

Photo-Assisted MOVPE Growth of ZnMgS on (100) Si

Angel Rodriguez, Jeremy Shattuck, Xiaoguang Zhang, Peng Li, David Parent¹, John Ayers and Faquir Jain

University of Connecticut, Department of Electrical and Computer Science Engineering,
Storrs, CT 06269-2157, U.S.A.

¹San Jose State University, Department of Electrical Engineering,
San Jose, CA, U.S.A.

ABSTRACT

This paper presents for the first time photo-assisted Metalorganic vapor phase epitaxial (MOVPE) growth of ZnMgS on Si (100) substrates. The growth was done using dimethylzinc (DMZn), bismethylcyclo-pentadienyl-magnesium ((MeCP)₂Mg), and diethylsulfide (DES) as zinc, magnesium, and sulfur precursors. Epitaxial characterization by X-ray Photoelectron Spectroscopy (XPS), and low - angle X-ray Diffraction (XRD) results are presented. Mg solid phase incorporation is estimated to vary from 0 to 60 percent. The epitaxial nature of the ZnMgS layers has been verified using the low-angle X-ray diffraction eliminating any interference from the Si substrate. It can be shown with this technique that the change in the ZnMgS peak position changes from 27.35 degrees to 26.5 degrees with an increase in Mg incorporation, compared with a Si control sample peak at 27.4 degrees. XRD results obtained have been verified with XPS data. Chlorine doping of the ZnMgS layer was also studied. Concentrations up to $3 \times 10^{15} \text{ cm}^{-3}$ were observed in the ZnMgS layer. Results of the n (ZnMgS:Cl) - p (Si) diodes fabricated are also presented.

INTRODUCTION

The availability of flat panel televisions, laptop computers and many other products during the past decade has been made possible by the development of flat panel displays (FPDs). FPD technologies include electroluminescent displays (ELDs), light emitting diode arrays, plasma display panels (PDPs), liquid crystal displays (LCDs), and flat cathode ray tubes (CRTs). Their applications generally fall into two broad categories: (i) High Information Content (HIC) or high pixel count displays having 50,000 to 10^6 pixels per frame (both monochrome and color), and (ii) lower pixel count displays as used in calculators, clocks, and other consumer products.

II-VI materials such as ZnCdSe have been used and proposed in the implementation of laser diodes emitting in the red through blue spectrum [1-3]. An application for this material system includes flat panel displays, which has the advantage of enabling the realization of transistor drivers in the silicon substrate.

Another application includes higher efficiency solar cells, which are also currently under investigation [4,5]. Advantages of using wide-band gap material in solar cells include lower losses in the window region, and lower ohmic losses. In addition ZnS and Si exhibit closely matched electron affinities.

EXPERIMENT & RESULTS

A vertical, stainless steel EMCORE reactor with a rotating, resistively-heated molybdenum susceptor was used for growth. All growth runs were carried out at 250 Torr, with a susceptor rotation of 350 rpm, and 14.25 slm of palladium-diffused hydrogen as the carrier gas. The photo irradiation was achieved using an Oriel Hg arc lamp operated at 150W electrical power. The ultraviolet irradiation was brought into the reaction chamber using a mirror and a quartz window, resulting in normal incidence on the sample. Neutral density filters were used to adjust the irradiation intensity. All irradiation intensities reported were measured using an intensity meter (manufactured by HTG) outside of the reaction chamber.

Prior to growth, the native oxide on the substrates was removed by an *in-situ* dry etch [6,7,8], using a dilute flow of hydrogen sulfide (H_2S) at a temperature of 900°C for one hour prior to the epitaxial growth. Then temperature was decreased to 360°C for the ZnMgS layer growth. The reactant mole fractions for the ZnMgS layers were 10^{-4} (DMZn), 4×10^{-4} (DES) and $1.8 - 7.4 \times 10^{-6}$ ((MeCP) $_2$ Mg).

The samples were characterized using a low-angle X-ray diffraction technique with a Bruker analytical X-ray System D5005 X-ray Diffractometer. The results of which are seen in Figure 1. With this technique the X-ray beam is incident on the sample at very small angles, usually $0.5^\circ - 5^\circ$, to confine the penetration of the X-ray beam to the epitaxial film only. In this system the sample is fixed, and the X-ray source is fixed after the angle of incidence as been selected. The detector head rotates from the initial 2θ angle to the final 2θ angle selected by the user.

