# RF Magnetron Sputtered Zinc Sulfide Thin Films and Their Applications to Thin Film Transistors

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## Abstract

In this work, zinc sulfide (ZnS) thin films are deposited by RF magnetron sputtering. By introducing hydrogen sulfide (H<sub>2</sub>S) as working gas, ZnS thin film with good stoichiometry (Zn:S = 1.2) is obtained. The effect of substrate temperature and H<sub>2</sub>S gas flow are also investigated. Bottom gate thin film transistors (TFT) using sputtered ZnS as active channel are fabricated and characterized for the first time. The ZnS TFTs exhibit a field effect mobility of  $1.4 \text{ cm}^2/\text{Vs}$  and on/off ratio of  $5.2 \times 10^4$ .

# Introduction

Zinc sulfide (ZnS), a II-VI compound semiconductor, has been investigated for many years [1] and has been applied in many areas [2]–[5], such as laser [2], light emitting diode [3], solar cell [4] and data storage devices [5]. However, for display device, ZnS is rarely applied into thin film transistor (TFT) as active channel. Several methods [6]-[10], such as molecular beam epitaxy [6], metal-organic chemical vapor deposition [7], metal-organic vapor phase epitaxy [8], chemical bath deposition [9] and sputtering [10], has been used for produce ZnS film. Among these methods [6]-[10], only sputtering is the low temperature, cost-effective and large-area technique.

In this work, ZnS thin film is obtained by RF magnetron sputtering. The impact of substrate temperature ( $T_s$ ) and H<sub>2</sub>S/Ar flow rate ratio (FRR) on ZnS film crystallization are investigated. Bottom gate TFTs using sputtered ZnS as active channel are fabricated and characterized for the first time. The ZnS TFTs exhibit a field effect mobility ( $\mu_{FE}$ ) of 1.4 cm<sup>2</sup>/Vs and on/off ratio of 5.2 × 10<sup>4</sup>.

# Film formation and characterization

RF magnetron sputtering method was utilized to fabricate ZnS thin films on bare glass substrate. The films were deposited at room temperature, 200°C, 300°C and 400°C  $T_s$ . The vacuum chamber was evacuated up to 5×10<sup>-6</sup> Torr base pressure using a turbo molecular pump. A commercially available high purity (99.99%) ZnS target was used for the sputtering. The working gas were Ar and H<sub>2</sub>S. The working pressure and power were fixed at 5mTorr and 80W respectively. The crystal structures and grain size of ZnS were analyzed by X-ray diffraction (XRD). The composition of sputtered ZnS film were analyzed by X-ray photoelectron spectroscopy (XPS).

Shown in Fig. 1 is XRD patterns of ZnS thin films grown at different  $T_s$ . Only Ar was employed as working gas. It can be observed that the deposited ZnS films are textured along (311). When the  $T_s$  increase to 300°C and 400°C, (111) peak is observed. Chemical compositions of each film at different  $T_s$  are summarized in Table I. For each film, O content are comparable to S content for when only using Ar as working gas.



Fig. 1. XRD patterns of ZnS thin films grown at different  $T_s$ .



	RT	200°C	300°C	400°C
Zn	53.11%	55.28%	55.25%	55.35%
S	16.07%	22.82%	23.88%	23.06%
0	29.54%	21.69%	19.94%	21.03%
С	1.26%	0.21%	0.93%	0.56%



Fig. 2. XRD patterns of ZnS thin films grown at different  $H_2S/Ar$  FRR.

Table II. Chemical composition of ZnS films for different  $H_2S/Ar$  FRR, measured by using XPS.

	FRR=0	FRR=0.25	FRR=0.375	FRR=0.5
Zn	53.11%	52.91%	50.45%	51.99%
S	16.07%	42.23%	41.09%	41.04%
0	29.54%	2.73%	3.91%	2.27%
С	1.26%	2.50%	4.54%	1.18%

To suppress O content, H<sub>2</sub>S was introduced when sputtering ZnS film. As shown in Fig. 2 is XRD patterns of ZnS thin films grown at different H<sub>2</sub>S/Ar FRR. Clearly, when introducing H<sub>2</sub>S, sputtered ZnS films are extremely textured along (111) plane even at room temperature. It can be also observed that best crystallization of ZnS film is obtained at  $H_2S/Ar$  FRR = 0.25. The gain size of ZnS at FRR = 0.25 are estimated as 20nm from Debye-Scherer formula [11]. Chemical compositions of each film at different FRR are summarized in Table II. Compared to ZnS film obtained at FRR = 0, ZnS films obtained at FRR = 0.25, 0.375 and 0.5 show nearly at 1:1 stoichiometric ratio of Zn:S. H<sub>2</sub>S can greatly suppress O content when sputtering ZnS film.

## Device fabrication and characterization

Fig. 3 shows a cross-section schematic of the proposed bottom gate TFT with ZnS thin film as active channel. Silicon wafer covered with 500nm thick thermal oxide was used as a substrate. First, a 50nm thick indium-tin-oxide (ITO) film was patterned into the gate electrode. 100nm thick SiO<sub>2</sub> А was consecutively deposited as the gate insulator using conventional plasma-enhanced by chemical vapor deposition (LPCVD) method at 300°C. A 50nm thick ZnS was deposited on the gate insulator by RF magnetron sputtering at room temperature. The H<sub>2</sub>S/Ar FRR was fixed at 0.25. After patterning this ZnS active layer by a liftoff process with an acetone solution, a 50nm thick Ti/Au was sputtered as source/drain electrodes by a liftoff process. Next, a 100nm thick SiN<sub>x</sub> was deposited by LPCVD at 300°C as passivation layer. Finally, gate, source and drain electrodes are opened by dry etching process.

For characterization, the HP 4156A semiconductor parameter is used to test the device electrical performance. TFTs used in this work have 50  $\mu$ m in width and 25  $\mu$ m in length. The  $\mu_{FE}$  is extracted from the following expressions [12],

$$\mu_{FE} = \frac{LdG_m}{W\varepsilon_{ox}V_{ds}}$$
$$G_m = Max(\frac{dI_{ds}}{dV_{qs}})$$

where d,  $\varepsilon_{ox}$ ,  $I_{ds}$  and  $G_m$  are physical gate dielectric thickness, gate dielectric permittivity, drain current and maximum of

transconductance at  $V_{ds} = -0.1$  V. The  $I_{on}/I_{off}$  ratio equals to maximum current over minimum current within the measured range.

Shown in Fig. 4 is transfer curves and output curves of ZnS TFT. It can be observed that such ZnS TFTs exhibits depletion mode characteristics [13]. The extracted  $\mu_{FE}$  and  $I_{on}/I_{off}$  ratio are 1.4 cm<sup>2</sup>/Vs and 5.2 × 10<sup>4</sup> respectively.



Fig. 3. A cross-section schematic of the proposed bottom gate TFT with ZnS as active channel.



Fig. 4. (a) Transfer curves and (b) output curves of ZnS TFTs.

#### Conclusion

In this work, ZnS thin films are deposited by RF magnetron sputtering. The effect of  $T_s$  and H<sub>2</sub>S/Ar FRR are investigated. Bottom gate TFT using sputtered ZnS as active channel are fabricated and characterized for the first time. The ZnS TFTs exhibit a  $\mu_{FE}$  of 1.4 cm<sup>2</sup>/Vs and  $I_{on}/I_{off}$  ratio of 5.2 × 10<sup>4</sup>.

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