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INVESTIGATION OF THE NEUTRAL-SOLUTION ETCH PROCESS FOR REFRACTIVE SOE ANTIREFLECTIVE SURFACES*

Alexander B. Maish
Sandia National Laboratories
Albuquerque, NM 87185 USA

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ABSTRACT

Antireflection of optically clear glass used in photovoltaic concentrator refractive secondary optical elements (SOE's) was investigated using the neutral-solution etch process developed by Schott Glass. Test coupons and SOE's made from barium zinc glass, which does not solarize under ultraviolet exposure, were successfully etched at the center point process variable conditions of 87°C and 24 hours. Reflectance of the plano-plano coupons dropped from 7.7% to 0.8%, with a corresponding increase in transmission from 91.7% to 98.5%. The etching process uses non-hydrofluoric, relatively non-toxic chemicals in a low-cost process well suited for use by photovoltaic system manufacturers during production.

ANTIREFLECTION COATINGS IN PHOTOVOLTAIC CONCENTRATORS

Optics plays a vital role in photovoltaic (PV) concentrator systems both at the cell and at the module level. At the cell level, manufacturers routinely use single or dual layer antireflection coatings to minimize cell reflection. Significant research has gone into identifying optimum cell surface geometries to trap light within the cell to maximize photon absorption (1). At the module level, light must be focused uniformly over the cell surface for best performance. In most PV collectors, Fresnel lenses are used for this purpose. They can easily provide the 10 to 22X geometric concentration ratios typically used in line-focus collectors and the 100 to 500X ratios used in point-focus systems. In addition to concentrating the light, optics plays an important role in compensating for both component and module misalignment. Secondary optical elements located near the photovoltaic cell redirect light onto the cell to correct for assembly tolerance and tracking errors. Both reflective cones and refractive optics have been used for this purpose.

Reflective secondary optical systems generally use flat anodized aluminum reflectors mounted around the cell. These systems are coupled with non-imaging primary Fresnel lenses designed to provide uniform illumination on the cell surface. The reflective secondaries normally do not serve a concentrating function and are not active unless misalignment occurs. Thus there is no optical loss associated with reflective secondaries under normal design conditions.

Glass secondary optical systems have evolved over several years. First generation glass secondary optical elements used the angled sides as totally internally reflecting (TIR) surfaces which functioned as round conical reflectors. Later, Varian used secondaries with domed tops which added some refraction but still used the TIR effect to achieve reflection off the sides of the element (2). The modern refractive glass secondary design was developed by Larry James under contract with Sandia National Laboratories (3). It does not use any reflection, and the sides of the element are completely non-active which eliminates any requirements for shape, surface finish or prevention of adhesive bonding to the sides. Instead it is configured with a domed front surface to redirect light directly onto the cell (Fig. 1). As with all glass secondary elements, the rear surface is flat so the element can be mounted to the front surface of the PV cell to eliminate reflection losses at an additional glass/air interface. These purely-refractive secondaries are coupled with an imaging primary Fresnel lens to project a "picture" of the square lens element onto the cell. Illumination profiles on the cell are much more uniform than with reflective secondaries resulting in a higher cell efficiency. Additionally, tolerance to misalignment and mistracking is better so that optimum module performance is maintained over a wider operating range. A major design constraint of refractive secondary systems, however, is that all the power-producing light must pass through the elements where it is subject to both reflection and absorption losses.

Antireflection coatings on both primary Fresnel optics and secondary refractive optics can provide a significant increase in the optical efficiency and thus the electrical output of PV concentrators. Roughly eight percent of the total energy is lost passing through the two air/acrylic interfaces of the Fresnel lens. If one uses a refractive secondary, another four percent (or more due to the large incident angles on the secondary's curved surface) are lost by reflections from the front air/glass interface. The predicted optical efficiency with a refractive secondary element with and without an optimal AR coating (i.e., no reflection losses) is shown in Fig. 2. The predicted efficiency increase for an optimal AR surface under normal tracking conditions is six percent. Assuming a $2 per watt system cost, 15% electrical operating efficiency, 880 W/m² direct normal illumination, and a nine inch square aperture, one can afford to

