FINAL REPORT
Evaluation of Glass Resin Coatings for Solar Cell Applications

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TABLE OF CONTENTS

Summary:

Using a variety of non-vacuum deposition techniques coatings have been implemented on silicon solar cells and arrays of cells interconnected on Kapton substrates. The coatings provide both antireflection optical matching and environmental protection.

Reflectance minima near 2% have been achieved at a single wavelength in the visible. Reflectance averaging below 5% across the useful collection range has been demonstrated. The coatings and methods of deposition were:

Ta_2O_5	spun, dipped or sprayed
$Ta_2O_5 \cdot SiO_2$	spun, dipped or sprayed
GR908 (SiO_2)	spun, dipped or sprayed

Total coating thicknesses were in the range of 18µm to 25µm.

The coatings and processes are compatible with single cells or cells mounted on Kapton substrates.

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Evaluation of Glass Resin Coatings for Solar Cell Applications

INTRODUCTION

The work reported below was designed to investigate the use of non-vacuum techniques to deposit active optical films on silicon solar cells and modules. An active optical film is one which interacts with incident optical radiation in a desirable fashion. These films are used to reflect, transmit or filter light. A further purpose is to provide protection to the substrate from heat, moisture and mechanical abrasion. The major impetus for research of this type is economic, although enhanced performance is desirable as well.

Present methods of protecting/enhancing silicon solar cells require vacuum-deposited films, cover glasses, or encapsulation. Vacuum deposition is expensive, cover glasses are bulky and mechanically difficult to handle, and encapsulation is not easily adaptable to modules or large areas. The advantages of non-vacuum coating with liquids are several-fold:

1) Rapidity of coating. There is no delay in pumping or loading.
2) Uniformity of material. Liquids are solutions. If properly mixed they are homogeneous by definition.
3) Flexibility of composition. With a proper choice of starting materials composition (and ultimate physical property, say index of refraction) is infinitely variable.
4) Potentially better film structure. Vacuum coatings involve highly energetic atoms or ions condensing on cold substrates. Unless done very slowly, thin films are always non-uniform and stressed to some extent.
5) Cost. As pointed out below, both equipment cost and material cost are relatively low for liquid coating.
6) Uniqueness of formulation. There are materials available as liquids which do not exist in forms suitable for vacuum deposition, primarily polymers.

Some effort was given to investigating a novel method of producing monocrystalline CdS on silicon substrates for the purpose of exploiting the combined efficiency of the two semiconductors. The results detailed below were less than successful.

Finally, a large portion of the time was spent in testing the films and materials produced. In view of the long, successful history of vacuum-deposited optical films it was important to check our progress at each step of the way. It's safe to say that much more testing remains to be done.

Materials I

This section describes Glass Resins in general, the modifications attempted, and the final multi-layer, non-vacuum film system adapted.

Glass Resins

"Glass Resin" is a term used by Owens-Illinois, Inc. to describe a family of polymers whose structure consists of alternating silicon oxygen bonds. The polymers can be classed generally as silicones. These thermo-setting polymers can be cured to clear, hard end products without fillers or catalysts. Table I summarizes the general properties of Type 650 Glass Resin polymer. This material contains more than eighty per cent silicon and oxygen.

TABLE I GLASS RESIN GENERAL PROPERTIES

PHYSICAL PROPERTIES	SPECIFIC GRAVITY	1.3
	FLAMMABILITY	NONFLAMMABLE
	TENSILE STRENGTH, PSI	3,500
	ELONGATION, PERCENT	APPROX. ZERO
	COMPRESSIVE STRENGTH, PSI	30,000
	FLEXURAL STRENGTH, PSI	5,000
	MODULUS OF ELASTICITY	
	FLEXURAL, PSI	200,000
	IMPACT STRENGTH, IZOD	
	(FT. LB./IN. NOTCH)	.03
	HARDNESS, ROCKWELL R SCALE	
	(1/4" THICK SAMPLE)	120-140
ELECTRICAL PROPERTIES	DIELECTRIC STRENGTH: (50MIL SAMPEL) SHORT TIME (VOLTS/MIL)	900
	DIELECTRIC CONSTANT: 60 CYCLES	4.1
	10^6 CYCLES	3.2
	DISSIPATION FACTOR: 60 CYCLES	30×10^{-4}
	10^6 CYCLES	70×10^{-4}
	ARC RESISTANCE: (SECONDS)	130-195
	VOLUME RESISTIVITY: (OHM-CM)	
	25°C	1×10^{14}
	75°C	2×10^{16}
THERMAL PROPERTIES	COEFFICIENT OF LINEAR EXPANSION (0-300°C) (IN./IN./°C)	13×10^{-5}
	THERMAL CONDUCTIVITY:	
	(BTU/FT^2/HR/°F/IN.)	1.0
	(CAL/CM^2/SEC/°C/CM	3.4×10^{-4}

Resin coatings offer exceptional transmission in the ultra-violet portion of the optical spectrum. Table II exhibits the optical properties of the material type 650.

TABLE II OPTICAL PROPERTIES

TYPE 650	
$n_D^{20}=1.42$	
WAVE LENGTH	PERCENT TRANSMITTED
3600 to 7000 A	85-95
3000 A	70
2300 A	60
1950 A	0.1

ULTRA-VIOLET LIGHT EXPOSURE: NO VISIBLE CHANGE AFTER 500 HOURS EXPOSURE 8 INCHES FROM A 400 WATT ULTRA-VIOLET SOURCE IN AIR (OUTPUT, 3000 to 4000 ANGSTROMS). Accelerated testing at the Desert Sunshine Exposure Test Center confirms the excellent stability of Glass Resin Polymer coatings.

Table III Radiation Exposure Data

RADIATION EXPOSURE TO COBALT-60 SOURCE: AFTER A TOTAL GAMMA RADIATION OF FIVE MEGARADS AT A RATE OF $3X10^{+5}$ RADS/HOUR, THE SAMPLES BECOME SLIGHTLY PINK
RESISTANCE IN COLOR. THIS PINK COLOR IS NOT PERMANENT. TRANSPARENCY WAS UNAFFECTED.

EXPOSURE TO ENRICHED URANIUM SOURCE: AFTER A TOTAL RADIATION OF TEN MEGARADS AT A THERMAL NEUTRON DENSITY OF $8X10^{12}$ NEUTRONS/CM^2/$SECONDS^{-1}$, THE SAMPLES BECOME SLIGHTLY PINK IN COLOR. THIS WAS ONLY A TEMPORARY EFFECT.

Generally speaking, coatings of Type 650 Glass Resin polymer at or above twenty-five microns (25 µm) thick on metal are severely stressed. Glass Resin Type 100 shares the same excellent properties of Type 650 as shown in Tables I and III, but is more flexible and thus allows higher thicknesses to be applied. Type 100 is less transparent in the ultra-violet region, however, and has a larger refractive index as shown in Table IV.

TABLE IV. OPTICAL PROPERTIES OF GR100

OPTICAL PROPERTIES		TYPE 100	
	REFRACTIVE INDEX	$n_D{}^{20}=1.49$	
	LIGHT TRANSMISSION	WAVE LENGTH	PERCENT TRANSMITTED
		3600 to 7000 A	90-95
		3000 A	80
		2850 A	20
		2800 A	0.2

Type 100 Glass Resin polymer contains slightly more than 60 percent silicon and oxygen.

Type 650M is a polyester-modified resin with increased flexibility over the base type 650. This flexibility is purchased at the expense of a slight decrease in optical transmittance in the ultra-violet region. Accelerated testing at the Desert Sunshine Exposure Test Center has shown no significant degradation is expected due to this loss of transmittance.

Some formulations of Glass Resins have been space-qualified. For information please see

-Combined Space Environment Effects on Typical Spacecraft Window Materials, Final Report, Contract NAS9-2939 Avco Corporation, Tulsa Division, July, 1965.

-IITRI Report C6027-16 for Jet Propulsion Laboratories, Stable White Coatings, June 30, 1965.

-IITRI-U6002-73 George C. Marshall Space Flight Center, Development of Space-stable thermal-control Coatings, January 31, 1969.

A third member of the Glass Resin family is Type 908. Type 908 contains in excess of fifty percent silicon and oxygen. It has excellent coating properties and is as flexible as Type 100. Type 908M, polyester-modified, is even more flexible.

Glass resins are available in flake or B-stage. The flake is readily soluble in a number of organic media. The general procedure for using Glass Resin is to dissolve the flake in a solvent appropriate for the particular coating method at a known solids level. The solids level, solvent properties, and coating method determine the resultant film thickness. After coating the substrates are dried (solvent removal) and exposed to high temperature for further curing. Curing is a matter of time and temperature. Satisfactory cure is adjudged by resistance to gentle abrasion with a acetone-saturated cloth or paper towel. Curing temperatures of 150°C to 180°C for Type 100 and Type 650 for twenty to forty minutes are generally sufficient at small film thicknesses. Thicker films require more careful drying and a longer cure time. Type 908 requires temperatures of at least 180°C for satisfactory curing.
Type 650 or 650M were not suitable for use on silicon, particularly solar cells with metal grids. At any thickness above 6 to 8μm (cured) the coatings cracked during curing. No combination of number of coatings or cure cycle would alleviate this problem. Type 650 may be combined with an acid for greater flexibility. This was not attempted.

Type 100 is probably the most flexible unmodified Glass Resin. Films could be produced on grid-metallized silicon at thicknesses of 14 to 16μm. If it was attempted to deposit the entire thickness in one or two passes, microcracks were noticed during or after curing. Some samples in the 13μm to 14μm also failed during humidity/temperature testing (see Testing).

Type 908 or 908M can be deposited on silicon solar cells to thicknesses of at least 25μm without any signs of cracking. The coatings must be carefully applied in thicknesses of 8μm or less, drying but not curing between each coat, and cured slowly for about two hours at 220°C to 230°C. Films of up to 35μm in thickness have been produced this way with no observable delaminations or cracks. Some samples with films of Type 908 above 20μm thick have failed in humidity/temperature cycling, however. Close observation of the samples indicated physical defects (pinholes) in the film were responsible.

The above results indicated that thicknesses of 20μm to 25μm with Type 908 were quite feasible. Glass Resin films alone on silicon are not particularly interesting, however, as the optical index of refraction n_o=1.42 offers little aid in reducing the large reflection loss of silicon. Modifications to the resins would possibly improve the thermal expansion and optical match.

Modifications to Glass Resin Polymers

In solution Glass Resins consist of random groups of silicon, oxygen and organic molecules. It should be rather easy to introduce limited amounts of liquid metallo-organic materials which could be incorporated into the polymer lattice during curing. By choosing materials similar to silicon it was hoped that even if direct substitution did not occur, the structure would be disturbed only slightly.

