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# Room-Temperature Synthesis of ZnS:Mn Films by H<sub>2</sub> Plasma Chemical Sputtering

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Polycrystalline ZnS and ZnS:Mn films were grown at 20°C by hydrogen plasma chemical sputtering. The films were deposited in a planer magnetron sputtering system with hydrogen gas from a sintered ZnS and ZnS:Mn targets. Xray diffraction measurements revealed that the (111) oriented cubic ZnS films were obtained on glass substrates. Growth rate decreased logarithmically with increasing Mn concentration in the target, which suggests that the Zn particles be formed by the chemical reaction between the hydrogen plasma and the target rather than the physical sputtering. The CdS and SrS film were also prepared by the HPCS method.

## 1. INTRODUCTION

Hydrogen plasma chemical sputtering (HPCS) process is an attractive deposition technique, by which the films are grown on the basis of the chemical reaction between the targets and the H<sub>2</sub> plasma. It enables us to fabricate the diamond-like-carbon, micro-crys-talline Si:H, and epitaxial CdTe films at low substrate temperature<sup>1-3)</sup>. However, the growth mechanism has been unexplained yet. The study on the film growth of various materials should be carried out for the sake of the explication of the growth mechanism and the applications.

The present work demonstrates the roomtemperature synthesis of the ZnS and ZnS:Mn films by the HPCS process for the first time. The growth of the CdS, SrS, and  $\mu$ c-Si:H films are also examined.

#### 2. EXPERIMENTAL PROCEDURE

The films were deposited with 7N pure hydrogen gas onto glass substrates. The substrate temperature was kept at  $20\pm10^{\circ}$ C during the deposition. The films were deposited from a 3-inch sintered ZnS, ZnS:Mn (0.5, 2.0wt%), CdS, SrS, and single crystalline Si target under the following conditions: gas pressures, Pr, ranging from 20 Pa to 200 Pa, the rf powers, Ps, varied from 100 to 400W, and a gas flow rate of 30 sccm. The films were characterized by X-ray diffraction measurement, Raman spectroscopy, EPMA and ICP. The plasma conditions were diagnosed by the optical emission spectroscopy.

- 3. RESULTS
- 3.1. ZnS Film Growth

Figure 1 shows a typical X-ray diffraction pattern from the undoped ZnS film with the thickness of 2 $\mu$ m. We see that the (111) oriented cubic ZnS film is obtained<sup>4)</sup>. Figure 2 shows the diffraction pattern measured with



Fig.1 X-ray diffraction pattern from the ZnS film.

the fixed 2  $\Theta$  at (111) diffraction. The halfwidth of the curve is 4.5°, which indicates that the films are highly-oriented. The diffraction measured from the (111) oriented single crystalline Si wafer is also given in Fig.2. The integrated intensities of the spectra from the ZnS films are about 5 times larger than that from the Si wafer. It indicates that the highly-crystallized ZnS film is deposited at room-temperature.

The pressure dependence of the crystallinity is summarized in Fig.3. The integrated intensity and the full width at half maximum (FWHM) of the (111) diffraction drastically increases and decreases as the pressure is raised from 50Pa to 80Pa. At Pr>80 Pa, the films have almost the same crystalline quali-



Fig.2 X-ray diffraction pattern measured from the ZnS film in scanning mode with the fixed 2  $\Theta$  at 28.7°. The pattern from the (111) Si wafer is also given.



Fig.3 Pressure dependence of the integrated intensity and the FWHM of the spectra at (111) diffraction.

ty. The average grain size estimated from theFWHM through the Scherrer's equation is 60nm.3.2. Mn Doping into the ZnS Film

The Mn doped ZnS films were deposited from the sintered ZnS:Mn(0.5wt%). Figure 4 shows the Mn concentration as a function of Pr. It reveals that the Mn doping into the ZnS films is realized, but its concentration drastically decreases from 0.7wt% to about 0.1wt% with increasing Pr from 20 Pa to 200 Pa. Since the EL devices require the Mn concentration more than 0.5wt% and our films deposited at Pr<50Pa have the poor crystallinity, we have not obtained the device quality films yet. The concentration control of the Mn element is now under way.

Figure 5 shows the pressure dependence of the growth rate and the FWHM. We see that the growth rate logarithmically decreases with increasing Pr. Its relation is similar to that the undoped ZnS film growth. This is asof cribable to the change of the reaction between the H<sub>2</sub> plasma and the target as discussed later. The values of the FWHM decreases with increasing Pr. which is the similar characteristic on the undoped ZnS growth. But the smallest value (0.19°) is larger than that of the ZnS. The values are affected neither by the growth rate, the Mn concentration in the films, nor the gas pressure, but by the content of Mn in the target, which suggests that



Fig.4 Pressure dependence of the Mn concentration in the ZnS:Mn films.

the plasma condition plays an important role in the film growth.

