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Transparent conductive coatings in the far ultraviolet

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ABSTRACT

In certain cases a space-borne optical instrument with a dielectric window requires a transparent conductive coating deposited on the window to remove the electrostatic charge collected due to the bombardment of ionized particles. Semiconductor and metal films are studied for use as transparent conductive coatings for the front window of far ultraviolet camera. Cr is found to be the best coating material. The theoretical search for the semiconductor and metal coating materials and experimental results for ITO and Cr films are reported.

1. INTRODUCTION

Some optical instruments flown on orbiting satellites have exterior dielectric windows. Due to bombardment by ionized particles, electrostatic charge accumulates on the window which may cause undesirable effects. This prompted investigation into the properties of a conductive transparent coating for use as a surface layer to remove the undesirable electrostatic charges.

Transparent conductive coatings combine high optical transmission with good electrical conductivity and have a number of interesting applications : liquid crystal and gas discharge displays, front electrodes for solar cells, heating stages for optical microscopes, IR reflectors, photoconductors in television camera vidicons, Pokell cells for laser Q-switches, and antistatic coatings.

Combining the properties of transparency and conductivity in the same coating material is not trivial and is only possible with certain semiconductors and with very thin and very low electrically resistant metal films. Thin metal films are widely applied as IR reflectors, but are not extensively used as transparent semiconductors.[1] In general, semiconducting oxides exhibit better electrical and optical properties than thin metal films. Also, metal films are not very resistant to abrasion and other forms of mechanical damage.

For applications in which transparency is much more important than electrical conductivity, SnO_2 is usually employed because its absorption edge occurs further into the UV than other oxide materials. In other classes of devices, in which transparency must be sacrificed for maximum conductivity, indium tin oxide (ITO) (In_2O_3;Sn) is ordinarily used because it yields the highest conductivity and because it can be etched easily.[1]

(NASA-CR-194632) TRANSPARENT CONDUCTIVE COATINGS IN THE FAR ULTRAVIOLET (Alabama Univ.) 8 p

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So far studies about transparent conductive coatings have focused only on the visible and IR regions. In the far ultraviolet (FUV) region, all optical materials are absorbing and reflection optics have been widely used. Therefore, a transparent conductive coating in the FUV region is a new problem to be addressed. Published materials for transparent conductive coatings in the visible and IR region were reviewed by Holland[2] in 1958 and Vossen[1] in 1977. These papers served as a starting point in our research to find FUV transparent conductive coatings.

2. INSTRUMENTAL REQUIREMENTS

The FUV imager[3] for the International Solar Terrestrial Physics (ISTP) mission is designed to image four features of the aurora : O I lines at 130.4 nm and 135.6 nm and the N_2 Lyman-Birge-Hopfield (LBH) bands between 140 nm ~160 nm (LBH short) and 160 nm ~180 nm (LBH long). The optical system contains three electro-mechanical devices : an entrance aperture door, a filter wheel, and a folding mirror. The purpose of the entrance door is to close the instrument during non-operating conditions (integration, launch, thruster burns), and to protect it. Because this instrument is used at altitudes between two and nine earth radii (RE), the entrance door is exposed to bombardment by ionized particles and no buildup of electrostatic charge is allowed. Also, in the event it should fail in the closed position, it is designed to work as a broad passband window for the entire FUV region. Our research goal was to develop a conductive coating to meet the following specifications.

a) substrate : 3" diameter, 0.125" thickness MgF_2 window
b) transmittance : > 50 % for entire FUV region
c) resistance : < 10 kΩ/□
d) should be stable chemically and mechanically

3. SEMICONDUCTOR MATERIALS

3.1. Conductivity

Oxide films, deposited by whatever means, appear to grow on oxide substrates as continuous films from the outset of deposition and do not have the island structure typically found in metal films. However, due to a smaller number of carriers compared to metal films, thicker films are required to achieve the same conductivity. Therefore, 200 nm to 400 nm thickness is usually required for semiconductor transparent conductive films in the visible and IR region.[4] For an antistatic film, less conductivity is required. Haas *et. al.*[5] achieved 700 Ω/□ with 36 nm In_2O_3 film and 6 kΩ/□ with 31 nm In_2O_3 +SnO_2 film for a space temperature control application.

The electrical properties of semiconductor films are very dependent on stoichiometry and the incorporation of impurities, either purposeful or inadvertent. Also they are relatively unstable, chemically, and depend on the fabrication parameters; fabrication process, starting material, substrate temperature, deposition rate, and annealing temperature and time. For nominally equivalent materials, even similar processes often result in quite different properties.