Ions chosen for trial were Ti (TiO_2:n=2.2), Al (Al_2O_3:^{n}=1.6), CeO_2 and $Mg_2Al_2O_4$. The latter two compounds were largely for the purpose of thermal expansion coefficient modification. In each case the following procedure was used: Glass Resin flake, either Type 100 or Type 908 was mixed with isopropanol to a total solids content of 25%. Appropriate amounts of the metallo organic solutions were mixed to yield the following metal ion ratios:

99 Si: 1 M
95 Si: 5 M
90 Si:10 M
80 Si:20 M
75 Si:25 M

For $Mg_2Al_2O_4$ the ratios were SiO_2: $Mg_2Al_2O_4$. Films of each material were obtained by dropping known amounts on a glass substrate spinning at a fixed speed. The solvents were removed by drying at 100°C for 15 minutes under a heat lamp. The samples were then baked at 150°C to 230°C for one hour and subsequently examined. Preliminary examination consisted of visual observation with a microscope, test for adhesion by abrasion, and solvent solubility with acetone immersion.

Al_2O_3 and $Mg_2Al_2O_4$ were rejected by a) the solutions, they precipitated immediately or b) the polymerized resin. Small white agglomerates were apparent in the cured resin films at every ration above 99Si: 1 Al or $99SiO_2$: 1 $Mg_2Al_2O_4$. The Al_2O_3 was apparently very hygroscopic as the small white particles were tentatively identified as aluminum hydrate. The small amount of alumina in the lowest ratio samples appeared to have no detectible effect on physical properties.

Samples with CeO_2 were rejected for low transmission or non-compatibility. The optical transmission dropped below 95% above the 1 Ce level. At the 1 Ce level no detectable increase in film flexibility was observed when deposited on silicon.

Ti acted much the same as Al with the exception that up to 10 Ti could be included in the cured film. The index of these films (90Si:10Ti) was slightly higher than 1.49, nearly 1.55. No increase in flexibility was apparent.

The above trials, as noted, were at low temperatures as they were aimed at modifying the polymer. A parallel set of experiments was completed to evaluate TiO_2 and solutions of $TiO_2 \cdot SiO_2$ alone as optical films on silicon.

These are described below.

It was concluded that little or no modification in the thermal expansion coefficient or refractive index of Glass Resins could be effected by substituting Ti, Al, or Ce for Si. The only attempt to substitute for SiO_2 (with $Mg_2Al_2O_4$) was also fruitless The polyester-modified Glass Resins do show a substantial increase in flexibility. Also however, the penalty for better flexibility was a decrease in the ultraviolet optical transmission and, possibly, stability in high UV-intensity environments.

Multi layer non-vacuum Films

Silicon solar cells require an anti-reflective layer on their front surface to achieve resonable efficiencies. Figure 1 shows the reflection from a bare, polished silicon surface. Some portion of the thirty-seven percent of reflected radiation can be recovered. A single layer with an optical thickness of one-quarter wave length can, in principle, provide an exact match (zero reflectance) at one wave length. It requires a multi-layer filter to obtain a low reflectance at several wave lengths. Ideally the optical response would be as shown schematically in figure 2.

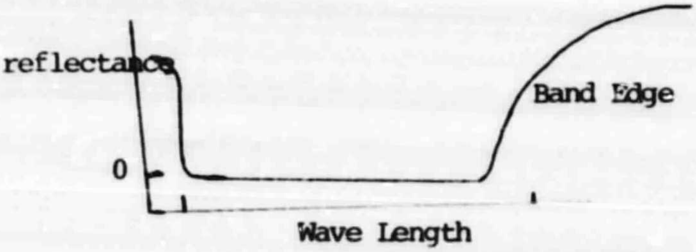


FIGURE 2. Ideal spectral response of coated silicon.

The aim of this work was to achieve both antireflection and physical protection (humidity, abrasion, etc.) with a minimum number of 'active' films. The Glass Resin coatings would be incorporated into the optical design as the last layer or layers and provide the bulk of the environmental protection. Figure 3 illustrates the theoretical optical response it was thought possible to achieve with a three-layer or four-coating.

The first experiments were performed with metallo-organic (MOD) solutions designed to yield TiO_2 after pyrolysis. The general procedure was to coat the samples, glass or silicon, with the MOD solution, dry under a heat lamp to remove the solvent and fire the samples in a continuous belt, air atmosphere furnace. TiO_2 films are easily produced on clean glass and silicon at temperatures above 300°C. Figure 4 shows the effect of temperature on optical transmission for TiO_2 films on glass. Notice that the peak transmission decreases as the films are fired at increasing temperature. This is interpreted as being the result of both film densification and an increase in the degree of oxidation. As the film oxidizes more completely the stoichiometry more nearly approaches TiO_2 and the refractive index increases. The TiO_2 films are hard, transparent and apparently pinhole-free. The refractive index approaches that of dense TiO_2. As shown in Figure 5 the TiO_2 films in the proper thickness can

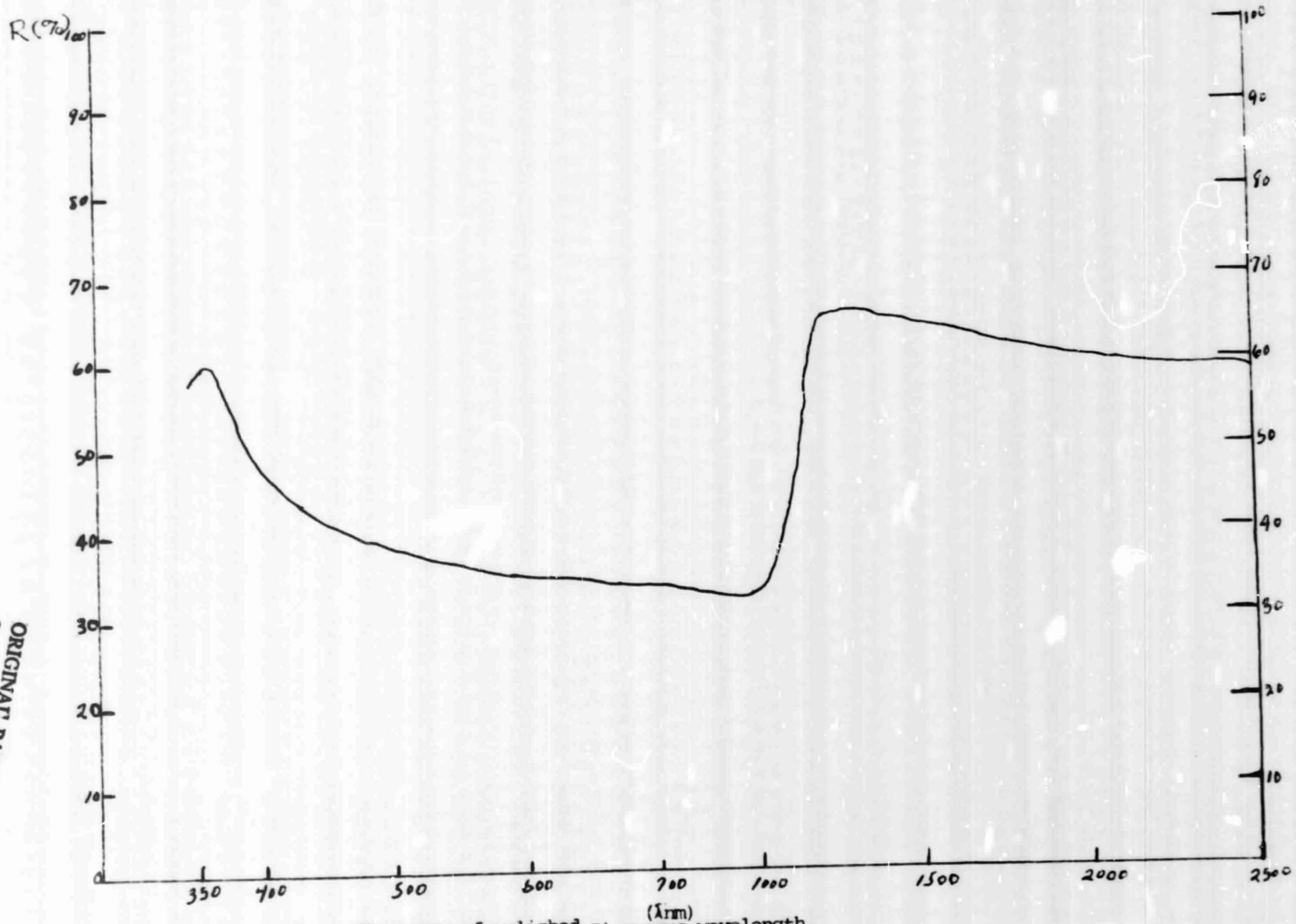
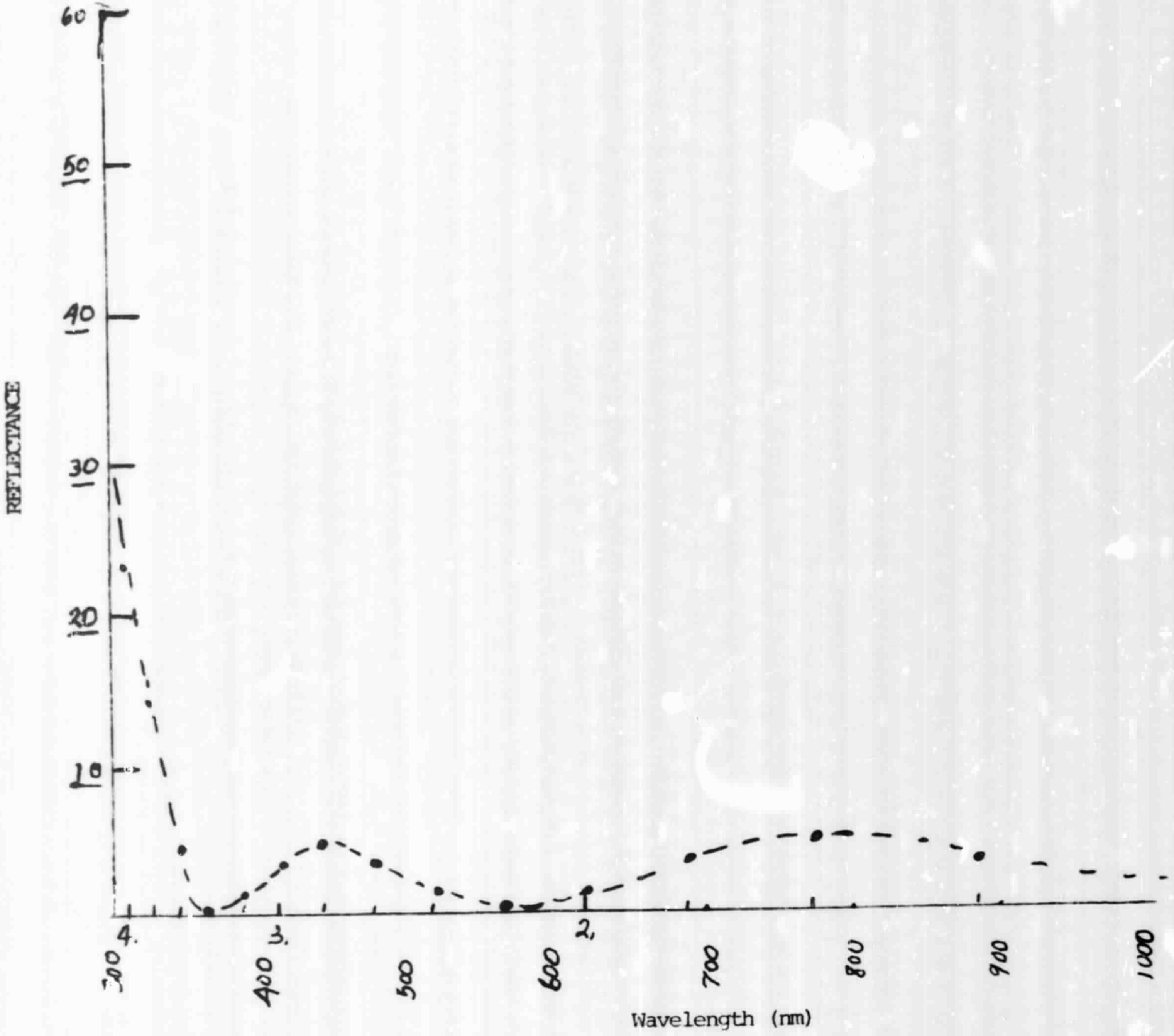


