TRANSPARENT ARCPROOF PROTECTIVE COATINGS: PERFORMANCE AND MANUFACTURABILITY ISSUES

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Abstract. Highly transparent thin films with moderately high sheet resistivity approximately 10^8 ohms·square^{-1} ($\Omega \cdot \square^{-1}$) are needed for protection of photovoltaic arrays and other spacecraft surfaces from static charging in space. They may also be useful for dust control on Mars and the Moon. Indium tin oxide (ITO) codeposited with the transparent insulator MgF_2 is promising for these applications, but it is difficult to deposit films with reproducible sheet resistivity. We report experiments on a small dual RF magnetron sputter coater, using plasma emission monitoring (PEM) to improve control of film composition. Results show that PEM is useful for composition control but must be supplemented by periodic in situ measurements of coatings' optical or electrical properties. We have successfully coated both rigid (glass, quartz) and flexible substrates.

Key words: arcproof coatings, spacecraft charging, dust management

1. Introduction

Charge buildup on nonconductive spacecraft surfaces, due to solar proton and electron emissions, can cause damaging arcing. The optimum protective coating for these surfaces would have a sheet resistivity approximately 10^8 ohms·square^{-1} ($\Omega \cdot \square^{-1}$) and must be highly transparent spectral range if used on photovoltaic arrays or optical windows. An excessively conductive surface is undesirable in low Earth orbit since it may lead to large current flow between the spacecraft power system and the conductive space plasma. Application of these coatings will require production coating of a variety of substrates ranging from flat glass to the complex, flexible polymeric structures of inflatable satellites [1].

Similar coatings may have dust control applications on the Moon and Mars, since the dust is held on surfaces by electrostatic charge.

Previous work [2] has shown that thin films of codeposited indium tin oxide (ITO) and MgF_2 can be made with the desired sheet resistivity and have the

J.I. Kleiman (ed.), Protection of Materials and Structures from Space Environment, 331–340.

