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ZnS THIN FILMS – AN OVERVIEW

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Abstract: ZnS thin film properties are overviewed in this research paper. These include absorbance, transmittance, optical band gap, refractive index and structure (on the basis of X-ray diffraction and scanning electron microscopy). It has been observed that these film properties are dependent on various parameters e.g. thickness of the film, deposition method, deposition rate, substrate material, substrate temperature, source temperature etc. In most of the studies ZnS thin films showed the best preferential orientation of crystallinity to (111) plane of cubic structure, however, hexagonal structure is also observed. ZnS thin films are found useful in various device applications.

Keywords: Absorption, deposition parameters, transmittance, optical band gap.

INTRODUCTION

Literature [Chopra 1969] shows that first of all Bunsen and Grove obtained metal films in 1852 by means of chemical deposition and flow discharge of sputtering, respectively. Faraday made metal films in 1857 by the thermal evaporation on explosion of a current carrying metal wire. The usefulness of the optical properties of metal films and the scientific curiosity about the behavior of two dimensional solids has been responsible for the immense interest in the study of science and technology of thin films. Earlier, the varied and irreproducible results often obtained on films led most workers to conclude that vapor deposited films represent a high state of disorder and that no two films are alike. This chaotic state of knowledge has actually been a blessing in disguise since it sustained and energized continued interest in thin film research.

The technology and understanding of films less than 1 micron thick have made tremendous advances in last 50 to 60 years, primarily because of industrial demand for reliable thin film microelectronics devices to fulfill the needs of the sputnik era. This progress has brought maturity and much scientific confidence in the use of thin films for basic and applied research. In addition to major contributions to a variety of new and future scientifically based technology, thin films studies have directly and indirectly advanced many new areas of research in solid state physics and chemistry which are based on phenomena uniquely characteristic of thickness, geometry and structure of films.

The thin films have mechanical, electrical, magnetic and optical properties which may differ from those of the bulk material and are used commonly in the form of a deposit on a suitable substrate for integrated circuits, resistors, capacitors, transistors and superconductors to name some examples [Thewlis 1979].

ZnS thin films have been found useful in various devices. The applications of ZnS thin films which cover a wide area of interest are:

- Antireflection coating for the solar cell [Bloss *et al*. 1988].
- Environmental friendly buffer layer as compared to CdS layer in CIS based thin film solar cell [Katsumi 1995].
- Wide band gap material for electroluminescent and opto-electronic devices [Tong *et al.* 1996].
- Photosynthetic coatings [Ndukwe 1996].
- Blue light emitting laser diodes [Hasse *et al.* 1991].
- As α - particle detector [Kashani 1996].

EFFECT OF DEPOSITION TECHNIQUES AND DEPOSITION PARAMETERS ON ZnS THIN FILMS

OPTICAL PROPERTIES

The results obtained by Nadeem and Ahmed [2000] and Ndukwe [1996] on the optical absorbance of ZnS thin films for wavelengths in the infrared (up to 1000nm) and visible spectrum showed that ZnS is practically non-absorbing in these regions. Similar behavior was observed by Hammer [1943] in the visible region. The ZnS films deposited on the glass substrate at room temperature have shown the enhanced absorption in the neighborhood of λ = 330nm [Huldt and Staflin 1959, Gonellian 1996] and 360nm [Nadeem and Ahmed 2000] and were expected to have a fine grained structure. The absorption peak shifts towards longer wavelength with increasing thickness. Ndukwe [1996] also observed that some ZnS films have high absorbance (~ 0.56) in the near infrared and low absorbance (~ 0.01 – 0.1) in the ultraviolet and visible region.

Multilayer filters using ZnS films cannot be used in the ultraviolet range because of strong absorption band at 365nm. For infrared filters the limitations does not appear to be one of absorption, the sphalerite is claimed to be transparent up to λ = 1200nm, but requires an excessive film thickness [Holland 1970].