3.3. Application of HPCS to the Other Films

The CdS, SrS, and µc-Si:H film growth by means of the HPCS process was examined. The CdS film was not obtained when the substrates were placed on the holder. Then we set the substrates on the side wall of the chamber. Figure 6 (a) shows the X-ray diffraction pattern from the 500nm-thick CdS film. It indicates that the highly-oriented CdS film can be obtained by the HPCS process. The crystalline structure was not identified since the (111)oriented cubic-CdS shows almost the same diffraction pattern as the (001)oriented hexagonal CdS.

Although the crystallinity was poor, we obtained the crystallized SrS film. Figure 6 (b) gives the X-ray diffraction pattern from the 100nm-thick SrS film deposited at 20°C. The pattern indicates that the poorly-oriented cubic SrS film can be formed by the HPCS process. However, the maximum growth rate was 0.5nm/min within our experiments. The result suggests that the reaction between H<sub>2</sub> plasma and the SrS target is not active enough to dissociate the elements from the target.

The  $\mu$ c-Si:H films can be obtained by the HPCS process<sup>5)</sup>. But in general the amorphous phase co-exists in the crystallized Si film.



Fig.5 Growth rate and FWHM as a function of  $\ensuremath{\mathsf{Pr}}$  .

We have studied the growth temperature dependence of the films and found that the films deposited at 400°C were composed of the highly-crystallized Si grains. Figure 7 shows the Raman spectra obtained from the µc-Si:H film prepared at 400°C on the quartz substrate. The spectrum at 519cm<sup>-1</sup> of the wave number shift corresponds to the c-Si Raman shift and the spectrum at 480 cm<sup>-1</sup> from the amorphous phase is not observed. We have also succeeded in the fabrication of the Sb doped µc-Si:H films from the Sb doped target. The results indicate that the HPCS process can produce the device quality films for the applications such as the thin film transistors.

## 4. DISCUSSION

The sputtering mechanism in the HPCS process is explained by the chemical reaction between the  $H_2$  plasma and the target since the mass of the hydrogen is too light to sputter the target physically. We consider that the S element is dissociate from the target by the chemical reaction through the gas phase molecule formation such as  $H_2S$ . There are two candidates to explain the Zn particle forma-



Fig.6 X-ray diffraction patterns from the CdS film (a) and the SrS film (b).





Fig.7 Raman spectra from  $\mu$ c-Si:H film prepared at 400°C.

Fig.8 Growth rate (a) and emission intensity (b) vs Pr. The Mn concentration is chosen as a parameter.

tion; one is the physical sputtering by the ion molecules such as  $H_2S^+$ ; the other is the chemical reaction between the Zn element and the H<sub>2</sub> plasma. Figure 8 (a) shows the pressure dependence of the growth rate as a parameter of the Mn concentration in the target. It is found that the growth rate strongly depends on the Mn concentration. Since the sputtering rate of the Zn element by the physical sputtering with Ar gas is in the same order of that of Mn, the result indicates that the Zn element is also formed by the chemical reaction.

The plasma conditions during the deposition was diagnosed by the optical emission spectroscopy. We observed the emission from the Zn, H and H<sub>2</sub> elements in the wavelength ranging from 200nm to 900nm. The intensity of the Zn emission at 213.8nm was monitored as a function of Pr as given in Fig.8 (b). At Pr < 150Pa, the intensity logarithmically decreased with increasing Pr and , at Pr>150Pa, it keeps the constant value. The pressure dependence is quite similar to that of the growth rate at Pr<150 Pa. It indicates that the Zn neutrals formed in the H2 plasma dominate the growth Above the value of Pr, the growth rate rate. decreasing, which suggests that the keeps

other factors such as  $H_2S$  molecules would play an important role in the film growth at Pr > 150Pa. It is not clarified whether or not the Mn elements are deposited through the chemical reaction process in the  $H_2$  plasma. 5.CONCLUSION

We have demonstrated the room-temperature synthesis of the ZnS and ZnS:Mn films by the hydrogen plasma chemical sputtering. The characterizations reveal that the highly-oriented cubic ZnS and ZnS:Mn films can be obtained by utilizing the HPCS process. The CdS and SrS films were also fabricated by the HPCS process.

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