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RESEARCH FOR LOW-APPLICATION-TEMPERATURE, ELECTRICALLY CONDUCTING, TRANSPARENT COATINGS FOR AIRCRAFT WINDSHIELDS AND RELATED COMPONENTS

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FOREWORD

This report was prepared by the Battelle Memorial Institute under USAF Contract No. AF 33(616)-342. The contract was initiated under Project No. 7312, "Finishes and Materials Preservation, Task No. 73125 "Transparent Conducting Coatings for Aircraft Materials", formerly RDO No. 616-13, "Optical Coatings for Aircraft Materials", and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Mr. J. R. Cannon acting as project engineer.

ABSTRACT

A survey of various methods for producing transparent conducting films at temperatures below 250°F and development studies of one method were conducted in a search for both low- and high-conductivity films. These films are needed for dissipation of static electrical charges and fog, frost, and ice from safety-glass aircraft enclosures.

Of approximately 12 methods investigated, the one chosen for more extensive study was the thermal conversion of metal films to transparent oxides. Evaporated indium films were successfully converted to transparent oxide films at temperatures below the bubbling temperature of the plastic laminate. Films with resistances below 500 ohms per square, measured in vacuum, were produced, but exposure of the films to air at atmospheric pressure caused the resistances to increase by at least two orders of magnitude.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. R. WHITMORE
Technical Director
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INTRODUCTION

This is the final report on investigations of transparent conducting coatings for application to safety glass below the bubbling temperature of the plastic laminate. The objectives of the work were the development of two types of coating, namely:

Type A: A low-conductivity coating needed for dissipation of static charges formed on external surfaces of transparent aircraft enclosures

Type B: A high-conductivity coating needed for removal of fog, frost, and ice on the interior and exterior areas of transparent enclosures by electrical heating methods.

The general requirements were good mechanical durability, low haze, optical transmission of white light of at least 85 per cent, and electrical stability for at least 250 hours during operation, even at high humidity, over the temperature range -65 to 250 F. In the Type A coating, the resistance range required was 1 to 10 megohms per square, and, for the Type B coating, the resistance should not exceed 100 ohms per square.

The approach to the problem involved a survey of various methods of producing coatings, with subsequent development of the most promising coating.

SUMMARY AND CONCLUSIONS

During the past year, a number of possible methods for producing transparent, conducting coatings on glass at temperatures of 250 F or less were investigated. Among the methods studied were those which have previously been used successfully to form films by utilizing high application temperatures. These methods were studied from the standpoint of determining the feasibility of their use in conjunction with low application temperatures. In addition, several general methods not previously used for the formation of transparent conducting films were investigated.

The methods which were studied are the following:

(1) Deposition of metal films from aqueous solutions for subsequent conversion to the oxide

(2) Precipitation of oxide films from solution

(3) Formation of oxide films by decomposing metallo-organic compounds

(4) Formation of oxide films by dipping heated glass in nonaqueous solutions of metal salts

(5) Formation of oxide films by impinging the metal-salt vapor on a hot glass surface

(6) Formation of oxide films by decomposing metal-salt vapors at low pressures

(7) Evaporation of metal oxide films

(8) Evaporation of metal films, followed by oxidation using these methods:

  (a) Wet chemicals

  (b) Electrical discharge in normal atmosphere

  (c) Heating under various environmental conditions

  (d) Glow discharge

(9) Formation of metal films by sputtering, followed by oxidation using:

  (a) Glow discharge

  (b) Conversion to the oxide by heating in an oxidizing atmosphere.

The methods of film formation listed above are discussed in the succeeding paragraphs.

The study of the deposition of metal films from aqueous solution was limited to attempts to produce cadmium films, since these films are difficult to prepare by vacuum evaporation. The objective was to develop a process similar to that used to form silver mirrors from a silver-salt solution.

A number of reducing solutions were tested on cadmium-salt solutions with the cadmium present as both uncomplexed and complexed ions. None of the reducing agents produced a metallic mirror. The only deposits obtained were white, amorphous, nonadherent deposits of what may have been cadmium oxide or hydrated oxide.

Tin oxide films were prepared by homogeneous precipitation(1) from aqueous and nonaqueous solutions of tin salts. Most of these films were nonconducting(2); a few films were prepared which had resistances of 500-1000 megohms between 1/2-inch probes(3). All films formed by this method were extremely hazy. It is not anticipated that films having the desired optical properties could be prepared by this method, even if suitable conductivity could be obtained.

Attempts were made to produce cadmium and tin oxide films both by dipping hot glass into metallo-organic solutions of dimethyl cadmium and tetramethoxy tin and by spraying these solutions onto hot glass. Only white, amorphous deposits were obtained in all cases.

Both TiO_2 and SnO_2 films were prepared by dipping heated glass slides into dilute alcoholic solutions of $TiCl_4$ and $SnCl_4$ and postheating the glass-film system for varying periods. Temperatures in the range 250-400 F were used for preheating and postheating. At 400 F, the resistances of the SnO_2 films were in the range 5-50 megohms between 1/2-inch probes and, for TiO_2 films, 10-50 megohms. At 300 F, SnO_2 films had resistances in the range 20-200 megohms, whereas TiO_2 films prepared at 300 F had resistances in the same range as those prepared at 400 F. Some small areas of these films had resistances as low as 1/2 megohm between 1/2-inch probes. Reducing the application temperature to 250 F resulted in the formation of films having resistances of 1000 megohms or more. The optical properties of all the dipped films were good; light transmission was 75 per cent or better, and little or no haze was detectable visually. This method of film application appears to be promising, at least for the formation of high-resistance films for static dissipation.

Film formation by impinging metal chloride vapors on glass heated to temperatures of 250 to 450 F was studied. Various apparatus designs were studied. Best film formation was obtained when the geometry of the apparatus was such as to prevent, as much as possible, the homogeneous gas-phase reaction between the metal chloride and water vapor. This precaution made a greater fraction of the materials available for the heterogeneous reaction at the hot glass surface. Principal emphasis was placed on the formation of SnO_2 films from $SnCl_4$. Some work was done using $TiCl_4$, VCl_4, $SbCl_3$, and $InCl_3$ to form the corresponding oxides. The latter materials were studied from the standpoint of their possible use as undercoat materials and impurity additions for tin oxide, as well as for their use as conducting films. The study of the effect of impurity additions to

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(1) The homogeneous-precipitation technique involves precipitation of a material by homogeneous-solution reaction with a precipitating agent. In this work, the reaction between the tin compound and the precipitating agent was carried out near the boiling point of the solution.

(2) Films having resistances greater than 1000 megohms between probes spaced 1/2 inch apart will be classified as nonconducting in this report.

(3) Resistance per square is approximately equal to 0.6 of the resistance between point probes 1/2 inch apart.

SnO_2 films was inconclusive because of the scatter in the resistance values obtained. The effect of undercoatings is discussed later in this section.

SnO_2 films formed by the vapor-impingement method at 250 F were generally nonconducting. However, conducting areas with resistances as low as 50 megohms between 1/2-inch probes were found on a few films. Films formed at higher temperatures (450 F) exhibited resistances as low as 0.2 megohm between 1/2-inch probes.

As in the case of the dipping method, the vapor-impingement method shows some promise for the formation of high-resistance coatings (static dissipation) but little promise as a method for the formation of low-resistance coatings.

In view of previous work at Battelle which indicated that the rate of formation of SnO_2 from $SnCl_4$ vapor is accelerated at low pressures to produce clear conducting films at temperatures as low as 550 F, it was decided to investigate the use of this method at lower temperatures. Using pressures in the range < 1 mm to 300 mm of mercury, it was found that conducting films were not produced at temperatures below 475 F.

Using the same apparatus at normal atmospheric pressures permitted formation of a film having a resistance of 25 megohms between 1/2-inch probes at an application temperature of 385 F. At 250 F, a film having a resistance of 100 megohms between 1/2-inch probes was produced.

Thus, although the use of reduced pressures at higher temperatures increased the rate of film formation, the opposite effect seemed to occur at lower temperature.

When SnO_2 films were applied by vapor impingement, dipping, and homogeneous precipitation to conducting SnO_2 films prepared at temperatures above 800 F, the double-layer films had resistances appreciably lower than the resistances of the single-layer, high-application-temperature films. If the double-layer film is treated as two resistances in parallel, it can be shown that the second SnO_2 layers had resistances of the order of 10^4 ohms per square, as compared with resistances greater than 10^8 ohms per square when applied singly. It is apparent from these results that the substrate has a large effect on the conductivity.

Films of TiO_2, VO_2, Sb_2O_3, and In_2O_3 were tested as possible substrates for improving the conductivity of SnO_2 films applied by vapor impingement. The scatter in the resistance values of SnO_2 films with and without undercoating was too great to permit any conclusions to be drawn as to the effects of these undercoating materials.

A rather extensive investigation on the formation of transparent conducting films by the oxidation of evaporated metal films was conducted. Primary emphasis was placed on films of indium, cadmium, and tin.

Initial attempts to oxidize metal films were made using wet-chemical methods. The metal films were treated with insoluble oxidizing agents applied both as a paste wet with 10 per cent NaCl solution and as a dilute aqueous slurry. Conducting oxide films were produced by these methods. The optical properties of all the films were poor, the films being extremely hazy.

In view of the fact that all the films formed from aqueous solution by homogeneous precipitation and systems containing water and insoluble oxidizing agents were extremely hazy, it did not appear that these methods, although producing conducting films, would warrant further investigation.

Some preliminary work was done on oxidation by electrical discharge, prior to completion of the glow-discharge apparatus, by treating the films with a Tesla coil (high-frequency generator) in normal atmosphere. Oxidation of indium films in this manner resulted in both conducting and nonconducting areas having very poor optical properties.

Attempts were made to oxidize evaporated tin and indium films by glow discharge. In the case of tin, there was no evidence of oxidation. Some indium films appeared to be at least partly oxidized, as evidenced by increases in light transmission during glow-discharge treatment. These indium films could be oxidized further by the regular thermal treatment. From the work thus far on glow-discharge conversion, this method appeared to be inferior to thermal oxidation.

Metal films were converted to oxides thermally under various environmental conditions. Initial conversions were conducted at pressures ranging from normal atmospheric up to about 80 psi and temperatures of 200 - 400 F. This work indicated that indium films could be converted to the oxide at 250 F, providing proper evaporation conditions were used in preparing the metal film. The minimum temperature requirement for oxidation of the other two metals, cadmium and tin, which were investigated was about 400 F. Resistances of all of the oxidized films were 10^4 ohms or higher, with very few films exhibiting the lower value.

Of all the methods studied in this survey, the thermal oxidation of metal films appeared to be the most promising. In view of the higher temperature required for the oxidation of tin and cadmium, emphasis was placed on the In-O system in the subsequent work. A study was made on the effects of evaporation parameters on the ease of oxidation of indium-metal films, and values of these parameters were determined that permitted thermal oxidation of indium films at temperatures of 250 F or less. Oxidation was conducted at pressures below atmospheric in order (1) to study the resistance changes of the films during deposition and the thermal oxidation procedures independent of the effect of environment and (2) to determine the effect of environment on the resistance of the resulting oxide films.

Metal films were heated by an electrical grid heater and by electrical load(1) during the oxidation procedure.

The best films obtained by thermal oxidation of evaporated indium metal had resistances of 300-500 ohms per square in vacuum, with film thickness being in the range 1000-2000 angstroms, as estimated from interference colors. The light transmission of these films was 75-85 per cent. On exposing these films to normal atmosphere, large resistance increases were observed. The films, after having undergone these resistance increases, also exhibited large photoeffects.

In the third phase of study, further considerations were given to the improvement and development of oxidized metal films. Emphasis was placed on investigations of the resistance stability of In-O films and the preparation of metal films by sputtering. Effort was directed toward stabilizing the resistance at the value in vacuum by the use of an overcoating. The best results thus far have been obtained by applying a SiO overcoating. The best overcoated films undergo resistance increases by a factor of 5 or 6, as compared with increases of about three orders of magnitude for similar unprotected films.

