Optical and electronic characterization of a ZnS/Mg thin film system

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ABSTRACT. ZnS layers are widely used in optics as high refractive index films in multilayer coatings as well as for protective purposes. We have deposited ZnS coatings on different metal films to prevent their surface degradation when exposed to the ambient. In particular, magnesium is a very active material that generates a diffusive oxide layer as soon as it is removed from the vacuum chamber. Here we are presenting an optical characterization of the ZnS/Mg/ZnS/Glass system, using Spectrophotometry, and the Drude and Lorentz models for the dielectric function. To determine the type and strength of the interaction between the ZnS and the Mg we performed a study of the interface using Auger electron spectroscopy and scanning electron microscopy.

1. INTRODUCTION

One of the problems associated to the techniques used to determine optical properties of materials, is that, in general, the solutions they produce are not unique [1–3]. This situation is dealt with by using complementary criteria to help us choose the “best” solution. These criteria are very often based on experience, on the overdetermination of variables or on the use of complementary experimental techniques. In this study, we try an alternative method based on the overdetermination of variables. Here we present results based on spectral transmittance (T) measurements on a metal film, magnesium, covered by a
stepped dielectric overlayer, ZnS, using a technique similar to the one first proposed by Vincent-Geisse [4].

2. Methodology

2.1. Sample preparation

The main purpose of this work is to perform the optical characterization of a metallic film protected from the environment by a dielectric overlayer that introduces the smallest possible alteration of the optical performance of the metal surface. Here we analyze in particular, the zinc sulfide protected magnesium film system.

The method for the determination of the optical properties is based on the experimental measurements of a vacuum deposited magnesium film of a given thickness, 30 nm, measured with a quartz microbalance in our case and over it, a stepped zinc sulfide overlayer: 0, 80, 160 and 240 nm thick steps for these samples (Fig. 1). The film deposition was done by thermal evaporation at a pressure of $4 \times 10^{-6}$ mbar and the ZnS overlayer was deposited without breaking the original vacuum conditions. At these pressures, however, it is impossible to avoid the formation of a thin magnesium oxide layer and it must be taken into account in the calculations.

The spectral transmittance curves for each zone are obtained with a PE 330 (185–2600 nm) spectrophotometer. It is worth while to note that the deposition of a magnesium thin film directly on glass may present some problems, for one, the uniformity is very poor. This problem disappears as thickness increases, but beyond a certain thickness, of the order of 100 nm, the film will become opaque and transmittance measurements will not be possible. By depositing a buffer layer of ZnS (30–50 nm) on the glass substrate and the magnesium film over it, very good quality films were obtained. The studied system was, therefore, ZnS/Mg/ZnS/Glass.
With the purpose of determining if there was any kind of interaction between the magnesium and the zinc sulfide at the interfaces, a study was performed by Auger Electron Spectroscopy, assisted with argon ion sputtering.

2.2. Determination of the optical properties: Curve fitting

By modeling the magnesium dielectric function $\epsilon$ with a Drude term $\epsilon_D$ for the visible region of the spectrum, plus a Lorentz term $\epsilon_L$ for the infrared [Eqs. (1), (2), (3)], the glass substrate with a Lorentz oscillator [Eq. (3)] using the values given by Palik [5] for the refractive index of zinc sulfide and assuming a non dispersive magnesium oxide layer $(n = 1.7, k = 0)$, it is possible to reproduce the experimental transmittance curves for each step, by modifying the oscillator parameters until the best fit is obtained:

$$\epsilon = \epsilon_L + \epsilon_D,$$

where

$$\epsilon_D = 1 - \frac{4\pi Ne^2}{m} \frac{1}{\omega^2 + i\Gamma\omega},$$

and

$$\epsilon_L = 1 + \frac{4\pi Ne^2}{m} \frac{1}{(\omega_0^2 - \omega^2) - i\Gamma\omega},$$
FIGURE 3. (a) Refractive index of Mg, real (continuous) and imaginary (dashed) parts, calculated from $\varepsilon^{1/2}$, with a Drude, $\varepsilon_D$, and a Lorentz $\varepsilon_L$ contribution. The isolated points, full for the real part $n$ and empty for the imaginary part $k$, were taken from the literature [6] for comparison.

FIGURE 3. (b). Refractive index of Mg considering only a Drude contribution.
where $N$ is the electronic density, $e$ and $m$ are the electron charge and mass respectively, $\omega_0$ and $\Gamma$ represent the oscillator resonance frequency and linewidth, respectively and $\omega$, the frequency of the incident field.

