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LASER WINDOW SURFACE FINISHING AND COATING SCIENCE

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

~~We report on~~ the objectives and the progress achieved in a program to study the surface finishing and coating of laser windows for high energy laser applications in the 10.6 ~~μm~~,xx 5.3 ~~μm~~, and 3.8 ~~μm~~ wavelength regions,* ~~Our~~ recent chemical-mechanical optical polishing procedures use 1,2-propanediol, whose surface etch rate appears to match the rate of formation of damaged surface layers produced during polishing. Polycrystalline windows approximately 5 cm in diameter and 1 cm

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thick have been polished flat to 1/4 fringe in the visible (better than $\lambda/120$ at 10.6 μm) with faces parallel to 2 arc sec, total optical absorption loss at 10.6 * ~~μm~~ of 0.0007 for a 1 cm thick piece was measured after polishing. ~~Our~~ recent coating efforts have placed emphasis on the use of three layer antireflection coatings produced in ultra high vacuum in an attempt to remove the absorption limitation of $> 0.1\%$ per surface for the two layer coatings produced previously which have prevented the achievement of a ~~our~~ program goal of $< 0.1\%$ coating loss per surface at 10.6 * ~~μm~~. With the new three layer coating designs xx ~~we have been able~~ to achieve coating absorption losses as low as 0.05% per surface for ZnSe/ThF_4/ZnSe designs. The rather high values of absorption index ~~($K = 1 \times 10^{-3}$)~~ for ThF_4 films used at 10.6 * ~~μm~~ can now be incorporated in our new designs and we can still achieve coatings with less than 0.1% absorption losses.

* micrometers

xx it was possible

(K = .003)

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I. INTRODUCTION

Hughes Research Laboratories (HRL) is engaged in a broad program to develop laser window surface finishing and coating technology. Extensive investigations are under way in many laboratories throughout the country, as well as at HRL to develop window materials that have both the low-optical absorption and the high tensile yield stress necessary to satisfy high energy laser system applications. Two classes of materials — the wide bandgap semiconductors and the alkali halides — have received major emphasis in these investigations. At present, serious limitations to window performance characteristics can exist because as the laser pulse duration is shortened and the peak power densities rise, the low damage threshold of the presently available coatings and surfaces can cause damage to occur below the bulk material damage threshold. This lowered damage threshold can be caused by the presence of pores and microcracks which can be present in window surfaces and coatings, and by the high optical absorption in the polished surfaces and coatings produced using presently available state-of-the-art surface finishing and coating techniques.

The goal of our program at HRL is to investigate the surface characteristics and the optical coatings applied to laser windows in order to develop optimized finishing and coating procedures so that the laser damage thresholds of the coatings and surfaces approximate as closely as possible the damage thresholds of the bulk window materials.

Our accomplishments in the initial phases of the program that we conducted in the period from 1 May 1973 to 31 October 1974 were reported in the final report, Contract AFCRL-TR-75-0041, entitled "Laser Window Surface Finishing and Coating Technology," January, 1975. We conducted a broad attack on some of the major problem areas in the surface finishing and coating of windows for use at the 10.6 μm CO_2 laser wavelength. Early emphasis was placed on the ability to prepare reproducible surfaces on single crystal KCl and polycrystalline ZnSe (Raytheon CVD material) which were free of impurities and were structurally representative of the bulk materials. Our success in this effort guaranteed that a "standard surface" was available for use in subsequent coating work which had as its goal the exploration of the potential of film preparation technologies other than sublimation or evaporation in conventional vacuum systems. These included deposition in ultrahigh vacuum, sputtering, physical vapor deposition, and chemical vapor deposition. Pulsed, 10.6 μm, laser damage studies were conducted with the goal of determining the damage thresholds and elucidating the damage mechanisms of the window materials, both in the bulk and on the surface, and the coatings applied to them.

An important aspect of the program was the extensive chemical, physical, and optical characterization of surfaces and films. The effort had a twofold goal: first, to track progress and aid in the conduct of the work on the various tasks, and second, to assess the potential of the various instruments and techniques. The various surface physics tools used included electron microprobe analysis, Rutherford backscattering of light ions, Auger electron spectroscopy, low energy electron diffraction, and scanning electron microscopy.

Carbon dioxide laser calorimetry to determine the 10.6 μm absorption of films and surfaces was used extensively. Other standard optical evaluation methods used were infrared spectrophotometry, attenuated total reflection spectroscopy, and 10.6 μm scattering and reflectance.

In addition a unique optical evaluation tool was designed and is under development in the form of a modulated light ellipsometer for use at 10.6 μm. This instrument can be used for the precise determination of the optical constants of surfaces and films and is expected to be competitive with calorimetry for the determination of absorption coefficients for interfaces and films.

This report covers the work performed on our continuing program for the period 2 June 1975 to 2 December 1975. The objective of our research continues to be the development of surface finishing and coating technology for halide and semiconductor laser windows for use in high-power infrared laser systems. The window materials to be investigated will include single and polycrystalline KCl, CaF_2, doped and alloyed alkali halides and ZnSe. The principal laser wave lengths of interest are 10.6 μm, 5.3 μm, 3.8 μm, and 2.8 μm.

II. TECHNICAL DISCUSSION

A. Surface Finishing

We are continuing to use chemical-mechanical polishing techniques in our optical finishing work to produce damage-free, low absorption surfaces on infrared windows. KCl is lapped and polished using standard high-quality optical finishing methods, with the use of special edge mounting techniques to avoid face damage, and the introduction of a chemical solvent on the final pitch polishing lap. Our findings from a Hughes Aircraft Internal Research and Development Study of grain growth in forging, when combined with our controlled slow etch-polish study for surface finishing, are providing a more thorough understanding of the causes of high surface absorption. Ways of minimizing this absorption are now evident to us, and we are applying this new knowledge to our polishing procedures and fabrication methods.

1. Solvents for Chemical Polishing

The rate of dissolution of surface material by a solvent during polishing must be controlled. The damaged surface layers must be removed as fast as they are formed, but the removal rates cannot be too high, or flatness is degraded. In addition, the solvent used must not attack the pitch lap. Our last Semiannual Report No. 1 (July 1975) describes the testing of 35 solvents for pitch compatibility, and the selection of six solvents. The chosen solvents are listed again in Table 1 along with their etch rates and structural formulae. Table 1 shows a range of etch rate of 30:1, from 0.11 to 3.3 μm per minute. These rates were measured on a KCl surface which had been etch-polished 2 minutes in concentrated HCl, a procedure which removes all disturbed material and leaves a smooth, polished surface, completely reproducible as a reference surface. Note that these solvents act to dissolve KCl by a chelating action, in which the OH^- ions form a complete five- or six-member ring with the K^+ ion. The increase in etch rate with availability of OH^- ion is evident (glycerin should have the highest rate, but its viscosity slows its etch rate).

