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SELECTIVE IR REFLECTIVE COATINGS DEVELOPMENT

Semi-Annual Report, July 24, 1978—January 24, 1979

By
A. R. Lefkow

January 1979

Work Performed Under Contract No. EM-78-C-04-4299

MASTER

Honeywell, Inc.
Systems and Research Center
Minneapolis, Minnesota

U.S. Department of Energy

Solar Energy

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COATINGS DEVELOPMENT

SEMI-ANNUAL REPORT
for the period 24 July 1978 - 24 January 1979

A.R. Lefkow

Honeywell Inc.
Systems and Research Center
2600 Ridgway Parkway
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Prepared for
The Solar Heating and Cooling
Research and Development Branch,
Office of Conservation and Solar Applications
United States Department of Energy
Under Contract No. EM-78-C-04-4299

FORWORD

This is the first semi-annual report describing the work performed at Honeywell, Inc., Systems and Research Center, for the U.S. Department of Energy under Contract No. EM-78-C-04-4299. The work has been supported by the Solar Heating and Cooling Research and Development Branch, Office of Conservation and Solar Applications, U.S. Department of Energy.

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Mr. A.R. Lefkowitz is the Project Principal Investigator. The coatings work was performed by G. Jorgenson, S. Tobias and J. Vaughn. The coatings analysis was performed by B. Durand.

ABSTRACT

Two low temperature deposition techniques, a glow discharge activation technique and an ion plating technique, were investigated as methods for coating thin plastic membranes with solar transparent, infrared reflective semiconducting oxides.

The glow discharge activation technique was shown to produce coatings with better optical properties than the ion plating technique. Repeatability of coating properties with the glow discharge technique has been a problem whose solution appears to lie in better deposition process control.

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SECTION I
INTRODUCTION

This is the first semi-annual Technical Progress Report on Contract No. EM-78-C-04-4299 and covers the technical progress made during the period from 24 July 1978 through 24 January 1979.

The objective of this program is the development of a cost effective method for coating thin plastic membranes with a solar transparent, infrared reflective coating for use as a heat mirror. Optical properties goals are 85%-90% solar transmittance and 90%-95% infrared reflectance at the peak of the room temperature black body radiation spectrum. To achieve these program goals, metal oxide semiconductor coatings, indium-tin oxide ($\text{In}_2\text{O}_3/\text{SnO}_2$), antimony doped tin oxide ($\text{SnO}_2:\text{Sb}$) and cadmium stannate (Cd_2SnO_4) were to be deposited using several non-conventional techniques that minimize substrate heating.

The objective of the first six months of this program (Phase I) has been the evaluation of the two deposition techniques selected for this program, i.e., a modified ion plating technique and a glow discharge activation technique. Coatings of indium-tin oxide, tin oxide and antimony doped tin oxide have been deposited in two separately configured ion plating systems. Tin oxide coatings have been deposited in the glow discharge

activation system. Comparison of the electrical and optical properties of coatings deposited by both techniques clearly indicates that the glow discharge technique is superior for this program.

A description of each coating system and the deposition process along with the results obtained is given separately below.

SECTION II

MODIFIED ION PLATING TECHNIQUE

Vacuum evaporation of metal oxide semiconductors ordinarily requires either a heated substrate or a post deposition heat treatment to produce transparent conductive coatings. Previous work done at Honeywell⁽¹⁾ has shown that an in-situ post deposition oxygen glow discharge in place of substrate heating or post deposition heating can produce thin ($\sim 100 \text{ \AA}$) tin oxide films with high conductivity. Films of this thickness are obviously not thick enough to provide the infrared reflectance required by this program. To ensure that high conductivity would be maintained throughout the bulk of a much thicker film the metal oxides were to be evaporated through an oxygen glow discharge.

Resistive Evaporation Ion Plating System

The first attempts at evaporating metal oxide semiconductors were carried out in the system shown schematically in Figure 1. The evaporation source was resistively heated rather than E beam heated primarily because an E beam will not operate at the chamber pressures required to sustain an oxygen glow discharge. Literature⁽²⁾ suggested that the oxides of indium and tin should evaporate at approximately 600°C , well within the capability of the resistively heated source. Unfortunately this turned out not to be the case. Source temperatures of 1500°C or greater were required to achieve any appreciable evaporation rates. The high temperatures are required because In_2O_3 and SnO_2 , both semiconductors, reduce to In_2O and SnO , both insulators, and the insulating oxides

require much higher evaporation temperatures. These evaporation temperatures are above the recommended limits of the sources used and radiant heating of the bell jar becomes excessive.