Figure 1. The reflectance of polished Si versus wavelength.

Figure 3 Calculated Reflectance
Three Layer Coating



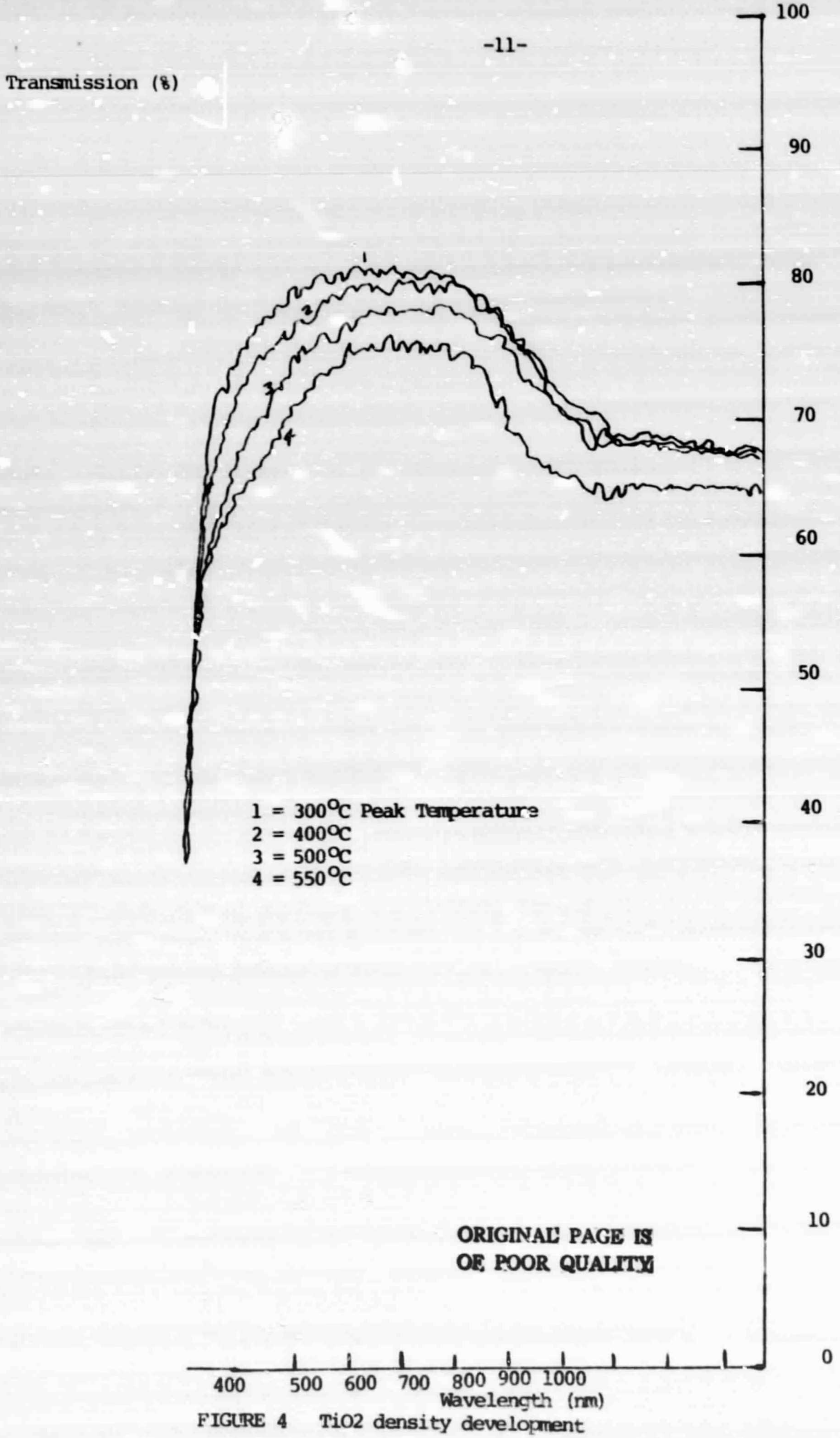


FIGURE 4 TiO2 density development

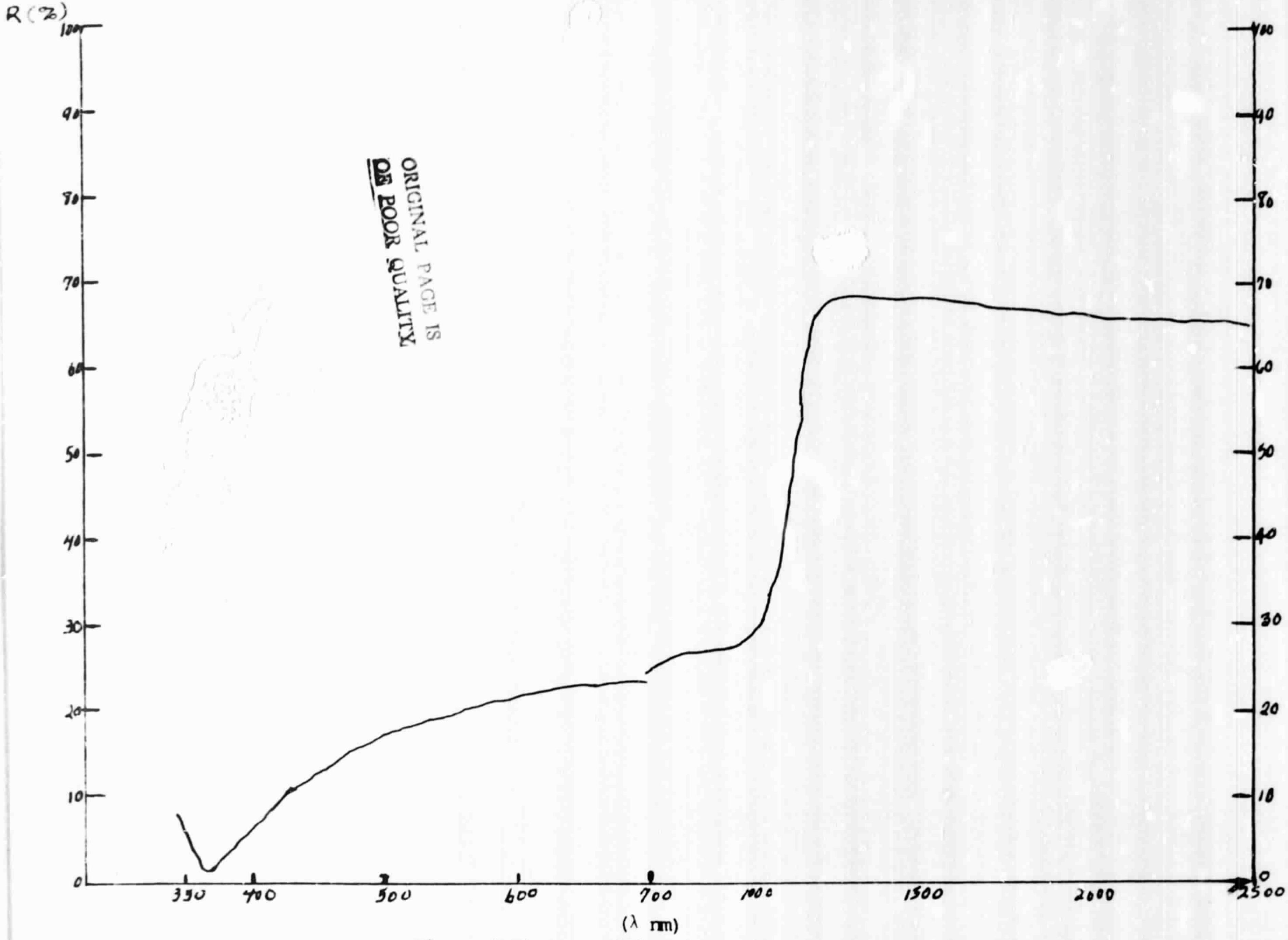


Figure 5 TiO_2 on silicon

provide an excellent match to silicon at a single wavelength.

To obtain a graded-index optical filter it was necessary to produce films with refractive indices between TiO_2 ($n \approx 2.2$) and SiO_2 ($n \approx 1.42$). The simplest approach was simply to manufacture or prepare solutions containing TiO_2 and SiO_2 in various proportions. This was done and the results are shown in Figure 6. The solutions are mutually soluble and apparently one can prepare an infinite series between the two end members. Figure 7 shows a combination anti-reflective/protective film on silicon. The spun coatings were

Material	Firing Temperature
TiO_2	350°C
$80\ TiO_2 \cdot 20SiO_2$	350°C
Glass Resin (3 layers)	230°C

Total film thickness was 18µm. Films similar to this have undergone extensive ultraviolet exposure moisture penetration, thermal shock and flexibility testing without any apparent deleterious effects (see testing, below).

