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EXPLORATORY DEVELOPMENT OF TRANS-
PARENT CONDUCTOR MATERIALS

G. Haacke

American Cyanamid Company

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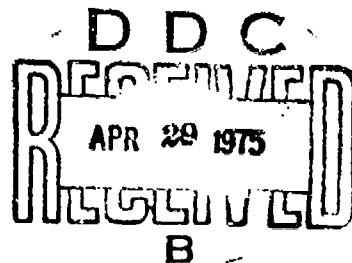
EXPLORATORY DEVELOPMENT OF TRANSPARENT CONDUCTOR MATERIALS

AMERICAN CYANAMID COMPANY

TECHNICAL REPORT AFML-TR-75-21

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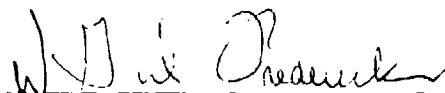
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This technical report has been reviewed and is approved for publication.



Robert M. Van Vliet
Project Engineer

FOR THE COMMANDER



William G. D. Frederick
Chief, Laser and Optical Materials Branch
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Air Force Materials Laboratory

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The development of electrically conductive cadmium stannate coatings with high visible transparency and high infrared reflectivity has been pursued. Efforts concentrated on the investigation of different deposition technologies, film doping, coating of various substrate materials, and film testing.		

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20. ABSTRACT

Chemical spray deposition and vacuum evaporation of cadmium stannate films has been evaluated and compared to radio frequency sputtering. The development of a spray technology has resulted in highly transparent films with 100 ohm/square electrical sheet resistance. Further improvements of this coating technique appear to be possible which could lead to sheet resistances approaching those of sputtered films (1-2 ohm/square). Vacuum evaporation of cadmium stannate did not result in acceptable films.

Doping experiments showed that interstitial cadmium and oxygen vacancies are effective dopants for maximum electrical conductivities. Indium and tantalum doping increase the infrared reflectivity to 90% beyond two micron.

Substrate materials investigated included silica, sapphire, soda-lime glass, Chemcor glass, alumina-silica glass, stretched acrylic, and polycarbonate. Adherence and abrasion resistance of cadmium stannate films on non-plastic substrates are excellent. Adherence to plastic substrates is excellent if a silica interlayer is deposited onto the substrate prior to cadmium stannate deposition. The temperature/humidity resistance of cadmium stannate coatings on all substrates investigated was found to meet specifications.

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FOREWORD

This report was prepared by the Chemical Research Division, American Cyanamid Company for the Air Force Materials Laboratory, Wright-Patterson Air Force Base under Contract No. F33615-74-C-5021. The author is Dr. G. Haacke.

The effort described was conducted in support of project #7371 and task #737102 for the Laser Window Branch of the Electromagnetic Materials Division during the period of January through December 1974.

The report was submitted by the author January 1975.

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Valuable contributions to the project were made by H. Ando, R. E. Evans, J. P. Falzone, L. A. Siegel, and C. F. Spiers.

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SECTION I

INTRODUCTION AND SUMMARY

A. INTRODUCTION

The number of practical applications for transparent, electrically conductive coatings grows with increasing film conductivity if a high optical transmission can be maintained. Coatings with electrical sheet resistances in the 10-100 ohm/square range (30-90% visible optical transmission) are available and find use in electro-optical devices such as displays, memories, etc. The range of applications could be broadened considerably if sheet resistances of 1 ohm/square and lower became feasible without decreasing the optical transmission much below 90%. One important application for such advanced coatings would be in solar cells where they could function as transparent frontwall (silicon cell) or backwall (CdS cells) electrodes.

Tin oxide and indium oxide are currently the best known transparent conductor materials and they are available commercially. Recently, a third material, cadmium stannate (Cd_2SnO_4), was found to have promising transparent conductor properties.^{1,2} From an investigation of its fundamental physical properties it was concluded that cadmium stannate is a viable candidate for transparent solar cell electrodes. Moreover, the mechanical properties of cadmium stannate thin films on glass indicated their potential utility as high conductivity coatings on aircraft canopies for the purpose of eliminating radio frequency interference from the cockpit.

The objective of this program was the development of cadmium stannate films with high visible transparency, low infrared transparency and high electrical conductivity for use on aircraft canopies and certain electronic devices. The program goals included development of deposition procedures for stable, adherent cadmium stannate films on various canopy surfaces and a feasibility study of fabricating a conductive x-y grid for high intensity electroluminescent displays.

The tasks of AF Contract F 33615-74-C-5021 have been complemented by a program which American Cyanamid Company has carried out with NSF/RANN support. The NSF/RANN sponsored work has been concerned with the development of cadmium stannate films for solar energy applications. Here the objectives are cadmium stannate films with approximately 1 ohm/square sheet resistance and 90% visible optical transmission and the incorporation of these films as transparent backwall electrodes in CdS solar cells. A further objective has been the utilization of the high infrared reflectivity of cadmium stannate in heat reflective greenhouse window coatings in solar heat collectors.

This report describes the work performed under AF Contract F 33615-74-C-5021 and discusses the results obtained during the course of this project. Included in the discussion are also those results of the NSF/RANN program which are relevant to the particular Air Force applications.

B. SUMMARY OF RESULTS AND CONCLUSIONS

Efforts during the program concentrated on four main tasks:

1. investigation of different deposition technologies for cadmium stannate films, 2. modification of the electrical and optical film properties by doping, 3. coating of different substrate materials and 4. cadmium stannate film testing.

Three deposition technologies have been evaluated: radio frequency sputtering, chemical spray deposition, and vacuum evaporation. The development of sputter deposition of cadmium stannate films has been most successful. Films with sheet resistances near 1.5 ohm/square and better than 85% visible transmission can be prepared on silica or glass substrates. The feasibility of chemical spray deposition for the production of transparent cadmium stannate films has been demonstrated. However, the electrical sheet resistances of these coatings are still high (~ 100 ohm/square) so that further development work will be required if the properties of sputter coated films are to be matched. The preparation of cadmium stannate films by vacuum evaporation was not successful.

Modification of the electrical and optical film properties by doping was attempted via partial cadmium or tin substitution to achieve larger band gaps, via substitutional doping to increase the electrical conductivity and by impurity additions to induce near infrared absorption. Larger band gaps were not achieved. Most effective dopants for maximum electrical conductivities were found to be interstitial cadmium and oxygen vacancies. Infrared absorption/reflection becomes

significant beyond 1.5 micron in optimal doped samples. Attempts to shift this absorption closer to the visible spectrum have not yet been successful. However, only a limited amount of time could be spent on this part of the program and further studies could well result in significant IR absorption below 1 micron. Highest IR reflection (90%) beyond 2 micron has been obtained in samples doped with indium or combinations of indium and tantalum.

Substrate materials investigated included silica, sapphire, soda-lime glass, Chemcor glass, alumina-silica glass, stretched acrylic, and polycarbonate. Adherence and abrasion resistance of cadmium stannate films on non-plastic substrates were found to be excellent. Adherence to plastic substrates is excellent if a silica interlayer is deposited onto the substrate prior to cadmium stannate deposition. Electrical sheet resistances as low as 10 ohm/square have been achieved on polycarbonate substrates. The abrasion resistance of cadmium stannate on plastic thus far has been poor. However, it was observed that the properties of the interlayer and the mode of cadmium stannate deposition influences the abrasion resistance. Further development work could lead to considerable improvement in this area.

The humidity resistance of cadmium stannate coatings on all substrates investigated was found to be excellent.

SECTION II

CADMIUM STANNATE FILM DEPOSITION

A. RF SPUTTERING

The deposition of cadmium stannate films by radio frequency sputtering from hot pressed Cd_2SnO_4 target plates results in coatings with highest electrical conductivity and lowest optical absorption in the visible spectrum. A total of ten deposition parameters was found to influence film properties. Of major importance are substrate temperature, plasma gas composition, gas pressure, RF tuning, and substrate bias.

If cadmium stannate is sputtered onto glass or silica substrates kept at room temperature the resulting coatings are amorphous. The amorphous nature of these samples limits their electrical conductivity to approximately $1,000 \text{ ohm}^{-1}\text{cm}^{-1}$ and if sheet resistances below 2 ohm/square are desired the visible optical transmission does not exceed 70%. Substrate temperatures of 500°C or higher induce film crystallization. These polycrystalline samples reach electrical conductivities as high as $3500 \text{ ohm}^{-1}\text{cm}^{-1}$ if all other preparation parameters are optimized.

The minimum substrate temperature necessary for film crystallization depends on the properties of the substrate but also on the plasma gas composition. Films sputtered in pure oxygen crystallize at temperatures almost 200°C below those required for an argon rich argon/oxygen mixture. Still lower substrate temperatures result when single crystal substrates are used. In the case of a single crystal spinel substrate film crystallization was achieved near room temperature.

Since most of the sputter deposition development was carried out under the NSF/RANN grant further details of this work will not be discussed here. A good representation of the electrical and optical properties of state-of-the-art sputter coated cadmium stannate films is shown in Figure 1 which depicts the optical transmission of a cadmium stannate film with 1.3 ohm/square electrical sheet resistance. The curve includes approximately 7% transmission and reflection losses of the vitreous silica substrate. By subtracting these losses we see that the average film transmission is 85% over a large part of the visible spectrum.

State-of-the-art sputtered cadmium stannate films are not single phase. Besides consisting of Cd_2SnO_4 they contain small amounts of CdO and CdSnO_3 .³ The secondary phases were found to reduce the free electron mobilities to values lower than would be expected for homogeneous single phase specimens. Corroborating evidence has been provided by extensive Hall effect measurements. Determination of the electron mobility μ as function of the free carrier concentration n in a given sample revealed that in sputtered films the mobility increases with electron concentration. An example of this dependence is shown in Figure 2 for two zirconium doped specimens. Besides the unexpected functional dependence of μ vs. n it can be seen that the mobility of the amorphous sample is higher than that of the crystalline film. Such behavior can be accounted for by the multi-phase film composition. It also indicates, however, that in single phase Cd_2SnO_4 we can expect considerably higher mobilities and, hence, lower sheet resistances than in current state-of-the-art coatings.