3.2. Transmittance

Previously reported studies about the optical properties of oxide semiconductor coatings have focused on the visible and IR regions where oxides have low absorption. The lowest wavelength reported was 200 nm. Hass *et. al.*[5] measured their In_2O_3 and In_2O_3 +SnO_2 coatings prepared by evaporation and sputtering down to this wavelength. They got 25% transmittance for a 36 nm In_2O_3 film and 23 % with a 31 nm In_2O_3 +SnO_2 film at 200 nm. Their spectral measurement results showed that there was less transmittance at the shorter wavelength.

Dobrowlski *et. al.*[4] reported optical constants of their ITO films (thickness 184 nm ~ 412 nm) formed by ion-assisted deposition down to a wavelength of 400 nm. At 400 nm, the absorption coefficients were 0.04 ~ 0.05, but increasing with a very steep gradient.

These prereported results showed that oxide semiconductors are very absorbing below 400 nm. Therefore, we need a very thin film to achieve the transmittance requirement.

3.3. Experimental results on the ITO coating

RF-sputtering was used to fabricate ITO coatings to test the possibility of using semiconductor antistatic films in the FUV region. ITO was selected as a trial material because it is reported to have the lowest resistance and the required conductivity could be achieved with minimum thickness. The sputtering target material was 99.99% {(In_2O_3)91% (SnO_2)9%} supplied by Angstrom Sciences. The initial vacuum was 4 ~ 5 X 10^{-5} torr and the Ar gas flow inlet was set to reach a vacuum of 5 X 10^{-2} torr during the sputtering. The oxygen valve was kept closed and the substrate was not heated.

Before deposition onto the MgF_2 substrate, masked and unmasked Pyrex 1/2" substrates were used for testing. We used the masked Pyrex coating to measure the thickness with a Talystep profiler and found the deposition rate to be 8 nm/min. This deposition rate was used to control the thicknesses afterwards keeping the parameters the same except for deposition time. The unmasked Pyrex substrate was used to measure the square resistance by the method of reference 6. In a 4 minute sputtering time, we obtained 5.7 kΩ/□ resistance which is very similar to Hass *et. al.*'s[5] result.

32 nm and 64 nm coatings are deposited on 1/2" diameter and 0.125" thickness MgF_2 substrates for optical measurements. Our optical measurement system which is located at the NASA Marshall Space Flight Center is explained elsewhere.[7] The transmittance at normal incidence and the reflectance at a 6° angle of incidence are shown in Figure 1. The reflectance remained around 15% through the entire FUV region and the transmittance decreased monotonically to the short wavelength side. The absorption loss increases at shorter wavelengths. This result seems consistent with Hass *et. al.*'s[5] and Doborowalsky *et. al.*'s[4] results. It is evident that ITO is not a good material for transparent conductive coatings in the FUV region. With these disappointing results further experiments to change the deposition parameters were abandoned.

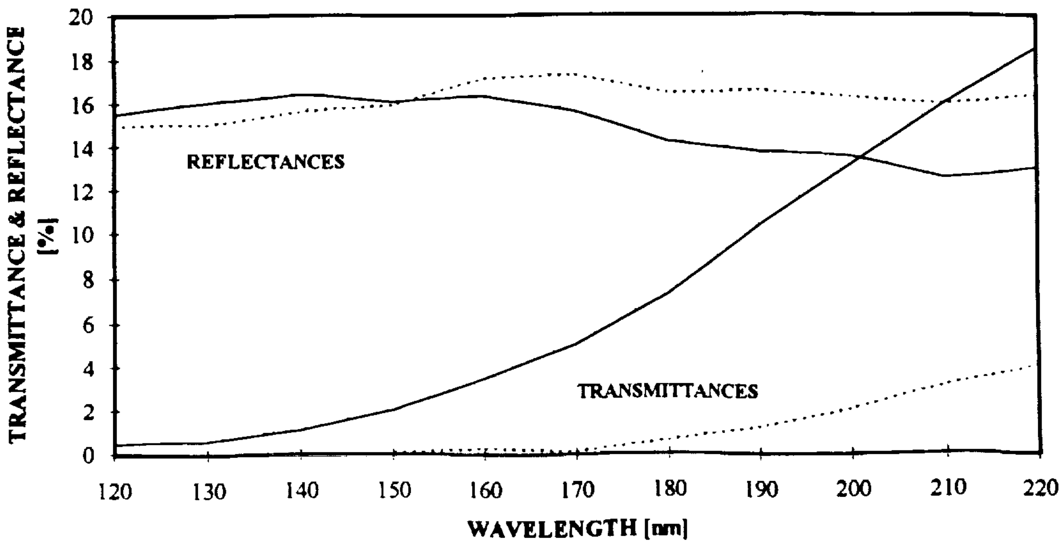

Figure 1. Measured transmittances and reflectances of 32 nm (solid lines) and 64 nm (dotted lines) ITO coatings on MgF_2 substrates.

