Study of Mid-Infrared Optical Properties of ZnS Thin Films by Spectroscopic Ellipsometry

Zhe Wang[1,*], Jun Xiao[1], Feng Miao[1] and Zi Ma[2]

[1]*College of Electrical & Information Engineering, Southwest University for Nationalities, Chengdu 610041, China*

[2]*Southwest Institute of Technical Physics, Chengdu 610041, China*

Abstract: In order to obtain the mid-infrared optical properties of ZnS thin films, ZnS films with different thickness were prepared on K9 glass substrate by electronic beam evaporation. They were denoted by A、B、C . The optical properties of thin films were studied by Spectroscopic Ellipsometry. The measured date of film A 、B、C were fitted by Brendel oscillator, and based on ZnS film properties and the film forming characteristic of the ZnS film, building the model"substrate(K9 glass)/EMA(50% K9 glass and 50% ZnS)/ZnS/rough surface layer(50% ZnS and 50% air)/air". The optical constants curve and thickness of ZnS thin film were got. The results shown that the evaluation function MSE is small when Brendel model is used in data fitting. Within the wavelength range of 3000nm ~ 12500nm, the ZnS thin films refractive index and extinction coefficient are reduced with increasing wavelength. The Extinction coefficient tends to zero near the long wavelengh. The thickness of ZnS measured value was closest to the theoretical value. The results have certain reference value to measurement and preparation of high quality ZnS thin film.

Keywords: Thin films, Optical constants, Ellipsometry, ZnS thickness of film.

1. INTRODUCTION

It is well known that ZnS is an important II-VI compound semiconductor materials. There are two structures of ZnS which are sphalerite (cubic) and wutzite (six type) crystal structure [1]. It is known to all that ZnS is an important material of the infrared transmission [2]. It also has good optical properties in infrared and far infrared range. Above all it has so many advantages, such as wide bandgap (about 3.77eV) [3], low dispersion of visible and infrared range [4]. Moreover it is widely used for Electroluminescence, flat panel display, and cathode luminescence. Depending on high refractive index (2.2~2.3) [4] ZnS is often used materials of mirror, broadband antireflection film and a dielectricfilter film. Ellipsometry measurements is the highest measurement accuracy of optical constants of materials method. whatsmore this method is non destructive to sample, can be carried out in situ measurement [5].

Up to now ZnS films have been studied by many times such as the study of optical properties of ZnS films with different deposition temperature by Yu [6], study of effect of substrate temperature on the properties of ZnS thin films by electron beam evaporation by Huang [7].

All of the above methods of study gets some useful conclusion, but there are also some disadvantages. Because the reliability of the ellipsometric results largely depends on the modeling [8, 9], it is very important to choice the oscillator. Research shows that dispersion models commonly used such as Cauchy model and Sellmeier model which can get accurate optical constants near the transparent zone of the intrinsic absorption band [10-12]. But it is low precision when these oscillator used in mid infrared. Brendel dispersion model can well simulate the molecules vibration absorption in the mid infrared range [13].

In this paper we described the electron beam evaporation processing of different thickness of ZnS films.Three physical models simulated ZnS structure. The optical constants of ZnS were obtained in mid infrared range.

2. EXPERIMENTAL PROCEDURE

There are 3-design thickness of ZnS thin films 115nm, 467nm, 652nm were prepared on K9 glass substrate by the TXX550- II box type vacuum coating machine.

They were denoted by A, B, C, Raw materials are ZnS (99.99%) particles. The vacuum is not less than 3×10^{-3}Pa. The temperature of deposition is 230^0C. Using method of optical extremum monitor it. The control center wavelength is 700nm. Using the German made SENTCH SE850F reflective spectroscopic

*Address correspondence to this author at the College of Electrical & Information Engineering, Southwest University for Nationalities, Chengdu 610041, China; Tel: 86-28-85522085; Fax: 86-28-85522085; E-mail: wanziwangzhe@163.com

E-ISSN: 2408-9834/15

ellipsometry measurement these samples. The incidence angle is 70^0. We get the 3 films ellipsometry parameter (Ψ and Δ) at the range of 3000nm~12500nm.