Several In-O films formed by the thermal conversion of evaporated indium films were subjected to d-c loads of 300 to 1100 watts per square foot. The load tests showed that the films were capable of withstanding high electrical loads without destruction by ionic conduction or film burn-out.

The work on sputtered films has been limited, up to the present time, to the formation of tin- and indium-metal films. Indium, unlike tin, was found to be difficult to sputter. Conditions (not necessarily optimum) were determined subsequently that permitted indium to be sputtered quite readily.

Several sputtered indium films were oxidized thermally in the vacuum system at a pressure of 6 microns of mercury and a temperature of 250 F. These sputtered films appeared to oxidize as readily as the most easily oxidized evaporated indium films. The best film obtained by this method thus far had a resistance of 600 ohms per square and a transmission of 75 per cent.

The sputtered indium films that were thermally converted were quite stable with regard to resistance changes on exposure to normal atmosphere. On aging in normal atmosphere at room temperature for 1 day, the resistance did not increase more than 10 per cent over the value in vacuum. After 20 days, resistances had increased by a factor of two. No attempts were made to oxidize sputtered tin films thermally.

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(1) The terms "electrical load" and "load heating" will be used in this report to designate heating by passing an electrical current through the film.

In addition, as a further check on glow discharge, both tin and indium sputtered films were subjected to glow discharge in an attempt to convert them to the oxides. The results were similar to those obtained when evaporated films were subjected to glow-discharge treatment. There was no evidence to indicate oxidation of tin films. Indium films were only partially oxidized.

It must be emphasized, with regard to sputtering and glow discharge, that only a small fraction of the many possible applications have been investigated, and even those applications that have been investigated have not been exploited to the full extent.

The methods which show the most promise in the formation of films with the desired electrical and optical properties are the formation of metal films by sputtering and formation by evaporation, followed by conversion to the oxide. The immediate problem with regard to evaporated films is to stabilize film resistance at the value obtained in vacuum (300-500 ohms). If this can be achieved, it is likely that stable resistances can be decreased to the desired 100 ohms per square or less, possibly by means of impurity additions or by the use of undercoat materials. From the small amount of work which has been done so far on thermal conversion of sputtered films, this method appears promising. From the evidence available, it appears that stability will be much less of a problem with the sputtered films.

DISCUSSION

A number of possible methods for producing transparent, conducting coatings at temperatures of 250 F or less were investigated during the past year. The results of these investigations are discussed in the following sections.

Deposition of Cadmium Films From Solution

One technique for producing an oxide film is to deposit a thin metallic film and subsequently convert it to the oxide. In view of the fact that cadmium oxide is known to form a transparent, conducting film on glass, and since cadmium films are difficult to prepare by vacuum evaporation, it was decided to investigate the possibility of forming cadmium films by a process similar to that used for the formation of silver mirrors from a silver-salt solution.

The primary problem was to find a reducing agent suitable to produce the cadmium deposit. Oxidation potentials indicated that hydroxylamine, ferrous hydroxide, methyl alcohol, sulfite ion, and thiosulfate ion might be sufficiently powerful reducing agents to reduce cadmium ion from basic solutions. In the case of the silvering process, the concentration of silver ion in solution is controlled by forming the silver ammonia complex.

Proper concentration control permits the oxidation reaction to occur heterogeneously on the glass surface while reducing the amount of reaction occurring in the body of the solution.

In the attempts to produce cadmium mirrors, various amounts of the reducing solutions were added to solutions containing varying ratios of cadmium and ammonia. In all tests, a thin, nonmetallic film was formed on the solution surface after the reducing agents were added. Glass plates immersed in these solutions for periods of 1/2 hour to 12 hours and subsequently dried had white, powdery deposits on the surface. Both the film on the surface of the solution and the deposit on the glass had the appearance of cadmium oxide or hydrated oxide. There was no evidence of the formation of the oxide as a precipitate in solution.

An attempt was made to reduce cadmium from a solution of the cadmium cyanide complex by using the cobaltous cyanide complex as a reducing agent. There was no reaction in this case, possibly because of the stability of the cadmium cyanide complex.

Oxalic acid was tested as a possible reducing agent in acid solution, but it also failed to reduce the cadmium ion.

The fact that the most powerful reducing agent used, cobaltous cyanide complex, is sufficiently powerful to reduce water, with the liberation of hydrogen, and yet did not reduce the cadmium ion to the metal indicated that the possibility of producing cadmium mirrors by this method is remote, particularly in aqueous solution.

Precipitation of Oxide Films From Homogeneous Solution

According to an article by Willard and Gordon in the Analytical Chemistry Journal for January, 1953, the precipitation of basic tin salts from homogeneous solution results in the formation of adherent tin oxide coatings on glassware. No information was available as to the optical and electrical properties of these films. The process, however, merited investigation, since the temperatures of film formation were well below the bubbling temperature of the plastic laminate in safety glass.

The following general principles apply to the formation of films by this method. All metallic ions which form colloidal and flocculent precipitates by heterogeneous precipitation methods tend to form films when precipitated homogeneously. Denser precipitates form more adherent films. Low-temperature (slow) precipitations do not give adherent films.

After investigation of the variables, concentration, rate, and temperature, a solution was prepared from which hazy, transparent, nonconducting films were obtained. The solution consisted of tin dissolved in hydrochloric acid, to which was added ammonium sulfate, sulfuric acid, and urea. In addition to urea, sodium trichloroacetic acid, ammonium carbamate, and sodium sulfite were tested as precipitants. All resulted in comparatively complete precipitation of the tin from solution; however, only the use of urea resulted in film formation on either the beakers or glass plates suspended in the solution.

In previous work at Battelle on SnO_2 films prepared by spraying $SnCl_4$ solution at high temperature, it was found that too high a concentration of water vapor in the atmosphere caused some haziness in the resulting films. Therefore, it was considered that precipitation from nonaqueous solution might reduce haze. The general procedure was to prepare a nonaqueous solution containing tin and generate water in situ as a precipitating agent. Three types of reaction were tried as methods for generating water: esterification, dehydration of a tertiary alcohol, and thermal decomposition of a hydrate. Only the latter method resulted in film formation. Chloral hydrate was decomposed to supply the water necessary for precipitation. Five hours were required to produce a film having resistance of greater than 500 megohms between 1/2-inch probes. There was no improvement in optical properties over those obtained in aqueous solution. The homogeneous-precipitation method shows little promise for formation of films with the desired optical properties and, therefore, investigation of this method was discontinued.

Formation of Oxide Films From Metallo-Organic Compounds

Many metallo-organic compounds are highly unstable with respect to thermal decomposition and hydrolysis. Since conducting oxide films have been formed by decomposition of the corresponding chloride on glass at high temperatures, it was thought that one possible means of reducing application temperature might be to use metallo-organic compounds which are more readily decomposed than the chlorides.

Dimethyl cadmium was prepared by a standard organic synthesis (see "Experimental Details"). Ether solutions of this material were used for dipping glass slides and for spraying onto glass slides. A powdery, white deposit (probably cadmium oxide) formed in all cases. It was nonadherent and nonconducting.

Tetramethoxy tin was tested as a possible material for forming SnO_2 films. The tin compound was prepared from tin tetrachloride and sodium methoxide. The supernatant liquid was removed from the reaction vessel and used as a spraying and dipping solution. This material was not obtained in the pure form, since attempts to distill it for purification resulted in tar formation. Again, only a white, powdery, nonconducting deposit was obtained.

From the limited amount of work done on the decomposition of metallo-organic compounds, it appeared that, although an oxide may be formed, it is not probable that conducting, transparent oxide films can be formed by this method.

Formation of Oxide Films by Dipping

The preparation of transparent, conducting oxide films by dipping hot (700 F or more) glass slides into nonaqueous solutions of metal chlorides is known. The applicability of this method in the temperature range 250 - 400 F was investigated. Initial experimental work involved the use of a stannic chloride-acetic acid-ethyl alcohol solution that previously had been found, by other investigators(1), to yield a conducting tin oxide film at temperatures above 700 F. Two general observations were made from this initial work. First, for low-temperature application, the glass slides not only must be preheated before dipping, but also must be heated after dipping to produce an adherent film. Second, the concentration of stannic chloride in the dipping solution must be lower for low application temperatures than for high application temperatures. Only white, powdery deposits were obtained with the more concentrated solutions when used at low temperature. In contrast to high-temperature dipping, in which case the stannic chloride is converted to the oxide immediately, it appeared that, at low temperatures, a thin film of solution containing $SnCl_4$ adhered to the glass. On postheating, the solvent then evaporated and the stannic chloride was converted to the oxide. If too much stannic chloride adhered to the glass surface, the deposit tended to be thick and nonadherent. It seemed probable that the amount of stannic chloride that adhered to the glass could be controlled by controlling the concentration of stannic chloride and also by choosing solvents of the proper viscosity. In attempts to employ the latter method of control, benzene, acetone, ethyl ether, methanol, and ethyl alcohol were tested as solvents. The glass plates were preheated and postheated at 240 F during this portion of the work, and solutions of various concentrations of stannic chloride were used.

Acetone solutions formed brown, powdery deposits that could be removed from the glass easily. Thin, transparent, nonconducting films were formed from the benzene, ethyl ether, ethyl alcohol, and methyl alcohol solutions. Film adherence was improved by longer postheating times in all cases. The best films were obtained from a solution of 2 parts stannic chloride and 100 parts by volume of methyl alcohol. Therefore, this solution was used for all subsequent work on dipped SnO_2 films.

In order to obtain conducting SnO_2 films, it was decided to investigate the dipping technique at 400 F, in the hope of obtaining information at this

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(1) McMaster H. A., "Conductive Coating for Glass and Method of Application", U. S. Patent 2,429,420 (October 21, 1947).

temperature on the factors affecting conductivity. At this temperature, the film resistances varied from greater than 1000 megohms ("nonconducting") to about 5 megohms between 1/2-inch probes. The variations in film resistance were not merely random scattering, but, rather, there appeared to be a trend in resistance with time of film preparation. The first films made exhibited higher resistance values than those prepared later. The possibility that aging of the stannic chloride solutions had some effect on the resistance of the resulting films was eliminated by comparing films formed from aged solutions with those formed from freshly prepared solutions. The resistance variations will be discussed in more detail later in this section.

The possibility of forming TiO_2 films by the dipping method was investigated at the same time as the possibility of forming SnO_2 films by dipping. A solution of $TiCl_4$ in 95 per cent ethanol was found to give the best TiO_2 films. The first films made were nonconducting, even when an application temperature of 400 F was used. However, after the $TiCl_4$ solution had aged for about 6 weeks, conducting films were obtained at this temperature. Film resistances generally were in the range 20 - 50 megohms between 1/2-inch probes. A small area on one of the films had a resistance of 1 megohm between 1/2-inch probes. Use of a freshly prepared solution again resulted in the formation of nonconducting films. This solution was then refluxed for 1 hour in an attempt to accelerate the aging process. After this treatment, films with resistances of 100 to 200 megohms between 1/2-inch probes could be prepared. The refluxed solution contained small amounts of white precipitate, but the solution aged at room temperature did not form this precipitate.

Additional TiO_2 and SnO_2 films were prepared subsequently by dipping, using application temperatures of 300 F and 250 F, as well as 400 F. The results are summarized in Table 1.

TABLE 1. EFFECT OF APPLICATION TEMPERATURE ON RESISTANCE OF TiO_2 AND SnO_2 FILMS

Type of Film	Application Temperature, F	Resistance Between 1/2-Inch Probes, megohms
SnO_2	400	5 - 50
SnO_2	300	20 - 200
SnO_2	250	Nonconducting
TiO_2(1)	400	20 - 50
TiO_2	300	20 - 50
TiO_2	250	Nonconducting

(1) Aged solution.