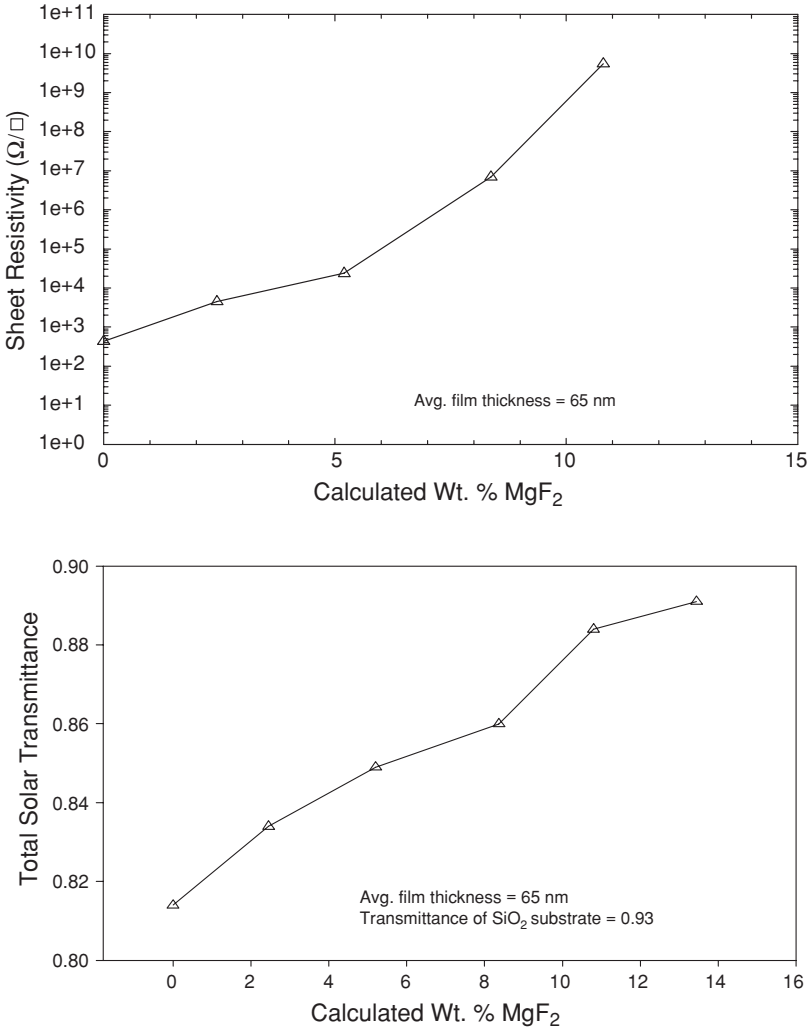

Figure 1. Sheet resistivity and solar transmittance of ITO–MgF_2 vs. composition [2]

extremely high solar optical transmittance needed for high-efficiency photovoltaic arrays, as shown in figure 1.

Unfortunately, the sheet resistivity of ITO–MgF_2 is rather sensitive to the MgF_2/ITO ratio, leading to irreproducible results when depositing coatings in laboratory-scale equipment [3]. Thus this material cannot be used unless a method is found for reliable industrial-scale coating deposition. Industrial deposition of transparent oxide coatings is frequently done by sputtering, using magnetron sputter guns driven by RF or medium-frequency current sources. To investigate the possibility of depositing ITO–MgF_2 by this technique, we have prepared films

using two independently powered RF magnetrons with, respectively, ITO and MgF_2 targets, facilitating adjustment of film composition. Since plasma emission monitoring (PEM) of sputter discharges is a technique well known to the vacuum coating industry, we investigated its use to control the composition of our films. We find that monitoring the intensity of ITO and MgF_2 plasma emission lines improves sample reproducibility but probably will have to be supplemented by periodic in-situ resistance or optical measurements for reliable production. It would clearly be helpful if sheet resistivity were less strongly dependent on film composition. We find that the addition of high-purity air (N_2/O_2 mixture) during deposition appears to accomplish this.

2. Experimental Techniques

A schematic view of the deposition chamber is shown in figure 2.

Films were deposited by simultaneous operation of two 5.1 cm diameter 13.56 MHz magnetron sputter guns. RF power (generally <100 W) to each gun was controlled independently to adjust film composition. Sputtering was carried out in argon gas at approximately 6 mTorr pressure. Samples normally were made without addition of oxygen or air because this system produces highly transparent, conductive ITO without it. The background pressure with argon turned off and pump throttle valve set as for deposition was $<2 \times 10^{-5}$ Torr. (Pressure with argon off and throttle wide open was typically $\sim 1 \times 10^{-6}$ Torr.)

Sample thickness was determined by readings of a single quartz crystal monitor (QCM) located near the sample. The QCM had been calibrated separately for MgF_2 and ITO by measuring films of each, deposited on optically flat quartz, with

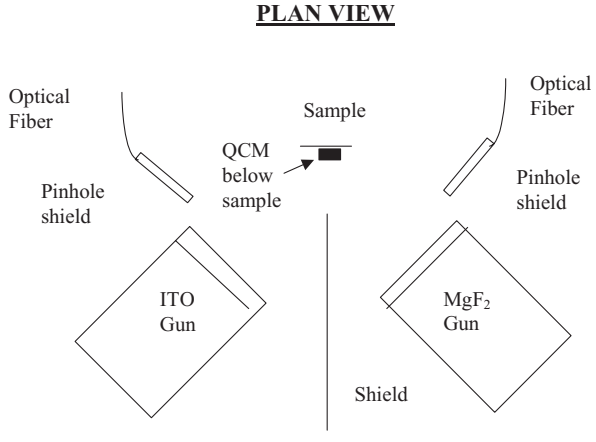

Figure 2. Layout of deposition chamber

a profilometer [4]. MgF_2/ITO composition ratios were estimated from deposition rate measurements made on each sputter gun at least once during each deposition run. (We had previously found the deposition rate to be approximately a linear function of RF power.)