4. METAL COATINGS

4.1. Conductivity

Metal films that have been studied for transparent conductive coating applications include : Au, Pt, Pd, Ag, Cu, Fe, and Ni.[1] However, Au is predominantly used.[8] Au is a noble metal that is chemically stable and has a very low electrical resistance.[9]

The most important factor for the conductivity of a thin metal film is island formation. Since, in nearly every case, metal atoms arrive with energies greater than kT (where T is the substrate temperature), it is found that some of the atoms reevaporate, some are directly reflected from the surface, and some lose their energy by moving about the substrate surface until a small cluster, or island, is formed at a site occupied by a nucleus. As the film gets thicker, there is a coalescence of the islands and a continuous film is obtained.

The implication of an island structure to transparent conductors is threefold.[1] First, the resistivity of such films is very high. Second, if the islands become quite large, they act to scatter incident light, rather than transmit it. Third, all other things being equal, a thicker film must be deposited to obtain sufficient electrical conductivity, but this results in more light absorption loss. Therefore, a thin continuous film material is better for this purpose than those materials which have lower bulk resistance.

Sennett and Scott[10] observed the structure of evaporated films of eight different metals in an electron microscope. They found that for Au and Ag, the thickness for which the aggregation began to merge was approximately 18 nm. With the resolution obtainable in their electron microscope, a Cr film as thin as 2 nm appeared to be continuous. Therefore, we selected Cr as the best coating material to get a required conductivity with a minimum thickness.

4.2. Transmittance

We attempted to theoretically estimate the transmittance using the optical constants of metal coating materials found in references 11 and 12. The transmittance, reflectance, and absorptance can be calculated by the standard matrix method with known optical constants of the film and substrate and the thickness of the film.[13] The calculated transmittances for 2 nm thickness of Pt, Au, Pd, Ag and Cr films on MgF_2 substrates are shown in Figure 2. We used the optical constants for a MgF_2 substrate from reference 14. As we can see there is little difference in transmittance for candidate materials in the FUV region. The optical constants of our candidate materials do not differ very much over the entire FUV region. Therefore, the reflectances from the top surface of the film, assuming very thick films, are similar and the absorption loss plays the critical role in determining the transmittance. Apparently, the extinction coefficients (i.e. the imaginary part of optical constant) are all of the same order of magnitude.

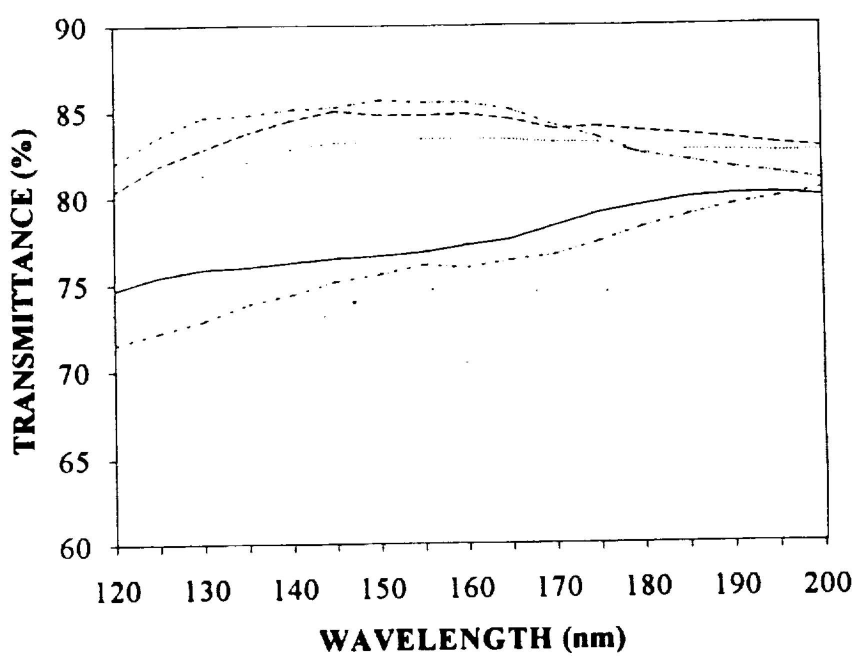

Figure 2. Calculated transmittances for the 2 nm thickness metal films on MgF_2 substrates : Pt (dashed and dotted line), Au (solid line), Pd (dotted line), Ag (dashed line), and Cr (dashed and double dotted line).