The ranges of resistance values given in the preceding table are the ranges in which most of the values fell. A few films with lower (1 megohm) resistances were prepared. Also, some with higher resistances were obtained. It is to be noted that SnO_2 films exhibited about a fourfold increase in resistance on decreasing the application temperature from 400 F to 300 F. TiO_2 films, on the other hand, had about the same resistance at both temperatures. In most cases, films formed at a temperature of 250 F were nonconducting; a few films had resistances in the range 500 - 1000 megohms between 1/2-inch probes.

During the investigation on SnO_2 and TiO_2 films formed by dipping, it appeared that film resistance was dependent on baking time. In order to test the effect of baking time, a series of SnO_2 and TiO_2 films was baked at 400 F for several days. Minimum resistances for both types of film were observed after approximately a 24-hour baking time, after which resistance again increased. The average minimum resistance for the films was 50 megohms for TiO_2 and 15 megohms for SnO_2 films. Continued baking finally resulted in nonconducting TiO_2 films, whereas the resistances of SnO_2 films were about 200 megohms after 7 days. Although these data indicate a minimum resistance after a baking time of about 1 day, they are not conclusive, since an additional factor, ambient humidity, was not controlled during the baking period.

In order to check the effect of ambient humidity on resistance during postheating, both SnO_2 and TiO_2 films were postheated for 1 day at 300 F in a controlled-humidity atmosphere. The data obtained showed that minimum resistance was obtained if the partial pressure of water vapor in the baking atmosphere was 70 to 80 mm of mercury. Using this optimum humidity, the effect of baking time on resistance was checked again. For TiO_2 films, the minimum resistance was obtained after about 1 day, as before. The data on SnO_2 films were more erratic, but indicated approximately a 1-day baking time for obtaining the minimum resistance.

The effects of added impurities were investigated by adding stannous chloride, antimony chloride, hydrogen fluoride, and indium chloride to the stannic chloride solutions. Stannous chloride was used to test the possibility of increasing the conductivity by controlling the valence of the tin in the oxide film. Additions of indium and antimony oxides and fluoride ion increased the conductivity of SnO_2 films formed at high temperatures (from previous work at Battelle). The scatter in the resistance values obtained was such that no conclusions could be drawn as to the effect of the impurity additions.

During these investigations on films formed by dipping, it was found that the temperature differential between the solution and the glass plate at the time the plate was dipped had an important effect on the resistance of the resulting film. If both the solution and the glass plate were heated prior to dipping, or if neither plate nor solution was heated, nonconducting films were formed, regardless of the length of the postheating treatment.

It appears that the solution-dipping method has some promise for the production of high-resistance coatings for static dissipation, but little or no promise for use in forming coatings having resistances of 100 ohms per square or less.

Formation of Oxide Films by Vapor Impingement

Attempts were made to form oxide films by passing the vapor from a volatile anhydrous metal salt over heated glass surfaces. The moisture required for conversion to the oxide was to be supplied from the surrounding atmosphere.

Preliminary Studies

Attempts were made to produce conducting SnO_2 coatings at temperatures ranging from 100 to 400 F, by bubbling dry air through anhydrous $SnCl_4$ and then flowing the $SnCl_4$-laden air over a hot glass surface. Only at temperatures of about 400 F could clear, conducting SnO_2 films be produced. The films were about 700 to 1000 angstroms thick, as estimated from interference colors, and exhibited resistances of about 5 to 20 megohms between 1/2-inch probes. At a glass temperature of about 250 F, only a very thin film and nonadherent powder were formed. Both were nonconducting. At a temperature of about 100 F, a wet coating was formed which immediately clouded and solidified. This material was probably the hydrated chloride. These latter films, when baked for periods of 10 to 60 minutes at temperatures from 200 to 400 F, were converted to clear nonconducting films. During the preparation of these SnO_2 coatings, the humidity was varied by introducing moist air in a concentric envelope around the cone of $SnCl_4$ vapor. The effect of added moisture was to increase the powder formation.

In addition to the $SnCl_4$-to-SnO_2 conversion, oxide-film formation was attempted, using SnI_4, $SbCl_3$, $CdBr_2$, and mixtures of $SbCl_3$, and $SnCl_4$ as the starting materials. With molten SnI_4 as the vapor source, no film was formed at temperatures up to 400 F. Clear, but nonconducting, coatings of antimony oxide could be prepared at temperatures as low as 220 F. Cadmium bromide gave only a white nonadherent deposit, even at 450 F. With mixtures of $SbCl_3$ and $SnCl_4$ containing less than 10 per cent $SnCl_3$ by weight, clear films having resistances of about 10 megohms between 1/2-inch probes were produced at 400 F.

In previous work at Battelle on high-application-temperature films, overcoating SnO_2 films with a thin layer of antimony oxide resulted in increased conductivity.

In the present work, posttreatment of conducting SnO_2 films produced at 400 F by flowing $SbCl_3$ vapor over the SnO_2 film at a glass temperature of 300 to 350 F resulted in a decrease in resistance from 5 megohms to 0.5

megohm between 1/2-inch probes. This decrease occurred only in those areas where a very thin film of Sb_2O_3 was deposited. In those areas where a thicker layer of Sb_2O_3 (as determined by change in interference color) was deposited, the resistance increased. Since Sb_2O_3 films are not conducting, it is believed that the decrease in resistance obtained by overcoating with very thin films of Sb_2O_3 is due to (1) formation of a low-resistance layer at the interface of the Sb_2O_3 and SnO_2 layers, possibly by diffusion of the Sb_2O_3 into the SnO_2, or (2) formation of a thin layer of conducting Sb_2O_3 due to the introduction of lattice strains in the Sb_2O_3 layer. As the thickness of the Sb_2O_3 layer is increased, the additional material probably is deposited in a structure which is nonconducting, thus providing an insulating top layer and increasing the over-all film resistance.

Addition of fluoride ion in spraying solutions used to form high-application-temperature SnO_2 in previous work at Battelle reduced the resistivity of these films. When $NH_4 \cdot HF_2$(1) or HF additions were made to $SnCl_4$ in the present work, no film formation was obtained at 350 to 400 F.

This preliminary work on film formation by vapor impingement permitted the following general observations to be made. First, for best film formation, the design of the apparatus should be such that the metal chloride vapor does not come in contact with the water vapor, except in a zone very close to the hot glass surface. Such a design would minimize the homogeneous gas-phase reaction between the two materials (water vapor and metal chloride vapor) and thus make more of the material available for the heterogeneous reaction on the hot glass surface. Secondly, the application temperature required to form conducting films seemed to be higher than the bubbling temperature of the plastic laminate of safety glass. Therefore, the design of the heating apparatus should be such that a temperature gradient is produced through the glass, so that the exposed surface is hotter than the back surface of the glass. The heating apparatus should also be designed so that a uniform temperature is maintained over the glass surface to which the film is applied.

Further Investigations With the Vapor-Impingement Method

The types of apparatus used in subsequent work are described under "Experimental Details". Glass plates were heated by (1) an electrical grid heater suspended from 1 to 2 inches from the glass surface, (2) a hot-air blast, and (3) placing the plates in an enclosed furnace. The first two methods permitted temperature gradients as high as 100 F to be produced between the front and back surfaces of the glass. However, temperature gradients of as much as 80 F were obtained over the front surface of the glass. The enclosed furnace used for heating, although not designed to

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(1) $NH_4 \cdot HF_2$ and HF additions to $SnCl_4$ are claimed to lower the resistance of the SnO_2 films; see Lytle, W.O., and Junge, A. E., "Electroconductive Products and Production Thereof", U.S. Patent 2,566,346 (September 4, 1951).

permit cooling of the back surface of the glass, probably could be adapted to this purpose if the heating method were otherwise satisfactory. The furnace heating had the advantage of maintaining a uniform temperature over the surface of the glass. With all methods of heating, the metal chloride and water vapor were introduced through separate inlets near the glass surface. Best results were obtained when both inlets were close together and near the glass surface.

The most satisfactory inlet design consisted of a set of concentric inlets placed close to the glass surface. An area approximately 3 inches in diameter could be filmed, using one set of inlets.

The results obtained with the electrical grid heater were erratic. Films were formed when using temperatures of 250 to 375 F. In some cases, SnO_2 films having a resistance of 100 megohms between 1/2-inch probes could be formed on 1/4-inch safety glass without bubbling the plastic, whereas, in other cases, the plastic was badly bubbled and the films were nonconducting. With the hot-air-blast method of heating, films were formed only directly in front of the hot-air outlet. Very large (80 F) temperature gradients were produced over the glass surface. In the case of the enclosed-furnace heating, results also were very erratic. It appeared that relative rates of introduction of water vapor and metal chloride vapor are important factors in determining the type of deposit formed. Too high a ratio of water vapor to chloride vapor results in a powdery deposit, whereas a low ratio results in no film formation. In a few cases, proper adjustment of rates of flow of water vapor and metal chloride vapor permitted formation, at 250 F, of SnO_2 films having resistances of 50 megohms between 1/2-inch probes.

Some work was done on use of undercoatings for vapor-impinged SnO_2 films. Undercoatings that were tested were MgF_2, TiO_2, VO_2, and PbO_2, all applied at temperatures below 300 F. The wide variations in resistance obtained with and without undercoating prevented drawing any conclusions as to the effect of these undercoatings.

As in the case of the dipping method, the vapor-impingement method shows some promise for use in the formation of high-resistance films for static dissipation, but little or no promise for the formation of low-resistance films.

Formation of Oxide Films by Decomposing Salt Vapors at Low Pressure

Information obtained during previous work at Battelle on high-application-temperature films indicated that the rate of formation of SnO_2 from $SnCl_4$ vapor is accelerated at low pressures, so that clear conducting films could be produced at temperatures as low as 550 F. Therefore, it was decided to investigate low-pressure decomposition at lower temperatures. The apparatus used is described under "Experimental Details".

Pressures in the range < 1 mm to 300 mm of mercury and temperatures in the range 250 to 284 F were used. In this pressure range, the only film that could be formed was deposited at 485 F. This film had a resistance of 500 megohms between 1/2-inch probes. At lower temperatures, either a hydrated film or no film was formed. Subsequently, $SnCl_4$ was introduced with the apparatus at atmospheric pressure. At 385 F, a film about 1000 angstroms thick (estimated from interference color) and having a resistance of about 25 megohms between 1/2-inch probes was formed. A film formed at 250 F about 700 angstroms thick had a resistance of 100 megohms between 1/2-inch probes. These films were formed in about 15 minutes.

Thus, it appears that, although the rate of film formation is increased by decreasing the pressure when high application temperatures are used, the opposite effect occurs at lower temperatures.

Duo-System Films

Differences in nucleation and growth of conducting and nonconducting SnO_2 films have been suspected as probable reasons for the difference in electrical resistivity of these films.

It was decided to deposit a second layer of SnO_2 on a highly conducting SnO_2 film in order to determine whether or not the structure necessary for low resistivity could be induced in the second layer by the first layer. Second layers of SnO_2 were applied by homogeneous precipitation, vapor impingement, and dipping and postheating onto low-resistance films produced by spraying $SnCl_4$ solution at temperatures of 1000 - 1200 F.

The results of this investigation are shown in Table 2.

The calculated resistance of the second layer is based on treating the double-layer system as two resistances in parallel. The thickness of the second layer was estimated, from interference color changes, to be 1000 angstroms. From these results, it is apparent that resistances of the order of 10^4 ohms per square can be obtained on the conducting substrate, whereas films formed under identical conditions on glass substrate have resistances of the order of 10^8 ohms per square or more.

The second layer formed by homogeneous precipitation, although showing some promise from the standpoint of electrical properties, exhibited poor optical properties (high haze). However, the beneficial effect of the SnO_2 undercoatings on the resistance of films formed by vapor impingement

TABLE 2. RESISTANCE CHANGES AFTER REFILMING OF CONDUCTING SnO2 FILMS

Method for Second Film Application	Application Temperature of Second Film, F	Usual Resistance of Second Film on Glass, ohms/square	Resistance of First SnO_2 Film, ohms/square	Final Resistance of Both Films, ohms/square	Calculated Resistance of Second Film, ohms/square
Vapor impingement	300	100 megohms up	12,000	4,000	6,000
	300	Ditto	6,000	3,000	6,000
Precipitation from solution	200	"	8,200	2,900	2,100
Deposition by dipping	250	"	3,400	3,000	25,000
	250	"	1,900	1,600	10,000

and dipping methods suggests that further investigation is warranted, particularly from the standpoint of producing high-resistance films for static dissipation.

