

# Epitaxial Growth of Non-polar ZnS on Sapphire Substrate by Mist Chemical Vapor Deposition

Koshi Okita<sup>1</sup>, Taiki Goto<sup>1</sup>, Yudai Tanaka<sup>1</sup>, Masato Takenouchi<sup>1</sup>,  
Zenji Yatabe<sup>2</sup> and Yusui Nakamura<sup>1,3</sup>

<sup>1</sup>Kumamoto Univ., Graduate School of Science and Technology

<sup>2</sup>Kumamoto Univ., Priority Organization for Innovation and Excellence

2-39-1 Kurokami Chuo-ku, Kumamoto 860-8555, Japan

Phone: +81-96-342-3842 Email:yusui@cs.kumamoto-u.ac.jp

<sup>3</sup>Kumamoto Phoenix

3-11-38, Higashi-machi, Higashi-ku, Kumamoto 862-0901, Japan

## Abstract

Non-polar ZnS layers were epitaxially grown on m-plane sapphire substrates by mist chemical vapor deposition at atmospheric pressure. For this growth, ZnO buffer layers were inserted between the ZnS and the sapphire because ZnO has an intermediate lattice constant.

## 1. Introduction

Zinc sulfide (ZnS) is abundant material and expected as promising material of light emitting diodes (LEDs), which can be operated in ultraviolet range at room temperature because ZnS has wide band gap of 3.54eV for zinc blende structure and 3.8eV for wurtzite structure and large exciton binding energy of 37meV.

Recently, to grow epitaxial ZnS layers, various methods and substrates have been studied. As the growth method, molecular beam epitaxy and metal organic chemical vapor deposition are used. As the substrates, GaAs and GaP are used, since lattice mismatch between ZnS with zinc blende structure and the two substrates are small [1,2].

In contrast, in this study, we used mist chemical vapor deposition (mist-CVD) [3]. This is because mist-CVD is a simple and low-cost growth method, which is operated at atmospheric pressure. Also in this study, we used low-cost sapphire substrates [4], but only polar ZnS epitaxial layer is reported to be formed on the sapphire substrates. In case of quantum well structures in LEDs, this polar plane has a demerit in light emission efficiency, because electrons and holes are separated by electric field due to piezoelectric and spontaneous polarizations [5]. Therefore, we tried to form non-polar ZnS epitaxial layers such as m-plane ZnS on m-plane sapphire substrates.

However, epitaxial m-plane ZnS layers were not formed directly on the sapphire substrates. On the other hand, we have already reported that m-plane ZnO single crystal were formed uniformly over 2-inch m-plane sapphire substrates by mist-CVD [6,7]. Based on this result, we used ZnO buffer layers because m-plane ZnO with wurtzite structure

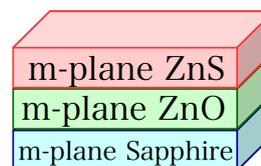


Fig. 1. Schematic diagram of the layer structure in this study. The ZnS layer was formed on the sapphire substrate with ZnO buffer layer by mist-CVD.

has an intermediate lattice constant between m-plane ZnS with wurtzite structure and m-plane sapphire substrate. So, in this study, we have tried the layer structure of m-plane ZnS/m-plane ZnO/m-plane sapphire substrate as shown Fig. 1.

## 2. Experimental Procedure

In all experiments in this study, both ZnO and ZnS layers were formed by mist-CVD on the m-plane sapphire substrates, where carrier gas of the mist was N<sub>2</sub>. Growth duration was 30 min for both ZnO and ZnS. As the first layer, ZnO buffer layers were formed at 600 °C with carrier gas flow rate of 8 L/min, using aqueous source solution of ZnCl<sub>2</sub> with a concentration of 0.1 mol/L.

As the second layer, ZnS layers were formed, using an mixed aqueous source solution with of 50 mL of ZnCl<sub>2</sub> with 0.1 mol/L with and 10 mL of CH<sub>4</sub>N<sub>2</sub>S with 0.5 mol/L, where atomic concentration ratio of Zn and S was 1:1. In order to investigate the best growth condition, ZnS layers were grown at various growth temperatures from 400 to 600 °C with a carrier gas flow rate of 8 L/min. After the best growth temperature was found, ZnS layers were grown at various flow rates of 1 to 8 L/min at constant growth temperature of 425 °C.

The grown ZnS layers were characterized using X-ray diffraction (XRD) measurements of  $\theta$ -2 $\theta$  and  $\phi$  scanning modes to identify vertical and lateral orientations, respectively. Scanning electron microscopy (SEM) is used to observe surface morphology of the ZnS layer. (SEM images are not shown here.)

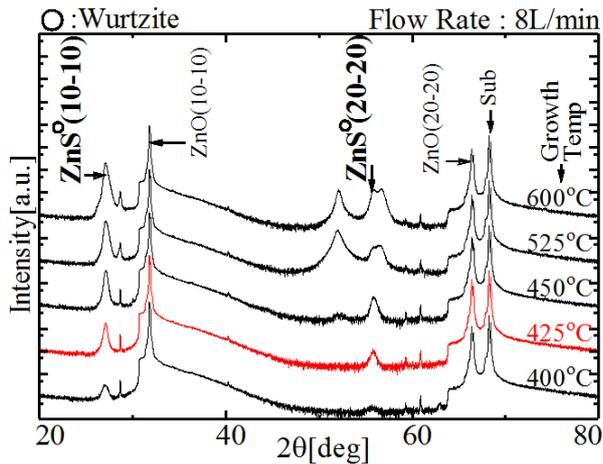


Fig. 2. The XRD results with  $\theta$ - $2\theta$  scanning mode of ZnS on ZnO at various growth temperatures of 400 to 600 °C with 8 L/min.