Rood [1951] reported that rapidly evaporated ZnS films had a high optical absorption and claimed that the deposition rate for producing good quality films should be about $0.16 nms^{-1}$. Polster [1952] found that the rapidly deposited ZnS films ($1.6 nms^{-1}$) had considerable light absorption, but the films formed at about $0.5 nms^{-1}$ had negligible absorption. He claimed that large ZnS crystals are formed at high deposition rates and this increased the amount of light lost by scattering within the film. The result was opposite to the general experience because the grain size of most substances falls as the rate of deposition increases. Decomposition of evaporant may explain the greater light absorption of rapidly deposited ZnS thin films. At high rates of evaporation corresponding to high source temperature, free zinc atoms may be trapped in the condensed film. At low evaporation rates decomposition may be less and there is also ample opportunity for free zinc atoms to oxidize either at the condensing surface or in the region of the source. Zinc oxide has a refractive index

comparable to that of ZnS and if present in the deposit would not be easily detected.

ZnS films prepared by Nadeem and Ahmed [2000] using resistive heating technique had high transmittance (60 – 99%) in the visible and near infrared region. ZnS thin films coated on Ge [Yamanishi *et al.* 1985] using ionized cluster beam (ICB) method were found to have a transmittance of 96%. So they are useful as an antireflection coating for the optical transmission window. Yamaguchi *et al*. [1996] deposited the (Cd, Zn)S thin films on Corning 7059 glass substrate using chemical bath deposition (CBD) technique for photovoltaic devices. Thin films with zero concentration of Cd demonstrated more than 70% transmittance at wavelengths longer than 600nm. ZnS films grown by Ndukwe [1996] had high transmittance (~ 64 – 98%) in the visible and near infrared region. He also observed that some of the films had low transmittance (~ 30 – 37%) in near infrared region and high transmittance (~ 78 – 98%) in the visible and ultraviolet region. The transmittance of ZnS films grown on polyester foils [Lindroos *et al*. 1997] using successive ionic layer adsorption and reaction method was more than 60% above 400nm.

The optical band gap of ZnS (α) and ZnS (β) at 300K is 3.8eV and 3.6eV [Hu and White 1983]. The band gap of ZnS thin films found by various scientists using different techniques has been summarized in Table 1.

Table 1: Comparison of Optical Band Gap energy of ZnS Thin Films

Scientists	Methods	Optical Band gap (eV)
Lindroos *et al.* [1997]	SILAR	3.44
Nomura *et al.* [1995]	MOVPE	3.5
Yamaguchi *et al*. [1996]	CBD	3.6
Biswas *et al.* [1986]	CBD	3.68
Ndukwe [1996]	CBD	~3.7 – 3.8
Nadeem and Ahmed [2000]	R - H	3.51 – 3.84

The refractive index of bulk ZnS is 2.4 [Hu and White 1983]. Hass *et al*. [1982] have reported that ZnS films deposited at high rates and low pressures are found to exhibit bulk values of refractive index when evaporated at room temperature. Hammer [1943] observed that the refractive index for thinner ZnS films were lower than those for thicker films. The presence of voids, more marked in the thinnest films gave rise to the mean refractive index below that of bulk material. Nadeem and Ahmed [2000], Ndukwe [1996] and Polster [1952] found that refractive index vary with the wavelength of the incident light, where as for the films analyzed by Nesmelov *et al.* [1984] refractive index seems to be dependent on the growth rate. Lindroos *et al.* [1994] grew ZnS thin films using successive layer adsorption and reaction (SILAR) technique on soda lime glass, ITO - and Al_2O_3 - covered glass and Si substrate. The refractive indices varied from 2.07 to 2.19 on glass grown ZnS films and from 2.15 to 2.30 on ITO – covered glass. The film thickness was

measured through out the film area and no correlation between film thickness and refractive index was detected. The refractive indices of ZnS:Mn films [Lindroos *et al*. 1995a] provided by transmittance spectra varied from 2.04 to 2.22 in films grown on glass and from 2.13 to 2.32 in films grown on ITO – covered glass. Takeda *et al.* [1995] studied the nonlinear optical properties due to the thermal effects in a prism – coupled ZnS thin films. He observed a change in the refractive index of ZnS films which was confirmed to be due to the temperature rise resulting from the absorption of incident light.

