

MOCVD growth of non-epitaxial and epitaxial ZnS thin films

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Thin films of ZnS have been deposited by MOCVD on both BaTa₂O₆/ITO/glass and Si substrates. Diethylzinc (DEZn) and H₂S are used for deposition on substrates heated to the 250–400°C temperature range. The microstructure and properties of ZnS films were studied by X-ray diffractometry (XRD), ultraviolet/visible spectrophotometry (UVS) and scanning electron microscopy (SEM). Films prepared on BaTa₂O₆/ITO/glass were polycrystalline with mixed cubic and hexagonal phases. The hexagonal structure dominated for film thicknesses < 700 nm, while the cubic structure dominated for film thicknesses > 700 nm. The bandgap energy of ZnS films decreased and the surface morphology became worse with the increasing film thickness. Upon annealing 200–600 nm films at temperatures of 450–550°C in H₂S for 1 h, the ZnS films developed an even stronger cubic (111) or hexagonal (002) preferred orientation. Polycrystalline ZnS films grown on Si(100) and (111) substrates tended to be cubic. Nucleation and growth rates on Si(100) substrates were initially faster than on Si(111) substrates. At 400°C, epitaxial growth of ZnS on Si(100) was achieved.

1. Introduction

Alternating current thin film electroluminescent (ACTFEL) devices used for light-emitting displays are based on metal–insulator–semiconductor–insulator–metal, MISIM, structures [1]. The MISIM structure is of great interest because each layer is transparent, and therefore light emitted from one layer can be transmitted through other layers with little energy loss. The two major problems in developing full color displays are achieving high brightness in the blue region of the spectrum and reduction of the drive voltage. There is strong evidence [2] that the luminescence efficiency may be increased and the driving voltage decreased through the growth of single crystal rather than polycrystal ZnS. In principle, single crystal ZnS can be achieved by using single crystal silicon as the substrate for fabrica-

tion of ACTFEL devices. Single crystal Si is an attractive substrate for the epitaxial growth of ZnS since these two materials are both cubic with a 0.4% room temperature lattice mismatch. Epitaxial ZnS thin films on high quality single crystal Si substrates could serve as a model material to investigate the luminescent properties of doped ZnS, eliminating the influence of extended defects.

Metal-organic chemical vapor deposition (MOCVD) has been successfully used to grow ZnS thin films [3,4]. MOCVD offers several advantages over halide CVD or physical deposition methods, such as low growth temperature, ease of controlling the impurity doping concentration and the potential for the growth of large-area thin films. In this study, diethylzinc (DEZn) and hydrogen sulfide (H₂S) in H₂ were used as precursors to grow ZnS. In this paper, the crystalline

structure and properties of ZnS thin films grown on both BaTa₂O₆/ITO/glass substrates and single crystal Si wafers are reported.

2. Experimental procedure

A modified Spire Model SPI-MOCVD 450 system was used for the growth of ZnS thin films. The system is a 4 gas-4 bubbler unit equipped with a fast switching run-vent manifold. The reactor is a horizontal design with an RF-heated

tilted susceptor. A turbopumped, load-lock system allows substrate insertion without exposing the reactor to air. The parameters used to grow ZnS thin films were as follows:

- growth temperature: 250–400°C
- reactor pressure: 50–80 Torr
- VI/II ratio: 50–200
- film thickness: 100 nm–2 μm.

The BaTa₂O₆/ITO/glass substrates used for the MOCVD growth of ZnS thin films were provided by Planar System, Inc. The 0.3 μm polycrystalline BaTa₂O₆ insulating layer and the 0.2

