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Growth and Characterization of ZnS Thin Films by Hot Wall Method

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Hot Wall법에 의한 ZnS 박막의 제작과 특성

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Abstract : *ZnS thin films were prepared on glass substrate at various deposition conditions by a HW apparatus and were systematically investigated the growth characteristics, in terms of deposition rates, absorption edges by a double beam spectrophotometer, and structural analysis by a x-ray diffraction. The deposition rates were increased with increasing the cell temperature and vapor pressure of sulfur, but were decreased with increasing substrate temperature. The optical characteristics of thin films depends on the deposition rates. The band gap energies of 3.46~3.52eV measured at room temperature are smaller than the theoretical value of 3.54eV, indicating that impurities exist in the crystal. All ZnS thin films are oriented in the (111) principal direction of a zincblende structure. By introducing the S vapor, optical and crystalline properties have been improved.*

Key words : *ZnS, Thin Film, Hot Wall Method, Band GAp Energy, Crystallinity, Crystal Structure*

요 약 : ZnS 박막을 Hot Wall 법에 의해 증발관 온도, 기판온도 및 외부로부터 유황(S)의 공급을 변수로 하여 제작하여 광학적, 결정 구조적 특성을 분석·검토하였다. 박막의 증착속도는 증발관 온도 및 S 증기압을 높일수록 증가하였으나 기판온도를 높이면 급격히 감소하였다. 박막의 광학적 특성은 증착속도와 밀접하게 관계하고 있다고 사료되며, 실온에서의 금지대 폭은 이론 값보다 작은 3.46~3.52eV를 나타내어 결정 중에 결함이 존재함을 알 수 있었다. 박막의 구조를 분석한 결과 어느 경우에 있어서나 섬아연광 구조의 (111) 주 배향성을 나타내었으나 회절 피크의 강도 및 반치폭으로부터 결정성은 대체로 양호하지 못했음을 알았다. 그러나, 기판온도 또는 S 공급 등의 제작조건에 따라 광학적, 결정적 특성이 개선되었다.

핵심용어 : 황화아연, 박막, Hot Wall법, 금지대 폭, 결정성, 결정구조

1. Introduction

Wide band gap II-VI compounds are one of the most promising materials for optoelectronic applications such as laser diodes(LDs) and thin film electroluminescent(EL) devices. Among these, ZnS compound has been used for phosphor, and has been intensively investigated for the full color EL displays and blue LDs which operate in the blue to ultraviolet region[1-2]. By many experimental studies on thin film growth, ZnS thin film has been grown by various deposition methods according to application fields. That is, a polycrystalline thin film for EL devices is mainly deposited by non-equilibrium methods such as electron-beam evaporation and sputtering[3], and epitaxial layer thin film for LDs is grown by near-equilibrium methods such as molecular beam epitaxy(MBE), atomic layer epitaxy (ALE) or metalorganic chemical vapor deposition(MOCVD) [4].

The performance of devices is known to depend strongly on the quality of films. In this sense, MBE or MOCVD which can control the atom unit is an excellent deposition apparatus. However, These techniques can not give easy access to use in individual laboratory due to their complex and expensive apparatus. Hot Wall(HW) equipment which permits the thin film deposition very near to thermodynamical equilibrium[5], stands on an equality of film deposition and is relatively simple and inexpensive compared to MBE. Hence, HW method has been widely applied for the growth of thin films, and the electrical and luminescence properties of CdTe thin fims fabricated by HW have been

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reported to be superior to those by MBE[6]. Therefore, HW is expected to be a useful deposition method in individual laboratory to obtain the high quality of ZnS thin film.

In this study, ZnS thin films were prepared on glass substrate at various deposition conditions by a standard HW apparatus and were systematically investigated the growth characteristics, in terms of deposition rates, absorption edges by a double beam spectrophotometer, and structural analysis by a x-ray diffraction.