Light from the plasma in front of each gun was collected by an optical fiber oriented approximately as shown in figure 2. Each fiber terminated in a short tube with a small hole at its outer end. This reduced the number of scattered particles reaching the fiber [5]. Emissions were analyzed by a two-channel grating spectrometer with wavelength resolution approximately 0.4 nm. Experiments showed that each fiber received a negligible amount of light from the other sputter gun.

Substrate temperature during deposition, estimated from thermocouple measurements, was $<40^{\circ}$C. Thus, it is likely that our samples were highly disordered or amorphous. However, this demonstrates the feasibility of coating flexible polymeric substrates.

Most samples discussed in this paper were deposited on borosilicate glass. However, we have successfully coated Mylar, Kynar, and Upilex. Each substrate was covered by an aluminum mask to produce a sample measuring 0.3×1.9 cm^2 with electrical contact arms along the edge. Electrical resistance measurements were made at room temperature in ambient atmosphere by four-terminal methods to eliminate the effect of contact resistance, using appropriate guarded cabling and high-input resistance electrometers.

3. Results and Discussion

3.1. PLASMA EMISSION

A typical PEM spectrum for each target is shown in figure 3. The spectra clearly are very different.

We chose to use ITO and MgF_2 lines at 453 and 384 nm, respectively, because they showed the best correlation with sheet resistivity. Higher resolution plots of these lines are shown in figure 4.

The possible benefits of composition control by plasma emission monitoring are shown in figure 5, where we plot sheet resistivity for the same samples vs. the MgF_2/ITO plasma intensity ratio and vs. the MgF_2 concentration determined by the quartz crystal monitor. Note the closer correlation of sheet resistivity to the intensity ratio than to the estimated MgF_2 concentration.

On the other hand, we sometimes found large shifts of sheet resistivity relative to plasma intensity ratio and QCM data, usually after opening the chamber to remove samples. This is shown in figure 6.

Based on these results, it appears that PEM can facilitate production of ITO–MgF_2 but must be supplemented by periodic in-situ measurements on coated products or witness coupons.

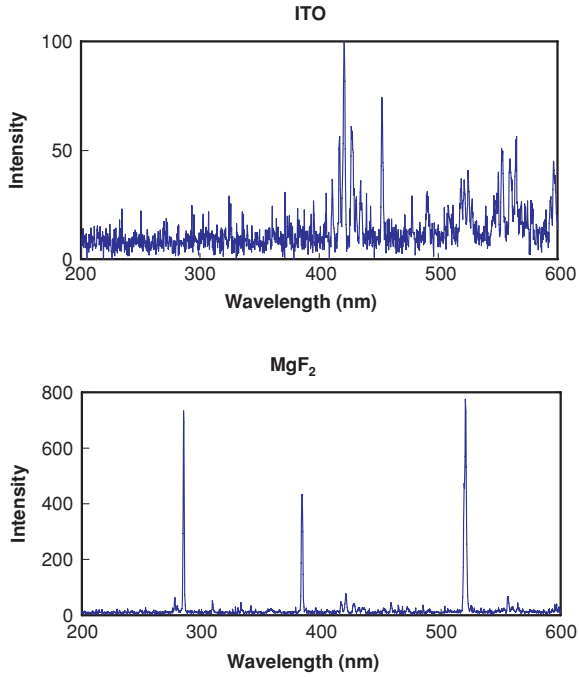

Figure 3. Broadband optical spectrum of each target's discharge. Intensity is measured in arbitary units

