Application Note: IR Materials

This application note presents the initial results from a study investigating the influence of Low Pressure IAD on the optical and physical properties of some commonly used metal fluorides used in the production of IR multilayer stacks.

It is generally understood, and has been widely reported in the literature [1-3], that there exists a fundamental problem regarding the deposition of materials such as YbF_3 and YF_3 when used as the low index material in combination with materials such as ZnS and ZnSe. Most of the metal fluorides show considerable water absorption bands in the 2.5 – 3.0 micron and 5-6 micron bands. The depth of the water absorption peak is, effectively, a measure of the porosity (or reduced density) of the film materials. Attempts to reduce this problem have mainly centered on deposition on heated substrates at temperatures in excess of 150°C or the application of Plasma Assisted IAD (PA-IAD).

Unfortunately, as the water absorption peak may be reduced with increasing substrate temperature, this will also be accompanied by an increase in film stress, often resulting in delamination and general film failure will often result. An added problem is that the high index materials used in the multilayer stacks (typically ZnS and ZnSe) are not particularly compatible with deposition on heated substrates. These materials possess a very low sticking coefficient even on unheated substrates. This program studied the effect on the water absorption peak by ion bombardment using oxygen ions. Two techniques were investigated, namely:

1. Pulsed IAD (P-IAD)
2. Continous IAD

The technique of P-IAD was developed to reliably produce stable metal fluoride films such as MgF_2 and CaF_2. The technique involves providing short duration ion bombardment to the depositing film. The main purpose is to provide sufficient energy transfer to the film matrix without introducing chemical changes. This technique has been documented elsewhere and will not be discussed further here.

Experimental preparations

All depositions were carried out in a Balzers BAK760 (30” box chamber) system and pumped by a diffusion pump. To reduce the water partial pressure, a cryogenic Meissner trap was used for all depositions. No heating of substrates was applied and the substrates were subjected to a temperature rise of a few degrees at completion of the depositions. The coating system is equipped with a Telemark Model 264 4-pocket (15cc pockets) and controlled by a Telemark Model 880 Deposition Controller. Control of the electron beam was with a Telemark Cheetah Programmable Sweep. The “shrinking circular” pattern was found to be ideal for these particular materials as it maintained very uniform evaporation from the entire surface of the crucible thus ensuring maximum use of available material. A 3-4 min pre-deposition soak at about 80% of deposition power was all that was required to melt down new material with minimal spitting. Ion source used was a 1.5 kW ST55 Ion Beam System using a nominal ion energy of 200 eV. Although the ST55 is capable of delivering very high ion fluxes, for this work only low ion doses were deployed to be consistent with the requirements of radiation-sensitive metal-fluorides. A Saintech Ion Current Monitor (ICM) was used for all depositions for monitoring the instantaneous ion flux. As will be seen, the implementation of an ICM is essential for the realization of full benefit from this process. Evaporation work distance is 500 mm and ion source to substrate distance is 400 mm. Base pressure of approx. 1e-6 mbar is normally achieved in 20-30 min from atmosphere using the high speed pumping of the Meissner coils. Typical run pressure is of order 5e-5 mbar for full-time IAD and about an average pressure of 2e-5 mbar for P-IAD. All deposition rates were controlled to 10 Å/ sec by quartz crystal controller.

Experimental Results

A series of YbF_3 film depositions were produced. Each film was deposited to a thickness of approximately 700 nm as indicated by the quartz thickness monitor. As a control, a single film was produced by electron beam evaporation with no ion assistance apart from an ion pre-clean. This was deposited at the standard deposition rate to an unheated substrate. All film depositions were optically monitored using single wavelength monitoring. The signal was recorded on a strip chart recorder. All substrates were subjected to a two minute pre-deposition clean with O+ bombardment. Pre-deposition cleaning was carried out while material soaking. Deposition commenced immediately following the ion cleaning. One film was produced with the P-IAD technique using a 50:50 duty cycle with a peak beam flux of 60 $\mu A\,cm^{-2}$. The beam ON time was set to 5.0 seconds with a 10 seconds period. Due to limitations of MFC response times, actual Beam ON times were of order four seconds, i.e. time required for beam flux to achieve maximum. A further two films were deposited using a full-time IAD mode. One film was produced using a 30 $\mu A\,cm^{-2}$ dose of oxygen ions while for the other film preparation the ion dose was doubled to 60 $\mu A\,cm^{-2}$. The ion dose that is incident at the plane of the substrate is a very important parameter in the IAD process. This parameter can be often seen to have little relationship to the parameters of the ion-generating plasma (beam current). This parameter needs to be set and maintained throughout the deposition process if consistency of product is to be realized. The spectral optical performances were obtained from a recording spectrophotometer and can be seen in Figure 1 below. Note that the typical water absorption peak can be seen in the spectral region around 3.0 and 6.0 microns. The red data (evaporated - no IAD) shows the largest absorption peak. The P-IAD performance has reduced the water peak slightly and further comment will be made below. The results obtained by continuous ion bombardment show considerable improvement with the film produced by the 60 $\mu A\,cm^{-2}$ ion dose approaching an ideal dose. From this it would appear that an ion dose of around 80-100 $\mu A\,cm^{-2}$ would be required to completely eliminate the water peak and produce a fully dense and stable film.