To alleviate the temperature problems, metals rather than metal oxides were used as source materials. Indium metal, for instance, evaporates at approximately 750°C rather than the 1500°C required for the oxide. To ensure that the condensing film would be fully oxidized, slow evaporation rates were used. Several thin ($100 \text{ \AA} - 200 \text{ \AA}$) films were deposited with surface resistivities between $15 \Omega/\square$ and $100 \Omega/\square$. Deposition times for these films were quite long, on the order of 30 minutes. The long deposition times were a result of evaporant material scattered by the background gas. Gas pressures of 1×10^{-3} torr to 5×10^{-3} torr are required to sustain a glow discharge and at these pressures the mean free path of an evaporated molecule is between 5 cm and 5 mm. The source to substrate distance is approximately 45 cm so the average evaporated molecule reaching the substrate will have undergone at least 10 scattering collisions.

Film parameters were not repeatable from run to run. The primary reason for this was radio frequency interference from the glow discharge power supply. The interference did not

Figure 1. Resistive Evaporation Ion Plating System

Figure 2. E-Beam Evaporation Ion Plating System

allow monitoring of any of the deposition parameters such as evaporation rate, background gas pressure or substrate bias voltage. As an example of this, the high background gas pressure caused conductive cooling of the source thus lowering the evaporation rate. To compensate for the cooling, the source current was increased but the amount of increase could not be monitored.

Although several thin coatings were deposited with low surface resistivities the majority of the depositions carried out in this system resulted in no coating at all, too metallic coatings or very powdery coatings.

Electron Beam Evaporation Ion Plating System

Because no control of the deposition parameters could be established in resistive evaporation deposition system, efforts were transferred to the electron beam evaporation system shown in Figure 2. In this system thick coatings are built up by depositing a number of thin layers ($50 \overset{\circ}{\text{A}} - 100 \overset{\circ}{\text{A}}$) with each layer being subjected to an oxygen glow discharge before the next layer is deposited. This method is slow and tedious but is known to produce coatings with appreciable conductivity⁽¹⁾. Because the deposition chamber is backfilled with oxygen for

the glow discharge activation after each thin layer is deposited, deposition parameters can be monitored and repeated. An electron beam rather than a resistively heated source was used so that metal oxides rather than metals could be evaporated.

The primary issue with this deposition technique was how thick a layer could be deposited before the glow discharge activation process is required. Depositions of films with several different thicknesses suggest that the thinner the deposited layer the more effective the glow discharge activation process becomes. This is true for all metal oxide films deposited, $\text{In}_2\text{O}_3/\text{SnO}_2$, $\text{SnO}_2:\text{Sb}$ and SnO_2 . The activation process takes place in the first minute of the glow discharge. (The glow discharge was turned on and off at one minute intervals with no decrease in resistivity seen after the first minute.)

Thin (⁰250 Å) films of In_2O_3 with surface resistivities as low as 6 $\Omega/\square$ were deposited in this manner. These films were quite dark (reduced) immediately after deposition. The subsequent glow discharge, although it reduced the films surface resistivity, failed to improve the optical characteristics of the films. Figures 3 and 4 show the visible transmittance (.35 μm to .75 μm) and infrared reflectance (2.5 - 40.0 μm) of one of the In_2O_3 films deposited using this technique. It can be seen that these films of In_2O_3 (or $\text{In}_2\text{O}_3/\text{SnO}_2$) will not meet the optical properties goals of this program.

Figure 3. Visible Transmission of 250 Å In_2O_3 Coating Deposited in Electron Beam System Shown in Figure 2. Film Deposited in Five Steps of 50 Å Each With One Minute Glow After Each Step. Surface Resistance = 90 $\Omega/\square$.

Figure 4. Infrared Reflectance of 250 Å In_2O_3 Coating Deposited in Electron Beam System Shown on Figure 2. Film Deposited in Five Steps of 50 Å Each With One Minute Glow After Each Step. Surface Resistance = 90 $\Omega/\square$.