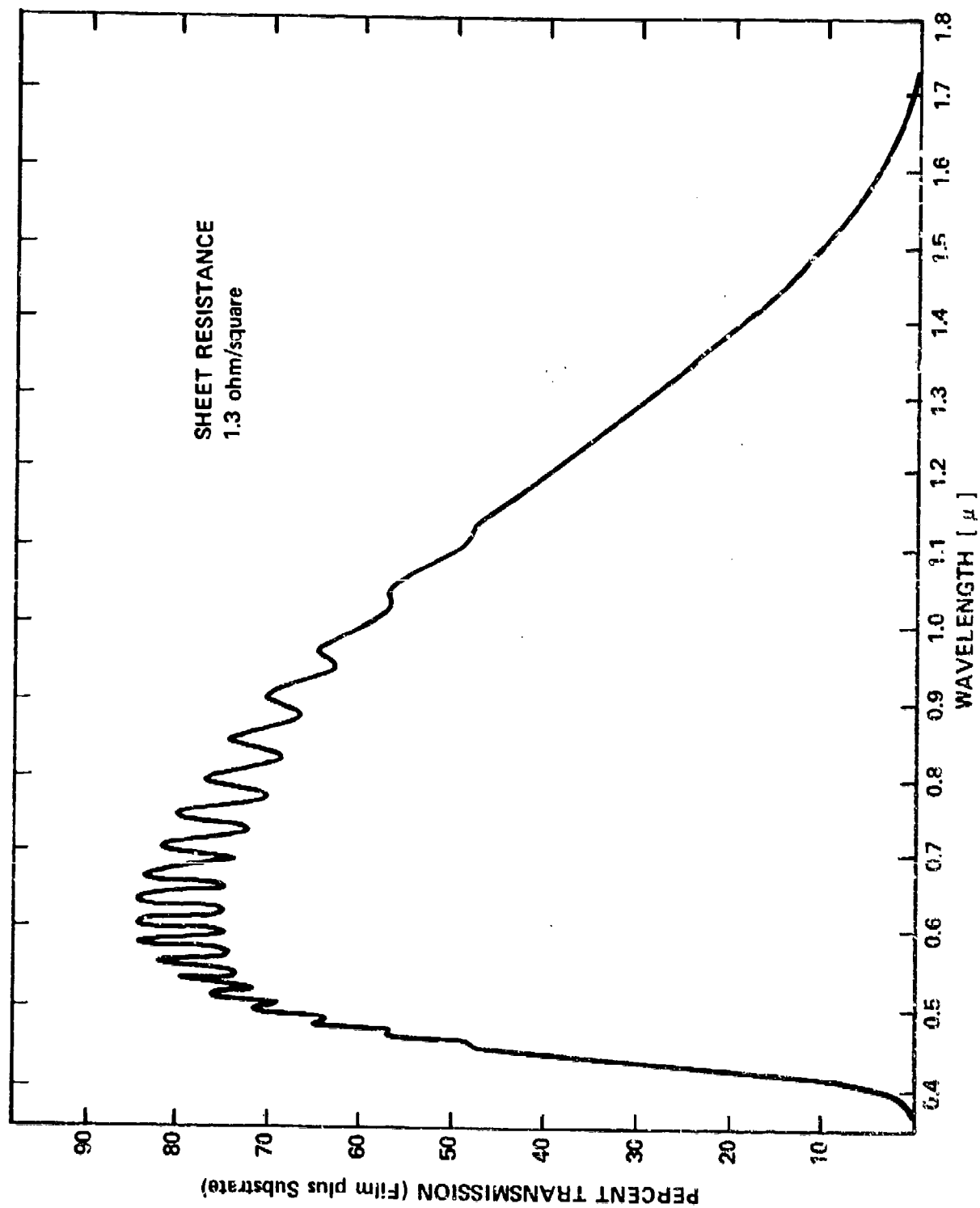


Figure 1. Optical Transmission of Cadmium Stannate Film on Quartz Substrate

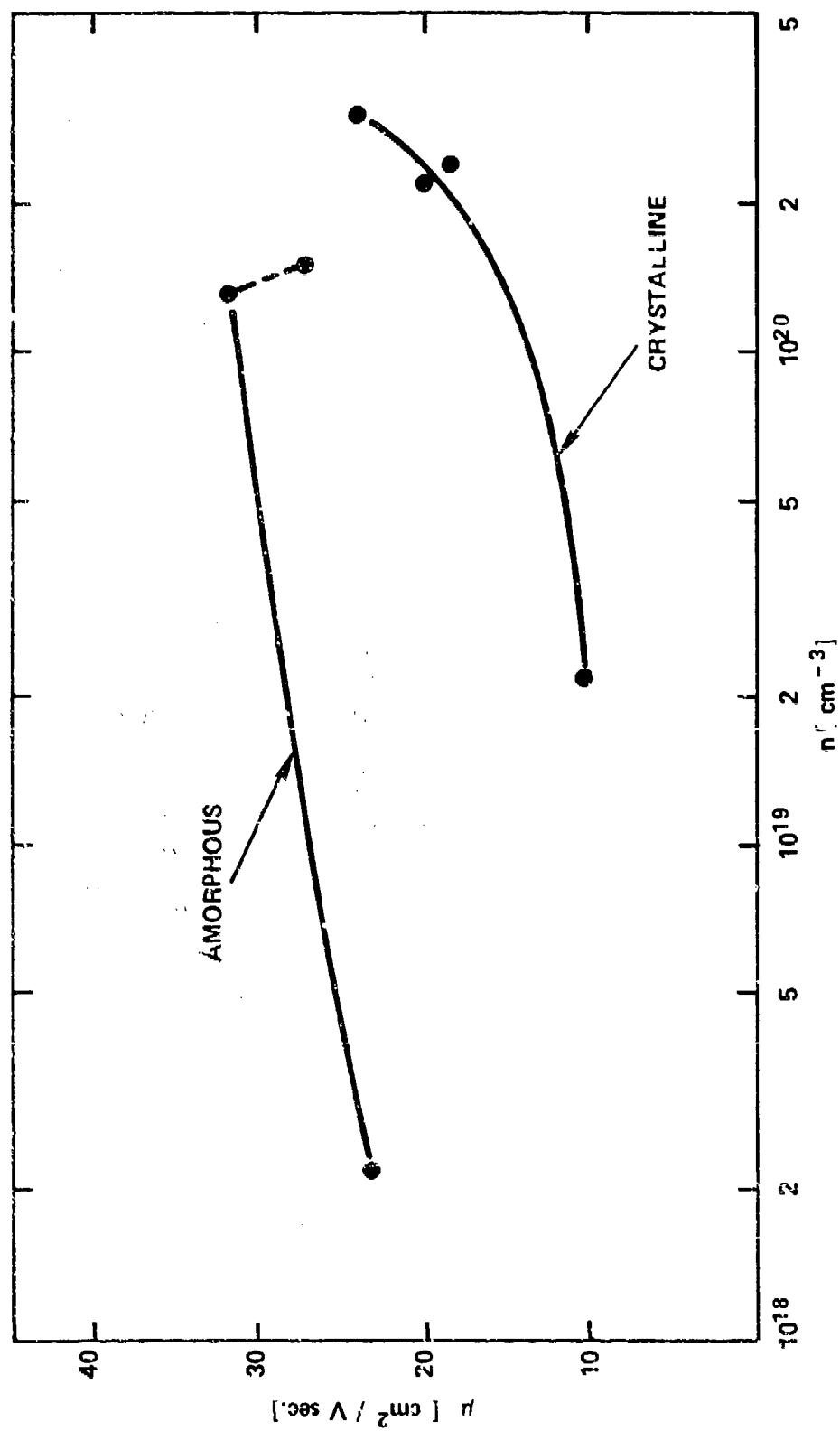


Figure 2. Hall Mobility vs. Carrier Concentration of Zr Doped Cd_2SnO_4 Films

The curves of Figure 2 are characteristic for doped as well as undoped samples. Mobilities between $45\text{--}50\text{ cm}^2/\text{Vsec}$ ($n > 10^{20}\text{ cm}^{-3}$) have been measured in some samples. The lower mobility values of Figure 2 are caused by the zirconium doping which appears to introduce additional carrier scattering. A similar effect has been observed with most other transition metal dopants.

B. CHEMICAL SPRAY DEPOSITION

The versatility of chemical spray deposition (CSD) and its potential economic advantage over sputter deposition has led to an investigation of its applicability to the preparation of cadmium stannate films. The principal of CSD consists of spraying a solution with the desired metal ions onto a hot substrate. Upon impact of the solution droplets on the substrate the solvent evaporates and the metal ions form oxides in the presence of oxygen. This method does not present major difficulties for the deposition of binary oxide coatings. However, if ternary oxide films are to be prepared formation of the ternary phase and avoidance of the binary components can pose severe problems.

None of the deposition parameters important for CSD can readily be subjected to a scientific analysis but has to be optimized empirically instead. Therefore, a simple experimental set-up was chosen which facilitated screening and could be modified easily.

For rapid heating and cooling clear fused silica slides were used as substrates. Most of the substrates measured between $1/4" \times 1/4"$ and $1/2" \times 1/2"$. They rested on a ceramic or stainless steel support inside a Cenco muffle furnace or a Thermolyne Type 1500 furnace. Substrate heating with a torch was attempted but a precise gas flow control and flame shaping would be necessary to adapt this mode of heating to routine spray coating experiments.

The substrate surface temperature and its change during spraying are critical film formation parameters. Hence, a thermocouple pressed against one point near the edge of the substrate surface. Its output was delivered to a recorder and a continuous temperature monitoring took place during spraying.

Suitable cadmium and tin salts for the spray solution can be chosen from SnBr_4 , SnCl_4 , CdBr_2 , CdCl_2 , and $\text{Cd}(\text{NO}_3)_2$. While during the early phases of the project clear cadmium stannate coatings could only be obtained from dissolved bromide salts refinements of the technology made possible the use of chlorides as well. The $\text{CdCl}_2/\text{SnCl}_4$ combination has been finally adopted for the basic spray solution because it allows greater flexibility in choosing a wide range of concentrations. In view of large scale applications, price and availability also favor the chlorides.

Water was found to be the best solvent for preparing the spray solution. Its complete or partial replacement by organic solvents was investigated since the patent literature^{4,5} reports on the beneficial effects of alcohols in solutions used for the deposition of conductive binary oxide coatings. Methanol as solvent leads to combustion of the spray and prevents film formation even if it is used only as a diluent of aqueous solutions. Similar observations were made with ethanol. Higher alcohols (butanol, octanol, ethylene glycol) in the spray solution are responsible for non-conductive white films. None of the alcohols or solvents added to the spray solutions produced better film properties than could be obtained from aqueous solutions.

A significant parameter for the spray deposition of cadmium stannate films is the Cd/Sn ratio in the spray solution. Caused by the greater volatility of cadmium and its compounds the Cd/Sn ratio in the solution has to be greater than two. Ratios of 20:1 were found to be necessary for the substrate temperatures maintained during most of the deposition experiments.

The importance of the substrate temperature for film formation has already been mentioned. During spraying this temperature can drop several hundred degrees. Such large temperature drops create appreciable amounts of amorphous phases in the films thus limiting their electrical conductivities. With the heating equipment available spray times could not exceed five seconds before the electrical film properties deteriorated. These deposition times resulted in film thicknesses of approximately 2000Å. The low thicknesses are considered to be the limiting factor in achieving low electrical sheet resistances.

Under the above experimental conditions CdSnO_3 forms if the initial substrate temperature is below but close to 900°C. The Cd_2SnO_4 phase appears when the starting temperature is higher than 900°C. However, Cd_2SnO_4 films always contain some CdSnO_3 because of the temperature drop during the spray process.

Extensive doping experiments (Section III) revealed that indium in the spray solution lowers the crystallization temperature by almost 100°C from 900°C to ~800°C. Several examples are shown in Table 1.

Table I

Influence of Indium Doping on Film Crystallization

Sample No.	Initial Substrate Temp.	In Doping	Resistance	X-ray
S11182-125A	760°C	yes	360 Ω	crystalline
S11182-127D	820°C	yes	70 Ω	crystalline
S11182-129F	770°C	no	320 Ω	amorphous
S11182-146B	900°C	no	100 Ω	crystalline
S11182-149E	920°C	no	250 Ω	amorphous
S11182-149F	900°C	yes	70 Ω	crystalline

Initial substrate temperatures of approximately 900°C are necessary to crystallize films sprayed with indium-free solutions (S11182-146B). If the solutions contain indium, crystalline samples form at initial substrate temperatures as low as 760°C. At this temperature crystallization is poor so that the film resistance is quite high (S11182-125A). Samples -149E and -149F were prepared from solutions with a Cd/Sn ratio of 40:1. Such films cannot be crystallized even at 900°C and indium is needed in the solution for crystallization.

The available time did not permit to check other additives for their influence on film crystallization. However, it is quite conceivable that lower substrate temperatures may be possible with additives other than indium.

Small additions of lead (1-2%) to the spray solution cause clearer films than lead free solutions. It appears that lead induces a better film crystallization which not only reduces surface roughness and, hence, light scattering, but also decreases the film resistivity. Coatings sprayed from solutions without lead have in general

sheet resistances in the 200-300 ohm range. If lead is present these resistances drop to 100-200 ohm. The optical transmission of a spray coated cadmium stannate film containing 2% lead is shown in Figure 3. This sample has a sheet resistance of 130 ohm/square and represents a typical example of state-of-the-art films prepared by CSD.

A series of CSD experiments were performed on silica substrates having thin oxide interlayers. The interlayers had been sputtered and were a few hundred angstroms thick. The results of these experiments are shown in Table II.

Table II

Influence of Interlayers on Electrical
Properties of Spray Coated Films

Sample No.	Interlayer	Resistance [ohm]
S11182-158F	control	220
S11182-159A	TiO ₂	280
S11182-161F	Al ₂ O ₃	200
S11182-163C	Nb ₂ O ₅	240
S11182-163G	Ta ₂ O ₅	230
S11182-158C	Cd ₂ SnO ₄	100,000
S11182-160F	CoO	800
S11182-161G	CuO	800
S11182-162D	Fe-oxide	800
S11182-163E	NiO	4,000
S11182-166D	WO ₃	600

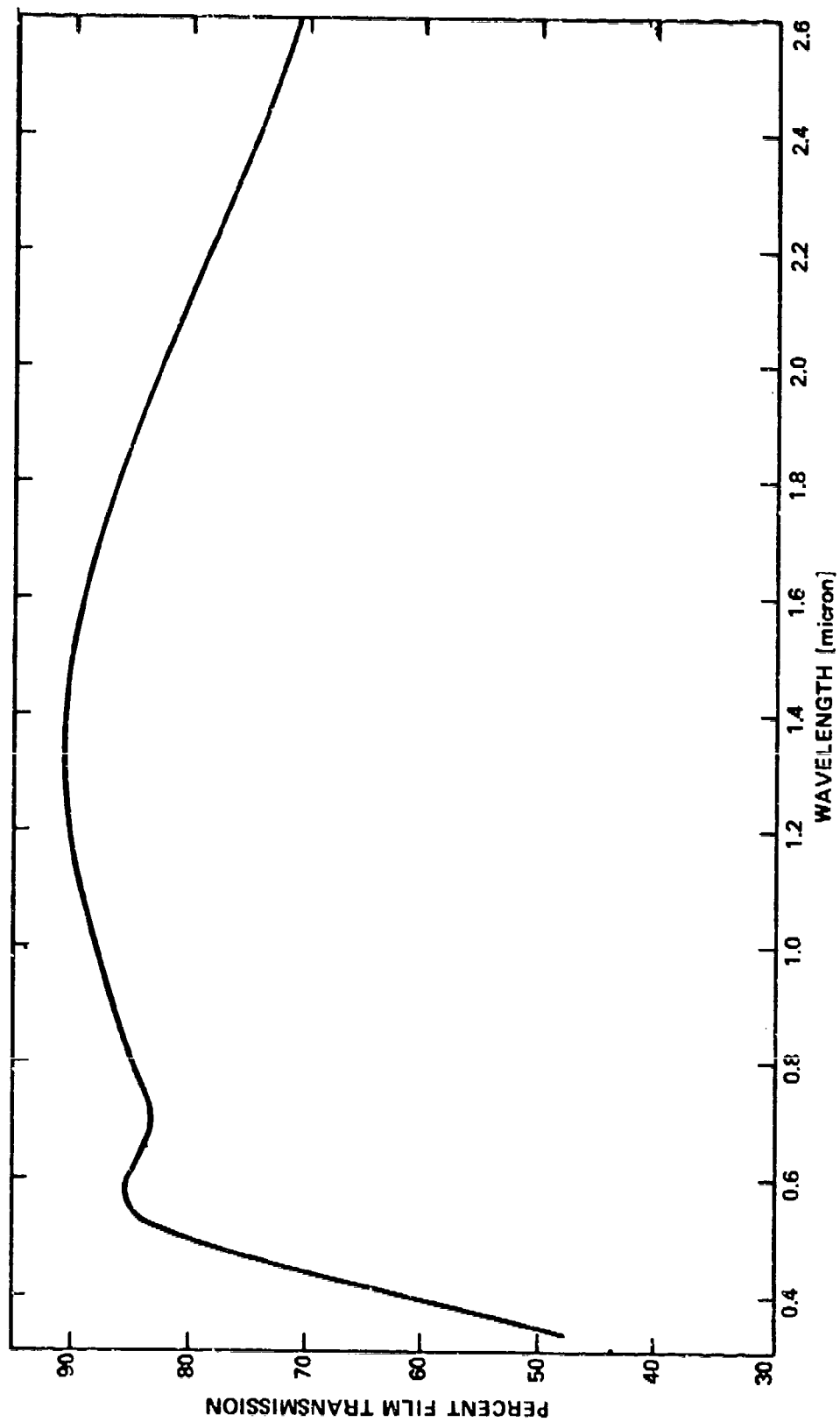


Figure 3. Optical Transmission of Spray Coated Cadmium Stannate Film

None of the interlayer materials led to lower sheet resistances although Al_2O_3 may have a small beneficial effect. The large resistance measured on samples sprayed onto Cd_2SnO_4 interlayers is surprising and inexplicable.

C. VACUUM EVAPORATION

Vacuum evaporation was investigated as an additional route to the deposition of transparent, conductive cadmium stannate films. Direct evaporation of Cd_2SnO_4 powder from a tantalum boat produces unidentified black deposits, even in an oxygen atmosphere.

Simultaneous evaporation of cadmium and tin from separate boats onto hot or cold substrates produces tin films which can be converted to SnO_2 by heat treatment in air. Cadmium was found to stick to the substrate only if it is evaporated from a CdO/SnO_2 mixture. No tin evaporates from this mixture so that a second boat for tin is still required. The resulting films are metallic but become yellowish transparent after short annealing in air. They consist of CdO and SnO_2 and have low conductivities.

