Improved Manufacturing Techniques for RF and Laser Hardening of Missile Domes

Phase I Technical Report

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July 1982

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Pacific Northwest Laboratory
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SUMMARY

This report summarizes key results and accomplishments during the first year of a Manufacturing Methods and Technology project to adapt an existing Pacific Northwest Laboratory (PNL) optical coating capability developed for high-power fusion-laser applications to the case of rf and laser hardening of plastic missile domes used by the U.S. Army (MICOM). The primary objective of the first year's work was to demonstrate rf hardening of Hellfire and Copperhead 1.06-micron missile domes by use of transparent conductive Indium Tin Oxide (ITO) coatings. The project thus involved adaptation of a coating material and process developed for flat glass components used in fusion lasers to the case of hemispherical or conical heat-sensitive plastic domes used on laser-guided missiles. Specific ITO coating property goals were an electrical sheet resistance of 10 Ohms/square, a coated-dome transmission of 80% or more at 1.06 micron wavelength (compared to 90% for a bare dome), and good adhesion. The sheet resistance goal of 10 Ohms/square was expected to result in an rf attenuation of 30 dB at the frequencies of importance.

Coating of the missile domes involved design, part fabrication, assembly and testing of a coating system for applying ITO in uniform thickness to temperature-sensitive parts with complex shapes. Achievement of the ITO property goals required careful and systematic optimization of deposition parameters. Metal electrode materials, to contact the ITO to the metal missile body, were selected, evaluated and optimized. Electrical and optical properties of hundreds of ITO and electrode coatings were measured. Thickness uniformity over the dome surface and adhesion to the plastic was measured on selected coatings. Procedures were also developed for cleaning the plastic before coating, and for fabrication of source materials used in the coating process. Finally, seventeen domes (fourteen Hellfire and three Copperhead) were coated and sent to MICOM for rf shielding tests and evaluation.

The first year's work successfully demonstrated the technical feasibility of achieving significant rf shielding with a thin transparent ITO coating. ITO coatings with 10 Ohms/square sheet resistance and 80% transmission at 1.06 microns were obtained on both Hellfire and Copperhead domes using a reactive magnetron sputtering process. Rf testing at MICOM on Hellfire domes showed greater than 30 dB attenuation in the high frequency range of interest and greater than 25 dB at low and medium frequencies whenever the ITO sheet resistance was less than 26 Ohms/square. Actual attenuations may have been higher since measurement at each frequency was limited by the output of existing power supplies. Copperhead domes yielded only 13 to 21 dB at the high frequency. However, the ITO on these domes was the most conductive made in the first year and the low attenuation is believed to be due to poor electrode thread coverage. A plasma-sprayed Zinc (Zn) electrode performed best on the Hellfire domes. Sputtered Nickel (Ni) electrodes did not appear to work well on either Hellfire or Copperhead domes. Tensile pull tests for ITO on polycarbonate (Hellfire) and polysulfone (Copperhead) plastics indicated adhesion of several thousand psi. The reactive magnetron sputtering approach appears promising for mass production coating of missile domes at a reasonable cost, but very precise control of deposition parameters is required. Procedures were developed for cleaning plastics before coating and for fabrication of In/Sn sputtering sources, and some of the coating process concepts and procedures needed for mass production were determined.

Future work is planned to include: 1) coating of more domes for additional rf tests as well as optical, environmental and field testing, 2) multilayer coatings for laser hardening, 3) production coating cost estimates, and 4) assessment of and improvement in production readiness leading to ultimate production implementation.

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INTRODUCTION

Pacific Northwest Laboratory^a achievement¹ of high resistance to laser-induced damage in transparent conductive ITO coatings for fusion laser applications suggested their use for both rf and laser hardening of plastic domes for laser-guided missiles and munitions. Of particular interest were the Hellfire and Copperhead missiles which are guided by 1.06 micron radiation from Nd:YAG lasers, a wavelength falling in the region of high transparency for ITO. A single layer of ITO with the proper conductivity (sheet resistance of approximately 10 Ohms/square) could provide rf shielding when the missile dome was electrically connected to the metal missile body. A multilayer interference filter, one layer of which is ITO, could provide both rf and laser hardening of the missile seeker simultaneously. The transparency of the ITO would allow hardening without impairing the domes 1.06 micron transmission (10% or less transmission loss). A Manufacturing Methods and Technology project was thus initiated to adapt the fusion laser coatings and coating process to the case of heat-sensitive plastics in hemispherical or conical shapes.

In the first year of the project, coating equipment and a process were demonstrated for applying transparent ITO coatings to Hellfire and Copperhead missile domes and significant rf shielding was achieved at the important frequencies. This report describes the equipment and process used and summarizes all results obtained for ITO coatings and associated metal electrodes. Recommendations for future work leading to production implementation of the coating and process are also included.

Perhaps the most significant accomplishment of this work is the technical demonstration that very respectable rf shielding can be achieved with a coating two orders of magnitude thinner than a skin depth at the frequencies of interest. Apparently, the rf shielding is a reflection phenomenon, and little if any of the rf attenuation results from absorption in these 1-micron thick films. The ability to achieve significant rf shielding in

^a Operated for the U.S. Department of Energy (DOE)
by Battelle Memorial Institute.

such thin films makes possible simultaneous optical transmission. The ideas demonstrated in this work for ITO at 1.06 micron wavelength thus may be extendable to other transparent or weakly absorbing materials for use with target designators working at wavelengths different from that of the Nd:YAG laser. In particular, narrow band gap semiconductor materials may possibly be used for rf shielding with lasers operating farther in the infrared.

CONCLUSIONS AND RECOMMENDATIONS

Reactive sputtering of ITO transparent conductive coatings on the inside of Hellfire and Copperhead domes appears to be a viable approach to rf hardening laser-guided missiles. Hellfire domes have been hardened to greater than 30 dB shielding at the important rf frequencies with a loss in 1.06 micron transmission of about 10% on some domes and less than 20% on others. Copperhead domes have also been coated with similar or better ITO coatings, but initial tests showed rf shielding of only 13 to 21 dB probably due to a poor metal electrode. The ITO used is about 1 micron thick, and has a sheet resistance between 3 and 26 Ohms/square. Its adherence to the plastics has been measured to be several thousand psi. The coating is applied in about 30 minutes in a vacuum deposition process involving sputtering of In/Sn metal in a reactive O₂ atmosphere. Electrical contact of the ITO to the missile body requires application of a metal electrode to the threaded region of the dome. Plasma sprayed Zn, which is applied in just a few minutes using a hand-held gun, appears to work well on Hellfire domes and should also be tried on Copperhead domes. Multilayer coatings of ITO and a second suitable material appear possible to also achieve laser hardening by interference filtering.

Logical and orderly implementation of the ITO approach to rf hardening should include the following major steps:

- additional rf testing on Hellfire domes to better define the sheet resistance specification range which produces the desired shielding
- rf testing of Copperhead domes with promising metal electrode materials such as plasma sprayed Zn
- optical testing on an operational missile system to check the coating's influence on seeker performance
- environmental testing to assess coating lifetime when exposed to humidity, temperature cycling, shock, etc.
- field testing on a fired missile

- laboratory exercises to assess production readiness of the process and to better define implementation strategies
- production coating cost analysis
- interaction with the dome contractor for technology transfer.

