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# SYNTHESIS AND PROPERTIES OF ZnS–EuS FILMS GROWN FROM VOLATILE COMPLEX COMPOUNDS

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## ABSTRACT

Deposition and characterization of films of ZnS, EuS and ZnS:Eu are described. The films have been prepared by chemical vapor deposition using new volatile complex compounds, dithiocarbamates of Zn and Eu, as precursors. Characterization includes X-ray diffraction, chemical analysis of the film composition, Raman spectroscopy, ellipsometry, and spectrophotometry. The spatial chemical homogeneity of the films has been determined using a recently developed method of differential dissolution and found to be uniform. Doping of ZnS by Eu with dopant concentration up to 0.3 at.% has been achieved. Effects of Eu doping on structural and optical properties of the films are presented. *Copyright © 1997 Elsevier Science Ltd*

KEYWORDS: A. thin films, A. chalcogenides, B. vapor deposition, D. crystal structure, D. optial properties

## INTRODUCTION

Preparation of $A^{II}B^{VI}$ films doped by rare-earth (RE) elements attracts significant attention due to their potential application in microelectronics. Incorporation of RE into the $A^{II}B^{VI}$ lattice and the mechanisms of isovalent and heterovalent replacement have been discussed in the literature since 1960. It has been shown for single crystalline materials synthesized at

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temperatures above 1000°C that the solubility of RE in ZnS is relatively small and lies in the interval of $10^{-4}$–$10^{-2}$ at.% [1,2]. Therefore, preparing homogeneous solid solutions for these systems presents significant difficulties, and doping, as a rule, results in dopant segregation and clusterization enhanced by extended structural defects or crystallite boundaries.

Fabrication of an electroluminescent device on the basis of ZnS:Eu films by magnetron sputtering has been described in the literature [3]. The concentration of Eu in the target was in the range from 0.05 to 0.80 at.%. No information on the Eu concentration and distribution in the film is available. Molecular beam epitaxy of ZnS:Eu films has been performed (4). Forms Eu incorporation into the ZnS lattice for single crystals at concentrations less than 1 at.% has been studied in (1,5). The Eu doping was performed by adding into the starting powders either metallic Eu or oxide $Eu_2O_3$, with Li often used as co-dopant. It has been established that a small fraction of europium is incorporated into the ZnS lattice as isolate substitutional $Eu^{2+}$ centers and europium mostly forms precipitates of various compositions (5,6).

Employment of volatile complex compounds (VC) and development of a chemical vapor deposition (CVD) process for these compounds create new opportunities for materials fabrication. For example, using as molecular precursors of Zn and Eu dithicarbamate compounds containing "ready made" sulfide fragments of type M-S may facilitate the sulfide formation of and promote the doping by Eu, as we have already shown for the ZnS:Mn system (7). The CVD procedure allows synthesis and doping to be performed in a one-step process due to heterogeneous interaction between the sulfides formed during VC decomposition. Doping in such a way, as well as the lower temperatures of the process, may promote the RE solubility in the ZnS matrix.

A new volatile compound of Eu has been employed in this work. The properties of the compound essential for applications as a precursor in a CVD process, such as temperature and pressure conditions, have been assessed. The paper presents results on the low-pressure CVD of ZnS–EuS films, the structure, composition, dopant distribution, and optical properties of the films.

## EXPERIMENTAL

We have used complex compounds of the class of dithiocarbamate, $ZnPhen(S_2CNEt_2)_2$ (hereafter referred to as compound 1) and $EuPhen(S_2CNEt_2)_3$ (compound 2) to prepare ZnS–EuS films. These VC are sufficiently stable under ambient conditions, nonhydroscopic, and low-toxic. The choice of compounds 1 and 2 for films synthesis is based on the fact that these compounds easily sublimate at relatively low temperatures. The temperature conditions for compound sublimation have been determined using differential thermal analysis/thermal gravimetry (DTA/TG).

