Slightly Conductive Transparent Films for Space Applications—Manufacturability and Durability

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ABSTRACT

Highly transparent, slightly conductive films of co-deposited indium tin oxide (ITO) and MgF₂ have possible applications for environmental protection of exterior surfaces of spacecraft. Reliable preparation of films with the desired sheet resistivity (~10⁸ ohms/square) is difficult because the electrical properties of ITO-MgF₂ are highly dependent on film composition. We have investigated the use of plasma emission monitoring to improve the reproducibility of films prepared by RF magnetron sputtering. While considerable improvement was observed, it appears that some in-situ electrical or optical characterization will be needed for reliable production coating with ITO-MgF₂. We have also done further evaluation of a possibly undesirable photoconductive effect previously observed in these films.

INTRODUCTION

Nonconductive exterior spacecraft surfaces can develop large electrostatic charges due to particles emitted by the sun or, on Mars, friction from windborne dust. This may lead to damaging arcing and/or dust adhesion on solar panels, windows and lenses. Protection of these surfaces requires a coating with sheet resistivity (Rₛ) ~10⁸ ohms/square (Ω/□), which for some applications must be highly transparent. Previous work has shown that co-deposited films of ITO and MgF₂ can be made with these characteristics and exhibit good durability under exposure to atomic oxygen, which is present in the earth’s upper atmosphere [1]. Application of these films will require production coating of a variety of substrates ranging from flat glass to the complex, flexible polymeric structures of inflatable satellites [2].

We are developing an ITO-MgF₂ deposition technique using two independently powered RF magnetron sputter guns with ITO and MgF₂ targets, respectively [3]. This method allows easy adjustment of film composition. However, Rₛ is strongly dependent on MgF₂/ITO ratio, causing large variations in Rₛ despite frequent sputter rate calibrations of each gun using a quartz crystal monitor (QCM) [3].

In this paper we report an attempt to use optical plasma emission monitoring (PEM) to facilitate reliable ITO-MgF₂ film deposition. We indeed find Rₛ to be more closely correlated to the relative intensities of MgF₂ and ITO emission lines than to film composition as calculated from QCM sputter rate measurements. However, it appears that PEM must be supplemented by period in situ measurements of film properties.

In addition, we present additional data on the photoconductivity of ITO-MgF₂ in short-wavelength visible light previously reported by us [3]. These results may be useful in future attempts to minimize this effect should it cause application problems.

EXPERIMENT TECHNIQUES

A schematic view of the deposition chamber is shown in Figure 1.

Plan View

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. Target-to-sample distance was

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~10 cm. Angle between each gun’s axis and sample normal was 45°. One target was 90wt%/10wt% In/Sn oxide, the other was MgF₂. The chamber was pumped by an oil diffusion pump and liquid nitrogen trap.

Sputtering was carried out in Ar gas at ~6 mTorr pressure. Samples were made without addition of oxygen or air because this system produces highly transparent conductive ITO films without it. The background pressure with Ar turned off and pump throttle valve set as for deposition was usually <2x10⁻⁵ Torr. (Pressure with Ar off and throttle wide open was typically ~1x10⁻⁶ Torr).

Sample thickness was determined by readings of a single QCM located near the sample. The QCM had been calibrated separately for MgF₂ and ITO by measuring films of each, deposited on optically flat quartz, with a Dektak profilometer [3]. MgF₂/ITO composition ratios were estimated from deposition rate measurements made on each 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 emitted by the plasma in front of each gun was collected by an optical fiber oriented approximately as shown in Figure 1. This orientation reduced coating of the fiber tip by particles on ballistic trajectories from the target. 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 [4]. Emissions were analyzed by a two-channel Ocean Optics grating spectrometer (two separate spectrometers with shared electronics) with resolution ~0.4 nm. Experiments showed that each fiber received a negligible amount of light from the other sputter gun.

Samples discussed here were deposited on borosilicate glass. Each substrate was covered with an aluminum mask to produce a sample measuring 0.3x1.9 cm² with electrical contact arms along the edge. Thermocouple measurements indicate that substrate temperature during deposition was <40°C. Thus it is likely that the samples are highly disordered or amorphous.