Laboratory work which should be pursued includes:

- coating and rf testing of thinner ITO
- improved deposition monitoring instrumentation
- eliminating some fine cracking which occurs in some coatings near the top of the dome
- improving thickness uniformity.

Thinner coatings would allow an increase in 1.06 micron transmission, a reduction in coating cost, and an increase in coating adherence and durability. Improved instrumentation would increase production yield and have long term cost benefits. Cracking, of course, must be eliminated, and improved thickness uniformity would maximize dome transmission and minimize the chances of adverse effects on seeker performance.

Finally, multilayer coatings should be examined to determine if laser hardening and rf hardening can be achieved in one coating process.

PROPERTIES OF ITO COATINGS

Of all transparent conductive coatings for use in the visible and near-infrared spectral regions, the $\text{In}_{2-x}\text{Sn}_x\text{O}_{3-y}$ (ITO) solid solution system has received the most attention to date because it simultaneously offers the highest conductivity and transmission. Maximum conductivity or minimum resistivity is obtained for $0.1 < x < 0.2$, with some of the Sn replacing In substitutionally and serving as a donor impurity.^{2,3} Oxygen vacancies also make a major contribution to the electron carrier concentration in ITO coatings. For a given Sn content, control of oxygen deviations from stoichiometry allows sensitive control of ITO conductivity. All of the work described in this report was done with a Sn content of 10 wt.% ($x = 0.2$).

The electrical and optical properties of the semiconductor ITO are intimately related. Generally speaking, there is a tradeoff between high optical transmission and low electrical resistivity. In addition, variation of the electron carrier concentration over several orders of magnitude, which accompanies resistivity changes, has significant effects on both the short-wavelength and long-wavelength transmission.

Figure 1 shows the wavelength dependence from 0.2 to 2.6 microns of the external transmittance of three ITO coatings with widely different electrical resistivities: 5×10^{-4} , 5×10^{-2} and 1 Ohm cm. Also shown is the transmission curve for a bare fused silica substrate. The two lower resistivity coatings are 0.63 microns thick. The high resistivity coating is 0.30 microns thick. A resistivity of 5×10^{-4} Ohm cm is very close to the minimum value attainable for ITO.^{2,3} A value of 1 Ohm cm corresponds to a coating which is nearly completely oxidized. Hence the coatings of Figure 1 represent extremes which clearly illustrate the differences between highly conducting and semiconducting (or insulating) coatings.

Note that all three coatings exhibit a short-wavelength absorption edge in the ultraviolet spectral region due to optically-induced interband electronic transitions. In general, fully oxidized ITO has an absorption edge

Figure 1. Transmission Spectra for Three ITO Coatings with Different Resistivities

of about 0.35 microns (3.5 eV), which shifts to longer wavelengths near 0.40 microns (3.1 eV) as absorbing oxygen vacancies are introduced to lower the resistivity. For very high oxygen vacancy levels, the absorption edge shifts back to shorter wavelengths, as shown in Figure 1, due to a Fermi level increase caused by the very high electron concentration. The latter shift is known as the Burstein effect.⁴

The interference pattern in the transmission curves for the coated substrates is due to constructive and destructive interference of light reflected from the air-coating and coating-substrate interfaces. Knowing the refractive index of the substrate, the index of the coating can be deduced at various wavelengths from the amplitude of the interference pattern.⁵ For the two higher-resistivity coatings of Figure 1, the index is 1.80 near 1 micron and 1.85 near 0.55 microns. The refractive index is dependent on deposition conditions, however, with values of 2.00 at 1 micron and 2.05 at 0.55 microns sometimes observed. For the low-resistivity coating of Figure 1, the index cannot be deduced accurately from the interference pattern amplitude because of absorption due to the large oxygen vacancy concentration. The percent absorption loss is roughly the difference between the transmissions of the coated substrate and the bare substrate near the maxima in the interference pattern. The loss for the low-resistivity coating is about 8% near 0.6 microns and about 15% near 1 micron. Note that the two higher resistivity coatings show no losses near either 0.6 or 1 micron.

The long-wavelength absorption edge also depends on the coating resistivity, as shown in Figure 1. For the low-resistivity coating, the transmission cutoff for wavelengths ≥ 1 micron is clearly evident. For the high-resistivity coating little loss is detectable even near 2.6 microns. The long-wavelength absorption edge in ITO is caused by metal-like free-carrier absorption which is responsible for an increase in the reflectivity and a concomitant transmission decrease.³ The increase in the reflectivity which accompanies the transmission decrease is shown very clearly for a highly conductive coating in Figure 2. Note that the coating absorption, defined as $100\% - \text{transmission} - \text{reflection}$, exhibits a peak or resonance

Figure 2. Transmission, Reflectance and Absorption Spectra for a Highly Conductive ITO Coating

near 1.65 microns. This long-wavelength absorption edge or "plasma frequency" shifts to shorter wavelengths with decreasing resistivity. For a resistivity of 5×10^{-4} Ohm cm the edge is between 1 and 2 microns as shown in Figure 2. For 1 Ohm cm resistivity, the edge is in the far-infrared.

The optimum resistivity for low sheet resistance and high transmission near 1.06 microns is about 10^{-3} Ohm cm. Thus, for a sheet resistance goal of 10 Ohms/square, the coating thickness must be approximately 1 micron. From Figures 1 and 2, it can be estimated that a coating with 10 Ohms/square resistance and a thickness of 1 micron will have a transmission loss of about 10% at 1.06 micron wavelength.

COATING PROCESS AND EQUIPMENT

COATING APPROACH

Low-cost mass-production coating of plastic domes with ITO requires a coating process which gives 1) high deposition rates, 2) little substrate heating, 3) precise deposition control and 4) uniform thickness over an approximately hemispherical shape. The coating process chosen for this work is reactive magnetron sputtering with a "point-like" source. Sputtering processes, in general, give precise deposition control. Magnetron sputtering yields high deposition rates and little substrate heating by using a permanent magnet behind the source to efficiently ionize the sputtering gas while confining the plasma to the source region so that little substrate bombardment occurs. The small-diameter or "point-like" source was chosen because it produces an approximately hemispherical distribution of sputtered material which will uniformly coat an approximately hemispherical substrate. If necessary, the distribution of sputtered material possibly can be tailored to conform more exactly to the substrate shape by proper design of the dark space shield or by adjustment of the gas pressure.

REACTIVE SPUTTERING DESCRIPTION

Deposition of ITO coatings by reactive sputtering requires an In/Sn metal source mounted on a dc electrode inside of a vacuum chamber. Sputtering is accomplished by introducing a low pressure (~ 2 mTorr) of an inert gas such as argon while applying a negative dc voltage (~ 200 V) to the source. A sustained discharge results and a plasma of Ar^+ ions and electrons forms in the region between the source and substrate. Attraction of Ar^+ ions to the negatively-biased source leads to bombardment, which in turn results in sputtering or atom-by-atom removal of material from the In/Sn source and subsequent transfer to the substrate. Addition of a reactive gas such as O_2 to the Ar permits deposition of the oxides of the source metal by reaction with the metal atoms as they travel to the substrate or while on the substrate surface.

COATING SYSTEM

Two coating systems were designed and built during the first year's work. The most recent design is shown schematically in Figure 3. This design is the simplest and least expensive to build and capitalizes on all of the deposition experience gained during the first year.

