Parameters of ZnS/Metal/ZnS Nanostructured Systems with Different Metal Layers

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Abstract— ZnS/metal/ZnS (ZMZ) nanomultilayer films with Au, Ag and Cu as a metal layer have been deposited on a glass substrate by thermal evaporation and then, were annealed in air at different temperatures from 100 to 300 ºC for one hour. Several analytical tools such as X-ray diffraction, four point probe and spectrophotometer were used to study the changes in structural, electrical and optical properties of the samples. XRD patterns show that the crystallinity of structures and also grain size of particles increases with increasing the annealing temperature. Improved electrical property (a sheet resistance of 7 Ω/sq for ZnS/Au/ZnS) and considerable improvement in the transmittance curves (86% maximum transmittance for ZnS/Au/ZnS) of the samples after heat treatment at 200 ºC was observed. Also, the optical constants of the ZMZ multilayer samples were calculated from transmittance and reflectance measurements. The figure of merit was applied on the ZMZ coatings and the most suitable films and annealing temperature for the application as transparent conductive electrodes were determined.

KEYWORDS: Transparent conductive coatings, Nanomultilayer films, Heat treatment, Vapor deposition, X-ray diffraction, Optical properties.

I. INTRODUCTION

There are increasing interests in transparent conducting coatings for the use in the variety of optoelectronics applications. The transparent conductive thin film requires high visible transmittance ($400<\lambda<700$ nm) and high infrared reflectance ($700<\lambda<3000$ nm), where λ is the wavelength. Also, these films exhibit high electrical conductivity ($>1\times10^6\ \Omega^{-1}\ m^{-1}$) [1].

Addition to the most common transparent conductive films such as ITO [2], SnO_2:F [3] and Al doped ZnO [4, 5], some researchers have proposed Dielectric/Metal/Dielectric (D/M/D) multilayer structures with much lower resistance as a good transparent conductive films [6-12]. These structures can suppress the reflection from the metal layer in the visible region, and achieve a selective transparent effect. It has been well established that oxidative surface treatment schemes, such as ultraviolet (UV)–ozone [13] and oxygen plasma treatments [14] and thermal annealing [15–21] of transparent conductive films, significantly enhances transparency and reduces resistivity.

Thus, in this work we have focused on D/M/D multilayer films with ZnS as the dielectric and Au, Ag and Cu as metal layers and investigated the effect of thermal treatment on the structural, electrical and optical properties of the ZnS/M/ZnS (ZMZ) multilayer samples. Several analytical tools such as X-ray diffraction (XRD), electrical resistivity and optical transmittance and reflectance measurements were used to investigate the effect of the thermal treatment on properties of ZMZ multilayer films.

II. EXPERIMENTAL PROCEDURE

Conductive transparent ZnS/Metal/ZnS nanostructures have been simulated through optimization layers thicknesses, as we did in our previous work [21], where used Gold, Silver and Copper materials as a metal layer and zinc sulfide as dielectric layers. The Table 1 presents the results of this simulation. Then the optimum structures were made on a glass substrate by thermal evaporation. The Glass substrates were cleaned sequentially by ultra-sonication in propanol, acetone and deionized water for 10 min, respectively. Then the substrates were dried in an oven keeping at 80 ºC temperature. The chamber, which was equipped with a load-lock system and diffusion pumps, had a base pressure of 10.64×10^{-4} Pa. The Metal (Au, Ag and Cu) and ZnS particles (99.9% purity) were heated in tungsten boats. The temperature of the substrates was about the room temperature during deposition. The film deposition rate was 0.1 nm/s. The thickness of each film was monitored in situ by a quartz crystal thickness measuring device. The multilayer films successively formed on the glass substrate without vacuum break. The thermal treatment was carried out in air for an hour and the temperature was varied from 100 to 300 °C. The sheet resistance of the ZMZ nanomultilayer structures was measured by means of a portable four-point probe. The optical transmittance and reflectance of the ZMZ nanomultilayer structures were also measured in the wavelength range 200–1100 nm by an ultraviolet (UV)/visible spectrometer (Ceintra 6). To investigate the microstructure of the ZMZ nanomultilayer structures with different annealing temperature, X-ray scattering examination was employed by X-ray diffraction measurements with 40 kV, 30 mA, Cu Kα radiation with wavelength of 1.54 Å (Philips), in the scan range of 2θ between 10° and 90° with a step size of 0.05 (2θ/s).

