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# Design and Fabrication of Multi-Layers Infrared Antireflection Nanostructure on ZnS Substrate

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$MgF_2$/ZnS thin films were deposited on ZnS substrates by physical vapor deposition (PVD) to investigate multi-layer antireflection (AR) coatings. The three-layers of $MgF_2$/ZnS/$MgF_2$ with optimized thicknesses were fabricated by PVD technique and studied by Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and field emission scanning electron microscope (FESEM). From FTIR spectroscopy it was found that in the wavelength range of 8–12 $\mu$m, the average transmittance of the double-side coated sample increases by about 26% and its maximum reaches about 98%. The FESEM figures indicate that all the samples were uniform, compact with good adhesion on ZnS substrate. The XRD pattern of the ZnS/$MgF_2$ multilayer which exhibits the presence of both pristine phases of $MgF_2$ and ZnS, respectively.

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## 1. Introduction

Zinc sulfide (ZnS) is an important wide band gap semiconductor which is widely used in infrared optics (windows, domes etc.) in the wavelength range of 8–12 $\mu$m. It has a refractive index of 2.2 at 10$\mu$m and a reflection loss of 24.7% (two surfaces) [1]. $MgF_2$ and $SiO_2$ are used as low refractive index material in the AR coating. Also, $MgF_2$ has been universally used due to low refractive index and high transmittance in ultraviolet region [2]. Therefore, ZnS with a high refractive index and $MgF_2$ with a low refractive index are commonly used for single- or double-layer AR coatings. Generally, refractive indices of ZnS and $MgF_2$ are known to be 2.354 and 1.377 at 630 nm, respectively [3, 4]. At present, many potential applications of ZnS and $MgF_2$ such as LEDs [5], solar cells [6], photo-detectors, photovoltaic cells, solar collectors, IR diodes [7, 8] are being explored. The thin films of ZnS and $MgF_2$ have been prepared by many deposition techniques such as thermal evaporation [9], sputtering [10], chemical bath deposition [11], SILAR [12], thermionic vacuum arc (TVA) [13], spray pyrolysis [14] and others [15, 16].

Most lenses and windows that are transparent in the ultraviolet region and used in optical systems have a high refractive index and therefore reflect a large part of the incidence radiation. Transmission and reflection coefficient of the surface is obtained using the following formula

$$\rho = \frac{n_0 - n_1}{n_0 + n_1}, \tau = \frac{2n_0}{n_0 + n_1}, \qquad (1)$$

where $\rho$ is the magnitude of the reflection, $\tau$ is the magnitude of the transmission, $n_0$ is the refractive index of the air and $n_1$ is the efractive index of the layer. To have the minimum reflection in a AR coating should equate the reflectance of two surfaces in the following equation

$$\frac{n_0 - n_1}{n_0 + n_1} = \frac{n_1 - n_s}{n_1 + n_s} \Rightarrow n_1 = \sqrt{n_0 n_s}, \qquad (2)$$

where $n_s$ is the refractive index of the substrate [1]. The relationship obtained above between the refractive index of the air, layer, and substrate is the minimum condition for reflection in an AR single-layer coating. To enhance the transmittance of infrared windows, it is essential to use the multi-layers antireflection coating. Several multi-layers coatings, consisting of low and high index materials, have been applied by researchers to enhance the transmission of ZnS in the range of 8–12 $\mu$m: $ThF_4$/ZnS [17], YF3/ZnS (only designed, not measured) [18], $YF_3$/ZrN [19], $YbF_3$/ZnS [20], and multilayer hard carbon [21].

In this work, multi-layer AR coating such as single layer, double- and triple layer was investigated with ZnS and $MgF_2$. ZnS and $MgF_2$ films were deposited by physical vaper deposition (PVD), and their optical properties were examined. Based on the optical constants of each material, single-layer, double-layer, and triple-layer AR coatings were designed and fabricated on the ZnS substrate. The film's thickness was found out using FESEM images with the help of the Digimizer software. The structural properties of samples were studied using X-ray diffraction and the IR transmission spectra was measured with an FTIR spectrometer.