2. Experimental procedure

A standard HW apparatus was employed, which is mounted in a vacuum chamber with an initial pressure of 1 $\times 10^{-4}$Pa[7]. Fig. 1 shows a schematic diagram of HW deposition apparatus, in which 4 evaporation walls and a substrate holder are equipped. The distance between a wall and the glass substrate is about 15mm. The resistively heated quartz tube was used as an ZnS evaporation wall. And sulfur(S) vapor was introduced to the ZnS wall to supplement S, which is supplied from a S furnace placed on the outside of the growth chamber. The S vapor pressure in the S furnace was controlled by a temperature of 200-300C. On growing the ZnS thin films, vacuum pressure were maintained at 6×10^{-3}Pa and at 2×10^{-2}Pa without and with supplying S, respectively. The S vapor pressure was reduced by a bellows valve.

ZnS thin films were grown using a ZnS powder source of 5N and S powder source of 6N. ZnS powder of 10g was put into a evaporation wall at one time. And to purge the gas and settle the evaporation pressure, ZnS powder in the wall was preheated for one hour at 850℃ which is higher than growth wall temperature.

A non-alkali glass of NA-40 was used as substrate, which is cleaned in ultra-pure water and acetone by an utrasonic cleaner to eliminate the surface contamination before being set in substrate holder. After the substrate was once heated to 550℃ and maintained for 10 minutes to promote the purity of surface, and decreased at the target temperature. The substrate was heated by about 15℃ per one minute to avoid the thermal damage or structural distortion, and after growth, the substrate was naturally cooled in the chamber.

The thin film growth were carried out at several parameters, that is, substrate temperature(T_{sub}) of 200℃~500℃, evaporation wall temperature(T_{ZnS}) of 550℃~850℃ and S supply. To pursue the settlement of vacuum pressure, S was supplied before 30 minutes to deposit.

The deposition rates were calculated by film thickness which is measured by Multiple Beam Interferometry using He-Ne laser beam. To estimate the optical properties, the optical transmission spectra were also measured using a conventional double beam spectrophotometer. The crystal structure and crystalline properties were investigated by x-ray diffraction(XRD) measurement. Cu-Kα (λ=1.5405Å) radiation was employed.

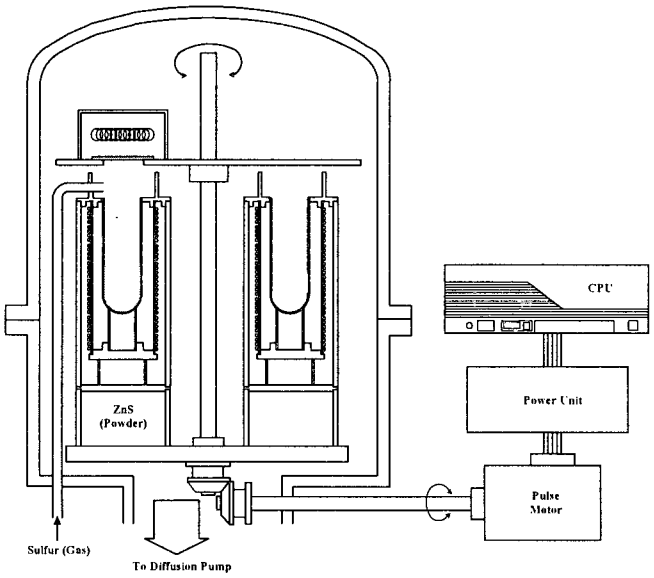

Fig. 1 Schematic diagram of vacuum chamber for hot wall equipment.

3. Results and discussion

3.1 Deposition rates

Fig. 2 shows the dependence of evaporation cell temperature on vapor pressure and deposition rates. Also, the line shows the theoretical saturated vapor pressure of ZnS. Open and closed circles indicate experimental vacuum pressure on evaporation wall temperature and deposition rates of thin film grown at T_{ZnS}=200℃, respectively.