The vacuum chamber in Figure 3 is a 14-inch (inner diameter) cylindrical vessel attached to a conventional oil-diffusion pumping station with a liquid nitrogen cold trap and a mechanical roughing/backing pump. Two sputtering sources are mounted on the baseplate at 120° positions with room for a third if needed. The sputtering sources are "Research S-gun" dc magnetrons purchased from Sputtered Films, Inc., Santa Barbara, CA. The substrate holder, shown in Figure 4, is simple carousel suspended from the chamber top plate with a differentially-pumped vacuum seal. Rotational position is indexable by external fiducial markings. The carousel table has three holes machined at 120° positions on the same diameter bolt circle as the sputtering sources. The holes are 4.620 inches in diameter, counterbored to 4.920 inches for half the plate thickness, so that both Hellfire and Copperhead domes drop simply and securely into place. For production coating, the carousel can be built to accomodate a larger number of domes, limited by the chamber inner diameter in the present case to three. The substrate table is electrically isolated from the center support with insulating washers and a bushing. The substrate table diameter is almost as large as the chamber inner diameter to eliminate coating the top part of chamber which necessitates cleaning. A rotatable shutter (0.062 inch stainless steel plate) enters through the center of the base plate with a differentially-pumped vacuum seal to allow cleaning and/or stabilizing of the source before coating. The two sources and the shutter can be seen in Figure 5. A window on the side of the chamber allows visual observation of the coating process using the light of the glow discharge. Two other ports are used for introducing the Ar/O₂ sputtering gas and monitoring its pressure with a capacitance manometer.

The original version of the sputtering system employed two very sophisticated substrate holders, which were later found to be unnecessary. A

Figure 3. Schematic Diagram of Dome Coating System

Figure 4. Carousel Substrate Holder

Figure 5. Sputtering Sources and Rotatable Shutter in Base of Coating System

holder was machined from a 6-inch Al rod to surround and fit exactly the outside of each dome type. The holder was water cooled, and was intended to cool the plastic substrate during deposition so that no melting or thermal expansion problems occurred. Each holder was also isolated from electrical ground, attached to an rf electrode, and surrounded by a co-axial dark space shield so that substrate sputter cleaning and bias deposition could be carried out to improve coating adherence and properties. It was later discovered that the magnetron sources and the low power levels required did not produce appreciable substrate heating. In addition, the optimum coating properties and good adherence were obtained without rf substrate etching or bias deposition. These findings led to the simple carousel holder of Figure 4.

Important ancillary equipment for the coating system includes sputtering source dc power supply, gas mixing valves, mass-flow meters and sputtering gases. This equipment can be seen in Figure 6. The power supply is a Sputtered Films, Inc. Model PS-60-4 (0-600 V, 0-4 A) dc supply which connects directly to the sputtering source. The current adjust on the supply was changed from a 1-turn to a 10-turn potentiometer for greater tuning sensitivity, and digital voltmeters with 1 V and 0.001 A resolution were added for precise reading of the sputtering source voltage and current. The gas mixing valves are Varian Model 951-5100 precision needle valves which allow adjustment of the individual Ar and O₂ flows from the regulated storage bottles to the chamber in flow increments of 0.01 SCCM. In series with each needle valve is a Teledyne-Hastings-Raydist Model NALL-5P Type H-5 (0-5 SCCM) transducer-type mass flow meter with digital readout to the nearest 0.01 SCCM. An MKS Baratron capacitance manometer (Type 310BHS-1 head, Type 170M-6C analog readout) is also used to monitor chamber pressure during deposition. The Ar and O₂ sputtering gases are 99.999% pure commercially bottled gases.

SPUTTERING SOURCE FABRICATION

For mass production coating of large quantities of domes, a supply of In/Sn sputtering sources will be needed. A source is expected to last for about 500 Hellfire domes and about 200 Copperhead domes, based on a coating

Figure 6. Dome Coating System and Support Equipment

thickness of 1 micron and the manufacturer's claim of 65% usage before re-cycling. New sources can be fabricated simply by casting into an Al mold on a conventional laboratory hot plate. The mold is machined to produce the desired target shape and size, or can be purchased from Sputtered Films, Inc. Indium and Tin shot (~1/8 inch size, 99.99% pure) are mixed in the proportion 72 grams In plus 8 grams Sn (10 wt.% Sn) in a Pyrex beaker. The beaker is placed on a hot-plate and heated until all the shot melts. After stirring with a glass rod, the molten mixture is poured into the Al mold which is also preheated on the hot-plate. The casting and mold are then allowed to cool. Immediately after pouring, some shaking of the mold is necessary for complete filling by the molten metal.

ITO DEPOSITION PARAMETER OPTIMIZATION

KEY CONCEPTS

Stoichiometric In_2O_3 is a transparent insulator. Adding Sn as a substitutional dopant reduces the resistivity of stoichiometric In_2O_3 to $\sim 10^{+3}$ Ohm cm. To achieve resistivities $\lesssim 10^{-3}$ Ohm cm, as required to meet the 10 Ohms/square property goal for this project, oxygen vacancies must be introduced by deliberately depositing coatings which are deficient in oxygen. Since too large an oxygen deficiency will result in a metallic, non-transparent coating, and since resistivity must be traded off against transmission, the number of oxygen vacancies must be precisely controlled. In near optimum ITO, approximately 1% of the oxygen sites must be vacant.

Control of the oxygen vacancy level in reactive sputtering is achieved by balancing the rate at which In/Sn metal is sputtered from the source against the rate at which O_2 is introduced into the chamber to react with the In/Sn. The rate at which In/Sn is sputtered is controlled by two parameters: the source voltage and the source current. The rate at which oxygen is introduced is the O_2 flow. Hence the three principal deposition parameters which must be controlled are source voltage, source current and O_2 flow. Each of the three can be monitored precisely with digital meters. The current is controlled simply by adjusting the set point on the constant current supply. Adjustment of the O_2 flow is made by opening or closing a needle valve. The target voltage is controlled by the valve between the vacuum chamber and the pumping station. Opening the valve slightly lowers the chamber pressure and raises the voltage induced on the source. Closing the valve slightly raises the chamber pressure and lowers the source voltage. For all deposition work reported here the argon flow was 4.30 SCCM.

With these concepts in mind, strategy for controlling the oxygen vacancy level in ITO is an iterative process. First, a coating is made with the current, voltage and O_2 flow set at values expected to yield transparent conductive ITO based on previous values used. Next the coating transmis-

sion and sheet resistance are measured. If the coating is highly transparent and resistive, it is too fully oxidized. Thus on the next deposition the current or voltage must be raised, to increase the metal content relative to oxygen, or the O_2 flow must be lowered. If the first coating is metallic or dark, the current or voltage must be dropped or the O_2 flow increased. This process is repeated until the desired coating properties are achieved.

For the particular application of ITO coatings on plastic domes, the range of currents is constrained by two considerations. First, coating economics dictate that deposition rates, which are determined primarily by the source current, be as high as possible. Second, plasma heating of the dome requires that source current not be too high because of thermal expansion or melting problems with the plastic. For the case of Hellfire domes, the optimum current is approximately 0.15 A which results in a deposition rate of 350 Å/min or 1 micron/30 minutes. For Copperhead domes, where less experience was gained the first year, the optimum current is at least 0.15 A and may be as high as 0.25 A.

