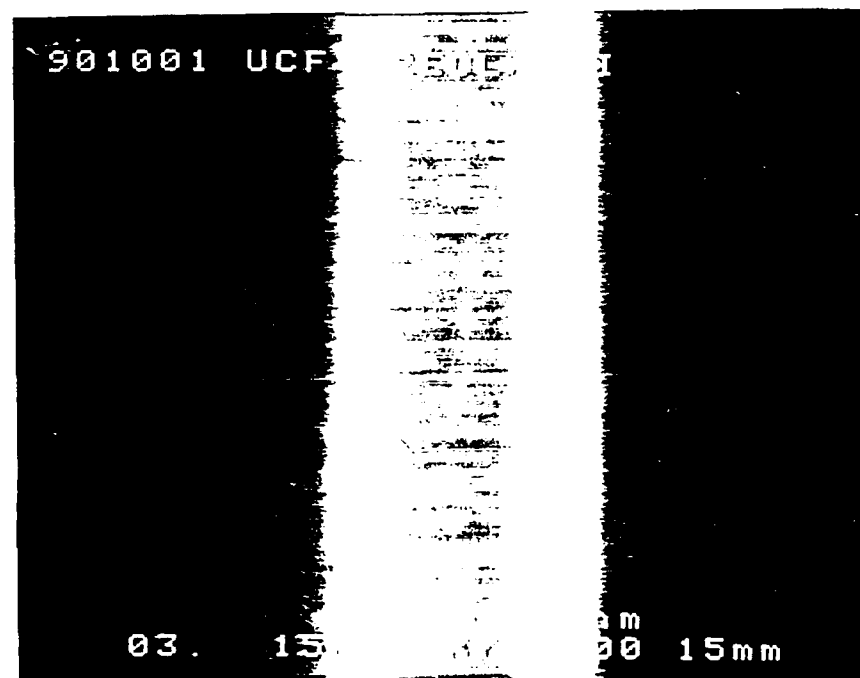
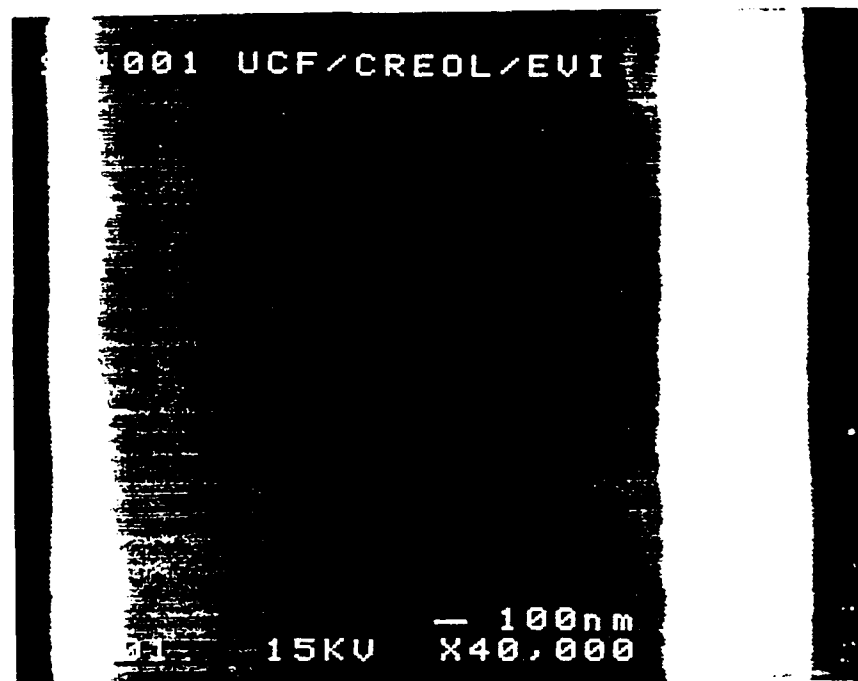


Fig. 12.(top)
 (bottom)

Cross-section of sample # 901001 (JSM-6400 at MAIC/UF).
 Detail of top layers next to the surface. The first three (RLVIP) layers from the top show as one bright band, not really resolved because of too high an electron emission.