Table 1. Etch Rates of KCl Versus Solvent Structure

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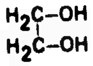
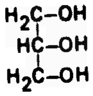
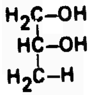
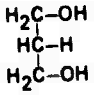
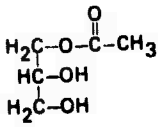
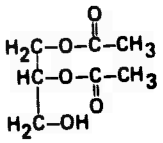
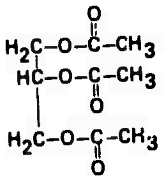
ETCHANT	ETCH RATE, μm/min	STRUCTURE
ETHANEDIOL	3.3	 $H_2C{-}OH$ $H_2C{-}OH$
GLYCERIN (PROPANETRIOL)	1.5	 $H_2C{-}OH$ $HC{-}OH$ $H_2C{-}OH$
PROPANEDIOL 1, 2	0.6	 $H_2C{-}OH$ $HC{-}OH$ $H_2C{-}H$
PROPANEDIOL 1, 3	0.3	 $H_2C{-}OH$ $HC{-}H$ $H_2C{-}OH$
MONOACETIN	0.3	 $H_2C{-}O{-}\overset{O}{\overset{\|}{C}}{-}CH_3$ $HC{-}OH$ $H_2C{-}OH$
DIACETIN 1, 2	0.1	 $H_2C{-}O{-}\overset{O}{\overset{\|}{C}}{-}CH_3$ $HC{-}O{-}\underset{O}{\underset{\|}{C}}{-}CH_3$ $H_2C{-}OH$
TRIACETIN	0	 $H_2C{-}O{-}\overset{O}{\overset{\|}{C}}{-}CH_3$ $HC{-}O{-}\underset{O}{\underset{\|}{C}}{-}CH_3$ $H_2C{-}O{-}\underset{O}{\underset{\|}{C}}{-}CH_3$

2. Chemical-Mechanical Polishing

Our recent optical polishing procedures use 1, 2-propanediol whose etch rate appears to match the rate of formation of damaged surface. This rate is somewhat self-controlling because more highly-damaged surface material etches at a higher rate than the less-damaged substrate, as can be seen in Fig. 1(b). The polishing procedure outlined below yields a flatness of 1/4 fringe (better than λ/120 at 10.6 μm), faces parallel to 2 arc seconds, with a total absorption at 10.6 μm of 0.0007 for a piece 1 cm thick. The KCl sample, forged from a RAP-grown boule of <100> axial orientation, was reduced 65% in height at 280°C, and had a grain size of 3 to 30 μm. This was accomplished as follows:

a. The forged blank is rounded to 2 in. diameter and grafoil lubricant is removed by grinding on wet silicon carbide papers of 320, 400 and 600 grit. This short exposure to water does not affect RAP KCl to a great depth (see Paragraph 4, below), so that subsequent finishing removes all trace of surface moisture.

b. Initial flat and parallel grinding is performed manually on dry aluminum oxide papers of 30 μm and 9 μm grit sizes (Imperial lapping film discs from 3M Company). Note that initial flat grinding of larger pieces can be done mechanically, since the aluminum oxide grinding papers may be mounted on a polishing machine. For small (2 in. diameter) windows, mounting for mechanical pregrinding is not necessary.

c. Final polishing is accomplished on a lap of swiss pitch (No. 73, medium soft), using a pressure of 0.8 psi at 18 rpm. Alumina of 0.3 μm size (Linde A) suspended in an etch-polish vehicle of propanediol 1, 2 is used for chemical-mechanical polishing. Single-side flatness is checked at frequent intervals with a Davidson plano-interferometer, using monochromatic mercury illumination.

d. Second-side polishing is accomplished by placing the delicate finished face against a metal flat covered with masking tape, and securing the blank to the flat using tape around the circumference. Final parallelism is measured with a Hilger and Watts autocollimator, flatness with the plano-interferometer (see c. above).

e. Final cleaning for optical measurements is a two-step process, using an ethyl alcohol (denatured) or 2-propanol rinse followed by a freon TF vapor degreaser.

The surface absorption of a polished sample can be lowered still further by dip-etching, since slow dip-etchants such as propanediol 1, 3, permit us to remove up to 1 μm with no measurable change in flatness. Also, as mentioned above, the lower etch rate of subsurface layers provides partial self-limiting of the etching process.

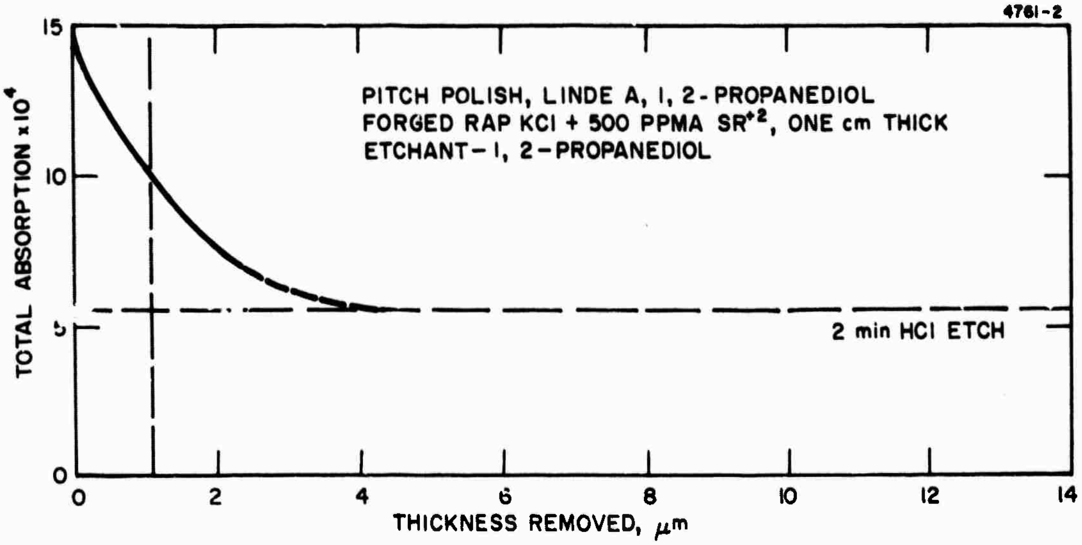
For scale-up, slow etchants permit flooding the surface of a window which is too large to be immersed.

3. Additional Uses for Slow Etchants

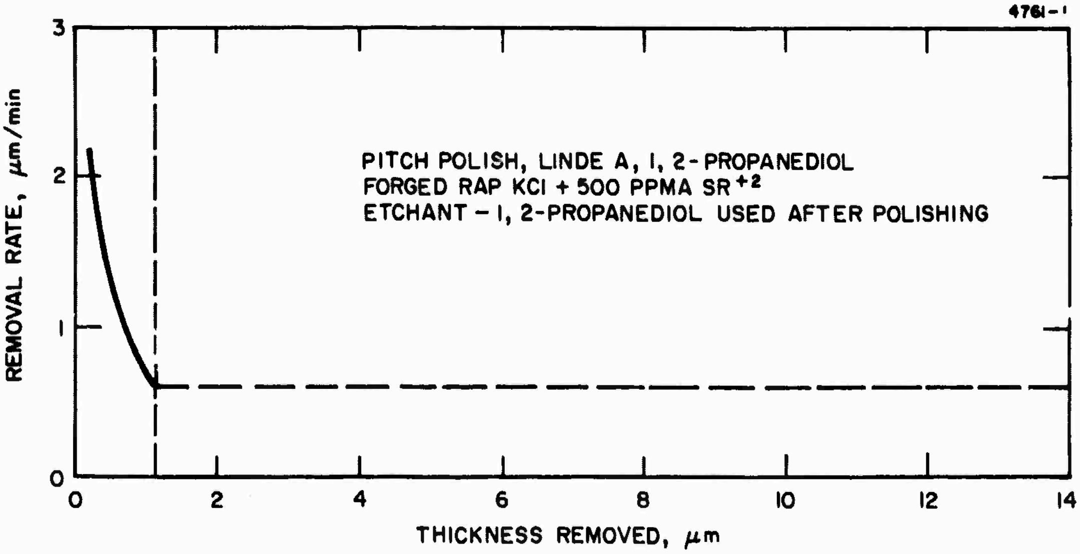
The ability to remove surface layers of KCl at rates down to 1100 Å per minute gives us a control of thickness removal within 300 Å. This permits examination of surface absorption, surface deformation, surface grains, embedded abrasive, and surface chemical action in a way not previously possible. This technique shows us variation of window absorption as thin layers are removed from optically-lapped surfaces (see Fig. 1(a)). Note that the initial total absorption of 15×10^{-4} drops rapidly as material is removed, then more gradually down to 5×10^{-4} after removal of 4 μm.