Since the Cd/Sn ratio in the evaporated films is difficult to control by using the two boat method flash evaporation of Cd_2SnO_4 powder was attempted. This approach yields reproducible Cd/Sn ratios close to two if the substrates are kept at room temperature. The films are metallic and can be converted to transparent CdO/SnO_2 films of moderate conductivity by heat treatment in air. However, all attempts failed converting these mixed oxide films to cadmium stannate by a special heat treatment. During these experiments cadmium oxide evaporated from

the films leaving a highly resistive tin oxide coating behind. To prevent this effect we attempted direct reaction to Cd_2SnO_4 during the evaporation by maintaining the substrate at high temperatures (up to 700°C) in oxygen atmosphere (approx. $5 \cdot 10^{-4}$ torr). However, under these conditions cadmium does not deposit onto the substrate.

In summary, the evaporation experiments suggest that vacuum evaporation is not a suitable method for the preparation of cadmium stannate films.

SECTION III

DOPING EXPERIMENTS

Doping experiments were carried out with cadmium stannate powder samples as precursor to actual film doping. Three classes of dopants have been studied: 1. dopants which increase the band gap and shift the fundamental optical absorption edge into the UV, 2. dopants which increase the IR reflection and/or shift the IR absorption edge closer to the visible part of the spectrum, 3. dopants which increase the electrical conductivity.

A. BAND GAP MODIFICATION

The apparent band gap of highly conductive Cd_2SnO_4 is 2.8 eV imparting a light green tint to thin films. If the band gap could be increased to at least 3 eV the preparation of colorless coatings may become feasible.

Partial substitution of tin by germanium in Cd_2SnO_4 was proposed as one means of increasing the band gap. Since Cd_2GeO_4 has been reported in the literature⁶ to have the same crystal structure as Cd_2SnO_4 we assumed that a solid solution system of the two compounds should exist.

By carefully mixing given ratios of CdO , GeO_2 , and SnO_2 and firing the mixtures at 1050°C the following compositions were synthesized: $\text{Cd}_2\text{Sn}_{.95}\text{Ge}_{.05}\text{O}_4$, $\text{Cd}_2\text{Sn}_{.90}\text{Ge}_{.10}\text{O}_4$, and $\text{Cd}_2\text{Sn}_{.85}\text{Ge}_{.15}\text{O}_4$. All three samples were after firing as bright yellow as Cd_2SnO_4 indicating that germanium had not been incorporated into the cadmium stannate lattice. This supposition was confirmed by X-ray analysis and diffuse reflection measurements. The diffuse reflectance spectra of Figure 4

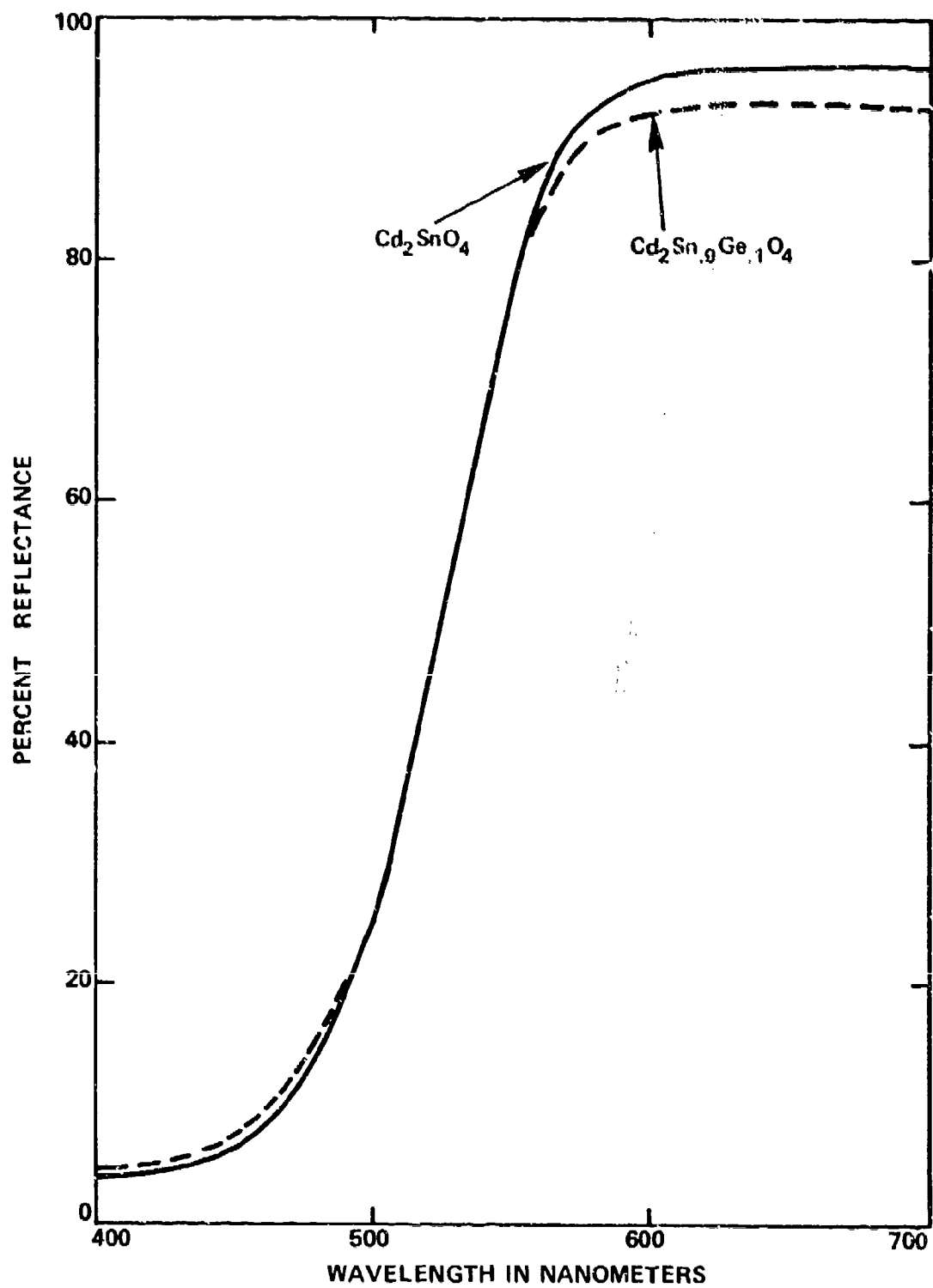


Figure 4. Diffuse Reflectance Spectra of Cd_2SnO_4 and $\text{Cd}_2\text{Sn}_{.9}\text{Ge}_{.1}\text{O}_4$ Powders

show that the optical absorption edge of the germanium containing sample has not been shifted towards shorter wavelengths. Similar curves were obtained for $\text{Cd}_2\text{Sn}_{.95}\text{Ge}_{.05}\text{O}_4$ and $\text{Cd}_2\text{Sn}_{.85}\text{Ge}_{.15}\text{O}_4$. Also, no shift of the lattice constants could be found in any sample.

Since preparation of single phase solid solutions of Cd_2SnO_4 and Cd_2GeO_4 by high-temperature synthesis from the binary oxide powders was not successful we attempted formation of these compositions as thin films by RF sputtering. Films were sputtered onto vitreous silica slides from a target of the nominal composition $\text{Cd}_2\text{Sn}_{.9}\text{Ge}_{.1}\text{O}_4$ (9:1 intimate mixture of Cd_2SnO_4 and Cd_2GeO_4). The deposition conditions were identical to those used for the preparation of crystalline cadmium stannate from Cd_2SnO_4 targets.

Film samples prepared from the $\text{Cd}_2\text{Sn}_{.9}\text{Ge}_{.1}\text{O}_4$ target under the above conditions did not crystallize. Their X-ray diffraction spectrum indicated only the presence of an amorphous phase. In addition, it was found that these films had high electrical resistivities while their optical absorption was higher than would be expected for a high resistivity Cd_2SnO_4 type sample. From these results it is concluded that a single phase $\text{Cd}_2\text{Sn}_{1-x}\text{Ge}_x\text{O}_4$ system is unlikely to exist.

A second possibility for increasing the optical band gap of Cd_2SnO_4 is the partial substitution of cadmium by calcium since Ca_2SnO_4 is isomorphous with Cd_2SnO_4 .⁷ High-temperature synthesis of $\text{Cd}_{2-x}\text{Ca}_x\text{SnO}_4$ powders was not successful. This failure may have been caused by the high reaction temperature ($>1400^\circ\text{C}$) required for Ca_2SnO_4 synthesis. At these temperatures Cd_2SnO_4 decomposes. Even a 10% substitution of cadmium by calcium cannot be achieved in the temperature range in which Cd_2SnO_4 is stable.

Sputter deposition was attempted from a target consisting of a mechanical mixture of CdO, CaO, and SnO₂ with the nominal composition Cd_{1.8}Ca_{.2}SnO₄. These experiments revealed a strong preferential sputtering of SnO₂. Since a determination of the proper target composition would have been time-consuming this approach was not pursued further.

During the CSD experiments the CdSnO₃ phase frequently occurred in the sprayed films. This compound, therefore, was synthesized as powder sample and its diffuse reflectance spectrum measured. Figure 5 shows that the band gap of CdSnO₃ is at least 3 eV. Hence, if coatings are required with low absorption in the short wavelength part of the visible spectrum CdSnO₃ could be a suitable choice.

B. IR OPTICAL PROPERTIES

For aircraft canopy coatings it is desirable to absorb and/or reflect as much of the infrared part of the solar spectrum as possible. This requirement is in contrast to the specifications for solar energy conversion devices which require transmission of the sun's light to at least 1.5 μ . Cadmium stannate doped with oxygen vacancies or interstitial cadmium is transmissive to 1.5 μ and well suited for coatings on solar energy devices. To shift the IR absorption to shorter wavelengths specific dopants will have to be found which introduce absorption peaks near 1 μ . Also, the infrared reflection of cadmium stannate doped with oxygen vacancies or interstitial cadmium does not exceed 80% below 10 μ . Special doping materials may lead to higher reflectivities.

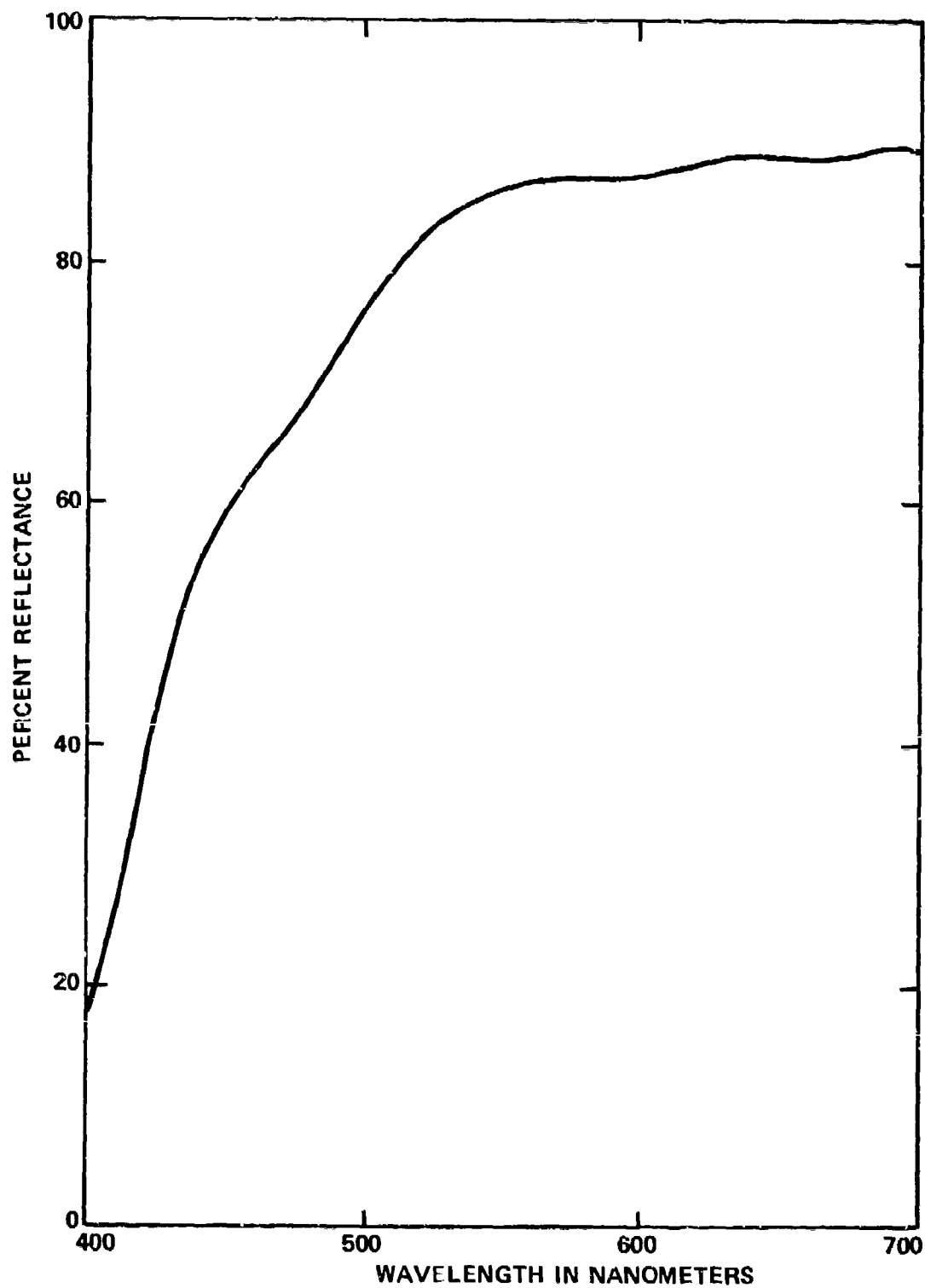


Figure 5. Diffuse Reflectance Spectrum of CdSnO₃ Powder

Trivalent indium is known to produce optical absorption near 1μ in some materials.⁸ Since indium is also a potential electron donor its influence on the electrical and optical properties of Cd_2SnO_4 was investigated. Initially, indium doped Cd_2SnO_4 powders were synthesized and their electrical resistance measured on pressed cylindrical pellets. All pellets had equal geometrical dimensions and were pressed under identical pressure. The electrical resistances measured between solder contacts on the end faces are listed in Table III.