A further study was carried out using yttrium fluoride (YF3) deposited in combination with zinc sulphide as an antireflection coating on substrates of ZnSe for the 5-10 micron band. The film stack was a 3-layer design using sub/YF3/ZnS/YF3/air. All films were deposited at 10Å/sec as per the YbF3. Once again, no substrate heating was applied. All layers were optically monitored at 400nm. The short wavelength was used as check for homogeneity and for any optical absorption. Film thicknesses were determined solely by the quartz crystal. A spectral scan of the completed film stack is shown in Figure 2 below. Although the spectral performance of the antireflection coatings is not particularly noteworthy, the absence of the water absorption peak is. As noted above, the deposition and IAD parameters for the YF3 were the same as for the YbF3 film preparations. Both of the YF3 layers were ion assisted with 60 $\mu A\,cm^{-2}$ oxygen ions while the ZnS layer was assisted with a greatly reduced dose of about 20 $\mu A\,cm^{-2}$.

The coated substrate used in this study was further studied for environmental performance according to MIL-C-48497A. The substrate passed the various adhesion tests as well as humidity and moderate abrasion. The substrate failed the salt fog test. The sensitivity of this test could be a fundamental limitation of the material itself and could be improved by addition of a single protective over-layer. Discussion on optical performance. All film depositions were monitored in transmission mode and in the visible. Substrate monitors of fused silica were used as it provides some measure of the refractive index which can be derived from turning points. The optical monitoring also provides useful information on the transparency of the material as it is deposited. The repeatability of the turning points also provides useful information as to the homogeneity of the depositing material. The table below provides some of the above information Film Prep. R.I @ 550nm Absorption Inhomogeneity YbF3 no IAD Approx. 1.46 none Showed considerable inhomogeneity YbF3 P-IAD 1.42* none Very slight YbF3 30μA dose 1.52 none negligible YbF3 60μA dose 1.54 none negligible 3-layer AR ** Not determined none None observed

Table 1. Presents an indication of the performance of the depositions from observations of optical monitoring. See notes below for explanations. The inhomogeneity shown by the film deposited by evaporation (no IAD) is to be expected and the low index is also consistent with a film displaying high porosity. The actual refractive index will likely change once exposed to air. The film deposited by P-IAD is very interesting. It was the only film to show an increase in transmittance which indicates it is depositing with a lower refractive index than the fused silica monitor. This is consistent with the results previously obtained by the author from earlier work done with the P-IAD of other metal fluorides such as MgF2 and CaF2. Further work is required but preliminary results indicate the P-IAD technique presents a unique opportunity to realize bulk properties for many of these metal fluorides. Although the small effect on reduction of the water peak was realized, there are ways to improve this result. This technique offers the best opportunity to realize full density without compromising optical purity. It is also noteworthy that, for the two films prepared with full-time IAD, increasing the ion dose showed a definite increase in refractive index. This is also consistent with the earlier work, mentioned above, for IAD of MgF_2, etc. Full-time IAD using oxygen bombardment showed a trend to higher indices with increasing ion flux. The higher ion dose causes some replacement of fluorine atoms by oxygen. In the case of magnesium fluoride, this produces an increasing percentage oxygen within the MgF film matrix leading to formation of MgO_xF_y. As the value of x increases, the increase in refractive index tends upward from 1.37 (MgF_2) $\rightarrow$ 1.6 (MgO). The author has measured the refractive index for MgF_2 to be as high as 1.43 at 550nm for full-time high dose oxygen ion bombardment.

Further Comments and Discussion

Further studies are planned. The benefits of producing multilayers using the above techniques are obvious;

1. Normal deposition rates can be deployed. Although the above films were deposited at only 10 Å/ sec, providing the ion to atom/molecule ratio is maintained, similar results should be realized for higher deposition rates. Compare to sputtering – both magnetron and ion beam (IBS). Both of these deposition techniques increase the atomic percentage of trapped argon leading to reduced optical properties and increased intrinsic stress with the added disadvantage of slow deposition rates

2. All films were deposited to unheated substrates. Although studies of residual stress have not been done, it is obvious that the films produced in this study are stable and

strongly adhering (passed MIL environmental tests).

3. The temperature rise of substrates from the deposition process is negligible because this is low-pressure IAD as distinct from Plasma IAD which is normally performed at higher pressures and results in high thermal radiation loads to the substrates. Normal run pressures for this process are the mid 10-5 mbar

4. While this study has focused on the two fluorides (YbF3 and YF3), the results should be also relevant to other metal fluorides. Study of other material is under consideration and will be reported on in due course.

5. The results of this initial study clearly demonstrate that the achievement of environmentally stable, dense and optically qualified metal fluoride films can be achieved using this technique of Low Pressure IAD.

References

1. “Effects of Water in Thin Film Coatings” Materion – Coating Material News Vol 9 Issue 1

2. “Optical properties and residual stress of YbF3 thin films deposited at different temperatures” Ying Wang, Yue-guang Zhang, Wei-lan Chen, Xu Liu. Presented at OIC Topical Meeting, Tucson AZ, 2007

3. “Long Term Stability of Low Index Mixed Fluorides” David Cushing Presented at the OIC Topical Meeting Tucson AZ, 2007