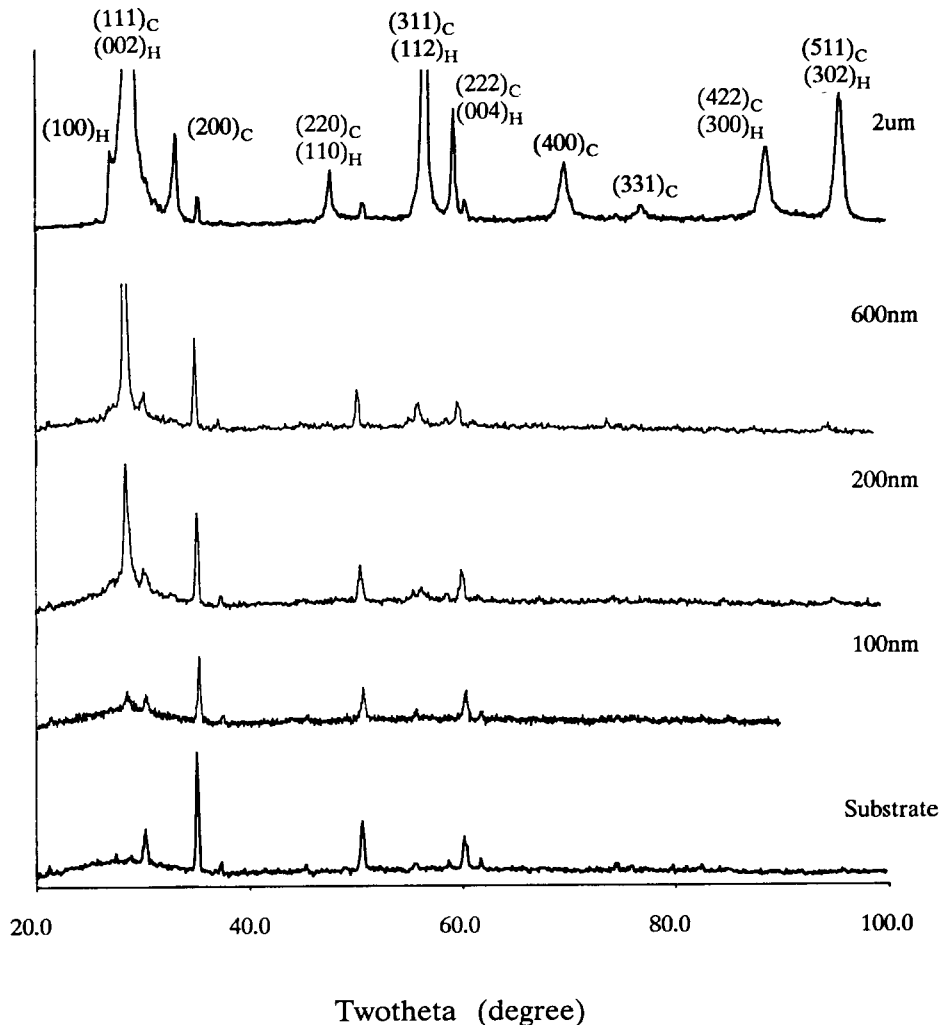


Fig. 1. XRD patterns of ZnS films grown on BaTa₂O₆/ITO/glass substrates by MOCVD; subscripts of H = hexagonal (2H), C = cubic (3C).

μm ITO electrode layer were sputter deposited. Before growth of ZnS, the substrate was cleaned sequentially in warm trichloroethane (TCE), acetone, methanol, rinsed thoroughly in deionized water, and blown dry with N_2 gas. After being degreased and cleaned using the above procedure, the Si substrate was etched in buffered oxide etch (BOE), rinsed in deionized water, and blown dry in N_2 gas, etched in dilute HF solution, then again blown dry in N_2 gas. All substrates were immediately transferred into the reactor after cleaning and the Si substrates were baked at 950°C in the presence of H_2 flow prior to commencing growth. In this study, an APD 3720 diffractometer was used for X-ray diffraction (XRD), a Perkin-Elmer Lamda 9 UV/VIS/NIR spectrophotometer (UVS) was used for bandgap analysis, and a JEOL JSM-6400 scanning electron microscope (SEM) was used for studying the topography.