Although the actual pressure except that in T_{ZnS}=550℃ is about ten times as high as theoretical saturated vapor pressure of ZnS, its slope is nearly equal to that of the theoretical saturated vapor pressure[8], which suggests that HW is deposition method near to thermodynamical equilibrium. The higher actual pressure may come from the difference between pressure measured in chamber and temperature measured in ZnS evaporation wall. The deviation

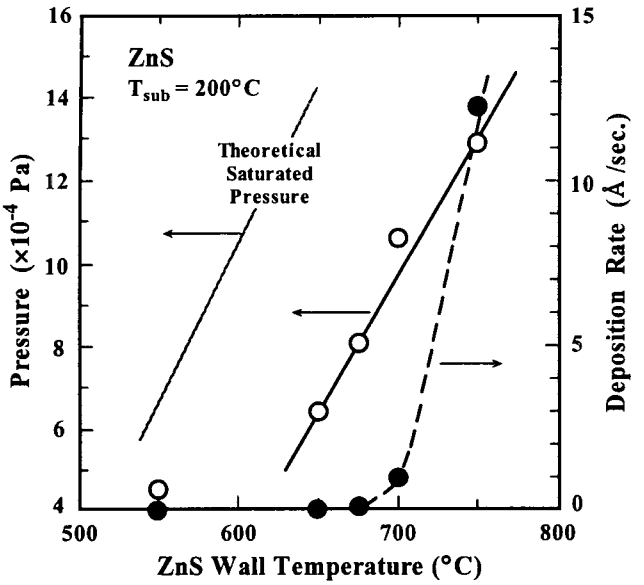

Fig. 2 The dependence of evaporation wall temperature on vapor pressure and deposition rates.

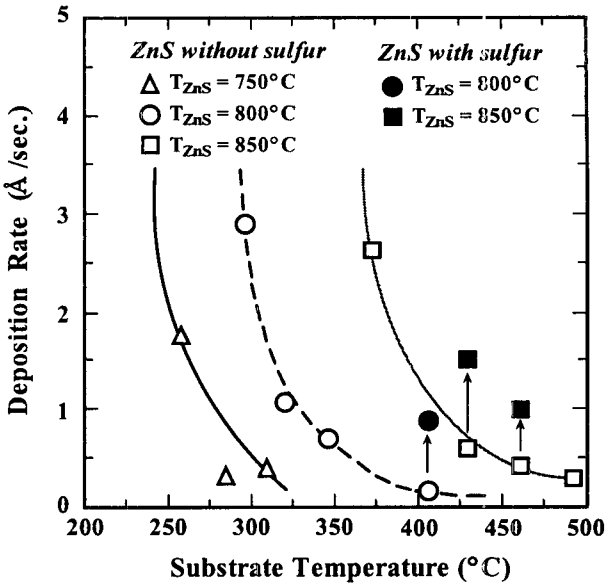

Fig. 3 The dependence of substrate temperature on deposition rates for ZnS films deposited at ZnS wall temperature of 750, 800 and 850℃, respectively.

from the plotting at T_{ZnS}=550℃ is due to the evacuation capacity of the apparatus.

The deposition rates increase steeply with increasing ZnS wall temperature after a thin film has started to grow at T_{ZnS}=700℃. The growing film sticked to substrate can be simply calculated by the difference of ZnS vapor quantity arriving at substrate Q1 which is under the control of the wall temperature and re-evaporation vapor quantity from substrate Q2 which is governed by the substrate temperature. Therefore, in case of T_{sub}=200℃ ZnS starts to deposit on the substrate by Q1>Q2 only when wall temperature increases to 700℃. That is, below T_{ZnS}=700℃, film is scarcely deposited. Above T_{ZnS}=700℃, however, Q1 increases steeply with raising the ZnS wall temperature whereas Q2 keeps nearly constant and hence, experimental results above T_{ZnS}=700℃ well explain that the deposition rates increase steeply with the increase of the arriving vapor quantity.

Fig. 3 shows the substrate temperature dependence of the deposition rates for ZnS films deposited at T_{ZnS}=750, 800 and 850℃, respectively. Open and closed circles indicate the deposition rates without and with introducing S vapor, respectively.

