

A Solution to the Adhesion Problem of Oxide Thin Films on Zinc Selenide Optical Substrates

M.B. Cosar^{1,2}, G.H. Aydogdu¹, H. Batman¹, A.E.S. Ozhan^{1,3}

¹*Aselsan Inc. Microelectronics, Guidance and Electro-Optics Division, Ankara, Turkey*

²*Middle East Technical University, Metallurgical and Materials Engineering Department, Ankara, Turkey*

³*Atilim University, Graduate School of Natural & Applied Sciences, Ankara, Turkey*

ABSTRACT

Zinc selenide optical substrates have high transparency within the 0.5- to 14.0- μm wavelength range. This makes them an attractive candidate for multiband imaging applications in optical components. In order to minimize reflection loss in visible, near-infrared, and mid-infrared applications, zinc selenide lenses are coated with multi-layered oxide thin films by physical vapor deposition method or ion beam deposition. In this study, a four-layer anti-reflective filter at 1.064 μm and between 3.6 and 4.9 μm is applied to zinc selenide using an ion beam deposition system. The filter is used for a dual-beam optical application. The filter is composed of metal oxide layers that have an adhesion problem on zinc selenide. In order to solve this adhesion problem they were heat-treated at 300°C for varying amounts of time prior to metal oxide coating. Treated samples were characterized in terms of their roughness, contact angle, morphology, refractive index, transparency, crystallography and chemical composition. Results show that it is possible to manufacture durable oxide thin film coatings on zinc selenide, by using a well-designed pre-treatment processes.

INTRODUCTION

Zinc selenide (ZnSe), which can be produced as cubic and hexagonal crystal structures, is generally preferred for dual- or triple-beam optic and laser system applications. ZnSe has 70 % average transparency between 0.5 and 14.0 μm and also has high importance at 10.6 μm for CO₂ laser applications due to lower absorption. Although ZnSe can be processed as a single crystal optical element, the polycrystal-

line structure is quite sufficient for optical applications and can be produced at a lower cost. Also, ZnSe optics have an advantage in optical design due to their high resistance to chemical reaction and thermal shock. ZnSe optics are also able to be fabricated with high purity, are easily shaped, and have low porosity [1–5].

The common way to produce ZnSe substrates is by chemical vapor deposition (CVD). A vertical furnace is fed with H₂Se gas in this method. Zn metal is heated and vaporized at a lower part of the furnace, and the vapor rises and reacts with H₂Se gas on the graphite mandrel at about 750°C. The quality of the ZnSe substrate mainly depends on the gas flow rate, type of base plate, pressure level, temperature, and deposition rate to the point of reaction on the graphite mandrel. In other words, these parameters determine the purity, porosity, density, particle, and grain size of the ZnSe substrate [3, 6, 7]. A final procedure for fabricating a polycrystalline ZnSe substrate into an optical element involves additional processing like grinding and polishing in order to give high optical quality, that is, a defect free structure [8, 9].

This study aims to find a solution to the adhesion problem of oxide coatings such as tantalum pentoxide (Ta₂O₅), silicon dioxide (SiO₂), hafnium dioxide (HfO₂), and titanium dioxide (TiO₂) on ZnSe. Oxide coatings are applied to minimize surface reflections, which are absolutely necessary for use in electro-optical systems. Optical design was made sequential using Ta₂O₅ for high-index and SiO₂ for low-index material. These materials were deposited by ion-beam deposition (IBD). It was seen that oxide coatings have a prob-

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lem adhering to the zinc selenide surface. Because of adhesion problems, anti-selective coatings do not survive well after deposition. The native oxide layer on ZnSe substrates was investigated in work by Masetti et al. [10]. Although the primary goal of Masetti's study was not the enhancement of coating adherence, it offered a process to remove polishing contamination and surface oxidation.

