Transparent Conducting Thin Films for Spacecraft Applications

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Abstract

Transparent conducting thin films are required for a variety of optoelectronic applications, automotive and aircraft windows as well as in solar cells for space applications. Transparent conductive coatings of indium-tin-oxide (ITO)—magnesium fluoride (MgF$_2$) and aluminum doped zinc oxide (AZO) at several dopant levels are investigated for electrical resistivity (sheet resistance), carrier concentration, optical properties, and atomic oxygen durability. The sheet resistance values of ITO-MgF$_2$ range from $10^2$ to $10^{11}$ ohms/$\square$, with transmittance of 75 to 86 percent. The AZO films sheet resistances range from $10^7$ to $10^{11}$ ohms/$\square$ with transmittances from 84 to 91 percent. It was found that in general, with respect to the optical properties, the zinc oxide (ZnO), AZO, and the high MgF$_2$ content ITO-MgF$_2$ samples, were all durable to atomic oxygen plasma, while the low MgF$_2$ content of ITO-MgF$_2$ samples were not durable to atomic oxygen plasma exposure.

Introduction

Transparent conducting thin film materials would have wide application for heat mirrors, opto-electronic devices, gas sensors, automotive and aircraft windows. The use of solar cells for space applications also requires slightly conductive coatings which are resistant to degradation caused by atomic oxygen and ultraviolet (UV) radiation.

The development of a conductive protective coating is essential for the operation and efficiency of photovoltaic systems for use in space environments. Atomic oxygen is the most predominant environmental species from an altitude of 180 km (97 nmi) to 650 km (351 nmi), and degradation by atomic oxygen and or UV radiation may cause optical property changes, thus affecting the performance of the system.

Another mechanism of degradation is surface charging, which might lead to pinhole formation in the protective coatings, as well as electronic interferences with the on-board spacecraft systems. A possible solution to this problem is to...
apply a surface coating material that is conductive, transparent, flexible, and resistant to atomic oxygen and UV radiation. To discharge surfaces that are being charged by space plasmas, a high resistivity to ground can be tolerated because the plasma charging currents are small. Materials applied over a dielectric area must be grounded at the edges and must have a resistivity less than 10^9 "ohms per square" (Ω/□) for geosynchronous orbit. The draining of surface charge for low Earth orbit (LEO) polar spacecraft applications, requires a surface resistivity of 108 Ω/□. Several candidate materials which might provide protection are transparent inorganic oxide coatings. To improve coating adherence, a 15 cm diameter source was operated with argon (Ar) at an ion energy of 1000 eV and an ion beam current of 35 mA. The water cooled substrate holder was located approximately 15.3 cm from the target and approximately 30.5 cm downstream of the 15 cm diameter source. To improve coating adherence, a 15 cm diameter ion source was operated with argon (Ar) at an ion energy of 250 eV and beam current of 35 mA to ion beam clean the substrates for 2 min prior to deposition. Air was also introduced during deposition of ITO-MgF2. Thin film coatings were sputter deposited on fused silica substrates at an average ITO-MgF2 deposition rate of 31 Å/min. Film thickness was measured on the fused silica substrates with a Sloan:Dektak IIa surface profiler. The film thickness ranged from approximately 900 to 1000 Å. The average deposition rate for AZO on fused silica substrates was 11 Å/min, the film thickness ranged from 200 to 650 Å.

A compromise between electrical conductivity and optical transparency is required. An increase in thickness of the conductive coating increases the electrical conductivity but it also decreases the optical transmittance.

Optical Properties

Optical measurements of coatings deposited on fused silica substrates were made with a Perkin Elmer Lambda 9 UV/VIS/NIR spectrophotometer operated with a 60 mm integrating sphere. Integrated solar transmittance and solar reflectance values were obtained by convoluting the spectral data into the air-mass-zero (AM0) solar spectrum. The accuracy of measurements are within ±2 percent. Figure 2 illustrates the spectral transmittance for ITO-MgF2, AZO and ZnO thin films on fused silica quartz. The transmittance of the ITO-MgF2 coating increases with an increase in MgF2 concentration. Spectral variations at approximately 820 nm and 1920 nm are due to the instrument filter changes.

The total transmittance and solar absorptance (α) for the thin films are shown in Table 1. The absorptance was calcu-
Table 1. Optical and Electrical properties of thin films