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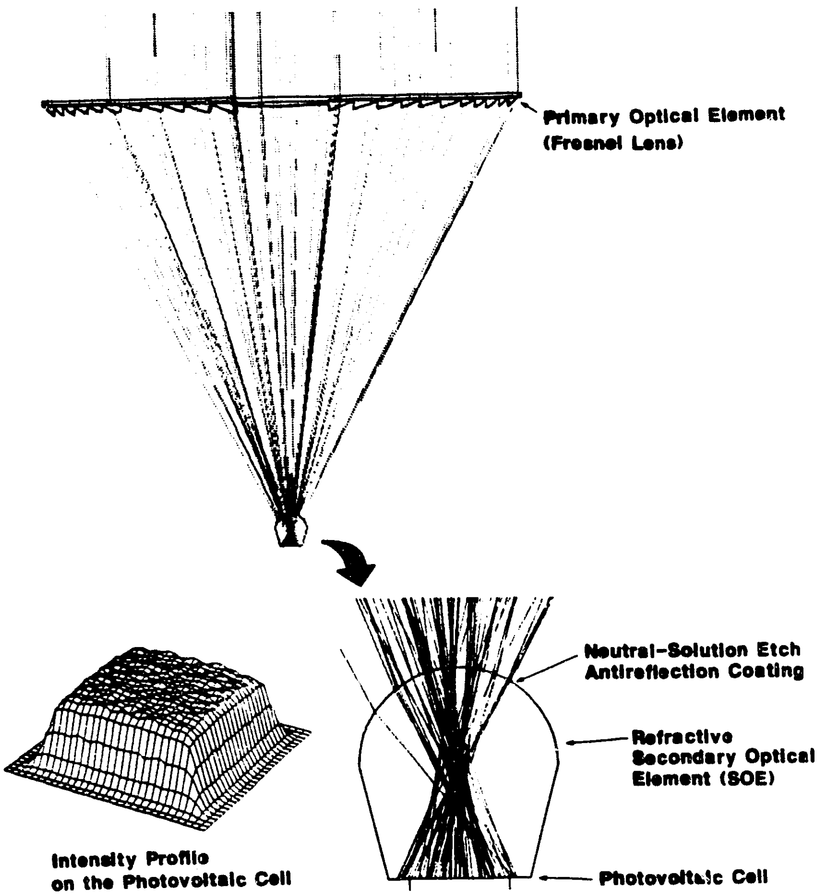

Figure 1 - Concentrating Photovoltaic Module Optics

spend 55¢ per cell assembly for each four percent improvement in optical performance or 82¢ for a six percent improvement.

Unfortunately no low cost method of applying AR coatings to acrylic Fresnel lenses has been developed. Traditional vacuum-deposited quarter-wavelength films, such as magnesium fluoride, are too expensive for use in PV modules. Coatings made of Solgel (curable liquid glass polymer) have been tried at Sandia, but the low curing temperatures dictated by the acrylic substrate limits the achievable density and hence the durability of the coating on the plano outer surface. An additional problem caused by the solution wicking into the facet valleys reduces performance when used on the facet side.

These AR coating methods also have drawbacks for use on glass secondary optical elements. Vacuum-deposited films are too expensive for use on the smaller areas of the refractive secondaries, even for single layer films. They are optimally effective for only limited wavelengths and incident angles. Since they are applied to the surface of the glass, they are dependent on a clean surface for bonding. Solgel films are also applied to the surface (using dip or spinning techniques), so adhesion is also dependent on surface preparation. The Solgel film thickness must be carefully controlled on the curved secondary front surface to achieve uniform AR effects, and the result is similar to the quarter-wavelength coatings in that the surface is only optimally effective for limited wavelengths and incident angles. Fortunately, another AR coating treatment process exists for glass secondary optical elements that avoids the limitations of the methods previously discussed.

NEUTRAL SOLUTION ETCH FILM DESCRIPTION

This paper discusses an investigation of the neutral-solution etch (NSE) process for achieving an AR film on glass secondary optical elements used in PV concentrators. This method promises to deliver a low cost coating technology which can be easily integrated into production lines by module manufacturers at their facilities. Because this process is performed at room pressure and low temperature, no expensive vacuum chambers are required. The film developed during the NSE process is structurally part of the glass so there is not a concern with delamination. The film thickness is controlled by process time and temperature so it is easy to obtain uniform thicknesses on curved surfaces.