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## 2. Design

The design was performed by the Essential Macleod program (Thin Film Center Inc.), that is a comprehensive software package for the design and analysis of optical coatings. In this software, the desired characteristic (transmission/reflection/absorption) is determined by optimizing the thickness of the high and low refractive index layers. The design of the multi-layers coating was done by using $MgF_2$ and ZnS on ZnS substrate. The optimization was performed by the simplex method at a reference wavelength of 10 $\mu$m. The arrangement and optimized thickness of the layers in the designed antireflection coating are as follows ZnS substrate/ $MgF_2$/ZnS/$MgF_2$/Air

## 3. Experimental

The deposition was performed by physical vapor deposition (PVD) technique in a vacuum chamber, by using the thermal boat. The deposition was performed at a pressure of $1 \times 10^5$ mbar. Polycrystalline ZnS (multispectral grade, 3 mm thick) were used as substrates. Before deposition, the substrates were washed with detergent in an ultrasonic bath. $MgF_2$ (purity: 99.99%) and ZnS (purity: 99.99%) were evaporated by thermal boat. During the deposition process, the substrate temperature was kept at room temperature. Layer thickness and deposition rate were measured by a piezoelectric crystal. The deposition rates were 1 and 0.5 nm/s for ZnS and $MgF_2$, respectively.

The film's thickness was found out using FE-SEM (MIRA3 TESCAN) side images with the help of the Digimizer software program. The structural properties of samples were studied using X-ray diffraction (ADVANCE–D8 model) equipped with Cuk= 1.5406 radiation source and the IR transmission spectra was measured with an FTIR spectrometer (Shimadzu-8400S).

## 4. Results and discussion

The structural analysis and phase purity of the $MgF_2$/ZnS films were determined by XRD pattern using X' Pert PRO Panalytical instruments, as shown in Fig. 1. This figure shows the XRD patterns of the single layer of $MgF_2$, two layer of $MgF_2$/ZnS, and three layers of $MgF_2$/ZnS/MgF2, respectively. Figure 1 represents the tetragonal phase of $MgF_2$ with estimated lattice constants $a = 4.611 \pm 0.006$ Å, $b = 4.613 \pm 0.011$ Å, $c = 3.022 \pm 0.017$ Å, comparable to standard lattice parameters $a = 4.625$ Å, $b = 4.625$ Å, $c = 3.052$ Å (JCPDS:721150) [22]. No impurity peaks were found in the XRD pattern. Similarly, Fig. 1 represents the cubic phase of ZnS layer with estimated lattice constants $a = b = c = 5.331 \pm 0.019$ Å as compared to the standard lattice parameters $a = b = c = 5.345$ Å (JCPDS: 800020) of ZnS [23, 24]. The XRD pattern of the ZnS/$MgF_2$ multilayer is shown in Fig. 1, which exhibits the presence of both pristine phases of $MgF_2$ and ZnS, respectively. Any additional peaks, as well as secondary phases were not observed in the combined phases of the ZnS/$MgF_2$ composite except pristine ZnS and $MgF_2$ peaks, which confirms that the lattice diffusion does not occur during the fabrication of alternate layers in the composite system. Comparing these data with those of single films, no extra peaks are found. Then it can be deduced that no other crystalline compound is formed during either the growth. $MgF_2$ peaks appear at the multilayers and in thin films. This has been interpreted as a transition from amorphous to polycrystal in this material. The size of the crystals of this sample was obtained with the Debye-Sherrer formula

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{3}$$

where $D$ is the crystal size, $\lambda$ is the wavelength of the X-rays, $\beta$ is the half-width of the peak, and $\theta$ is Bragg's angle. In the case of three layers the obtained $\theta$ was 0.45°, while crystal size for final coating was 21.81 nm. By increasing the number of layers crystallinity increases.