The auto-consistency test for the technique consists simply in that the solution obtained for one of the steps, must be also a solution for the other three, leaving only as parameters for the fit the thicknesses of the magnesium film and the zinc sulfide steps. The range of variation of the thicknesses for the fitting procedure is very limited since we already have an experimental value given by the quartz microbalance. However, there is always an uncertainty due to the precision of the instrument and to the geometry of the deposition set up.

3. Results

3.1. Optical spectroscopy

The results obtained with the above mentioned technique are presented in Figs. 2a, 2b, 2c and 2d, where the dotted line represents the experimental values of the corresponding zone and the continuous line represents the theoretical fit obtained with the following parameters for the Drude and Lorentz expressions for magnesium:

<table>
<thead>
<tr>
<th>Model</th>
<th>Strength</th>
<th>$\omega_0$</th>
<th>$\Gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drude</td>
<td>67.00</td>
<td>0.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Lorentz</td>
<td>13.00</td>
<td>0.805</td>
<td>0.3700</td>
</tr>
</tbody>
</table>

It can be observed from Fig. 2 that, for a better fit, a small taper in the films must be considered, where the thickest part is the one that was closer to the corresponding
Figures 3a, b, and c, show the refractive index, $\varepsilon^{1/2}$, real part (continuous line) and imaginary part (dotted line), where Fig. 3(a) contains both Drude and Lorentz contributions, represented by Fig. 3b and 3c, respectively. Figure 3a shows also the only data reported in the literature [6] we could find (dots), for the refractive index of magnesium. The coincidence for the real part is reasonably good, however for the imaginary part, our values were consistently higher. One possible explanation is that the film is partially transmitting, which means that the trajectory of the light beam is longer due to multiple reflections, appearing to be more absorbing. For this reason, the optical constants of the film may differ from those in the bulk.

The refractive index of glass used in the calculations was obtained from the Lorentz expression, Eq. (3), and the refractive index of ZnS, by interpolation of the experimental data reported by Palik [5].
3.2. Electronic spectroscopy: Auger

The purpose of performing Auger electron spectroscopy on our samples was to analyze layer by layer and interface by interface to obtain the relative concentration of participating elements in each region of the sample and also determine possible chemical interactions or element interdiffusion as we probe through its cross section. Using argon ions, a crater was dug on the sample and a series of spectra were taken starting at the surface, Fig. 4, along the wall of the crater, all the way to the substrate.

Figure 5 corresponds to the interior of the ZnS film where an almost stoichiometric relation between zinc and sulphur can be observed. Figure 6 corresponds to the ZnS-Mg interface where the three elements, Zn, S and Mg appear, plus an important oxygen peak. For a given position of the probe beam, peaks of magnesium and oxygen appear in a proportion that suggests MgO, Fig. 6. It is for this reason that a MgO film was included in the calculations for the dielectric function.
FIGURE 6. Auger spectrum of the ZnS-Mg interface.

In Fig. 7 the interior of the Mg film is analyzed and the presence of Zn and more notoriously of S are acknowledged. There are several possible explanations for this situation, the presence of residual evaporation material in the deposit chamber is one. However, any explanation we may consider must take into account the effect of the electron beam on the materials of the sample. In particular, it seems to have an important effect on magnesium, causing this element to migrate away from the beam. This phenomenon is being carefully studied and will be reported elsewhere.

4. CONCLUSIONS

By comparing the results obtained by the stepped overlayer technique based on transmittance measurements, with the scarce data available in the literature, we can say that the agreement is reasonable good, as can be seen in Fig. 3a, even though only transmittance measurements were used. The knowledge of the optical properties is now expanded from 300 to 2500 nm.
The oscillations that appear superimposed on the transmittance curves of Figs. 2a, b, c and d, are due to interference. The fact that the calculated maxima and minima coincide with the experimental values, tells us that the film thicknesses are well estimated.

The fact that the curve fitting is not that good for thicker overlayers may indicate that the modeling of the dielectric functions was oversimplified. It may also be necessary to take into account that the ZnS–Mg interface may be considered as a cermet where metal particles (Mg) are embedded in a dielectric (ZnS) and include it in the calculations.

The Auger spectra seem to indicate that all layers are slightly contaminated and that, presumably, there may be some chemical interaction between the elements of the different layers. This result may imply that ZnS is not the best coating for magnesium. Another important piece of information from the Auger analysis is the indication of the presence of a MgO thin layer over the metallic Mg, even though the deposits were made at pressures of the order of 10^{-6} Torr.
ACKNOWLEDGEMENTS

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REFERENCES