At any ZnS wall temperature, deposition rates decrease exponentially with increasing the substrate temperature. As mentioned above, this result implies that because Q1 remains constant by the constant wall temperature and Q2 decreases abruptly by increasing the substrate temperature, the film is more slowly deposited.

The deposition rates with S supply considerably increase compared to those without S supply. This result can be explained by the increase of the effective bonding of Zn-S by introducing S vapor, in which, if without S supply, Zn atoms not to be bonded with S have been evacuated by S defect. It is also confirmed that this result is coincident with the sulfur pressure dependence of the deposition rates shown in Fig. 4.

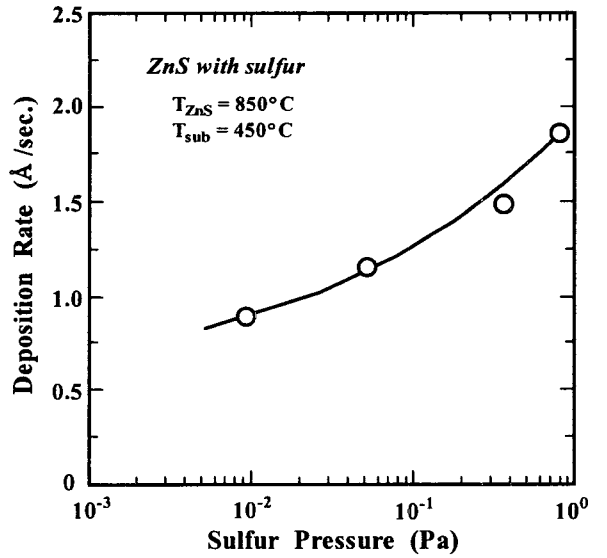

Fig. 4 The dependence of sulfur pressure on deposition rates.

Fig. 4 shows the dependence of sulfur pressure on deposition rates. Although thin films were deposited at constant wall temperature of 850℃ and at constant substrate temperature of 450℃, the deposition rates increase with increasing the S vapor pressure.

3.2 Optical characteristics

In order to evaluate an absorption edge for ZnS thin films, optical transmission spectra have been measured at room temperature using an UV-visible beam spectrophotometer. Fig. 5 shows the typical transmission spectra of ZnS thin films deposited at various substrate temperatures. The thickness of each sample is about 1 μm. As can be seen in Fig. 5, the fundamental absorption edges shift noticeably toward the shorter-wavelength side with increasing the substrate temperature except the case of T_{sub}=500℃, which implies that optical properties improve with increasing the substrate temperature up to 450℃.

However, if ZnS wall temperature kept constant, the deposition rates decrease with increasing the substrate temperature as shown in Fig. 3. Taking into consideration of this result, the optical characteristics of films with the nearly same deposition rates which are deposited by controling the substrate and wall temperature have been investigated. Fig. 6 shows the transmission spectra of ZnS thin films deposited at about same deposition rates of 0.5Å /sec. Independent of the substrate and wall temperature, little change in spectra are nearly observed, which suggests that optical characteristics do not depend on the substrate temperature but mainly on the deposition rates.

It is known that the oscillations appear in the longer-wavelength region of the transmission curve due to the interference between film surface and substrate interface, which indicates the smoothness of the film surface. But the oscillations in the films are not observed clearly.

It is not easy to determine exactly the absorption edge energy, i.e., band gap energy(Eg) from this type of measurement. Several methods have been reported for the determination of the absorption. In this paper, the usual procedure of plotting $\alpha h\nu$ versus $h\nu$ to obtain Eg. The absorption coefficient α is deduced by approximating the transmittance as $\exp(-\alpha t)$, where t is the film thickness. According to a simple theory, the fundamental absorption can be written as $(\alpha h\nu)^2=A(h\nu-Eg)$ for a direct transition material[9]. By extrapolation of the linear portion of the $(\alpha h\nu)^2-h\nu$ curves to the abscissa, the energy gap Eg of the films were estimated.