3. Results and discussion

3.1. ZnS on $\text{BaTa}_2\text{O}_6/\text{ITO}/\text{glass}$

Samples grown to different thicknesses with $T_{\text{sub}} = 350^\circ\text{C}$ and $\text{VI/II} = 100$ were studied with X-ray diffraction (XRD), and the diffraction spectra are shown in fig. 1. These spectra show that the ZnS thin films on $\text{BaTa}_2\text{O}_6/\text{ITO}/\text{glass}$ were polycrystalline. Under a thickness of 200 nm, the XRD peaks were mainly from the $\text{BaTa}_2\text{O}_6/\text{ITO}/\text{glass}$ substrate. When the film thickness was in the range of 200–700 nm, the peak near 28.5° (2θ) was very strong indicating a preferred orientation. This peak can be attributed to either the 3C cubic (111) or the 2H hexagonal (002) planes [5,6]. Besides this strongest ZnS peak, peaks at 2θ 's of $\sim 56^\circ$ and 95° are also evident in fig. 1. However, the XRD patterns from ZnS did not change with thicknesses over the range of 200–700 nm. As the thickness of the film increased to $2\ \mu\text{m}$, additional diffraction peaks were detected at 2θ 's of 33° , 47° , 59° , 69° , 74° and 88° . The diffraction peaks often can be assigned to either the cubic or the hexagonal crystal structure. The exceptions to dual assign-

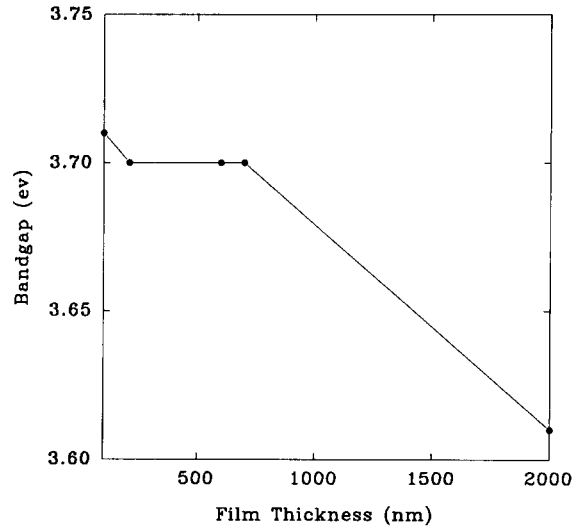


Fig. 2. Bandgap energies of ZnS films grown on $\text{BaTa}_2\text{O}_6/\text{ITO}/\text{glass}$ by MOCVD.

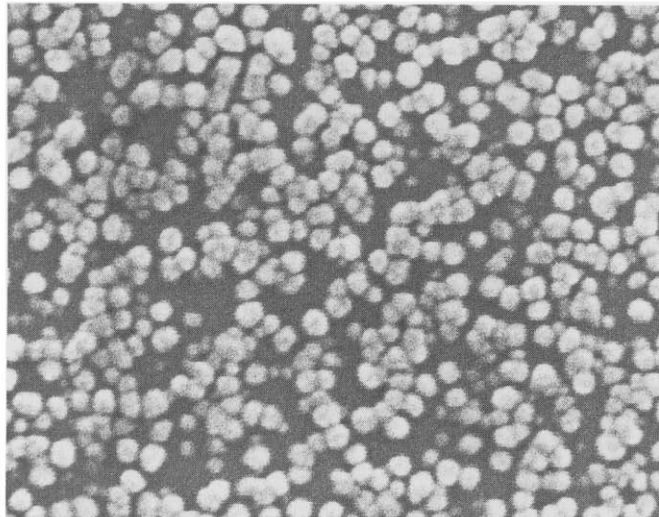
ment are the three peaks at about 27° , 33° and 69° . The peak at 27° corresponds to ZnS hexagonal (100) reflection [6] and cubic ZnS does not have a peak at this position. The other two peaks at $\sim 33^\circ$ and 69° correspond to ZnS cubic (200) and (400) reflections [5] and hexagonal ZnS does not have peaks at these positions. The XRD pattern from a $2\ \mu\text{m}$ ZnS film matches the cubic structure, although a small fraction of a hexagonal phase still exists as evident from the relatively small (100) hexagonal peak at $\sim 27^\circ$.