4. Absorption and Grain Growth

Deformed KCl grows grains in the presence of moisture, according to recent results obtained in a Hughes Internal Research and Development Study. While this study involved KCl deformed by press forging, we recognize that optical surface finishing by grinding, lapping, and polishing can produce local highly-disturbed surface



(a)



(b)

Fig. 1. Absorption at 10.6 μm and etch rate of KCl versus thickness removed.

layers which are also sensitive to moisture. We tested this effect by grinding single crystal KCl on 600-grit (fine) silicon-carbide paper both with and without the presence of moist air. Grinding was followed by a very light etch (≈100 Å), and revealed equiaxed grains when moisture was present, and grain-free deformed material when moisture was excluded. This agrees with Hughes study of forged materials.

We can lower total window absorption by chemically removing disturbed surface layers. (Figure 1(a) shows the amount of removal required.) One assumption has been that crystalline distortion alone is responsible for high surface absorption. The above results suggest that this is not so, because the grains that grow in the presence of moisture are equiaxed and stress-free, but still show high absorption. Therefore, moisture and OH^- ion may be entirely responsible for high surface absorption, with deformed material contributing only through its high affinity for OH^- ion. This view is supported by the fact that press-forged KCl has not shown increased bulk absorption over that of the single crystal. We may obtain strong supporting evidence by measuring absorption of a single crystal, ground, lapped and mechanically polished under moisture-free conditions. If total absorption is no higher than for the same crystal with disturbed material removed, the absorptive role of OH^- and moisture will be verified.

The KCl prepared by reactive atmosphere processing (RAP) and subsequent deformation is more resistant to grain growth caused by moisture than non-RAP KCl (shown by Hughes study of forged material). During surface finishing, this passivity to moisture pickup, aided by our nonaqueous chemical solvents, results in low total absorption (0.0007 for a piece 1 cm thick).

We believe that control of moisture during fabrication and surface finishing, combined with low internal OH^- content and passivity to moisture conferred by RAP, will lead to KCl windows of higher quality. These will have extremely low absorption, stable structure both internally and on the surface, and reliable high strength.

B. Laser Window Coating Studies

In this element of the program, it is our object to prepare antireflection (AR) film coatings on potential infrared laser window materials by three techniques; evaporation, sputtering, and chemical vapor deposition. The films will be compared to determine the method of preparation of the optimum AR coating for high energy laser windows.

During this report period, the major emphasis has been in the evaporative deposition of 10.6 μm AR coatings on single and polycrystalline KCl under ultra high vacuum (UHV) conditions.

1. Ultrahigh Vacuum Coating Studies

The objectives of the study during this period were to design and construct a UHV system which would permit the deposition of coatings on both surfaces of a window material during a single pump down, to deposit some two layer AR coatings to compare the effect of conventional and UHV systems, and to deposit three layer AR coatings under a range of conditions.

a. Apparatus — Results of previous UHV studies demonstrated the necessity of depositing AR coatings on both surfaces of a window material during a single pump down. It had been observed that exposure of the AR coating to a 250°C bake out processing of the system resulted in the thermal stress cracking of films deposited on KCl substrates.

As a consequence, a new UHV system having the following characteristics was designed and fabricated. Disk shaped samples of window materials, 25 mm in diameter and from 5 to 15 mm thick, are lightly clamped in a support ring. This is shown in Fig. 2. This structure is pivoted, so that the sample can be flipped over and both sides can be exposed during a single run. Four samples are mounted on a rotating fixture. Deposition is on one sample at a time. Thus during a single run, four samples can be AR coated on both surfaces. Also four different AR coating designs can be tested in one run. The overall system is shown in Fig. 3 and an interior view is shown in Fig. 4.

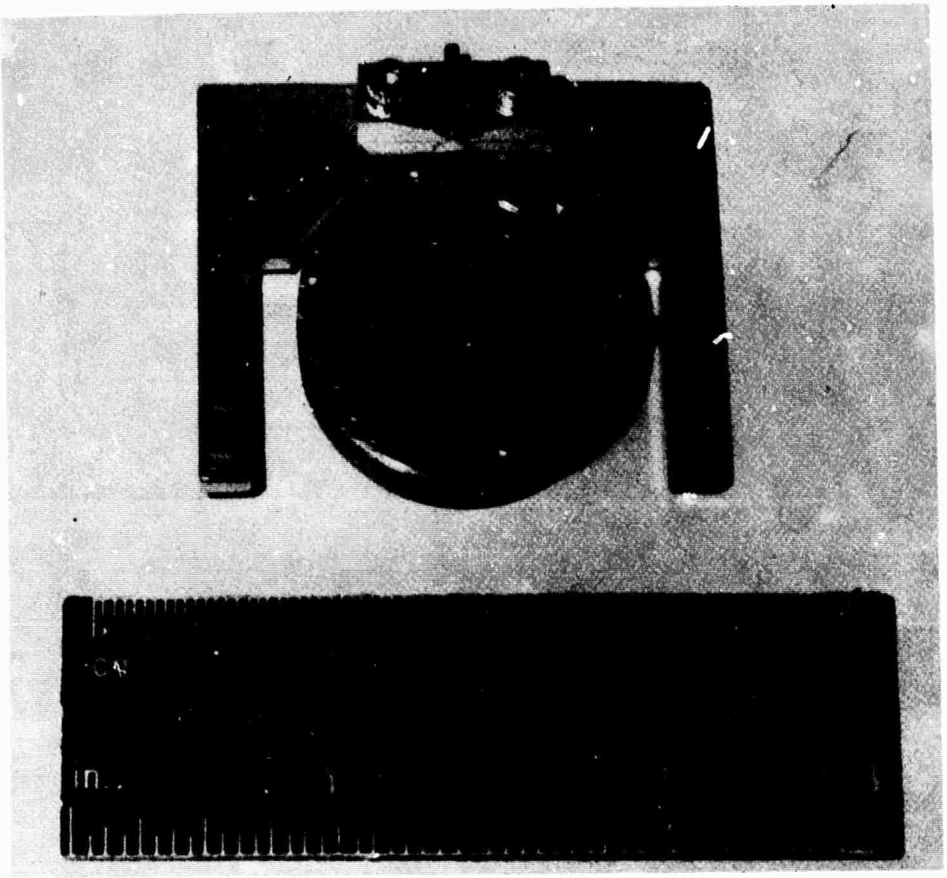


Fig. 2. ZnSe sample mounted in UHV sample holder.