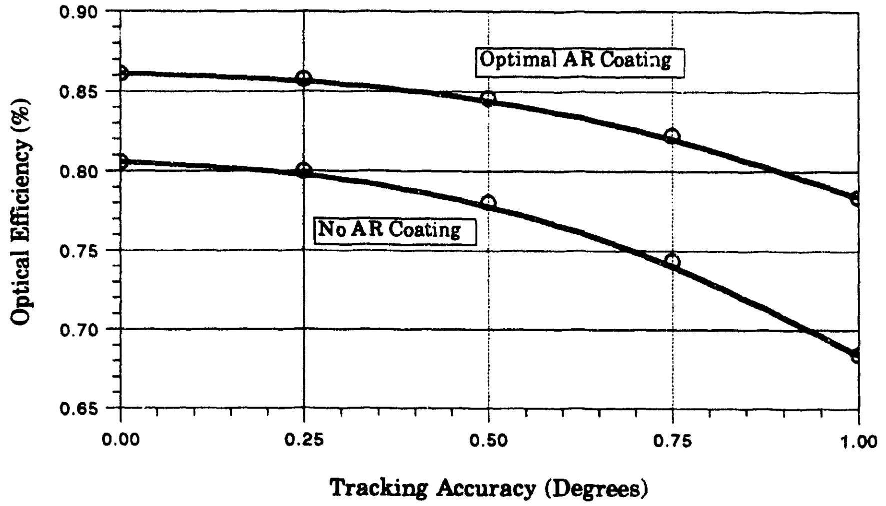

Figure 2 - Predicted Refractive SOE Optical Efficiency With and Without Antireflection Coating

Unlike most etching processes, non-hydrofluoric, relatively non-toxic chemicals (sodium phosphate and aluminum chloride) are used in deionized water to form a near-neutral solution (pH 7.7). This is of vital importance to manufacturers in this era of chemical and environmental safety. The resulting film forms a graded index of refraction antireflection coating, so the AR effect is over a broader range of wavelengths and incident angles than with a quarter-wavelength or Solgel film. In this application, both the broad wavelength and incident angle acceptance are important, but especially the latter since much of the light hits the curved secondary's top surface at non-perpendicular incidence angles.

NEUTRAL SOLUTION ETCH PROCESS DEVELOPMENT

Schott Glass developed and patented the neutral-solution etch process for generating antireflection films in the 1980's for use with high power laser optics (4,5,6,7,8). The process was able to reduce reflection losses very significantly, from 4% to 0.1% per surface. Currently, Schott is licensing the technology to interested companies.

During the process development, Lee Cook and others conducted extensive research using Schott's BK-7 optically clear borosilicate glass to determine the underlying chemistry and the critical process variables. The mechanism believed to create the AR film is one of partial leaching of the metal ions in the glass by alkali/proton ion exchange forming a porous layer having a graded index of refraction. Removal of these metal ions and generation of a porous silicate skeletal structure are important in modifying the refractive index. An additional reaction of network dissolution also occurs which is important in the film formation kinetics.

Several important variables were identified that affect the film formation rate. The most critical variables are process temperature, glass surface to solution volume ratio (S/V), the concentration of the solution chemicals, and the glass annealing rate. Discovery that the S/V ratio is a critical variable which controls the reaction rate was the key to enabling the process to be consistently reproduced from batch to batch. By maintaining the S/V ratio, one can also scale the process up to larger sizes of glass. Low S/V ratios slow the film formation rate, producing AR films with better uniformity, lower reflectance, and greater durability. Cook's studies showed that both the annealing rate and the temperature affect the alkali/proton ion exchange rate, while the network dissolution is affected by the S/V ratio and the amount of silica in solution.

The process variables that do not have to be carefully controlled are almost as important to the usefulness of NSE in production settings as those that are critical to film formation. Cook found that AR film uniformity can be achieved without stirring or controlling solution flow rates over the glass surface, even for irregularly-shaped parts. Solution transport is not needed because diffusion from the glass is the rate-determining process for film formation. The process is also insensitive to other variables, such as sample loading time and solution heating and cooling time, because the reaction times are on the order of hours, not minutes. In fact, optical glass surfaces up to 90 cm in diameter have been coated in a production scaleup described in (7). Finally, using a near-neutral solution containing low-toxicity chemicals rather than hazardous hydrofluoric acid etch solution simplifies handling and compliance requirements, critical issues to a manufacturer.

