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ANTI-REFLECTION COATINGS APPLIED BY ACID LEACHING PROCESS

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By
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MASTER

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Motorola Inc.
Semiconductor Group
Phoenix, Arizona

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QUARTERLY TECHNICAL REPORT NO. 1

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THE JPL LOW-COST SOLAR ARRAY PROJECT IS SPONSORED BY THE U.S. DEPARTMENT OF ENERGY AND FORMS PART OF THE SOLAR PHOTOVOLTAIC CONVERSION PROGRAM TO INITIATE A MAJOR EFFORT TOWARD THE DEVELOPMENT OF LOW-COST SOLAR ARRAYS. THIS WORK WAS PERFORMED FOR THE JET PROPULSION LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY BY AGREEMENT BETWEEN NASA AND DOE.

PROJECT NO. 2370

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1.0 SUMMARY STATEMENT

This report covers the first three months of a nine-month program to study the production of anti-reflective coatings for glass solar module covers by means of a silica-saturated fluosilicic acid etch.

The efforts of the program during this first quarterly period have been to set up the process and begin production of filmed sample glass plates. To this end, a temperature-controlled bath has been prepared, large quantities of the filming solution have been formulated, and production of samples has begun using empirically determined processes.

2.0 INTRODUCTION

During the period from 1930 to 1950, extensive research was directed at methods of producing antireflective films on glass for use in optical equipment. During World War II, work on these methods became particularly intense, and several methods were developed into workable processes. In the late 1940's and early 1950's vacuum deposition methods advanced to the point where these were (and still are) used extensively in the optical industry, displacing the earlier chemical processes.

One of the most successful processes was developed by S. Milton Thompson, the details of which were published in the RCA Review, March, 1951. Unlike the present vacuum deposition techniques, Thompson's method is applicable to very large and/or irregularly shaped surfaces, requires very simple process equipment, and is inexpensive.

The technique depends for its operation on the structure and composition of soda-lime glass. Soda-lime glass is composed of a matrix of silicon dioxide in which are embedded ions of calcium and sodium. The antireflective

method of Thompson uses an acid which selectively dissolves and removes the sodium and calcium ions from the silicon dioxide matrix. This leaves a "skeleton" of porous silicon dioxide in a thin layer over the surface of the glass. The skeletonized layer has a lower refractive index than that of bulk glass and its thickness can be controlled by duration of exposure to the acid so that an effective antireflection film results.

From elementary optical theory, the most effective antireflective film has the following characteristics:

$$n_f = \sqrt{n_g}$$

$$n_f d_f = \frac{1}{4} \lambda$$

where

n_f = refractive index of the film

n_g = refractive index of the bulk glass

d_f = thickness of the film

λ = wavelength of incident light.

The above equations define the requirements for films which extinguish surface reflections. As can be seen from inspection of the equations, extinction is possible for only one particular wavelength when a film of constant refractive index is used.

The film's refractive index demanded by the above equations can not be provided by any known solid substance. A close approach to the required refractive index is provided by the skeletonized silicon dioxide layer formed in Thompson's method because of the microscopically porous nature of the layer. The result is a film which very strongly reduces reflections from a glass surface at a particular wavelength and provides strong attenuation of reflection of neighboring wavelengths as well.

In practice, the acid etch consists of a 1.25 M aqueous solution of fluosilicic acid (H_2SiF_6), saturated with silicon dioxide at room temperature. During use, the acid solution is warmed to speed the filming reaction; a temperature of 45°C is found to be convenient. In addition, the acid is supersaturated in silicon dioxide by the addition of boric acid. The supersaturation in silicon dioxide is a necessary part of the process. It is also the most difficult process requirement to meet. Only over a narrow range of supersaturation will there be any formation of film. Moreover the supersaturation degree differs for different brands or batches of soda-lime glass. As with any supersaturated solution, instability results; the solution spontaneously reverts to saturated form by the precipitation of silicon dioxide. Thus, frequent additions of boric acid are required to maintain a successful acid composition.

3.0 TECHNICAL DISCUSSION

The experimental facility now in use consists of a hot plate with external thermistor temperature probe. The hot plate maintains the temperature of water contained in a stainless steel tank, within which rests a polypropylene container containing the acid solution. A magnetic stirrer is provided to continuously agitate the acid solution. A tightly fitting lid is maintained on the container to prevent evaporation. At a temperature of 45°C , the temperature variation of the acid bath is typically $\pm 1.0^\circ\text{C}$.

3.1 METHOD OF PRODUCTION

The acid bath is prepared by dilution of commercial fluosilicic acid. As obtained from the supplier, fluosilicic acid is in the form of a 23% aqueous solution. To prepare 1.25 molar fluosilicic acid, approximately 670 ml of

the commercial acid is diluted to 1 liter. To this is added 20 grams of precipitated silicon dioxide (commercially known as "silicic acid"). The mixture is agitated continuously over a period of several hours to promote dissolution of the silicon dioxide. After agitation, the mixture is filtered through paper to remove undissolved silicon dioxide. The solution is then stored at room temperature until needed.

Glass is prepared for filming by a wash and etch sequence. Glass as received from the manufacturer is first rinsed briefly in water to remove dust and gross surface contamination. The glass is then submerged for thirty minutes in boiling detergent solution consisting of 12 ml of Joy dishwashing detergent per liter of deionized water. (Physical abrasion of the glass surface is not employed.) After a brief rinse to remove detergent, the glass is etched for 1 min. to remove the weathered surface layer present on most soda-lime glass. The etch used is a 10% by volume solution of hydrofluoric acid in water. Following a rinse in water, the glass is placed in the fluosilicic acid filming solution.