The photoabsorption edge of these ZnS films was determined to be near 350 nm and it shifted to longer wavelength as the film thickness increased. This indicates that the bandgap energy of the ZnS films decreased as the film thickness increased, as shown in fig. 2. The bandgap energy of ZnS has been reported to be 3.54 eV [7] for the cubic phase and 3.80 eV [8] for the hexagonal phase. For ZnS exhibiting mixed cubic and hexagonal phases, the bandgap energy has been reported to decrease as the fraction of the cubic phase increased [9,10]. The data in fig. 2 demonstrate that a larger portion of the cubic phase was present in thicker film which resulted in a lower bandgap. As the film thickness increased to $2\ \mu\text{m}$, the bandgap energy decreased from 3.70 to

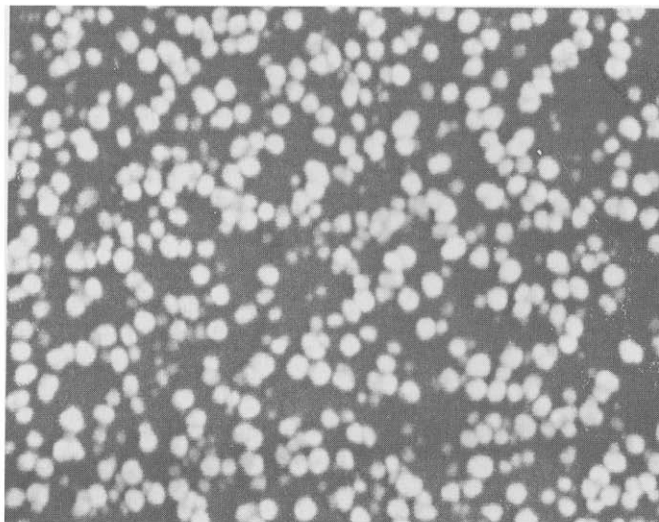
3.61 eV and XRD data show that the cubic crystal form dominates. Thus, a transition in crystal structure from initially hexagonal at thicknesses < 700 nm to cubic at $2 \mu\text{m}$ thickness is indicated by the XRD and photoabsorption data. It was also observed by SEM that the surface became rougher as the thickness of ZnS films increased.

To test for recrystallization and grain growth, 200–600 nm ZnS samples were annealed at 450 or 550°C in H_2S for 1 h. After annealing, the

XRD peaks shifted to slightly larger 2θ angles. This shift is probably due to relief of stress within the ZnS films. The intensity of the ZnS peak at $\sim 28.5^\circ$ increased while that of the other ZnS peaks remained the same. This suggests that the ZnS films develop an even stronger cubic (111) or hexagonal (002) preferred orientation after annealing. The bandgap energies of annealed ZnS films were slightly lower by 0.01 eV. The surface morphology of the thin films became smoother after annealing.



ZnS/
Si(100)



ZnS/
Si(111)

Fig. 3. SEM photomicrographs of polycrystalline nucleation of ZnS on Si(100) or (111) wafers.

3.2. ZnS on Si

Photomicrographs of ZnS grown for short times on Si(100) and (111) substrates are shown in fig. 3. Discrete ZnS particles were seen, and they were more numerous and larger on Si(100) as compared to Si(111) after 1 min of growth at 400°C. This demonstrates that nucleation is three-dimensional and ZnS had a higher nucleation and growth rate on Si(100) as compared to Si(111). Cross section SEM shows that after 1 h growth, ZnS films on Si(100) substrates can reach thicknesses of 3 μm giving a growth rate of 0.83 nm/s. ZnS films grown on Si(111) at the same time reached thicknesses of only 300 nm, corresponding to a lower growth rate of 0.17 nm/s. A

continuous ZnS film on both Si substrates was observed after 5.5 min of growth, but the surface became rougher at longer growth times.