NSE PROCESS DETAILS

The films developed during the neutral-solution etch process result from a series of complex chemical reactions which are described in detail in (8). The etch solution contains sodium phosphate (Na_2HPO_4) and aluminum chloride ($AlCl_3$) in deionized water. The sodium phosphate generates an ion-exchange alkali leach front which grows into the glass leaving a silica-rich (SiO_2) layer. The alkali flux leaving the surface generates a high pH surface gradient, and the silica begins to dissolve and flow into solution. Thus the alkali flux controls the rate of dissolution. The porous silica layer is stabilized by adsorption of Al^{3+} which comes from the aluminum chloride. In fact, a solution containing only sodium phosphate without aluminum chloride can be used to remove an existing film. The Al^{3+} adsorption thus produces a stable silicate inner skeletal layer. The silica leaving the surface reacts with Al^{3+} in solution to form aluminosilicate colloids which are adsorbed onto the surface. It is this polymerization from the solution that produces the aluminosilicate outer layer. Scanning electron micrographs indicate that the pore size is on the order of 40 to 60Å.

Experiments run at Schott Glass indicate the film growth and the reflection minima wavelength increase linearly with time. The relationship with temperature is nonlinear, but Schott did not study the reaction enough to determine the character of the relationship. Temperature affects the process rate dramatically. Film growth occurs at a rate of about 24 nm per hour at a process temperature of 87°C and drops to about half that (10 nm per hour) at 80°C (10). At temperatures much above 87°C, bubble formation can begin to be a problem as the boiling temperature is neared. The S/V ratio affects the process by determining the silica concentration of the solution and thus the growth rate of aluminosilicate colloids. Glass annealing and surface treatment affect the network density and thus the alkali diffusion rate. Fire polishing, which is used on the curved refractive secondaries to smooth them, generates an alkali-depleted zone near the surface which requires additional process time before the leached alkali reaches the glass surface, starting the etch process.

Cook developed a baseline set of process variables for BK-7. S/V ratio was set at 0.2 cm^{-1}, process temperature at 87°C, the glass was fine-annealed with standard grinding and polishing procedures, and the solution concentration was 0.035 moles per liter of sodium phosphate and 0.001 moles per liter of aluminum chloride. Only Teflon, polyethylene, or polypropylene tools and apparatus were used since metals, rubbers, and, of course, glass can affect processing. Contaminants can coat the surface and prevent etching, so parts are carefully degreased prior to etching. Even finger prints on the edge of the glass are sufficient to form streaks on the surface of the glass during etching.

Although Cook optimized the process variables for BK-7 glass, this glass cannot be used for refractive secondary optical elements in PV concentrators because it "solarizes" or turns color under concentrated ultraviolet (UV) light. Solarization is a process which has been known for many years and is due to an exchange of electrons from trace metals in the glass (9). Secondary optical elements made of BK-7 were actually tried in a PV concentrator, and despite the use of UV blockers in the primary lens, the secondaries turned slightly purple and shattered. This was due to the heat generated by absorption of light under the several thousand suns of illumination at the focal point within the glass. Candidate optically-clear glasses were identified which do not solarize, but the process variables for NSE film generation are not known for them. This paper discusses an investigation of the effect of the critical process variables on AR film formation for one new glass composition.

NSE FILM DURABILITY

Although etched surfaces can endure unchanged for many months, they are mechanically somewhat fragile. One can remove fingerprints with lens paper and an alcohol rinse, but moderate abrasion can remove the AR film. Heat treating to partially sinter the surface can improve mechanical durability. If soaked in water the AR film degrades, over a few days at 20°C and over 24 hours at 80°C. Acids also degrade the film by removing the protective Al^{3+}.

Although some films have lasted many months with no increase in reflectivity, others reverted to original reflectance within months due to adsorption of hydrocarbons, probably from plastic outgassing. Flushing with ethyl alcohol restored the low reflectance of the samples at Schott. Testing is needed to see if this will cause a problem in PV concentrator module applications. Moisture absorption by the film was also observed to reduce reflectivity. It too was reversible.

EXPERIMENTAL SETUP

An experiment was designed at Sandia to evaluate the NSE process on barium zinc glass and to characterize the effects of process variables, specifically temperature and time. To minimize the number of experimental variables, values for the S/V ratio and solution composition were held constant at the values used by Schott Glass in their process for BK-7 glass. A S/V ratio of 0.204 cm^{-1} was used with the solution chemical composition previously described. The experiment is a main effects test with factor interaction, which requires testing at the center point of the experimental space (24 hour process time and 87°C process temperature) and at the four corners (12 and 36 hours process time and 82°C and 92°C process temperature).

The steps used in the Sandia investigation are listed in Table 1. Processing is relatively simple and was performed in programmable laboratory oven to enable process automation of times at temperature. The glass parts were degreased, heated to the process temperature in a precise volume of etch solution at the process temperature, held for the process time, and then cooled and rinsed.