Two different approaches were studied to improve adherence of thin films on ZnSe substrates as a pre-study. First, IBD equipment parameters like deposition rate, deposition temperature, beam voltage, and current were changed; however, they did not show enhancement of coating adherence. The second approach was changing the substrate cleaning procedure. Optical lenses were mainly cleaned with acetone using soft paper. Ultrasonic cleaning and plasma cleaning were tried in hopes of supplying a better surface for coating; unfortunately, these did not supply better surfaces for thin film deposition on ZnSe substrates. This study is aimed at solving the coating adherence problem by heat-treating the substrates at 300°C before the coating process. It was thought that high temperature heating would remove the organic residues that come from polishing solutions. In addition, it causes to reorganize the substrate surface molecules, or create a new surface composition to create a suitable surface for oxide thin films. Oxide coatings deposited on ZnSe substrates after high-temperature pre-treatment of ZnSe did not peel off after the humidity and the tape peel test, which were conducted following military testing standards.

EXPERIMENTAL PROCEDURE

Six pieces of ZnSe samples, 1" (2.54 cm) diameter and 1 mm thick (produced by Umicore) were annealed at 300°C on the hotplate at 5 min. (SN1), 10 min. (SN2), 15 min. (SN3), 20 min. (SN4), 25 min. (SN5), and 30 min. (SN6) durations. One sample (SN0) was also analyzed without any treatment. Before the heat treatment, the substrates were cleaned with dry nitrogen and rinsed with acetone. To examine the adherence performance of the treated ZnSe substrates, Ta₂O₃ and SiO₂ were deposited by (Veeco Spector) ion-beam sputtering configured with two radio frequency (RF) inductively coupled plasma ion beam sources. A 16-cm-diameter grid ion beam source was used for deposition while a 12-cm-diameter source was used for assisted deposition; 99.999 % pure tantalum (Ta) and silicon dioxide targets were used with a 30-sccm oxygen flow rate. Target materials were sputtered by typical ion-beam energies with 1250 eV beam voltage and 600 mA beam current. Finally, the coated samples were exposed to a relative humidity of 95 to 100 % at 49°C for a period of 48 hours.

After the heat treatment, uncoated ZnSe substrates were investigated by spectrophotometer, X-ray diffractometer, X-ray photoelectron spectroscopy, X-ray fluorescence, optical microscopy, contact angle measurement, and white light interferometer (WLI). Transmittance spectra of the films were measured with a (UV-VIS-NIR) Perkin Elmer Lambda 950 spectrophotometer, and fast-Fourier transform infrared (FTIR) spectroscopy was used for infrared measurements. The refractive index was obtained from the "Essential Macleod" optical thin film calculation software via mathematical approximation. Crystallographic analyses were made by an X-ray diffractometer (XRD), Rigaku using Cu K α radiation (1.54 Å). The elemental composition of the films was analyzed by X-ray photoelectron spectroscopy (XPS) (Thermo K-Alpha) from the surface of samples and X-ray fluorescence (XRF) (Rigaku ZSX primus II- 30 kV and 100 mA) from the deeper regions at a micron depth. Surfaces were observed by optical microscopy (Nikon-LV). Contact angle measurement was measured with the KSV Contact Angle Measurement System. A Zygo-white light interferometer was used for surface roughness analysis.

RESULTS AND DISCUSSION

XPS Results

In order to understand the effect of the heating process on the surface of ZnSe (within 8–10 nm depth), the sample was first analyzed by XPS. In this measurement, the main purpose was to obtain the chemical composition of surface and ratio of elements. For this reason, samples were measured in survey mode shown in Figure 1. In addition, Table 1 summarizes the change in elemental percentages with heat treatment. The amount of selenium (Se) decreases with increasing heating time. This occurred because Se reacts with oxygen coming from water in the atmosphere. The main volatile product is selenium dioxide and elemental sele-

