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 MgF_2 have possible applications for environmental protection of exterior surfaces of spacecraft. Reliable preparation of films with the desired sheet resistivity (~10^8 ohms/square) is difficult because the electrical properties of ITO-MgF_2 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-MgF_2. 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 (R_s) ~10^8 ohms/square (Ω/□), which for some applications must be highly transparent. Previous work has shown that co-deposited films of ITO and MgF_2 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-MgF_2 deposition technique using two independently powered RF magnetron sputter guns with ITO and MgF_2 targets, respectively [3]. This method allows easy adjustment of film composition. However, R_s is strongly dependent on MgF_2/ITO ratio, causing large variations in R_s 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-MgF_2 film deposition. We indeed find R_s to be more closely correlated to the relative intensities of MgF_2 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-MgF_2 in short-wavelength visible light previous 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.

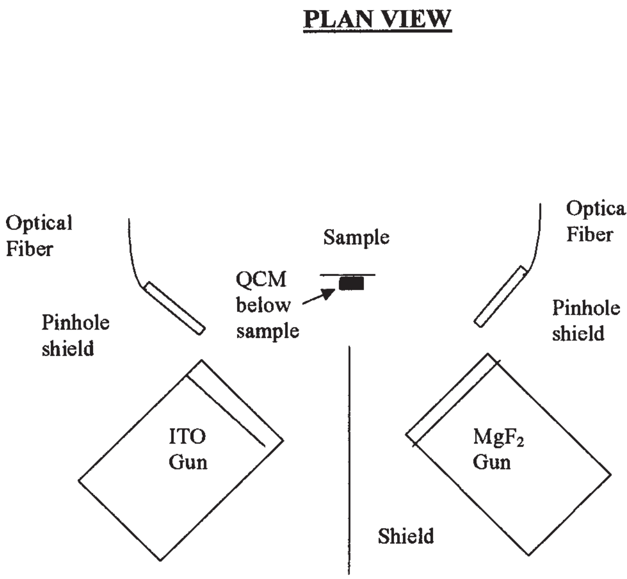

Figure 1: Layout of deposition chamber.

Films were deposited by simultaneous operation of two 5.1 cm diameter 13.56 MHz magnetron sputter guns. RF power (generally <100W) to each gun was controlled independently to adjust film composition. Target-to-sample distance was

~10 cm. Angle between each gun's axis and sample normal was 45°. One target was 90wt%/10wt% In/Sn oxide, the other was MgF_2. 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 $\sim 1x10^{-6}$ Torr).

Sample thickness was determined by readings of a single 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 a Dektak profilometer [3]. MgF_2/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 cm^2 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/m^2.

RESULTS AND DISCUSSION

Plasma Emission

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

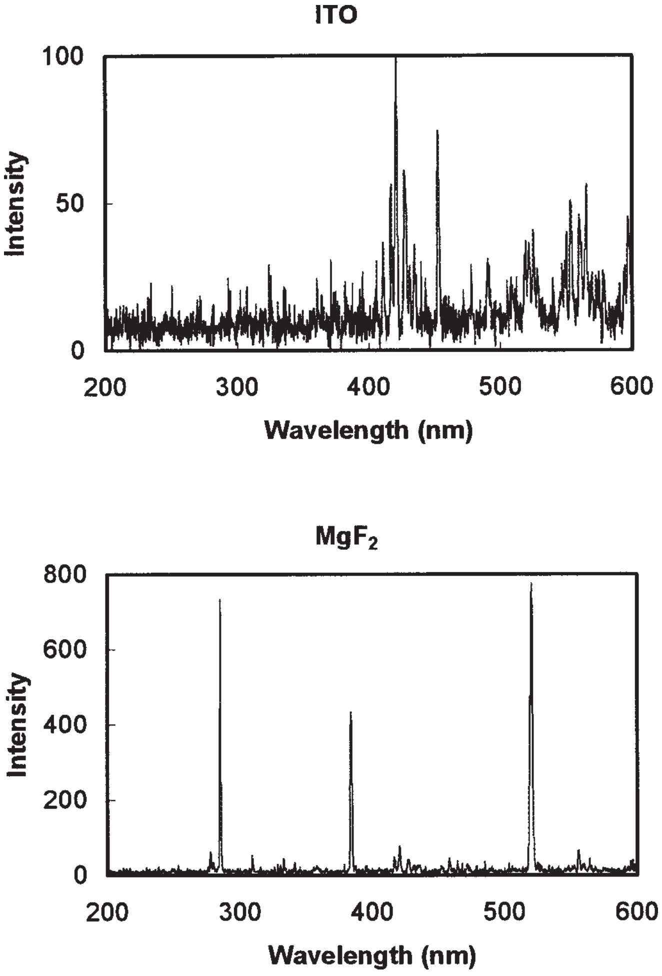

Figure 2: Broadband optical spectrum of each target's discharge. Intensity is measured in arbitrary units defined by the spectrometer manufacturer.

To decide which PEM lines to use, we compared the measured R_s of several samples with the intensity ratios of several pairs of ITO and MgF_2 lines. The best correlation was obtained using ITO and MgF_2 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].