Evaporation of Metal Oxide and Sulfide Films

Some preliminary investigations were made on evaporated metal oxide and sulfide films. Two types of deposit can be obtained by evaporating some metal oxides. At low pressures (10^{-4} mm or less), metallic films are obtained, whereas at higher pressures (several microns), oxide films are formed. In the case of metal sulfide, evaporation results in the formation of the sulfide film even at pressures as low as 10^{-4} mm of mercury. The use of the metal oxide as the source material for vacuum evaporation was of interest, both for the formation of metallic films for conversion to the oxide and for direct evaporation of the oxide film.

The oxide films that were evaporated directly were In_2O_3 and SnO_2. Even at higher pressures (up to 50 microns), the deposits appeared to contain some unoxidized metal, as evidenced by the fact that the transmission increased upon subsequent thermal oxidation of the films. Resistances in the range 1 - 100 megohms between 1/2-inch probes were measured for SnO_2 films and 0.1 - 1.0 megohm for In_2O_3 films. Maximum light transmission was 70 per cent, even after the thermal-oxidation treatment.

The sulfide films produced by direct evaporation were CdS, In_2S_3, and PbS. These sulfides were nonconducting and could not be converted to the oxide at temperatures below the bubbling temperature of the laminate. The PbS films were opaque, and the CdS and In_2S_3 films had a yellow transmission color and transmitted approximately 60 per cent of white light. This work on oxides and sulfides was conducted at the same time as work on the oxidation of evaporated metal films, and the promising results obtained by the latter method seemed to warrant discontinuing the work on the direct evaporation of oxides in order that maximum effort could be directed to the investigation of the oxidation of metal films.

Formation of Oxide Films by Oxidation of Evaporated Metal Films

Survey of Oxidation Methods

Preliminary work on the formation of oxide films by the oxidation of evaporated metal films included a survey of several possible methods of oxidizing the metal films. The metal films used for this survey were tin, cadmium, and indium films deposited by vacuum evaporation of the metals at a pressure of about 10^{-4} mm of mercury. The methods of oxidation studied were heating the metal film in air and oxygen, exposing the film to mixtures of air with corrosive vapors (HCl, $TiCl_4$, and $SnCl_4$) at 250 F, subjecting the film to high-frequency electrical discharge (Tesla coil) in air, oxidizing the films electrolytically, oxidizing in solutions of soluble oxidizing agents, oxidizing the films with insoluble oxidizing agents(1), and oxidizing by glow discharge.

Metal films were heated to temperatures in the range 250 - 400 F at air pressures in the range 1 - 750 mm of mercury. Some conversion of tin films to the oxide was obtained at temperatures of 350 F or higher. In general, only small areas of the films were oxidized, and these areas were nonconducting. Indium films heated under similar conditions formed transparent conducting oxides at temperatures of about 400 F. Resistances of the order of 10^4 ohms per square were obtained. At 350 F, less complete conversion was obtained and, again, resistances were of the order of 10^4 ohms per square. At 300 F, only isolated areas of the films were oxidized, but these areas were conducting. Resistances of the transparent areas were of the order of 10^6 ohms per square. There was no apparent correlation between the pressure during conversion and the degree of conversion to the oxide.

Metal films exposed to corrosive vapors of HCl, $SnCl_4$, and $TiCl_4$ were converted to nonconducting films having poor optical properties.

Films subjected to high-frequency electrical discharge were converted to oxides having very poor optical properties. Light transmission was 30 - 50 per cent, and the films were extremely hazy. For the most part, the oxidized areas were nonconducting, but a few film areas exhibited resistances of the order of 10^6 ohms per square.

Films of tin and indium were subjected to a glow discharge with air as the discharge gas at a pressure of 100 microns. Although dependent upon the length of time the discharge was continuously maintained, the film temperatures rose to 250 to 350 F, in general. As a result of this treatment, a partial conversion of the indium films to the oxide was effected. The fact that the conversion was only partial was deduced from the fact that films which had been glow discharged, underwent further conversion when subsequently heat treated (as described in a later section of this report), as evidenced by increases in transmission. The resistance changes associated with the conversion were erratic. Because of the rise in film temperature to about 250 F, and the incompleteness of the conversion, this method was considered to be inferior to the thermal conversion of evaporated films. Tin films were also subjected to the same glow-discharge treatment. No conversion could be produced.

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(1) The insoluble agents were applied to the film as pastes and also as slurries in which the films were immersed.

Electrolytic oxidation of indium films was attempted with sulfuric acid solutions similar to those used for anodizing aluminum. Also, alkaline solution (sodium carbonate) and a neutral solution (sodium chloride) were tried. In all cases the indium films were oxidized, but they either peeled or dissolved in the electrolyte.

Attempts were made to oxidize indium films in solution using sodium bismuthate, ammonium persulfate, and potassium permanganate as oxidizing agents. In neutral solution, these oxidizing agents were without apparent effect. In acid and alkaline solutions, the film was destroyed.

Since some insoluble oxidizing agents are known to cause the formation of adherent oxide coatings on bulk metals, it was decided to investigate their use as oxidizing agents for metal films. A paste was formed by wetting the insoluble material with distilled water or a 10 per cent sodium chloride solution. The metal film was first covered with a strip of filter paper wet with the same solution as that used to make the paste. The paste was then applied over the paper separator. In addition to filter paper, Methocel and gelatin strips were tested as separators. The oxidizing agents that were tested were MnO_2, $AgIO_3$, $Hg(IO_3)_2$, $Hg_5(IO_6)_2$, $Pb(BrO_3)_2$, $AgBrO_3$, $AgMnO_4$, Ag_2CrO_4, and $Pb(IO_4)_2$. The contact time between the oxidizing agent and the metal film ranged from 10 minutes to 24 hours. The only materials that oxidized the indium films were MnO_2, $AgMnO_4$, and $Pb(BrO_3)_2$. The films oxidized with MnO_2 were extremely hazy, and the resistances were of the order of 10^5 ohms per square. The use of $AgMnO_4$ resulted in a deposit of what appeared to be MnO_2 on the surface of the film. When this deposit was removed by rubbing with a rough cloth, an adherent coating similar to that formed when using MnO_2 as the oxidizing agent was exposed. $Pb(BrO_3)_2$ oxidized the indium films rapidly (10 minutes); however, the oxide often dissolved as it was formed. In those cases in which the film did not dissolve, the optical properties were poor and resistance was of the order of 10^5 ohms per square or higher.

The same oxiding agents were tested on tin films. None oxidized the metal completely, and the oxidized areas were nonconducting.

Cadmium mirrors were treated with MnO_2, $AgMnO_4$, and $Pb(BrO_3)_2$. The $Pb(BrO_3)_2$ completely oxidized the cadmium in about 2 minutes, whereas MnO_2 and $AgMnO_4$ required about 1/2 hour for complete oxidation. In all cases, the oxide did not adhere to the glass.

Attempts were also made to oxidize metal films by immersing them in a rapidly stirred slurry of oxidizing agent and water. In almost all cases the film was removed from the glass. In those cases in which a film remained on the glass, the adherence was poor and the optical properties were inferior to those of the films oxidized using the oxidizing agent as a paste.

Summary of Survey Investigations

The preliminary work on the oxidation of metal films indicated that all methods involving solutions, pastes, or corrosive vapors, in those cases in which oxidation occurred, resulted in films having very poor optical properties, namely, low transmission and high haze values. Conversion by glow-discharge treatment also showed little promise.

Some of the other methods, such as dipping and postheating and vapor impingement, showed some promise for producing the high-resistance coatings but little promise for making coatings capable of meeting the low-resistance requirements. The precipitation of oxide films from solution, the decomposition of metallo-organic compounds, and direct evaporation of sulfides and oxides showed little, if any, promise for either type of coating. The one method that showed the greatest promise for formation of low-resistance films with the desired electrical and optical properties was thermal oxidation of metallic indium films. There was also indication that the conditions under which the metal films were prepared had an important effect on the ease of oxidation of the film. Thicker films definitely were found to be more difficult to oxidize than thinner films. In subsequent work, emphasis was placed on the thermal-conversion methods and controlled evaporation conditions.

Atmospheric-Pressure and High-Pressure Thermal Conversion of Metal Films to the Oxide

The preliminary work on thermal conversion of metal films to the oxide indicated that temperatures higher than the bubbling temperature of the plastic laminate in safety glass might be required to oxidize metal films completely. The information obtained by communication with a glass manufacturer indicated that safety glass might be heated to temperatures higher than 250 F without detrimental effect to the plastic laminate, provided the heating is done under high pressure. Therefore, thermal conversion was investigated at pressures of air and oxygen as high as 80 psi, as well as at atmospheric pressure. For atmospheric-pressure conversions, the films were heated in an enclosed oven and also by use of an infrared heat lamp.

High-pressure conversion was conducted in a small bomb. In the initial work, the bomb was heated to the desired temperature in a furnace. Indium-metal films prepared from indium oxide at evaporation pressures ranging from about 0.1 to 20 microns were oxidized at pressures of air and oxygen up to 80 psi and temperatures varying from 250 to 400 F. At temperatures of 300 F or more, no significant differences were obtained with indium films prepared at different pressures or oxidized at different pressures. The transmission of the oxidized films was about 75 per cent, and resistances were in the range 10^4 - 10^6 ohms per square. However, at a temperature of 250 F, only those indium films that were prepared at higher pressures (about 20 microns) could be oxidized. These oxidized films had resistances similar to those obtained at higher temperatures.

Some safety glass plates included in the above work bubbled around the edges at 350 F and a pressure of 80 psi. It was believed that there were rather large temperature gradients throughout the bomb when it was heated in air in a furnace. It is quite likely that the regions near the walls of the bomb were considerably hotter than the center region of the bomb. In order to obtain a uniform temperature throughout the bomb, it was heated by immersion in a constant-temperature oil bath for subsequent work; using this method, safety glass could be heated to 350 F under a pressure of 65 psi without detrimental effect to the plastic laminate. Indium films vacuum evaporated both from the metal and from the oxide at pressures ranging from 0.1 to 20 microns of mercury were treated under various oxygen and air pressures in the temperature range 250 - 400 F.

All the In-O films made by heating with the oil bath were nonconducting. Indium films could be oxidized at temperatures as low as 250 F, providing they were made at pressures of about 10 microns or more. Cadmium and tin films could not be oxidized at temperatures below 400 F, and even at this temperature most films were oxidized only in random areas.

Atmospheric-pressure conversions conducted in an enclosed furnace or by heating with an infrared lamp resulted in the formation of In-O films with about 75 per cent transmission and resistances as low as 10^4 ohms per square. Here, again, the pressure during evaporation seemed to have an important effect on the ease of conversion of the metal film; films formed at high pressures (10 microns or more) were readily oxidized at temperatures in the range 250 - 300 F.

The following conclusions were drawn from this work on various methods of thermal conversion.

(1) There appears to be no advantage to the use of high pressures during conversion other than that safety glass can be heated to a higher temperature without bubbling the laminate. The resistances of films oxidized at high pressures are generally higher than the resistances of similar films oxidized at atmospheric pressure. If the In-O system is an excess-metal oxide, the greater resistance at higher pressures may be caused by the inclusion of oxygen or other gases in the film.

(2) The temperature at which a metal film can be oxidized is dependent on the pressure during evaporation.

(3) Indium can be oxidized more easily than can cadmium or tin.