3. THE DATA FITTING

In order to get a reliable fitting data we shuold obtain K9 ellipsometry parameter before. Figure **1** is the K9 glass ellisomtry parameter (Ψ and Δ) of measured and fitted. The evaluation function MSE is 1.25, so the dispersion model can be used for the base model of the experimental group.

In order to study the infrared optical properties of ZnS thin films, the author established 2 physical models of Table **1**. Table **1** shows the physical model I is the monolayer ZnS films cover on K9 glass substrates,and ZnS layers is the Brendel oscillator model [14]. The physical model II is EMA (effective medium approximation) on K9 glass substrate, up layer is themonolayer ZnS film. The rough surface layer is between ZnS layer and Air layer.

Table 1: Two Kinds of Physical Models for ZnS Films

I	II
	Air
	Rough
Air	ZnS
ZnS	EMA
K9	K9

The film A fitted with physical model I when the initial thickness is set to 115nm. After that the fitting result Figure **2** was obtain. And the tkickness of film A 110.86nm was got. The evaluation function MSE is 4.047.

It was EMA (effective medium approximation) that was introduced to describe the mixture of ZnS flim and K9 galss. EMA layer designed as hybrid ZnS film and the K9 glass [15]. The proportion of ZnS thin films linear increase form 0 to 100% with the increase of the thickness [16]. In addition considering the surface of ZnS films is rough, so introduce the layer of rough which contains 50% air and 50% ZnS films.When the

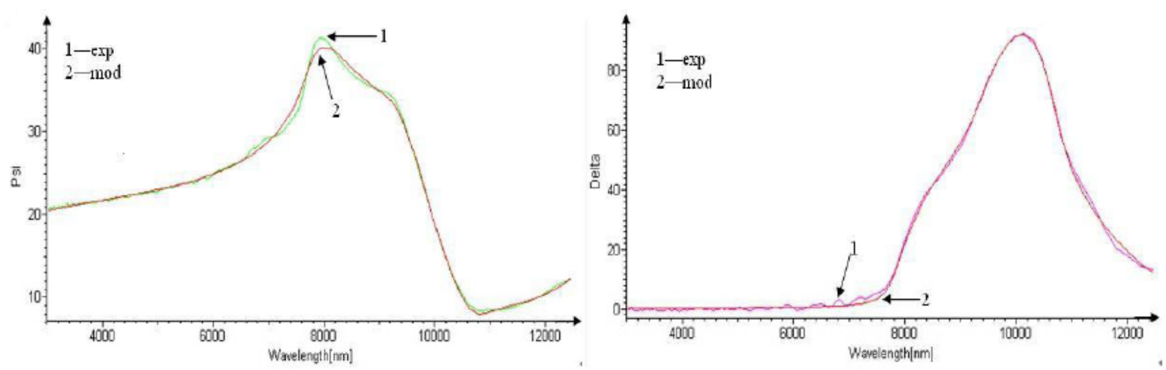

Figure 1: Measured and fitted results of Ψ and Δ of K9 glass.