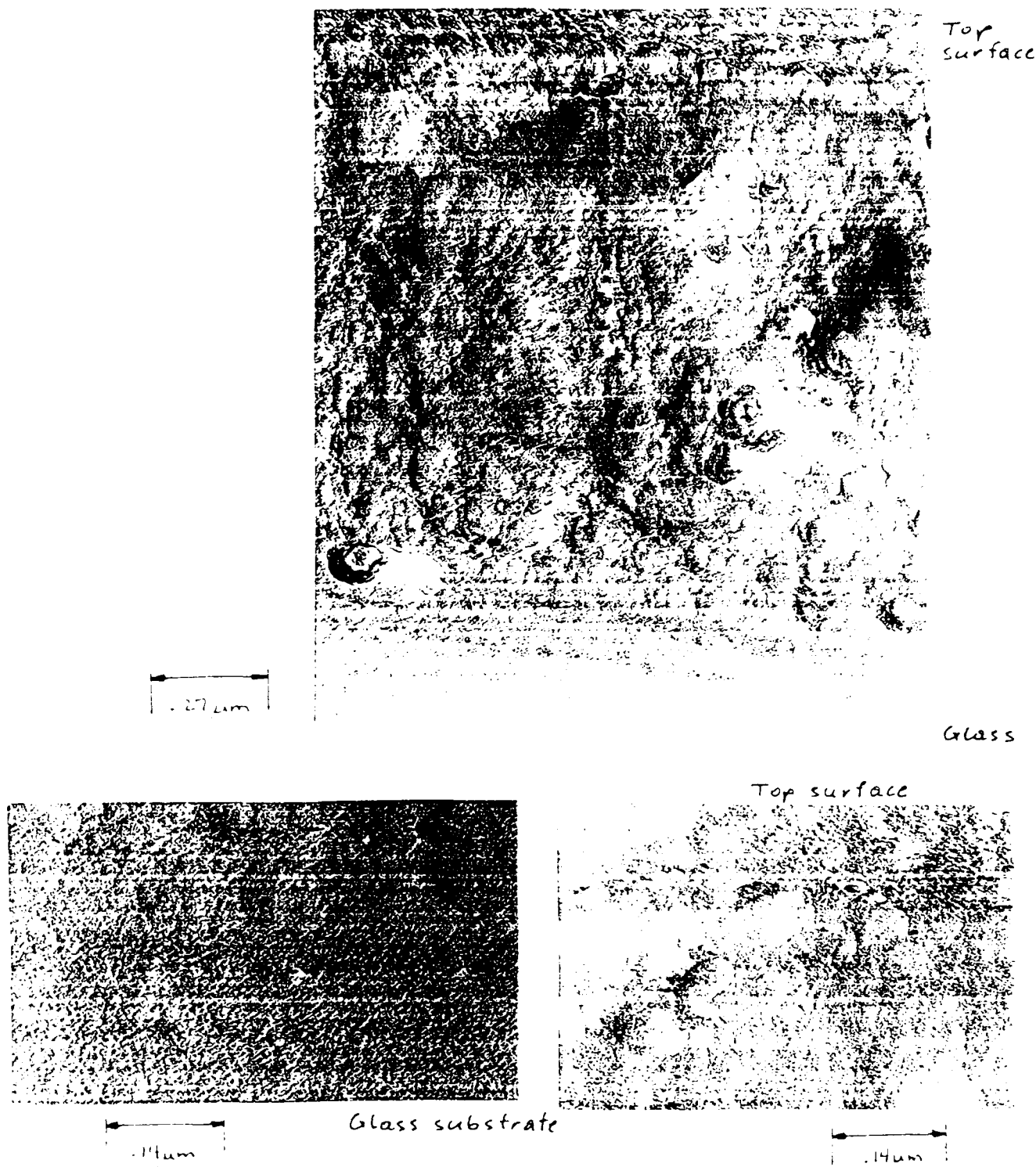


Fig.13.(top)

Cross-section of sample # 900915, taken from a Pt-C/C replica with the JEM 200 CX at MAIC/UF

(bottom left) Detail of layers next to the substrate, showing the first two (RLVIP) layers being denser than the following (EB) ones.

(bottom right) Detail of top layers next to the surface. Although the last layer has been deposited by RLVIP, it is not as smooth as the first two at the bottom, because the intermediate electron beam deposited layers with their granular structure produced a rough surface.