Table 1 Simulated optimum thickness of glass/ZnS (d_3)/Metal (d_2)/ZnS (d_1) structures.

Metal	d_1 (nm)	d_2 (nm)	d_3 (nm)	n
Au	37.0	16.5	42.5	3.2
Ag	35.1	18.3	38.6	4.9
Cu	41.5	17.6	47.7	4.0

III. RESULTS AND DISCUSSIONS

A. *Structural Properties*

The high angle XRD pattern of the prepared ZnS/Metal/ZnS thin films is shown in Fig. 1.

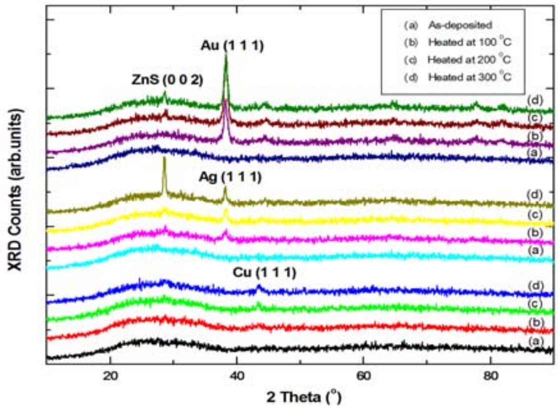

Fig. 1 XRD patterns of ZMZ nanomultilayer films with different metal layers (Au, Ag, Cu) annealing at various temperatures.

The X-ray diffraction measurements of the ZMZ films for 2θ scans between 10 ° and 90 ° have been obtained at different annealed temperatures. It can be seen that before the heat treatment, the films are amorphous but after annealing, the films show only two maximum peak intensities. The maximum intensity peak at $2\theta = 28.68°$ is contributed by ZnS films corresponds to the (002) predominant orientation. Other peak is related to Metal films. Diffraction angles observed at $2\theta = 38.269°$, $2\theta = 37.934°$ and $2\theta = 43.473°$ are belonged to the diffraction peak of Au, Ag and Cu, respectively, corresponding to the cubic structure with (111) predominant orientation. The peak intensities are enhanced by increasing annealing temperature. Also the influence of the annealing temperature on grain size of the metal layers in the ZMZ thin films is investigated. The crystalline size was calculated by Scherrer's formula [22]

$$D = 0.89\,\lambda / \beta\,Cos\theta \tag{1}$$

where D is the grain size, λ (1.54056 $\overset{o}{A}$) is the wavelength of X-ray radiation, β is the full width at half maximum (FWHM) of the diffraction peak and θ is the Bragg diffraction angle of the XRD peak. The average grain sizes of the films annealed at various temperatures were estimated and are presented in Table 2. It can be seen that the particle size increases with increasing the annealing temperature. However, it was revealed that ZnS/Cu/ZnS multilayer film showed diffraction pattern without a diffraction peak at 100 ºC annealing temperature, indicating that it was amorphous in structure. It seems that nucleation temperature of ZnS/Cu/ZnS multilayer film is higher than two other structures.

Table 2 The grain size (crystalline size) of metal in ZMZ nanomultilayer structures with various annealing temperatures.

Structure	Annealing Temperature [ºC]	2θ [°]	β	Particle Size [nm]
ZnS/Au/ZnS	100	38.22	0.48	17±1.8
	200	38.17	0.40	21±2.6
	300	38.31	0.24	35±7.2
ZnS/Ag/ZnS	100	38.19	0.96	9±0.4
	200	38.29	0.48	17±1.8
	300	38.22	0.29	29±4.9
ZnS/Cu/ZnS	100	-	-	-
	200	43.51	0.63	13±1.0
	300	43.65	0.40	21±2.6

B. *Electrical properties*

The sheet resistance changes of the ZnS/Metal/ZnS nanomultilayers prepared with Au, Ag and Cu as the metal layer as a function of thermal treatment temperature are shown in Fig. 2.