<table>
<thead>
<tr>
<th>Thin Film</th>
<th>Total Transmittance</th>
<th>Solar Absorptance</th>
<th>Total Reflectance</th>
<th>Thickness (Å)</th>
<th>Sheet Resistance (Ω/□)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO</td>
<td>0.720</td>
<td>0.140</td>
<td>0.140</td>
<td>1000</td>
<td>10^4</td>
</tr>
<tr>
<td>ITO/MgF₂ (I - low)</td>
<td>0.750</td>
<td>0.130</td>
<td>0.120</td>
<td>1000</td>
<td>10^4</td>
</tr>
<tr>
<td>ITO/MgF₂ (II - high)</td>
<td>0.835</td>
<td>0.022</td>
<td>0.123</td>
<td>959</td>
<td>10^4</td>
</tr>
<tr>
<td>ITO/MgF₂ (III)</td>
<td>0.790</td>
<td>0.064</td>
<td>0.146</td>
<td>1115</td>
<td>10^4</td>
</tr>
<tr>
<td>ITO/MgF₂ (VI)</td>
<td>0.763</td>
<td>0.093</td>
<td>0.145</td>
<td>1042</td>
<td>10^4</td>
</tr>
<tr>
<td>ITO/MgF₂ (VII)</td>
<td>0.774</td>
<td>0.068</td>
<td>0.159</td>
<td>1158</td>
<td>10^4</td>
</tr>
<tr>
<td>AZO (II)</td>
<td>0.833</td>
<td>0.013</td>
<td>0.153</td>
<td>624</td>
<td>10^4</td>
</tr>
<tr>
<td>AZO (III)</td>
<td>0.906</td>
<td>0.012</td>
<td>0.082</td>
<td>200</td>
<td>10^4</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.792</td>
<td>0.038</td>
<td>0.171</td>
<td>1068</td>
<td>10^4</td>
</tr>
</tbody>
</table>

lated from the reflectance and transmittance data. Values are typically an average of two to five samples. A decrease in is obtained with an increase of MgF₂ in the ITO films.

Atomic Oxygen Durability

Atomic oxygen exposure was conducted in a ground based-plasma facility (SPI Plasma Prep II). Atomic oxygen was generated in a small quartz vacuum chamber by RF (13.56 MHz) dissociation of air at a pressure of approximately 90 mtorr. The typical effective atomic oxygen flux during exposure was approximately 8x10¹⁵ atoms/cm²-sec based on the erosion of Kapton in the plasma compared with known erosion in low Earth orbit (LEO). Samples were exposed to atomic oxygen effective fluences between 5.4 and 6.4x10²¹ atoms/cm². Although the atomic oxygen flux is accelerated compared to what would be experienced in LEO, and the energy is lower (0.04 eV compared to 4.5 eV in LEO), plasma exposure can provide a good qualitative feel for material durability in LEO.

The changes in the spectral total transmittance of ITO-MgF₂ upon exposure to atomic oxygen can be seen by comparison on the plots shown in Fig. 3. Figure 3(a) shows the spectral total transmittance of ITO-MgF₂ (high MgF₂ concentration) before and after exposure to an atomic oxygen fluence of 5.39x10²¹ atoms/cm². Figure 3(b) shows the total spectral transmittance for a sample with a low dopant level of MgF₂ before and after atomic oxygen exposure to an effective fluence of 5.39x10²¹ atoms/cm² or to same effective fluence as high MgF₂. Figure 4 shows the total spectral transmittance for AZO (2 percent Al) before and after atomic oxygen exposure.

Figure 3.—Total spectral transmittance. (a) ITO/MgF (high MgF) Before and after atomic oxygen exposure. (b) ITO/MgF (low MgF) before and after atomic oxygen exposure.

Figure 4.—Total spectral transmittance of AZO before and after atomic oxygen exposure.
The integrated solar optical properties (total transmittance ($\tau_t$), specular transmittance ($\tau_s$), total reflectance ($\rho_t$), specular reflectance ($\rho_s$) and absorptance) of all samples exposed to atomic oxygen, prior to and after exposure, are listed in Table 2. The ITO-MgF$_2$ samples with apparently lower MgF$_2$ content (I and VII) have initially lower total transmittance (0.748 and 0.774, respectively), similar to the ITO without any MgF$_2$ (0.720), and these samples are found to decrease in transmittance and increase in absorptance with atomic oxygen exposure. This behavior is very similar to the reaction of ITO to atomic oxygen plasma exposures. Decreases in transmittance of ITO samples are generally attributed to the UV radiation which is present during plasma ashing. The addition of greater amounts of MgF$_2$ to ITO (II and IV) not only results in greater initial transmittance (0.855 and 0.842, respectively), but these samples are found to increase in transmittance with atomic oxygen exposure (to 0.870 and 0.895, respectively). The solar absorptance of the lower MgF$_2$ content films (I and VII) increased from 0.105 and 0.068 to 0.256 and 0.176, respectively. While the absorptance of the higher MgF$_2$ content films (II and IV) increased and decreased, respectively. These changes in the optical properties of the high MgF$_2$ content ITO samples may be attributed to index of refraction changes associated with oxidation of the MgF$_2$. ITO-MgF$_2$ (II) increased from 0.020 to 0.049, while ITO-MgF$_2$ (IV) decreased from 0.039 to 0.020. Both the AZO and the ZnO films reacted similarly when exposed to atomic oxygen. Both the AZO (II) and the ZnO (II) films increased in total transmittance from 0.833 and 0.792 to 0.845 and 0.838, respectively, and increased in solar absorptance from 0.008 and 0.038 to 0.019 to 0.046, respectively. All samples except one (ITO-MgF$_2$ (VII)) experienced a decrease in both total and specular reflectance with atomic oxygen exposure. The sample which did not decrease in reflectance, increased only slightly, from a total reflectance of 0.159 to 0.167. In general, with respect to the optical properties, the AZO, ZnO, and the high MgF$_2$ content ITO-MgF$_2$ samples, were all found to be durable to atomic oxygen, while the low MgF$_2$ content ITO-MgF$_2$ samples were not durable to UV containing atomic oxygen environments.