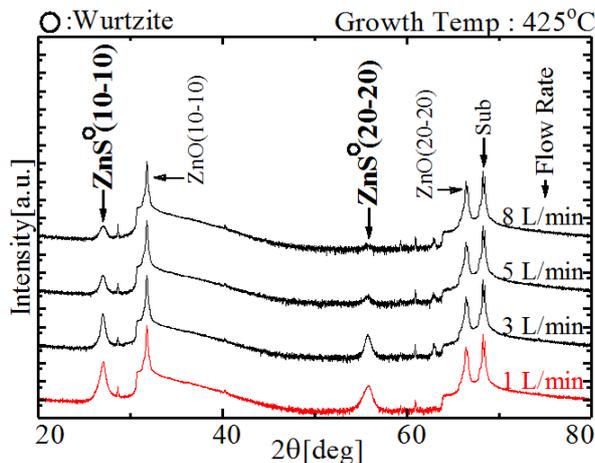


Fig. 3. The XRD results with  $\theta$ - $2\theta$  scanning mode of ZnS on ZnO at 425 °C with various flow rates of 1 to 8 L/min.

### 3. Results and Discussion

Figure 2 shows XRD results of ZnS layers on ZnO buffers grown at various growth temperature of 400 to 600 °C with a constant flow rate of 8 L/min. In case of the growth temperature of 450 to 600 °C, ZnS diffraction peaks other than m-plane of (10-10) and (20-20) appeared, and intensity of ZnS diffraction peaks decreased as growth temperature decreased, which is probably due to decrease of the ZnS thickness. Therefore, the best growth temperature is found to be 425 °C, because only the m-plane ZnS of (10-10) and (20-20) were observed at 425 °C and 400 °C, and the intensity at 425 °C is bigger than that at 400 °C.

Figure 3 shows XRD results of ZnS layers on ZnO buffers grown with various flow rates of 1 to 8 L/min at a constant growth temperature of 425 °C. The m-plane ZnS diffraction peaks of (10-10) and (20-20) were observed in the samples with all flow rates, and intensity of ZnS diffraction peaks increased as the flow rate decreased. It is probably due to increase of the ZnS thickness. Therefore, the best flow rate

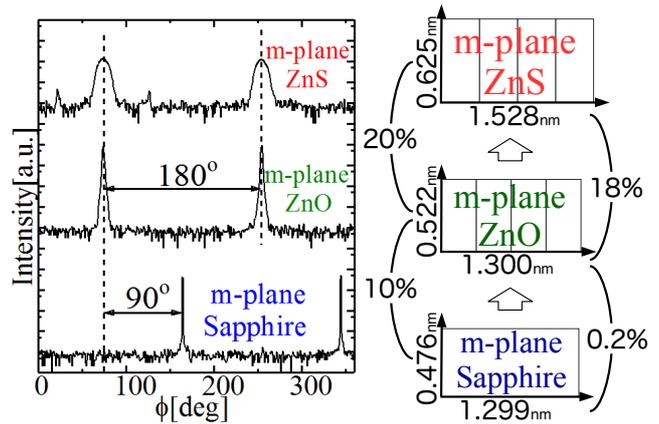


Fig. 4. The XRD results with  $\phi$  scanning mode of the best ZnS on ZnO grown at 425 °C with the flow rate of 1 L/min.

is found to be 1 L/min, because diffraction peak intensity of the m-plane ZnS of (10-10) and (20-20) is biggest at the flow rate of 1 L/min.

To investigate in-plane orientation of the m-plane ZnS layer grown at the best condition at 425 °C with the flow rate of 1 L/min, XRD measurement with  $\phi$  scanning mode was performed. Figure 4 shows XRD results with  $\phi$  scanning mode of the best ZnS layer on ZnO buffer. In Fig. 4, two ZnS peaks spaced by 180° were observed similarly to ZnO peaks, which indicates that the m-plane ZnS layer was epitaxially grown on m-plane ZnO. In addition, these ZnS and ZnO layers were also epitaxially grown the sapphire substrate, where four small ZnS and ZnO lattices are on one large sapphire lattice as domain matching epitaxy. However the full width at half maximum of the ZnS peaks were wide, thus the crystallinity of ZnS was not very good. This result is probably due to large lattice mismatch between ZnS and ZnO as the illustration in Fig. 4. This result indicates that the crystallinity of ZnS layers should be more improved.

### 4. Conclusions

The m-plane ZnS epitaxial layers were grown on m-plane ZnO buffer layer formed on m-plane sapphire substrate by mist-CVD.

### Acknowledgements

We would like to express sincere thanks to Professor Ichikawa of Kumamoto University for their support of XRD measurement. This work was partly supported by JSPS KAKENHI Grant Number 15K05991.

### References

- [1] S.Nakamura, et.al, *Jpn.J.Appl.Phys.* **40** (2001) 6993.
- [2] K.Ichino, et.al, *Phys.Status Solidi C9* (2012) 1744.
- [3] J.G.Lu, et.al, *J.Cryst.Growth* 299 (2007) 1.
- [4] Y.-Z.Yoo, et.al, *J.Cryst.Growth* 237-239 (2009) 1594.
- [5] K.Koike, et.al, *Jpn.J.Appl.Phys.* **43** (2004) 1372.
- [6] H.Tanoue, et.al, *Appl.Phys.Express* **8** (2015) 125502.
- [7] H.Tanoue, et.al, *Phys.Status Solidi A* (2017) 1-7.