SYSTEMATIC TUNING OF PARAMETERS

Systematic tuning of deposition parameters in an iterative process to achieve the optimum tradeoff between transmission and resistance is illustrated in Figure 7 for the case of 0.15 A source current and 190 V source voltage. By systematically stepping through O_2 flows, a flow which produces high transmission and low resistance can be found. Note in the top curve that, at high O_2 flows, the ITO is transparent and transmission at 1.06 microns approaches that of the bare dome. At lower flows, the coatings are darker and lower in transmission. The sheet resistance curve at the bottom shows a minimum near the transition from transparent to opaque. The data of Figure 7 indicate the optimum deposition conditions are 0.15 A, 190 V and 1.86 SCCM O_2 which will result in an ITO sheet resistance of 20 Ohms/square and a transmission of 79% at 1.06 microns.

An alternate approach to tuning the deposition parameters is to fix the

Figure 7. Systematic Tuning of O₂ Flow to Obtain Transparent Conductive ITO

current and O_2 flow while varying the voltage, as shown in Figure 8. Here the current is 0.15 A and the O_2 flow is 1.88 SCCM. Note in the upper curve that low voltages result in high transmission, because at these voltages In/Sn is sputtered more slowly and is fully oxidized by the O_2 flow. At higher voltages, In/Sn is sputtered more rapidly than it can be fully oxidized and the ITO becomes dark or even metallic. The lower curve again shows that the sheet resistance exhibits a minimum near the transition from transparent to opaque ITO.

Systematic tuning data are shown in Figure 9 for the case of 0.20 A source current, 220 V source voltage and stepwise selection of O_2 flow. Note that the higher current requires a higher voltage for near optimum tuning. Also note that in Figure 9 the range of O_2 flows selected is broader than that of Figure 7, so that the ITO ranges from all metal at low flows to fully oxidized at higher flows. The resistance again exhibits a minimum near the transition point.

Typical operating conditions are summarized in Table 1 for Hellfire domes. Copperhead domes can be deposited using the same conditions, or can be coated more rapidly by raising the source current and adjusting the source voltage appropriately.

Figure 10 shows the optimum operating voltage for any current selected between 0.15 and 0.4 A, for an argon flow of 4.3 SCCM and an O_2 flow near 2 SCCM. In practice, the current is selected to yield the best compromise between deposition rate and substrate heating. Figure 10 is then used to select the optimum voltage for the current selected, and the O_2 flow is varied in the region of 2 SCCM until the optimum ITO is obtained.

The dependence of deposition rate for near-optimized ITO on source current is shown in Figure 11. Rate increases approximately linearly with current over the range examined. A current of 0.15 A appears to be the optimum for Hellfire domes. At this current the deposition rate is about 500 Å/min for a new source, gradually dropping to about 350 Å/min for a heavily used source. Thus the time required to coat Hellfire domes with

Figure 8. Systematic Tuning of Source Voltage to Obtain Transparent Conductive ITO

Figure 9. Systematic Tuning of O₂ Flow at Higher Source Current

TABLE 1. Process Conditions For Sputtering ITO On Hellfire Domes

Sputtering System	dc Magnetron ("S-gun")
Source Current	0.150 A
Source Voltage	~170 V
Ar Flow	4.3 SCCM
O ₂ Flow	~2 SCCM
Ar/O ₂ Pressure	~3 mTorr
Source-Substrate Spacing*	3 inches
Deposition Rate	350 - 500 Å/min

* Center Top Source to Inside Top of Dome

Figure 10. Optimum Source Voltage as a Function of Source Current

Figure 11. Dependence of Deposition Rate on Source Current for Hellfire and Copperhead Domes

1 micron thick ITO is between 20 and 29 minutes, depending on source age. For Copperhead domes, a current of 0.15 A results in a rate of 100 Å/min for a heavily used source and probably 150 Å/min for a new source because the Copperhead is taller and has 2.5 times the surface area. Thus coating time would be between 67 and 100 minutes for 1 micron thick ITO. However, the Copperhead domes never showed any of the cracking effects of plasma heating experienced with the Hellfire domes for currents higher than 0.15 A, so that higher rates can probably be realized for Copperhead domes by using higher current.

VACUUM HEAT TREATMENT OPTION

An alternative to controlled deposition of ITO as described above is deposition of fully oxidized or stoichiometric ITO followed by vacuum heat treatment to produce the oxygen deficiency required for conductive coatings. This approach was pursued early in the first year, and much data was generated on times and temperatures required for treating ITO. However, the process does not appear to be attractive for low-cost, mass-production coating, so that details will be omitted here. The key result is that the times required for successful heat treating were very long at temperatures which the plastic domes can withstand. The maximum temperature for heat treatment without melting for Hellfire (polycarbonate) domes is 140°C. The maximum temperature for Copperhead (polysulfone) domes is 170°C. At these temperatures, heat treatment requires several days and sometimes a week for a 1 micron thick coating.

METAL ELECTRODE SELECTION AND DEPOSITION

ELECTRODE COATING SCHEMES

A metal electrode appears to be desirable for ensuring electrical contact between the ITO and the missile body. The Hellfire coil housing to which the coated domes are threaded during rf testing at MICOM was specially outfitted for this project with a plasma sprayed Zn coating which contacts the outer flat surface of the Hellfire domes. Since the ITO coatings are applied only to the inside of the domes, a metal electrode was needed to contact the ITO with this outer flat surface. Contact requires continuity across the dome threads. For the Copperhead domes, the threads are inside the dome and the entire coil housing is metal.

The electrode geometries selected for Hellfire and Copperhead domes are illustrated in Figures 12 and 13, and pictures of coated domes are shown in Figures 14 and 15. Each dome is first coated on the inside with 1 micron thick ITO.

To electrically mate with the Zn-coated coil housing the Hellfire electrode must extend and be electrically continuous across the outermost flange surface, through the threads, across the bottom flat surface, and up inside the dome to the beginning of the optically polished region. The thickness of the electrode should not be more than standard machining tolerances (a few 0.001 inch) to avoid problems when the dome is threaded onto the coil housing. If the coil housing were made of metal or Zn-coated across its top gasket groove, it might not be necessary to coat the threads of the Hellfire domes.

The Copperhead electrode requires continuity only through the threads so that the ITO coating above the threads contacts the all-metal coil housing when the dome is screwed into place. However, some additional contact may be achieved by extending the metal below the threads and across the dome bottom surface. For additional rf shielding, the electrode on the Copperhead can be extended up the interior surface to the optically polished region.

HELLFIRE COATING SCHEME

NOTE: COATING THICKNESSES
ARE GREATLY EXAGGERATED
FOR CLARITY

Figure 12. Hellfire Coating Scheme

COPPERHEAD COATING SCHEME

NOTE: COATING THICKNESSES
ARE GREATLY EXAGGERATED
FOR CLARITY

Figure 13. Copperhead Coating Scheme

Figure 14. Uncoated and Coated Hellfire Domes

Figure 15. Uncoated and Coated Copperhead Domes

FIGURE OF MERIT

Several properties appear to be important for proper performance of an electrode material. For good rf shielding, low electrical resistivity is needed. To resist galling in the threads after screwing on and off several times, hardness appears to be an important electrode property. Finally, the very large linear thermal expansion coefficient of both polycarbonate ($68 \times 10^{-6}/K$) and polysulfone ($56 \times 10^{-6}/K$) suggests selection of a metal with a similarly large expansion coefficient.