In view of these conclusions, the following program was adopted for further work. First, the investigation of the oxidation of evaporated metal films would be restricted, at least temporarily, to indium films, since this material showed the most promise with regard to oxidation at a temperature of 250 F. Second, since pressure during evaporation has such an important effect on the ease of conversion of the metal films, a survey would be made on the effect of evaporation parameters on film structure and, thus, on ease of conversion. Third, oxidation would be carried out, if possible, at reduced pressures in the vacuum system in an attempt to attain lower film resistances (since high-pressure conversion had been shown to give oxide films of higher resistance than those converted at atmospheric pressure). It was believed that this program would permit determination of the effect of the evaporation parameters on the ease of oxidation of the metal film and on the electrical and optical properties of the resulting oxide film.

Low-Pressure Thermal Oxidation of Evaporated Indium Films

A brief literature survey was made to determine the effects of evaporation parameters on the structure of evaporated indium films. Parameters that are known to affect the film structure are evaporation rate, pressure during evaporation, source-to-substrate distance, and substrate temperature. The information available as to the effect of these parameters on structure indicates that decreased evaporation rate, increased pressure, and increased source-to-substrate distance all favor the type of structure that is easily oxidized. The effect of substrate temperature on ease of oxidation was not apparent, since two opposing trends are possible with different substrate temperatures. Increased substrate temperature was shown to favor the formation of films whose structure differs from the bulk metal structure (this is desirable, from the standpoint of ease of oxidation). However, increasing temperature tends to anneal the film after it is deposited. The over-all effect of substrate temperature insofar as ease of conversion is concerned was not known.

The general procedure used in investigating the evaporation parameters was as follows. Evaporation pressures of 10^{-5} mm and 6 microns of mercury were used. The first value is that maintained with the diffusion pump connected to the vacuum system, and the latter value was that maintained by using only the forepump. The pressure could be conveniently maintained constant at these two values during the evaporation procedure. Evaporation rates were varied in such a manner that indium films having a resistance of 20 kilohms per square were produced in periods ranging from 2 to 20 minutes. Power input to the evaporator coil was maintained constant during the formation of each film. The quantity of indium in the coil was such that only a small fraction of the total amount was used during a given evaporation. It was believed that sufficiently close control could be maintained over the evaporation rate by this procedure, unless film characteristics were extremely sensitive to small changes in evaporation rate. Source-to-substrate distance was varied from 5 to 15 cm, and substrate temperatures investigated were in the range from slightly above room temperature to 220 F.

Film resistance was measured during the evaporation procedure and, after evaporation was completed, the films were permitted to age at room temperature in vacuum until a constant resistance was attained. The films formed by slow evaporation exhibited no resistance change during aging at room temperature, whereas those prepared with a rapid evaporation rate generally required about 10 minutes to attain a constant resistance. This final constant resistance was always higher than the resistance immediately after evaporation.

Two possible reasons for changes in resistance of rapidly evaporated films on room-temperature aging are apparent. One possibility is that rapidly evaporated films anneal during the room-temperature aging, whereas slowly evaporated films anneal as they are formed. It is expected, however, that annealing should be accompanied by resistance decreases. The second possible reason is that films formed at rapid rates take up more oxygen or other gases after formation, whereas slowly evaporated films have equilibrium amounts of gas included during the evaporation. The inclusion of gases would be expected to increase the resistance, as was observed in this work.

After the films had attained constant resistance at room temperature, they were heat treated at 200 F until a constant resistance was attained at this temperature. The films were heated with an electrical grid heater suspended parallel to and about 2 inches from the film surface. The final resistance, with a few exceptions, was lower than the room-temperature resistance. The resistance decrease could be due either to outgassing or to further annealing, or to both. The films were then heated to about 250 F. In some cases, oxidation began to occur at about 230 F, as evidenced by rapid increases in optical transmittance. In those cases in which a noticeable rate of oxidation did not occur at 250 F, sufficient air was introduced into the vacuum system to increase the pressure to about 1 cm of mercury.

The following observations were made on the effects of the various evaporation parameters on the ease of oxidation of the metal film.

Evaporation Pressure

Films formed at pressures of 10^{-5} mm could not be oxidized at 250 F, regardless of the values used for the other evaporation parameters. Films formed at a pressure of 6 microns could be oxidized at 250 F, providing suitable values were used for the other parameters.

Substrate Temperature

Increasing the substrate temperature, with the values of the other evaporation parameters maintained constant, resulted in the formation of films that were increasingly difficult to oxidize. When the substrate temperature was 220 F during evaporation, the films could not be oxidized, even with prolonged (several days) heating at 250 F.

Source-to-Substrate Distance

The effect of source-to-substrate distance on ease of oxidation is illustrated in Table 3.

TABLE 3. EFFECT OF SOURCE-TO-SUBSTRATE DISTANCE ON EASE OF OXIDATION OF EVAPORATED INDIUM FILMS

Film	Source-to-Substrate Distance, cm	Evaporation time, minutes	Transmission After Conversion, per cent	Resistance of Metal Film, kilohms/square	Resistance[1] of Oxide Film, kilohms/square
1-4-1	5	14.5	65	18	1.9
12-27-1	10	18	72	10	6.2
12-23-1	10	15	80	16	2.6
12-29-2	15	17	85	20	1.6
1-4-2	15	18	90	20	2.8

(1) Prior to exposure to air at atmospheric pressure (to be discussed later).

The films were oxidized at 230 to 250 F. The pressure used during the evaporation and oxidation of the above films was 6 microns of mercury. The variations in evaporation period used in preparing these films are not sufficiently large to produce any noticeable effect on the ease of conversion, as shown by the investigation of the effect of evaporation rates (discussed later).

The light transmissions of films formed at greater source-to-substrate distances are highest, indicating more complete conversion to the oxide. In addition, films formed at the 15-cm distance were converted much more rapidly, with oxidation beginning in some cases at 230 F, whereas those films made at 5- and 10-cm distances did not oxidize much below 250 F. It is possible that the effect of substrate distance was entirely due to the greater heating effect of the source on the substrate at shorter distances, since no provisions were made for cooling the substrate during evaporation. At a distance of 5 cm, the substrate was heated to about 150 F, whereas, at the 15-cm distance, the substrate temperature was about 100 F. As was previously pointed out, the use of elevated substrate temperatures during evaporation causes subsequent oxidation of the films to be difficult.

Evaporation Rate

The effect of evaporation rate on the ease of oxidation of indium films is illustrated in Table 4. Actual rates are not given, since film thicknesses were not known. The evaporation times given are the times required for the film resistances to reach the values given in the third column of the table. These times, then, for films of equal resistance, may be considered to be rough measures of the evaporation rates(the longer the time, the lower the rate). Of course, the correspondence is not necessarily quantitative, since films made with different rates may have different resistivities. Films prepared at lower evaporation rates were more completely oxidized, as evidenced by the high light transmission. In general, they also had lower resistances than those prepared at higher evaporation rates. A source-to-substrate distance of 15 cm and a pressure of 6 microns of mercury were used during formation of the films. The films were oxidized at a temperature of 250 F and a pressure of 6 microns of mercury. In some cases for which the higher evaporation rates were used, small amounts of air, sufficient to increase the pressure to about 1 cm of mercury, were introduced to permit the oxidation to proceed. The time required for oxidation was generally 5 minutes or less. Those films that were not completely oxidized in this period did not appear to undergo any significant amount of oxidation when heated at 250 F for 1/2 hour either at reduced pressure or at atmospheric pressure. However, most films that transmitted from 50 to 75 per cent of white light increased in transparency on subsequent aging for several days at 230 F in air at atmospheric pressure. The effects of aging are discussed in a later section of this report.

TABLE 4. EFFECT OF EVAPORATION RATE ON EASE OF CONVERSION

Film	Evaporation Time, minutes	Resistance of Metal Film, kilohms/square	Resistance(1) of Oxide Films, kilohms/square	Transmission, per cent
1-20-1	3	20	12	25
12-28-1	2	46	5.6	65
1-27-1	5	20	3.4	80
12-29-1	7	21	2.1	80
1-4-2	10	20	2.8	90
12-29-2	17	20	1.6	85

(1) Prior to exposure to air at atmospheric pressure.

As a result of the investigation of the evaporation parameters, a set of values, not necessarily optimum, was selected for the preparation of metal films that could readily be converted to the oxide. A source-to-substrate distance of 15 cm and a pressure of 6 microns of mercury were used for further work. The evaporation rate was adjusted so that a period of 10 to 20 minutes was required to produce a metal film having a resistance of 20 kilohms per square. The substrate temperature was about 100 to 110 F, since no provisions were made for cooling to eliminate the slight heating of the substrate due to radiation from the evaporation source.

A number of films were made with the above values for the evaporation parameters. The resistances of the oxide films made from these metal films (with resistances of approximately 20 kilohms per square) ranged from 1.3 to 3 kilohms per square, and light transmissions were in the range 80 - 88 per cent.

Multiple-Layer Films

A few attempts at making multiple-layer films during the preliminary work on the In-O system indicated that films of good transparency low resistance could be formed by this method. Two methods of producing multiple-layer In-O films were studied. The first method consisted of depositing and converting a single-layer indium film, subsequently cooling the substrate, and then depositing and converting a second metal layer. The other method consisted of depositing and converting a single-layer film, followed by the deposition of additional indium on the substrate maintained at 250 F, thereby effecting simultaneous deposition and oxidation of the indium. Attempts to deposit and to oxidize the metal simultaneously on a heated (250 F) glass substrate did not yield the oxide, but gave a metal film that could not be converted to the oxide by prolonged heating at 250 F. If, however, a single-layer oxide film was applied to the glass first, simultaneous evaporation and oxidation of an additional layer could be effected, providing a slow evaporation rate was used.

The first method, evaporation followed by oxidation, permitted the formation of a double-layer film having a resistance of 700 ohms per square and a light transmission of 75 per cent. Aging in air for several days at 230 F increased the transmission to 80 per cent. Resistance changes on aging will be discussed in a later section.

The second method, simultaneous evaporation and oxidation, permitted the formation of several double-layer films having resistances of 340 to 520 ohms per square and light transmissions of 50 to 65 per cent. Aging at 230 F for several days increased the light transmission to 75 to 88 per cent.

Oxidation of Evaporated Indium Films at Low Pressures by Application of a D-C Load

As discussed in a later section of this report, during load testing of In-O films prepared as described in the previous section, some films that were incompletely oxidized (light transmission of 50 to 75 per cent) were further oxidized (light transmission of 80 to 85 per cent) by prolonged application of a d-c load of about 100 volts. Therefore, it was decided to investigate application of a d-c load as a method of heating films for conversion to the oxide.

In order to obtain a power input sufficient to heat the films to 250 F in the vacuum system, it was necessary to begin with metal films having resistances no greater than 2000 ohms per square. This limitation on the maximum resistance was due to the limitation on the applied voltage. Voltages higher than about 150 volts caused breakdown of the bus bar-film junction. In this work, silver-paint bus bars were applied to the glass before depositing the film. Apparently, this resulted in thinner film and higher resistance at the junctions, which, in turn, caused localized heating and burn-out when the load was applied. The evaporation conditions used when preparing these films were identical to those described in the previous section, except that films of greater thickness were made.

Indium films having resistances as low as 500 ohms per square could be oxidized readily with a d-c load at a pressure of 6 microns and at a temperature of 250 F, provided that an evaporation time of not less than 30 minutes was used to prepare the metal film.

Using the load-heating method, single-layer In-O films having resistances in the range 400 to 1000 ohms per square in vacuum and light transmissions of 80 to 90 per cent were prepared.

Double-layer films formed by the method of simultaneous evaporation and oxidation in conjunction with load heating exhibited resistances in the range 200 - 300 ohms per square in vacuum and had light transmissions as high as 85 per cent.

Load heating has certain advantages over external grid heating. Load heating permits oxidation of thicker metal films than is possible with grid heating. Furthermore, load heating apparently heats the film to the desired temperature with less heating of the substrate than is the case with the grid heater.

Testing of In-O Films Under D-C Loads

In-O Films, prepared by thermal conversion of evaporated metal films, were subjected to d-c loads to determine: (1) their ability to withstand high electrical loads, (2) whether or not the conductivity is primarily electronic, and (3) the effects of heating by the electrical load on the optical properties of the films.

