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A solution to adhesion problem of oxide thin films on Zinc Selenide optical substrates

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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 multi band imaging applications in the optical components. In order to minimize reflection losses for visible, near-infrared and mid-infrared applications, Zinc Selenide lens are coated with multi-layered oxide thin films by physical vapor deposition method or Ion Beam Deposition. In this study, four-layer dual beam anti-reflective coating design at 1.064 μm and between 3.6 and 4.9 μm is applied using Ion Beam Deposition system directly on Zinc Selenide substrates. Because of solving the adhesion problem which is observed after the coating of oxides on Zinc Selenide substrates, they were treated at 300 °C for varying amounts of time before coating oxides. Treated samples were examined in terms of their roughness, contact angle, morphology, refractive index, transparency, crystallography and chemical composition. It is found that it is possible to manufacture durable oxide thin film coatings on Zinc Selenide, utilizing well designed pre-treatment processes.

1. Introduction

Zinc Selenide (ZnSe) which can be produced at cubic and hexagonal crystal structures, is generally preferred at 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 CO_2 laser application due to less absorption. Although it can be processed at single and polycrystal structures, polycrystal structure is quite sufficient for optical applications and it supplies lower production cost. ZnSe substrates also have advantageous at high resistance to the chemical reactions and thermal shocks, producibility with high purity, easily shaping and low porous nature [1–6].

The common way to produce ZnSe substrate is Chemical Vapor Deposition (CVD). A furnace which is at vertical direction is feed with H_2Se gaseous in this method. Zn metal is heated and vaporized at below part of the furnace and the vapor rises and reacts with H_2Se gas on the graphite mandrel at nearly 750 °C. Quality of the ZnSe substrate mainly depends on the flow amounts of gaseous, type of base plate, pressure level, temperature and deposition rate to the point of production. In other words, these parameters mainly determine the purity, porosity, density, particle and grain size of the ZnSe [3,7]. As a final procedure for using as a lens, CVD growth ZnSe substrates are grinded and polished following the optical techniques to have optic quality. Due to the polycrystalline structure, it is difficult to obtain defect free surfaces with ZnSe and it is required additional effort [8,9].

This study is aimed to find a solution to adhesion problem of oxide coatings such as Tantalum Pentoxide (Ta_2O_5), Silicon Dioxide (SiO_2), Hafnium Dioxide (HfO_2) and Titanium Dioxide (TiO_2) on ZnSe. Oxide coatings are applied to minimize surface reflections which is absolutely necessary to use them in electro-optical systems. Optical design was made sequential using of Ta_2O_5 for high index and SiO_2 for low index material. These materials were deposited by Ion Beam Deposition (IBD) method. It was seen that oxide coatings have a problem to adhere on the Zinc Selenide surfaces. Coatings did not survive after deposition process. In Masetti work, native oxide layer on ZnSe substrates were investigated [10]. Although the primary goal of that study is not the enhancement of coating adherence, they offered a process to remove polishing process contamination and surface oxidation.

Two different approach were tested to improve adherence of thin films on ZnSe substrates as a pre-study. Firstly, IBD equipment parameters like deposition rate, deposition temperature, beam voltage-current and assisted deposition were changed, however they do not show enhancement in coating adherence. Second approach is about the change in cleaning procedure of substrates. Mainly, optical lenses are cleaned with acetone using a soft paper. Ultrasonic cleaning and plasma cleaning is tried to supply better surface for coating, unfortunately, these surfaces do not supply better area for thin films. This study aims

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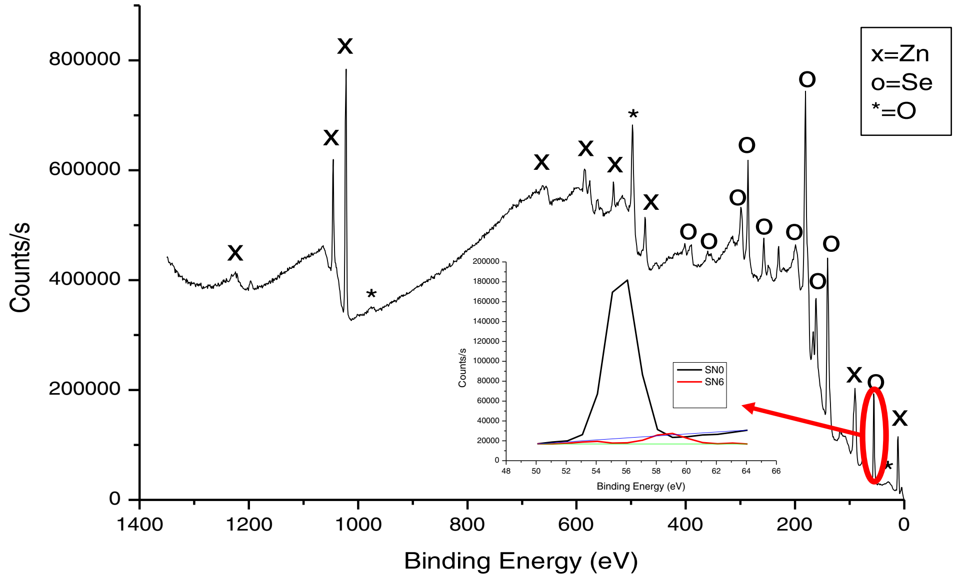