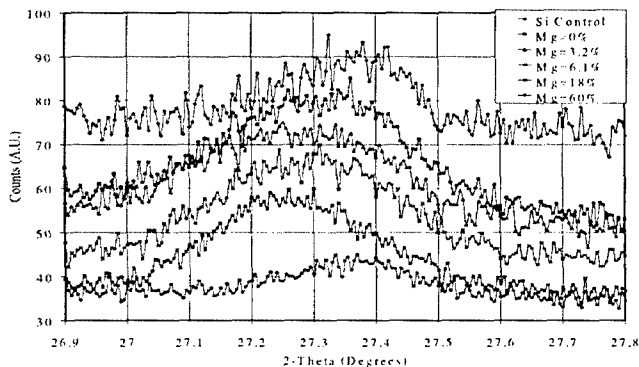


Figure 1. Low-angle X-ray diffraction curves measured at room temperature, for different Mg compositions of x for $\text{Zn}_{1-x}\text{Mg}_x\text{S}/\text{Si}(100)$ heterostructures. The $\text{Zn}_{1-x}\text{Mg}_x\text{S}$ epitaxial films were grown at 360°C with $35\text{mW}/\text{cm}^2$ UV irradiation intensity.

The samples were also sent to Evans East for XPS analysis, where the surface of the sample was examined initially by low-resolution survey scans to determine which elements were present. Then high-resolution depth profiles were acquired, as seen in Figure 2. The samples were profiled (sputtered) using a 3kV Ar^+ ion beam ($3.5 \times 3.5 \text{ mm}^2$ raster) and high-resolution scans of the elements were obtained every $37.5\text{\AA}$ (assuming a SiO_2 sputtering rate).

The quantification of the elements was accomplished by using the atomic sensitivity factors for a Physical Electronics Model 5700Lsci ESCA spectrometer.

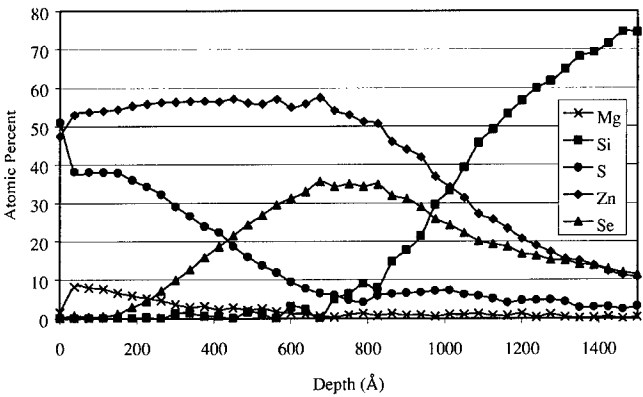


Figure 2. XPS results for run number 1261, for 6.1% composition Mg in the solid phase. The $\text{Zn}_{1-x}\text{Mg}_x\text{S}$ epitaxial film was grown at 360°C with 35mW/cm² UV irradiation intensity.

From the results obtained with XPS the percent Mg in the solid phase of ZnMgS versus percent $(\text{MeCp})_2\text{Mg}$ in the gas phase was determined as seen in Figure 3.

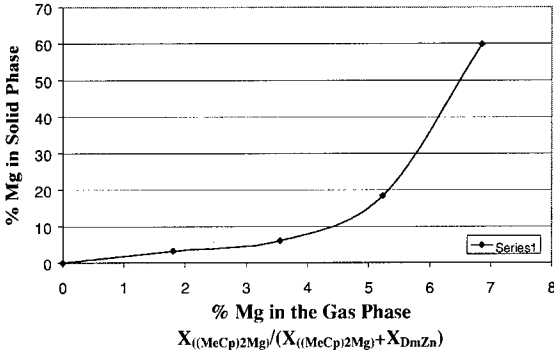


Figure 3. Percent Mg in the solid phase of ZnMgS (as determined by XPS results) versus percent $(\text{MeCp})_2\text{Mg}$ in the gas phase. The $\text{Zn}_{1-x}\text{Mg}_x\text{S}$ epitaxial films were grown at 341°C with 35mW/cm² UV irradiation intensity.

Thickness measurements were done by the Filmetrics F20 system, an optical non-destructive thickness measurement system. The results of which are presented in Figure 4.

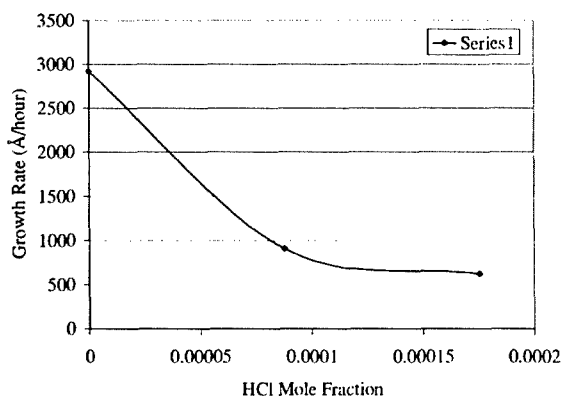


Figure 4. Growth rate of $\text{Zn}_{1-x}\text{Mg}_x\text{S}$ epitaxial films doped with HCL versus HCL mole fraction. The $\text{Zn}_{1-x}\text{Mg}_x\text{S}$ epitaxial films were grown at 360°C with no UV irradiation, and without a buffer layer.