Tin oxide and antimony doped tin oxide provide much better visible transmission than the indium compounds discussed above. The surface resistivities of these films are however, higher than that of indium oxide, $3 \text{ K}\Omega/\square$ compared to $6 \Omega/\square$ for the same thicknesses. There is essentially no difference between tin oxide and antimony doped tin oxide films in surface resistivity, visible transmittance and infrared reflectance.

Efforts were concentrated on depositing a thick film of tin oxide to determine if the optical properties goals of this program are attainable with this deposition method. A film with a total thickness of $4000 \text{ \AA}$ was deposited in 80 different steps of $50 \text{ \AA}$ each with a one minute glow discharge after each step. This film took four days to deposit. The surface resistivity of this film is $\sim 1.5 \text{ K}\Omega/\square$. The film is quite soft and surface resistivity is therefore very difficult to measure with a four point probe. The optical properties of this film are shown in Figures 5 and 6. Thicker films will give higher infrared reflectance but lower visible transmission and will take much longer to deposit.

Because of the poor results obtained to date in both of the ion plating systems used, no further efforts are planned along these lines. High quality films are probably attainable by this method if the material can be evaporated through an oxygen glow discharge. To do this would require a multiple chamber, differentially pumped system which is not available at this time.

Figure 5. Visible Transmission of 4000 Å Thick SnO_2 Film Deposited in Electron Beam System Shown in Figure 2. Coating Deposited in 80 Steps of 50 Å Each with One Minute Glow After Each Step. Surface Resistance = $1.5\text{K } \Omega/\square$.

Figure 6. Infrared Reflectance of 4000 Å Thick SnO_2 Film Deposited in Electron Beam System Shown in Figure 2. Coating Deposited in 80 Steps of 50 Å Each With One Minute Glow After Each Step. Surface Resistance = $1.5\text{K } \Omega/\square$.

SECTION III

GLOW DISCHARGE ACTIVATION SYSTEM

The glow discharge deposition process is one of the methods chosen for this program because it is a non-thermal technique for depositing metal oxide semiconductors that will minimize damage to thin plastic substrates. Chemical vapors from an organo-metallic compound such as tetramethyltin, $\text{Sn}(\text{CH}_3)_4$, are combined with oxygen and activated by introducing the mixture into a radio frequency electrical discharge. The tin and oxygen then combine, either in the glow or on the substrate or both, to form a tin oxide semiconducting coating, SnO_x , where $1 < x < 2$. Antimony doping, with a material such as trimethylantimony, $\text{Sb}(\text{CH}_3)_3$, is possible and should be quite uniform and controllable. In theory, films of In_2O_3 , $\text{In}_2\text{O}_3/\text{SnO}_2$ and Cd_2SnO_4 can also be deposited using this technique. Because of toxicity and safety problems, only films of SnO_x have been deposited to date.

Glow Discharge Deposition System

The glow discharge deposition system is shown schematically in Figure 7. The system is essentially an RF sputter system with the target replaced by a gas diffuser that also serves as the cathode mount. The diffuser ensures that the premixed gases are distributed uniformly throughout the plasma. This gives uniform coating properties over large area substrates. The organo-metallic compound is held under vacuum in a separate chamber and its vapors are bled through a needle valve/flow-

Figure 7. Glow Discharge Activation Deposition System

meter combination, combined with oxygen and delivered to the deposition system through the gas diffuser.

Deposition Procedure

In a typical deposition the following sequence of events take place:

- (1) Load substrate into system
- (2) Evacuate system to 5×10^{-6} torr
- (3) Set organo-metallic & oxygen partial pressures
- (4) Throttle gate valve to obtain desired deposition pressure (total system pressure)
- (5) Turn on RF power, set to desired level
- (6) Allow deposition to proceed for desired length of time
- (7) Shut off RF, shut off organo-metallic & oxygen flows
- (8) Evacuate deposition system
- (9) Vent to air & remove substrate

Deposition Parameters

The deposition process parameters and their effects on the coatings produced are listed in Table 1. All of the process parameters, with the exception of the DC bias voltage developed on the cathode, are externally controllable and their effects on the coating are well known. The bias voltage is a complicated function of all of the other process parameters and can have a significant effect on coating properties.