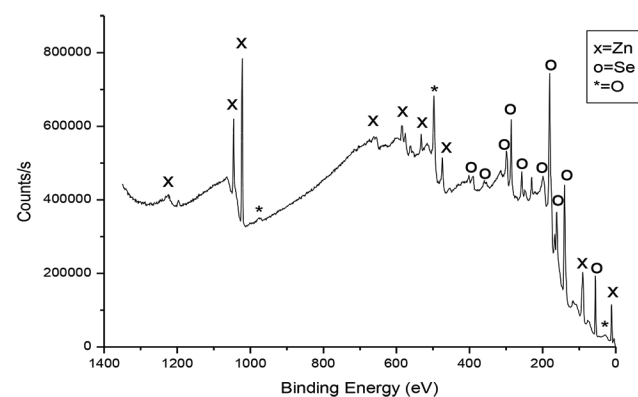


Figure 1. X-ray photoelectron spectroscopy (XPS) binding energy spectra of the ZnSe substrate.

mium, which can leave from the sample in a gaseous form. Therefore, ZnSe experienced loss of Se upon heating. On the other hand, ZnO is the only non-volatile product of this reaction, and it was observed that the relative amounts of Zn₂O and the Zn/O ratio decreased from 1.43 to 0.81. This means that the remaining zinc atoms combine with oxygen from the ambient environment to form ZnO.

Table 1: Elemental composition of different heat-treated ZnSe substrates analyzed with XPS

sample	Zn (2p3)(%)	Se (3d)(%)	O (1s)(%)
SN0	26.56	54.87	18.57
SN1	29.73	44.21	26.06
SN2	31.82	29.13	39.05
SN3	33.75	16.95	49.29
SN4	36.39	7.70	55.91
SN5	37.36	6.98	55.67
SN6	43.39	3.55	53.06

XRF Results

The XRF measurement technique was used to understand the effect of heating which is observed not only on the surface but also at a deeper level (within a few microns). However, because the XRF system is capable of detecting lighter elements down to only fluorine, oxygen cannot be detected. As a representative result of analysis, the elemental composition of the SN0 sample was 54.4 % Se and 45.2 % Zn and, for the SN3 sample, it is 54.5 % Se and 45 % Zn. This means that there is no change in Zn/Se composition ratio between the non-heated treated sample and the 15-minute heated sample. It can be said that the reaction and evaporation are taking place only at the sample's surface region. When the XPS and XRF results are compared for untreated samples, it can be seen that Zn/Se ratio obtained from XPS and XRF equals 0.48 and 0.83, respectively. This result also proves that Se decreases in the surface region.

XRD Results

When all the curves were overlapped, common diffraction (2 θ) peaks of ZnSe composition were at 27.4° (111), 45.5° (220), 53.8° (311), 65.8° (400), and 72.6° (331) shown in Figure 2. All the diffraction peaks are well matched with the peak of ZnSe. Also, the additional peaks at 47.4° (102), 66.3° (200), 67.9° (112), and 72.5° (004) correspond to the diffraction peak of ZnO. Although all diffraction peaks of ZnSe are observed for all samples, their intensities and highest peaks change from sample to sample. Fang et al. explain the

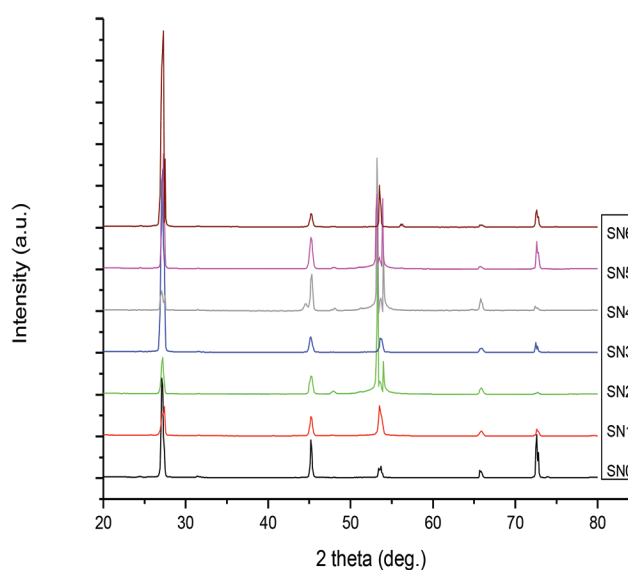


Figure 2. X-ray diffraction (XRD) spectra of seven ZnSe substrates, with different heating parameters. ZnSe peaks are at 27.4° (111), 45.5° (220), 53.8° (311), 65.8° (400), and 72.6° (331). Also, the peaks at 47.4° (102), 66.3° (200), 67.9° (112), and 72.5° (004) correspond to ZnO.