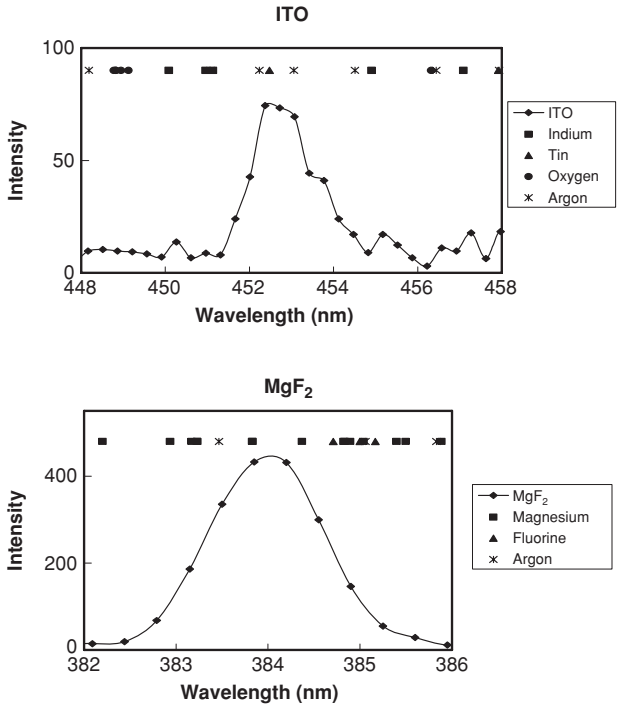

Figure 4. Higher-resolution spectra of the monitored plasma emissions, together with data on relevant elemental emission lines

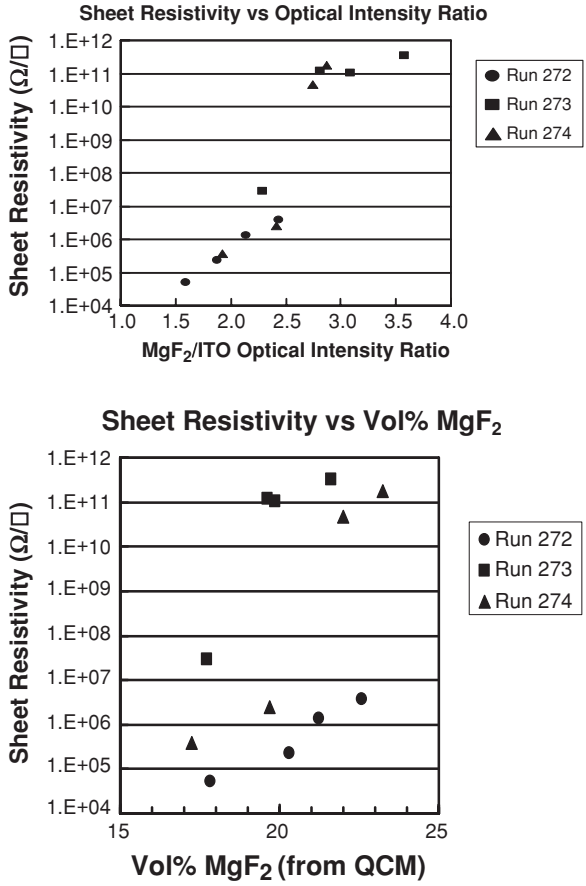

Figure 5. Sheet resistivity vs. MgF_2/ITO intensity ratio (upper graph) and vs. estimated MgF_2 concentration (lower graph). Sample thickness 400 Å on glass

3.2. COATING STABILITY

The sheet resistivity of several films measured at room temperature is plotted vs. time since deposition in figure 7 (glass substrates) and figure 8 (Upilex substrates). All samples were stored in ambient air.

As noted by the authors of [2], sheet resistivity generally increases over time, probably due to absorption of atmospheric oxygen. However, the stability is similar to that of [2] even though our films are somewhat thinner. In addition, we note that stability of our films on Upilex substrates appears to be similar to that of films on glass. Some films in figures 7 and 8 show unusually large resistivity increases. The reason for this is unknown, and the films' microstructure has not been examined.