Although the response of the TiO_2-based filters is quite good, there are materials which are better. The prime reason for considering a different filter is to obtain a better response near the uv bandedge. The compound Ta_2O_5 has a large refractive index and is transparent to lower wave lengths in the uv than TiO_2. Figure 8 exhibits the uv transmission of TiO_2 and Ta_2O_5 films derived from MOD solutions. Proceeding as above, the correct compositions were chosen to achieve the best optical matching and performance. The optimal system, on average, was as follows.

Ta_2O_5	300°C
$75\ Ta_2O_5 \cdot 25SiO_2$	300°C
Glass Resin 908 (3 to 7 layers)	230°C

Film thicknesses from 18µm to 28µm are easily achieved by multiple applications of Glass Resin 908.

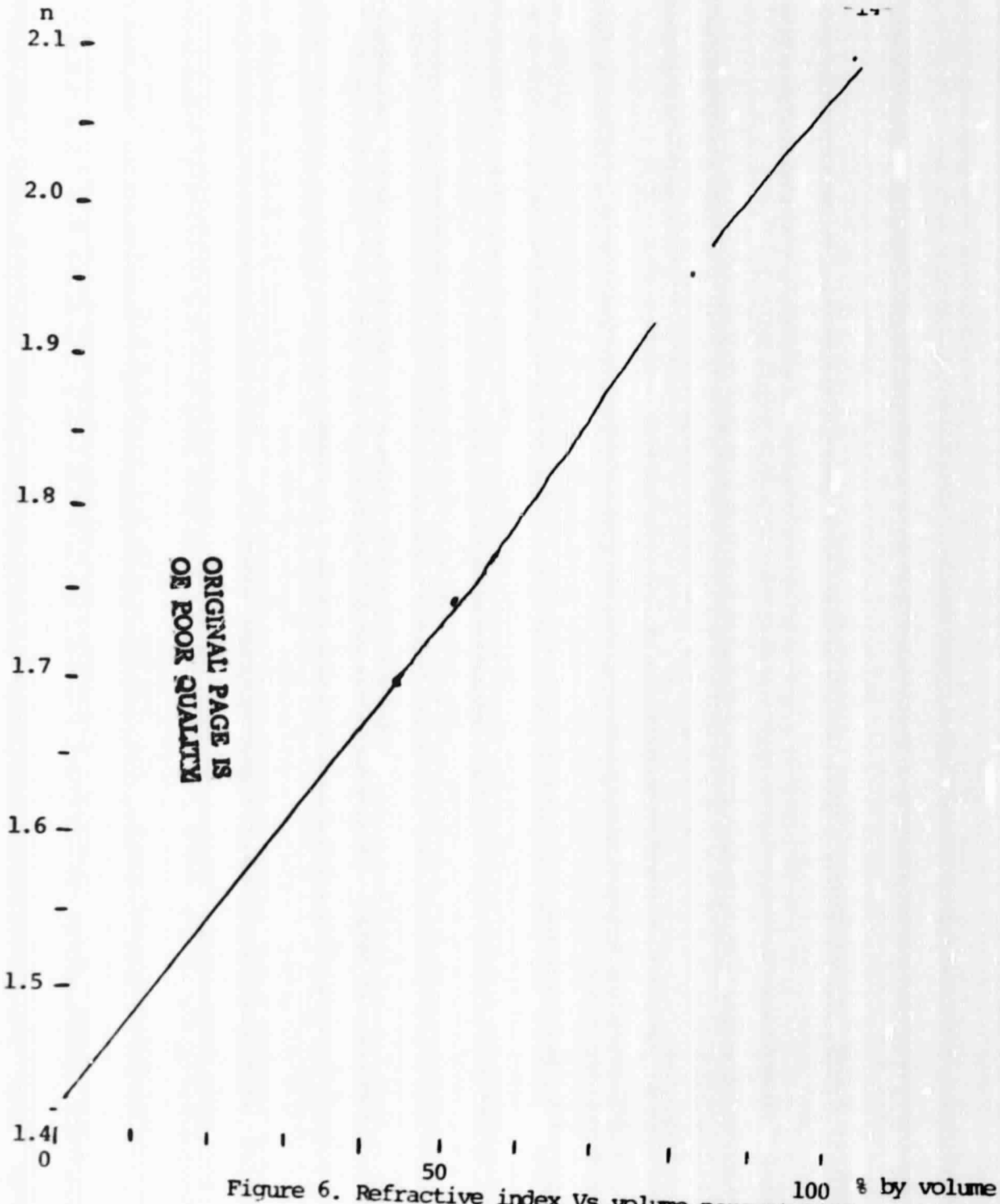


Figure 6. Refractive index Vs volume percent TiO2

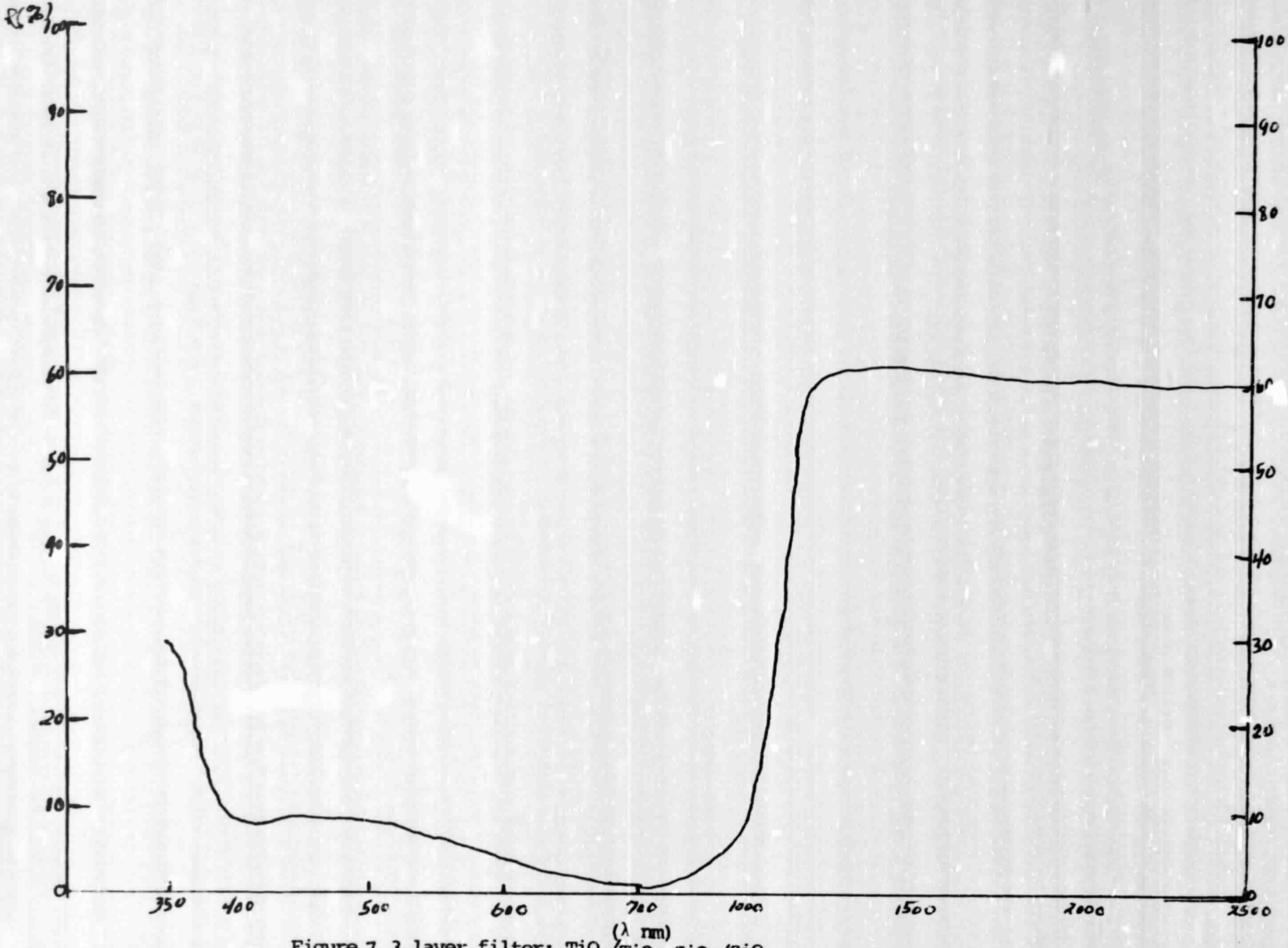


Figure 7.3 layer filter: TiO_2/TiO_2 SiO_2/SiO_2

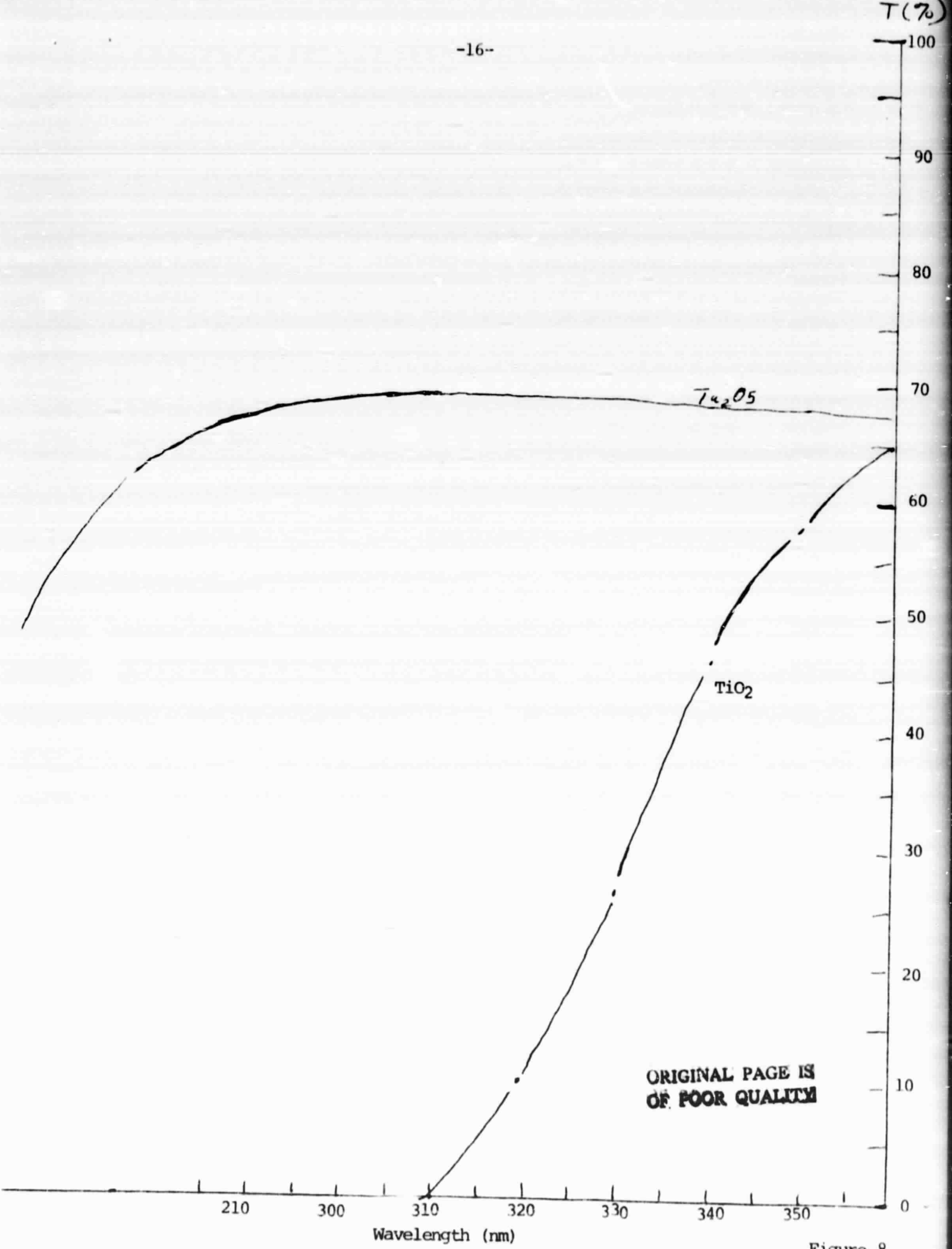


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Figure 8

Sample Preparation

Proper procedure for coating substrates requires a number of operations: cleaning, solution preparation, deposition, drying, pyrolysis/cure, testing, and quality control. Each step is important and requires care. It is the intent here to share our experience in coating with the reader. No claim is made that this is the optimal technique, but it has been successfully used for thousands of samples. The instructions are general in the sense that all substrates must be cleaned, solutions measured, etc., but specific to antireflection coatings on glass and silicon with Ta_2O_5 solutions and the deposition method used.

Cleaning

The purpose of cleaning is to remove any organic contaminant from the surface and, in the case of silicon, to remove thermal oxide. The following procedure must be carefully followed.

1. Prepare cleaning solutions:
    a. Non-phosphate detergent in hot deionized water. Alconox works well. Water temperature about 55°C.
    b. Deionized water rinse at 20°C.
    c. Nitric or chromic acid. Thirty percent acid by volume.
    d. Deionized water rinse at 20°C.
    e. Hydrofluoric acid. Three percent by volume.
    f. Deionized water rinse at 20°C.
    g. Electronic grade ethyl or isopropyl alcohol.

The samples, glass or silicon, are immersed in the above solutions b thru g after manual or automatic scrubbing in detergent. Do not use an ultrasonic cleaner. Steps e and f can be omitted for glass. In the case of silicon, leave the cells immersed under the alcohol until immediately before coating.

Air dry with filtered air.

Glass surfaces are clean when deionized water poured on the surface flows off uniformly from every portion of the area. Electronic grade alcohol is water free and tends to have the least alkali and transition metal ion contamination.

Solution Preparation

We discuss here three solutions: Ta_2O_5, $Ta_2O_5 \cdot SiO_2$, and GR908 all in alcohol solvents.

The Ta_2O_5 solutions are prepared to yield Ta_2O_5 on a weight basis. A convenient formula to use, for example, is 46 gram of tantalum ethoxide in 454 gram of isopropanol. This yields 5% Ta_2O_5. The Ta_2O_5 solutions can also be prepared with tantalum chloride, $Ta\,C\ell_5$, which is soluble in absolute alcohol. These solutions tend to age: bottle life is about three months at room temperature. A strong acetic acid smell is the hint that the material is no longer to be trusted.

Partially-hydrolzed tetraethyl silicate is mutually soluble with tantalum ethoxide and isopropanol. As mentioned in the text, the second layer is not particularly critical as to thickness but the refractive index should be correct. We've found that a five per cent solution of 75 $Ta_2O_5$25 SiO_2 by weight works well.

Glass Resin is available as a B stage polymer in flake form. One simply dissolves the desired amount in a solvent to obtain the solids content desired. A five percent solution in isopropanol works well for multiple spin coats; a twenty-five percent solution in 4 parts alcohol, 1 part xylene, seems to spray quite nicely.

Deposition

As an example of filter manufacture the deposition of Ta_2O_5 and $Ta_2O_5 \cdot SiO_2$ by spinning and GR908 by spraying is explained.

The cell or module is placed on the spinner head and the vacuum chuck engaged. A drop of Ta_2O_5 in isopropyl alcohol is placed on the center of the substrate. Drop size is roughly 0.05 mℓ to 0.10 mℓ. The drive is activated which brings the module to 1500 rpm within one half second and maintains the speed for five seconds. Deceleration is also controlled. An alternate method is to place the drop on the spinning substrate.

The substrate is removed, dryed and fired. $Ta_2O_5 \cdot SiO_2$ coating is applied in a similar fashion.

Glass Resin 908 is mixed at a 25% solids basis in 4 alcohol: 1 xylene and placed in a container for spraying. A non-pressurized spray is used. Single, uniform light coats are applied to a substrate which is held vertically or nearly so. The coating is dryed at 110°C for 5 minutes and another layer applied. This is repeated as required. Do not overdry the glass resin coatings as once cured the resin acts like a silicone and will not accept further coating.

Drying

Drying is a non-critical, solvent-removal step. At Pantek an infrared lamp ten inches above the substrate allows an even heating to 110°C. About ten to fifteen minutes is sufficient.

Pyrolysis/Cure

The tantala-containing materials must be pyrolyzed at 300°C or above to develop the necessary density. Below 300°C the refractive index is lower than 2.08, an indication that the films are not completely dense. A suitable cycle is an endless belt furnace which allows five to six minutes dwell at 300°C. Time and temperature are important; within limits, the hotter the better. Firing below 300°C and for less than five minutes is not recommended.