Table 1. Glow Discharge Deposition System Parameters

Parameter	Expected Effect on Coating
RF Power	Affects growth rate, conductivity
Syst. Pressure	Affects growth rate, conductivity
Gas Flow Rate	Primary effect on stoichiometry
Partial P Ratio	Affects stoichiometry, conductivity
Electrode Spac.	Primarily affects growth rate and uniformity
Time	Affects coating thickness
Cathode Bias Voltage	Unknown - suspect major effect
Substrate Bias Voltage	Unknown - major effect may be on film growth rate

Cathode Bias Voltage Effects

The cathode bias voltage controls the velocity with which electrons created near the cathode enter the plasma. These electrons are responsible for creating the ionic species from which the film is formed. As the electron velocities vary the ionization rates of the gas constituents, tetramethyltin (TMT) and oxygen, will vary. It is reasonable to assume that the collision cross sections of TMT and oxygen with these electrons are not equal but are functions of the electron velocity. This implies that as the accelerating voltage varies, the ratio of oxygen to tin ions in the plasma and the resulting film stoichiometry will vary. Film composition then can range from SnO_x + polymerized TMT to SnO_x ($1 < x < 2$) to SnO_2 depending on the cathode bias voltage.

The effects of changing the bias voltage for depositions using otherwise identical parameters are shown in Table 2. In general, high bias voltages (> 450 V) lead to high resistivity films, low bias voltages (< 300 V) lead to SnO_2 + polymerized TMT films which may or may not be conducting and bias voltages between 350 V and 450 V yield clear (no polymer incorporation) conducting films.

In addition to bias voltage changes caused by power and pressure variations from deposition to deposition, there are also changes that occur during deposition. This is caused by the

Table 2. Effect of Bias Voltage on Coating Parameters

Coating No.	Deposition Conditions				Coating Parameters	
	Pressure	O ₂ /TMT Ratio	Input Power	Bias Voltage	Surface Resist. ($\Omega/\square$)	Coating Appearance
80	30 m torr	2.375/1	45W	350V	1K	Clear
83	30 m torr	2.375/1	55W	490V	71K	Cloudy
84	30 m torr	2.375/1	65W	500V	∞	Clear
87	30 m torr	2.375/1	45W	370V	12	Clear
88	30 m torr	2.375/1	55W	390V	250	Clear
89	30 m torr	2.375/1	65W	450V	2.4K	Clear
91	40 m torr	2/1	45W	350	∞	Clear
98	40 m torr	2/1	45W	270	3.0K	Cloudy

conductive coating being deposited on the ceramic insulators separating the cathode from the grounded diffuser. As the insulators become coated and increasingly conductive, the bias voltage decreases and part of the input power is dissipated in the insulator coating instead of in the plasma. When the insulators are stripped or replaced the bias voltage increases. The bias voltage therefore changes in an uncontrolled manner and may be largely responsible for lack of coating repeatability.

Several design modifications to the cathode/diffuser assembly will be made to prevent coating buildup on the ceramic insulators. In addition, an electrical network to control the bias voltage is being developed.

Coating Results To Date

During the first phase of the program, efforts have been concentrated primarily on varying those parameters that have the greatest effect on coating properties. RF power, total system pressure and oxygen/organo-metallic partial pressure ratios have been varied to produce high growth rate, clear, conductive films. Repeatability, the ability to reproduce a set of coating parameters with a given set of deposition parameters, has not been good. A given set of deposition parameters, power, flow rate and partial pressure ratio will produce a clear conductive coating at 20 μ pressure but not at 30 μ pressure. In fact, a significantly different partial pressure ratio has had to be found for each deposition pressure used.

Table 3. Coatings Deposited at a System Pressure of 20 μ

Coating No.	O ₂ /TMT Ratio	RF Power	Bias Voltage	Deposition Time	Film Growth Rate (Å/Min)	Surface Resist. ($\Omega/\square$)
54	2/1	45W	450V	$\frac{1}{2}$ hr	63	40
55	2/1	55W	470V	$\frac{1}{2}$ hr	50	45
56	2/1	65W	>500V	$\frac{1}{2}$ hr	35	17.5
57	2/1	35W	360V	$\frac{1}{2}$ hr	23	105
58	2/1	25W	320V	$\frac{1}{2}$ hr	37	385
79	2/1	55W	450V	1 $\frac{1}{2}$ hr	-	14