crystallographic orientation of ZnSe substrates in their study [11]. According to that study, anisotropy of growth rate in different crystal directions with high gas flow velocity is the main reason for the change of the peak intensity. Also, although preferential orientation is expected at [111], it can be changed by thermal treatment. According to Lemasson's work, [422] and [331] are the preferred orientations under low-pressure CVD growth conditions [12], because atoms tend to travel randomly and gather at preferred orientation sites.

Surface Roughness and Contact Angle Results

To analyze the effect of heating the wetting characteristic of ZnSe surfaces, contact angle measurements were applied to the samples. The main expectation was to change the surface as a result of possible reactions or modifying atomic orientation. These changes directly affect the surface energy, which causes change in the wetting behavior. The results show a correlation between the wetting contact angle and adherence of thin film oxide coating on ZnSe substrate by heating of the substrates. While increasing heating time, contact angle increases. A similar effect was observed in the roughness value of the surface, which is an important parameter for thin film coatings. Effect of roughness on adherence of the coating depends on the matching of coating material and substrate. In this case, surface roughness for the samples increases with heating time in the range 0.6–2.2 nm in the area 300 μm \times 300 μm . The increase in the amount

of surface irregularities causes high surface roughness, as shown after the humidity test results where samples with high roughness make a stronger bond with the coating.

xSpectral Transmittance and Refractive Index

While enhancing the adhesion of ZnSe of anti-reflective oxide films, the processes should not make any change in their optical properties. For this reason, visible to near-infrared spectral transmittance measurements were made

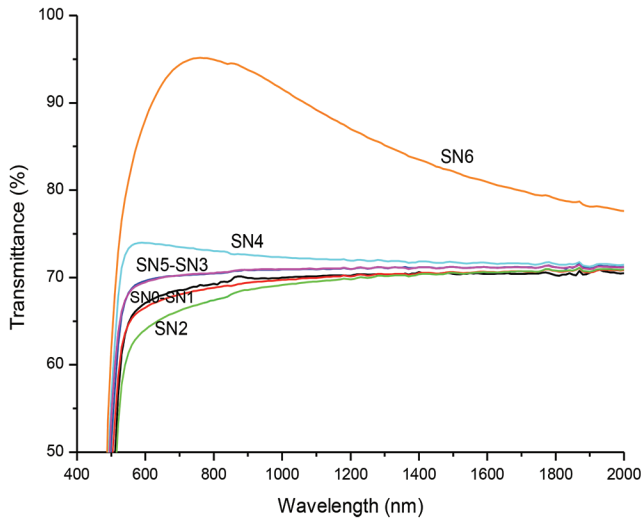


Figure 3. Spectral transmittance of seven ZnSe substrates at visible and near-infrared

(Figure 3). The visible and near-infrared optical transmittance of samples between SN0 and SN5 are similar, while SN6 showed significantly higher transmittance, possibly resulting from the formation of different compounds with a decrease in Se composition. For the other curve, SN1 was the same as SN0. SN2 was a little below SN0, and SN3 and SN5 were a little above SN0 in transmittance. These curves are acceptable in using ZnSe for any application. However, SN4 shows higher transmittance than SN3 and SN5, and using this sample in near-infrared application is questionable. Therefore, heat treatment time should not be more than 15 minutes to remain on the safe side for the samples between SN3-SN5 and applications in the wavelength between 8000-12000 nm. All the samples (except SN6) can be used without any issue. The change in refractive index of ZnSe should also be considered when making an optical design using ZnSe substrates.