Electrical resistance measurements were made in ambient atmosphere by the four-terminal method to eliminate the effect of contact resistance. Measuring current was 1 pA-100 µA. Guarded cabling and high input resistance electrometers minimized errors due to the high resistance of some samples.

Photoconductivity experiments were performed with the sample in a light-tight box equipped with a blue light emitting diode (LED). The LED has a rather narrow optical bandwidth with peak emission at ~430 nm (photon energy ~2.9 eV).

Light intensity at the sample, determined approximately by measuring beam diameter and total power (using an optical power meter), was ~20 W/m².

RESULTS AND DISCUSSION

Plasma Emission
A typical PEM spectrum for each target is shown in Figure 2. The spectra clearly are very different.

![Figure 2: Broadband optical spectrum of each target's discharge. Intensity is measured in arbitrary units defined by the spectrometer manufacturer.](image)

To decide which PEM lines to use, we compared the measured Rₚ of several samples with the intensity ratios of several pairs of ITO and MgF₂ lines. The best correlation was obtained using ITO and MgF₂ lines at 453 nm and 384 nm, respectively. Higher resolution plots of these lines are shown in Figure 3, together with the wavelengths of relevant elemental emission lines [5].
Figure 3: Higher resolution spectra of the monitored ITO and MgF₂ emissions, together with data on relevant elemental emission lines.

The benefits of PEM are illustrated in Figure 4, where we plot Rs for the same samples vs. MgF₂/ITO plasma intensity ratio and vs MgF₂ concentration determined by the QCM. Note the closer correlation of Rs to the intensity ratio than to the estimated MgF₂ concentration.

Figure 4: Sheet resistivity vs. MgF₂/ITO intensity ratio (upper graph) and vs. estimated MgF₂ concentration (lower graph).

On the other hand, the plasma intensity ratio alone is insufficient to adequately predict Rs. An example is shown in Figure 5, where we plot Rs vs. intensity ratio for high and low RF power settings. Note also that the data of Figure 5, for unknown reasons, are quite different from those of Figure 4.
Based on our findings to date, it appears that PEM can improve production of ITO/MgF$_2$ but must be supplemented by periodic in situ measurements on coated products or witness coupons. We will soon test methods for in situ characterization of electrical and optical properties of this material to see if a simple, reliable technique can be found.

Photoconductivity

We have previously reported substantial reductions in $R_s$ of ITO/MgF$_2$ in the presence of low-intensity visible light, particularly at the blue end of the spectrum [3]. At that time our samples were deposited on quartz substrates. In those samples, the relative change in $R_s$ increased monotonically with dark resistance; the strongest photoconductivity effects were observed in samples with dark $R_s \sim 10^{11} \, \Omega/\square$. Our more recent samples, deposited on borosilicate glass, also exhibit photoconductivity as shown in Figure 6, where we plot the change in $R_s$ vs. time in the presence of blue LED illumination.

In these recent films, however, the photo effect is strongest in samples with dark $R_s \sim 10^8 \, \Omega/\square$ and essentially disappears in high-resistance samples, as shown in Figure 7.
The abrupt disappearance of photoconductivity when dark $R_s$ exceeds $\sim 5 \times 10^9 \Omega/\square$ suggests a change of some sort in the electrical conduction mechanism that apparently did not occur in earlier samples deposited on quartz [3]. Further investigation of this matter could lead to future coatings with reduced photoconductivity.

CONCLUSIONS

A technique for preparation of slightly conductive transparent coatings by co-deposition of ITO and MgF$_2$ from independent RF magnetron sputter guns has been enhanced by the addition of a plasma emission monitor. By controlling the ratio of ITO and MgF$_2$ line intensities rather than RF power, we have improved the controllability and reproducibility of the coating’s sheet resistivity. However, the relationship between sheet resistivity and line intensity ratio depends on RF power levels and other variables. Thus it appears that some in situ electrical or optical property measurements will be needed to monitor and re-calibrate the deposition process. We are beginning experiments on these techniques.

The photoconductivity observed previously in ITO-MgF$_2$ has been studied in more detail. The effect is most pronounced in samples with dark sheet resistivity $\sim 10^8 \Omega/\square$ and is absent in samples with dark sheet resistivity $>5 \times 10^9 \Omega/\square$. The cause of this behavior is unknown.

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