Based on these three important properties of electrical resistivity, hardness and expansion coefficient, a simple figure of merit was devised to be the product of expansion coefficient and hardness divided by the resistivity. Calculation of the figure of merit allowed straightforward comparison of metals and selection of the most promising candidates. Using handbook data for the bulk materials,⁶⁻⁸ Table 2 was constructed to rank the various candidates.

The most promising candidates appear to be Ni and Zn. Ni ranked first in figure of merit, and is straightforward to deposit by several techniques including sputtering and electrodeposition. Be ranked second, but was eliminated for health reasons. Mg ranked third, but was eliminated because of pyrophoric behavior in vacuum coating chambers. Fourth and fifth were W and Zn, respectively, of which Zn was selected because it is easy and inexpensive to deposit by plasma spraying and because it is the same material used on the Hellfire coil housing.

SPUTTERED Ni ELECTRODES

Ni in smooth, hard, shiny and conductive form is easily deposited by sputtering on many substrates, including plastics. Ni coating of Copperhead and Hellfire domes by sputtering, however, is difficult because the threads are not accessible to line-of-sight deposition. Ni electrodes were attempted on several domes of each type by sputtering so that rf shielding tests could be carried out on the ITO coatings. Deposition was made at much higher sputtering gas pressures than normally used so that collisions of sputtered Ni atoms with Ar atoms might scatter Ni into thread regions

TABLE 2. Selection Of Electrode Metal For ITO-Coated Domes

<u>Metal</u>	<u>Bulk Resistivity</u>	<u>Expansion Coefficient</u>	<u>Bulk Hardness</u>	<u>Figure of Merit*</u>	<u>Rank</u>
Ni	6.85×10^{-6} Ohm cm	$13.3 \times 10^{-6}/K$	300 Bhn	582	1
Be	4.50	12.1	175	471	2
Mg	4.45	25.2	50	283	3
W	5.65	4.5	325	231	4
Zn	5.92	34.2	30	173	5
Mo	5.2	5.4	152	158	6
Al	2.65	25.2	15	143	7
Cr	13	5.9	220	100	8
Ta	12.4	6.5	152	80	9
Nb	13	7.0	133	72	10
Ti	43	8.5	250	49	11
V	25	7.9	138	44	12
Cd	7.40	30.6	10	41	13
Zr	41	5.5	200	27	14
Sn	11.0	19.8	10	18	15

* Expansion Coefficient x Hardness/Resistivity

not accessible to line-of-sight incidence. This approach appeared to work in that the threaded area was visibly coated and dc resistance measurements across the threads indicated only a few ohms. However, sputtering at high gas pressures is impractically slow, and the Ni in the threads appears to wear poorly when threaded to and unthreaded from the coil housing several times, so that other contacts should be sought.

Ni for the Hellfire domes was applied by rf sputtering from a 5-inch diameter flat-plate Ni source in 100 mTorr of argon at a power level of 100 Watts. The dome was laid top down on a water-cooled table located about 3 inches from the target. A round, flat polycarbonate plug was inserted to avoid coating the inside optical surface. The outside was protected by an annular shield. A target larger in diameter than the dome is needed for the Hellfire domes because the threads are outside. Higher power could not be used because of substrate heating which can melt polycarbonate. Under these conditions, the Ni deposition rate was approximately $5.5 \text{ \AA}/\text{min}$. A Ni coating 1 micron thick would have required 30 hours for deposition. As shown in Table 3, the rf sputtered Ni exhibited resistivity in the range 20 to $65 \times 10^{-6} \text{ Ohm cm}$ compared to $6.85 \times 10^{-6} \text{ Ohm cm}$ for bulk Ni. Typical deposition conditions are summarized in Table 4.

Ni for the Copperhead domes was applied by dc magnetron sputtering using the same system and sources used for IT0. Here a source smaller in diameter than the dome is desirable because the threads to be coated are inside. The inside optical surface was protected from the Ni with a round, flat polysulfone plug. The outside surface was protected by the substrate table (See Figure 3). Deposition conditions used were source voltage of 170 V and source current of 0.40 A. For a full-length electrode up to the optical surface, an argon sputtering gas pressure of 10 mTorr worked well and yielded a deposition rate of $72 \text{ \AA}/\text{min}$ or 1 micron/138 min. For coating the threads only, 25 mTorr Ar worked best, and the deposition rate was $54 \text{ \AA}/\text{min}$ or 1 micron/185 min. Higher deposition rates can be achieved at higher power levels at the risk of overheating the plastic plug. As shown in Table 3, the magnetron sputtered Ni showed resistivity of $13 \times 10^{-6} \text{ Ohm cm}$, within a factor of 2 of bulk material. Typical deposition conditions

TABLE 3. Resistivity Results For Metal Electrodes

<u>Material/Preparation</u>	<u>Resistivity ($10^{-6}\Omega\text{cm}$)</u>	<u>Sheet Resistance For 1 μm Thickness (Ω/Square)</u>
Bulk Ni*	6.85	0.0685
RF Diode Sputtered Ni	20 to 65	0.20 to 0.65
Electroless Ni Plating	100	1
Magnetron Sputtered Ni	13	0.13

Bulk Zn*	5.92	0.0592
Plasma Sprayed Zn	12 - 44	0.12 to 0.44

*Handbook value, ref. 7.

TABLE 4. Process Conditions For Sputtering Ni On Hellfire Domes

Sputtering System	rf Diode
Source Diameter	5 inches
Ar Pressure	100 mTorr
rf Power	100 W
Source-Substrate Spacing*	3 inches
Deposition Rate	5.5 $\text{\AA}/\text{min}$

* Center Top Of Source To Inside Top Of Dome

are summarized in Table 5.

ELECTROLESS NI ELECTRODE

Electroless Ni plating was investigated briefly as a potentially low cost technique for coating threads by submersion in a coating bath. Electroless Ni plating is the catalytic reduction of Ni ions in an aqueous solution of hypophosphite ions.⁹ The Ni reduction takes place on the surface of the catalyst. Metals belonging to Group VIII of the periodic table (i.e. Fe, Co, Ni, Pd, etc.) are known catalysts. A small-scale batch plating system was assembled to study the electroless Ni plating of ITO. Several experiments showed that ITO is not catalytic for this reaction. ITO was Ni plated when immersed in the plating bath while in contact with Ni, although approximately 25 minutes was required to initiate plating. Experiments produced excellent results for ITO-coated glass but poor results for ITO-coated polycarbonate. With glass substrates, the Ni was smooth, hard, adherent and had a resistivity of 100×10^{-6} Ohm cm. With polycarbonate substrates the Ni frequently peeled. It appeared that the plating bath was lifting the ITO coating off the plastic as if the plastic were being dissolved. Deposition rates were typically 0.0005 inch/hr.

