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Substrate temperature effect on the nanoscale multilayer ZnS/Ag/ZnS for heat mirror application

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Nanoscale multilayers of ZnS/Ag/ZnS were deposited on Corning glass substrates at different substrate temperatures. The depositions were carried out in high vacuum using electron beam deposition technique at 20, 60, 100 and 150 °C, respectively. The optical and electrical performance of each single layer and the accomplished ZnS/Ag/ZnS multilayer system were characterized using spectroscopic ellipsometry analysis, XRD and finally AFM. Based on these analyses and associated theories, such as the characteristic matrix theory, the optimized multilayer system was speculated and tested. Crystallographic structures of the films were studied by X-ray diffraction. In addition to X-ray diffraction, morphological characterizations were carried out by AFM in order to observe the deposited particle size, packing and roughness of the films. The optimum performance was achieved at the substrate temperature of 60 °C.

Keywords: *energy saving; nanosized ZnS; spectroscopic ellipsometry (SE); matrix theory; electron beam vapor deposition*

1. Introduction

The fascinating phenomenon of heat mirror and its potential applications have motivated scientists and engineers. Intense research has taken place to discover new materials, to understand the physics that underlies the properties of heat mirrors, and to develop new applications for these materials. Modeling the properties of multilayers with different thicknesses of dielectric and metal films has been an important subject of interest.

Thin multilayer dielectric/metal/dielectric (D/M/D) system with heat reflectance was built for better thermal storage performance and high transparency in the visible and reflectance in the infrared ray (IR) regions. As the dielectric layer, ZnS was chosen because of its high refractive index, ease of deposition and low cost, although other compounds, e.g. WO_3 and TiO_2 have also been tested [1]. The metal in common use is Ag due to its low absorption of light in the visible region but Au and Cu have also been taken into account. The leading parameter of optical performance for any optical system, e.g. heat mirror is the refractive index that is sensitive to wavelength, scattering of incident light and multilayer thickness. Structural and optical properties of such multilayer systems and the effect of annealing have been investigated. The ZnS/Metal/ZnS multilayer film, in addition to low resistivity and high optical transmittance, has a good chemical and thermal stability, which led to its extensive applications in optical devices and heat mirrors [2]. The coating was employed for transparent conductive oxide (TCO) in optical devices as well as for heat mirrors [3]. There are numerous reports on theoretical and experimental studies of the devices [4, 5].

Fan et al. [6] reported that if a film of metal is embedded between two dielectric layers as a mirror layer with high reflection, this multilayer system could suppress the reflection from the metal layer in the visible region, and achieve a selective transparent effect. Design and construction of an improved nanometric ZnS/Ag/ZnS/Ag/ZnS transparent conductive electrode and the effect of annealing on its characteristics, has been studied [7]. In an effort to improve the properties of transparent conductors (TC), a set of multilayer coatings consisting of three alternating layers of metals and high refractive index dielectrics has been developed.

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Design and optimization of these coatings was carried out using the electromagnetic equations and the characteristic matrix theory. Optimum thickness was predicted for each layer and the most suitable materials were chosen [8]. The influence of Ag thickness on structural, optical, and electrical properties of ZnS/Ag/ZnS multilayers was the subject of studies performed by Leng et al. [9].

An extended review was carried out on ZnS thin films and the optical properties of the films were studied in a variety of circumstances. The absorbance/transmittance/reflectance spectra, band gap, refractive index, extinction coefficient, optical conductivity, complex dielectric constant were studied for different thicknesses of the layers [10]. Although some studies were carried out on the resistance and transmission properties of ZnS/Ag/ZnS multilayers for transparent electrodes in flat display applications [8, 11], not much attention focused on the curved surfaces of the multilayer, reported in the literature [12].

Referring to the former studies, electron beam assisted deposition technique is a preferred method to produce high quality thin films [13]. In addition, the effect of substrate temperature on optical and electrical properties of semiconductors was investigated by Suganya et al. [14].

The present study is focused on a ZnS/Ag/ZnS multilayer array with optimum optical properties of dielectrics with low IR radiation reflection and high transmittance in the visible region. The ZnS/Ag/ZnS multilayer with nano-dimensions was deposited by electron beam evaporation of the elements in a vacuum system. The crystal structure of the films, topography, optical and electrical performance and the depth profiles of the glass/ZnS and glass/ZnS/Ag samples were studied in details. The effects of substrate temperature on the properties of the glass/ZnS sample were investigated. Annealing which is an important process to modify the nanostructure of ZnS/Ag/ZnS film will be the subject of the next report.