Table 4. Coatings Deposited at a System Pressure of 30 μ

Coating No.	O ₂ /TMT Ratio	RF Power	Bias Voltage	Dep. Time	Film Growth Rate (Å/Min)	Surface Resist. ($\Omega/\square$)
87	2.375/1	45W	370V	1 hr	58	12
88	2.375/1	55W	390V	1 hr	91	250
89	2.375/1	65W	450V	1 hr	83	2.4K

Table 5. Coatings Deposited at a System Pressure of 40 μ

Coating No.	O ₂ /TMT Ratio	RF Power	Bias Voltage	Surface Resist. ($\Omega/\square$)	Coating Appearance
90	2.375/1	45W	375V	∞	Clear
94	1.75/1	45W	290V	1.7K	Cloudy
95	1.875/1	45W	290V	10K	Cloudy
99	1.9/1	45W	470V	7.8K	Cloudy
100	2/1	45W	470V	4.8K	Cloudy
101	2.125/1	45W	480V	∞	Clear
102	2.25/1	45W	480V	∞	Clear

The best deposition parameters to date for deposition pressures of 20 μ , 30 μ , and 40 μ respectively are shown in Tables 3, 4, and 5. The gas partial pressure ratios can be seen to be different for each deposition pressure used and, in fact, no satisfactory ratio could be found for a deposition pressure of 40 μ for the range of input powers used. The partial pressure ratios that were tried for 40 μ deposition pressure ranged from 1.75:1 to 2.375:1 (O_2 /TMT).

Film growth rates as functions of input power are shown in Figure 8 for deposition pressures of 20 μ and 30 μ . Growth rates are obtained by dividing the film thickness by the deposition time. Except for the data point at 20 μ , 25 W, both sets of pressures show an initial increase in growth rate followed by a subsequent decline. The higher pressure, 30 μ , shows a higher growth rate at higher input powers. This higher growth rate is consistent with more material present to form a film at a total system pressure of 30 μ than at 20 μ . The decrease in growth rate beyond the peak is believed to be related to the increased bias voltage developed at the higher pressures changing the ratio of the ions of the gas constituents.

The relationship between surface resistance and input power for the coatings of Figure 8 is shown in Figure 9. As expected, the surface resistance decreases with increasing power for a deposition pressure of 20 μ . This decrease in surface resistance

Figure 8. Film Growth Rate ($\text{\AA}/\text{Min.}$) Vs. RF Input Power (W)

Figure 9. Surface Resistance ($\Omega/\square$) Vs. Input Power (W)

is caused by ions impacting the substrate surface with higher energies at higher power levels. Higher energy ions hitting the substrate surface result in a film with larger crystalline size and lower resistance. The increase in resistance with increasing power at a deposition pressure of 30 μ was unexpected. The explanation for this appears to be an excess of oxygen as compared to tin ions in the plasma, the excess again being caused by the increased bias voltage.

Figures 10 and 11, and 12 and 13 show the visible transmission and infrared reflectance of the best films deposited to date at a total system pressure of 20 μ and 30 μ respectively. The effects of coating thickness on reflectance can also be seen in Figure 11. The dashed curve ("A") shows the reflectance of a 1500 $\text{\AA}$ thick deposit. At this thickness the coating does not mask the absorption effects (a dip in reflectance from 5 μm to 10 μm) of the glass substrate. Curve "B" shows the reflectance of an 11000 $\text{\AA}$ thick deposit that masks some of the absorption effects of the glass substrate. In Figure 13 the effects of substrate material on the reflectance can be seen. Both glass and mylar substrates were used in this deposition and the effect on the reflectance is quite different. Curve B represents the mylar substrate and does not show the broad absorption band from 5 μm to 10 μm that is characteristic of SnO_x coatings deposited on glass substrates. Instead, the absorption bands of mylar are present, at 8 μm ,

Figure 10. Visible Transmission of 11000 Å Thick SnO₂ Film (Dep. No. 79)

Figure 11. Infrared Reflectance of $1,500 \text{ \AA}$ (Curve A) and $11,000 \text{ \AA}$ (Curve B) Thick SnO_2 Films. Curve A = Dep. No. 54, Curve B = Dep. No. 79

Figure 12. Visible Transmission of 5,800 Å Thick SnO₂ Film
(Dep. No. 87)

Figure 13. Infrared Reflectance of $5,800 \text{ \AA}$ SnO_2 Film (Dep. No. 87) Deposited on Glass (Curve A) and Mylar (Curve B) Substrates.