It was observed that the sheet resistance of the films was decreased monotically with annealing temperature by an increase in annealing temperature from 100 to 200 ºC. While further increasing of the temperature up to 300 ºC, leads to significant increase of the sheet resistance. These results are in agreement with Klöppel et al. report [23]. Basically the low sheet resistance in these multilayer films is considered as a result of the fact that sheet conduction occurs mostly within the metal films which inherently have a good ductility. The results show that the ZMZ films with highest conductivity can be realized by using the Au as the intermediate layer because Au is more conductive than other metals used in this study.

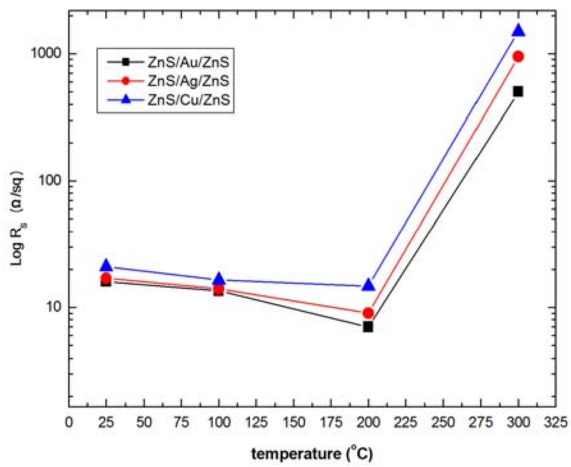

Fig. 2 The sheet resistance of ZMZ nanomultilayer films as a function of annealing temperature.

Sheet resistance of ZnS/Au/ZnS films achieved to the 7 Ω/cm^2 at 200 ºC annealing temperature. It seems that the enhancement of metal layer crystallinity and reduction of grain boundary scattering of multilayer system might results in the decrease of the sheet resistance of the samples annealed up to 200 ºC [21]. However, one can observe significant increase of sheet resistance with increase in annealing temperature up to 300 °C. It seems that this is basically due to severe inter-diffusion of atoms at the Metal/ZnS interfaces. In the other words, metal atoms diffuse through ZnS layers and Oxygen atoms diffuse through metal layers, which results in the oxidation of the metal layers. Therefore, the sheet resistance increases at higher temperatures.

C. *Optical transmittance*

Information concerning optical transmittance is important in evaluating the optical performance of transparent conductive films. It was observed that the optical transmission of the ZMZ films in the visible wavelength region improves with increasing annealing temperature up to 200 ºC and then by further increasing the annealing temperature up to 300 °C, the optical transmission decreases. Transmittance spectra in the UV and visible wavelength regions of the ZMZ films, annealed at 200 ºC are shown in Fig. 3. As can be seen, transmittance of (86%) for ZnS/Au/ZnS structure is higher than other structures. The increase in optical transmittance with increase in temperature can be attributed to the increase of structural homogeneity and crystallinity. Also, it seems that the reduction of transmittance is due to surface roughening of metal layer during annealing and diffusion of metal atoms into ZnS layer that resulted in more scattering of the incident light and reduction of the transmittance [24].

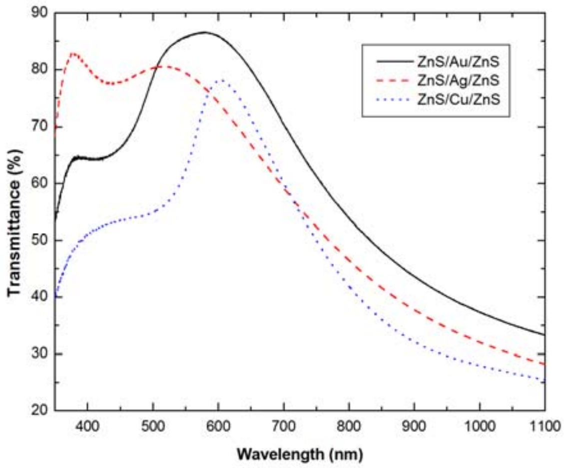

Fig. 3 Optical transmission spectra of ZMZ nanomultilayer films annealed at 200 ºC temperature.