2. Experimental

ZnS nano grains and Ag powder with high purity (99.99 %) were selected as deposition resources. The powders were filled in sequence into a graphite boat. The substrate was Corning glass (Corning 7059) cleaned sequentially by ultrasonication in acetone and deionized water for 10 min. Then, it was dried in a high purity N_2 gas stream just before positioning in the vacuum chamber. The vacuum system employed in this research was "Edwards AUTO 306, Sputtering System". At the first stage, the substrate was fixed in a sample holder equipped with a homemade heater box to vary the substrate temperature from 20 to 200 °C. The heater box was simply a Kendal wire placed in a small box and connected to an external power supply. The ZnS was filled in a graphite boat situated in the foreseen place. Then, the system was closed and evacuated to a base pressure of approximately $\sim 1 \times 10^{-3}$ Pa. Subsequently, the sample was further cleaned in the vacuum system by exposing to glow discharge for 5 min before deposition. The deposition was initiated in the electron beam mode with evaporating rate of about 0.1 $nm \cdot s^{-1}$. First, ZnS was deposited on the substrate at different substrate temperatures of 20, 60, 100 and 150 °C. Substrate temperatures were controlled using a thermocouple (K type) monitored by a microvoltmeter, while deposition was continued. For evaluating substrate temperature effects on the properties of ZnS thin films, the prepared films were characterized by SE, AFM, XRD and IR plus visible light spectroscopy. The optimized sample was selected for further operations; e.g. the sample was annealed at different temperatures. Second stage of the design was the Ag film deposition on the ZnS film. The deposition was carried out as in the first stage. Finally, at the third stage, ZnS was deposited on Ag and the multi-layer system composed of three layers was formed. The thickness of the layers was measured using a quartz crystal thickness monitor. The measurements were also calibrated by a spectroscopic ellipsometer "Model SENTECH SE800" in the range of 190 to 800 nm incident wavelength and at the angles of 50, 60, and 70° with incident beam perpendicular to the sample. The study of ZnS/Ag/ZnS interfaces by the spectroscopic ellipsometry revealed that the interlayer between the Ag and ZnS layer contained a physically mixed layer and a compound semiconductor layer. Based on these studies, according to the characteristic matrix theory, complete searching strategy was carried out to optimize the system [3].

The optical properties, such as refractive index and electrical performance of Ag and ZnS films with nano-dimensions were investigated [8, 9]. Surfaces under test have to be sufficiently even and parallel to each other. SE is capable of defining the refractive index in imaginary and real part as ($n = n_{rel} + ik$) and the depth-profiles of a multilayer structure. In physics, the imaginary part of a complex index of refraction is called "extinction coefficient", which also relates to light absorption. Extinction coefficient is a measure of how strongly a substance absorbs light at a defined wavelength. In the regions, where the extinction coefficient is zero, there is no absorption. Typical data of optical parameters, (refractive index and extinction coefficient) are shown in Fig. 1. This allowed us to select an optimum substrate temperature for ZnS/Ag/ZnS multilayer. In addition to the optical constants and the thickness assessments of the samples, spectroscopic ellipsometry measures the change in polarization state of the light reflected from the sample surface. The measured values are the ellipsometric parameters, delta (Δ), and psi (ψ). These values are related to the ratio of reflection coefficients r_p and r_s assigned to p and s polarized light, respectively, as follows:

$$\rho = \frac{r_p}{r_s} = \tan(\Psi)\exp(i\Delta) \qquad (1)$$

where ρ is the ratio of reflection coefficients and i is imaginary unit. In case of thin film layers, information about the thicknesses is included in ψ and Δ and the thickness of each layer can be determined by best fitting between the experimental and calculated data by usual thin film optics calculations, as shown in Fig. 2 [15].

The film structural analysis was accomplished by XRD "Philips X-ray diffraction system with the settings of 40 kV, 30 mA, CuKα wavelength of 1.540598 Å in the scan range of 2θ between 10° and 90° with 0.05 2θ s^{-1} step size. Surface morphologies and roughness of the films severely affected the optical properties due to surface

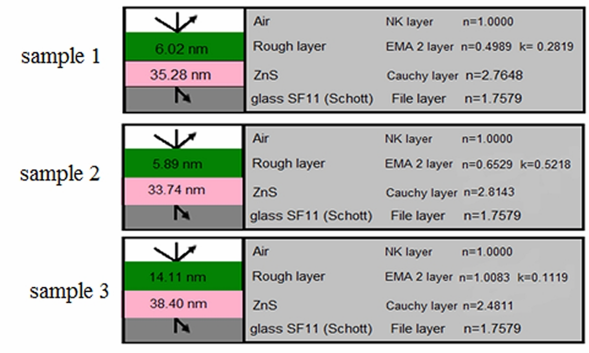

Fig. 1. Print screen of monitored data for thickness and optical parameters of samples 1, 2 and 3.

scattering. Scanning Probe Microscopy (SPM) monitored the morphologies at the non-contact (NC-AFM) mode. The SPM was Park Scientific Co. USA and non-contact AFM mode was employed to preserve the film surface and avoid damage.