Quasi-equilibrium thermogravimetry (Derivatograph Q–1500–D, MOM Company, Hungary) has been used in the regime of constant mass loss rate (0.3 mg/min) to determine the temperature conditions and character of evaporation. At a given vapor pressure about 6.8 Torr, compounds 1 and 2 sublimate without decomposition at temperatures 253°C and 223°C, respectively. The optimal temperature range 220–260°C for co-evaporation of the VC of Zn and Eu has been established as a result of this study.

The films have been prepared by thermal decomposition of compound 1 or 2, or both, in vacuum on hot substrates in a chamber evacuated by an oil-diffusion pump with a liquid-nitrogen trap to the pressure $6 \times 10^{-7}$ Torr. The substrate temperature was stabilized in the range 450–530°C by a PID temperature controller RIF-101. The temperature was monitored using a chromel-alumel thermocouple. Halogen lamps were used as heaters.

A special evaporator has been designed for simultaneous evaporation of Zn and Eu compounds from an open surface. It is possible to control the ratio of the components and to provide necessary molecular flow densities during the process to sustain high and stable growth rates of the films. At temperatures used in the evaporator (200–260°C), the total pressure in the chamber varies in the range $10^{-5}$–$10^{-4}$ Torr. This allows work in the regime of a molecular vapor stream.

Glass, fused quartz, and silicon wafers [(111) orientation] have been used as substrates (substrate areas from 0.5 to 54 $cm^2$). All substrates were cleaned carefully by a special procedure right before the loading. This procedure is described as follows: The glass and fused quartz are washed in a detergent solution, rinsed in distillate water, and immersed in $H_2SO_4$:$K_2Cr_2O_7$:$H_2O$ (184:6:100 by mass) for 24 h. Then the substrates are thoroughly washed in distilled water and dried in a flow of boiling propan-2-ol. The silicon substrates are treated by a polished technique (8). The thickness of the residual oxide layer on silicon, according to ellipsometry, is 9–13 Å. During one deposition experiment, different substrates can be used by placing them in the isothermal zone.

Film characterization included X-ray diffractometry (XRD), Raman spectroscopy, chemical phase analysis, ellipsometry, and spectrophotometry. The XRD of the samples was carried out using DRON-UM 1 (R = 192 mm, Cu K$\alpha$ radiation, Ni filter, and scintillation detector with amplitude discrimination) in the range of 2 theta angles from 5 to 70° at room temperature. Raman spectroscopy was performed using a spectrometer Triplemate (SPEX) with multichannel registration (detector O–SMA, SI) in geometry of backscattering. 488 nm $Ar^+$ laser line was used for excitation.

For chemical composition analysis of the films, a new method of differential dissolution has been used (9). The procedure includes dissolution of the film in a reactor of the apparatus described in ref. 9. The films are dissolved in the flow of a $HNO_3$ solvent with concentrations increasing from 0.01 M to 0.1 M. The amounts of Zn, S, and Eu passed into the solution are determined every 15 sec using atomic emission spectroscopy (AES) with an inductively connected Ar plasma reactor (uncertainty about 3–5%). Routinely about 150–200 points obtained have been used to reconstruct the kinetic curves of dissolution for these elements and their stoichiogram (molar ratio Zn/S, Eu/S, and Eu/Zn). This method allows the chemical composition to be determined as a function of film depth for each phase in the film.

The refractive indices and film thicknesses have been determined using ellipsometry (ellipsometer LEF–3M, $\lambda = 632$ nm) and spectroscopy in the region of visible light (spectrophotometer SF–18). First, the film thickness was estimated from the reflection spectrum. Then the inverse problem of ellipsometry was solved using the one-, two-, and three-layer films model (10).