9 μm and 12 μm . These absorption bands are not as deep or broad as the SiO_x absorption (5 - 10 μm) of glass, accounting for the improved reflectance of the film on mylar as compared to glass.

Film Composition

As mentioned above, film composition varied from SnO_x + polymerized TMT to SnO_x ($1 < x < 2$) to SnO_2 depending on the deposition parameters. Several early samples were analyzed using Mass Spectroscopy to determine their chemical composition and to try to relate the composition to the measured surface resistivities. These films are listed in Table 6. Only film no. 18, the lowest resistivity film, was clear. All of the rest had a cloudy appearance indicating that some polymer was incorporated in the films.

The analysis of each film is given below and an explanation of the peaks at the cited mass charge ratio (m/e) numbers is given in Table 7.

The mass spectrometer scans for Sample 18 (20 ohms per square) showed nothing except background air peaks. This coating appears to be extremely clean.

Sample 20 (60 ohms per square) showed a slight trace of an aliphatic organic material at a probe temperature of 350°C . At a temperature of 450°C a peak was noted at m/e 41.

Table 6. Glow Discharge Deposited Films Subjected to Mass Spectroscopy Analysis

Coating No.	Deposition Press. (μ)	Power Watts	O ₂ /TMT Ratio	Bias Voltage	Surface Res. ($\Omega/\square$)	Film Appearance
18	20	35	2/1	370V	20	Clear
20	100	35	2.15/1	300V	60	Cloudy
27	20	35	2/1	340V	-	Cloudy
29	20	35	2/1	375V	27	Cloudy

Table 7. Mass/Charge (m/e) Numbers and Most Probable Species

<u>Mass Spectra Peak Number</u>	<u>Most Probable Species</u>
14*	N
15	CH ₃
16*	O ₂
17*	OH
18*	H ₂ O
28*	N ₂
30	CH ₂ O
31	CH ₃ O
32*	O ₂
40*	A _r
41	CHCO
42	CH ₂ CO
43	CH ₂ CHO
44*	CO ₂

- Higher number peaks
result from more com-
plex aliphatic organics.

*Background Species

At 600°C peaks were seen at m/e 78, 41, 39, and 27, and at 700°C peaks are obtained at m/e 78, 77, 42, 41, 27 and 15. Trace amounts of other m/e values were also observed at 600°C and 700°C.

Sample 29 (26.8 ohms per square) showed the second largest amount of material. At 400°C peaks were noted at m/e 31 and 15. At 450°C peaks were noted at m/e 43, 42, 31, and 15 and at 500°C peaks were noted at m/e 42, 31, 30 and 15. No significant peaks were observed above 500°C.

Sample 27 at 350°C showed a peak at m/e 15; at 450°C peaks were seen at m/e 31, 27 and 15; and at 500°C peaks were seen at m/e 43, 42, 31, 30, 27, 26 and 15. Again no significant peaks were observed above 500°C.

The peaks at m/e 14, 16, 17, 18, 22, 28, 29, 32, and 44 are from background air and should be ignored. The peak at m/e 15 is due to a methyl group. The peak at m/e 27 is due to CH_3CH_2 . The peaks at m/e 30, 31, and 43 contain one and two carbon atoms respectively with an oxygen atom and several hydrogen atoms included. The peaks at m/e 77 and 78, may be aromatic, but in general they appear to be aliphatic material. The organic material may be coming from the organic portion of the organotin compound that is used for deposition. The small differences in relative amounts of material may be due to differences in the amount of scrapings that were placed in the Mass Spectrometer. However, the temperature above which no significant peaks were

observed may be indicative of the amount and type of material that was deposited. The mass spectra not resulting from background air, are indicative of organic materials contained in the films.

The dirtiest films, those with the most polymer incorporation, are numbers 20 and 27, those deposited with the lowest bias voltages (300 and 340 volts respectively). The m/e 41 peak at 450°C for coating number 20 indicates a high level of concentration of this species. The m/e 77 and 78 peaks of this film are longer "chain" aliphatics and are not present in the other films. This data tends to confirm that the bias voltage is at least a factor in determining coating quality.