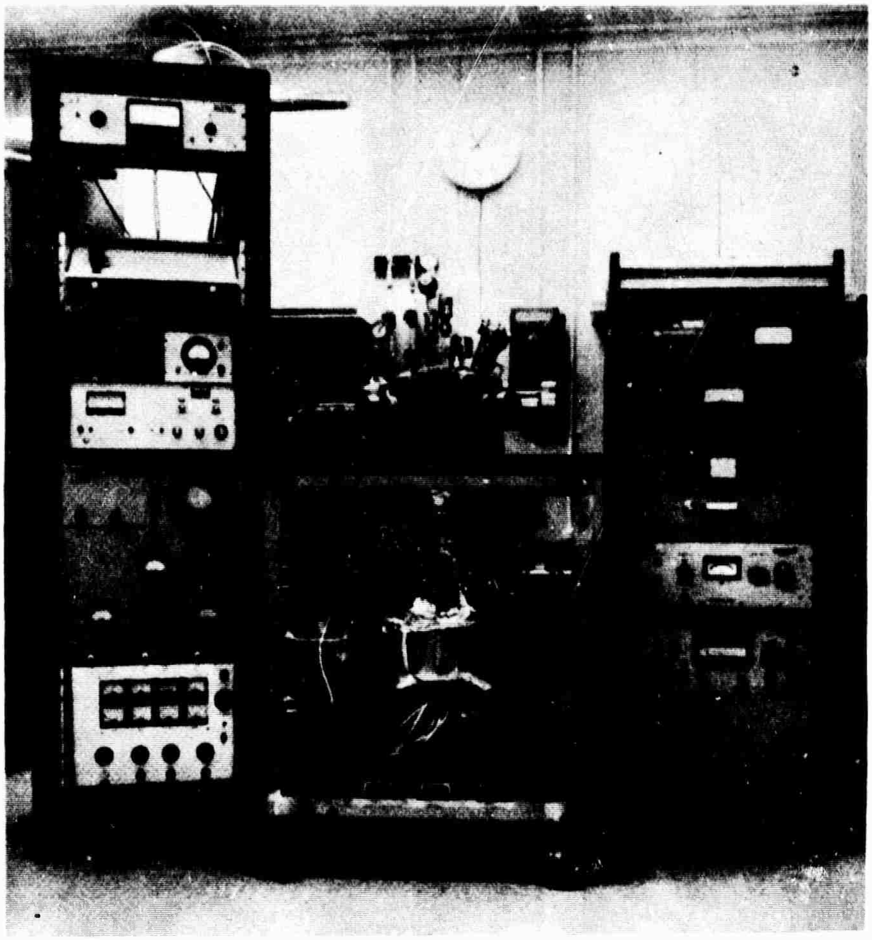


Fig. 3. UHV system for film deposition studies.

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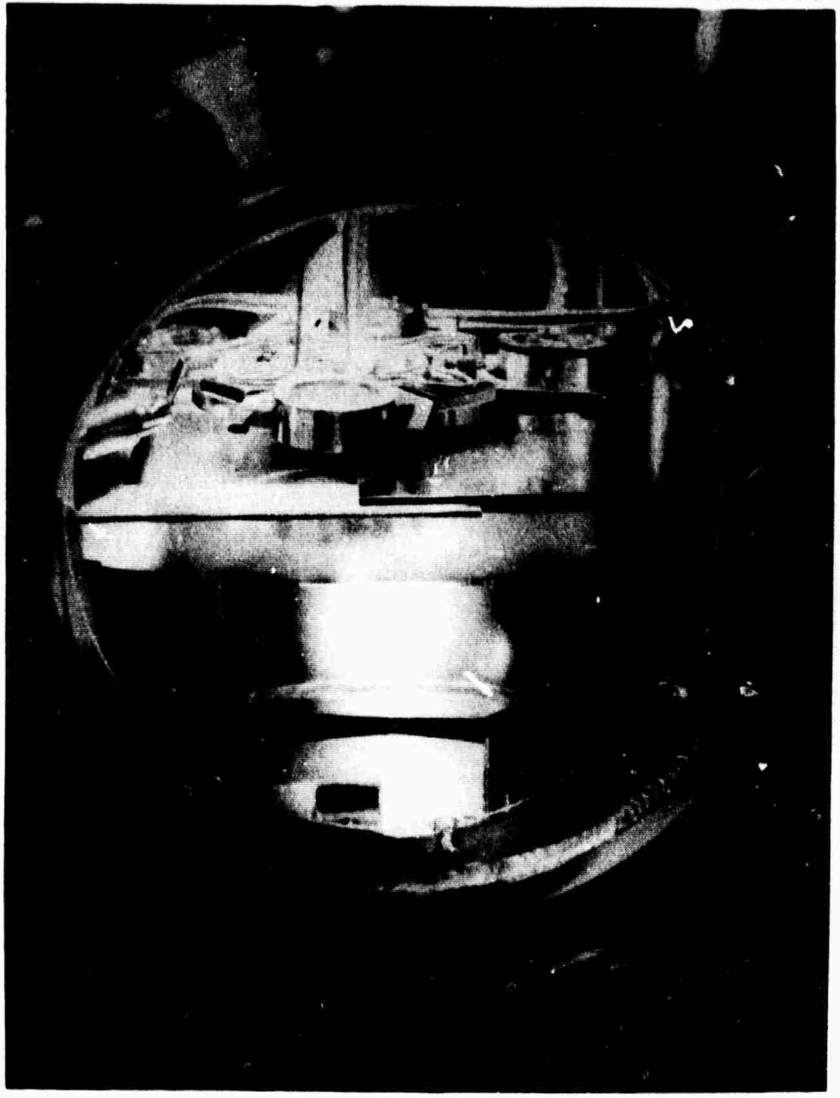

Fig. 4. Interior view of UHV system.

The samples can be heated either by conduction from a coaxial sheath heater, which is brazed to the sample holder, or by radiation from a quartz iodine lamp which is mounted inside the system. The temperature is monitored by means of a Chromel-Alumel thermocouple. A nitrogen or oxygen gas glow discharge is used to condition the sample surfaces before the deposition of the coatings.

The coating materials are evaporated from directly heated Knudsen sources. Due to the directionality of the sources and their location (about 15 cm from the samples), the sources have good efficiency. This is essential for the deposition of eight AR coatings during a single run. The coating thickness is measured during the deposition by a transmission monitor which consists of a synchronously chopped light source, a suitable bandpass filter, and a phase modulated detection circuit. A quadrupole mass spectrometer is used to analyze the gases present in the system before the deposition and those evolved during the evaporation.

b. Two Layer Coating Studies — The first two runs made in this system were of two layer ZnSe and ThF_4 coatings on KCl and ZnSe substrates. The purpose was twofold: (1) to fabricate AR coatings of designs that were being used in the conventional vacuum deposition, for comparison of the two systems, and (2) to de-bug the UHV system. The coating designs, which were determined under Contract F33615-73-C-5044 for the Air Force Materials Laboratory, are presented in Table 2.

The results of a large number of tests made under conventional vacuum conditions and two runs made in the UHV system indicated that the best AR films on KCl of these designs had an absorption of about 0.2% per surface. This implied that the k value assigned to ThF_4 was too low. Tests performed in UHV indicated that the minimum k value was 7×10^{-4} under ideal conditions and that a value of 1×10^{-3} was a realistic design value. A revised set of parameters is presented in Table 3.