Oikkonen *et al.* [1985] grew ZnS thin films from anhydrous zinc acetate and hydrogen sulfide by atomic layer epitaxy (ALE) at 290^{o}C to 330^{o}C. Thickness of the films ranged from 110 to 1350nm. The average crystallite size was 40-80nm depending upon the film thickness. These values were more than one half of those observed earlier for ZnS thin films grown by ALE from $ZnCl_2$ and H_2S and two or three times of those found in the films grown by electron beam evaporation.

STRUCTURAL PROPERTIES

The effect of growth temperature on the crystal structure of ZnS thin films grown using ALE was studied by Lahtinen *et al* [1985]. The crystal structure of polycrystalline ZnS thin films grown from Zn $(CH_3COO)_2$ at 300 – 375^{o}C was mainly cubic whereas ZnS layers grown from $ZnCl_2$ at 425 – 500^{o}C were predominantly hexagonal. The growth rate of crystalline ZnS films on (111) – oriented Si by molecular beam epitaxy (MBE) was studied by Yokoyama and Ohta [29] and found to be dependent on the substrate temperature.

Lindroos *et al.* [1994] found that the films grown on Al_2O_3 and Si (111) were inhomogeneous and of poor quality. The XRD analysis showed that ZnS films were polycrystalline and presumably cubic. Some preferential (111) orientation was detected. The films were found to begin to crystallize for a thickness of 30nm. The annealing (3 h, at 500^{o}C and N_2 atmosphere) increased the intensity of (111) line and decreased the half width correspondingly. The S/Zn ratio was approximately 0.8 and it increases with thickness. The ZnS films were found to contain uniformly distributed oxygen.

Manganese – doped ZnS thin films were deposited on glass, ITO – and Al_2O_3 – covered glass, quartz and CaF2 by Lindroos *et al.* [1995b] using SILAR method. The appearance of ZnS:Mn films (studied by scanning electron microscopy, SEM) was rougher to pure ZnS films. However, the annealing for 3 hours at 500^{o}C in nitrogen atmosphere flattened the films. No cracks were detected by SEM. According to XRD studies, ZnS:Mn films grown by SILAR at room temperature and normal pressure on an amorphous glass substrates were polycrystalline and presumably cubic. Some preferential [111] orientation was detected. The annealing for 3 hours at 500^{o}C in nitrogen atmosphere increased the intensity of the

peak. The S/Zn ratio was 0.85. After annealing for 3 hours at 500^{o}C in nitrogen atmosphere the S/Zn ratio slightly increased to 0.9 and the amount of oxygen was reduced.