Several In-O films on window glass were subjected to d-c loads of 300 to 1100 watts per square foot. Extended tests were carried out only at the lower power dissipations, since the plates broke after a few minutes when heavily loaded, even in moving air.

Subsequently, In-O films were applied to heat-shock-resistant Vycor glass by the evaporation-conversion process and tested in moving air. One film was tested at 530 and 950 watts per square foot. A second film was tested at 430 watts per square foot. The tests on these films and on the films on glass showed that the films were capable of withstanding high electrical loads without destruction by ionic conduction or burn-outs. The Vycor-based films underwent resistance fluctuations during the tests. It is not known whether or not the glass-based films fluctuated in resistance, since the resistances were measured only at the start and end of the tests. For one film, the over-all change after 250 hours was small. In the case of the second film, the change was greater, and, after 168 hours, the film failed at the bus bar. No further tests were made. During load testing of the films, optical transmissions increased, indicating further oxidation. Also, there were some resistance changes. In some cases, the resistances increased, and in other cases, they decreased. The data are presented in Table 5.

TABLE 5. D-C LOAD TESTS ON In-O FILMS

Film	Load, watts/sq ft	Initial Resistance, ohms/square	Final Resistance, ohms/square	Duration of Test, hr
1-13-1	300	2000	2000	24
1-13-1	500	2000	--	0.5 (glass broke)
1-15-1	220	5500	--	0.25 (glass broke)
1-29-1	380	2200	--	0.5 (glass broke)
2-16-1	600	2300	2600	15.0
2-16-1	1100(1)	2500	--	0.25 (glass broke)
2-19-1	1080(1)	2100	--	0.25 (glass broke)
3-10-1	530(1)(2)	11000	10000	250
3-10-1	950(1)(2)	10500	9600	50
3-9-3	430(1)(2)	8750	14000	168 (bus bar junction failed)

(1) Tested in air stream of table fan.

(2) On Vycor glass.

Oxidation of Sputtered Metal Films by Glow Discharge

Attempts were made to convert several sputtered indium and tin films to the oxide by means of a glow discharge. The data are presented under "Experimental Details". The films were sputtered on glass in an argon atmosphere (at about 75 microns) with current densities of 3 to 6 milliamperes per square inch. The tin films had resistances of 10 to 10^6 ohms per square and light transmissions of 0 to 60 per cent. The indium films had resistances of 200 to 50,000 ohms per square and light transmissions of 0 to 50 per cent.

The films were subjected to a glow discharge at pressures of 40 to 125 microns. The film temperatures rose to 275 to 390 F during treatment. There was little or no conversion in the case of the tin films. Transmissions remained unchanged. A few of the films did undergo slight increases in resistance. In the case of the indium films, some oxidation was effected. However, in general, the light transmissions of the converted films were lower than those previously obtained by thermal conversion.

Four of the indium films that had been subjected to glow discharge were subsequently heated in air at a pressure of 6 microns and temperatures of 200 to 300 F to determine whether or not further conversion could be effected. The films were heated directly by passing a direct current through the films (load heating). In all cases, the light transmissions of the films were increased by the thermal treatment. The resistances and transmissions of the films after the load-heating conversion were in the ranges 270 - 1900 ohms per square and 24 - 80 per cent, respectively.

In view of the poor results obtained with glow-discharge conversion, both with sputtered metal films and with evaporated films (discussed previously), the glow-discharge conversion method is considered to be unpromising. It is not certain that <u>any</u> conversion can be attributed to the presence of the discharge, since film temperatures rose to 250 to 300 F during treatment, so that the limited conversion obtained may have been merely thermal conversion.

Oxidation of Sputtered Indium Films at Low Pressures by D-C Load Heating

Two indium films formed by sputtering were converted to the oxide by heating with a d-c load to a temperature of 250 F, at a pressure of 6 microns of mercury. The initial resistances of the metal films were 620 and 1600 ohms per square. After oxidation, the films had resistances of 475 and 410 ohms per square, respectively, in vacuum. The light transmission of these films was 75 per cent. Why the higher resistance-metal film had the lower resistance after oxidation cannot be determined from the limited amount of data available on sputtered films. It appears likely that more rigid control of the sputtering conditions must be exercised before consistent results can be obtained.

Thickness of In-O Films

Attempts were made to determine the thickness of a few In-O films interferometrically. The method requires that a suitable film edge, obtained either by scratching the film or by shadowing during film deposition, be available for measurement. It was found that the In-O films were so difficult to scratch that it was not possible to scratch through the films without scratching the glass substrate.

Film-thickness measurements were made on two indium metal films having resistances of 20 kilohms per square. These films were found to be 160 and 180 angstroms thick. Although the thickness change on oxidation is not known, these thickness values for metal films indicate that those In-O films (prepared by thermal oxidation of 20-kilohm-per-square metal films) probably are a few hundred angstroms thick.

The thicknesses of In-O films prepared by load heating of 500- to 1000-ohm-per-square metal film were estimated from the interference colors to be in the range 1000 - 2000 angstroms.

Resistance Instability of In-O Films

After evaporated indium films were oxidized at 250 F, they were permitted to cool to room temperature in vacuum. They were then exposed to air at atmospheric pressure. This exposure resulted in marked increases in resistance (a factor of two to six in 5 minutes). The films were then removed from the vacuum system and aged for several days at 230 F in air at atmospheric pressure. This aging was accompanied by an additional increase in resistance. The resistance increases were in the range of one to three orders of magnitude. Subsequent aging in the dark at room temperature for several days resulted in further resistance increases. The final high resistance differed from the resistance in vacuum by two to four orders of magnitude. In general, the resistance increase at each stage of the aging process was greatest for those films having the highest initial resistance.

The two sputtered indium films that had been converted thermally exhibited only small resistance increases on exposure to air and subsequent aging at room temperature.

The resistance changes of some low-resistance, thermally-oxidized, sputtered films, are shown in Table 6.

TABLE 6. RESISTANCE INSTABILITY OF In-O FILMS

Film	R_1, Resistance in Vacuum, ohms/square	R_2, Maximum Resistance After Aging in Air at Atmospheric Pressure, ohms/square	$\frac{R_2}{R_1}$
		Evaporated Films	
1-6-1	700	500,000	700
2-4-1	570	400,000	700
1-15-1	520	10,000	19
2-1-2	510	170,000	330
1-20-2	470	60,000	120
1-31-1	340	2,400	7
2-4-2	300	70,000	230
2-11-2	200	85,000	420
		Sputtered Films	
3-11-1	470	1,000	2.1
3-11-2	390	635	1.6

In addition to being smaller, the resistance increases of sputtered films occur much more slowly than is the case for evaporated films. The highest resistance values given in the table were attained after about 5 days in the case of the evaporated films and 20 days for the sputtered films. After 1 day's exposure to the atmosphere, the resistance of sputtered films had increased only about 10 per cent.

Reversibility of Resistance Changes of In-O Films

Several In-O films prepared by thermal conversion of evaporated indium films were tested for the permanence of the resistance increases. After the films had attained a high resistance on prolonged exposure to air, they were again placed in the vacuum system and heated to 200 F. The resistance decreased to approximately the same value as obtained before exposure to air. Cooling to room temperature in vacuum resulted in only a slight resistance change. Upon again exposing these films to air for prolonged periods, resistance increases similar to those observed on initial air exposure occurred.

This behavior suggests that the resistance instability of In-O films is largely due to inclusion of gases in the film on exposure to air.

Photoeffect in In-O Films

In-O films which had undergone large resistance increases on aging in the dark (in air) were observed to undergo large resistance decreases when illuminated. The resistance decreases varied from one to three orders of magnitude, with the largest changes occurring for films with the highest initial resistance in vacuum.

One film was subjected to three light-dark cycles, after which the film resistance was stable with respect to light-dark cycling.

No photoeffect was observed with thermally oxidized, sputtered films.

Stabilization of Resistance of In-O Films

Preliminary investigations have been made on stabilization of the resistance of In-O films formed by the thermal conversion of evaporated indium films. Since there is evidence that the resistance changes are due to inclusion of gases in the film on exposure to air, it was believed that application of a protective coating might serve to stabilize the resistance.

The films used for the stabilization studies were prepared as described in the section of d-c load heating. Overcoatings of MgF_2 and SiO (which are known to form durable, transparent films) were tested for their protective properties. These protective coatings were applied by vacuum evaporation at a pressure of 10^{-4} mm of mercury.

Magnesium fluoride overcoatings seemed to reduce the rate of resistance increase on exposure to air. However, after prolonged exposure to air, the resistance increased to about the same value as that for unprotected slides.

Silicon monoxide films were prepared both by evaporation of SiO and by evaporation of a 50-50 mixture of silicon and SiO_2.

Films were formed more rapidly by the evaporation of SiO and had better protective properties than did those films formed from the Si-SiO_2 mixture.

Although the resistance was not completely stabilized by a protective SiO overcoating, some improvement resulted. The resistances increased by a factor of four to six after prolonged air exposure, as compared with increases of about three orders of magnitude for similar films without protective coatings.

The photoeffect on SiO-protected In-O films was also much smaller than that for unprotected films. The resistance of protected films changed by about 20 per cent under light-dark cycling, as compared with about two orders of magnitude for unprotected film.

EXPERIMENTAL DETAILS

Solutions for Homogeneous Precipitation of SnO_2 Films

Tin oxide films were precipitated from a solution prepared as follows. A stock solution was prepared from 12 grams of tin and 800 ml of 50 per cent by weight aqueous HCl solution. After the tin had completely dissolved, the solution was transferred to a flask, to which was added 400 ml of aqueous HCl (specific gravity 1.18) and then diluted 2 to 1 with H_2O. To 20 ml of this solution were added 1 gram of ammonium sulfate, 4 ml of HCl (specific gravity 1.18), 60 ml of H_2O, 15 ml of H_2SO_4, and 100 ml of H_2O containing 20 grams of urea. Glass plates were immersed in this solution, and the solution was heated to the boiling point. Other solutions were also used in which sodium trichloroacetate, ammonium carbamate, and sodium sulfite were used in place of urea.

The solution, which was prepared to precipitate SnO_2 by forming water *in situ*, consisted of 45 cc of water, 50 cc of glycerol, 50 grams of chloral hydrate, and 1 cc of stannic chloride. At room temperature, no SnO_2 was precipitated. However, when the solution was heated to 220 F, the additional water made available by the decomposition of the chloral hydrate caused precipitation of SnO_2.

Preparation of Metallo-Organic Compounds for Decomposition to the Oxide

Dimethyl cadmium was prepared as follows. Three hundred cc of 2N methyl magnesium bromide in dibutyl ether was placed in a 500-cc flask fitted with a stirrer, reflux condensor, and gas-inlet tube. The apparatus was flushed with dry oxygen-free nitrogen. One hundred grams of $CdBr_2$, prepared by heating $CdBr_2 \cdot 4H_2O$, was added to the methyl Grignard. This mixture was allowed to stand for about 65 hours, and the dimethyl cadmium was distilled off under vacuum and dissolved in dibutyl ether for dipping and spraying solutions.

Tetramethoxy tin was made by reacting tin tetrachloride and sodium methoxide in methyl alcohol. After reaction ceased, the supernatant solution was poured off and used as a dipping and spraying solution.

Solutions of Metal Salts Used to Form Oxide Films by Dipping

The solution that gave the best results in the formation of conducting SnO_2 films by dipping consisted of 2 parts anhydrous stannic chloride dissolved in 100 parts by volume of methyl alcohol.

Conducting TiO_2 films were formed by dipping in a solution prepared as follows. Five parts of anhydrous $TiCl_4$ were dissolved in 100 parts of 95 per cent ethanol. After aging 6 weeks or longer at room temperature, the solution was diluted using 3 parts of the more concentrated solution in 100 parts of absolute ethanol.