Table 2. Optical Characteristics for Two Layer AR Coatings

Substrate	Coating	Optical Thickness	Absorption, % per Surface	Reflectance, % per Surface
KCl	ZnSe-ThF_4	0.041-0.332	0.11	0
KCl	ZnSe-ThF_4	0.459-0.168	0.07	0
ZnSe	ThF_4-ZnSe	0.132-0.052	0.02	0
These values were predicted using a k value for ThF_4 of 3.6×10^{-4}.				

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Table 3. Revised Optical Characteristics of Two Layer AR Coatings

(ThF_4 k = 1×10^{-3}, ZnSe k = 6.8×10^{-5})

Substrate	Coating	Optical Thickness	Predicted	
			Absorption, % per Surface	Reflectance, % per Surface
KCl	ZnSe-ThF_4	0.041-0.332	0.30	3×10^{-5}
KCl	ZnSe-ThF_4	0.459-0.168	0.20	4×10^{-5}
ZnSe	ThF_4-ZnSe	0.132-0.052	0.10	3×10^{-3}

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Based on this work it was concluded that it would not be fruitful to continue the study of these two layer AR coatings. A Hughes Aircraft Internal Research and Development Project was undertaken to produce three layer AR coating designs which could meet the contractual goals.

c. *Three Layer Coating Studies* — The three layer AR coating design has a number of advantageous features. The thickness of the ThF_4 film can be reduced, thereby reducing the optical absorption. The ZnSe is divided into two films, which should reduce the film stress problems. Another significant feature can be seen in a comparison of Figs. 5 and 6, which are plots of the electric field distribution in two and three layer AR coatings.

In the two layer AR coating, the maximum electric field occurs in the ThF_4 film which has high absorption. In the three layer AR coating, the ThF_4 film is located at the point of minimum electric field. The design parameters for the three layer AR coatings are presented in Table 4.

Preliminary experimental studies on the coatings incorporating As_2S_3 were performed in a conventional vacuum system. The results were reported in the first semiannual report. During this report period the major emphasis was on the UHV deposition of the ZnSe/ThF_4 AR coating on single and polycrystalline KCl.

Table 4. Optical Characteristics of Three Layer AR Coatings on KCl

Coating Material	Optical Thickness	Predicted	
		Absorption, % per Surface	Reflectance, % per Surface
ZnSe/ThF_4/ZnSe	0.28/0.057/0.123	0.05	1×10^{-4}
As_2S_3/ThF_4/As_2S_3	0.28/0.060/0.120	0.05	9×10^{-5}
ZnSe/KCl/ZnSe	0.224/0.092/0.116	0.02	5×10^{-5}
As_3S_3/KCl/As_2S_3	0.265/0.074/0.116	0.02	2×10^{-6}

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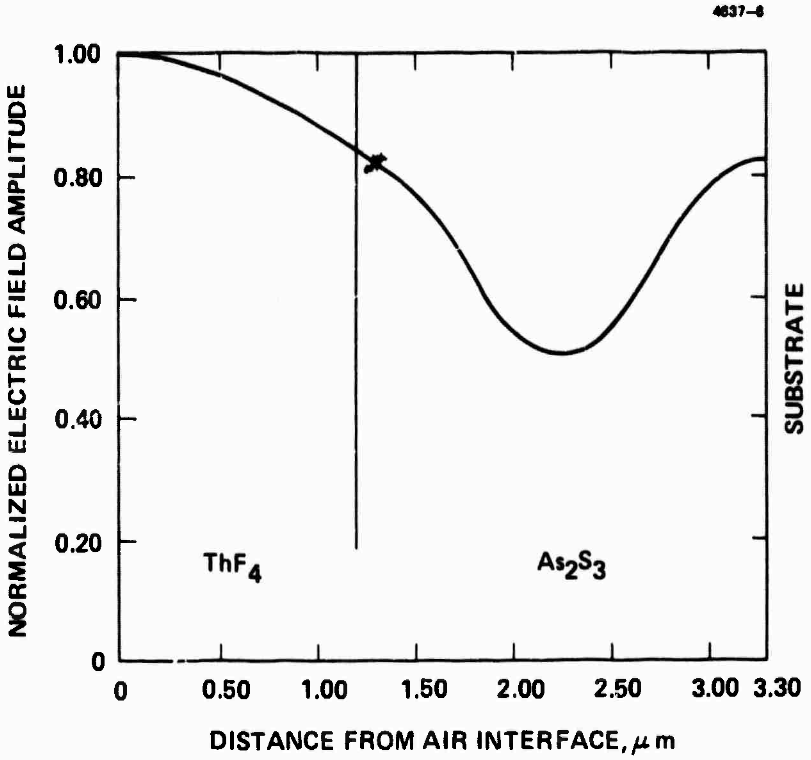

Fig. 5. Electric field distribution in AR coated KCl.

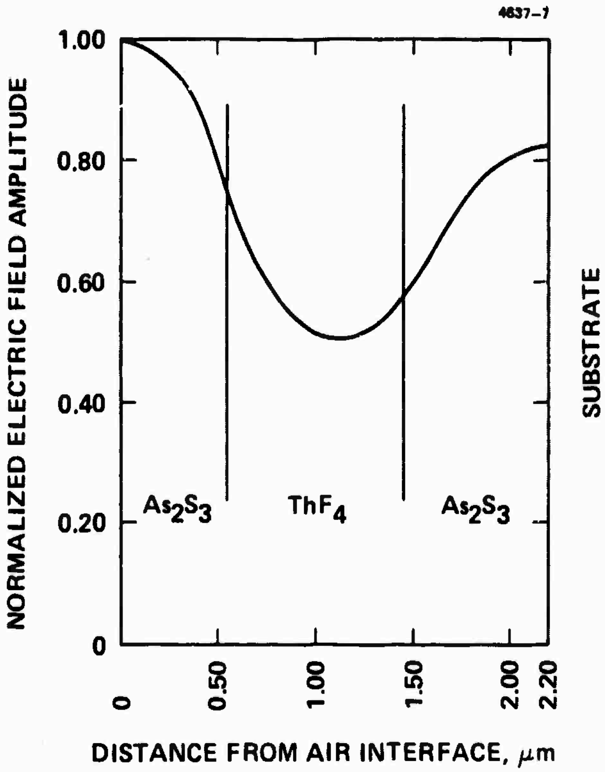

Fig. 6.
Electric field distribution in AR coated KCl.

The objectives of the UHV study were to determine the effects of substrate temperature, crystalline nature of the substrate, surface treatment of the substrate and vapor deposition rate on the performance characteristics of the AR coating. In previous studies, coatings of ThF_4 deposited under conventional vacuum conditions exhibited absorption bands at 2.8 and 6.1 μm unless the substrates were heated to above 100°C during the deposition of ThF_4. Depositions made at 150°C did not have any water bands, but did exhibit a tendency to craze and crack. This is believed to be associated with the difference in the coefficients of expansion of KCl and ZnSe.

Coatings were deposited in the UHV system at substrate temperatures of 150°, 137°, 78° and 23°C. There was no noticeable difference between these coatings in either the 10.6 μm absorption or in the transmission spectrum. This is in direct contrast to the situation in conventional vacuum systems. We believe the most probable explanation to be that the partial pressure of water is about 10^{-7} Torr in a conventional system and is measured at 10^{-11} Torr in the UHV system.