Table III
Indium Doped Cadmium Stannate Powders

<u>Sample</u>	<u>Resistance [ohm]</u>
Cd_2SnO_4	10,000
$\text{Cd}_{1.98}\text{In}_{.02}\text{SnO}_4$	130
$\text{Cd}_{1.98}\text{In}_{.02}\text{SnO}_4$ (annealed)	40
$\text{Cd}_{1.84}\text{In}_{.16}\text{SnO}_4$	15

The data in Table III indicate that indium is a donor element in Cd_2SnO_4 powders when substituting for cadmium. Sputtered samples, however, exhibit a different behavior. Doping action of In^{3+} has not been found in these films. A reason for this observation may be the multi-phase composition of sputtered films which was mentioned earlier; indium could accumulate preferentially in the secondary phases. Such preference may also account for the absence of the expected absorption peak near 1μ in indium containing sputtered films.

Further elements introduced as doping impurities into Cd_2SnO_4 powders included titanium, zirconium, niobium, tantalum, molybdenum, tungsten, and rhenium. In none of these samples diffuse reflectance spectra detected significant absorption near the infrared. In contrast, less than one percent copper decreases the diffuse reflectance to approximately 50% at 0.6μ . Figure 6 shows the influence of copper when replacing cadmium. The $\text{Cd}_{1.98}\text{Cu}_{0.02}\text{SnO}_4$ (CuCl) sample may actually contain less copper than indicated since it was doped with CuCl, part of which may have been volatilized during synthesis. Extrapolation of the curve of Figure 6 points to the onset of a strong absorption between 0.9 and 1.0μ so that copper may be a candidate for shifting the IR absorption in cadmium stannate films towards shorter wavelengths.

A target plate was fabricated from a cadmium stannate powder with 2 at % Cd substituted by copper ($\text{Cd}_{1.96}\text{Cu}_{0.04}\text{SnO}_4$). Thin films sputtered from this target did not show the expected near IR absorption (Figure 7). A slightly higher absorption occurs over the whole spectrum than in copper free samples. However, the infrared reflectivity of cadmium stannate coatings increases in the presence of copper. This can be seen in Figure 8 which shows the specular IR reflectance of the samples of Figure 7. It is interesting to note that the hemispherical-angular reflectance of copper doped Cd_2SnO_4 films is higher than the specular reflectance and reaches 90% (Figure 9). The curves of Figure 9 were measured at the Honeywell Systems & Research Center and we are grateful to Dr. R. P. Heinisch for his cooperation.