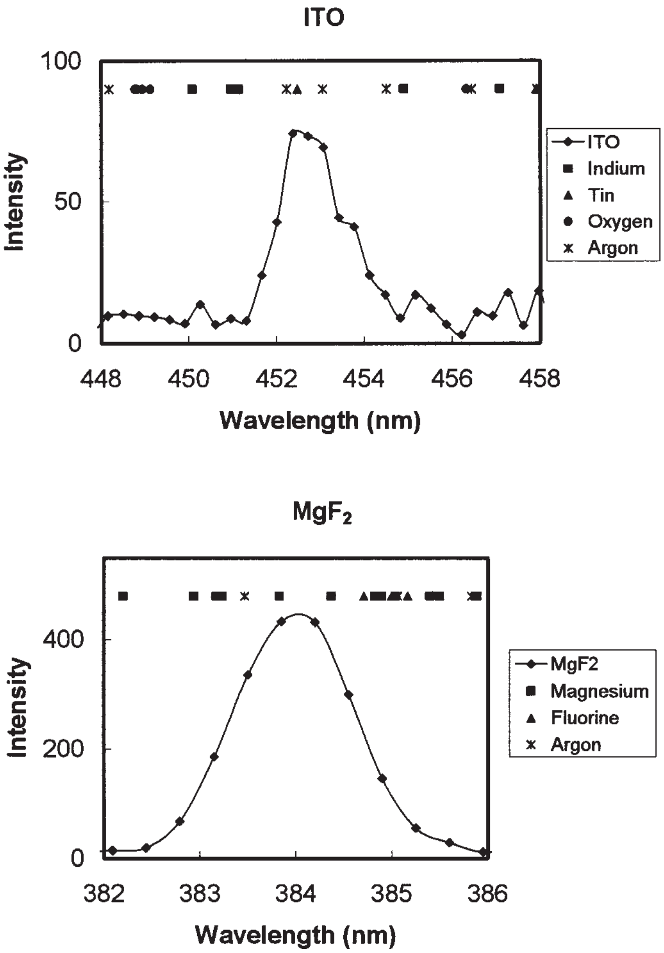

Figure 3: Higher resolution spectra of the monitored ITO and MgF_2 emissions, together with data on relevant elemental emission lines.

The benefits of PEM are illustrated in Figure 4, where we plot R_s for the same samples vs. MgF_2/ITO plasma intensity ratio and vs MgF_2 concentration determined by the QCM. Note the closer correlation of R_s to the intensity ratio than to the estimated MgF_2 concentration.

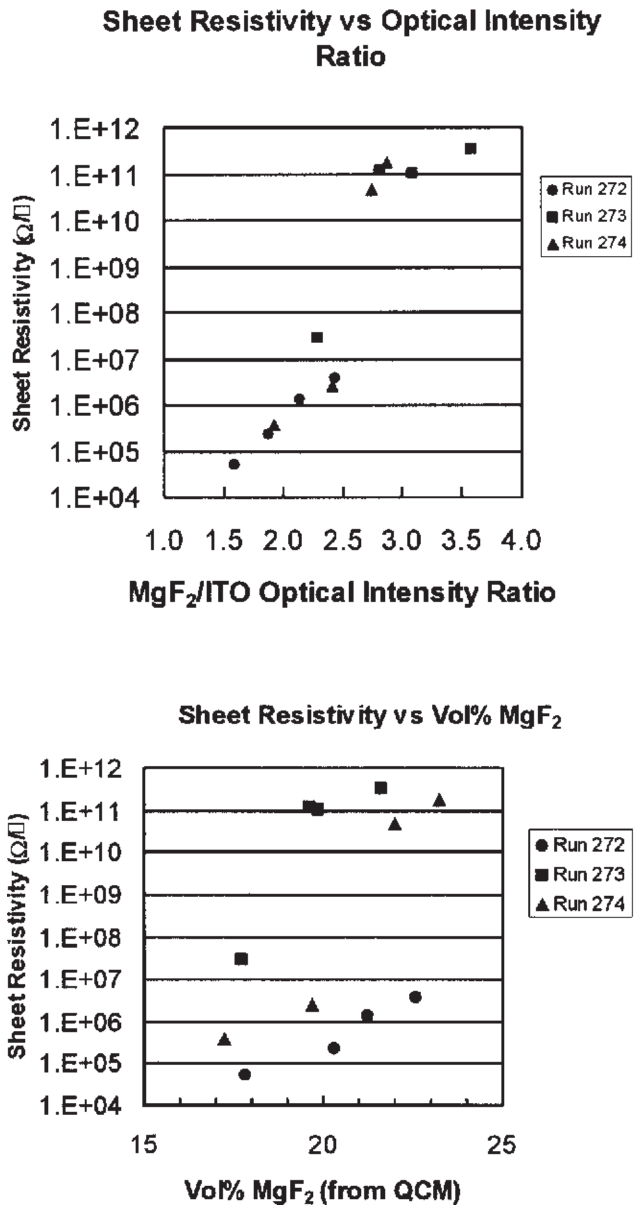

Figure 4: Sheet resistivity vs. MgF_2/ITO intensity ratio (upper graph) and vs. estimated MgF_2 concentration (lower graph).