3. Results and discussion

Uniform ZnS films were prepared by PVD method described in the literature [16]. The SE analysis was carried out by comparison the real measurement results with the data obtained by appropriate modeling of the SE system in a way recommended by the Company, (Fig. 1 and Fig. 2). Fig. 2 shows an image of SE used to estimate the real efficiency of the layers and optical parameters for sample 3. The measurements were taken at the angles of 50°, 60° and 70° with respect to the normal to the layer surface. In our case, the Cauchy model provided an adequate description of the dielectric function [17].

So far, the optical response was treated with a three-layer model in a mean-field sense [18]. Such a model is applicable if each layer is treated as a uniform mixture of the host and guest materials with their respective bulk optical dielectric constants. Once the surface roughness of a crystalline material extends beyond a monolayer, the three-layer model scheme is proposed to interpret the experiment [19]. The scheme assumes that on average the atoms/vacancies within an atomic/molecular layer at the same height with respect to the substrate surface experience the same mean electric field. The pores in the dielectric medium are supposed to be spheroidal and the porous film can be considered as a random composite medium. Bruggeman suggested that in this case the dielectric response of each layer is a complex quantity $\varepsilon = \varepsilon_1 + i\varepsilon_2$ with a real and imaginary part, ε_1 and ε_2, respectively. Within the layers, the calculations are carried out based on a self-consistent effective medium approximation (EMA) [20].

In theory, the contributions from surface atoms, including those at step edges, can be neglected, and in some cases it is successful [19, 21]. Such an assumption is questionable if vacancies are included, thus, the electric field due to the vacancies is expected to be different from that in the corresponding filled region, (atoms/molecules).

In this work, the EMA used to describe surface roughness of the layers was the Bruggeman EMA model (SE software), that was working well with the sphalerite/wurtzite structure of ZnS films [22]. Fig. 1 summarizes the data obtained by the model to monitor the quality of the samples.

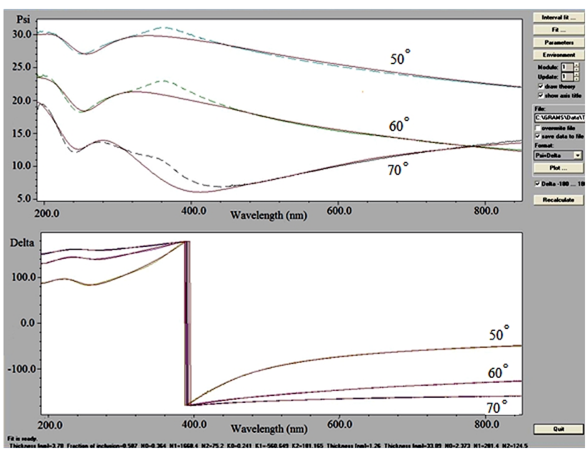

Fig. 2. Data analyzed by ellipsometry (dash line) well-matched with the data acquired from ellipsometry based on EMA, (solid line).

Fig. 2 shows an acceptable match between the raw data (dash lines, obtained for the samples) and ellipsometry model (solid lines, obtained from EMA) for delta (Δ), and psi (ψ) parameters.

Characteristic matrix theory predicts the thickness of ZnS film consisting of two parts, i.e. solid and rough parts. The fitted thickness for samples 1, 2 and 3 are 35.28 nm, 33.74 and 38.40 nm for the solid part and 6.02, 5.89 and 14.11 nm for the rough part, respectively. The refractive index of the sample is affected by the substrate temperature. Experimental results confirm that a temperature increment above 60 °C decreases the refractive index, whereas for samples 1 (20 °C), 2 (60 °C) and 3 (100 °C) it is 2.76, 2.81 and 2.48, respectively. It can be seen that sample 2 has optimum expected properties, due to denser layers, low roughness and higher refractive index. Fig. 2 presents SE calculations and measurements for the samples 1, 2, 3 and 4 at different temperatures.