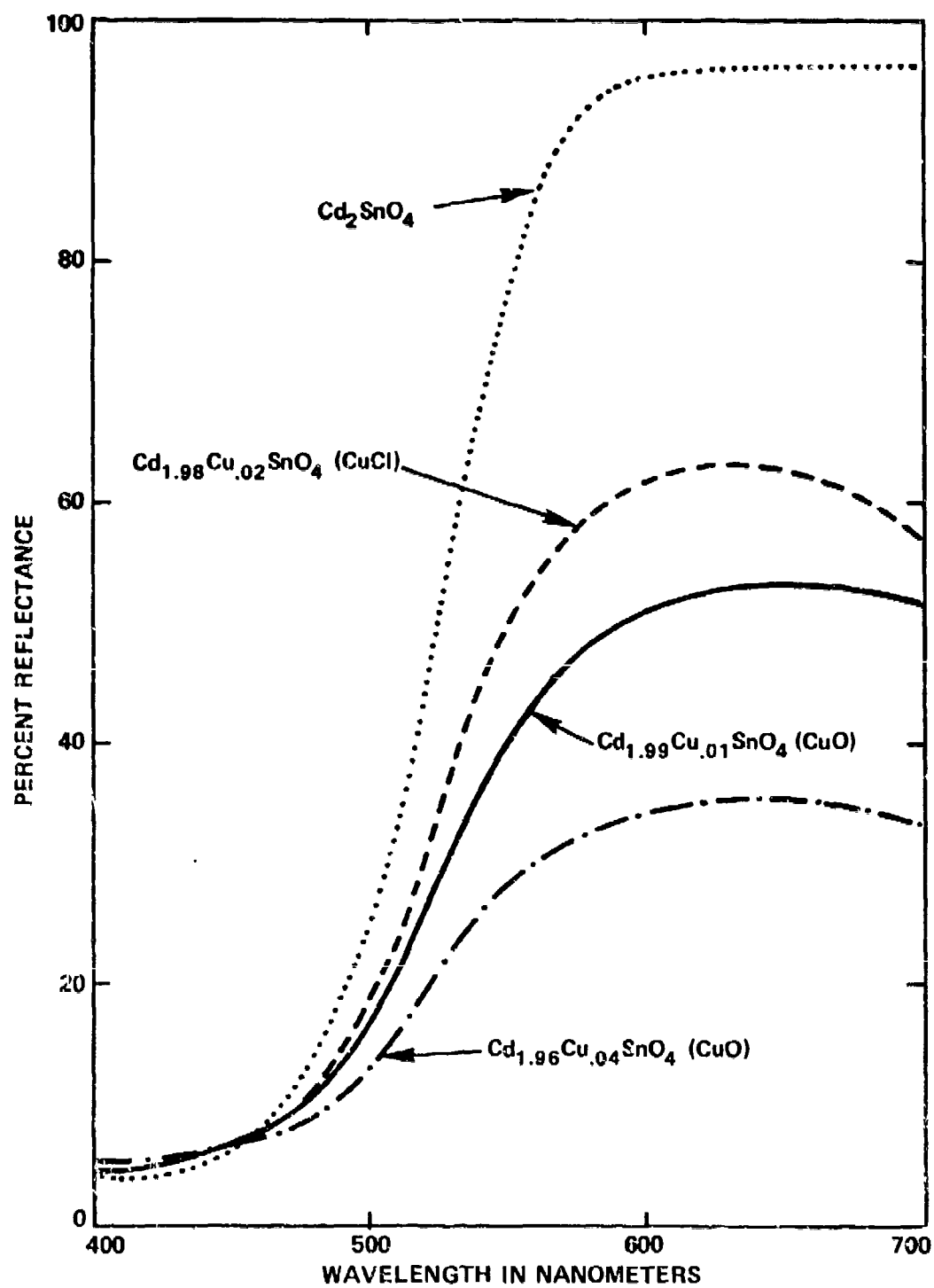


Figure 6. Diffuse Reflectance Spectra of Copper Doped Cd_2SnO_4 Powders

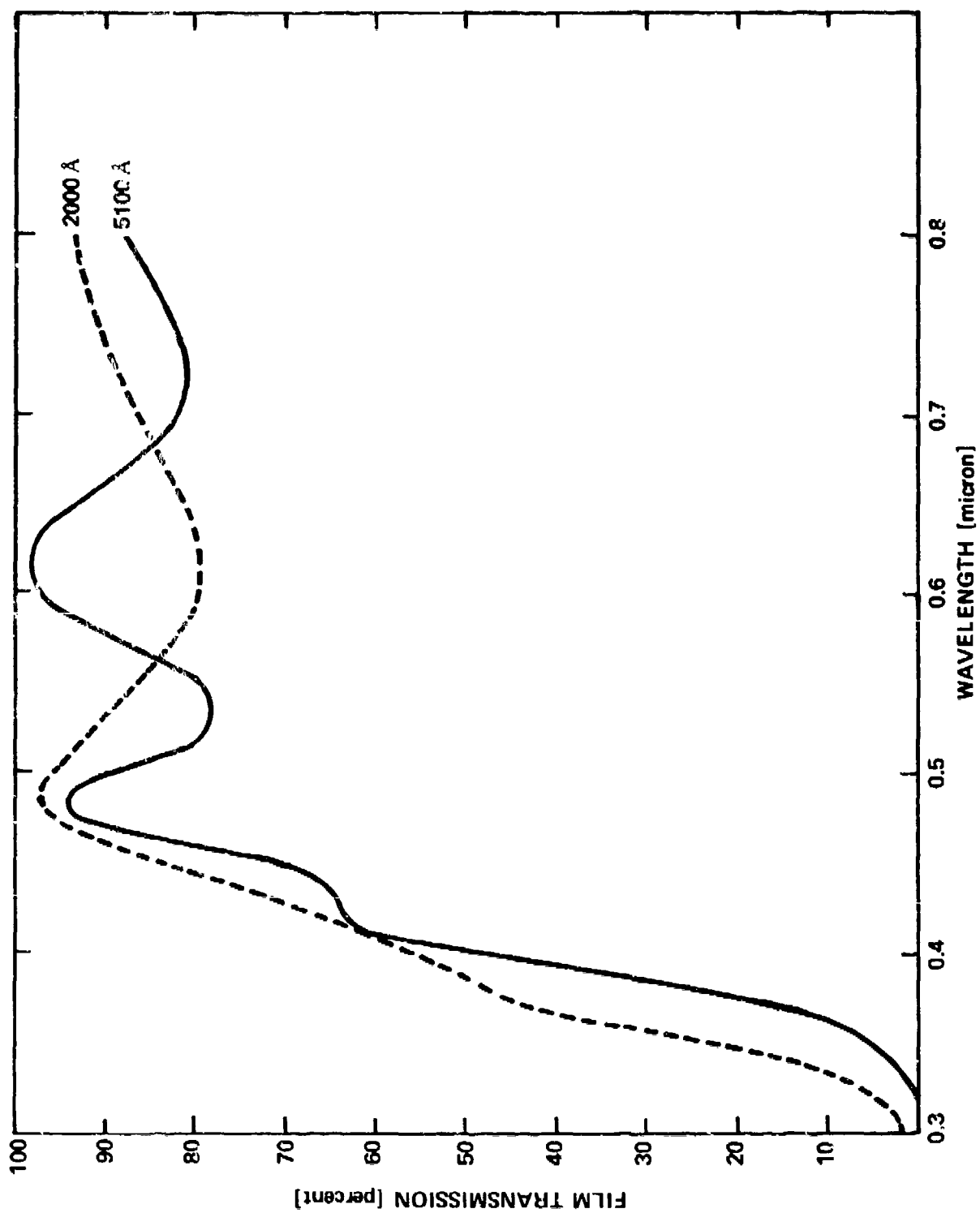


Figure 7. Optical Film Transmission of Copper Doped Cd_2SnO_4 Films

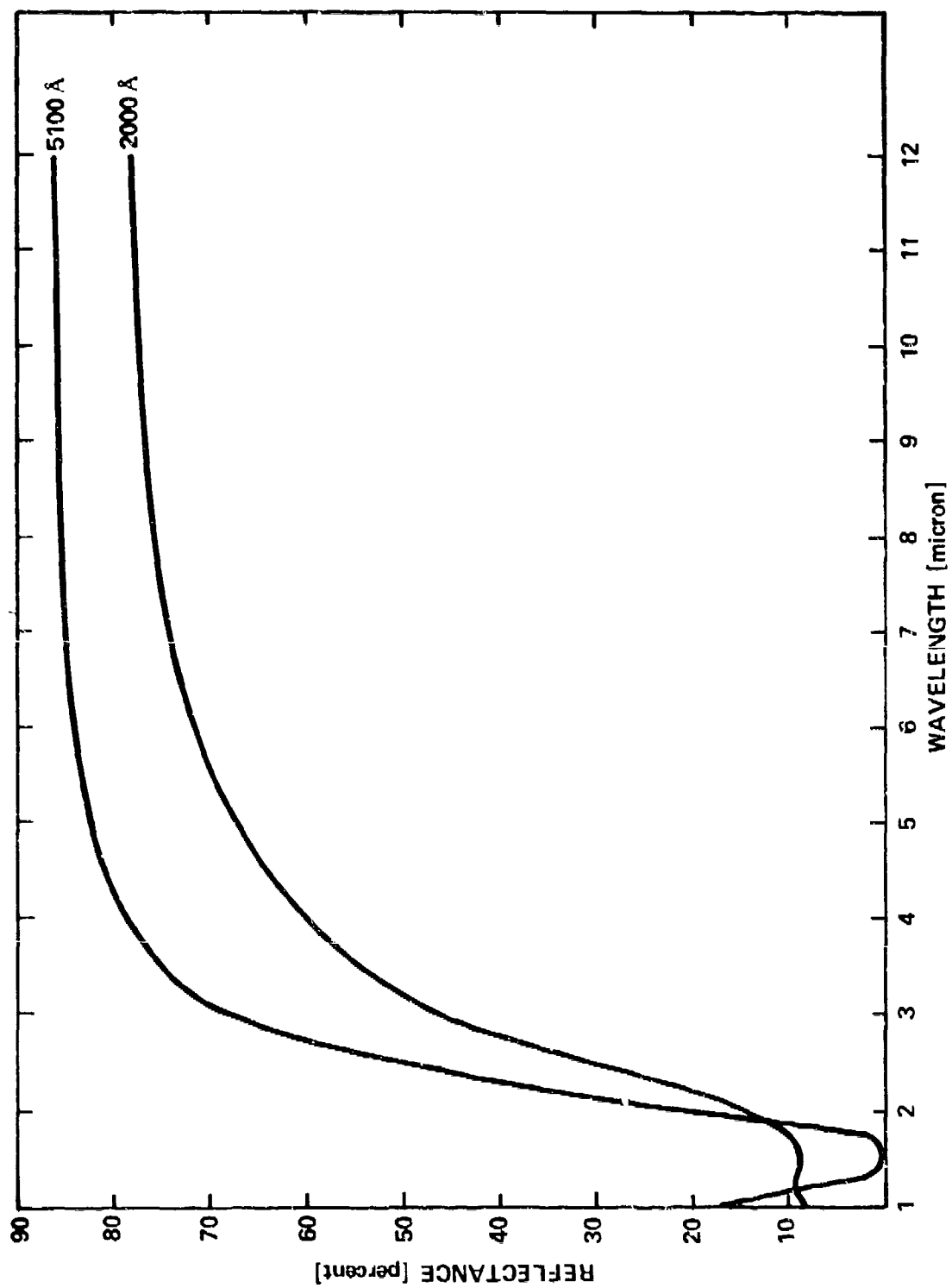


Figure 8. Specular Reflectance of Copper Doped Cd_2SnO_4 Films

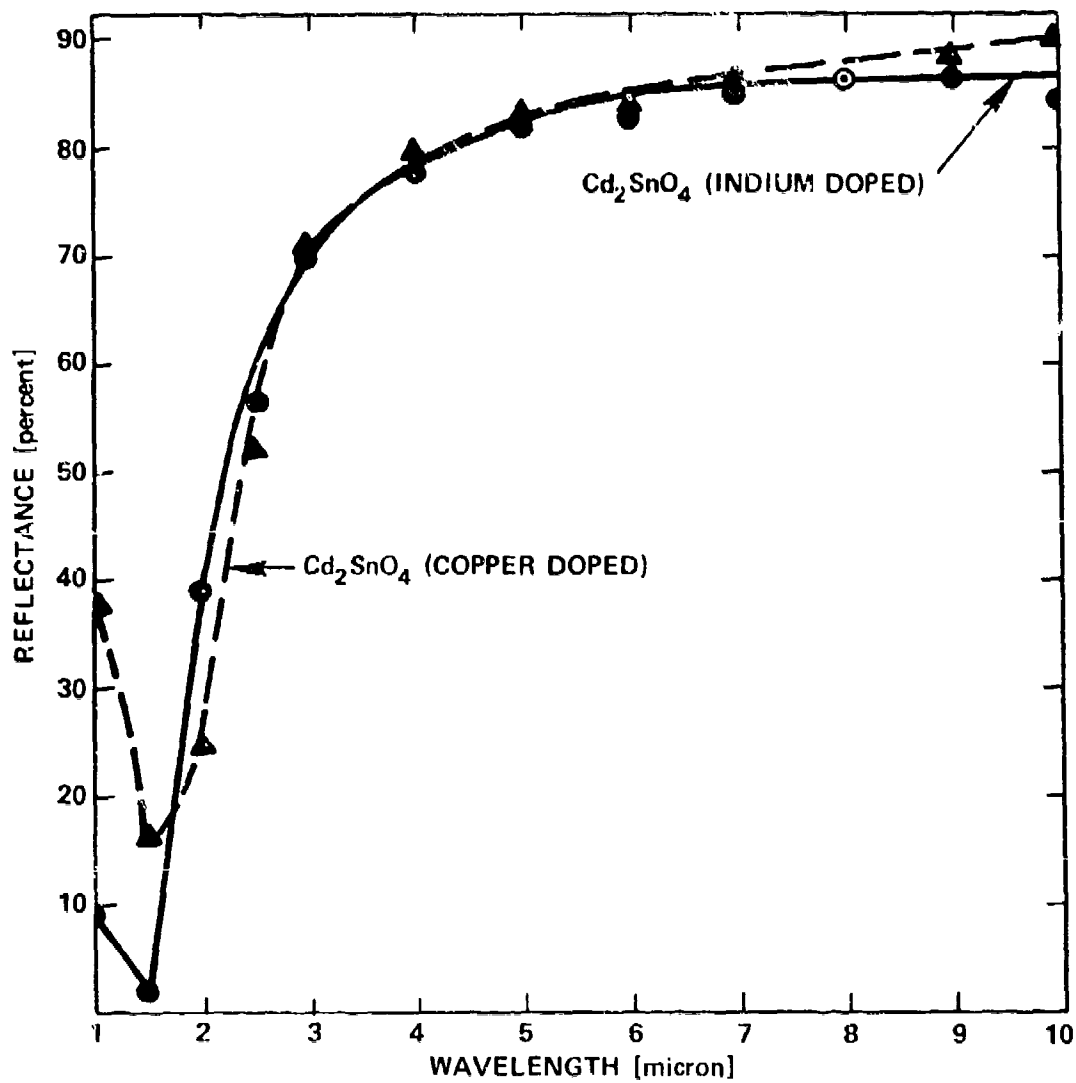


Figure 9. Hemispherical-Angular Reflectance of Cd_2SnO_4 Films
(Measured by Honeywell Systems and Research Center)

Besides copper several other elements improve the IR reflectivity of cadmium stannate coatings. Indium doped samples were found to have the highest specular reflectivity. Figure 10 shows several examples. This figure also demonstrates that film crystallization is important for achieving high IR reflectivities.

C. ELECTRICAL CONDUCTIVITY DOPING

Fifteen elements were investigated as candidates for electron donors in cadmium stannate powders. Seven elements did increase the electrical powder conductivity and shifted the fundamental optical absorption edge towards shorter wavelengths. They are assumed to be donor dopants and include indium, antimony, tantalum, niobium, vanadium, tungsten, and molybdenum.

Electron donor properties in RF sputtered films have been proven for tantalum only. It is suspected that the other six elements mentioned above accumulate in the secondary phases or along grain boundaries where they are electrically inactive. Besides tantalum, oxygen vacancies and interstitial cadmium are known electron donors in sputter coated cadmium stannate films.

Screening experiments were carried out utilizing CSD by adding water soluble salts of the investigated elements to the spray solution. The electrical resistance of the sprayed films was measured by a simple two-probe method. The results of these experiments are summarized in Table IV.

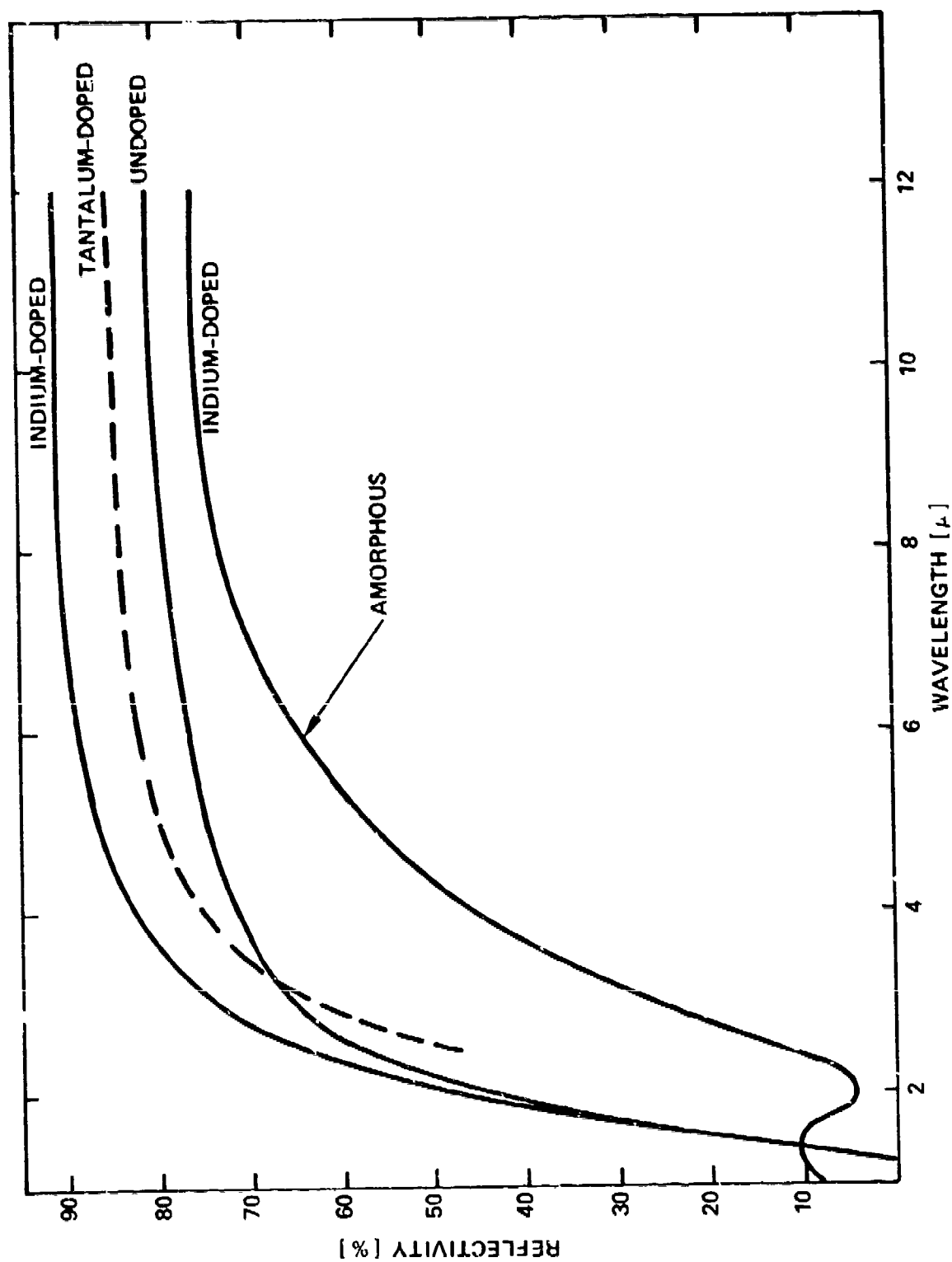


Figure 10. IR Reflectivity of Doped and Undoped Cd_2SnO_4 Films

Table IV

Doping of Spray Coated Cadmium Stannate Films

Sample	Dopant	Resistance [ohm]
S11182-132G	Al	250
S11182-139E	Ta	180
S11182-137B	Nb	380
S11182-178A	Nb + H ₂ O ₂	130
S11182-138A	Sb	200
S11182-130E	Sb + In	120
S11182-132F	B	3M
S11182-138G	Te	10M
S11182-133A	V	2K
S11182-129E	Co	340
S11182-133B	Cr	500
S11182-133C	Mo	28K
S11182-141F	Zr	280
S11182-140A	Ti	180
S11182-146B	Ti + H ₂ O ₂	100
S11182-151C	Cu	200
S11182-152A	Fe	400
S11182-153C	Li	250
S11182-153A	Rh	270

Several doping concentrations were investigated for each element. Table IV lists the lowest resistance value obtained for each element. As can be seen, several elements (B, Te, Mo) increase the

film resistance by orders of magnitude which in the case of boron may be due to acceptor properties (thermo-electric power measurements on boron doped samples were inconclusive).

Films sprayed from solutions without dopants have sheet resistances of approximately 200 ohm/square. Hence, Table IV shows that some improvement of the electrical properties can be obtained by adding impurities to the solution; these are Nb(+H₂O₂), Sb/In, and Ti(+H₂O₂). In all of these cases sheet resistances of 100 ohm/square can be obtained. The above dopants behave similar to lead (Section II, B). Therefore, it appears that the improvement of film properties achieved with these elements may be caused by better film growth during spraying rather than true doping action.

Additions of indium salts to the spray solution have been extensively investigated since in this way sheet resistances as low as 50 ohm/square could be achieved. However, it is doubtful whether indium is a true dopant in spray deposited cadmium stannate films. Small additions of indium chloride (one percent) to the Cd/Sn solution do not change the film resistivity. To lower the resistance into the 50 ohm range more than ten percent indium has to be present in the spray solution. The X-ray spectra of these films contain only cadmium stannate lines with no indication of indium oxide. However, electron microprobe results show that indium is present in concentrations beyond its solubility limit in cadmium stannate. We are, therefore, inclined to assume that the low resistivity samples contain a certain concentration of an amorphous indium oxide phase.

In addition to the elements discussed above eleven rare earth elements were screened. These elements included lanthanum, praseodymium, cerium, neodymium, samarium, europium, terbium, holmium, erbium, thulium, and ytterbium. Slightly improved electrical properties (10-20%) were observed in samples containing terbium or thulium. Neodymium and erbium additions resulted in higher sheet resistances while the rest of the above elements did not change the electrical resistance of the spray coated films.

SECTION IV

COATING OF DIFFERENT SUBSTRATE MATERIALS

A. SILICA

Most of the cadmium stannate films were prepared on vitreous silica substrates. This material was chosen as a matter of convenience since depositions were mainly performed at higher temperatures (400°C - 950°C). To achieve maximum conductivity of sputtered films a post-deposition heat treatment is required (10 min., 650°C , Ar). Although many glass substrates withstand this temperature sample handling procedures are much simpler with silica slides.

Superior transparent electrode properties like those shown in Figure 1 have thus far been achieved with silica and sapphire substrates only. However, the results of depositions onto other substrate materials suggest that electrical and optical properties equivalent to those obtained with silica should be feasible after adjustment of the relevant preparation conditions.

B. SAPPHIRE

Sputter depositions were carried out with single crystal sapphire substrates to obtain information on the influence of substrate morphology on film properties. The results of these experiments show that the electrical properties of sputtered cadmium stannate films on sapphire are similar to those on vitreous silica. However, higher optical transmissions can be obtained. As an example Figure 11 shows the transmission of a film deposited onto a 1" x 1" single crystal sapphire substrate (c-axis in plane). Although this film has an electrical sheet

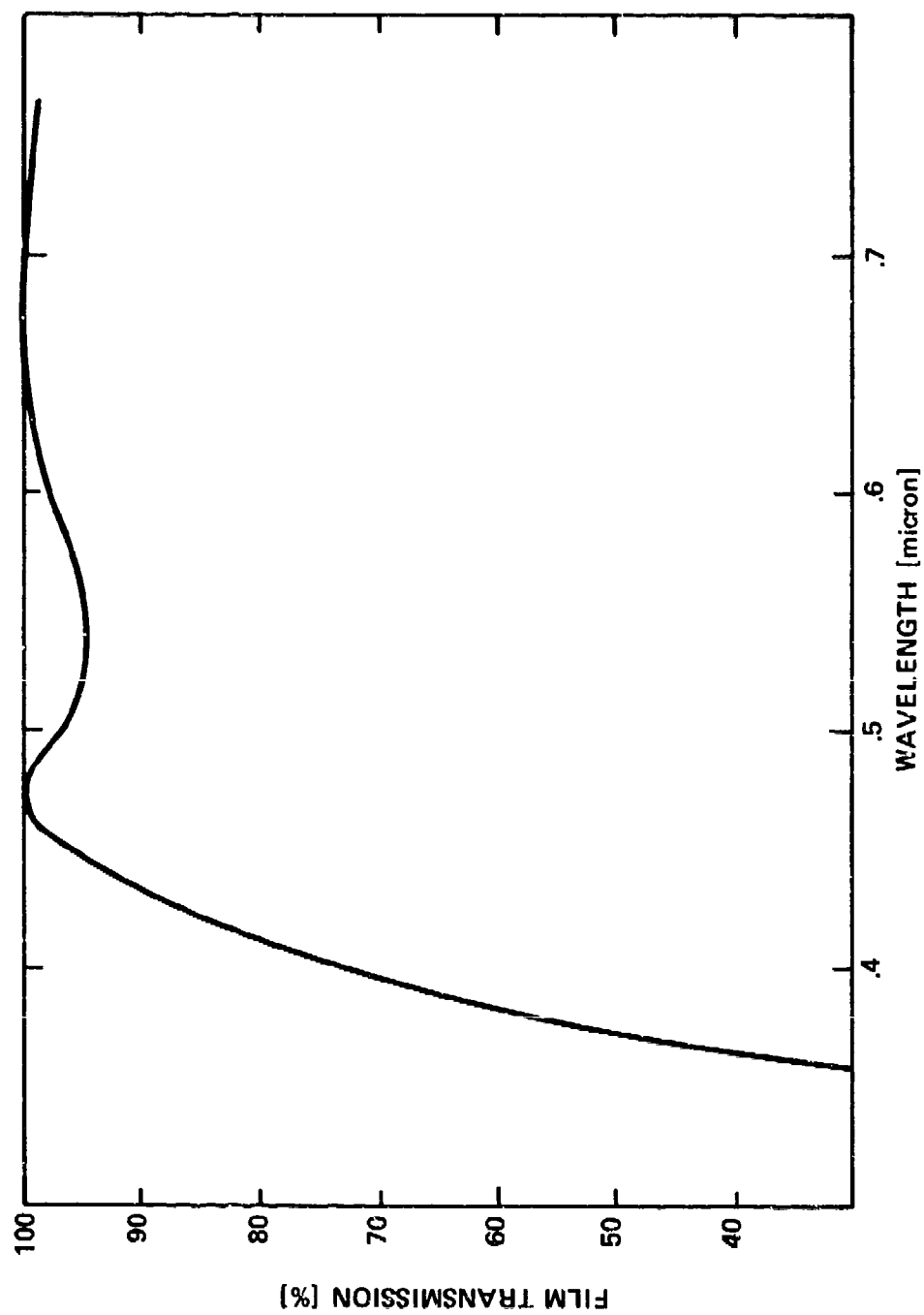


Figure 11. Optical Transmission of Cd_2SnO_4 Film (9 ohm/square) on Sapphire Substrate

resistance of 9 ohm/square it can be calculated that by increasing its thickness sheet resistances of 1 ohm/square and visible transmissions higher than 90% are possible.