PLASMA SPRAYED ZN ELECTRODE

Plasma spraying is a very rapid, low cost method for applying a Zn electrode to plastic. Zn is sprayed in fine molten droplet form when it is controllably introduced as a powder into a stream of ionized compressed Ar/He passed through an electric discharge gun. With this technique, the electrode on the Hellfire domes was applied to a thickness of 0.001 to 0.002 inch inside and outside of the domes in about 3 to 6 seconds with the dome spinning on a rotating table. The setup is shown in Figure 16. A polycarbonate plug was inserted into the dome and held in place with simple tension fasteners to prevent coating the optical surface. The plasma spray equipment used is a commercially available Plasmadyne Plasma Spray Gun (Model # SG-100) fitted with a plastic electrode for deposition of low-melting-point metals (Part # 5400). Typical process conditions for this sprayed coating are listed in Table 6. As shown in Table 3, sprayed

TABLE 5. Process Conditions For Sputtering Ni On Copperhead Domes

Sputtering System	dc Magnetron ("S-gun")
Source Current	0.400 A
Source Voltage	170 V
Ar Pressure	10 mTorr (full-length electrode)
Ar Pressure	25 mTorr (thread electrode)
Source-substrate Spacing*	6.25 inches
Deposition rate	54 - 72 Å/min

* Center Top Of Source To Inside Top Of Dome

Figure 16. Plasma Spraying of Zinc Electrode on a Hellfire Dome

TABLE 6. Process Conditions For Plasma Spraying
Zinc Electrode On Hellfire Domes

Plasmadyne Gun	Model # SG-100
Plastic Electrode	Part # 5400
Zinc Powder Size	44 - 74 Microns
Zinc Purity	99.5%
dc Amps	600
dc Volts	38 - 40
Arc Gas (argon)	70 psi
Auxiliary Gas (helium)	55 psi
Powder Gas (argon)	40 psi
Standoff	4 - 5 inches
Coating Thickness	0.001 - 0.002 inches
Spray Time	3 - 6 seconds (inside, bottom and outside)
Grit Blasting	80 mesh aluminum oxide @ 60 psi for 3 minutes

Zn coatings were measured to have resistivities of 12 to 44×10^{-6} Ohm cm, or 0.0031 to 0.011 Ohms/square sheet resistance for a thickness of 0.0015 inches. Before applying an adherent coating to plastic, the plastic must be roughened by light grit blasting for about 3 minutes with 80 mesh aluminum oxide powder ejected at 60 psi. The same rotating table and plastic plug are used for grit blasting as Zn spraying. Grit blasting is done before dome cleaning.

DOME CLEANING AND PRECOATING PREPARATION

NEW DOME CLEANING

Many cleaning solvents and procedures were examined throughout the first year of the program to 1) remove fingerprints and other grease, 2) maximize coating adhesion, and 3) avoid "water spots" left on the dome after drying. The essence of the problem is that both polycarbonate and polysulfone degrade rapidly (explosively) in all common laboratory degreasing solvents such as acetone, trichloroethylene and benzene. Weaker solvents such as freons and alcohols do not harm the domes, but they do not remove fingerprints either. The best cleaning procedure identified is outlined step-by-step in Table 7. An interesting and potentially useful observation was that polysulfone was much easier to clean than polycarbonate. Copperhead domes appeared to be hydrophobic; aqueous cleaning solutions bead or form drops, and roll off the dome when tilted leaving no water spots. Hellfire domes required blow drying with clean compressed gas (He or N₂) and sometimes showed water spots which were always exaggerated after ITO coating.

ACID ETCHING FOR RE-USE

Both polycarbonate and polysulfone appear to be unaffected by inorganic acids over a period of minutes to several hours at room temperature. Hence ITO coatings not meeting performance specifications can be etched off. After drying, the domes can be recoated.

Best etching results are normally obtained by submersion in moderate-strength HCl (50/50 HCl and H₂O) for approximately 15 minutes if the coating is about 1 micron thick. Fully oxidized ITO etches nicely. Dark oxygen-deficient ITO etches most slowly and sometimes requires more concentrated HCl, a small addition of HNO₃, or about 1 hour etching time. Metallic-looking ITO or In/Sn etches very rapidly.

TABLE 7. Cleaning Procedure For New Hellfire and Copperhead Domes

1. Soak for 30 minutes in lukewarm solution of 97/3 water and household ammonia.
2. Scrub non-optical surfaces and especially threads with a soft tooth brush using above solution.
3. Wash inside optical surface gently with cotton balls using above solution.
4. Repeat Steps 1-3 with Liquinox detergent solution.
5. Soak in lukewarm distilled water and rinse well.
6. Blow dry with clean compressed helium or nitrogen, paying particular attention to optical surface to be coated.
7. Inspect for particulate, grease, water spots, etc.
8. Use anti-static ionized gas gun on all surfaces to minimize pickup of dirt and lint.

TEST RESULTS FOR ITO COATED DOMES

All coated domes were measured by PNL for sheet resistance, resistance uniformity, spectral transmission from 0.2 to 2.3 microns, and transmission at 1.06 microns. In addition, adherence to polysulfone and polycarbonate was measured on selected samples. Domes were then sent to MICOM for rf shielding evaluation. In first year activity, 14 Hellfire and 3 Copperhead domes were made with ITO coatings considered sufficiently good to warrant rf evaluation. Properties of these coatings and the rf shielding they produced is described in the following sections.

RF SHIELDING

Table 8 summarizes key properties and rf shielding results for 14 ITO-coated Hellfire domes. ITO coating thicknesses from 1.0 to 5.6 microns were evaluated, and 1 micron thickness was found to be sufficient. Use of thinner coatings may be possible if further reductions in ITO resistivity can be made or if higher sheet resistance is found to produce acceptable shielding. Sheet resistances between 3.6 and 92 Ohms/square were investigated, with significant shielding found for all. Two early domes with much higher sheet resistance were found to provide no measurable shielding. The last 4 domes coated showed 1.06 micron transmissions of 74% or greater, and 2 were 82%. This compares well to the project goal of 80% transmission. 9 domes were outfitted with a sputtered Ni electrode, 2 with plasma-sprayed Zn, and 3 early domes had no metal electrode. Performance of the electrodes is discussed below.

Domes tested at MICOM for rf attenuation were mounted on a Hellfire missile body with an operational seeker in an anechoic chamber. The rf power level necessary for loss of target correlation was measured at three frequencies and corresponding missile body aspect angles known to influence Hellfire seeker performance. In this report, these three frequencies (and corresponding aspect angles) will be referred to as high, medium and low. Coated domes were always compared to uncoated domes to determine relative rf attenuation in decibels.

TABLE 8. Properties and rf Shielding Results for ITO
Coated Hellfire Domes Produced in First Year

Coating #	ITO Thick. (microns)	Sheet Resist. (Ohm/sq.)	% T. @ 1.06	Electrode (microns)	Comments	Shielding Results
45 I (H-1)	1.3	165,000	89	0	-	No effect.
45 L (H-2)	1.3	24,200	88	0	-	No effect.
45 L (H-2)	1.3	92	65	0	Heat Treated	15 dB @ hf
49 Q (H-5)	5.64	26	--	0.5 Ni	Heat Treated	19 dB @ hf
49 P (H-4)	5.25	28	47	1.0 Ni	Heat Treated	> 20 dB @ 3 f's
54 G (H-6)	4.51	12	55	1.5 Ni	-	> 24 dB @ 3 f's
54 H (H-8)	4.62	28	68	1.5 Ni	-	> 28 dB @ 2 f's
54 I (H-7)	4.84	10	50	1.5 Ni	-	> 30 dB @ 3 f's
56 W (H-10)	0.99	26	63	0.2 Ni	-	> 30 dB @ hf
56 X (H-11)	1.16	21	63	0.2 Ni	-	> 30 dB @ hf
58 I (H-12)	1.79	14	82 ± 2	50 Zn	-	> 30 dB @ hf
58 J (H-13)	1.79	21	82 ± 2	0.4 Ni	-	> 30 dB @ hf
60 M (H-15)	1.26	3.6	74	0.3 Ni	-	> 30 dB @ hf
60 N (H-14)	1.05	7.1	78	50 Zn	-	> 30 dB @ hf

f = frequency, hf = high frequency; see text for explanation.