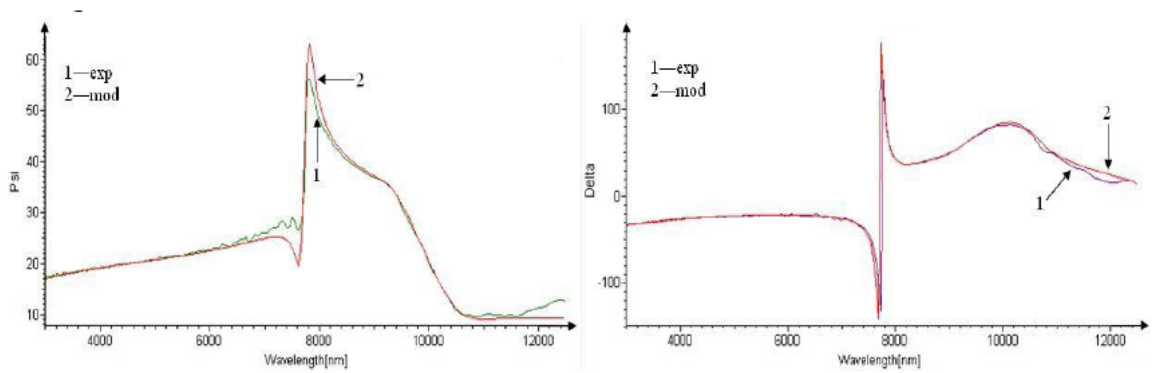

Figure 2: Measured and fitted results of Ψ and Δ of A by model I.

model II was used the initial thickness of EMA layer is set to 3nm, the initial thickness of ZnS layer is set to 115nm, the initial thickness of rough surface is set to 5nm. Figure **3** is the result of this simulation.

The results show that the thickness of EMA layer is 0, rough surface layer is 2.90nm, ZnS film thickness is 109.33nm, the evaluation function of MSE is 4.022.The Comparison between the results of 2 simulations can be seen the MSE of physical model I smaller 0.025 than the physical model II. The thickness of EMA is 0, the gap and the mixture and does not affect the optical properties in this band, so that the EMA does not exist. Rough surface layer is considered to be the cause of MSE smaller. Figure **4** shows the optical constants curve of ZnS films by inversion calculated.

From Figure **4** we can know that both the ZnS film refractive index and extinction coefficient decrease with the increase of wavelength. Refractive index from 2.2981 at 3000nm reduced to 2.222 at 12500nm. The extinction coefficient is 0.0025 at 3000nm, and tends to 0 at the long wavelength.

The same method was used to simulation the film B and film C. The initial thickness of ZnS layer of thin film B is set to 467nm. Figure **5** shows the measured and fitted results of Ψ and Δ of B by model I .MSE is 2.978.

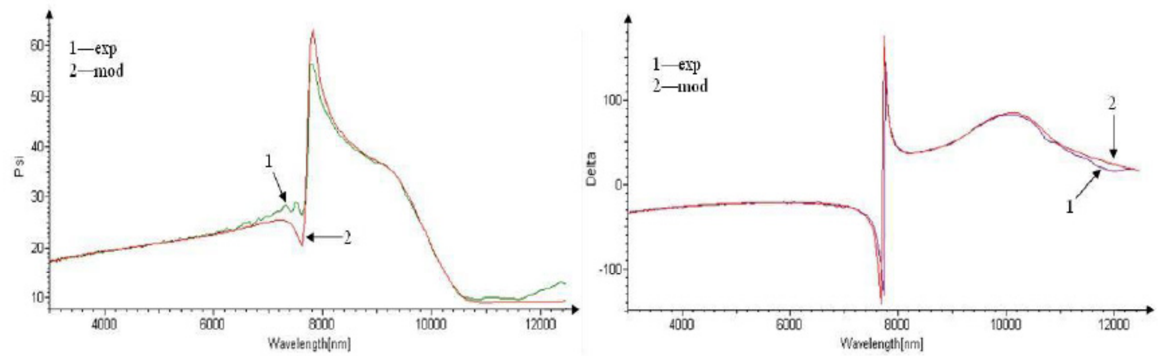

Figure 3: Measured and fitted results of Ψ and Δ of A by model II.