C. GLASS

In accordance with the contract requirements deposition of cadmium stannate films onto soda-lime glass, alumina-silica glass, and Chemcor glass was carried out. RF sputtering was employed for these experiments which were pursued to establish conditions for the coating of well adhering, stable films. Electrical sheet resistances in the 5-10 ohm/square range were sought. Time limitations did not allow to prepare samples with sheet resistances closer to 1 ohm/square. However, the results suggest that such resistance values should be attainable.

1. Soda-Lime Glass

Cadmium stannate was coated onto 2" x 2" x 0.085" soda-lime substrates purchased from Melvin Freed, Inc., Perkasie, Pa. Deposition procedures developed for fused silica substrates could be applied. Subsequent annealing revealed that the soda-lime slides acquired internal stresses during sputtering which severely bend the samples when annealed according to the fused silica procedures. A new procedure had to be developed starting at lower temperatures (400°C) and gradually raising the temperature to 580°C. The final temperature is lower than the optimum (650°C) which results in 20% lower conductivities. Figure 12 gives an example of the optical transmission of cadmium stannate on soda-lime glass.

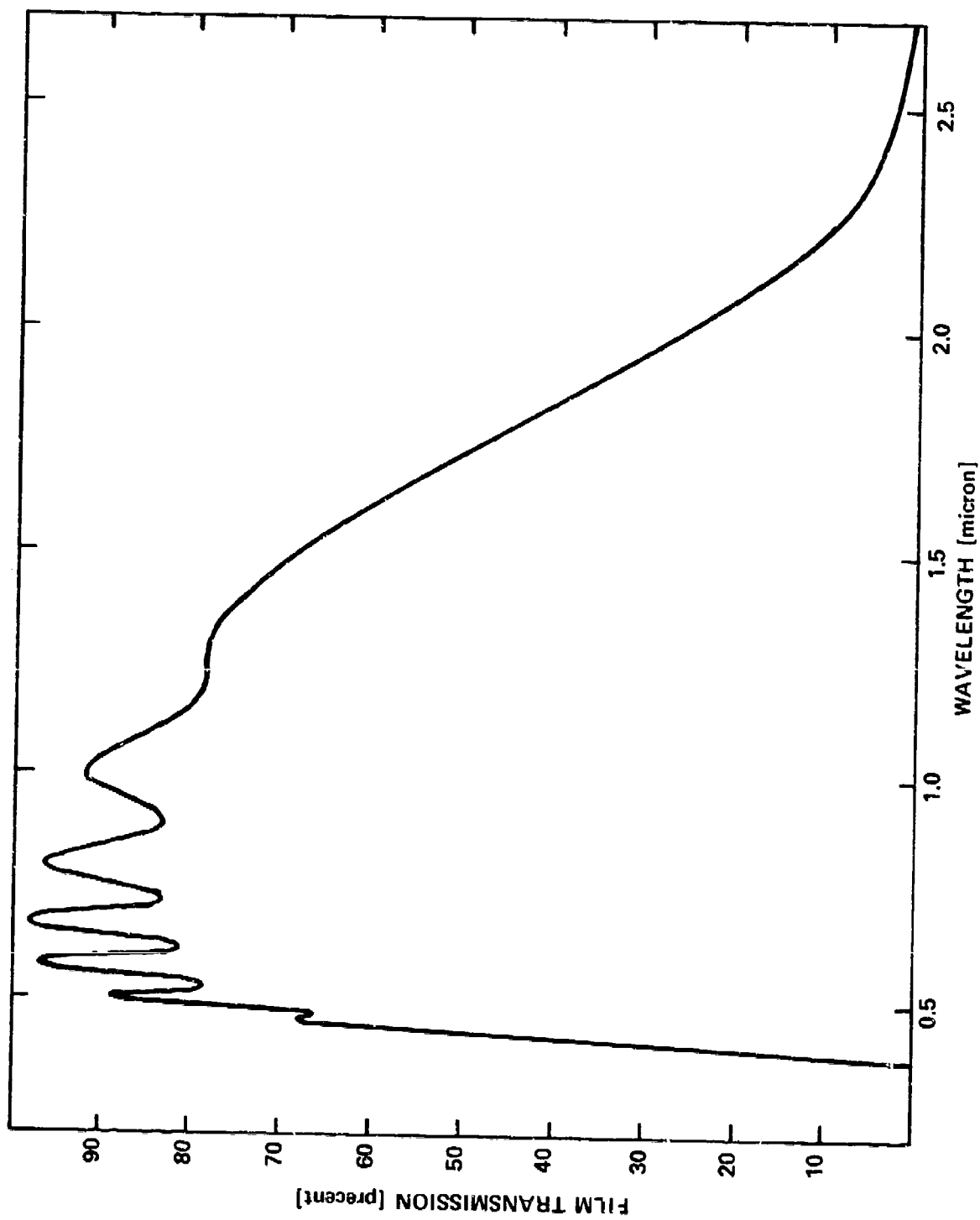


Figure 12. Optical Transmission of Cd_2SnO_4 Film (9 ohm/square) on Soda-Lime Glass

2. Alumina-Silica Glass

Substrates were obtained from Corning Glass Works (Corning 1720, 2" x 2" x 1/8"). Standard silica deposition procedures proved to be adequate. No difficulties developed during annealing. The optical transmission of a sputtered cadmium stannate film on a Corning 1720 substrate is shown in Figure 13.

3. Chemcor Glass

Chemcor #0313 substrates (2" x 2" x 0.085") from Corning Glass Works were used for these experiments. Since Chemcor loses its strength at temperatures above 450°C a low temperature deposition procedure had to be developed which also excluded annealing. Best results can be obtained when the films are sputtered onto substrates kept near room temperature and the plasma gas consists of a 5% O₂/95% Ar mixture. These films are amorphous and, hence, their transparent electrode properties will not be as good as those shown in Figure 1. However, the optical transmission of these films will be high if sheet resistances in the 10-15 ohm/square range are sufficient. Figure 14 shows the optical transmission of a cadmium stannate film on Chemcor with 5 ohm/square sheet resistance.

D. PLASTICS

High temperature requirements for CSD exclude this deposition method for the coating of plastic substrates. Radio frequency sputtering was used instead. A serious problem encountered with plastic substrates was film adhesion. A large difference in coefficient of thermal expansion between cadmium stannate and the plastics is probably

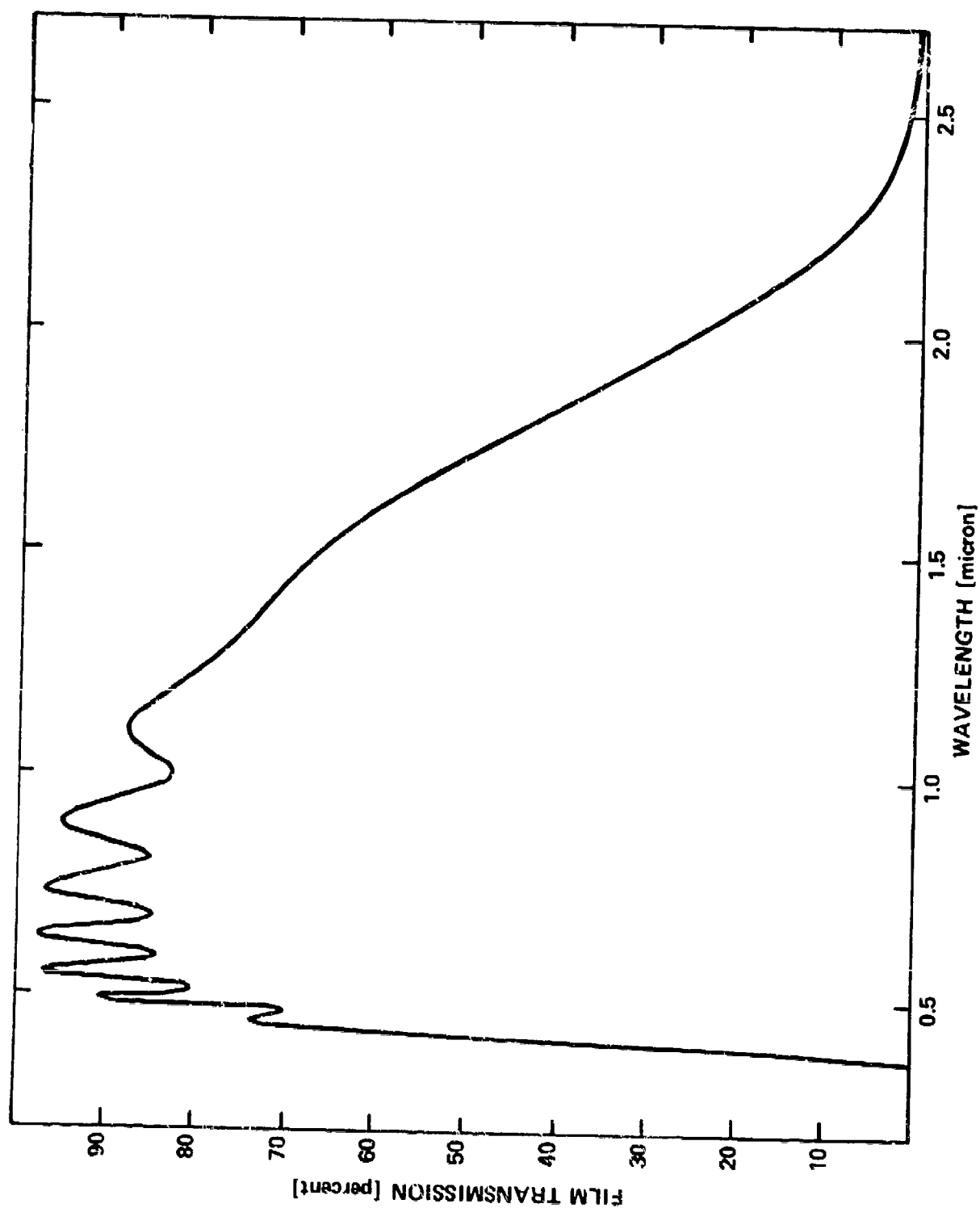


Figure 13. Optical Transmission of Cd_2SnO_4 Film (7 ohm/square) on Corning 1720 Glass (Alumina-Silica)

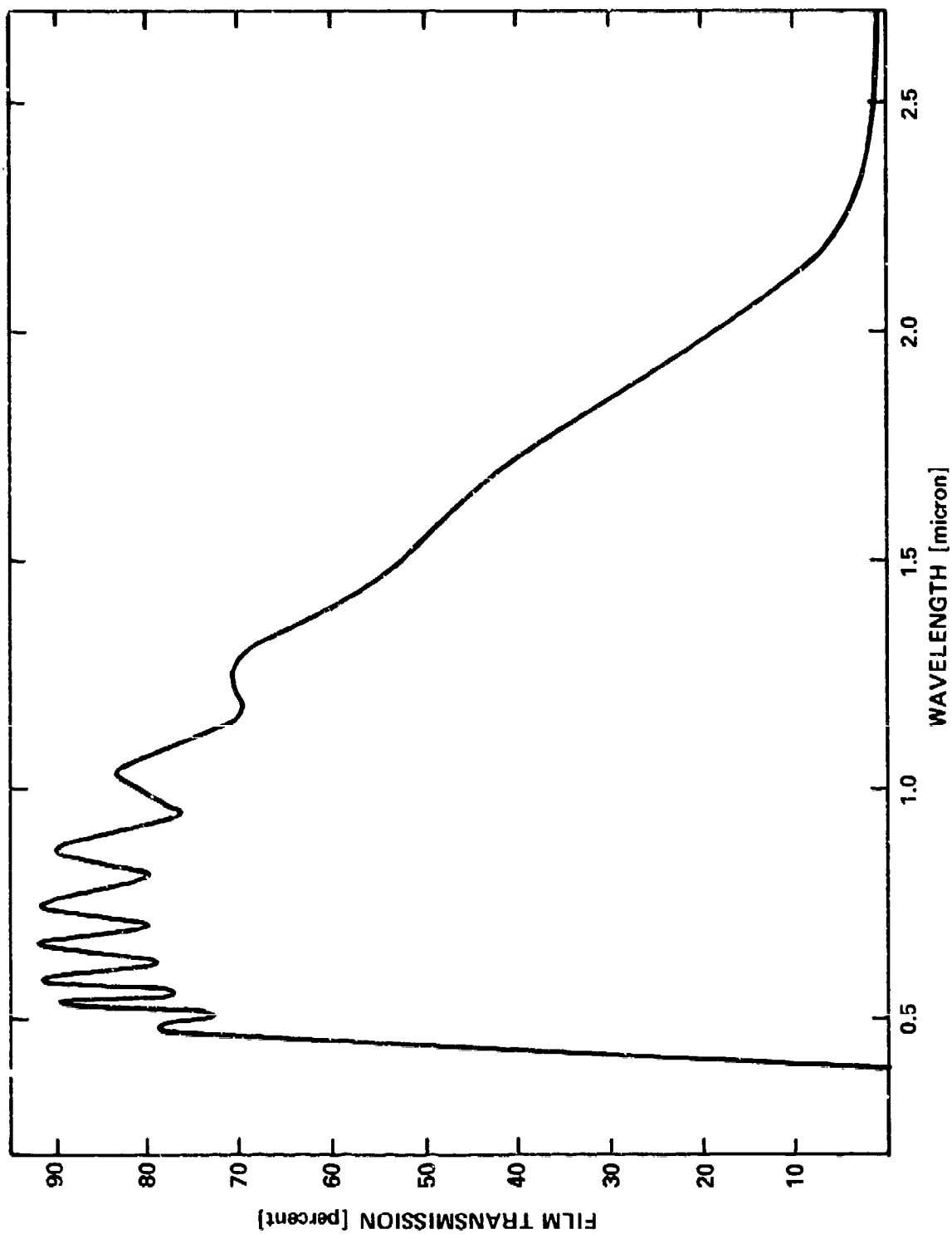


Figure 14. Optical Transmission of Cd_2SnO_4 Film (5 ohm/square) on Chemcor 0313 Glass

the cause for this problem since it occurs mainly at high sputtering rates which lead to excessive surface heating. Even at low RF power input (200 watts) care has to be taken to relieve residual thermal stresses. It is important not to remove the coated samples from the sputtering unit immediately after deposition but to allow slow substrate cooling, at 200 watts RF power the substrate heats to approximately 100°C.