Another aspect of this work is the study of the effect of the crystalline nature of the substrate on the AR coating. In the past, single crystal KCl has been used as a substrate in nearly all of the studies. As polycrystalline KCl is being considered for laser windows, we have begun to incorporate polycrystalline samples in our studies.

After some initial runs in which the coating design was validated, a polycrystalline sample was included in each run. There is no visual difference in the samples after the mechanical polishing process. After etching, the single crystalline KCl has a clear "gem like" appearance while the polycrystalline KCl has a dull cast which is associated with the many small crystal facets.

After being coated, there is a slight visual difference between the two types. While the single crystal samples remain very clear, the polycrystalline samples have a slight dullness in appearance. In contrast, there has been no discernible difference at 10.6 μm in either absorptance or reflectance. While the work is still preliminary, as it is based on 17 single crystal and four polycrystalline samples, we feel that the evidence that polycrystalline materials can be used is very good. Our future plans are to increase the number of polycrystalline samples to the point where they are used exclusively.

Because of the accidental failure of the glow discharge power supply, two of the runs were made without use of this surface treatment. While there was no discernible difference in the optical properties of these eight samples when contrasted to the 13 other samples, three of the nonglow discharge treated samples have subsequently developed surface crazing when handled, while none of the 13 treated samples have failed. This indicates a strong correlation of film adhesion with surface conditioning by glow discharge.

Preliminary experiments were made to determine if the rate of evaporation of the AR coating materials would affect their optical performance. Thus far, the rates have been varied by a factor of about 2 to 3. So far, there is no indication of any difference in optical performance. Future experiments will be made over a larger range of evaporation rates.

The overall summary of the optical characteristics of UHV deposited three layer ZnSe/ThF_4/ZnSe AR coatings (c.f. Table 4) is as follows. A total of 24 samples were coated. Three were accidentally deposited at 250° to 260°C instead of 150°C, due to an error in specification of thermocouple material. These cracked on removal from the holders indicating a very large thermal stress. These are not included in our discussion. An initial sample had an AR coating which was too thick and peaked at 11.0 μm rather than the desired 10.6 μm. Another sample was scratched by the flipper arm while in the vacuum system and so could not be evaluated for optical performance.

Of the remaining 19 samples, six samples had a 10.6 μm absorptance of 0.05 to 0.06% per surface, six samples had 10.6 μm absorptance of 0.07 to 0.085% per surface and three samples were in the range of

0.09 to 0.10% per surface. These results are in good agreement with the theoretical value of 0.05% per surface based on k values of 1×10^{-3} for ThF_4 and 6.8×10^{-5} for ZnSe.

Of the 19 samples, eight have reflectance losses at 10.6 µm of less than 0.06% per surface and three were in the range of 0.07 to 0.1% per surface. Thus more than half of the samples exceeded the contractual goals of 0.1% absorptance and reflectance losses per surface. A typical transmission spectrum for such a coating is shown in Fig. 7.

The good surface of the scratched sample was subjected to a scotch tape test. It was not affected by five applications of scotch tape No. 810. Two samples (B 109 RF 3 and B 129-10) have been subjected to laser damage tests. The results are presented in Section II-D. Sample B 109 RF 3 is a polycrystalline sample which has a 10.6 µm reflectance loss of 0.10% per surface and a 10.6 µm absorptance loss of 0.07% per surface. Sample B 129-10 is a single crystal sample having a reflectance loss of 0.02% per surface and an absorptance loss of 0.10% per surface. As the laser damage test is a destructive one, we selected two average samples rather than the best for those first tests. During the next quarter, we plan to extend the laser damage tests to some samples having lower values of absorptance losses.

As suitable tests are designed, some of these $ZnSe/ThF_4/ZnSe$ AR coatings will be subjected to humidity tests. Also further scotch tape tests will be performed. As these are destructive tests, they will be performed after a point when it is certain that there are no further optical tests required for these samples.

During the next quarter we will study the UHV deposited ZnSe/KCl/ZnSe AR coating (c.f. Table 4) which has a theoretical absorptance loss of 0.02% per surface. A majority of the substrates will be polycrystalline KCl. The substrate temperature and surface conditioning have been fixed by the present work, while the study of the effect of deposition rate will be extended in the next quarter.

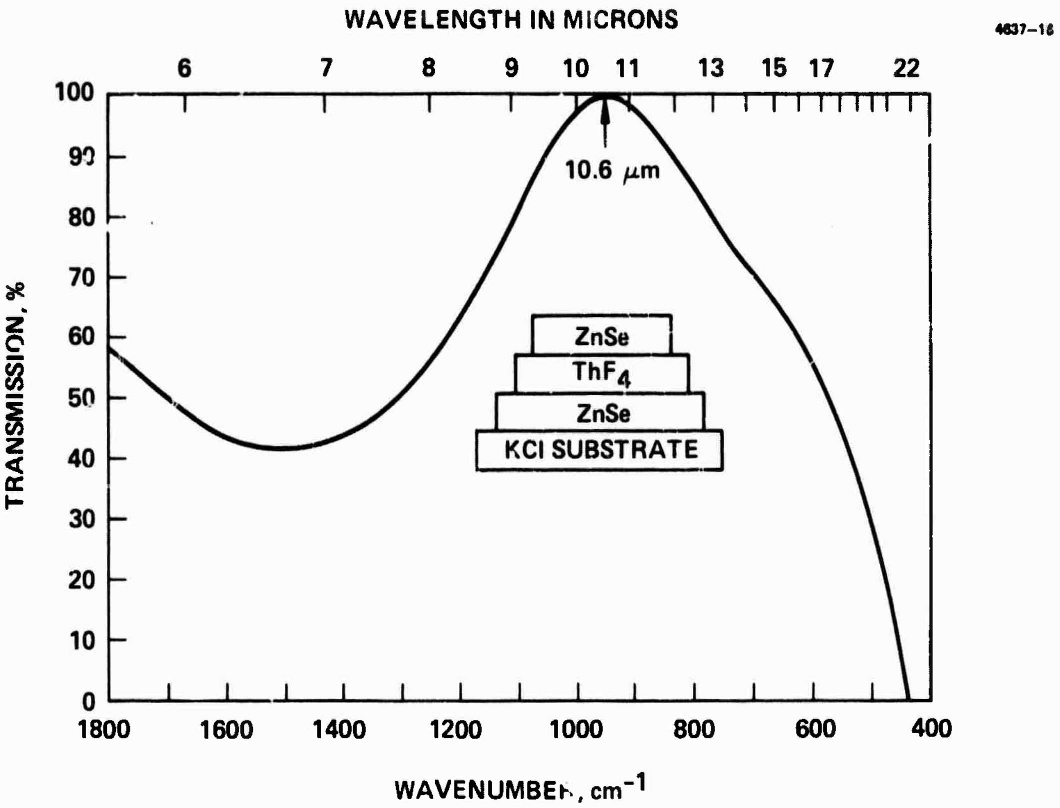

Fig. 7. Experimental spectral response of three layer AR coated KCl.

C. Optical Evaluation

Most of the problems delineated in the previous report (Semiannual Technical Report No. 1) have been resolved and, with some additional modifications which are essentially complete, calibration of the ellipsometer and diagnostic checks should be concluded in the near future. Detailed descriptions of the changes made since the last report are given below.