The ZnS films were cubic and had a strong preferred orientation with their (400) and (111) planes being parallel to the Si(100) and (111) planes, respectively. For growth at a lower temperature (400°C), polycrystalline films were generally observed. However, after increasing the Si wafer baking time at 950°C in H_2 and decreasing the reactor pressure from 80 to 50 Torr, an epitaxial layer of ZnS was grown on Si(100) at 400°C, as shown in fig. 4. This procedure presumably removed the surface oxide which eliminated three-dimensional growth. This same procedure did not result in epitaxy on Si(111), consistent

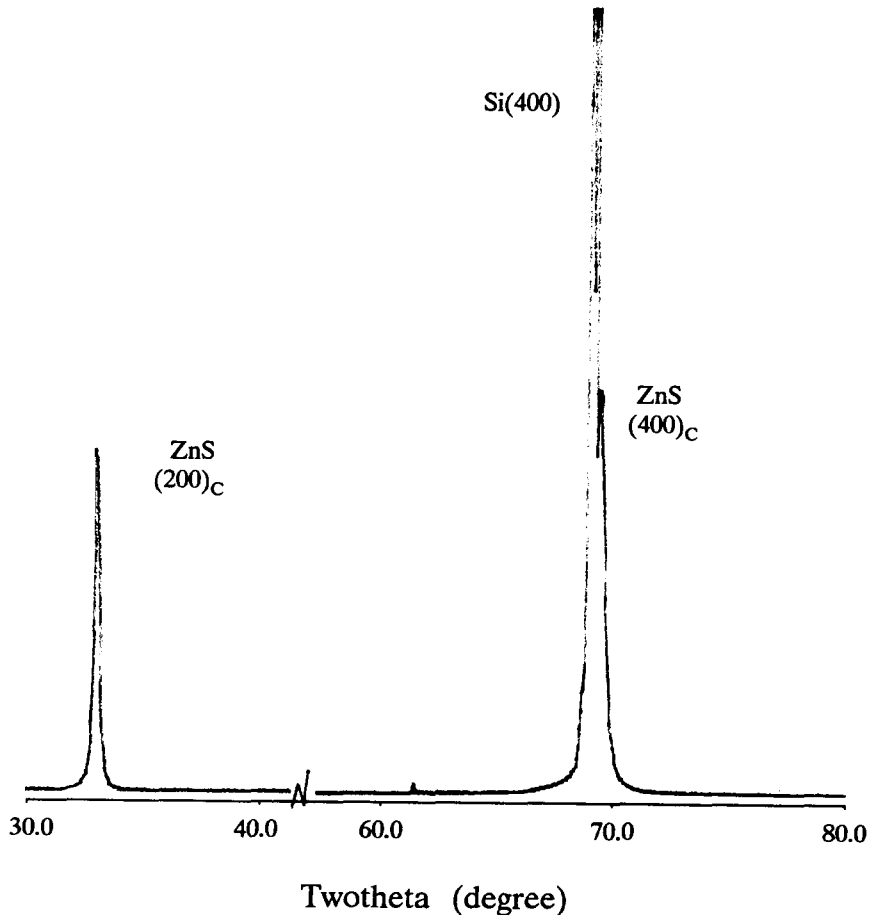


Fig. 4. X-ray diffraction pattern of epitaxial ZnS layer grown on Si(100) by MOCVD.

with the suggestion [7] that Si(100) is best suited for epitaxial growth.

4. Summary

Films of ZnS grown on both BaTa₂O₆/ITO/glass and Si substrates by MOCVD have been studied. The films grown on BaTa₂O₆/ITO/glass were polycrystalline. Under 700 nm, their crystal structure was hexagonal, as shown by ultraviolet spectroscopy, and textured with the (002) hexagonal planes parallel to the substrates as shown by XRD. Films 2 μm thick were mainly cubic, with a surface roughness which increased with thickness. ZnS films on Si were initially polycrystalline with faster nucleation and growth rates on Si(100) as compared to (111). Epitaxial ZnS was grown on Si(100) substrates at 400°C after rigorous surface cleaning procedures.

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