Two substrate materials were investigated: 1. polycarbonate, 2. stretched acrylic. Stretched acrylic samples (2" x 2" x 3/32") were received through the courtesy of Goodyear Aerospace Corporation. Lexan sheet (3/32" thick) from General Electric was used for polycarbonate substrates.

1. Polycarbonate

Initial attempts of coating Lexan with cadmium stannate concentrated on selecting sputtering parameters which would prevent film reticulation. This task was accomplished by limiting film preparation to low RF powers (200-300 watts) and not exceeding deposition times of one hour. Coatings with sheet resistances near 500 ohm/square can be fabricated in this way. Multiple one hour depositions lead to sheet resistances as low as 180 ohm/square.

To overcome the limitations placed on the preparation of low sheet resistance films by the above procedure the effect of interlayers on film adhesion has been investigated. Metal oxide interlayers were evaporated onto Lexan substrates and cadmium stannated films subsequently sputtered onto them. Interlayer materials investigated include SiO, SiO₂,

Al_2O_3 , TiO_2 , Ta_2O_5 , Sb_2O_3 , MgO , Cr_2O_3 , and CaF_2 . Improved cadmium stannate adhesion resulted from some of these materials and higher RF powers could, therefore, be applied during sputter deposition.

At 400 watts RF power and one hour deposition time cadmium stannate films were coated onto interlayers of titanium, tantalum, and antimony oxide which did not reticulate. Their electrical sheet resistances were between 20-30 ohm/square. Deposition onto SiO and SiO_2 under the same conditions resulted in film reticulation.

A second one hour sputtering at 400 watts RF onto the above non-reticulated samples was only partially successful. Films deposited onto the antimony oxide interlayers reticulated completely (infinite sheet resistance). Later experiments showed that antimony oxide interlayers can sustain cadmium stannate coatings of limited thickness only so that antimony oxide has been dismissed as interlayer material.

The second one hour coatings onto tantalum and titanium oxide interlayers developed a few fine cracks. Otherwise, these films were clear and had sheet resistances as low as 12 ohm/square. From these results it appears that tantalum as well as titanium oxides are viable candidates for interlayers. However, vacuum evaporation of these oxides is difficult so that work with evaporated TiO_2 and Ta_2O_5 interlayers was not pursued further.

Evaporated MgO interlayers appear to have a good potential. After a one hour deposition at 300 watts RF cadmium stannate films with sheet resistances between 15-20 ohm/square were obtained. These samples showed numerous fine hairline cracks which were not visible in the uncoated magnesium oxide films. Further work would be required to solve this problem.

Investigation of the properties of SiO and SiO₂ as interlayer materials was pursued since the silicon oxides appear to offer a more economic approach than other candidate materials (TiO₂, Ta₂O₅, MgO). Work with silicon monoxide was abandoned after it became clear that the electrical properties of the cadmium stannate coatings on SiO and their adherence was equivalent to those on SiO₂. Cadmium stannate on silicon dioxide offers the advantage of higher optical transmission because the SiO₂ interlayers are completely colorless while the intrinsic brownish color of SiO thin films induces additional absorption in the composite Cd₂SnO₄/SiO coating.

The problem of crazing observed initially in a number of cadmium stannate coatings on SiO₂ can be prevented. It occurs when the SiO₂ interlayers are evaporated too fast. Hence, slow SiO₂ evaporation results in crack-free cadmium stannate films. Furthermore, the interlayer thickness should not exceed 0.6 to 0.7 micron. Otherwise, crazing becomes more likely.

Deposition conditions have been established under which cadmium stannate films can be reproducibly sputter coated onto Lexan substrates having evaporated SiO₂ interlayers. With 300 watts RF power electrical sheet resistances of approximately 15 ohm/square are obtained

after 2 hours sputtering. Lower sheet resistances result if the deposition time is increased. These films adhere strongly to the substrates and pass the standard tape test. Figure 15 shows the optical transmission of a cadmium stannate film on Lexan with a SiO_2 interlayer.

In view of an economical interlayer deposition on large area substrates exploratory experiments have been carried out by chemically coating SiO_2 onto Lexan. The general approach⁹ consists of spin coating solutions of tetraethylorthosilicate onto the substrates and subsequently evaporating the solution under controlled conditions. Clear, smooth SiO_2 films (identified by IR reflection) can be deposited by this method. Non-reticulating cadmium stannate films have been sputtered onto these interlayers. Their electrical sheet resistances are similar to those deposited onto evaporated SiO_2 interlayers.

We have also been successful in spin coating titanium oxide onto plastic substrates by using solutions of tetrabutyltitanate. These interlayers are clear and smooth and well adhering, clear cadmium stannate films (30 ohm/square) could be coated onto Lexan.

The results of the interlayer experiments are summarized in Table V.

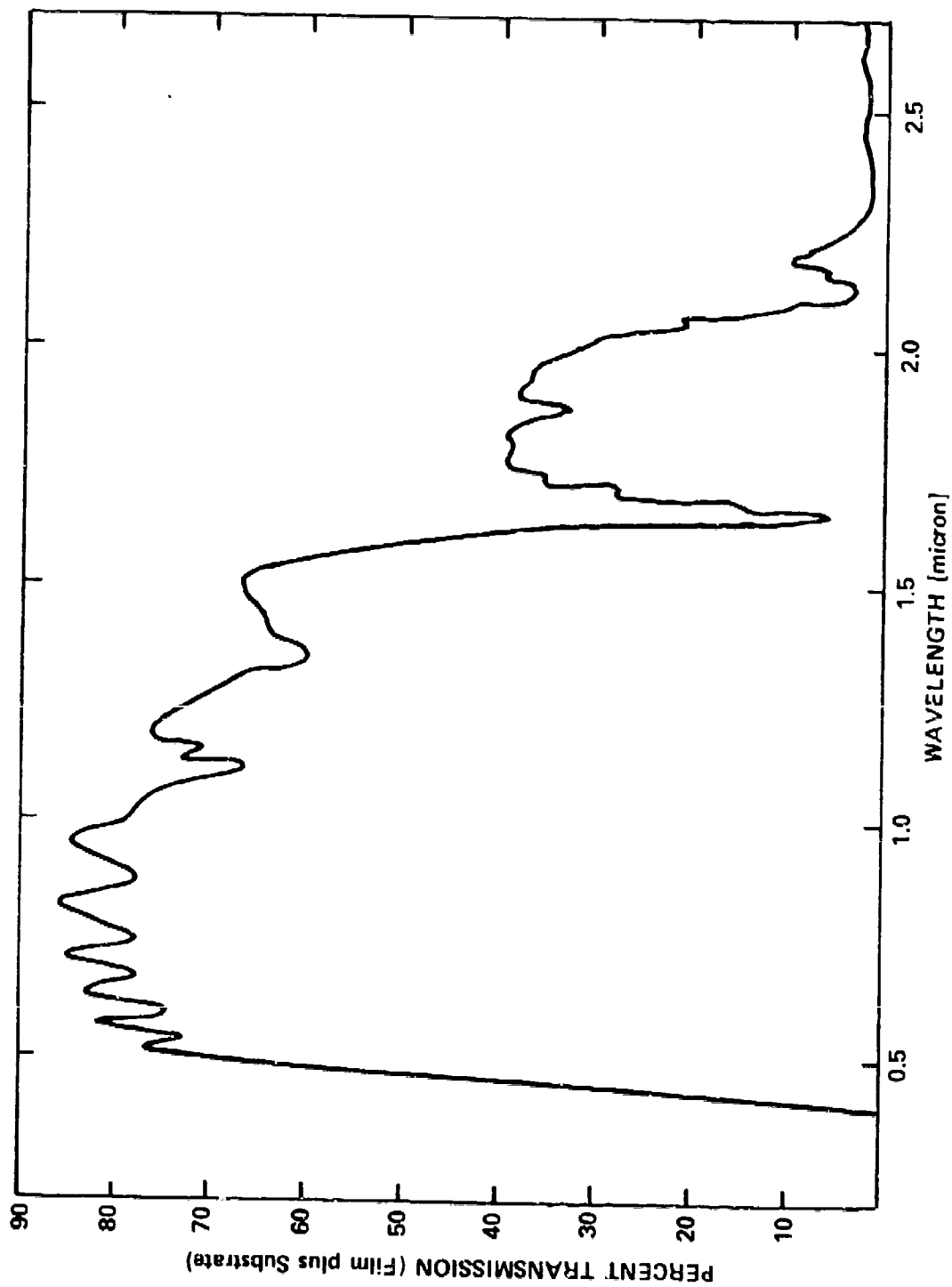


Figure 15. Optical Transmission of Lexan Substrate Coated with Cd_2SnO_4 Film (8 ohm/square) and SiO_2 Interlayer

Table V

Effect of Interlayers on Cadmium
Stannate Films on Plastic Substrates

Interlayer Material	Deposition Method	Cd_2SnO_4 Adhesion	Lowest Sheet Resistance Achieved [ohm/square]	Remarks
SiO	Evaporation	good	18	
SiO_2	Evaporation	good	8	
SiO_2	Spin Coating	acceptable	28	
TiO_2	Spin Coating	acceptable	29	
TiO_2	Evaporation	good	12	
Ta_2O_5	Evaporation	good	12	some crazing
Sb_2O_3	Evaporation	good	20	thick films retic.
MgO	Evaporation	good	17	crazing
Al_2O_3	Evaporation	reticulates	--	
Cr_2O_3	Evaporation	initially good	100	later reticulation
V_2O_5	Evaporation	partial reticulation	30	
CaF_2	Evaporation	reticulates	--	

According to Table V best results were obtained with SiO_2 interlayers. However, some of the other materials may be as good or even better than SiO_2 if developed further. Available time and funds did not permit, for instance, to evaluate the mechanical properties of the cadmium stannate films as a function of interlayer material. Here, additional work could lead to greatly improved properties.

2. Stretched Acrylic

The results obtained with Lexan have been applied to stretched acrylic substrates. However, the temperature constraints are more severe since stress release occurs at $\sim 100^{\circ}\text{C}$. If the stretched acrylic substrate is exposed to this temperature it relaxes to its original shape.

If the substrate temperature is carefully monitored silicon dioxide interlayers can be evaporated onto the acrylic without stress release. Observing the same precautions for maintaining a low substrate temperature during sputtering of cadmium stannate well adhering coatings can be deposited. Cadmium stannate films have been coated in this way onto stretched acrylic which have sheet resistances between 20 and 30 ohm/square. These sheet resistances were obtained with 200 watts RF power and two hours deposition time. Figure 16 shows the optical transmission of one of these samples.

Spin coating of SiO_2 and TiO_2 interlayers has been also achieved on stretched acrylic substrates. Non-reticulating Cd_2SnO_4 layers were sputtered onto these substrates.

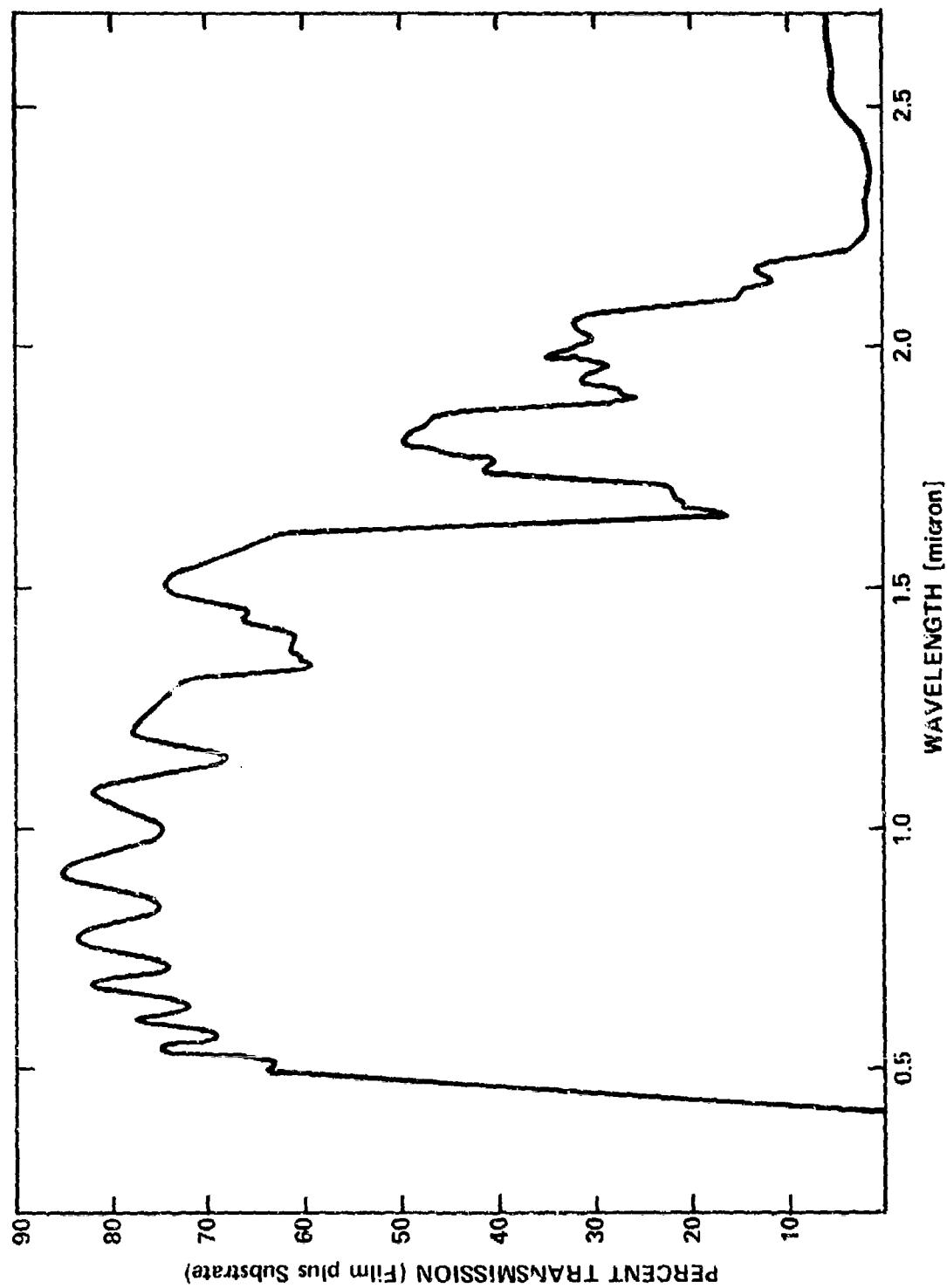


Figure 16. Optical Transmission of Stretched Acrylic Substrate Coated with Cd_2SnO_4
Film (26 ohm/square) and SiO_2 Interlayer

SECTION V

FILM TESTING

A. ELECTRICAL MEASUREMENTS

Electrical sheet resistances were routinely measured by a standard 4-point probe technique. Spray coated films which often had non-uniform thickness were evaluated by 2-probe measurements.