Microscope Images

Microscopic imaging of a surface is the final analyzing technique before coating (Figure 4). SN0 is like a smooth surface so no surface details could be seen. Heat treating of ZnSe indicated some structure growth, which increased from SN1 to SN6. This could be related to the removal of Se-rich surface compounds or the orientation of atoms at one diffraction plane. Some samples showed surface defects that were mainly residues of organics. Twinning structures

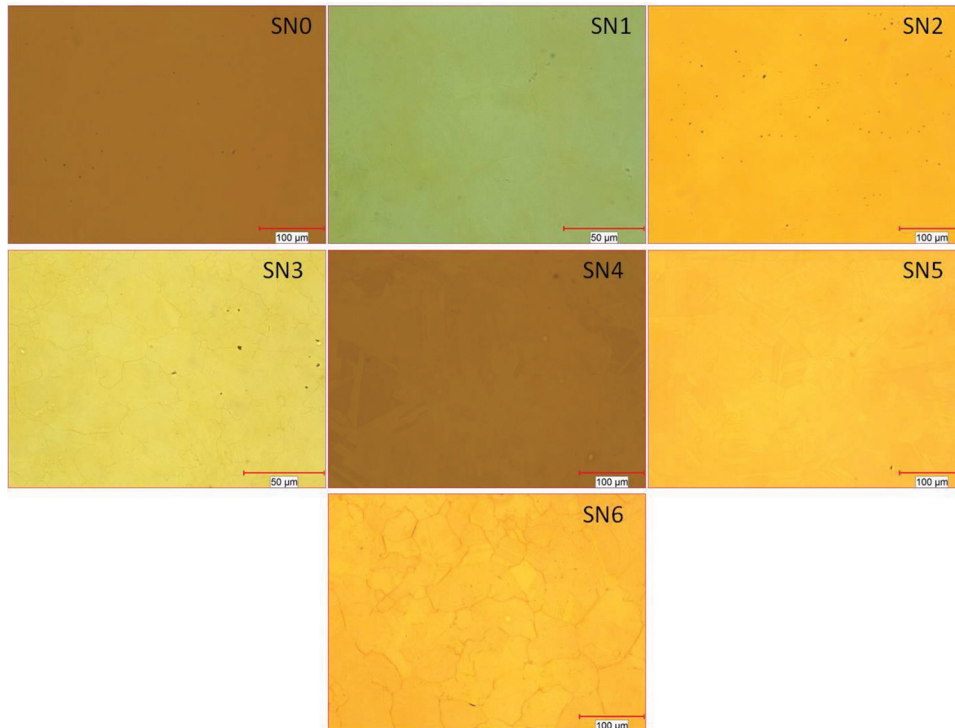


Figure 4. Microscopic surface images of seven ZnSe substrates.

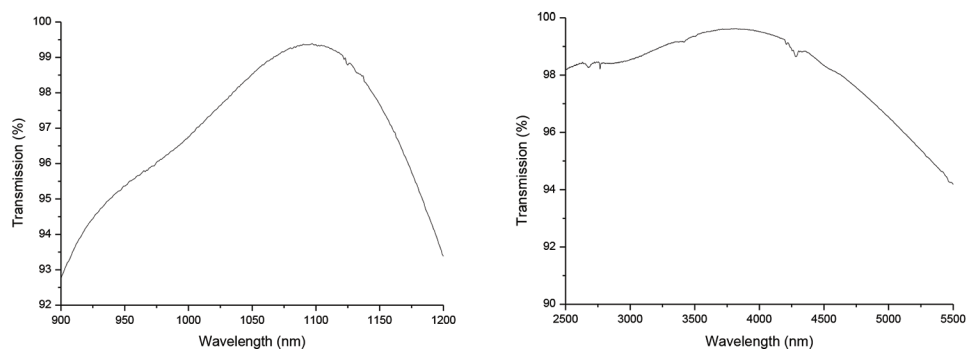


Figure 5. Spectral transmittance of four-layer oxide-coated ZnSe substrate. Transmittance for near-infrared range, 900–1200 nm (left) and for the mid-infrared, 2500–5500 nm (right). The laser wavelength is at 1064 nm.