Apparatus Used for Vapor Impingement on Hot Glass

The various types of heating arrangement used for the formation of oxide films by vapor impingement on a hot glass surface are shown in Figure 1. With the heating-grid arrangements (a), (b), (c), Figure 1, inlets for $SnCl_4$ and water vapor were installed between the heating grid and the glass surface. A cold-air blast could be directed on the back side of the glass plate, so that a high front surface temperature could be maintained without bubbling the plastic laminate of the safety glass. A temperature gradient of about 100 F existed between the front and back surfaces of 1/4-inch glass when the front surface was heated to about 300 F. The vertical heating arrangement shown in part (c) (Figure 1) produced large temperature gradients from the bottom to the top of the glass plate. The horizontal arrangements shown in parts (a) and (b) produced a more nearly uniform surface temperature.

Use of the hot-air-blast arrangement shown in part (d) resulted in large temperature gradients over the glass surface. Areas directly in front of the outlets were 50 to 80 F hotter than other areas, although the outlets were only about 1 inch apart.

Heating with an enclosed furnace [part (e), Figure 1] gave the most uniform surface temperature. Although the furnace used was not designed for cooling the back surface of the glass, this method of heating could be adapted for this purpose. In the initial work, the vapors were passed in the bottom inlet of the furnace. This procedure resulted in film formation over only a small area at the bottom of the plates. Subsequently, the top inlets were used and glass tubing was used to prevent mixing of the metal chloride and water vapor until just prior to reaching the glass surface.

The inlets that gave the best results with all the heating arrangements were made of two concentric tubes. The water-vapor inlet, made of 6-mm glass tubing, was sealed inside a 10-mm glass tube that served as the stannic chloride inlet. These inlets, when placed perpendicular to and

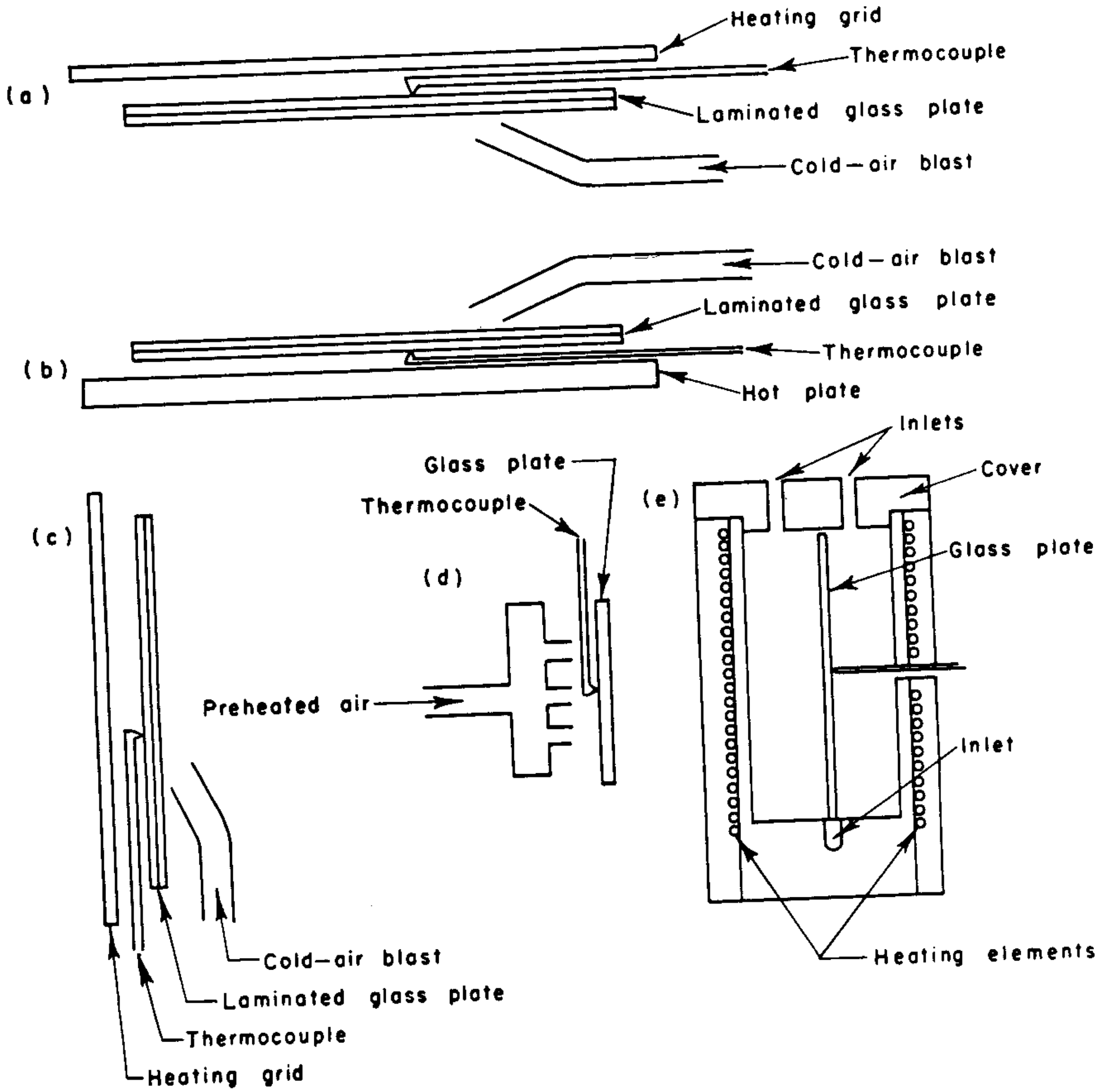

FIGURE I. TYPES OF HEATING ARRANGEMENTS FOR FORMATION OF OXIDE FILMS BY VAPOR IMPINGEMENT ON A HOT GLASS SURFACE

A-7162

about 1/4 inch away from the glass surface, permitted filming of an area about 3 inches in diameter.

Apparatus and Procedure for Low-Pressure Decomposition of Metal Chloride Vapors

A schematic diagram of the apparatus used for investigating film formation by low-pressure decomposition of metal chloride vapor is shown in Figure 2.

The reaction chamber was evacuated and air (about 50 per cent relative humidity) was bled into the system to the desired pressure. The pressure range < 1 mm to 300 mm of mercury was investigated. The leak rate was adjusted to maintain the desired pressure, and $SnCl_4$ vapor was flowed into the system, with and without helium, so as to obtain a preselected higher pressure (50 mm to 600 mm of mercury). The $SnCl_4$ was introduced through a nozzle directed toward the heated glass plate.

Vacuum-Evaporation Apparatus and Evaporation Procedure

The vacuum apparatus used to prepare the evaporated metal, metal oxide, and metal sulfide consisted of a bell jar 18 inches in diameter and 30 inches high mounted on a metal base plate. The base plate was fitted with electrical leads, vacuum-gage inlets, and vacuum-pump inlets. Vacuum was maintained by a large forepump capable of maintaining a pressure of a few microns and an oil diffusion pump, which, when used in conjunction with the forepump, was capable of maintaining pressures of 10^{-4} mm of mercury or less.

When powdered materials (metal oxides or metal sulfides) were to be evaporated, cylindrical tantalum tubes into which a small (1/8 inch) hole was drilled were used as the holders. This type of holder construction prevented ejection of the powdered materials from the holder during heating. For the evaporation of metals, both tantalum boats and tungsten helical coils were used as holders. The helical coils were found to be superior to the boats in that they did not radiate as much heat to the substrate.

The evaporation rate was controlled by maintaining a constant power input to the holder and using a sufficient quantity of source material that only a small fraction of the amount was removed during the evaporation period.

Substrate temperature was measured by means of a thermocouple attached to external leads on the vacuum system.

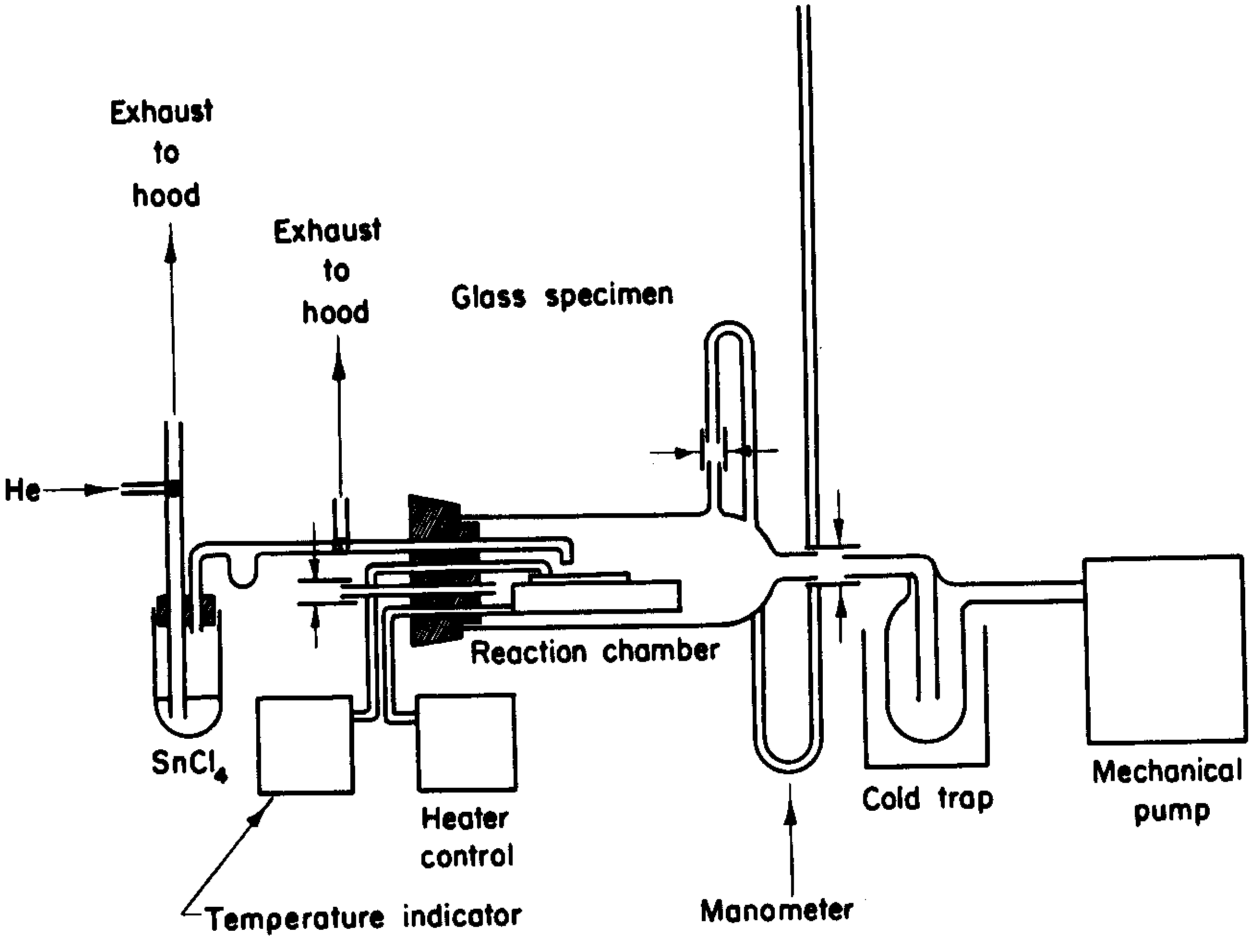

FIGURE 2. APPARATUS FOR LOW-PRESSURE VAPOR-DECOMPOSITION STUDIES

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Bus bars were applied to the glass substrate using air-dried silver paint. The substrates were then held in position in the vacuum system by means of two holders attached to the bus bars. The other ends of the holders were connected to the external leads of the vacuum system to permit continuous resistance readings to be made during evaporation and oxidation. Relative evaporation rates were estimated by the rate of change of resistance with time during the evaporation procedure.