The glass used, in this project is 2.5 mm thick Lustraglass[®] low iron soda-lime glass, manufactured by ASG Industries, Inc. The glass is not currently being manufactured, but is still available from some suppliers.

The addition of about 6 ml of 4% boric acid per liter of fluosilicic acid solution is necessary to raise the supersaturation level of silicon dioxide sufficiently to produce film. The supersaturation level falls off slowly, so that an additional one or two milliliters of 4% boric acid must be added daily to maintain the solutions filming properties.

3.2 DETERMINATION OF BATH COMPOSITION

As noted earlier, control of the degree of supersaturation of the bath is important. At present, no analytical technique is known of determining

the proper bath composition. The range of composition over which the filming reaction occurs is narrow. In order to determine the correct composition, a method described by Thompson must be used on a daily basis.

Into a series of test tubes are placed equal volumes of the fluosilicic acid etch solution. In the tubes are also placed increasing amounts of boric acid solution, such that each tube contains a sample of solution with a different degree of supersaturation. After bringing the tubes and their contents to operating temperature, freshly cleaned slivers of the same type of glass as is to be etched on a large scale are inserted into the tubes and allowed to etch, typically for an hour. After etch, the slivers are rinsed and examined for film. The composition which produced the best film is then duplicated in the large bath by direct scale-up of the boric acid content.

The method requires at least an hour-and-a-half to perform. Even though its use usually results in a large bath that operates satisfactorily, occasionally further adjustment of the large bath is required, either by the repetition of the test tube trials or on the basis of the operator's experience. To allow the widespread use of this filming solution, some other method of analysis needs to be found.

3.3 AREAS OF PROGRESS

The program efforts to date have concentrated on the production of samples of filmed glass for later testing, and as such, little tabular or other data has been generated. Several observations on the nature of the bath and its operation have been made, and these bear discussion in that they effect the success of the filming process.

3.3.1 OBSERVATIONS

Surprisingly, some aspects of etch bath operation and behavior have been found to be different from those originally reported by Thompson. Pyrex vessels are not suitable for containing the fluosilicic acid solution as these show signs of attack in as little as two weeks of continuous use. Vessels composed entirely of plastic polyethylene, polypropylene, methyl methacrylate, etc.) are preferred. The use of plastic vessels also allows them to be rinsed with hydrofluoric acid occasionally to remove deposited silicon dioxide such as SiO_2 deposits hasten the deterioration of the bath. The precipitation of silicon dioxide from the bath is unexpectedly large, inasmuch as the original reference suggests filtration once a month. It was found necessary to filter the bath at least once every two days; daily filtration is often necessary. The speed of spontaneous degeneration was also found to be greater than expected. At times, the bath has a useful life of one or two hours before addition of boric acid is necessary to restore it. Although filtration of the bath helps in reducing the speed of degeneration (by removing particles on which silicon dioxide can precipitate), a hydrofluoric acid etch of the vessels used was also done with some success in slowing the degeneration. Nevertheless, precipitation is such that provisions for continuous filtration may be necessary for large baths. By operating the filming bath at a constant 45°C , and employing daily filtering, daily change to HF-cleaned etch vessels, and daily replenishment of evaporated solution, as well as use of an air-tight cover, low rates of degeneration were found, amounting to a need for 2 ml of 4% H_3BO_3 to be added per liter of filming solution per day.

4.0 PROJECTED ACTIVITIES FOR THE NEXT THREE MONTHS

Work during the next three months will cover four areas: production of filmed glass samples, testing of samples by abrasion, testing of samples by chemical exposure, and testing of effects of process variations.

Progress on sample production is being made with the preparation of several dozen samples weekly. The samples are inspected and those that are optimized are collected for future testing. Preparations are in progress for abrasion testing, including the acquisition of the necessary equipment. Testing will begin in the next few weeks. At the same time, chemical testing equipment is being readied. The chemical tests will involve exposure to detergents and water both by stationary soaking and under the influence of ultrasonic agitation. Additional tests will involve exposure of samples to concentrated atmospheric pollutants (sulfur dioxide, oxides of nitrogen, carbon dioxide, etc.). Plans for conducting these tests are being reviewed. Process variations will be studied after testing is underway. The variations will occur in three areas: composition of etch bath, duration of etch, and temperature of etch bath. Plans for these studies will be prepared in the near future.

5.0 RECOMMENDATIONS

No specific recommendations are made at this time.

6.0 CURRENT PROBLEMS

No problems have presented themselves.

7.0 WORK PLAN STATUS

Although the program was delayed by late arrival of the glass used in sample production, work is within a few days of schedule.

8.0 ACTION ITEMS

No urgent action is required on any item.

9.0 NEW TECHNOLOGY

No reportable new technology has been identified.

10.0 PROGRAM AND DOCUMENTATION MILESTONES

Activities associated with the program are shown in the Program and Documentation Milestone Charts -- Figures 1 and 2 contained in Appendix 1.

APPENDIX I

PROCESS STEPS	1979 MONTHS								
	APR	MAY	JUN	JUL	AUG	SEPT	OCT	NOV	DEC
Set Up Facility									
Determine Process									
Produce Samples									
Test Abrasion									
Test Chemical Resistance									
Test Process Variations									
Cost Analysis									

FIGURE 1

DOCUMENTATION MILESTONE CHART	MONTHS								
	APR	MAY	JUN	JUL	AUG	SEPT	OCT	NOV	DEC
Monthly Financial Management Review		▲	▲	△	△	△	△	△	△
Technical Letter Progress Report		▲	▲		△	△			
Quarterly Technical Report				▲			△		
Draft Final Report								△	
Final Report									△
Program Plan	▲								
Baseline Cost Estimate	▲								

FIGURE 2