Curing glass resins is a combined solvent removal and cross-linking operation. The larger the number of discrete, single-layer films, the longer the cure cycle. For GR908, 200°C for thirty minutes per layer of 5 μm is required.

Testing

Testing these films during and after processing is crucial for performance control. Aside from quality control, pinholes, etc., the key parameter is optical thickness defined as the product of physical thickness and refractive index at a particular wavelength. The best measurement technique would be to use a reflectometer between each coating layer deposition. A reflectometer will yield a plot of reflectance versus wavelength. For the single Ta_2O_5 layer the plot should show a minimum at $\frac{\lambda}{4} = nd$, where λ is the optical wavelength n the optical refractive index and d the coating thickness. If n is known, λ is measured and d can be deduced. An optical index of $n = 2.02$ to $n = 2.08$ is produced with Ta_2O_5 deposited as above.

After a time the eye becomes a good judge of thickness by noting the hue of the coating. Note that the eye detects the sum of white light minus the color at which $\frac{\lambda}{4} = nd$. Also note that dried films will not yield the proper hue as the film contracts during firing and the index increases.

The second layer, Ta_2O_5 SiO_2, on top of Ta_2O_5 yields a reflectometer plot which exhibits a broad maximum nearly centered in the visible portion of the spectrum.

The final coating or coatings of GR908 should yield a film which appears light blue to the eye and has a spectrum similar to Figure 7. The minimum reflectance should be 3% or less.

Quality Control

Aside from the purely functional parameter of reflectance, the films must be pinhole-free and optically transparent. Pinholes or cracks can usually be detected visually with a low-power microscope and reflected light.

An excellent quality control check is to generate I-V curves under a calibrated light source. If the light source is constant in time, the short-circuit current (at a constant temperature) is measure of coating gain or reflectance.

Miscellaneous

A short mention of masks should be included. To keep the coating from covering metallized leads they should be protected with a maskant. The maskant must prevent coating but be itself easily removed. Pantek uses tape for large contacts and a slurry of baking soda in water for small areas. The baking soda is strong enough after drying to with stand spinning but weak enough after pyrolysis to be rinsed away.

Deposition Methods

Liquids are relatively easy to deposit on substrates. Methods in common use today by industries such as electronics and automotive manufacture are capable of excellent uniformity and reproducibility. Low viscosity liquids such as we are concerned with here can be painted, dipped, sprayed or dropped on rotating substrates. Each technique has particular advantages and disadvantages.

Dipping

A considerable amount of time and effort has been expended by electronics industry equipment suppliers in the design and construction of controlled-withdrawal dip coaters. This equipment is used by many firms to coat printed circuit board laminates with medium and low viscosity solutions. The procedure is as follows: a substrate is lowered into a tank of the coating solution at a rather rapid rate. It remains stationary for a period of time and is then withdrawn at a slow, constant rate. Coating thickness is a function of solution viscosity and withdrawal rate and can be remarkably predictable and reproducible. An advantage of this technique is the ease with which large areas can be coated. Another benefit is the relative solution usage efficiency: what is not deposited on the substrate drains back into the dip tank for reuse. Obviously the liquid either cannot be highly volatile or must be carefully monitored for solution solids content and viscosity.

A disadvantage of dipping is the lack of discrimination: both sides and the entire area will be coated unless masked. Masking involves the choice of a non-contaminating material compatible with the subsequent processing steps which can be easily and completely removed. There are a number of commercial resist materials which appear to meet these requirements. Another problem with dipping is the formation of a thick meniscus on the lower edge. If the solution is viscous the lower edge can build up to a thickness several times that of the top or center.

Pantek uses dipping extensively on surfaces of revolution (tubes, primarily) and large area samples. The choice of solvents is reasonably critical for this process and is a compromise between drying speed, (too fast can cause thickness variations), and viscosity.

Spraying

Many liquids are sprayed with automatic or semi-automatic equipment in industry. The technique is applied to relatively thin, fractional micron thicknesses as well as films several thousandths of an inch thick. Methods of air and liquid mixing have been developed which allow the use of liquids over a wide range of viscosity. Spraying is quick and convenient for small and large areas. There are several disadvantages to spraying:

1. Spraying is wasteful. In most cases the over-spray is not recoverable.
2. It is difficult to achieve uniformity, both in thickness and coverage.
3. Solvent/diluent properties are critical.

In spite of these problems, spray-coating is well-suited to relatively thick films and large areas.

Spin-Coating

This method involves rotating the substrate at a relatively high rate of speed and dropping controlled amounts of solution on the surface. Used primarily for applying thin coatings of photoresist in the electronics industry, it is an excellent technique for relatively small areas. Coating thickness is controlled by varying the rate of rotation and solution composition.