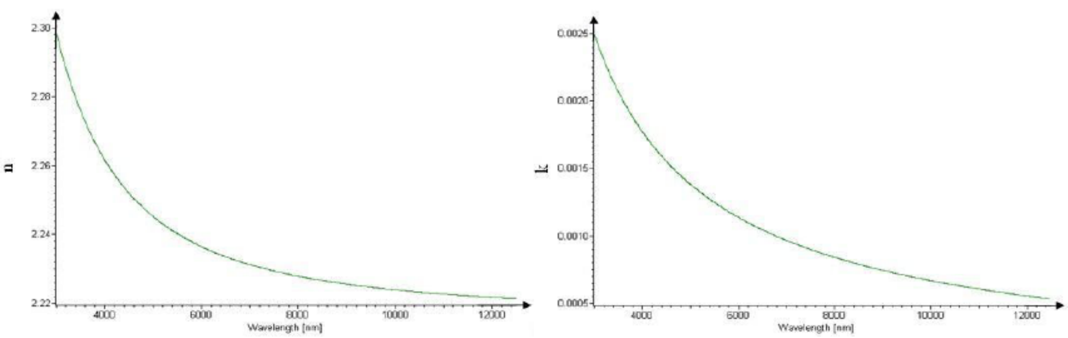

Figure 4: Calculated reflactive index and extinction coefficient of ZnS (A).

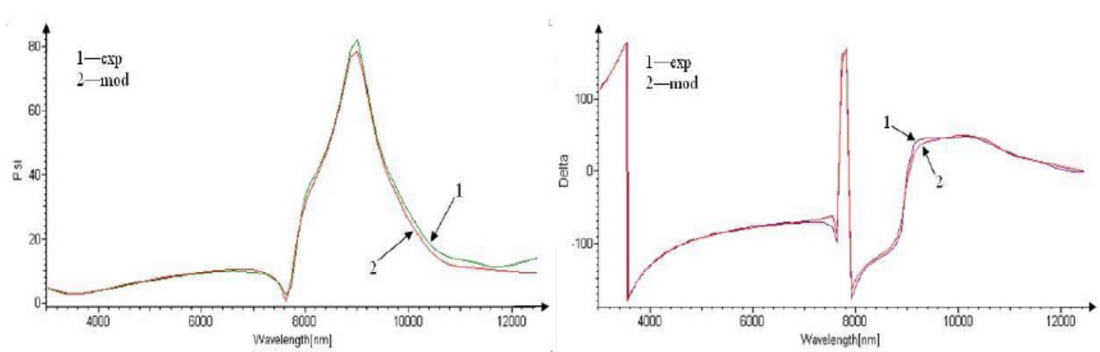

Figure 5: Measured and fitted results of Ψ and Δ of B by model I.

The thickness of ZnS layer of film B is 446.51nm. Figure **6** shows the measured and fitted results of Ψ and Δ of B by model II. The evaluation function MSE is 2.956, ZnS thickness is 444.07nm, the thickness of the EMA layer is 0,the thickness of rough surface layer is 3.56nm.

It can be found that the thinckness of ZnS is samller 22.93nm than design thickness. Figure **7** shows the optical constants curve of film B by inversion calculated.

Figure **8** is measured and fitted results of Ψ and Δ of C by model I.The initial thickness of ZnS layer is set to 652nm. MSE is 3.853. Fig.9 is measured and fitted results of Ψ and Δ of C by model II. The initial thickness of ZnS layer, EMA layer and rough surface layer are set to 652nm, 3nm and 5nm. So we got MSE which is 3.674,thickness of ZnS layer which is 639.75nm, thickness of EMA layer which is 0nm and thickness of rough surface layer is 3.14nm.