Fig. 7 shows the substrate temperature dependence of optical band gap energies. The open and closed circles

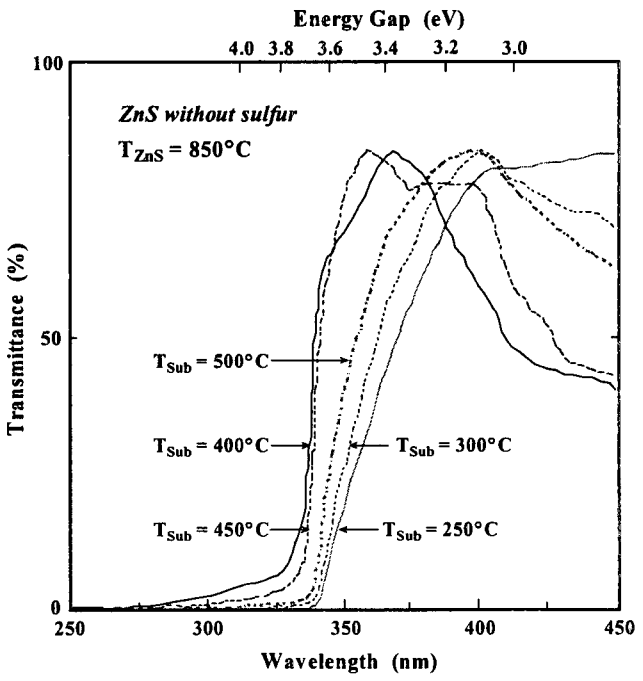

Fig. 5 UV-visible transmission spectra of ZnS thin films grown at various substrate temperatures.

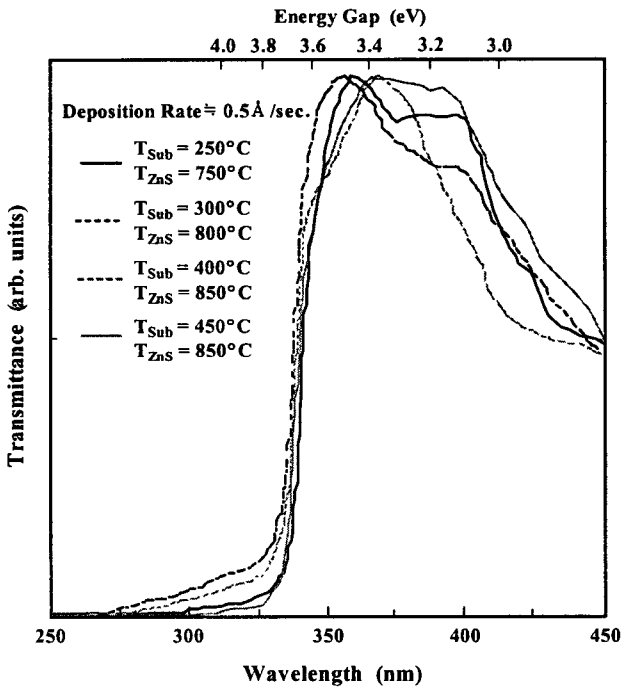

Fig. 6 UV-visible transmission spectra of ZnS thin films grown at about same deposition rates of 0.5Å/sec.