D. *Estimation of the optical band gap*

The relationship between absorption coefficient and optical band gap of nanomultilayer films assuming a direct allowed transition can be expressed as [25]:

$$(\alpha h\upsilon)^2 = A\left(h\upsilon - E_g\right) \tag{2}$$

where α is the absorption coefficient corresponding to frequency υ and A is a constant. The optical band gaps of the samples were determined by extrapolating the linear portion of the curve from the plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$ [26].

Fig. 4 shows the variation of the optical band gap, E_g, of the ZMZ nanomultilayer films having Au, Ag and Cu as a metal layer, as a function of the annealing temperatures.

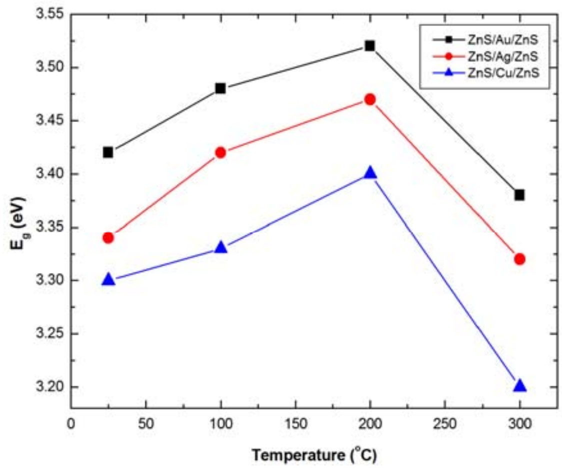

Fig. 4 Variations of the *Eg* of the ZMZ nanomultilayer systems with annealing temperature.

The E_g of ZMZ films increases as the annealing temperature increases. However, optical band gap decreases when temperature exceeds 200 ºC. The variation in the optical band gap according to Burstein–Moss effects can be attributed to carrier concentration, and the resistivity of the samples. Thus, increase in carrier concentration led to filling of the conduction band and blocking of the lowest states, results in wide optical band gap. However, with increasing the annealing temperature up to 300 ºC, carrier concentration of all films decreases due to increasing of oxygen concentration in the metal films and consequently the optical band gap becomes narrower.

E. *Investigation of refractive index*

The reflectance of the ZMZ nanomultilayer films as a function of wavelength are shown in Fig. 5.

The refractive index (n) of the samples is determined from the following equation [27]:

$$n = \frac{1+R}{1-R} + \left[\left(\frac{R+1}{R-1}\right)^2 - \left(1+k^2\right)\right]^{1/2} \tag{3}$$

where $k = \alpha\lambda/4\pi$ is the extinction coefficient. The refractive index values for the ZMZ nanomultilayer films as a function of wavelength are shown in Fig. 6.

Refractive index values at 550 nm for all structures are listed in Table 1. It can be seen that in this wavelength the $n_{ZnS/Au/ZnS} < n_{ZnS/Cu/ZnS} < n_{ZnS/Ag/ZnS}$. It is interesting to say that the n values (at 550 nm) of most of the ZMZ multilayer samples are much higher than the n value (at 550 nm) for the ZnS single crystal $n = 2.62$ [28].

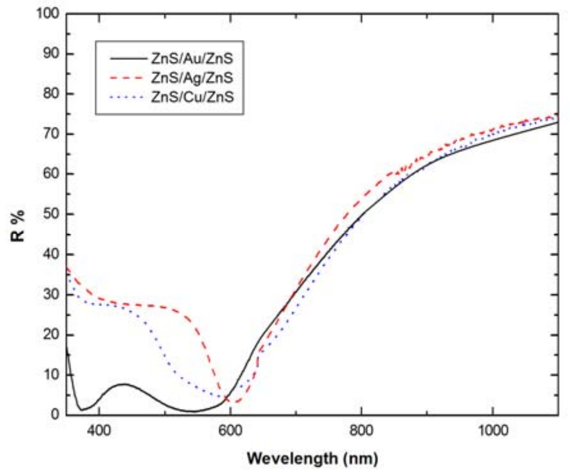

Fig. 5 Optical reflectance spectra of ZMZ nanomultilayer films annealed at 200 ºC temperature.