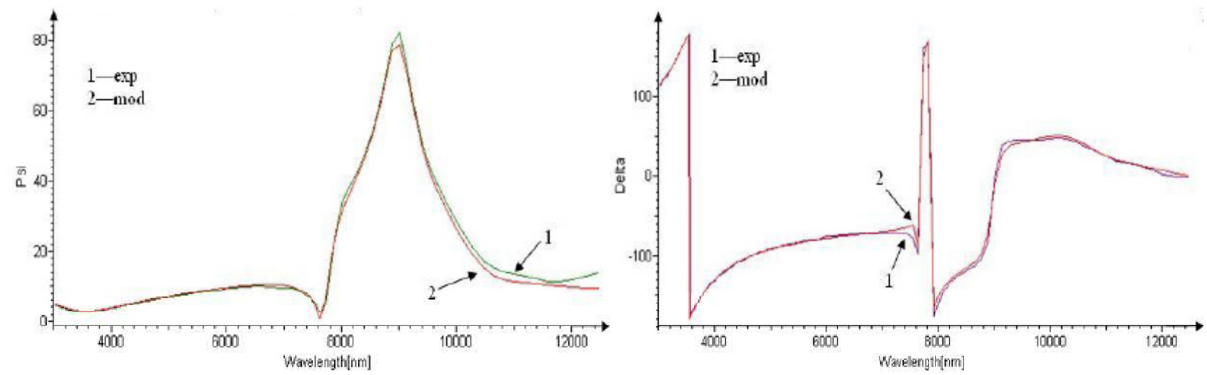

Figure 6: Measured and fitted results of Ψ and Δ of B by model II.

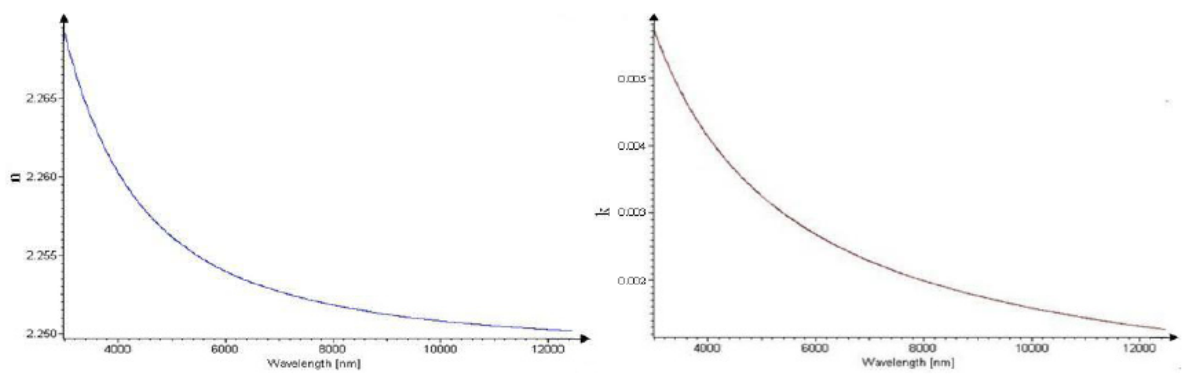

Figure 7: Calculated reflactive index and extinction coefficient of ZnS.

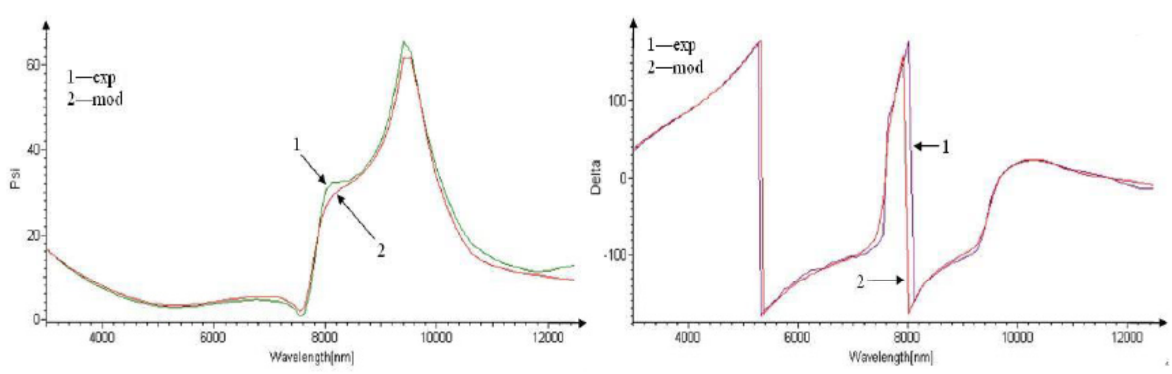

Figure 8: Measured and fitted results of Ψ and Δ of C by model I.