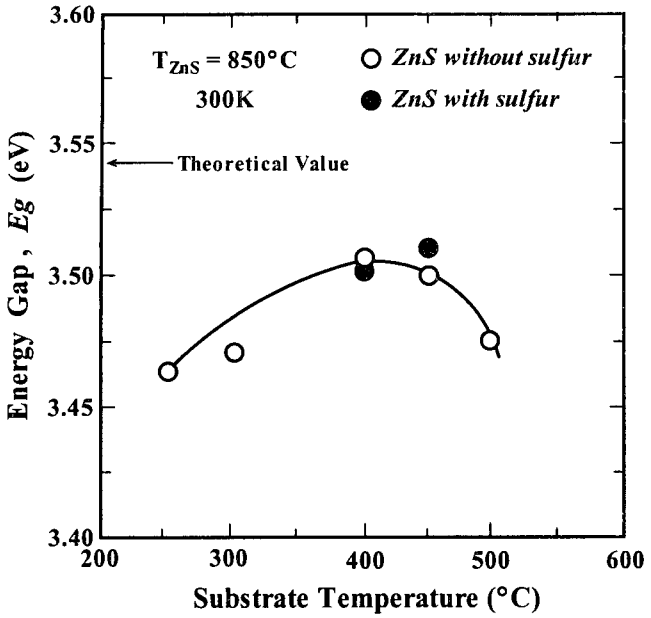

Fig. 7 Substrate temperature dependence of optical band gap energies. The open and closed circles indicate those of ZnS film prepared without and with sulfur, respectively.

indicate those of ZnS film prepared without and with S supply, respectively. it is reported that the optical band gap energy of ZnS with a Γ-Γ direct transition is 3.54eV at 300K[10].

All the experimental values with 3.46~3.52eV are narrow compared with theoretical value. Also, taking into consideration of the gentle slope of tale in the transmission spectra shown in Fig. 5, the films are considered to remain somewhat defective due to the impurity contents and/or structural defects.

The Eg comes close to theoretical value with increasing the substrate temperature, and the optical properties of films deposited at T_{sub}=400 and 450℃ are superior. By introducing S vapor, Eg becomes greater in the substrate temperature of 450℃, where decreases in T_{sub}=400℃. It may result from the crystal quality.

3.3 Crystal structure and crystallinity

The structural characteristics of the ZnS thin films are investigated by XRD measurement. Fig. 8 shows typical XRD patterns of ZnS thin films deposited at T_{sub}=400 and 450℃. For reference, the pattern of ZnS powder is also shown. The thickness of each sample is about 1 μm.

All the thin films show all peaks which are appeared in

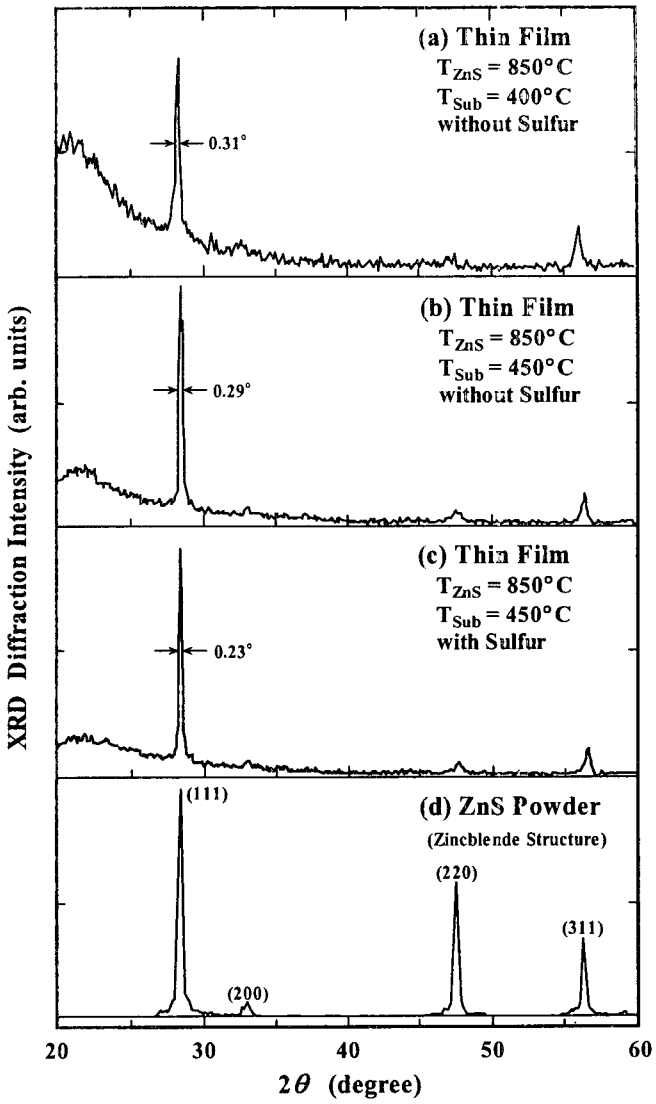

Fig. 8 X-ray diffraction patterns of ZnS thin films grown at Tsub.=400 and 450℃. The pattern of ZnS powder is also shown.