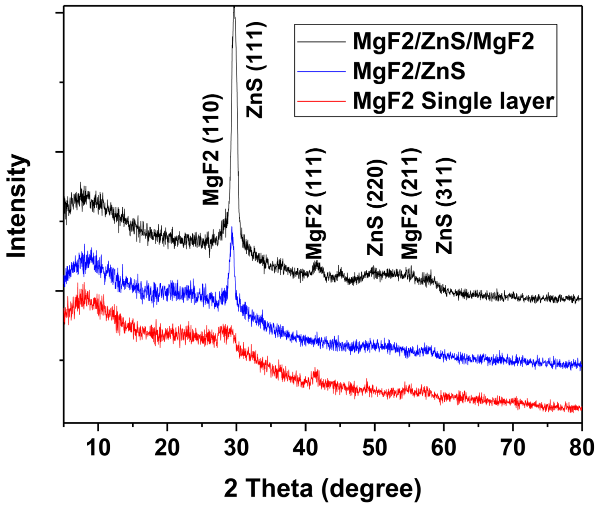

Fig. 1. The XRD patterns of the single layer of $MgF_2$ two layer of $MgF_2$/ZnS, and three layers of $MgF_2$/ZnS/$MgF_2$.

The FESEM 3D image was used to measure the thickness of the $MgF_2$/ZnS films. Figure 2 represents the cross- section views of (a) $MgF_2$ single layer, (b) $MgF_2$/ZnS, and (c) $MgF_2$/ZnS/$MgF_2$ deposited on ZnS substrate. The thickness of films was obtained after processing by using digimizer software. The thickness of the $MgF_2$ single layer was estimated to be 210 nm. The thickness of multilayers was estimated: ($545 \pm 20$ nm) $MgF_2$ / ($482 \pm 17$ nm) ZnS and ($402 \pm 14$ nm) $MgF_2$ / ($237 \pm 8$ nm) ZnS / ($119 \pm 6$ nm) $MgF_2$. The figures indicate that all the samples were uniform, compact with good adhesion on ZnS substrate.

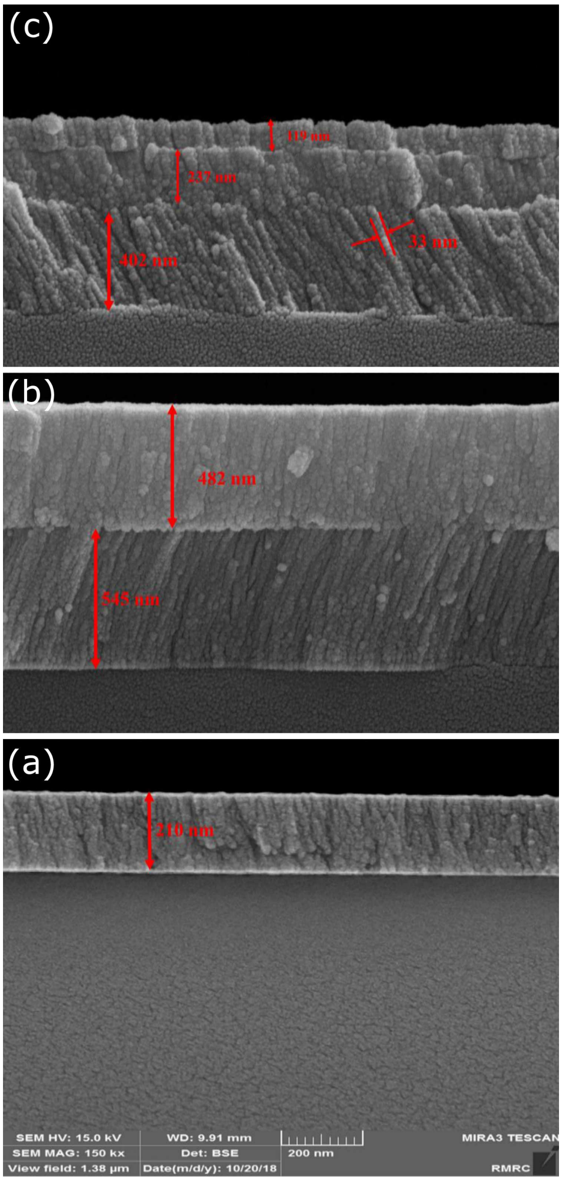

Fig. 2. The cross section views of (a) $MgF_2$ single layer, (b) $MgF_2$/ZnS and (c) $MgF_2$/ZnS/$MgF_2$ deposited on ZnS substrate..