Fig. 1. Survey of XPS spectra of ZnSe substrate as a representative and zoomed Se elements of SN0 and SN6 at 50-64 eV binding energy.

to solve adherence problem making a heat treatment of substrates surface at 300 °C before coating process. It was thought that heating at high temperature can remove the organic residues coming from solutions used for polishing, can reorganize the substrate surface molecules or can 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, do not peel-off after the humidity and following adhesion test which is applied according to military standards.

2. Experimental procedure

Six pieces ZnSe samples with 1″ diameter and 1 mm thick (produced by Umicore) are annealed at 300 °C with the rate of 10 °C/min on the hot-plate at 5(SN1)-10(SN2)-15(SN3)-20(SN4)-25(SN5) and 30(SN6) minutes durations and then samples were taken in turn and cooled down at the ambient temperature in 1 h. This is repeated at five times for testing repeatability. Also, one sample (SN0) is 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, Ta_2O_5 and SiO_2 were deposited by (Veeco Spector) ion beam sputtering which was configured with two RF inductively coupled plasma ion beam sources. 16-cm diameter grid ion beam source was used for deposition while 12-cm one is for assisted deposition. 99.999% purity of Tantalum (Ta) and Silicon Dioxide targets were used with 30 sccm oxygen. Target materials were sputtered by typical ion beam energies with 1250 eV beam voltage and 600 mA beam current. Finally, the coated samples was exposed to a relative humidity of 95 to 100% at 49 °C for a period of 48 h and then adhesion test was applied with tapping method according standard of MIL-F-48616.

After the heat treatment, uncoated ZnSe substrates are investigated by spectrophotometer, X-ray diffractometer, X-ray photoelectron spectroscopy, X-ray Fluorescence, Optical Microscopy, contact angle measurement, white light interferometer. Transmittance spectra of the films were measured with a Perkin Elmer Lambda 950 spectrophotometer. 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, Rigaku (XRD) using Cu Kα radiation (1.54 Å). The elemental composition of films was analyzed by X-ray photoelectron spectroscopy (XPS) (Thermo K-Alpha) from surface of samples and X-ray Fluorescence (XRF) (Rigaku ZSX primus II- 30 kV and 100 mA) from the deeper regions as micron level. Surfaces were observed by Optical Microscopy (Nikon-LV). Contact angle measurement was analyzed by KSV contact angle measurement system. Zygo-white light interferometer is used for surface roughness analysis.

3. Results and discussion

3.1. XPS results

To understand the effect of heating process on the surface of ZnSe (with only the 8–10 nm depth), they are firstly analyzed by X-ray photoelectron spectroscopy method. In this measurement, main purpose is to obtain the chemical composition of surface and ratio of elements. For this reason, samples are measured in survey mode shown as a representative and indicated a drastic variation of selenium (Se) amount between the samples SN0 and SN6 in Fig. 1. In addition, Table 1 summarizes the change in elemental percentages of Zn (zinc), Se and O (oxygen) elements at certain orbital stage with heat treatment. The amount of Se decreases with increasing heating time. This event can be related that Se elements give a reaction with the O atoms coming from water molecules, humidity and atmosphere. The main volatile product is selenium dioxide and selenium molecules can leave from the sample at gas form. Therefore, ZnSe expose to realistic Se loosing. On the other hand, ZnO is the only non-volatile product of this reaction and it can be observed from the relative ratings of Zn and O (Zn/O) which decreases from 1.43 to 0.81. This means that remaining zinc atoms picks oxygen from environment to form ZnO.

Table 1
Elemental composition of different amount heated substrates with XPS at certain orbital stage.

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