High frequency rf attenuation as a function of ITO sheet resistance is summarized in Figure 17 for all Hellfire domes measured in the first year. The most recent results (labeled 4-82) consistently indicate that > 30 dB is attained for sheet resistance < 26 Ohms/square, dropping off to 15 dB at 92 Ohms/square, provided that the Zn electrode is used or that Cu adhesive tape is used to assist the Ni electrode in the thread region. Earlier results (labeled 12-81) were less consistent and indicated between 18 and > 36 dB for sheet resistances < 26 Ohms/square, but some of these domes had very fine cracks and some peeling near the apex where rf might penetrate. The unassisted Ni electrode domes (and 1 Zn electrode dome where the thread region was known to be poorly coated) consistently yielded shieldings of 13 to 23 dB.

Medium and low frequency attenuation data are summarized in Figures 18 and 19, respectively. Fewer data are available for these frequencies because of power supply limitations. In addition, 4 of the 5 measurements in each figure were made on old domes (12-81) some of which were slightly cracked and peeling. Nevertheless, half of the domes showed attenuations > 30 dB at medium and low frequencies. Moreover, looking at each dome individually, the medium and low frequency attenuation is either the same or higher than the high frequency attenuation.

Properties and rf shielding obtained on ITO coated Copperhead domes are summarized in Table 9. Here only 3 domes were coated, 1 very early in the project and 2 near the end of the first year. The 2 recent domes had an ITO coating 1.2 microns thick, sheet resistance of 2 to 4 Ohms/square, Ni electrodes and 1.06 micron transmissions of 62 and 75%. One Ni electrode covered the full length of the non-optical region. The second electrode covered the threads only. Attenuations measured at the high frequency were 20 and 13 dB, respectively. Since the ITO coatings here are more conductive than those made on successful Hellfire domes, the surprisingly low attenuation is probably due to the Ni electrode which may not have adequately coated the thread region. Attenuations of 13 to 20 dB are quite similar to those observed on Hellfire domes with Ni electrodes and no Cu tape (13

Figure 17. High Frequency rf Shielding Results as a Function of ITO Sheet Resistance

Figure 18. Medium Frequency rf Shielding Results as a Function of ITO Sheet Resistance

Figure 19. Low Frequency rf Shielding Results as a Function of ITO Sheet Resistance

TABLE 9. Properties and rf Shielding Results for ITO
Coated Copperhead Domes Produced in First Year

<u>Coating #</u>	<u>ITO Thick. (microns)</u>	<u>Sheet Resist. (Ohm/sq.)</u>	<u>% T. @ 1.06</u>	<u>Electrode (microns)</u>	<u>Comments</u>	<u>Shielding Results</u>
44 C (C-1)	5	-	58	0	-	No effect.
60 K (C-12)	1.19	3.7	62	0.23 Ni	Full-Length electrode	20 dB @ hf
60 L (C-13)	1.20	2.6	75	0.32 Ni	Thread electrode	13 dB @ hf

f = frequency, hf = high frequency; see text for explanation.

to 23 dB, as shown in Figure 17). Plasma-sprayed Zn electrodes will be tried on Copperhead domes in future work.

In summary, the rf data accumulated to date indicate that an ITO thickness of 1 micron, an ITO sheet resistance < 26 Ohms/square and a plasma-sprayed Zn electrode will yield > 30 dB attenuation at the high frequency and the same or better at the medium and low frequency. The Ni electrode (despite its hardness, smoothness and appearance) appears to fail in the thread region because of the line-of-sight nature of the sputtering coating process.

TRANSMISSION/SHEET RESISTANCE TRADEOFF

High conductivity or low sheet resistance in ITO requires some loss in transmission at 1.06 micron wavelength because the same electrons responsible for the electrical conductivity are responsible for free carrier absorption. This tradeoff was measured for ITO coatings on Hellfire and Copperhead domes and is shown in Figure 20. Also shown for comparison is the 1.06 micron transmission of bare polycarbonate and bare polysulfone. For sheet resistances > 100 Ohms/square, the coating causes very little ($\leq 1\%$) absorption loss and the 90% transmission of the bare plastic is obtained. With decreasing sheet resistance, the transmission falls off and drops to 60% at 2 Ohms/square. At 10 Ohms/square, the transmission is 80%. These values are the project goals.

Also note that all ITO coatings in this Figure have thicknesses of about 1 micron. If adequate rf shielding can be obtained for thinner coatings, the transmission of the coated dome can be increased because the dome transmission is approximately given by $T_0 \exp(-\alpha t)$ where T_0 is the transmission of the bare dome, α is the ITO absorption coefficient, and t the coating thickness.

For example, at 10 Ohms/square with $T_0 = 0.90$ and $t = 1$ micron, T is 0.80 in Figure 20 and α is calculated to be 1178 cm^{-1} . If t is now decreased to 0.53 microns, the new transmission would be $0.90 \exp[-(1178 \text{ cm}^{-1})(0.53 \times 10^{-4} \text{ cm})] = 0.846$, or an increase of almost 5%. ITO coating thicknesses

Figure 20. Tradeoff Between Sheet Resistance and 1.06 Micron Transmission

are limited by interference reflection effects to values of 1.06, 0.79, 0.53 and 0.26 microns.

SPECTRAL TRANSMISSION

The spectral transmission of an ITO coated dome and a bare Hellfire dome are shown in Figure 21 for wavelengths between 0.2 and 2.6 microns. This ITO coating has a thickness of 1.79 microns and a sheet resistance of 21 Ohms/square. Note that the transmission at 1.06 microns (indicated by an arrow) is 82%. Also note that the ITO filters out radiation between 0.3 and 0.4 microns due to its optical band edge, and partially filters radiation between 1.06 and 2.3 microns due to free carrier absorption. Neither polycarbonate nor polysulfone transmits at wavelengths > 2.3 microns.

ADHERENCE

Quantitative coating adherence measurements were made on about 10 polycarbonate and 3 polysulfone specimens using a tensile pull method with an epoxy-bonded stud. Measurements were made for the plastics cleaned with various solvents and procedures. For polycarbonate, the measured force/area required to remove the ITO from the plastic was 2400 to 6050 psi for liquid detergent cleaning, 1560 psi for sputter etching, and 740 psi for bead blasting. For polysulfone, detergent cleaning yielded 3050 to 8790 psi adherence.