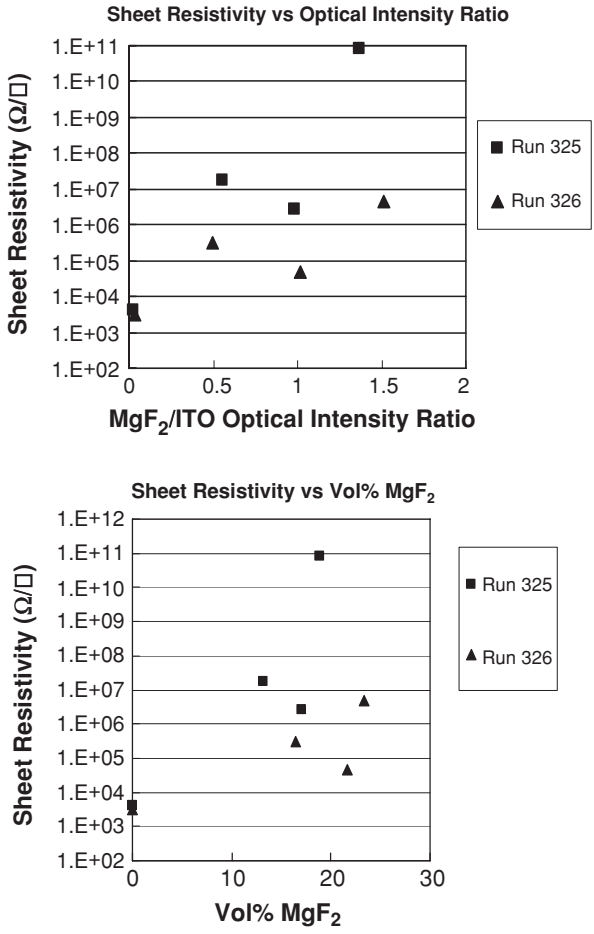

Figure 6. Data similar to figure 5, but showing poor correlaton of sheet resistivity with PEM and QCM data

3.3. EFFECT OF AIR INJECTION

The effect of injecting a small amount of high-purity air during deposition is shown in figure 9, where we plot sheet resistivity vs. MgF_2 concentration with and without air injection.

Argon flow rate was 0.9 SCCM in both cases, so the partial pressure of air was approximately 10% of the total pressure.

Although there is considerable scatter in the data, the addition of air appears to make sheet resistivity less dependent on composition. Note that figure 9 shows a considerably higher MgF_2 concentration than do figures 5 and 6. We believe this is due to a calibration error in the QCM data of figure 9, which were taken early in

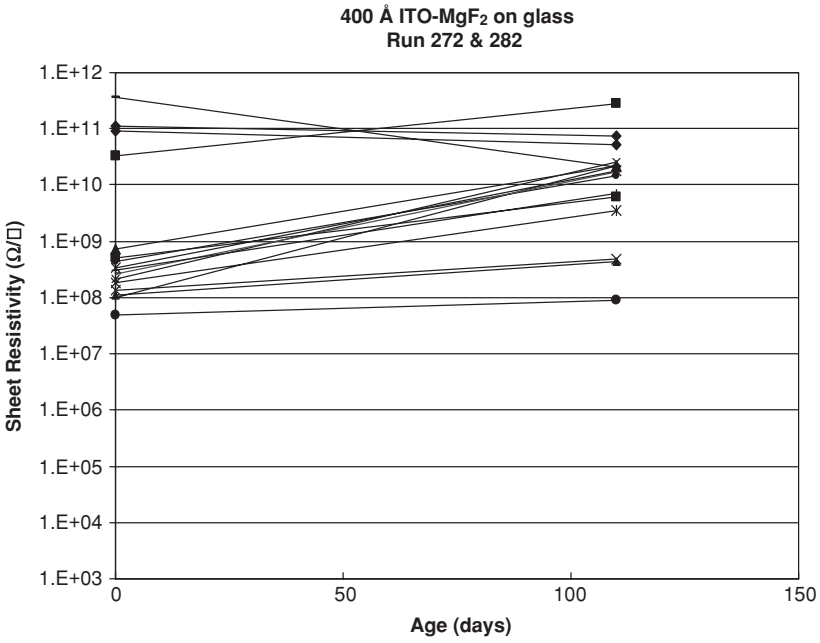

Figure 7. Sheet resistivity vs. time since deposition (glass substrates). Samples stored in ambient air

the project, that does not affect the remainder of this paper. It appears impossible to correct for this error in a reliable manner, so we have not attempted to do so.