Hall effect measurements were performed on selected samples (e.g., Figure 2). Highest electron mobilities measured thus far came close to $50 \text{ cm}^2/\text{Vsec}$. Hole mobilities could not be determined since p-type Cd_2SnO_4 does not appear to exist.

The temperature dependence of the electrical conductivity was measured for a number of samples between -196°C and $+200^\circ\text{C}$. In view of the high carrier concentration highly conductive Cd_2SnO_4 films are degenerate and, therefore, their electrical conductivity should be only moderately temperature dependent. The example in Figure 17 confirms this projection.

B. ADHESION AND ABRASION RESISTANCE

Film adherence was measured by applying a strip of 3M tape No. 250 to the coated specimen and removing the tape by a snapping pull at 90° to the substrate. The film should not be separated from the substrate during this test.

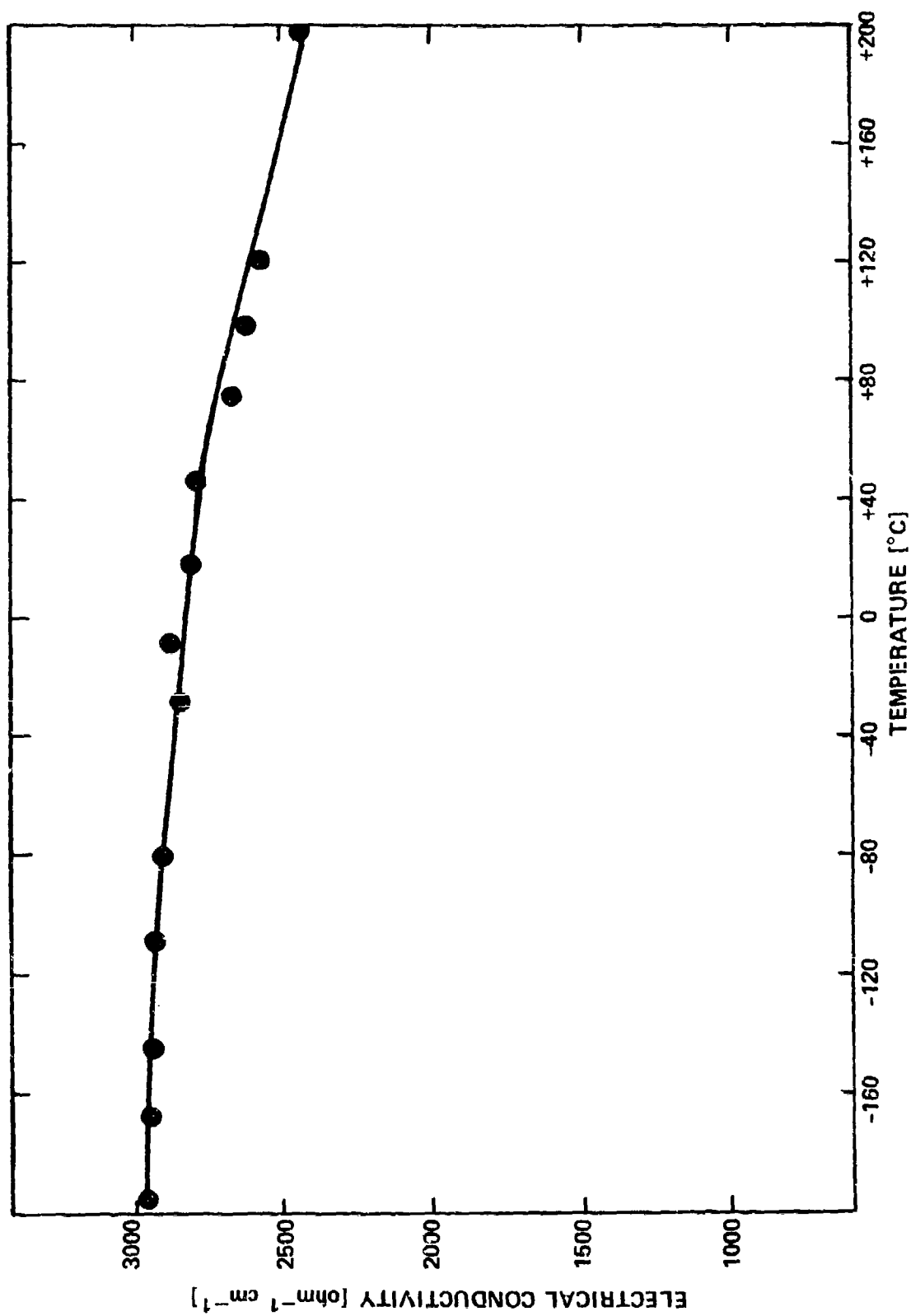


Figure 17. Temperature Dependence of Electrical Conductivity of Sputtered Cadmium Stannate Film

Cadmium stannate films coated onto silica or glass substrates have never failed the above test. They can be removed only by acid etch or with a diamond stylus. Coatings deposited onto plastic substrates without an interlayer do not pass the tape test if sheet resistances below 100 ohm/square are required. Certain interlayers greatly improve film adhesion for low sheet resistance coatings. Table VI summarizes the results of the adhesion tests.

Table VI
Adhesion of Cadmium Stannate Films
onto Plastic Substrates

Sample No.	Substrate	Interlayer	Tape Test
S11373-45 (34D)	Lexan	Sb ₂ O ₃	failed
S11373-45 (35D)	Lexan	Ta ₂ O ₅	passed
S11373-45 (42B)	Lexan	TiO ₂	passed
S11373-51 (20F)	Lexan	SiO	passed
S11373-51 (32C)	Lexan	SiO ₂	passed
S11373-51 (48C)	Lexan	Cr ₂ O ₃	failed
S11373-51 (50B)	Lexan	MgO	passed
S11373-66 (57D)	Lexan	V ₂ O ₅	passed
S11373-74 (71G)	Lexan	SiO ₂ (spin coated)	passed
S11373-79 (68G)	Stretched Acrylic	SiO ₂ (spin coated)	failed
S11373-79 (77A)	Stretched Acrylic	SiO ₂	passed
S11373-81 (78C)	Stretched Acrylic	TiO ₂ (spin coated)	failed
S11373-82 (78A)	Lexan	TiO ₂ (spin coated)	passed

Abrasion resistance was tested with a reciprocating arm type abrasion unit. The abrader pad material was kindly provided by Goodyear Aerospace Corporation and consisted of flocked neoprene rubber (0.06 inch thick). The abrasive film was 3M PSA Lapping Sheet (12 micron grit) with water used as lubricant. 3,000 cycles were run at 20 cycles per minute and 1 psi shoe pressure.

The results obtained for silica and glass substrates depend on the deposition conditions. If the substrate is kept at room temperature during sputtering severe abrasion occurs. Films deposited at 400°C and higher have a good abrasion resistance. In the case of silica and alumina-silica substrates only a few barely visible scratches can be discerned after the test. Cadmium stannate films on Chemcor or soda-lime glass remain clear, however, many fine scratch marks appear if these samples are observed under reflected light.

More severe abrasion is observed on cadmium stannate coatings deposited onto plastic substrates. Films on Lexan with evaporated SiO₂ interlayers are heavily scratched after the 3,000 cycles have been completed. On stretched acrylic substrates with evaporated SiO₂ interlayers streaks begin to show after the first 100 cycles and most of the cadmium stannate is removed after approximately 1,000 cycles. The substrate itself is also heavily abraded.

C. HUMIDITY RESISTANCE

Humidity resistance of cadmium stannate films on different substrates was determined in accordance with MIL-STD-810, Method 507, Procedure V. Prior to humidity exposure the coatings were scribed with a diamond stylus. Film adherence was checked by applying 3M No. 250 tape at 90° to the scribe and pulling the tape as in SECTION V, B. All samples were subjected to the tape test at three points in time: 1. before humidity exposure, 2. two hours after commencement of exposure to humidity, 3. at the end of total humidity exposure (20 days).

Most samples showed excellent humidity resistance and passed the above tests. Table VII summarizes the results of these experiments.

Table VII
Temperature-Humidity Resistance of
Cadmium Stannate Films

Sample No.	Substrate	Interlayer	Tape Test	
			2 hrs.	20 days
S11309-154	silica	none	pass	pass
S11373-83 (77B)	stretched acrylic	SiO ₂ (.5 μ)	pass	pass
S11373-81 (77A)	stretched acrylic	SiO ₂ (.5 μ)	pass	pass
S11373-79 (77A)	stretched acrylic	SiO ₂ (.5 μ)	pass	pass
S11373-81 (78C)	Acrylite	TiO ₂ (spin coated)	failed	--
S11373-82 (69C)	Lexan	SiO ₂ (.35 μ)	pass	pass
S11373-66 (65A)	Lexan	SiO ₂ (.3 μ)	pass	pass
S11373-82 (78A)	Lexan	TiO ₂ (spin coated)	pass	failed
S11373-83A	Lexan	none (60 μ /in)	pass	pass

SECTION VI

DISCUSSION AND CONCLUSIONS

The preceding discussions have shown that cadmium stannate is an excellent transparent conductor material. Current state-of-the-art properties (1.5 ohm/square, 85-90% visible transmission) have been achieved despite the fact that these coatings are not yet single phase Cd_2SnO_4 but contain CdO and CdSnO_3 as well. For this reason it is expected that further improvements of the transparent electrode properties of cadmium stannate will become feasible if single phase films can be prepared.

The heat reflecting properties of cadmium stannate beyond $3\ \mu$ were greatly improved by doping. Efforts to increase the optical absorption/reflection in the $1\ \mu$ wavelength region have not yet been successful. Since a significant portion of the solar energy falls into this spectral region higher absorption or reflection would enhance the utility of aircraft canopy coatings by reducing air conditioning requirements in the cockpit. Therefore, further work seems desirable. Failure to introduce additional absorption in cadmium stannate films near $1\ \mu$ by impurities is believed to be caused at least in part by the presence of secondary phases. Hence, a general improvement of the film composition should aid efforts to introduce the desired absorption peaks. From observations made on cadmium stannate powders it appears likely that first row transition metals are promising doping candidates for further investigations.

The experiments with different substrate materials have shown that cadmium stannate can be coated onto a variety of transparent substrates. Glasses of widely varying properties are suitable in most cases although deposition and annealing conditions have to be optimized for each individual material. Inclusion of polycarbonate and acrylic plastics in the list of useful substrate materials is considered a major accomplishment of this contract work since extensive attempts to coat plastics were unsuccessful several years ago. The adherence of cadmium stannate coatings onto plastic substrates now is excellent. Improvements are needed for their abrasion resistance. Progress in this area is most likely to result from work on the interlayer.

The contract work has also produced first time data on the environmental stability of cadmium stannate thin films. Although the stability of Cd_2SnO_4 paint films was tested and found outstanding before commencement of this contract information on the stability of film properties was mainly based on conjecture. Experiments on the temperature/humidity stability have now demonstrated that cadmium stannate films have excellent properties in this respect.

APPENDIX

FABRICATION OF X-Y GRID STRUCTURES

Experiments were carried out to coat 4" x 4" substrates with cadmium stannate and to generate a conductive bar pattern for utilization as X-Y grids in electroluminescent display devices.

The sputtering unit available for these experiments accepted targets of 5" diameter only. It had been set up for depositing uniform coatings onto 1" x 1" substrates. Major changes had to be instituted inside this unit to facilitate the coating of 4" x 4" substrates. Installation of a new and larger substrate heater and several radiation shields changed the RF tuning parameters completely. The resulting cadmium stannate films had poor electrical properties. Re-tuning improved the electrical conductivity. However, the larger current required to maintain optimum substrate temperatures produced a sufficient magnetic field for creating a plasma pinch so that uniform film thickness could not be obtained over the total substrate area.

Two approaches are possible for generating the bar pattern: 1. during deposition by using a mask, 2. after deposition by photo-etching. Experience with sputtering through masks onto a hot substrate has shown that this approach does not lead to a good definition of the mask boundaries due to thermal expansion. Non-uniform interference fringes

along the edges of the film segments are the result of this effect.

It was, therefore, decided to sputter the cadmium stannate films first and subsequently generate the bar pattern by standard photo-etching procedures.

A photo mask was prepared showing a bar pattern with four lines per inch and $3/16$ " line width. This mask was used for all experiments. The thickness of cadmium stannate films with sheet resistances below 5 ohm/square caused non-uniform film removal during etching. Hence, most of the experiments were carried out with coatings having 5-10 ohm/square sheet resistance. Conditions were established under which a satisfactory bar pattern can be etched in these films.

If grids are desired in films having sheet resistances close to 1 ohm/square the above experiments indicate that photo-etching alone will not be sufficient to generate a clean bar pattern. For such films a combined approach will have to be developed consisting of sputtering through a mask and photo-etching. The mask will have to be specially designed so that smaller portions of the growing film will be masked than will be ultimately etched away. In this way the subsequent photo-etching steps will have to be applied to considerably thinner portions of the film (only the fringed edges) and sharply defined edges should result.

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