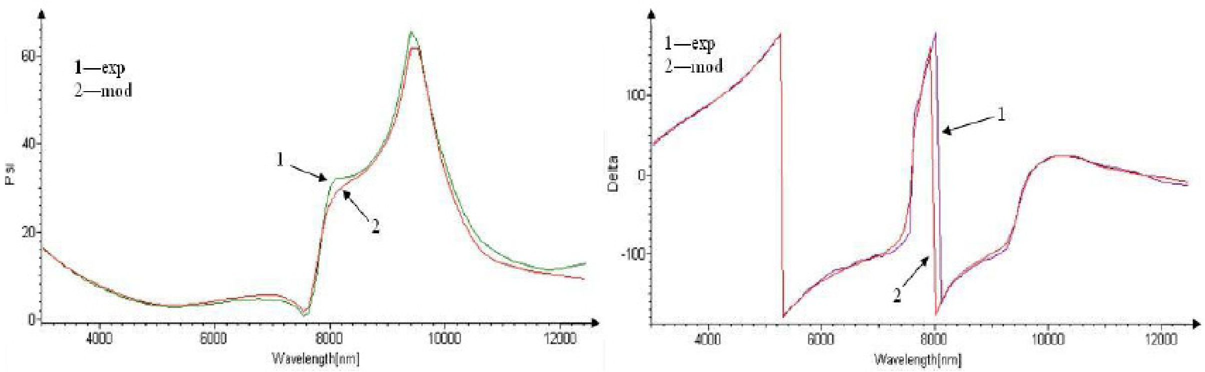

Figure 9: Measured and fitted results of Ψ and Δ of C by model II.

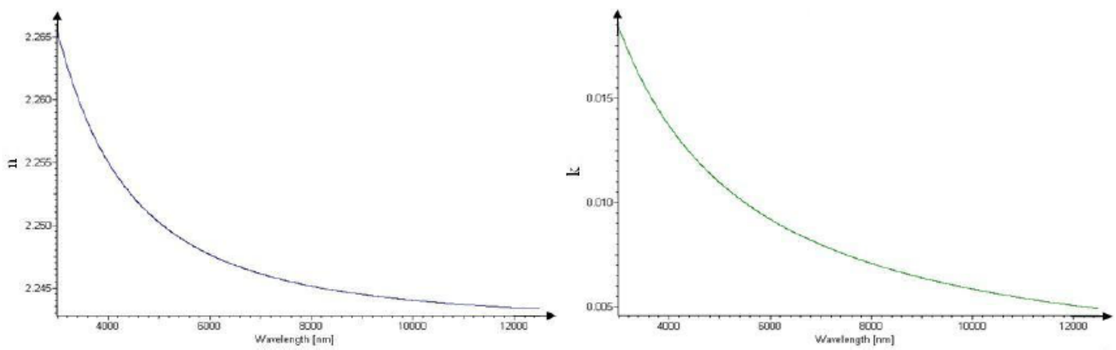

Figure 10: Calculated reflactive index and extinction coefficient of ZnS.

Figure **10** shows the optical constants curve of film B by inversion calculated. The Table **2** shows the parameters of all films. As can be seen from Table **2** the refractive index of ZnS films more than 2.22, the extinction coefficient is small at the wavelength of 10000nm. It can be found that the refractive index decreases with increasing wavelength and the extinction coefficient decreases with increasing wavelength in the wavelength range of 3000nm ~ 12500nm. ZnS films is normal dispersion in this range. ZnS films molecular vibration absorption peak is not within the wavelength range.

4. CONCLUSIONS

By electron beam evaporation on k9 substrate prepared ZnS films of different thicknesses. Using ellipsometry to study optical properties of them at 3000nm ~ 12500nm range. Two physical models designed to fit the film. The results show that: Brendel model can fit the measured data. The EMA layer do not affect the optical properties of ZnS films at this wavelength range. The refractive index decreases with increasing wavelength and the extinction coefficient decreases with increasing wavelength in the wavelength range of 3000nm ~ 12500nm.

ACKNOWLEDGMENT

This work was supported by the Funds for innovative research (No: CX2014SZ129), Southwest University for Nationalities.