The barium zinc glass SOEs were provided by Alpha Solarco, a photovoltaic concentrator module manufacturer using refractive SOEs in its module design. The University of Dayton Research Inst. glass shop fabricated the flat glass coupons needed to monitor the optical properties. A boule was cored, sliced, and mechanically polished on both surfaces to obtain test coupons which were 3.81 cm in diameter and 3 mm thick. From the work performed at Schott, it was known that the annealing rate and surface treatment

Table 1 NSE Process Steps

- Premix etch solution.
- Scribe and degrease glass samples.

Immediately prior to etching:

- Clean samples in an isopropyl alcohol bath.
- Rinse and warm samples in a warm (40°C) deionized water bath.
- Place samples in warm (60°C) etch solution in a covered polypropylene cup in a lab oven.
- Ramp temperature up to process temperature at 30°C per hour.
- Hold at process temperature for process time.
- Ramp temperature down to 60°C at 30°C per hour.
- Rinse and cool samples in warm (40°C) deionized water bath.
- Dehydrate samples with an isopropyl alcohol rinse and air dry.

affect the process time but not the resulting quality of the AR film. Additional samples were mechanically polished and subsequently reannealed and fire polished to duplicate the surface finish of production secondary elements. These were not received in time to complete the main effects and interaction studies before publication, but several center-value runs were made with the mechanically polished samples which are described below.

The etch solution was prepared by adding 19.88 grams of sodium phosphate (Na_2HPO_4) (0.035 moles per liter) and 0.969 grams of aluminum chloride ($AlCl_3$) (0.001 moles per liter) to four liters of deionized filtered water. The sodium phosphate mixes best at elevated temperatures (above 60°C) but mixing can be done at lower temperatures. Although the useful life of the solution is not known, samples were successfully etched at Sandia using a mixture 16 months old stored at room temperature.

Polypropylene cups with lids (250 ml) were used as etch chambers. A pinhole was placed in each lid to prevent collapse of the cup during cooldown. Evaporation was less than 2% (by volume) at nominal conditions. No stirring was used during processing, as previously discussed.

The glass and all tools underwent a standard degreasing process using Freon, acetone and isopropyl alcohol. Exam gloves or tools made of polyethylene, polypropylene or PTFE (Teflon) were used to handle the samples. Immediately prior to etching, a room-temperature isopropyl alcohol wash was used as the final cleaning step. A hot plate was also used to heat deionized water to 40°C for rinsing samples before and after processing to minimize thermal shock. After etching, another isopropyl alcohol rinse was used to dehydrate the glass surfaces and avoid water spotting.

A blown air laboratory oven was used to heat the samples in this experiment. It was refitted with a digital temperature controller which provides up to seven time and temperature setpoints for automatic heat-up, soak and cool-down. In addition it can be cycled repeatedly. A thirty minute dwell at 60°C was used to preheat the solution prior to adding the glass sample. The chamber was heated to the desired process temperature over the period of an hour, and was cooled to 60°C over the same period after processing. A Teflon coated thermocouple was used to monitor solution temperature.

Additional equipment not previously mentioned included a graphite-based Teflon beaker for use on the hot plate, a Teflon drying rack for the glass coupons, a Teflon graduated cylinder to measure etch solution volume, and plastic jugs for storing unused and waste etch solution.

RESULTS

Some initial etch results were obtained from Schott Glass on barium zinc coupons before Sandia completed its experimental setup. Ms. Sally Pucilowski at Schott Glass ran three coupons at various processing conditions. The sample prepared at the center point conditions, i.e., 87°C processing temperature and 24 hours processing time, etched fairly well (Fig. 3). This sample exhibited a total (both surface) reflectance of 1.6% and a transmittance of 97.6% (AM 1.5 solar photon average over the silicon response band). The major reflectance minima was 0.9% at about 900 nm, but reflectance increased to the 4-5% range beyond the silicon response band (1300-2000 nm). Samples run at 60°C for 23 and 48 hours showed no AR effect and had reflectances of 5.8% and 6.7%, and transmittances of 93.2% and 92.3%, respectively.