## RESULTS AND DISCUSSION

As has been shown previously, ZnS films from ZnPhen($S_2CNEt_2$)$_2$ can be prepared at T = 400–450°C (7). In the present work, films of cubic ZnS were deposited on different substrates at T = 450–530°C. The crystal structure improves when the substrate temperature increases. This follows from the increase of reflex intensities and reduction of the half-width of reflexes on diffractograms. When only compound 2 is used as precursor, EuS films are formed at substrate temperatures 490–530°C. Simultaneous evaporation of Zn and Eu compounds leads to deposition of ZnS:Eu films for substrate temperatures 490–530°C. The lowest substrate temperature is limited by the temperature of decomposition of both Zn and

TABLE 1
Characteristics of ZnS–EuS Films

| Sample | $T_{dep}$ (°C) | Eu concentration $C_{Eu}/(C_{Zn}+C_{Eu})$ in evaporator (at.%) | Eu concentration $C_{Eu}/(C_{Zn}+C_{Eu})$ in film (at.%) | Film thickness (nm) |
|---|---|---|---|---|
| 1 | 490 | 0 | 0 | 535 |
| 2 | 520 | 0 | 0 | 700 |
| 3 | 490 | 0.09 | 0.003 | 577 |
| 4 | 490 | 0.21 | 0.12 | 577 |
| 5 | 490 | 0.40 | 0.2 | 530 |
| 6 | 530 | 0.66 | 0.42 | 235 |
| 7 | 510 | 0.74 | 0.6 | 540 |
| 8 | 500 | 0.83 | 1.1 | 1365 |
| 9 | 510 | 0.9 | 0.41 | 416 |
| 10 | 530 | 1.5 | 1.3 | 480 |
| 11 | 515 | 1.7 | 1.4 | 220 |
| 12 | 510 | 3.9 | 1.9 | 810 |
| 13 | 530 | 6.9 | 4.8 | 280 |
| 14 | 530 | 100 | 100 | 220 |
| 15 | 490 | 100 | 100 | 560 |

Eu VC resulting in the sulfides formation. The highest value of substrate temperature is restricted by interactions of the sulfides with the substrate materials and by contamination of the films by products of decomposition of VC. Interaction effect has been established by detection contamination of the films by Si from the substrates using chemical analysis. The interaction of sulfides with glass substrates begins at T = 520°C. For quartz and silicon, such interaction has not been observed up to 530°C. However, starting at 530°C, black inclusions of carbon have been observed in the films. Deposition conditions (temperatures of evaporator and substrates, molar ratio of Zn and Eu compounds, thermal treatments) have been varied in the range 490–530°C. Some parameters of the process and composition of the films are presented in Table 1.

It can be seen from Table 1 that, as a rule, the increase of Eu VC fraction in the evaporator leads to the increase of Eu concentration in the film. The difference observed between these two concentrations may be explained by an incomplete sublimation for both volatile compounds, as well as by insufficient accuracy of Eu determination, when Eu in the analyzed solution is in the range $10^{-7}$–$10^{-6}$ mol/ml. The deposition rate depends on a number of parameters, including, first of all, the temperatures of the substrate and evaporator and the vapor pressure. At optimal conditions, the deposition rate of 20 nm/min can be achieved. The film thickness is uniform over the substrate area $6 \times 9$ cm$^2$. The thickness of the films on silicon substrates is systematically higher than on glass substrates. As a result of this study, conditions of reproducible deposition of ZnS:Eu films with a controllable doping level have been found.

The structures of the films have been studied by XRD and Raman spectroscopy. The X-ray diffractograms of ZnS (curve a), EuS (curve f), and ZnS:Eu (curves b, c, d, and e) films on quartz or glass substrate are shown in Figure 1. According to XRD phase analysis, reflexes for polycrystalline films correspond to cubic (β) and/or hexagonal (α) modifications of ZnS, and cubic modification of EuS. The exact identifications of the ZnS phases is complicated by