REFERENCE

[1] Fang J, Holloway PH, Yu JE, *et al.* MOCVD Growth of Non-epitaxial and Epitaxial ZnS Thin Films [J] Applied Surface Science 1993; 70(71): 701-706 http://dx.doi.org/10.1016/0169-4332(93)90605-B

Table 2: The Parameters of ZnS Thin Films

	Thickness/nm	Wavelength/nm	Refractive Index (*n*)	Extinction Coefficient (*k*)	MSE
A	109.33	10000	2.2241	0.0008	4.022
B	444.07	10000	2.2526	0.0138	2.956
C	639.75	10000	2.2442	0.0062	3.674

[2] Salavati NM, Loghman EMR, Davar F. Controllable synthesis of wurtzite ZnS nanorods through simple hydrothermal method in the presence of thioglycolic acid [J]. Journal of Alloys and Compounds 2009; 475(1-2): 782-788 http://dx.doi.org/10.1016/j.jallcom.2008.08.041

[3] JIU Zhi Xian, ZHANG BinLin, YAO Ning. ZnS thin film deposited by pulsed lasers and its luminescent characteristic [J]. Laser Technology 2004; 28(6): 621-624

[4] YANG H, HUO CS, YU HZ. Preparation of CVD ZnS polycrystalline material for infrared optics [J]. Journal of Applied Optics 2008; 29 (1): 57-61.

[5] Yu TY, Zhu FR, Liu DQ, Zhang FS. Design and Deposition of Broadband IR Antireflection Coatings on ZnS Lenses [J]. Acta Optica Sinica 2005; 25 (2): 0253-2239

[6] VEDAM K. Spectroscopic ellipsometry: a historical overview [J]. Thin Solid Films 1998; 1(9): 313-314.

[7] Yang Kun, Wang Xiangzhao Research Progress of Ellipsometer [J]. Metrology & Measurement 2007; 44(3): 108-112.

[8] Yu TY, Qing Y. Investigation of the crystal and optical properties of ZnS thin films deposited at different temperature [J]. Acta Physica Sinoca 2013; 62(21): 111-115.

[9] Huang H, Cheng S, Huang B. Influence of Substrate Temperature on Properties of ZnS Films Prepared by Electron-beam Evaporation [J]. Journal of Optoelectronics Laser 2009; 20(3): 355-358

[10] XU Junqi , FENG Xiaoli. Optical Constants of Multi-layer Thin Films Investigated by Spectroscopic Ellipsometry [J]. Opto-Electronic Engineering 2008,37(3): 1004-1009

[11] ZHAO Shuang, WU Fuquan. The study on dispersion equation and thermal refractive index coefficient of quarts cryst al [J]. Acta Photonica Sinica 2006, 35(8): 1183-1186.

[12] SU Weitao, Li Bin, *et al*. The Fitting of Optical Constants of Infrared Coating Materials and Application in Broadband Antireflection Coatings [J]. Acta Photonica Sinica 2008; 37(3): 1004-1009.

[13] SHI Gang , LI YaJun, *et al*. Effects of in-situ annealing on the structure and photoluminescence of ZnS thin films prepared by RF sputtering [J]. Journal of Infrared and Millimeter Waves 2011; 30(6): 507-510.

[14] BRUGGEMAN DAG. The dielectric constants and conductivities of mixtures composed of isotropic substances [J]. Annals of Physics, 1935, 24: 639-791.

[15] HU R, CHENG L, YANG ZH J. Optical thin film refractive index and thickness testing technology and research [D]. Nanjing, Nanjing University of Science and Technology 2004:16-17.

[16] ZHAO Weibiao, REN Jie. Growth mechanism of atomic layer deposition of ZnS thin films: a denisty functional theroy study. Molecular Science [J]. 2012, 28(4): 280-284

Received on 15-03-2015 Accepted on 30-03-2015 Published on 01-04-2015

http://dx.doi.org/10.15379/2408-9834.2015.02.01.5