Furthermore, good agreement was found between the actual and estimated thickness of the samples. Nanostructure thickness was measured using digimizer software, as can be observed in Fig. 2c. The' average thickness of the nano-columns was about 30 nm. Durability and environmental tests were performed on the samples by MIL-F-48616 (Salt spray: 24 h, 6.5–7.2 pH, 35 °C; Adhesion: 1 pull by scotch tape; Humidity: 24 h, 95–100% RH, 49 °C; Abrasion: 10 rubs by cheese cloth) and the $MgF_2$/ZnS/$MgF_2$ multilayer have successfully passed durability and environmental tests.

Figure 3 shows the theatrical and experimental spectra, both in the range from 8 to 12 $\mu$m. We have considered two different cases: uncoated ZnS substrate and three-layer antireflection coating on one side of the substrate. It is obvious that the coating greatly enhances the IR transmission. The maximum transmittance is 78% for the uncoated ZnS substrate. With the deposition of the three-layer antireflection coating on the one side of the substrate, the maximum transmittance reaches 98%. The average transmittance increases by 26% and reaches 93%, in the wavelength range of 8–12 $\mu$m. As seen from the figure, there is a good agreement between the calculated and experimental results, especially for the one side coated case. It should be noted that to obtain the best possible agreement, we first obtained the tooling factor (thickness of film on substrate/thickness displayed on the monitor) for ZnS and $MgF_2$. Then, after repeating the deposition process for several times and by using the "reverse engineering" mode of the software, the best choice for the monitor thickness was obtained. The discrepancy between the calculated and experimental spectra is more pronounced at about 8–8.5 $\mu$m for the one side coated case. Generally, the discrepancy may be attributed to tooling factor-calibrating errors, monitoring errors during layer deposition [25] and packing density of deposited coating materials [26].

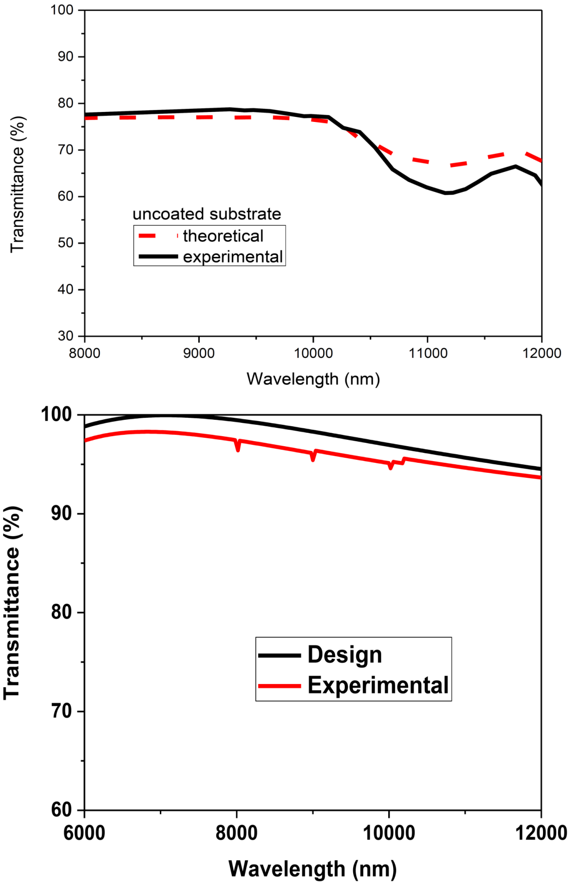

Fig. 3. The theoretical and experimental spectra, both uncoated ZnS substrate and three-layer anireflection coating, shown in the range from 8 to 12$\mu$m.

## 5. Conclusion

We have studied the design, fabrication, and characterization of the multi-layer antireflection coating consisting of ZnS and $MgF_2$ on ZnS substrate. The three-layers coating ($MgF_2$/ZnS/$MgF_2$) with optimized thicknesses was fabricated by the PVD technique. From FTIR spectroscopy it was found that in the wavelength range of 8–12 $\mu$m, the average transmittance of the double-side coated sample increases by about 26% and its maximum reaches about 98%. The FESEM figures indicate that all the samples were uniform, compact with good adhesion on ZnS substrate. The XRD pattern of the ZnS/$MgF_2$ multilayer which exhibits the presence of both pristine phases of $MgF_2$ and ZnS, respectively.

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