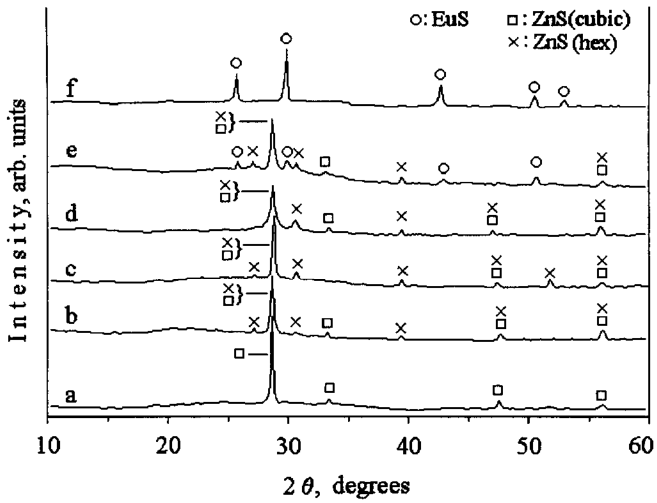

FIG. 1

X-ray diffraction spectra of ZnS, EuS, and ZnS:Eu films synthesized from compound 1 (curve a, sample 2), compound 2 (curve f, sample 14), and compounds 1 and 2 (curves b–e, samples 7, 8, 11, and 13, respectively).

a considerable overlap of the diffraction reflexes belonging to α-ZnS and β-ZnS. Identification of the hexagonal modification follows from the observed closest stereographic projections of reflexes (102) and (101) with angular positions 39.64° and 30.56°, respectively. The presence of the cubic modification has been checked using the (200) reflexes at 33.14°. In this case, the closest directions overlap with the reflexes of the hexagonal modification. The EuS films do not have a preferable orientation, all reflexes on the diffractograms are well-defined, and the ratio of the intensities is close to values presented in Table 1.

Effects of Eu doping starts to appear at very low concentrations of Eu in ZnS. The cubic ZnS reflexes become broader and the reflexes of hexagonal ZnS appear. At Eu concentrations more than 2 at.% (curve e), the reflections observed on the diffractogram can be attributed to the ZnS and EuS phases; the structural nonhomogeneity of the films increases. It appears that the incorporation of Eu results in disorder of the cubic ZnS structure and may cause defect formation in the layers.

Raman spectra of films on glass or silicon are shown in Figure 2. It can be seen that all main features for crystalline ZnS and EuS are present: first order modes at 275 $cm^{-1}$ (TO phonon), at 350 $cm^{-1}$ (LO phonon) for ZnS (curve a), and at 240 $cm^{-1}$ for EuS (curve e), as well as lines of the second order for ZnS, and the double frequency at 480 $cm^{-1}$ for EuS (11–13). In the spectra of ZnS:Eu films (curves b, c and d), the intensities of lines related to ZnS phase decrease rapidly, and at Eu concentration in the films of about 5 at.% (curve d), together with weak modes of ZnS, the EuS modes have been observed. One explanation for such variation is that the ZnS lattice is significantly affected by the presence of Eu atoms. The defects formation violates the selection rules for the perfect ZnS lattice, and the shape and intensity of observed Raman scattering reflects the density of phonon states of the crystal structure with defects, rather than the process of scattering in the center of Brillouin zone of a perfect lattice.

Kinetic curves of differential dissolution of each element Zn, Eu, and S, for pure ZnS (a), EuS (b), and ZnS:Eu (c) samples are presented in Figure 3. Also shown are the stoichiograms

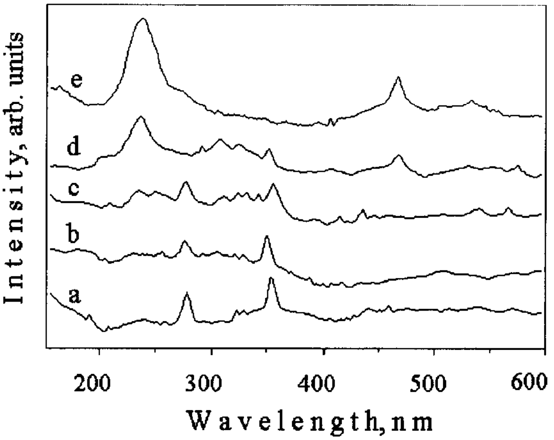

FIG. 2

Raman spectra of ZnS, EuS, and ZnS:Eu films, synthesized from compound 1 (curve a, sample 2), compound 2 (curve e, sample 14), and compounds 1 and 2 (curves b, c, and d, samples 7, 8, and 13, respectively).