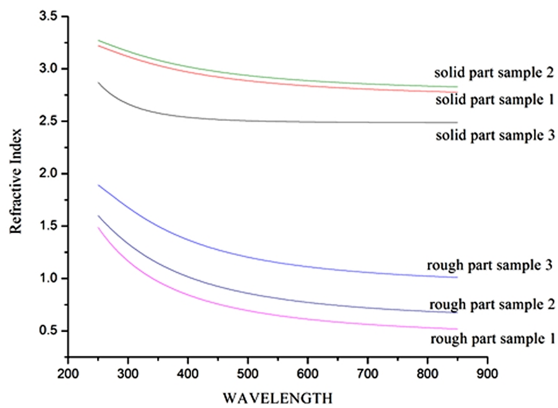

Fig. 3. Refractive index of both rough layer and bias region (solid part) for samples 1, 2 and 3.

In our study, the substrate temperature up to 60 °C resulted in a decrement in the grain size, but further temperature increase caused an increment in grain size. Fig. 3 shows refractive index variations of sample 1, 2 and 3 in the incident light range of 250 nm to 850 nm. The refractive index has increased with the increase of the thickness due to the grain size variation. The obtained data are not in contradiction with the result of Leftheriotis et al. [8] for 15 nm thickness, although the SE data obtained by characteristic matrix theory present different arrangements of the rough and solid parts in Fig. 3.

The XRD analysis indicates that ZnS films have zinc blende structure with (1 1 1) and wurtzite

Table 1. Calculated by SE at 627.8 nm and measured parameters of the films deposited at different temperatures.

Parameter	Sample 1	Sample 2	Sample 3	Sample 4
Substrate temperature	20 °C	60 °C	100 °C	150 °C
Thickness measured by thickness monitor	15 nm	15 nm	15 nm	15 nm
Refractive index (solid part)	2.76	2.81	2.48	–
Refractive index (rough part)	0.4989	0.6629	1.0083	–
Thickness of solid part of the layer (SE)	35.3 nm	33.7 nm	38.4 nm	–
Thickness of rough part of the layer (SE)	6.02 nm	5.89 nm	14.1 nm	–
RMS roughness (SE)	0.6 nm	0.6 nm	11.2 nm	–
Percent of vacancies (roughness's fluctuations)	2 %	1 %	15 %	–

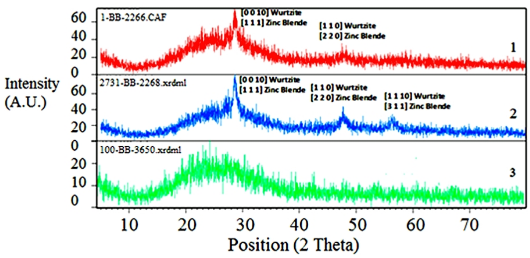

Fig. 4. XRD patterns of ZnS films 1, 2 and 3 deposited at 20 °C, 60 °C and 100 °C, respectively.

structure with (1 1 0) preferential orientations, whereas the diffraction patterns sharpen with the increase in substrate temperatures [23]. XRD patterns of ZnS thin film deposited at 20, 60 and 100 °C are shown in Fig. 4. The goniometric patterns were taken at a normal angle because the low angle was not available on that time, so the spectra are little inferior. Sample 1 (at the room temperature, 20 °C) displays two low intensity peaks that refer to both wurtzite and zinc blend structures of ZnS. In sample 2 (at the temperature of 60 °C) there are three sensible peaks as indicated in Fig. 2. These peaks are stronger and wider, indicating that sample 2 has a series of polycrystalline planes with diminutive particles. Sample 3 (at the temperature of 100 °C) does not have any crystalline structure observed in the spectrum. Thus, the XRD patterns show that sample 2 is favorable for further study.

Morphology and nanostructures of the surfaces play an important role in the optical properties of the films. Detailed studies of the films surface