If we neglect the interference effect between multiple reflected waves in the thin film, the ratio of the transmitted light intensity I to the light intensity Io is given by the relation :

$$\frac{I}{I_o} = \exp(-\frac{4\pi}{\lambda}kd) \qquad (1)$$

Because the values of k are close to 1, the thickness, d, should be smaller than 6 nm to get $I/I_o > 0.5$ for a wavelength of 120 nm. Au and Ag are not suitable for our purposes.

4.3. Experimental results on the Cr coating

For reason explained in section 4.1, Cr was selected as our trial material. Cr is fairly inert chemically. Because of its high corrosion resistance, it has been vacuum evaporated to form mirrors on glass, used for electroplated or evaporated cathodes in Geiger counters with chemically active gas fillings, and as electrodeposited anti-corrosion layers for the external mountings of electron tubes.[9]

We deposited Cr by the evaporation method with an e-beam gun in a 2 X 10^{-5} torr vacuum. The source material was 99.9 % granulate type supplied by Balzers. In order to get good adhesion, the substrate was heated to 200 °C and the deposition rate was slow.(4 nm/min) Before deposition on the MgF_2 substrate, a Pyrex substrate was used to find the film thickness which satisfied the conductivity requirement. The thickness and deposition rate were monitored by a Quartz crystal monitor which was calibrated using the Talystep thickness profiler.

It was found that only a 1 nm thickness Cr coating had good conductivity, with 2.15 kΩ/□ of resistance. We monitored the change of the resistance of the Cr coating (thicknesses of 1 nm and 2 nm) which had been kept on a lab shelf without any special care. We measured the square resistance once a week for the first three months and once a month afterward. There has been no change in the resistance in 6 months. This also means that the coatings adhere so well that the probes for the resistance measurement do not make any serious scratches.

Figure 3 shows the transmittance measurements of the 1 nm and 2 nm Cr coatings. The transmittance of the 1 nm film satisfies the requirement but has a very low transmittance compared to the calculated transmittance. The reason can be explained by four possibilities. First, the optical constant we used from the reference is different from that of our coating material. Second, the coating is oxidized and has different properties than pure Cr. Third, the absorption of the substrate and the reflection from the bottom surface of the substrate are not included in the calculation. Fourth, scattering loss is not calculated.

5. SUMMARY

ITO and Cr thin film materials were tried as antistatic coatings for a FUV camera window.In the ITO case, at least a 32 nm thickness was required to achieve the desired resistance and it had a severe absorption loss so that it could not be used as a transparent conductive window material. Instead, Cr films were found to be good for this purpose. Only 1 nm film thickness was required to provide conductivity and the transmittance was higher than 50 % between the wavelengths of 123 nm and 220 nm. Our Cr coating did not show signs of aging or deterioration for six months and also had good mechanical adherence.

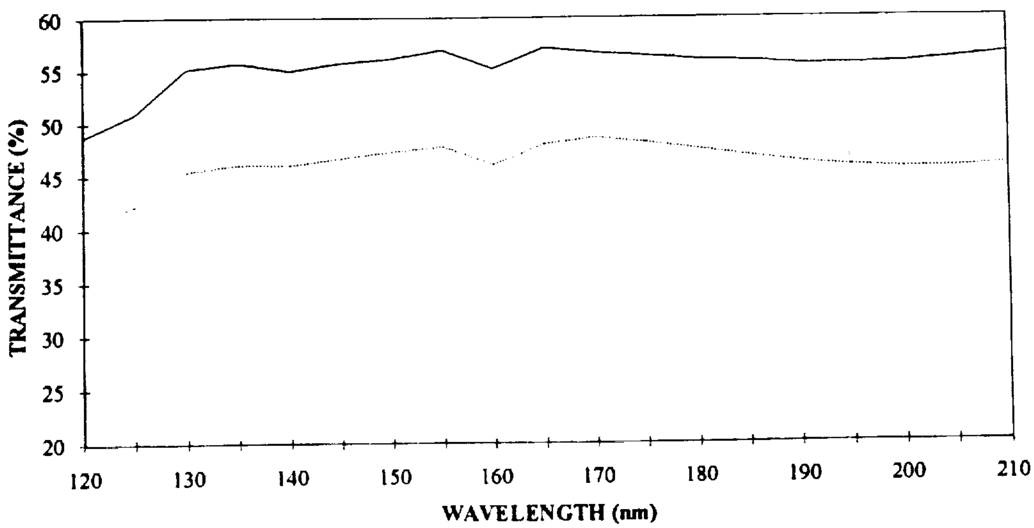

Figure 3. Measured transmittances of 1 nm (solid line) and 2 nm(dotted line)Cr coatings on MgF_2 substrates.

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