The waveguide laser was replaced by an amplitude stabilized conventional CO_2 laser. Amplitude stabilization was achieved via a feedback loop to the PZT mounted grating in the laser cavity fed by a signal at the "dc" frequency (180 Hz) picked off a beam splitter by a polyvinylidene Fluoride (PVF) pyroelectric detector. The system is similar to the feedback stabilization scheme for the CO_2 laser in our apparatus used to measure low level reflectance and scattering but is capable of faster response to amplitude instabilities. The waveguide laser exhibited short term instabilities which can probably be ascribed to a design defect in the electrodes. Recent models of the waveguide laser have corrected this defect and our particular laser will be modified to correct the design defect. The conventional laser is mounted so that the polarization of the beam is approximately $+45^\circ$ to the plane of incidence (all angles measured in the direction of k of the laser). The actual laser polarization is $+35^\circ$ but is corrected by the wire grid polarizer.

Absolute alignment of the wire grid polarizers presented a formidable problem as all the standards available were in the visible and did not overlap the wavelength range of the ZnSe wire grids. It was decided to make use of the He-Ne alignment beam and its diffraction by the wire grid. A screen was fabricated with closely spaced lines accurately parallel to the ellipsometer bench and therefore parallel to the plane of incidence. The ZnSe wire grids are rotated until the diffracted and zero order spots fall on the same line on the screen. At this position, the lines of the wire grid are perpendicular to the plane of incidence and the passing axis of polarization is parallel, i.e., 0°. Some complications did arise due to a slight wedge (approximately 1 minute) at about 35° to the lines of the grating in one of the ZnSe polarizers. This wedge causes the diffracted beams to be displaced slightly but the small error (on the order of 1°) introduced can be corrected. As a final test the two polarizers were aligned independently and their extinction positions were as calculated, ±0.05°. The above procedure yields alignment accuracy of 0.1° and, as shown in a previous paper,[1] no first order errors are introduced for angular misalignment of the polarizer and analyzer when their positions are ±45° relative to the plane of incidence. Such alignment accuracy should therefore be more than sufficient.

The optical stabilization scheme for the photoelastic modulator (PEM) described in the previous report was successful. A GaAs LED and Si detector are mounted in the housing of the PEM so that they look through the ZnSe PEM near an edge so as not to obstruct the main beam. Near IR polarizers (Polaroid Type HR) are used at approximately ±45° before and after the ZnSe. This arrangement generates a signal at 2ω which is porportional to the amplitude of the retardation, ϕ, of the modulator. This signal can be fed back to the voltage supply of the PEM in a stabilization loop similar to that used in the laser stabilization above. The GaAs LED was chosen because the retardation amplitude is an inverse function of the wavelength and at shorter wavelengths changes sign too rapidly to be useful for stabilization at 10.6 μm.

The electronics package which had been used to drive the PEM has been shown to be unreliable. The specifications on the components allowed little or no room for the inevitable variations so that a particular drive circuit would work under some conditions but not others. We have designed and bench tested a different drive circuit which will eliminate this problem. In addition, it will produce a sine wave drive

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[1] S. D. Allen, A. I. Braunstein, M. Braunstein, J. C. Cheng and L. A. Nafie, "A 10.6 μm Modulated Light Ellipsometer," presented at the Int. Conf. on Optical Properties of Highly Transparent Solids, Waterville Valley, N.H.

voltage at the crystal instead of the square wave which was used in the initial package. It is suspected that some of the error signal at the drive frequency, ω, that is detected might be a result of the odd harmonics present in the square wave drive. In any case, since the crystal in the PEM responds only sinusoidally, a sine drive seems desirable.

The PbSnTe detector was chosen initially for the ellipsometer because of its frequency independent response. The requirement of a dewar and consequent LN_2 supply plus the low signal/noise ratio of the particular detector used led to an alternative choice of detector. A pyroelectric detector of $LiTaO_3$ has been briefly tested as a replacement and seems to exhibit the requisite characteristics. Its signal/noise ratio is considerably better than the PbSnTe, but its sensitivity is frequency dependent and will have to be calibrated. The poor noise figure of the particular PbSnTe detector we have used to date is not inherent and steps will be taken to improve its response. For calibration and diagnostic tests, however, the pyroelectric detector will be much easier to use and will be more reliable. Use of the $LiTaO_3$ detector will require the substitution of a voltage mode preamplifier for the current to voltage converter used with the PbSnTe detector.

Efforts to obtain better wire grid polarizers on annealed ZnSe substrates are still in progress. Several paths are being investigated toward this goal including: continuation of the joint effort with California Institute of Technology; purchase of an Ar laser and set up of complete polarizer fabrication at HRL, and subcontracting with J-Y Optical or Bausch and Lomb Optical for fabrication of the gratings.

Immediate plans include the integration of the new PEM drive electronics and the $LiTaO_3$ detector into the electronics and subsequent calibration of the 1/2 in. ZnSe modulator and the requisite diagnostic checks. It is expected that we should be able to take data shortly thereafter.

D. Laser Damage Studies

1. Objectives

Our previous work suggests that 10.6 μm laser damage is limited by localized defects and that coatings are the least resistant optical elements. The highly satistical thresholds we have seen have made extensive tests necessary to obtain meaningful numbers.

The new three layer ZnSe/ThF_4/ZnSe AR coatings made in a UHV system, and the ThF_4/As_2S_3 made in a HV system have been selected for study during this period.

2. Accomplishments

Data was taken at several pulse lengths on two samples of each film system. This is presented in Tables 5 and 6 for the ZnSe/ThF_4/ZnSe UHV material (on KCl) and in Table 7 for the ThF_4/As_2S_3 system (on KCl).

Data is taken by beginning at a low flux level and progressively increasing the flux on the same site by about 15% while the site is simultaneously observed with a 50x microscope. Just prior to each shot, the microscope light is turned off to allow easier detection of laser induced sparks usually associated with breakdown. Damage is defined as any visible change in the surface. In some cases a subtle change occurs without the emission of a flash of light. In the case of As_2S_3, the first shot has the effect of removing scattering centers from the film; in effect, cleaning the film of inclusions. This was observed in 1973 (Ref. 2), and is a rare example where an initially observed change does not result in further deterioration of the film. In the case of the ZnSe coatings, the smallest observable change in surface has been found to signal further deterioration on succeeding

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[2] V. Wang, A. Braunstein, M. Braunstein, J. E. Rudisill, and J. Y. Wada, "Pulsed CO_2 Laser Damage Studies of Metal and Dielectric Coated Mirrors," NBS Spec. Pub. 387, Laser Induced Damage in Optical Materials: 1973, May 15-16, 1973, Boulder, CO.