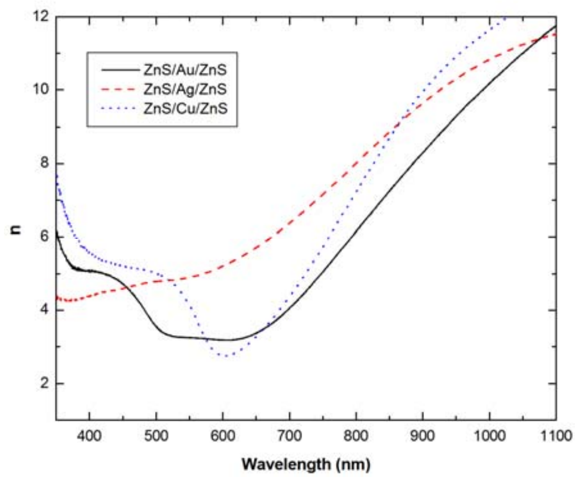

Fig. 6 Variation of the refractive index of the ZMZ nanomultilayer systems upon wavelength.

The figure of merit (F_{TC}) as suggested by Haacke [29] was used for comparing the performance of ZMZ multilayer films which were annealed in differnt temperatures. F_{TC} is defined as:

$$F_{TC} = \frac{T^{10}}{R_S} \tag{4}$$

where T is the transmission at wavelength 550 nm and R_S is the sheet resistance of the transparent conducting oxide.

A plot of the figure of merit versus the annealing temperature is presented in Fig. 7.

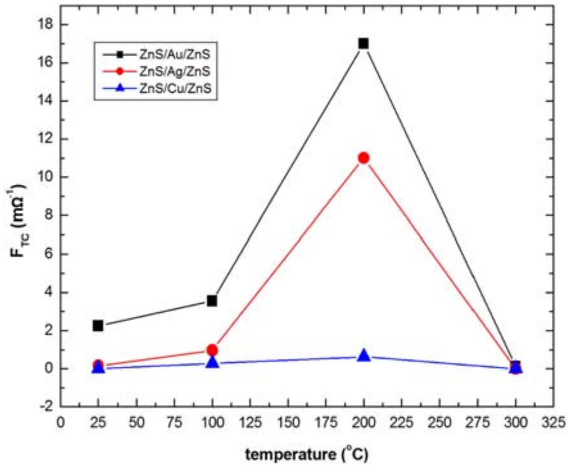

Fig. 7 The figure of merit of ZMZ nanomultilayer systems versus annealing temperature.

It is shown that by increasing the annealing temperature, the F_{TC} value increases and the maximum F_{TC} value of the ZMZ multilayer films could be obtained at 200 °C. Further increases of the annealing temperature, however, led to a decrease in F_{TC} value. The structure with Au as a metal layer has maximum value of figure of merit. Therefore, ZnS/Au/ZnS multilayer film which is annealed in 200 °C is a promising structure for transparent conducting oxide.

IV. CONCLUSION

The ZnS/Metal/ZnS nanostructured systems with Au, Ag and Cu as the metal layer have been prepared on a glass substrate at room temperature. To investigate the effect of annealing treatment on the structural, electrical and optical properties of the structures, the samples were annealed in air at different temperatures from 100 ° to 300 °C for an hour. The XRD patterns show that crystallization improves as a result of the annealing. Results are indicated that the sheet resistance decreases slowly with the increase in the annealing temperature and achieves a minimum value of 7 Ω/sq at 200 °C for ZnS/Au/ZnS structure. Significant increase in sheet resistance occurs with the increase in the annealing temperature up to 300 °C. Optical transmittance of different structures increases by heat treatment and then decreases by increasing temperature up to 300 °C. In conclusion, the annealing temperature has an important role in controlling structural, electrical and optical properties of the nanostructured multilayer films and the ZnS/Au/ZnS structure is a promising candidate to use as a transparent conductive oxide.

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