The growth mechanism of ZnS thin films [Lindroos *et al* 1995b] on a glass substrate using SILAR method was found to be a combination of different growth modes. It includes dominating two – dimensional as well as dominating three dimensional modes during different stages of growth causing either roughening or smoothing of surface. On mica substrate the initial growth mode of ZnS thin films was two dimensional [Lindroos *et al.* 1996]. The growth rate of ZnS on poly (vinyl chloride) (PVC) and poly carbonate (PC) [Lindroos *et al.* 1996] was found to be higher than the corresponding growth rate on glass substrate reported previously [Lindroos *et al.* 1994]. That was found to be due to rougher surfaces of polymers as compared to glass. Those inhomogeneities favored initial film growth more than flat surface. According to X-ray diffraction analysis the ZnS films deposited on PVC substrate, preheated with KOH, were polycrystalline and possibly cubic, as were films on glass [Lindroos *et al.* 1994]. However, the crystallinity was not as good as that of the films grown on glass. Annealing at 70^{o}C in air for 46 hours decreased slightly the intensity of the peak at 2θ = 28.6 of ZnS films deposited on PVC. ZnS films grown on PC showed no peak in XRD, so they were considered amorphous. The films grown by chemical bath deposition, despite the normally higher deposition temperatures were found to be amorphous [Grozdanov 1995]. ZnS films grown on PVC & PC were slightly Zn rich. The SEM images of ZnS films on PVC & PC revealed that the films were continuous and rather smooth. Compared with ZnS thin films on glass [Lindroos *et al.* 1994], the films on polymers were rougher. Deposition was also attempted on polystyrene and polyterephthalate substrate [Lindroos *et al.* 1996] but resulting films were inhomogeneous.

Polyester foils were used as substrate for ZnS thin films [Lindroos *et al.* 1997] grown by SILAR method. The growth rate of ZnS thin films was found to be higher on polyester as compared to glass substrate. That may be because of the rougher surface of polyester and thus films grown on polyester were rougher and inhomogeneous. XRD measurements revealed that ZnS films on polyester substrate, pretreated with $SnCl_2$ solution were amorphous up to approximately 250nm thickness, above that thickness, the films were polycrystalline. A weak diffraction peak at 2θ = 29.0 presumably corresponding to (111) reflection of cubic ZnS was detected.

Epitaxial growth of ZnS on GaP (001) substrate using ZnS compound as a source material of Zn and S was achieved by Kanie *et al.* [1994]. They showed that ZnS epilayer lattice in the plane of interface is deformed to match substrate lattice when the layer is grown at substrate temperature of 240^{o}C. The results were studied by XRD. The critical thickness of ZnS layers was observed to vary with substrate temperature. The critical

thickness was observed to be thinner than 200nm for layers grown at T_{sub}= 240^{o}C and much thinner than 200nm for layers grown at T_{sub} = 160^{o}C.

Devyatykh *et al.* [1996] observed the effects of chemical vapor deposition (CVD) conditions on the average grain size of ZnS deposits by micro-structural analysis. Grain size was found to increase with deposition temperature and H_2S concentration. The degree of orientation of ZnS grains along the growth direction was found to be virtually independent of deposition conditions. High quality ZnS thin films were grown using metal organic chemical vapour deposition (MOCVD) by Kina *et al.* [1996]. XRD spectra of ZnS thin films prepared at various substrate temperatures showed that highest peak diffraction intensity at 2θ = 28.6. All ZnS thin films showed the best preferential orientation of crystallinity to (111) plane of cubic structure at 200^{o}C of substrate temperature. When substrate temperature was increased, the crystal structure transformed to hexagonal from cubic. Under 300^{o}C of substrate temperature the crystal structure was cubic, but at 370^{o}C the crystal structure was hexagonal. SEM showed that the grain size of films deposited at substrate temperature of 200^{o}C was larger as compared to the films prepared at other substrate temperatures.

The successful growth of high quality (111) oriented cubic ZnS thin layer grown on Si (111) substrate by metal organic vapour phase epitaxy (MOVPE) process using zinc dithiocarbamate complex as precursor was achieved by Nomura *et al* [1995]. The growth rate of ZnS films was observed to vary with source temperature and substrate temperature. A comprehensive study has been reported [Tong *et al* 1996] of chemical and metal organic molecular beam epitaxial (CBE / MOMBE) growth of ZnS on Si and GaAs (100) substrates for applications in advanced electroluminescent displays and for optoelectronic device integration. SEM studies showed that ZnS on GaAs had better surface morphologies than film grown on Si, despite smaller lattice mismatch between ZnS and Si (0.46%) as compared to GaAs (4.4%). However, XRD pattern showed that the ZnS thin films were of same quality.

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