were also seen. Twins could be already present in the system or could be formed during annealing [12]. Grains can be grown on surrounding neighbors during annealing, causing twinning. Formation of twinning structure is related to formation of new phases at higher energy than the original phases. In addition to twinning, grain size increased with time at high temperature and probably created low scattering at grain boundaries. The Gavrishchuk study explains the CVD ZnSe growth parameters and grain size relation [13].

Humidity Test Results

All ZnSe samples between SN0 and SN5 were coated with a four-layer anti-reflective (AR) dual band coating designed for high transmittance at 1064 nm and 3600- to 4900-nm-wavelength regions. The AR coating was applied by IBD. Ion beam deposition UV-VIS-NIR spectroscopy and FTIR spectroscopy were used to get the results. As shown in Figure 5, average transmittance value was 98.9 % at 1064 nm and 98.8 % on average between 3600 and 4900 nm. After coating, samples were exposed to a humidity test. A tape test was applied according to MIL-F-48616 [14] to the samples after the humidity test to determine coating adhesion. Figure 6 shows the tape test result that was applied after the humidity test. Except for SN0 and SN1, all samples passed the tape test. Some local defects can be seen in samples between SN4 and SN6; they were formed after the heat treatment. While heat treating, the color of samples changed

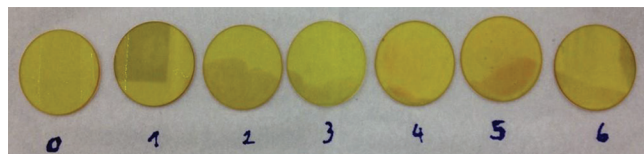


Figure 6. Images of ZnSe substrates after tape adhesion test. The numbers refer to SN0, SN1, and so on. SN0 and SN1 did not pass the the test.

from yellow to orange. After cooling to room temperature, the colors returned to the original yellow color. Color change is related to the electronic band gap and defect sites. Lengthy heat treatment gave irreversible effects to the samples. Transmittance results of samples between SN4 and SN6 show little effect on the near-infrared region while they show no effect on the mid-infrared regions, so it is advised that they should not be used.

CONCLUSION

In conclusion, ZnSe optical substrates were heat treated for different lengths of time to solve the adherence problem of coated AR oxide thin films. Heat-treated samples were analyzed using XPS, XRF, XRD, WLI, contact angle measurement, UV-VIS-NIR spectroscopy, FTIR spectroscopy, and microscopy. The heat-treated samples were coated with four-layer Ta₂O₅ and SiO₂ with an IBD system. After deposition, coated substrates were exposed to a humidity test and a tape adhesion test.

When the XPS and XRF results were considered together, it is obvious that elemental changes were realized at the near surface regions. At the treatment temperature, surface low energy elements reacted with ambient oxygen and produced volatile selenium products. Therefore, a sharp decrease of selenium concentration was noticed. Longer annealing times caused more selenium loss from the surface by diffusion.

Heat treatment was a good and simple solution to enhance the bonding strength between the AR coating and ZnSe substrate. After 10 minutes of heat treatment, all the coating samples resisted the tape test and did not peel off, while, for the samples between SN4 and SN6, transmittance and refractive index measurements showed little deviation from the untreated sample, and microscopic examination showed

some local defect sites. Therefore, usage of these samples can be problematic for some optical parameters, although transmittance changes were not a big concern.

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FOR MORE INFORMATION:

M. B. Cosar, ASELSAN, Microelectronics, Guidance and Electro-optics, Cankiri Yolu 7. km Akyurt, Ankara, 6750, Turkey, mbcosar@aselsan.com.tr, 90/3128475300 / 5581