Coating Of Plastic Substrates

Although most depositions have been carried out using glass substrates, plastic substrates have also been coated. Curve "B" of Figure 11 shows the best results on a plastic substrate to date. The substrate is 2 mil thick mylar and appears to have better infrared reflectance than the glass slide (curve "A") coated in the same deposition. The better infrared reflectance is caused by the Mylar substrate not having the broad, deep infrared absorption bands of glass.

Coatings were also deposited on 1 mil substrates of polyethylene and polyvinyl fluoride (Tedlar). Although not damaged during the deposition, these substrates did have a tendency to curl up due to the stresses in the SnO_x coating. The polyethylene substrate curled up so tightly that it could not be uncurled for optical or electrical properties measurements. Surface resistivities of the films on Tedlar and Mylar are on the order of 15 - 40 $\Omega/\square$. These resistivities were measured using a four point probe technique and because the substrates are soft may not be particularly accurate. However, a glass slide coated at the same time had a surface resistance of 15 $\Omega/\square$. The deposition conditions used for these films are given in Table 8.

The visible transmission and infrared reflectance of these coatings are shown in Figures 14 and 15. From the wavelength spacing of the interference fringes in Figure 14 the film thickness is determined to be approximately 6600 $\text{\AA}$ giving a film growth rate of 55 $\text{\AA}/\text{min}$. This is reasonably close to deposition no. 54 of Table 3 which used the same externally controllable deposition parameters.

Table 8. Deposition Conditions Used to Coat
Mylar, Tedlar and Polyethylene Sub-
strates

Deposition Pressure	20 μ
RF Power	45W
Electrode Spacing	2.0 in.
O ₂ /TMT Ratio	2/1
Bias Voltage	370V
Deposition Time	2 hr.

Figure 14. Visible Transmission of SnO_2 Coatings on 2 Mil Mylar and 1 Mil Tedlar (Dep. No. 130)

Figure 15. Infrared Reflectance of SnO_2 Coatings on 2 Mil Mylar and 1 Mil Tedlar (Dep. No. 130)

SECTION IV

CONCLUSIONS AND RECOMMENDATIONS

Modified Ion Plating Technique

Two versions of a modified ion plating technique were attempted: 1) evaporation through an oxygen glow discharge, and 2) E-beam evaporation of a series of very thin films with an oxygen glow discharge treatment after each layer. Although these techniques show some promise for producing films with the types of characteristics sought in this program, they do not appear to be the means for achieving the program optical properties goals. Therefore, no further activities using this technique are planned or recommended

Glow Discharge Activation Technique

We have shown that thin plastic foils can be coated with a conductive oxide (SnO_x) using the glow discharge activation technique. To date it has not been possible to achieve the program goal of 90%-95% infrared reflectance at 10μ , the peak of the room temperature black body radiation spectrum. It is doubtful, in view of the thickness and reflectance of the films produced so far, whether tin oxide films alone will be able to achieve this goal. Antimony doping, using $\text{Sb}(\text{CH}_3)_3$ - trimethylantimony, will be necessary in spite of the toxicity and handling problems involved in using that compound.

It is apparent that better process control is necessary in order to be able to reproduce a given set of coating parameters. This is particularly true for controlling organo-metallic flow rates and cathode bias voltages. Bias voltage control will be achieved by a redesign of the cathode/diffuser system to prevent deposition of a conductive coating on the ceramic insulators and by designing a voltage control circuit that will allow external adjustment of the bias voltage.

SECTION V

FUTURE PLANS

In the immediate future, the effect of cathode bias voltage on coating properties, particularly coating stoichiometry, will be more fully investigated. The redesigned cathode/diffuser and voltage control circuit should allow control of this parameter that is adequate to determine its effect.

After the cathode bias voltage effects have been determined and can be satisfactorily controlled we will study the effects of different doping levels of trimethylantimony. Optimum doping levels will be determined.

It will be necessary to deposit thicker films than those made to date to achieve the desired infrared reflectance. If films can be deposited with other characteristics that are satisfactory, attempts will be made to build up their thickness to improve their infrared reflectance. It will be of interest to determine the film thickness necessary to mask the absorption bands of the various substrates.

References

1. W.T. Boord, "Exploratory Development of Antistatic Coatings for Use on Aircraft Transparencies", AFML-TR-76-116, Honeywell, Inc., July 1976.
2. "Handbook of Thin Film Materials", Sloan Technology Corp., Materials Division.