On the other hand, the plasma intensity ratio alone is insufficient to adequately predict R_s. An example is shown in Figure 5, where we plot R_s 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.

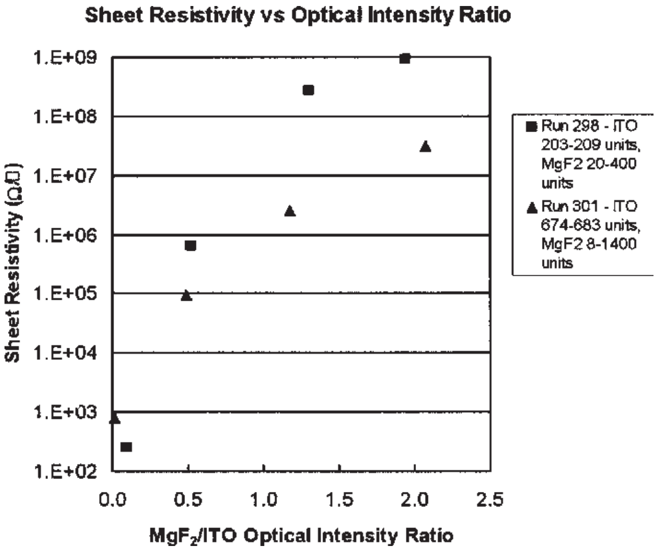

Figure 5: Sheet resistivity vs MgF_2/ITO intensity ratio for high and low RF power settings (see legend).

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 ~10^{11} Ω/□. 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.

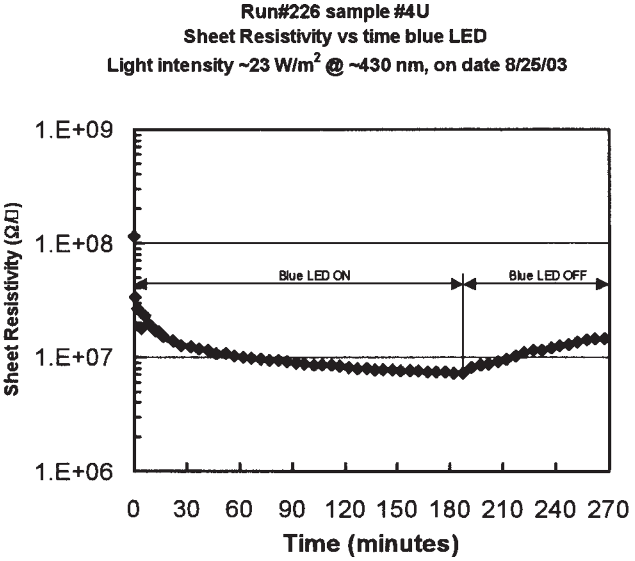

Figure 6: Effect of blue light on sheet resistivity of ITO-MgF_2 on glass.

In these recent films, however, the photo effect is strongest in samples with dark R_s ~10^8 Ω/□ and essentially disappears in high-resistance samples, as shown in Figure 7.

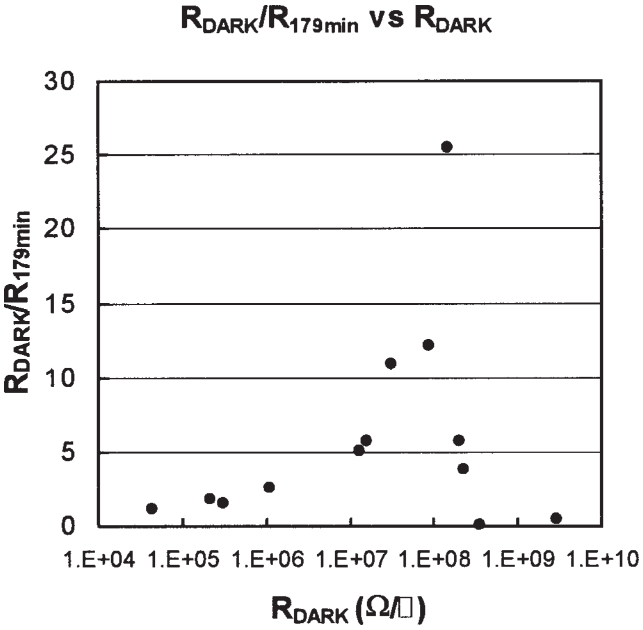

Figure 7: Ratio of dark resistance to resistance after 179 minutes of exposure to blue LED light, plotted vs. dark sheet resistivity. (Ratios < 1 indicate a small increase in resistance when light is applied).

The abrupt disappearance of photoconductivity when dark R_s exceeds ~5x10^9 Ω/□ 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 ~10^8 Ω/□ and is absent in samples with dark sheet resistivity >5x10^9 Ω/□. The cause of this behavior is unknown.

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