Chlorine doping levels were measured with an AC Hall Effect setup, using the Van der Pauw Method. Since the substrate was not semi-insulating a multi-layer model[9] had to be used to extrapolate the parameters of the epitaxial layer, listed in Table 1.

Table 1. Results from Room Temperature AC Hall Effect Measurements

Sample #	#1280	#1281
Electron Hall Mobilty $\mu_n(\text{cm}^2/\text{V-s})$	2.420×10^3	2.650×10^3
Electron Carrier Concentration(cm^{-3})	2.375×10^{15}	3.058×10^{15}
Conductivity (mhos)	0.9196	1.296
$R_{\text{Hall}}(\Omega)$	2.632×10^3	2.044×10^3
Cl mole fraction	8.771×10^{-5}	1.754×10^{-4}
p-type Si Substrate Conductivity (mhos)	0.1148	

The current - voltage (I-V) charateristics were obtained with an HP 4145B Semiconductor Parameter Analyzer. The results are shown in Figure 5.

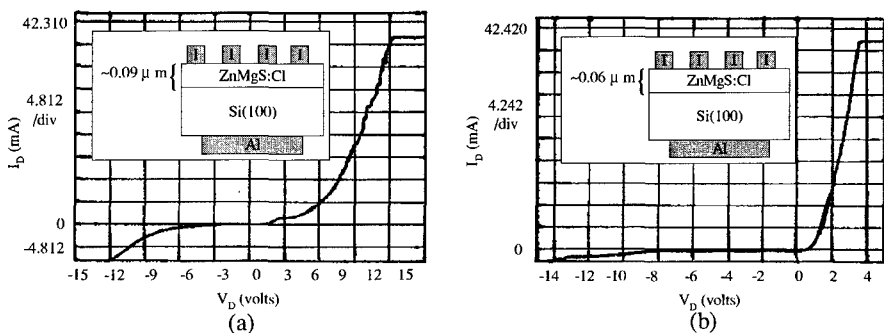


Figure 5. Current - Voltage characteristics of n-type $\text{Zn}_{1-x}\text{Mg}_x\text{S:Cl}$ / p-type Si diodes: (a) sample #1280 (b) sample #1281, (structure shown in insert).

CONCLUSION

This paper presents for the first time photo-assisted MOVPE growth of ZnMgS on Si (100) substrates. Epitaxial characterization by XPS, shows a Mg solid phase incorporation from 0 to 60 percent in the epitaxial layer. The epitaxial nature of the ZnMgS layers has been verified using the low-angle X-ray diffraction eliminating any interference from the Si substrate. It was shown with this technique that the change in the ZnMgS peak position changes from 27.35 degrees to 26.5 degrees with an increase in Mg incorporation, compared with a Si control sample peak at 27.4 degrees. XRD results obtained were verified with XPS data. Chlorine doping of the ZnMgS layer was also studied. Concentrations up to $3 \times 10^{15} \text{ cm}^{-3}$ were observed in the ZnMgS layer. Results of the n (ZnMgS:Cl) - p (Si) diodes fabricated were also presented.

REFERENCES

1. Washizuka, A. Mikami. "A 14.4-in Diagonal High Contrast Multicolor Information EL Display with 640×128 Pixels." *IEICE TRANS. Electron.* E81C (November 1998): pp. 1725-1732.
2. F. Jain. "Electroluminescent Flat Panel Displays Using MOCVD Grown ZnS and Ternary Compounds for Enhanced Blue Emission." *Proposal, University of Connecticut.* (1998).
3. G.P. Crawford. "A Bright New Page in Portable Displays." *IEEE Spectrum.* 37 (October 2000): pp. 40-46.
4. M.B. Spitzer, S.M. Vernon, and C.J. Keavney. "Passivation Techniques for Silicon Solar Cells."
5. G. Landis, J. Loferski, R. Beaulier, P. Sekula-Moisé, S. Vernon, M. Spitzer, and C. Keavney. "Wide-Bandgap Epitaxial Heterojunction Windows for Silicon Solar Cells." *IEEE Transactions on Electron Devices.* 37 (February 1990): pp. 372-380.
6. P. Smith. "Preparation and characterization of ZnS thin films produced by metalorganic chemical vapor deposition." *J. Vac. Sci. Technol.* A7 (May/June 1989): pp. 1451-1455.
7. T. Yokogawa, H. Sato, and M. Ogura. "Growth of ZnSe/ZnS strained-layer superlattices on Si substrates." *Journal of Applied Physics.* 64 (November 1988): pp. 5201-5205.

8. P. Rai-Choudhury, and A.J. Noreika. "Hydrogen Sulfide as an Etchant for Silicon." Journal of the Electrochemical Society: Electrochemical Technology. 116 (April 1969): pp. 539-541.
9. L.F. Lou, and W.H. Frye. "Hall effect and resistivity in liquid-phase-epitaxial layers of HgCdTe." Journal of Applied Physics. 56 (October 1984): pp. 2253-2267.