The main disadvantage to spinning is the formation of a thicker film at the substrate edge due to surface tension holding liquid on the edge. For a typical Ta_2O_5 film at Pantek of 600Å, the very edge can measure as much as 670Å. Within limits this effect can be minimized by proper solvent choice. Solvents with very low viscosities also have low surface tension.

Control of Properties

Below is a chart which compares the various coating techniques and estimates the degree of control possible for the properties of thickness and uniformity.

METHOD	FILM THICKNESS	PLUS OR MINUS	HOW ACHIEVED	SIZE	UNIFORMITY	HOW ACHIEVED	DISTRIBUTION
Dipping	1000Å	20Å	Solvent Addition	$100in.^2$	±5°A per inch	Solvent Boiling point/withdrawal Rate	Bottom Thickest
Spraying	5µm	.05µm	Solids Content	$10in.^2$	± 0.1µm per substrate	Solvent type/substrate travel rate	Variable
Spinning	600Å	10Å	Solids Content Rotation Rate & Time	$10in.^2$	± 5Å per inch	Rotation speed, solvent viscosity	Edges Thickest

This chart is helpful only as a guide to what is possible for the particular set of materials used in this work and represents the best achievable.

Films

This section discusses films in general, the basic questions of uniformity and stress, and in particular the graded-index system of Ta_2O_5, Ta_2O_5, · SiO_2 and SiO_2.

Stress

Large internal stresses are known to develop in thin films during their growth. The presence of such stress at the interface thin film & semi-conductor has a considerable effect on its mechanical properties, electron-transport mechanisms, magnetic, optical properties, etc.

The evaluation of such stress is important because thin films have unusually high tensile strength, which is related to their structure, growth, & the high density of defects built up during their deposition which appear principally as dislocations. Various methods may be used to perform measurements either mechanically, thermally, optically, electrically etc.

The bending measurement is the most common method in the mechanical approaches to stress evaluation. If a film adheres strongly to its substrate, such combination will bend because of stresses in the film e.g. if the film length tends to contract but is restrained by the substrate, the film is in a state of tension, or, if the film tends to expand, it will be in a state of compression by the substrate. Compression or expansion is either measured by the cantilever method or the deflection method.In the first case the substrate is clamped at one end & in the second it rest on knife edges. In either case the deflection can be measured in a variety of ways, mechanically with a stylus, or any electromechanical approaches, magnetic, optic, capacitive etc.

The deflection α of a bending plate [illegible] used to express a stress P in equilibrium with a strain

$$P = \frac{\alpha E_s D^2}{3L^2 t\ (1-\gamma_s)} \left(1 + \frac{E_F}{E_s} \frac{t}{D} \right) \qquad (1$$

Where S & F are suffixes for substrate & film respectively

E Young modulus
D, t thicknesses of substrate & film respectively
L face length of substrate
γ Poisson's ratio

For a very thin deposit t << D (1) simplifies to (2

$$P = \frac{E_s D^2}{6rt\ (1-\gamma_s)}$$

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Where r is the radius of curvature of the bent substrate. If the film is anisotropic the displacement α_z perpendicular to the isotropic substrate plane of (x, y)

$$\alpha_z = \frac{3\ (S_x - \gamma S_y)}{E_s t^2}\ X^2 + \frac{3(S_y - \gamma S_x)}{E_s\ t^2}\ Y^2$$

S_x & S_y are the stress components along x & y direction. The bending plate or cantilever measures directly the force St = F Differences in thermal expansion between film & substrate can be expressed as a function of the thermal coefficient of expansion, i.e. the strain S_{th} is,

$$S_{th} = E_f \left[\int_{T_1}^{T_2} \alpha_s\ (T) dt - \int_{T_1}^{T_2} \alpha_F\ (T) dt \right]$$

$$S_{th} = (\alpha_s - \alpha_F)\ E_F\ DT$$

$DT = T_2 - T_1$, and the same remarks apply with regards to compression or tension as a function of the respective signs & magnitudes of α. For conductive films or substrates the stress effects may be obtained as a function of dimensions & resistivity ρ from the resistance R

$$R = \frac{\rho L}{WD}$$

with stress R changes will be

$$d\ \ell n\ R = d\ \ell n\ \rho + d\ \ell n\ L - d\ \ell n\ W - d\ \ell n\ D$$

if the sample is isotropic with the stress P applied

$$\frac{d\ \ell n\ R}{d\ P} = \frac{d\ \ell n\ \rho}{d\ P} + \frac{K}{3}$$

Where K is the volume compressibility $(- \partial\ \ell n\ V/\partial P)_T$

If the substrate is bent such that its radius of curvature of bending is constant along the direction L, the strain in that direction is S_L & in the W direction $- \gamma_s\ S_L$, thus

$$\frac{DL}{L} = S_L \; ; \quad \frac{DW}{W} = - \gamma s \, S_L \; ; \quad \frac{DD}{D} = - \gamma F \left(\frac{1 - \gamma_s}{1 - \gamma_F} \right) S_L$$

The fractional change in resistance can be found for a given change in bending stress longitudinal with the substrate

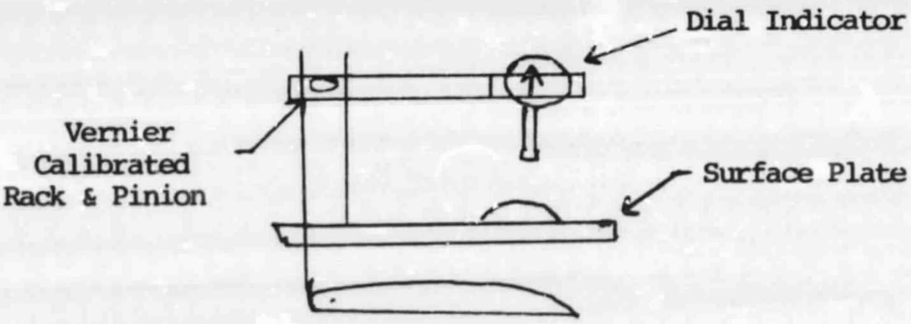
$$\frac{d \, \ell nR}{d \, s_L} = \left(\frac{d \, \ell n \, \rho}{dP} \right) \left(\frac{-1}{K} \right) \left(\frac{1 - \gamma_s}{1 - \gamma_F} \right) \left(1-2 \, \gamma_F \right) + \frac{1 + \gamma_s - 2 \, \gamma_s \, \gamma_F}{1 - \gamma_F}$$

which is valid for the case where the substrate is bent in the direction to the current flow.
When streched (or bent) in a direction transverse to the current flow

$$\frac{d \, \ell n \quad R}{d} = \frac{(d \, \ell n \, \rho)}{dP} \; \frac{(-1)}{K} \; \frac{(1 - \gamma_s)}{(1 - \gamma_F)} \; \frac{(1-2 \, \gamma_F)}{} - \frac{(1+ \gamma_s - 2 \, \gamma_F)}{1 - \gamma_F}$$

In the particular case of solar cells manufactured from 2 mil (50.8µm) thick silicon, the substrate is highly deformed as received. This is undoubtedly due to the difference in mass of silver deposited on front and back. The front of the cell is invariably bowed up in the center. The methods described above were investigated for quantifying the degree of stress. After repeated attempts to detect changes in the conductivity with stress the electrical methods were abandoned. Our best guess is that the ductile electrical contact material flowed sufficiently on a microscopic level to relieve most of the strain.

On a routine basis the degree of stress was estimated using a modified Ames gauge and equation (2) above. Pictured below is the apparatus.



An initial zero was set with the dial indicator on the wafer or surface plate and then again on the top of the deformed wafer. The difference in vernier readings would be the deformation, h. This quantity is related to the radius of curvature.

Deformation could also be measured with a light section microscope for very small (10µm) deflections. The trend we saw was a decrease in h with the addition of coatings up to a point. Tabulated below is the measured h and t, film thickness, versus a typical coating sequence.

SAMPLE	h	t	MATERIAL	TEMP. CYCLE
As received	0.0152"	0	--	--
1st	0.0147	600Å	Ta_2O_5	300°C, 5 minutes
2nd	0.0131	500Å	$75Ta_2O_525SiO_2$	300°C, 5 minutes
3rd	0.003	15μm	GR908	230°C, 1 hour

The 3rd coating, GR908, was actually deposited four times with a drying step between each coat. If the entire 15μm was deposited at one time the stress in the film was too high and cracks appeared. A number of experiments with one, two, three, etc. coats of GR908 showed that the change in h tended to decrease after two or three coats. This indicates that the effect is not simply one of mass addition to the front surface.

Experiments on simply exposing a bare cell to similar temperature cycles (above) showed no permanent change in h. Apparently the effect is not due to annealing either the silicon or the metallization.

An interesting effect was noticed during the thermal shock testing in which immersing a thin cell in liquid nitrogen would reverse the curvature. That is, the deflection would go to convex from concave. This occurs whether the cell is anti-reflection coated or not. The metal-covered back surface obviously contracts much faster than the silicon. It is not clear why the cells retain this 'set' and no change in the gross electrical properties of short-circuit current and open-circuit voltage could be ascribed to this change in configuration

Multiple thin coats of material minimize trapped solvent and intrinsic stress.

Uniformity

Of great concern during this work was the question of uniformity: could these non-vacuum techniques yield reproducible optical films? The answer seems to be maybe. Figure 9 exhibits the results of depositing Ta_2O_5 films on glass substrates eight times on two separate days with two independent batches of liquid at a five percent solids level. The curves are of optical transmission versus wave length. Tests such as these, less than six percent variation in optical thickness, yield confidence that the materials and methods are indeed reproducible.