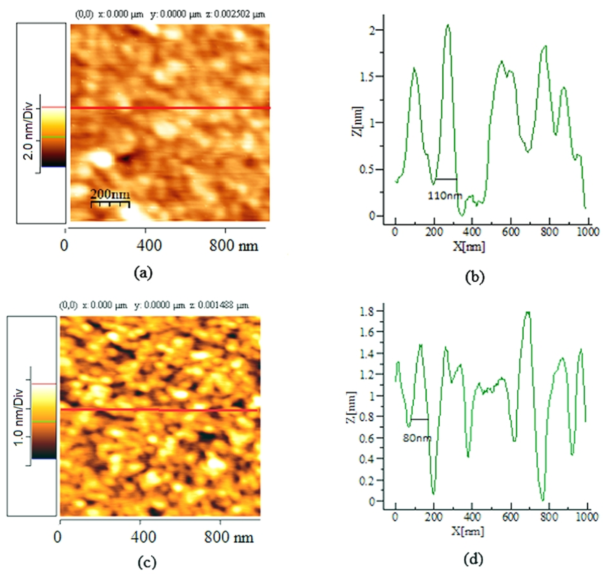

Fig. 5. (a) AFM image of a zinc sulfide thin film deposited on a Corning glass substrate at room temperature, (sample 1); (b) profile of the surface in the direction shown in (a); (c) ZnS thin film deposited on the substrate at 60 °C, (sample 2) and (d) profile of the surface in the direction shown in (c).

structures, particle size and roughness were carried out by AFM. Fig. 5 displays AFM images of the samples 1 and 2. Sample 2 has a minimum grain size of about 80 nm comparing to 110 nm of sample 1, which improves optical parameters because of smoother top layer, therefore, the lower scattering from the surface.

Table 2. Statistical parameters of samples 1, 2, 3 and 4 obtained from AFM data.

Roughness results:	Sample 1	Sample 2	Sample 3	Sample 4
RMS roughness:	0.621	0.608	10.152	14.108
Peak to peak:	6.201	5.624	88.370	67.725
Roughness average:	0.476	0.473	7.912	11.563
Average height:	2.301	2.900	28.005	30.983

Fig. 6 shows the AFM images of samples 3 and 4. Samples 3 and 4 have bigger grain sizes of about 200 to 380 nm compared to 110 nm of sample 1. The size degrades the optical parameters because of high fluctuation on the surface, therefore, extreme scattering.

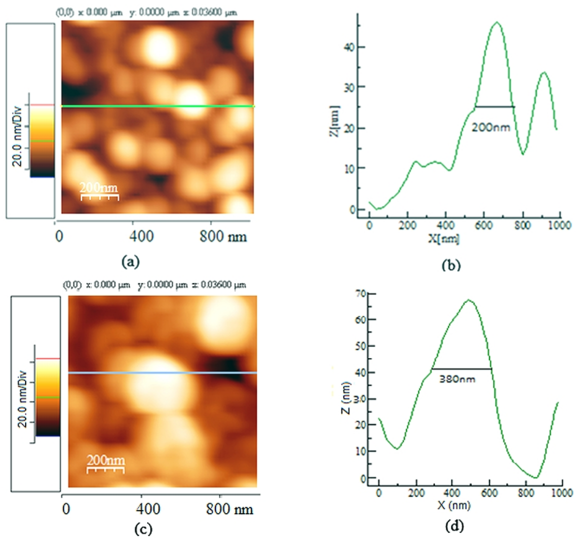

Fig. 6. (a) AFM image of a ZnS thin film deposited on a Corning glass substrate at 100 °C, (sample 3), (b) profile of the surface in the direction shown in (a), (c) ZnS deposited on the substrate at 150 °C, (sample 4) and (d) profile of the surface in the direction shown in (c).

The more prominent roughness in the profiles of the films resulted in the lower mean refractive index in comparison with the bulk material. However, the variation of refractive index of ZnS films due to the temperature increment resulted from absorption of the incident light [24].

Table 2 presents the statistical data obtained by AFM software; the data of samples 1 and 2 have insignificant deviations, but the parameters of samples 3 and 4 deteriorated drastically.

4. Conclusions

ZnS/Ag/ZnS thin films were deposited in a PVD system by electron beam evaporation. The effect of substrate temperature on the structure and optical properties of ZnS and ZnS/Ag/ZnS thin films was studied. The study focused on the roughness, crystal structure and grain size of the deposited films. The film obtained at 60 °C substrate temperature had smaller grain sizes compared to the films prepared at 20, 100 and 150 °C substrate temperatures. The increase of the temperature from 60 to 150 °C resulted in an increase in RMS values of the surface roughness from 0.6 nm to 11.57 nm. SE analysis showed that the film rough part thickness increased with the temperature increment, while the refractive index decreased. This is due to the valley and the hills modification in the films. AFM images of the ZnS, Ag and ZnS/Ag films deposited at 20, 60, 100 and 150 °C substrate temperatures confirm the statement. It can be concluded that the films roughness is highly influenced by the substrate and annealing temperatures; the last will be the subject of our further studies.

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