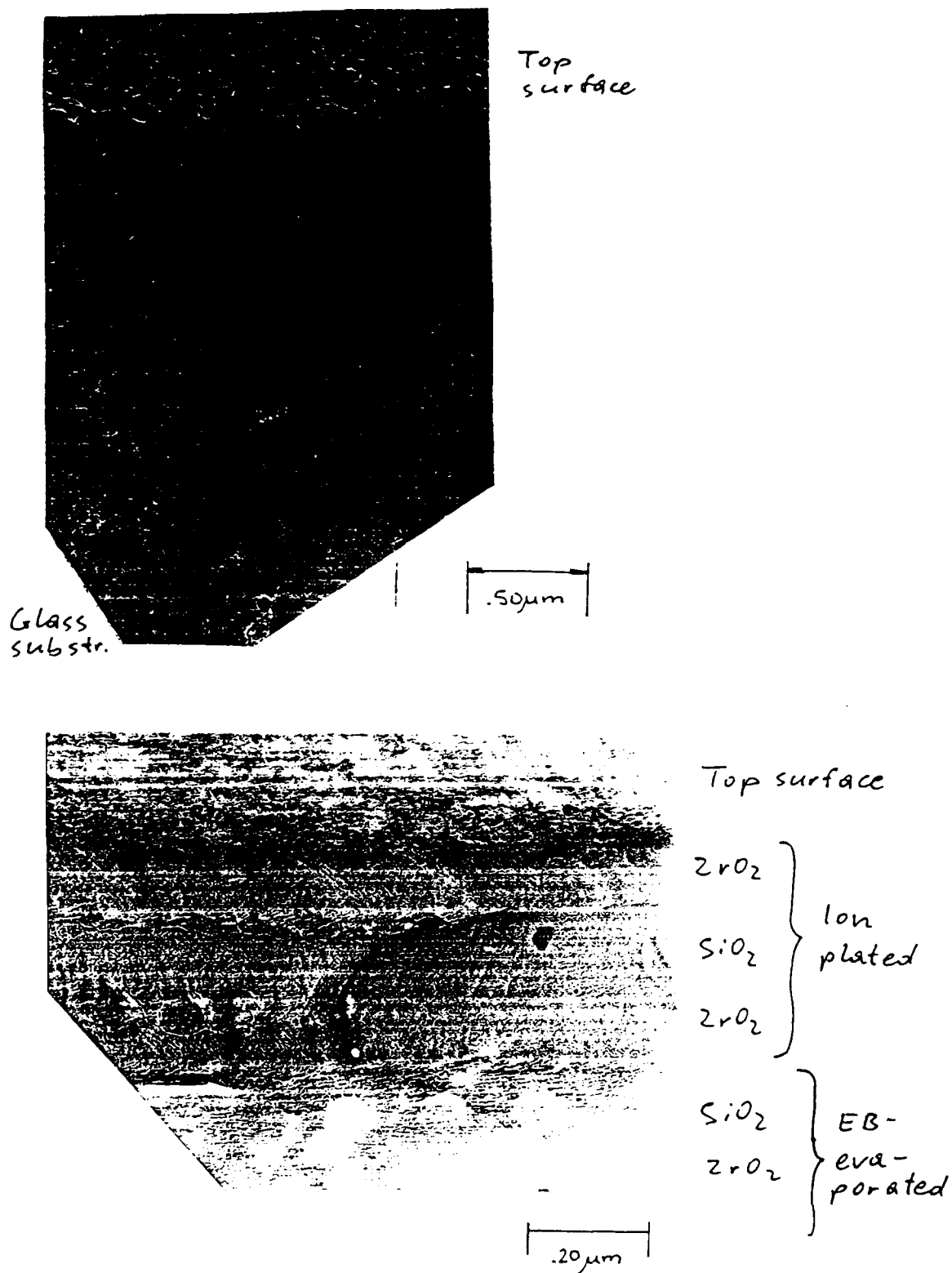


Fig. 14.(top)

(bottom)

Cross-section of sample # 901001, taken from a P-C/C replica with the JEM 200 CX at MAIC/UF

Detail of top layers next to the surface. The first three (RLVIP) layers from the top are better resolved than in the SEM micrograph (Fig. 12), showing denser structure than the electron beam evaporated layers.

Conclusions and Outlook

This feasibility study showed indeed promises for the compatibility of hard, dense dielectric coatings with polycarbonate lenses, particularly when they come with an organic (or lacquer) hard coat. The key issue of keeping the chamber temperature during film deposition low for the protection of the plastic lenses was reasonably well achieved, but may bear some further improvement in the proposed second phase of this development. It is particularly important for the envisioned deposition of all-RLVIP multilayer stacks, which we expect to have further improved imperviousness to ambient humidity and practically no spectral shift with changing temperature. For increased durability of our RLVIP dielectric multilayer coatings on plastic (PC) substrates in extreme field conditions, we need to conduct further and more detailed studies as to tailor intrinsic thin film stress and adhesion without compromising coating hardness and optical performance, possibly using different materials and/or co-deposition of dissimilar oxides.

Acknowledgements

The P. I. would like to thank his associate, Dr. K. Balasubramanian, Research Scientist at CREOL, for his invaluable support of and contributions to the successful completion of this feasibility study. Mr. Jeff Richmond, B. S. in Engineering Technology, was instrumental in designing and implementing the additional internal heat sinks and associated water chiller. Mr. Karsten Montkau and Mr. Xue-Qun "Jim" Hu, International Visiting Scientists holding M. S. equivalent degrees from their respective home institutions, operated the Balzers BAP 800 coating equipment in a professional, routine manner. Thanks are also due to Balzers High Vacuum Products of Hudson, N.H., who support the general operation of the BAP 800 with a no-cost service and maintenance agreement, which allows its utilization to the fullest extent.

The electron microscope investigations were carried out, in part, by Drs. A. Morrone (TEM) and R. Crockett (SEM) at the Major Analytical Instrumentation Center (MAIC), University of Florida (UF) in Gainesville. The P. I. received also some support in electron microscopy from Mr. Ed Principe, graduate student at the Dept. of Mechanical Engineering, UCF, and Miss Karin Karpinchik, senior undergraduate student of Physics and student assistant at CREOL. Last but not least, the P. I. would like to acknowledge the fine collaboration with Mr. J. J. Walls, Technical Director of ECI, in conducting this study.

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