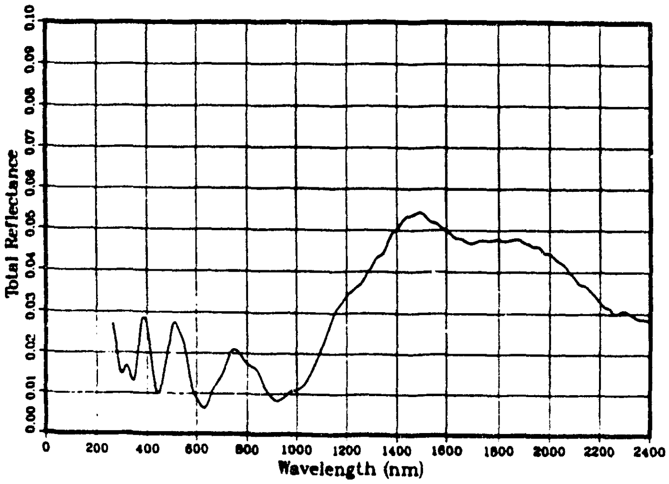

Figure 3 - Barium Zinc Glass Coupon
Total Reflectance After Etching by Schott Glass

At Sandia, two mechanically polished flat coupons were etched under the center point conditions. Optical property measurements showed an excellent AR film resulted (Fig. 4). The total reflectance dropped from 7.7% to 0.8%, with a corresponding increase in transmittance from 91.7% to 98.5%. The main reflectance minima appeared to be between 700 and 800 nm, but reflectance values were very low (between 0.3% and 2%) across the full range of measurement from 300 nm to 2500 nm. Such a broad range of low reflectance indicates that a graded index of refraction was indeed

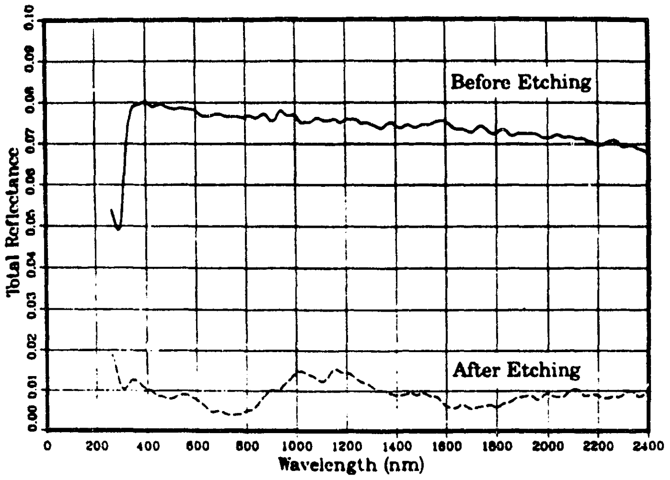

Figure 4 - Barium Zinc Glass Coupon
Total Reflectance Before and After Etching by Sandia

achieved on the samples. Absorption in the 3 mm thick sample was 0.7% which translates to a 5% absorption in a 2 cm thick refractive secondary.

Refractive secondaries etched at the center point conditions showed excellent reduction of reflection to the eye. Transmission and reflection measurements are difficult to make due to the element's non-planar surfaces, but preliminary measurements using a single wavelength 632.8 nm laser showed transmission above 94%.

Some BK-7 samples were also etched with poor results. The glass surface became opaque, and surface examination revealed relatively large pitting, cracking and flaking of the surface. Schott Glass found that if the etch process were allowed to run too long, the porous film layer became too thick and began delaminating due to differential stress mechanisms. This may have occurred in this instance. For some reason the etch process may have proceeded more rapidly than expected. Further investigation is planned.

SUMMARY

Barium zinc glass, which does not solarize under UV exposure, was tested to see if the neutral-solution etch process would successfully reduce reflectance and increase transmission. Mechanically-polished barium zinc coupons were successfully etched at the center point process variable conditions (87°C and 24 hours). Reflectance dropped from 7.7% to 0.8%, and transmission rose from 91.7% to 98.5%. Fire-polished refractive secondaries also appeared to etch well. Single wavelength (660 nm) measurements showed transmission was above 96%. Lens/cell tests are planned to quantify performance improvement under operating conditions, and a two-factor interaction main effects test will be completed to identify optimum processing conditions.

ACKNOWLEDGMENTS

Many people provided valuable assistance in this research effort. In addition to etching several glass samples, Ms. Sally Pucilowski of Schott Glass spent a great deal of time on the phone providing valuable information on the process. Rod Mahoney (Electronic Materials Applications Div., Sandia) provided sample optical analyses. Elaine Buck (Sandia) assisted in component acquisition and degreasing operations. Don Carroll of Alpha Solarco and Doug Wolf of the University of Dayton supplied the glass samples for the project. I thank them all for their efforts.

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