In a very simple model, the gravitational force required to remove the typical ITO coating from plastic would be that for which the coating weight per unit area would equal the tensile pull adhesive strength. In other words mg/A should be compared with the measured adhesion numbers above, where m/A is the coating mass per unit area and g the gravitational field. In terms of the coating density ρ and thickness t , $mg/A = \rho t g$. For ITO, $\rho = 7.2 \text{ g/cm}^3$ and $t = 1 \text{ micron} = 10^{-4} \text{ cm}$. Since the normal gravitational field is 980 cm/s^2 , $\rho t g = 0.706 \text{ dynes/cm}^2 = 1.02 \times 10^{-5} \text{ psi}$. For a gravitational field 10,000 times greater than normal, such as that encountered during firing of Copperhead missiles, the coating weight per unit area

Figure 21. Spectral Transmission of a Coated and an Uncoated Hellfire Dome

is 0.102 psi. Thus the effective gravitational force/area exerted by the mass of the coating is a factor of 10,000 smaller than the smallest adhesion numbers reported above.

ITO OPTICAL AND ELECTRICAL CHARACTERIZATION

Reasonably extensive characterization of the optical and electrical properties of the hundreds of ITO coatings made was necessary to provide guidance in coating optimization and to assess progress toward project property goals. Equipment and techniques used for these measurements are described in the following sections.

SPECTRAL TRANSMISSION MEASUREMENTS

Transmission of coated and uncoated Hellfire and Copperhead domes was measured from 0.3 to 2.3 microns wavelength, the region of transparency of the plastics, using a Beckman model 5270 dual-beam, double-monochromator, ratio-recording, UV-VIS-NIR spectrophotometer. Both dome types were inserted directly into the sample chamber. Hellfire measurements were always made at normal incidence to the top center. Copperhead measurements were made slightly off center and slightly off normal incidence because of a non-optical projection at the top center. For routine measurements on domes, transmission measurements are accurate and reproducible to $\pm 1\%$, and are limited primarily by focusing effects on the small-area detector caused by the curved dome surface. Calibration is accomplished using windows of known transmission, such as fused silica. The spectrophotometer is interfaced to a desk top computer for digital data storage at 0.001 micron intervals from 0.3 to 0.8 microns and at 0.004 micron intervals from 0.8 to 2.3 microns. Digital data are processed and plotted with a second desk top computer and a plotter. Typical spectrophotometer data are shown in Figure 21 for a coated and an uncoated Hellfire dome. The spectral transmission of Copperhead domes is identical to Hellfire domes at 1.06 microns (90%) and in general between 0.6 and 2.3 microns. The principal difference occurs in the blue-green region between 0.3 and 0.5 microns where the Copperhead transmission is always lower, resulting in the yellowish appearance of polysulfone.

1.06 MICRON TRANSMISSION MEASUREMENT

Transmission measurements at 1.06 microns wavelength were made two ways, with the spectrophotometer described above and with an optical bench apparatus which allows measurements at all points on the dome. An example of a 1.06 micron spectrophotometer measurement is indicated by the arrow in Figure 21. The optical bench apparatus is shown schematically in Figure 22. This apparatus uses a large-area detector (4 cm^2) so that it is relatively immune to focusing effects associated with curved sample surfaces. In practice, the detector output is recorded for a bare dome or no dome and then for a coated dome. The ratios of coated dome output to bare dome output and coated dome to no dome give the relative attenuation and absolute transmission, respectively. The transmission of bare Copperhead and Hellfire domes at 1.06 microns is 90%. The 10% loss is Fresnel reflection. Transmission accuracy and reproducibility estimated from measurements on known window materials is presently about $\pm 1\%$ due to multiple reflections between the detector, which is not anti-reflection coated at 1.06 microns, and the inner surface of a dome. Thus the accuracy is the same as for the spectrophotometer. However, the optical bench apparatus can be used for measurements at all points on the dome rather than just the top center.

REFRACTIVE INDEX MEASUREMENTS

ITO refractive index can be estimated from spectrophotometer curves such as Figure 21. The oscillation in the transmission curve between 0.5 and 1.06 microns for the coated dome is due to the difference in refractive index between plastic and ITO. The oscillation is caused by constructive and destructive interference of light reflected from the ITO/air and ITO/plastic interfaces as the wavelength of light varies through multiples of the ITO thickness. The indices of polycarbonate and polysulfone are both very close to 1.90 at 1.06 microns.¹⁰ Using this index number and the amplitude of the oscillation, the approximate index of the ITO can be calculated using standard equations.⁵ Typically, the index of the ITO is 1.90 ± 0.05 . The method is only approximate in this particular case because ITO

A - TUNGSTEN LIGHT SOURCE
 B - INFRARED FILTER
 C - GRATING MONOCHROMATOR
 D - FOCUSING LENS
 E - DOME UNDER TEST

F - SOLAR CELL DETECTOR
 G - SLIDING DOME HOLDER
 H - DIGITAL AMMETER
 I - OPTICAL BENCH

Figure 22. Optical Bench Apparatus for Measuring 1.06 Micron Transmission

absorption is not negligible. More sophisticated calculations are required to compute both the real and imaginary parts of the index.

THICKNESS UNIFORMITY MEASUREMENT

Using the spectrophotometer data of Figure 21 and the approximate refractive index as calculated in the previous section, the ITO thickness can be deduced. The oscillations in the transmission curve satisfy the relation $4nt = m\lambda$, where $m = 1, 3, 5, \dots$ for minima and $m = 2, 4, 6, \dots$ for maxima, n is the ITO refractive index, t is the ITO thickness and λ is the wavelength of the m th extrema. When the correct m value has been associated with each λ , the product $m\lambda$ is a constant, and the thickness is $m\lambda/4n$. Thickness measurements with this method are reproducible to $\pm 0.5\%$ on domes. Thickness accuracy is determined by the accuracy with which n is known. Of principal concern to this program is not the absolute thickness, but the wavelengths at which the transmission peaks occur. If a coating thickness of approximately 1 micron is desired for rf shielding, the $m = 8$ peak should occur at 1.06 microns for maximum dome transmission.

Employing the above procedure at different points on the dome, the thickness uniformity can be measured. Several domes tested during the year indicated thickness uniformities of $\pm 6\%$. No systematic attempt has yet been made to improve the uniformity because more important issues have required attention.

SHEET RESISTANCE MEASUREMENTS

Sheet resistance measurements were made using the standard van der Pauw 4-point method.¹¹ Spring-clip probes were attached to each dome at 4 equally spaced points, as shown in Figure 23. A dc power supply was used to provide current to the coating, and an electrometer for measuring the induced voltage. A specially constructed switch box was used to permute voltage and current contacts and to reverse the current. The current was measured by using the electrometer to measure the voltage across one member of a set of precision series resistors mounted in the switch box. Sheet resistance measurements can be reproduced to $\pm 2\%$ with this method. The ac-

Figure 23. Van der Pauw 4-point Sheet Resistance Measurement Apparatus

curacy of the method is determined by the calibration of the series resistors and the electrometer, each of which is accurate to about $\pm 1\%$.

For rapid, but less accurate, sheet resistance measurements, a simple method requiring only a hand-held ohmmeter was developed. If 2 points on the coating about 1/2 inch apart are touched very lightly with the probes of an ohmmeter set for the lowest readable resistance scale, then the sheet resistance in Ohms/square is approximately 1/5 the indicated resistance in Ohms plus 6.5 Ohms. For example, if the ohmmeter reads 50 Ohms, the sheet resistance is 16.5 Ohms/square. This approximate relation was derived by making 2-point ohmmeter and 4-point van der Pauw measurements on the same coatings, plotting the results as in Figure 24, and least squares fitting to a straight line.

Figure 24. Graph for Converting 2-point Ohm Meter Measurements into Sheet Resistance Values

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