When multiple coats are involved, some care must be used in method of deposition. It is possible to spray coat these optical films, but reproducibility is suspect, simply because of spray uniformity, uncalibrated coating weight, and solvent evaporation. We have found that if it is necessary or desirable to spray coat cells it is best done with multiple passes and dilute solutions. This allows for measurement

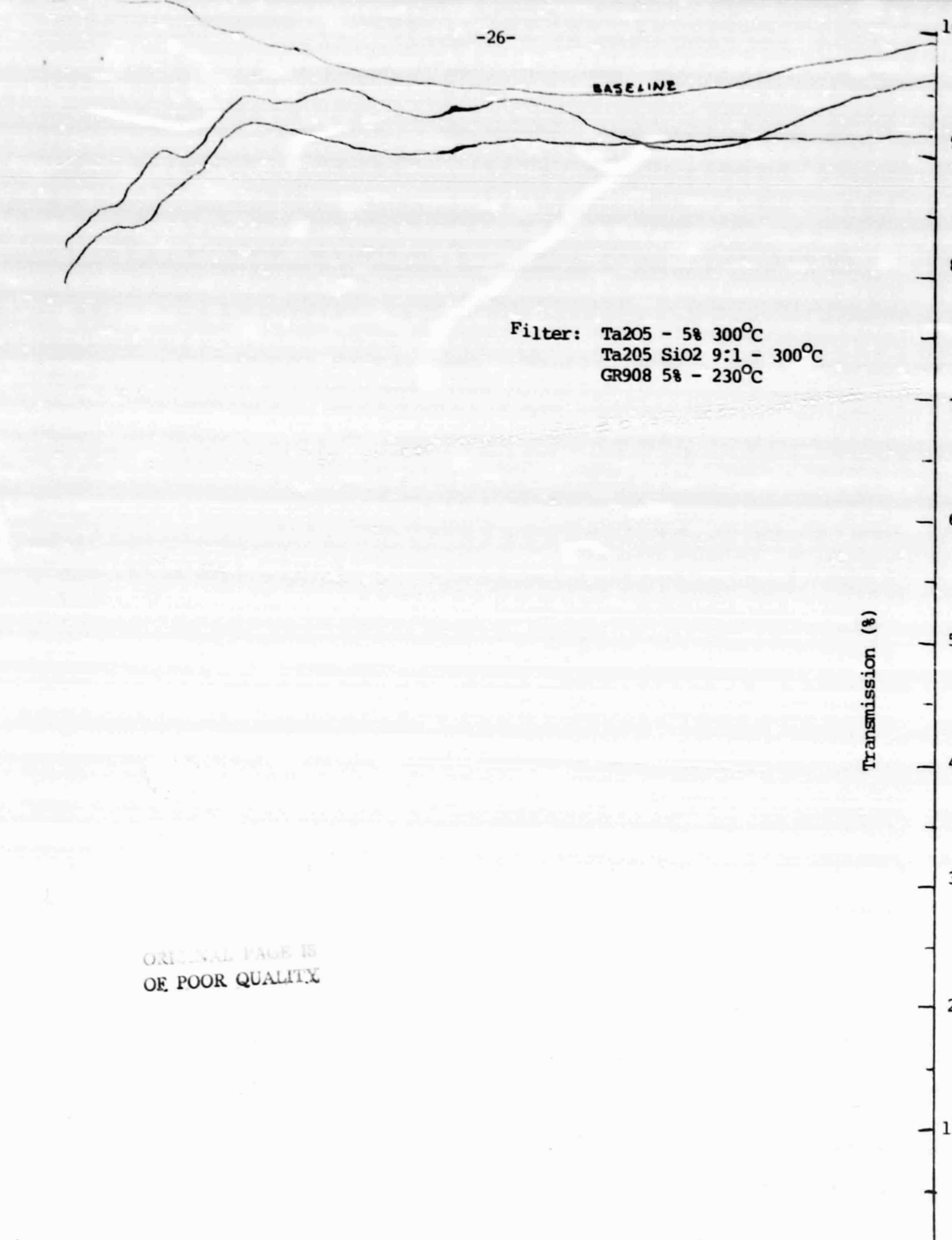


Figure 9 Transmission of two 3 layer filters

between coats and the possibility for adjustment. It also increases the time required for any set of coatings. For non-critical heavy coatings such as the Glass Resin, spraying is ideal. Computer simulation has shown that in a three-layer filter the thickness of the second and third layers is much less critical than the first. An error of 10% in physical thickness merely shifts the position of the minimum reflectance by one or two percent.

Modules of two by three interconnected cells (2mil thick) were furnished to us for coating. Some modules were simply interconnected, others had been bonded to a flexible Kapton substrate. In general this configuration would cause no difficulty in coating. In practice, however, the thin cells retained their deformation after bonding and the Kapton was not flat. Most of the modules were sprayed rather than spun.

Kapton sprayed with Glass Resin coatings and exposed to temperatures as high as 250°C for one to three hours showed no degradation in flexibility or other gross physical properties. As near as we could tell, no cell delamination occurred during curing.

The only serious problem encountered with coating the modules was one of silicone contamination on the surface. Sometimes the GE silicone bonding agent would creep over the cell edges. Glass Resin will not bond or coat over silicone.

Materials II

In this section is described attempts to deposit CdO and ZnO from metallo-organic solutions onto silicon substrates, convert to Cd Zn/S and obtain essentially single crystal material by a controlled withdrawal method.

CdO and ZnO are easily deposited and developed on glass substrates by spraying liquid organometallic solutions and subsequent pyrolysis. One firm markets thick film inks which develop CdO. Another company has inks which deposit thick CdS films. Dr. Hanlet had demonstrated in earlier work that CdS crystals could be grown in relatively large size on substrates[1]. The oxides can be reduced to CdS or ZnS by heating in sulfur atmosphere at low temperatures. The reaction proceeds easily but slowly to yield 100% sulfide.

Every attempt made to deposit CdO or ZnO on silicon in uniform, thin layers was unsuccessful. The films would appear to be uniform in the liquid state and also after drying. Upon examination microscopically the fired films were very poorly adhered: Abrasion with a soft paper tissue would remove them. Many combinations of time, temperature, surface treatment and thickness were attempted. The films acted as though they contracted away from the silicon. Two different cyrstallographic orientations of silicon, polished and unlapped, were tested with negative results.

Conversion of CdO into CdS was attempted with glass substrates and silicon. The films on glass were moderately smooth and adherent. The films on silicon fell off. It is possible that the thermal expansion coefficient of CdO and ZnO are sufficiently greater than that of silicon that no thermally stable film can be achieved at these relatively large thicknesses (1μm to 3μm). Because of these difficulties the experiment was abandoned.

1. J. M. Hanlet Facsimile Scanner Final Report. Navy Dep. Electronic Division March 1971, contract N00039-68-C-0557.

Testing

In addition to the usual quality checks, this contract required a substantial amount of environmental testing. These tests were designed to a) stress the coatings severely to determine their integrity and b) investigate the degree of protection offered to silicon solar cells. Cells were tested with a single coating and multilayers. Wafers of various thicknesses and a variety of coatings were measured and remeasured. Some cells failed. Some cells were incorrectly coated and tested. Some results are suspicious because of instrumental aberrations. For clarity and ease of interpretation this section is a summary of the test results. Examples of the results will be exhibited for typical cells and wafers.

Optical Transmission

Optical transmission of these coatings was measured on a glass witnesspiece which received identical coatings to the silicon cells. The measurements were made on a dual beam Beckman spectrophotometer model DK1 or DK2. In all cases internal transmission was greater than 95%. Internal transmission measures the losses in a coated substrate against or subtracted by the substrate properties and after correcting for reflection. Figure 11 is an example of the raw transmission data. Note two things about these data:

(1) correcting for the base line variation shows an absolute transmission which varys from 94% to 97% over the range 400nm to 1300nm and

(2) the regular peaks and valleys in the transmission are due to interference in the film. From the positions of these peaks one can deduce the total film thickness. These data are in-valuable as a check on physical thickness measurements.

All samples measured had excellent optical transmission. This is to be expected in such thin films. The only cause of lower transmission would be scattering in the film itself caused by dust or dirt or cracks, etc.

Warpage/Distortion

As mentioned in the text, a mechanical measurement of radius of curvature can be used to judge stress in the composite film and substrate. Shown below is one of a series of measurements. Note that the absolute change in h is proportional to the thickness (mass) applied, but that the change between 10μm and 17.3μm is much less than that between 5μm and 10μm. It is entirely

COATING	THICKNESS*	CURE	h
1. -	0	-	0.0171"
GR908	5.2μm	230°C-30 min	0.0128
-	0	-	0.0170
2.GR908	10.0μm	230°C-60 min	0.010
3. -	0	-	0.0174"
GR908	17.3μm	230°C-90 min	0.0094"

*Single deposition.

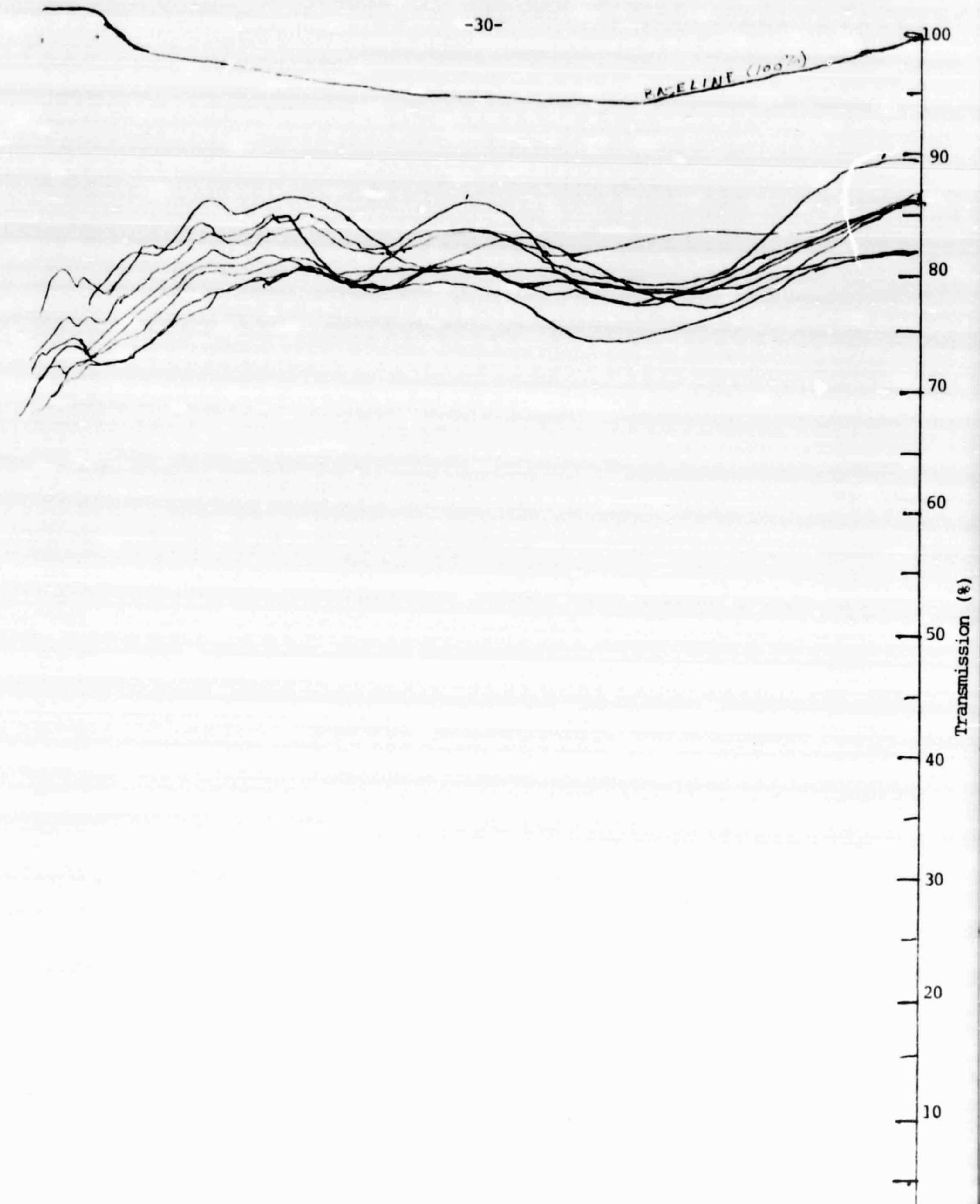


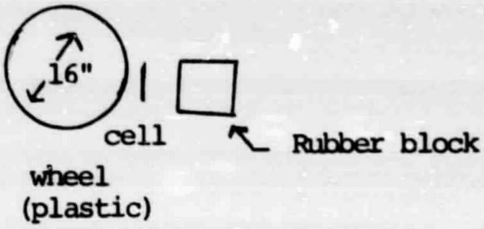
Figure 10. Optical transmission of eight samples, 6 layers each

possible that measurements such as these are meaningless due to a different intrinsic stress in the films as a function of thickness.