### Electrical Properties

Sheet resistance measurements were made on film samples using pressure contacts on wire leads attached with conductive silver paint. In general, alternating current (19.5 Hz) was used for samples with sheet resistance below 104 $\Omega/\square$, direct current was used for samples with higher resistance. Four-lead techniques were used whenever possible; however, some high-resistance samples were measured by two-lead methods. Power dissipation in samples was kept below 15 $\mu$W to avoid self-heating effects. Hall measurements were made by similar techniques in a magnetic field of 1.2 Tesla to obtain information on carrier concentration and mobility.

Our results on the electrical properties of ITO-MgF$_2$, ZnO, and AZO films are summarized in Table 3. The Hall data suggest that adding MgF$_2$ to ITO reduces carrier concentration and mobility, both increasing the resistance. This raises the question of stability, since the resistance of pure ITO films, prepared to have low carrier concentration and mobility, changes drastically when heated.

The sheet resistance of several samples were measured after atomic oxygen exposure, are shown in Table 4. These preliminary results suggest that the electrical properties are affected by atomic oxygen exposure. More tests are planned to investigate the effects of atomic oxygen on the electrical properties of these coatings.
Table 3. Electrical properties of thin films at room temperature

<table>
<thead>
<tr>
<th>Thin Film</th>
<th>Thickness (Å)</th>
<th>Sheet Resistance (Ω/□)</th>
<th>Carrier Concentration (electrons/cm³)</th>
<th>Mobility (cm²/(V·s))</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO</td>
<td>1000</td>
<td>10¹</td>
<td>10⁶</td>
<td>17 - 20</td>
</tr>
<tr>
<td>ITO/MgF₂ (I)</td>
<td>1000</td>
<td>10²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ITO/MgF₂ (II)</td>
<td>959</td>
<td>10³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ITO/MgF₂ (III)</td>
<td>1115</td>
<td>10⁴</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ITO/MgF₂ (VI)</td>
<td>1042</td>
<td>10⁵</td>
<td>≥ 10⁶</td>
<td>≤ 1</td>
</tr>
<tr>
<td>ITO/MgF₂ (VII)</td>
<td>1158</td>
<td>10⁶</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AZO (I)</td>
<td>559</td>
<td>10⁷</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AZO (II)</td>
<td>624</td>
<td>10⁷</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AZO (III)</td>
<td>150</td>
<td>10¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>1068</td>
<td>10¹</td>
<td>10⁶</td>
<td>5.8</td>
</tr>
</tbody>
</table>

Table 4. Sheet resistance of thin films before and after atomic oxygen exposure

<table>
<thead>
<tr>
<th>Thin Film</th>
<th>Sheet Resistance (Ω/□) (Before AO Exposure)</th>
<th>Sheet Resistance (Ω/□) (After AO Exposure)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO/MgF₂ (III)</td>
<td>1 x 10⁷</td>
<td>8 x 10⁹</td>
</tr>
<tr>
<td>ITO/MgF₂ (VII)</td>
<td>5 x 10⁷</td>
<td>1 x 10⁹</td>
</tr>
<tr>
<td>AZO (II)</td>
<td>1 x 10⁷</td>
<td>2 x 10⁹</td>
</tr>
</tbody>
</table>

Conclusions

Transparent conductive coatings of indium-tin-oxide (ITO)-magnesium fluoride (MgF₂) and aluminum doped zinc oxide (AZO) were prepared by ion beam sputter deposition. Simultaneous ion beam sputter deposited indium-tin-oxide (ITO) and magnesium fluoride (MgF₂) at several dopant levels were investigated for electrical resistivity, optical properties and atomic oxygen durability. Results show sheet resistance values of ITO-MgF₂ range from 10² to 10¹¹ Ω/□, with transmittance of 75 to 86 percent. The AZO films investigated show a sheet resistance value of 10⁷ to 10¹¹ Ω/□ and transmittance of 84 to 91 percent. In general, with respect to the optical properties, the AZO, ZnO, and the high MgF₂ content ITO-MgF₂ samples, were all found to be durable to UV containing atomic oxygen, while the low MgF₂ content ITO-MgF₂ samples were not durable to UV containing atomic oxygen environments.

References


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## Subject Terms

- Thin films
- Electrical properties
- Optical properties
- Atomic oxygen
- Inorganic coatings