The data of figure 9 for zero air flow suggest an abrupt increase in sheet resistivity at a "critical" MgF_2 concentration, the origin of which is unknown. It

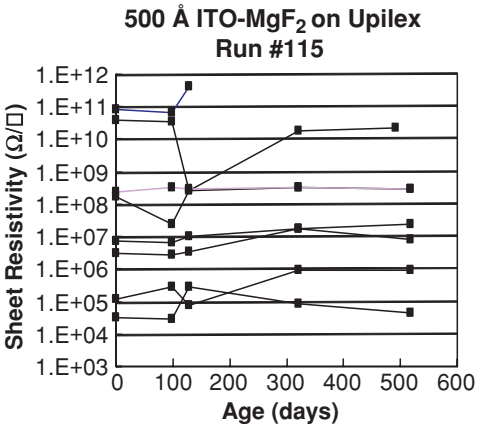

Figure 8. Sheet resistivity vs. time since deposition (Upilex substrates). Samples stored in ambient air

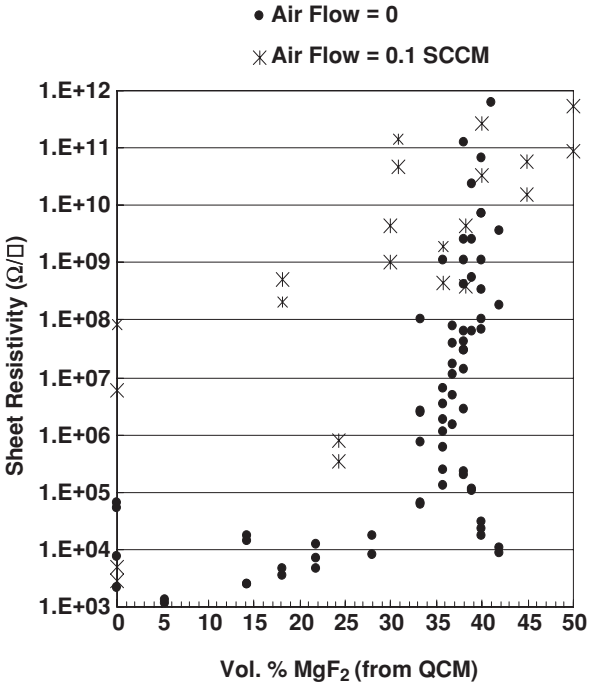

Figure 9. Sheet resistivity vs. MgF_2 concentration with and without addition of air. Argon flow 0.9 SCCM in both cases

might indicate a compositional metal–insulator transition or the onset of electron percolation between conducting and insulating granules.

4. Conclusion

ITO–MgF_2 coatings have been successfully deposited by sputtering from dual RF magnetrons. Control of film composition using intensity measurements of plasma emission lines improves reproducibility of sheet resistivity. These techniques are familiar to the vacuum coating industry. However, plasma emission monitoring will probably have to be supplemented by in situ measurements of coating properties. Since high-resistance measurements would be difficult in the vicinity of the sputter discharge, measurement of optical properties would be preferable. We find that the reflectance of ITO–MgF_2 diminishes as sheet resistivity increases, suggesting that simple reflectance measurements might suffice.

The dual-magnetron method has been used to deposit ITO–MgF_2 on flexible polymeric substrates that are increasingly of interest for space applications.

Stability of the coating on polymers appears to be similar to that on glass provided flexure is limited.

Preliminary data suggest that injecting high-purity air during deposition may make sheet resistivity less strongly dependent on film composition. This could be very helpful in production.

In the next several months we will investigate the durability of ITO–MgF_2 under vacuum ultraviolet exposure, in situ optical and electrical properties measurement methods, and the benefits of air injection.

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