Table 5. Multiple Shot Damage Thresholds in Three Layer $ZnSe/ThF_4/ZnSe$ UHV Deposited AR Coatings at 10.6 µm (J/cm^2)

Spot Size — 140 µm

Sample		Pulse Length			
		0.6 µsec	1.9 µsec SLM	4 µsec	6 µsec SLM
B129-10	Average Threshold	20	60	—	140
Run 36	No., Standard Deviation	6, σ = 13	6, σ = 45	—	5, σ = 42
Single Crystal KCl	Range	8-45	14-145	—	92-200
B109-RF3	Average Threshold	26	140	110	235
Run 34	No., Standard Deviation	7, σ = 11	6, σ = 10	4, σ = 10	5, σ = 190
Polycrystalline KCl	Range	11-36	97-200	95-115	99-570+

T1818

Table 6. Single Shot Damage Thresholds in Three Layer ZnSe/ThF$_4$/ZnSe UHV Deposited AR Coatings at 10.6 μm (J/cm^2)

Spot Size 140 μm

Sample		Pulse Length			
		0.6 μsec	1.9 μsec SLM	4 μsec	6 μsec SLM
B129-10	Average Threshold	7	36	—	46
Run 36	No., Standard Deviation	3, $\sigma = 2$	4, $\sigma = 11$	—	5, $\sigma = 29$
Single Crystal KCl	Range	5-9	26-49	—	33-72

T1819

Table 7. Multiple Shot Damage Thresholds in ThF$_4$/As$_2$S$_3$ HV Deposited AR Coatings at 10.6 μm (J/cm^2)

Spot Size — 140 μm

Sample		Pulse Length		
		0.6 μsec	1.9 μsec SLM	6 μsec SLM
B71-18	Average Threshold	47	37	63
(Single Crystal KCl)	No., Standard Deviation	5, $\sigma = 20$	11, $\sigma = 25$	5, $\sigma = 12$
	Range	28-74	16-105	54-83
B71-6	Average Threshold	40	141	152
(Single Crystal KCl)	No., Standard Deviation	2, —	5, $\sigma = 50$	3, $\sigma = 5$
	Range	29-50	68-190	113-120

T1820

shots. In both cases, damage is seen to nucleate on visible scattering sites in the film, suggesting that localized inclusions or defects are the limiting damage mechanism.

The data in Tables 5 through 7 are expressed in J/cm^2. The peak power density is obtained by dividing the energy density by the equivalent pulse length. A further enhancement of peak power on a nanosecond basis occurs during those pulses which are multilongitudinal, partially mode-locked (0.6 μsec and 4 μsec). Below the given values for average flux, the number of data points used to obtain the average are given along with the standard deviation. The third line lists the minimum and maximum thresholds observed (range). The threshold is defined as the last pulse energy at which no damage was observed.

The data of Tables 5 and 6 strongly suggest a power dependent damage threshold. Table 7 appears to show a general trend toward improvement with longer pulses, but the effect of rapid temporal modulation upon the threshold (mode-locked 0.6 μsec pulse) is unclear.

3. Future Plans

Tests are continuing upon these samples at different focal spot sizes. It has been found that there is a general tendency for the damage threshold to increase with smaller spot sizes. For samples containing randomly distributed, localized inclusions, this is thought to be the result of the greater probability of a small beam to miss inclusions. Thus, to assess the probable damage threshold for very large beams, tests at several beam diameters are needed. This information can further be used to estimate the average inclusion spacing if tests at enough spot sizes are made.

III. SUMMARY

Our recent chemical-mechanical optical polishing procedures use 1,2-propanediol whose surface etch rate appears to match the rate of formation of damaged surface layers. The polishing procedure outlined in Section II-A-2 for forged polycrystalline KCl window blanks yields a flatness of 1/4 fringe in the visible (better than λ/120 at 10.6 μm), faces parallel to 2 arc seconds, with a total optical absorption loss at 10.6 μm of 0.0007 cm^{-1} for a window of approximately 5 cm in diameter and one cm thickness. The surface absorption of a polished sample can be lowered still further by dip-etching, since slow etchants such as 1,3-propanediol permit removal of up to 1 μm of surface with no measurable change in flatness.

Antireflection (AR) coating at 10.6 μm for KCl using 2 layers (i.e., ThF_4/ZnSe) have optical absorption higher than the 0.1% absorption loss per surface which is the goal of our program. This is a result of the high absorption in the ThF_4 films. Our recent efforts have placed emphasis on the use of three layer AR coatings produced in ultra-high vacuum in an attempt to remove this limitation from achieving our program objectives. Three layer AR coatings using ZnSe/ThF_4/ZnSe have been produced on a number of KCl window surfaces with experimental results in agreement with our theoretical predictions that the coating loss could be kept <0.1% per surface. A number of coated KCl windows produced have 0.05 to 0.06% loss per surface. It has been possible to achieve these excellent results using the three layer designs because the ThF_4 film is placed in the coating stack at a location where the electric field is minimized. AR coating designs for 10.6 μm applications which use ThF_4 films can be produced with absorption loss less than 0.1%, even though the K value for the ThF_4 films is as high as 1×10^{-3} by using three layer designs.

Optical evaluation work continues to place major emphasis on 10.6 μm-calorimetry for obtaining surface and coating optical absorption loss data routinely. The work on the modulated light ellipsometer is continuing in an attempt to provide stable electronic drive circuitry and improved components so that reliable operation and optimized signal-to-noise ratios can be maintained.

Pulsed 10.6 μm laser damage data is reported for the recently prepared three layer ZnSe/ThF_4/ZnSe AR coatings produced in a UHV system and also for two layer ThF_4/As_2S_3 coatings produced in a HV system. Damage threshold data was taken at several laser pulse lengths on two samples of each film system. Both multimode (MM) and single longitudinal mode (SLM) laser beam characteristics were used for measurements. A tendency toward higher damage threshold seems to be indicated when using the single longitudinal mode beams or longer pulse lengths.

IV. CONSULTATIONS AND VISITATIONS

Extensive consultations were held with NWC, (China Lake), and DARPA Materials Science Office in regard to progress and developments on the Laser Window and Coatings Programs supported by AFWL, AFML, AFCRL, and DARPA.

Dr. Harold Posen (AFCRL) and Captain Harry Winsor (DARPA) visited Hughes Research Laboratories and were given a comprehensive technical review of the status of the Laser Window Surface Finishing and Coating Science Program.

V. PRESENTATIONS

The following papers were presented at the Seventh Annual Conference on Damage in Laser Materials, July 1975, at Boulder, Colorado and are to be published in the conference proceedings.

Single and Multilongitudinal Mode Damage in Multilayer Reflectors at 10.6 μm as a Function of Spot Size and Pulse Duration

V. Wang, C. R. Giuliano, and B. Garcia

Improvements in the Breakdown Threshold in Alkali Halides at 10.6 μm

V. Wang, C. R. Giuliano, S. D. Allen, and R. C. Pastor

The following papers were presented at the Fifth Laser Window Conference, December 1975, at Las Vegas, Nevada and are to be published in the conference proceedings.

State-of-the-Art Coating and Future Directions

M. Braunstein (invited paper)

Optical Finishing of KCl Windows to Minimize Absorption in the Infrared

R. Pastor, A. Timper, R. Turk, and M. Braunstein

Low Absorption Antireflection Coatings for KCl

M. Braunstein, J. E. Rudisill, A. I. Braunstein, and D. Zuccaro

Antireflection Coatings for CaF_2 Laser Windows Operating at 5.3 μm

J. E. Rudisill, M. Braunstein, and J. Bowers

Coating Materials for Chemical Laser Windows

A.I. Braunstein, M. Braunstein
J.E. Rudisill, J.A. Harrington and
D. Gregory

Multilayer Enhanced Dielectric Mirrors for 10.6 μm

M. Braunstein, A. I. Braunstein, and B. Garcia

A New Mechanism for Inhibiting Grain Growth in Forged KCl

A. C. Pastor, R. C. Pastor, R. R. Turk,
A. Timper, and R. L. Joyce