Apparatus and Procedure for Thermal Oxidation

During initial work on thermal conversion in the vacuum system, films were heated by an electrical grid heater suspended parallel to and about 2 inches from the film. The heater was on the side of the substrate opposite the side to which the film was applied, so that the evaporation source, substrate, and heater could be installed in permanent positions. In the event that films were to be deposited on safety glass, a movable heater would have to be installed to permit heating from the film side, in order to minimize the heating of the plastic laminate.

When films were heated by application of a d-c load, the electrical leads were attached to the film through the external leads on the substrate holder. Current passage was then interrupted at intervals to permit resistance measurement to be made through the same leads. The air-dried silver-paint bus bars were found to be inadequate for this work, since the film-bus bar junction broke down at about 80 volts. In order to permit application of higher voltages, thin gold bus bars were applied to the glass plates. These bus bars were then covered with air-dried silver paint, with the exception of a narrow edge, which was overlapped by the In-O film. Using these bus bars, about 150 volts could be applied to the film without breakdown of the bus bar junction.

The Glow-Discharge and Sputtering System

The combination glow-discharge and sputtering system consists of three principal parts:

(1) The discharge chamber
(2) The discharge electrodes
(3) The discharge power supply.

The discharge chamber consists of a glass bell jar sealed with a gasket to an aluminum base plate and evacuated with a mechanical pump. Atmospheres of various gases can be introduced through a controllable gas leak. The vacuum gauge first used on the system was of an ionization type. However, the readings were not correct when the glow discharge was maintained in the chamber, so a Pirani gauge was substituted. Four electrical lead-throughs in the base plate provide the connections for internal electrical measurements. A part in the bell jar is used to introduce the high voltage for the glow discharge. The base plate is the other electrode. Because of the heat generated in the glow discharge, the temperature of the aluminum base plate rises during operation. Therefore, copper tubing was attached to the base plate and tap water circulated through it. This eliminated the vaporizing of the indium sheet cathode that occurred during several of the early sputtering experiments.

As stated above, one of the discharge electrodes is the base plate. The other electrode is a 4-inch-square aluminum plate supported either by a rod and clamp arrangement attached to the high voltage lead-through or by a glass cylinder resting on the base plate. Electrode spacings of 1/4 inch to 18 inches are possible.

The discharge power supply provides a d-c voltage that can be varied from 0 to 5000 volts and is capable of delivering currents up to 200 milliamperes. This current is delivered to the discharge chamber by an insulated high-voltage cable and lead-through in the bell jar and by a ground lead to the base plate.

Sputtering of Metallic Films

Sputtering is a method of preparing thin films. A transfer of metal from a bulk source material, usually the cathode, to the substrate is effected when the gas in the space between is ionized by an electric field. The rate of deposition of material is dependent upon the ionizing-current density, the voltage applied to the discharge electrodes, the type of gas and residual pressure, the metal to be sputtered, and the geometrical relationship between the sputtering material and the substrate.

The substrates for the tin and indium films were glass microscope slides. Since the formation of metal films is sensitive to contamination of the glass surface, all slides were thoroughly cleaned prior to the sputtering. The first method used consisted of scrubbing in hot detergent, and then rinsing in hot water. Films formed on slides cleaned in this way had a streaked appearance, indicating inadequate cleaning of the surface. The second cleaning method was to hold the glass slides in the flame of a Bunsen burner for several minutes. Films formed on slides treated in this way showed no evidence of nonuniformities due to contaminated slides.

The sputtering of the tin and indium films was carried out in the following way. The material to be sputtered, either tin or indium in sheet form, was placed on and hand pressed to the base plate. The substrate was placed over and parallel to this sputtering cathode at the desired distance. The substrate was supported at each end by appropriate lengths of glass tubing. Cathode-to-substrate distances of 1 inch gave films of the desired thickness in about 15 minutes. The proper sputtering atmosphere and pressure were obtained as follows: With the gas inlet and air inlet closed, the bell jar was pumped down to a pressure of about 25 microns. The pump was then turned off and argon was admitted to the bell jar until a pressure equal to atmospheric had been reached. The gas inlet was then closed and the system again was pumped down to 25 microns. After the bell jar was filled with argon once more and pumped down, the argon leak was adjusted so that, with the mechanical pump running, the pressure in the bell jar was less than that desired to carry out the sputtering. The power-supply voltage was then applied between the cathode and anode (located above the substrate) and the potential adjusted to provide the desired operating current. Since the gas pressure and sputtering current density are not independent, several readjustments were made to reach the desired value of each parameter. The sputtering voltage was turned off when it was desired to terminate the film deposition.

Indium films with transmissions of 0 to 50 per cent and resistances per square of 200 to 50,000 ohms were sputtered. The conditions used were argon pressures of about 75 microns, current densities of about 3 to 6 milliamperes per square inch, times of about 5 minutes, and cathode-substrate distances of 1 inch.

Tin films with transmissions of 0 to 60 per cent and resistances per square of 10 to 10^6 ohms were sputtered. The conditions were the same as those used for indium.

Glow-Discharge Conversion of Metallic Films

Films of tin and indium were subjected to the glow discharge. The substrates were held parallel to the base plate (which is one glow-discharge electrode) at a distance of 1 inch. The discharge gas was air. Variation of the air pressure from 40 to 125 microns had no effect on the conversion. Times of exposure were varied between 2 and 45 minutes, with no effect on the conversion. During the glow discharge, the temperature of the film rose to between about 275 and 310 F at a pressure of 75 microns, within 5 minutes. At 50 microns the temperature reached about 390 F, and at 100 microns it reached about 240 F. Also, there were differences in temperature of 10 to 20 C, depending on the geometrical orientation of the film, the lower temperatures being obtained when the film was perpendicular to the discharge electrodes. In order to keep film temperatures down near 250 F, it was necessary to use intermittent exposures for the low-pressure discharges. The effect of the glow discharge on the optical transmission of tin films was unmeasurable. In general, film resistances remained unchanged, although in a few cases there were slight increases.

TABLE 7. CHANGE IN RESISTANCE PER SQUARE OF INDIUM-METAL FILMS DUE TO GLOW DISCHARGE AND THERMAL CONVERSIONS

		Resistance per Square		
Film	Metal-Film Optical Transmission, per cent	Metal Film, ohms	After Glow Discharge, ohms	After Load Heating at 250 F, ohms
In-3-4-1	0	140	60	
In-3-4-6	0	2.5 K	1.3 K	
In-3-3-5	0	2.2 K	70	
In-2-26-2	< 1	1 K	70	310
In-2-26-3	< 1	1 K	70	
In-3-11-2	6	1.6 K	Not treated	410
In-3-4-2	6	34 K	2.2 K	
In-3-1-1	8	250	300	
In-3-4-4	11	9.5 K	3.4 K	
In-2-26-1	11	600	700	270
In-3-4-3	12	15 K	3.5 K	1.9 K
In-2-26-4	16	10 K	60	
In-3-1-2	19	12 K	3 K	
In-3-3-3	20	9 K	2 K	990
In-3-3-2	22	20 K	4 K	
In-3-11-1	40	620	Not treated	475
In-2-26-6	48	50 K	150 K	

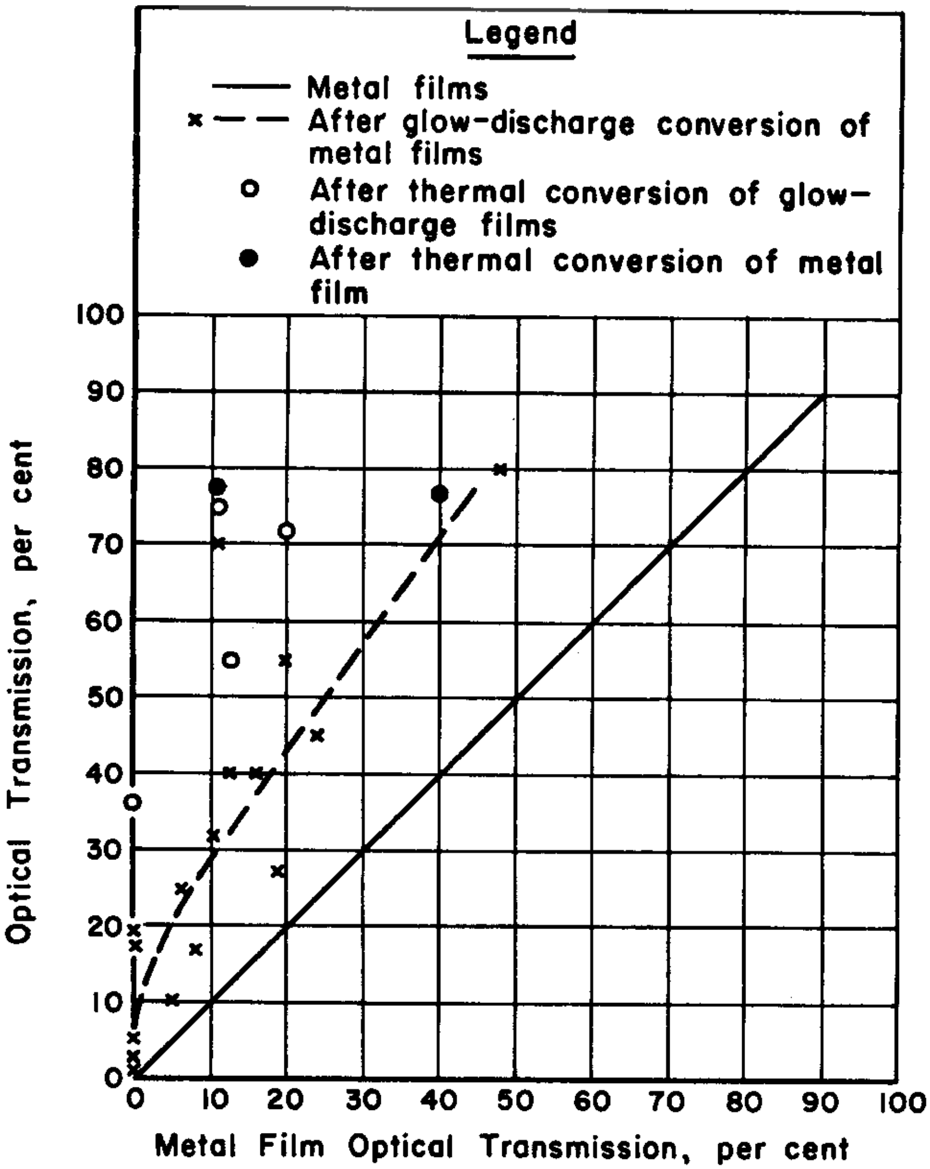

FIGURE 3. CHANGE IN OPTICAL TRANSMISSION OF INDIUM METAL FILMS BY GLOW-DISCHARGE AND THERMAL CONVERSION

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The effect of the glow-discharge treatment on the sputtered indium films is shown in Figure 3 and Table 7. Figure 3 shows the optical transmission of converted indium films plotted as a function of the optical transmission of the initial indium film. The change in optical transmission is used as a measure of the conversion from indium to In-O; therefore, the 45-degree line represents the unconverted metal films. The crosses show the effect of the glow-discharge treatment on indium films. The circled crosses represent films that were subjected to glow discharge first, and then subjected to load heating between 200 and 300 F at a pressure of 6 microns. The solid circles represent sputtered indium films converted by load heating at 250 F without prior glow-discharge treatment. Table 7 shows the resistance changes accompanying the conversion of the films shown in Figure 3.

Testing Procedures

For resistance measurements of portions of large film areas, point probes spaced 1/2 inch apart were used. In some cases, air-dried silver bus bars were applied to the plates and electrical connection was made to these through pressure clips.

Transmission and haze measurements were made using an apparatus designed according to the specifications set forth in the contract, namely, Federal Specification LP 406 B, Method 3021.

Aging tests were carried out in a stainless steel, thermostated oven that had an accuracy of control of ± 3 degrees F in the neighborhood of 200 F.

Load tests were conducted using a controlled-output d-c power supply. Some tests were conducted in still air at room temperature; others were conducted in moving air, the samples being mounted in the airstream of a table fan.