Our conclusions were that the thin films applied to silicon did not stress or deform the silicon and in fact served to relieve the deformation due to the metallization.

Flexibility

Flexibility was measured qualitatively by bending the 2 centimeter square cells or wafers or an eight inch radius wheel. Schematically, the cells were bent



both with the coating facing the wheel and facing away. The orientation was such that the substrate edge was parallel to the axis of rotation of the wheel. As mentioned above, cracking was observed visually in two cases:

a) Coatings above a certain thickness, no matter how applied and
b) above a certain thickness when applied in one deposition.

The cracks were generated where the film was deposited over the metallization.

The limits for Glass Resin Materials are shown in Table V.

TABLE V

RESIN	FILM THICKNESS AT WHICH 50% SAMPLES CRACKED	FILM THICKNESS AT WHICH MULTIPLE THIN FILMS CRACKED
TYPE 650/650M	6μm	8μm
GR100	14μm	16μm
TYPE 908	30μm	35μm

Thermal Shock

Coated cells were subjected to two rates of thermal shock. In one case the cells were placed on an aluminum block in a fast response oven. The oven was cycled repeatedly from -184°C to + 100°C. The oven approaches a (set) temperature at the rate of over 100°C per second. In this very reproducible cycle no failures were observed on any cells which had multiple Glass Resin coatings below the thicknesses given above.

A second test consisted of holding coated cells by tweezers and immersing them under the surface of liquid nitrogen. After thirty seconds the cells were removed. After another thirty seconds they were reimmersed for a total of fifteen or more times. No failures occurred as observed by visual examination and electrical measurements after humidity exposure. The above statement is only true for coatings at or below the value mentioned in the first column of Table V.

Water/Humidity Testing

Visual observations for cracks or delamination in coatings are coarse and non-qualitative. A test for degradation of coated silicon solar cells should include power measurements as the expected effect of humidity and water incursion is to degrade optical transmission or increase leakage resistance. In the absence of an optical simulator, an inexpensive GE projection lamp and a 'standard' cell allows the measurement of open circuit voltage and short circuit voltage and short circuit current in a reasonably reproducible fashion. The technique is as follows: A GE type H projection lamp bulb is connected to 110 VAC through a variable transformer. A standard cell from NASA or commercial sources* is placed on a copper measuring plate. Under illumination the short circuit current is measured and the light intensity adjusted until the known value under air mass 0 or air mass 1 is achieved. Cells of unknown characteristics are then measured under similar conditions and compared to the parameters of the standard cell.** This technique yields results which are reliable guides to the improvement or lack thereof due to a particular coating or treatment.

Cells have been measured using the above technique after three types of treatment: immersion in boiling water, exposure to 90% relative humidity, and during and after exposure to uv radiation under humid conditions. Suffice it to say that the results of water and humidity testing have shown no problem with properly applied coatings. This does not mean that failures, i.e., reduced power output after environmental exposure have not occurred. It says that these films under discussion can provide a limited amount of environmental protection with their thickness. Table VI shows some results of measuring coated cells before and after boiling water exposure.

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*A 'standard cell' is one whose light I-V curve has been obtained at a known temperature in apparatus whose characteristics are traceable and acceptable by NASA/NBS standards.

**The author expresses his gratitude to Mr.Jim Avery of Solar Technology for acquainting him with this idea and method. Mr. Jack Broder of NASA-Lewis Research Center cleverly suggested that with proper design one could incorporate the standard cell into a self-correcting circuit which yields calibrated values no matter what the temperature or illumination level. The author thanks Mr. Broder.

TABLE VI. Short circuit current and open circuit voltage before and after 30 minutes in boiling water. Coating is $Ta_2O_5/Ta_2O_5 \cdot SiO_2$/GR908 (4 coats). Coating thickness is 18μm ± 4μm, cell thickness 12 mil

	Before			After		
SAMPLE NO.	Isc	Voc	T (°C)	Isc	Voc	T(°C)
1	420 ma	570 mv	31	520 ma	570 mv	31
3	440	570	33	540	563	32
8	580	574	30	570	573	30
9	590	571	30	520	570	30
18	580	573	26	580	591	26
23	580	570	30	530	575	30

Uniformity/Reproducability

Nine cells (2 mil thick) were coated in one lot with Ta_2O_5, $Ta_2O_5 \cdot SiO_2$ and GR908 (4 coats). All cells were measured before coating with the simulator and measured Isc=100 ma ± 5 ma and Voc=540mv + 5mv at 27°C. Table VII is the result of the measurement after coating.

TABLE VII. Uniformity of coating nine cells in one lot. Coating thickness is 20μm + 2μm.

SAMPLE NO.	Isc (ma)	Voc (mv)	T (°C)
27	118	541	26
28	125	547	26
29	130	541	27
30	125	536	27.5
31	120	534	27.5
32	120	542	27
33	130	543	27
34	110	523	28
35	110	533	28

uv exposure

Cells were placed in a Weatherometer and exposed to 1.5 suns equivalent ultraviolet exposure. Some cells failed early, most survived with some degradation in output. Table VIII summarizes the results.

TABLE VIII. Weatherometer testing. 430 hrs. at 1.5 equivalent suns (uv) and 83°F.

Cell No.	Coating	Total Thickness	Result
4	Single layer TiO_2 plus GR908	18µm	Isc decreased 57% in 4320 hrs. Voc decreased 5% in 4300 hrs.
8	Ta_2O_5, $Ta_2O_5 \cdot SiO_2$, GR908	20µm	No change in Isc,Voc in 4320 hrs.
9	Single layer Ta_2O_5 plus GR908	14µm	No change in 4320 hours.
15	TiO_2, $TiO_5 \cdot SiO_2$ GR100	15µm	Direct short after 100 hrs.
16	Same as 15	15µm	Isc decreased 10% in 4320 hrs. Voc decreased 3% in 4320 hrs.
17*	Ta_2O_5; $Ta_2O_5 \cdot SiO_2$, GR908	28µm	Isc decreased 12% in 4320 hrs. Voc decreased 1% in 4320 hrs.
21*	Same as 17	28	Isc decreased 20% in 4320 hrs. Voc decreased 1% in 4320 hrs.
25	Same as 17	24	Isc decreased 10% in 4320 hrs. No change in Voc
92A	Uncoated commercial cell	-	Grid lifted in 48 hours.

*Note: coating started to lift off @ 96 hours; pinholes.

DISCUSSION OF RESULTS

The results presented above clearly demonstrate that non-vacuum deposition methods are applicalbe to film generation on silicon solar cells and modules. Thin, uniform coatings with reproducible optical properties are easily generated. In common with vacuum techniques, uniformity of coating will be more difficult as the size increases. In principle, however, the techniques of dipping and spraying are applicable to nearly any size. This is one of the three real advantages of using liquids for deposition.

Another prime advantage of liquids is the ability to form solutions between end members with much different values of a particular physical property. The sample in the text is that of refractive index, but other properties may be of interest. There is the possibility of optical filters, narrow band or cut-off type. Fluorescent dyes may be easily incorporated into these alcohol-based systems. Conductive, transparent films integrated into the optical filter are also possible.

The third potential advantage of the work described above lies in the possibility of achieving light-weight hermetic covers with the use of Glass Resins. These hopes are somewhat dashed by the preliminary findings above. Glass Resin films are not hermetic.

Recently it became obvious that the carefully worked-out procedures for wafers do not yield the same results on cells. First of all, the metallization causes non-uniform deposition whether it be spun, dipped, or sprayed. Although the grid lines are very thin, they are projections which the liquid finds convenient to hang onto. Even the very fluid solutions apparently have sufficient surface tension to build up several angstroms thicker around the lines than between them. This is most apparent in the Ta_2O_5 layer where color variations are easily seen. Secondly, the standard coating procedure calls for the silicon to be given a mild H F etch (3% H F acid by bolume, 30 seconds) immediately before coating. When the 2 mil cells are metallized some number of them, roughly forty percent, will lose the grid lines. The metal is not well-adhered and floats free. If the front surface is clean and free from silicone contaminants it is still possible to obtain good even coatings without the acid wash, however, there is some unknown amount of thermal SiO_2 present on the cell surface. The liquid-deposited Ta_2O_5 will either a) interdiffuse with the SiO_2 and yield a smaller than expected refractive index or b) the structure will be $Si \cdot SiO_2 \cdot Ta_2O_5$ rather than $Si \cdot Ta_2O_5$ and thus cause a less-effective optical matching.

The discussion of cost and production of these films were judged to be inappropriate in this report.

RECOMMENDATIONS AND CONCLUSIONS

Thin films of Ta_2O_5, $Ta_2O_5 \cdot SiO_2$ and Glass Resin deposited on silicon from liquid solutions in the proper sequence and thickness can provide both antireflection properties and environmental protection. The coatings can be applied by dipping, spinning or spraying silicon cells or interconnected arrays. Total thicknesses of 30μm or less can be achieved by multiple depositions.

The extent to which the films protect silicon cells is not yet clear; the electrical properties of coated cells changed after 4300 hours at 83°F and under an illumination equivalent to 1.5 suns. More testing of the Glass Resin films fired at different times and temperatures is required.

The integration of a highly conductive, transparent film into an optical filter should be investigated. In view of the low mass of these films, the system should be evaluated and considered for use in space arrays.