Zn/Eu in the (c) case (the similarity of Zn and S or Eu and S kinetic curves is obvious). From these (a, b) pictures, we conclude that pure ZnS and EuS are highly stoichiometric, independent of the film thickness. In the (c) case, the figure shows dissolution of a tricomponent sulfide with Eu/Zn ratio 0.006 ± 0.002. The sulfide is considered to be a solid solution ZnS:Eu, since the XRD patterns of the film show no indications of second phases.

Studies of the samples by monochromatic nulling ellipsometry and visible light spectrophotometry have provided information on the uniformity of optical properties across the films and revealed additional details of the film structure. The refractive index value $n$ for ZnS films evaluated based on a three-layer model has been shown to be the same for all three layers (curve a on Fig. 4). This indicates that the films are uniform. The ZnS films are essentially nonabsorbing and their refractive index values are similar to, or slightly less than, the known refractive index value for crystals, $n = 2.35$. This may be related to the presence of voids in the films. For EuS films (curve b in Fig. 4), the values of the refractive index decrease in the range $n = 2.4$–$2.0$ at $\lambda = 632$ nm. For ZnS:Eu films, a similar three–layer analysis gives a different value of refractive index for each of the layers, with a systematic decrease as a function of distance from the substrate (curve c in Fig. 4). As the refractive index values for ZnS and EuS at 632 nm are similar, the changes of $n$ with the film thickness may be caused by a nonuniform distribution of structural defects across the film. Further, we have observed an increase of the absorption coefficient. Therefore it can be concluded that Eu doping strongly affects the optical properties of the films.

## CONCLUSIONS

It has been shown that volatile complex compounds $ZnPhen(S_2CNEt_2)_2$ and $EuPhen(S_2CNEt_2)_3$ can be successfully used as precursors for CVD deposition of ZnS and EuS films in the temperature range 490–530°C. ZnS films doped by Eu have been obtained using simultaneous evaporation of Zn and Eu VC. The properties of ZnS films are very sensitive to doping, as has been shown in this study, by a variety of methods. Conditions for the formation of

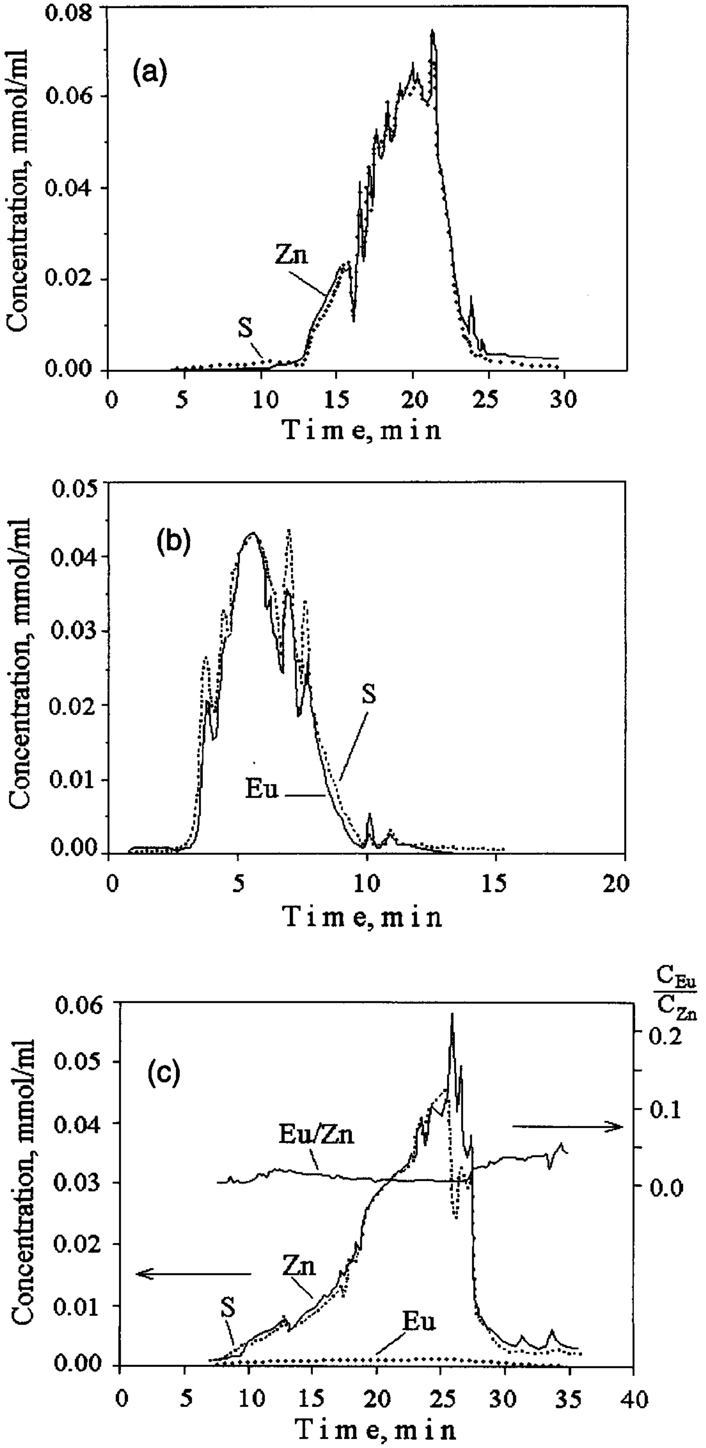

FIG. 3

Kinetic curves of solution for ZnS film (sample 2) (a), for EuS film (sample 14) (b), and kinetic curves of solution and stoichiogram for ZnS:Eu film (sample 7) (c).

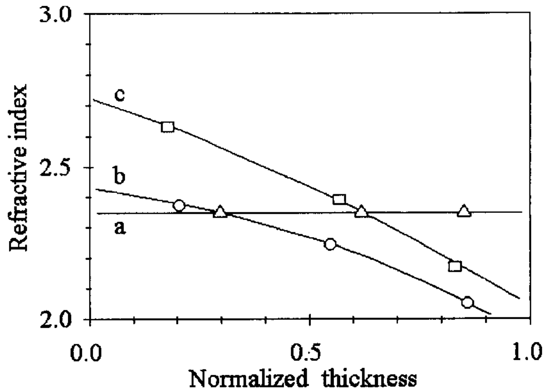

FIG. 4

Variation of the refractive index evaluated based on a three-layer model for ZnS (curve a), EuS (curve b), and ZnS:Eu (curve c) films.

homogeneous solid solution of ZnS:Eu with concentration up to 0.3 at.% have been found. This concentration is observed to be uniform for the whole thickness of the film and is higher than that known for single crystals, about 0.02 at.% (2). Two factors may be responsible for this increase of Eu solubility: (i) the higher disorder (relative to that of a single crystal) of the films prepared at moderate temperatures and (ii) stable transport conditions for the constituent elements provided by the CVD process. At these deposition conditions, the solubility of Eu in ZnS films reaches 0.3 at.%, which is much higher than the value for ZnS single crystals.

The structure of ZnS films shows significant disordering even at small amounts of EuS in the alloy. The stress relieving in disordered structures depends on the distance from the film/substrate interface and leads to the observed dependence of the refractive index on the film thickness.

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