the pattern of ZnS powder, but diffraction intensity of each peak differs from that of powder. That is, the pattern of powder shows the strong peaks originating from (111), (200), (220) and (311) planes, but the pattern of thin films shows one strong peak at the diffraction angle, 2θ of 28. 6° and three weak peaks due to the (111) orientation of the zincblende structure, indicating that ZnS film tends to grow in the polar [111] direction despite of high substrate temperature of 450℃.

Full width at half maximum(FWHM), $\Delta 2\theta$ of the 111 reflection for the films deposited at T_{sub}=400 and 450℃ is a 0.31° and 0.29°, respectively. By the Scherrer's equation [11], the film deposited at T_{sub}=450℃ has larger crystal

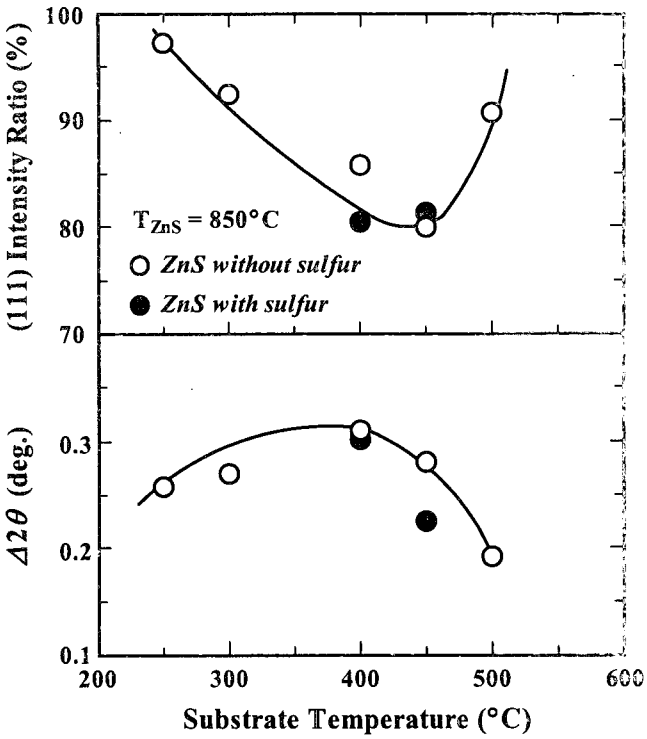

Fig. 9 The dependence of (111) intensity ratio and FWHM on substrate temperature. The open and closed circles indicate those of ZnS film prepared without and with sulfur, respectively.

particles and has a stronger diffraction intensity compared to those of the films deposited at T_{sub}=400℃, implying that the former is superior to the latter in a crystalline quality. By introducing S vapor, $\Delta 2\theta$ becomes more narrow to 0.23° and intensity is stronger, indicating the crystal properties are improved

Fig. 9 shows the substrate temperature dependence of the (111) intensity ratio and FWHM of the 111 reflection for the ZnS thin films deposited at T_{ZnS}=850℃. The open and closed circles indicate those of ZnS film prepared without and with introducing S vapor, respectively. The (111) intensity ratio represents the ratio of (111) peak intensity to the sum of (111), (200), (220) and (311) peak intensities which are appeared within a XRD scanning range of 20~60°.

From the intensity ratio and FWHM, the film deposited at T_{sub}=500℃ is considered to have a good crystalline quality. For the films deposited at the substrate temperature of 400 and 450℃, the preferential orientation in the [111] direction and $\Delta 2\theta$ is relatively poor. This results on the crystalline quality disagree with the optical results shown in Fig. 7, for which further investigation is considered to be necessary. In the case of introducing S vapor, no variation of the preferential orientation was not observed, but $\Delta 2\theta$ has been improved. On the whole $\Delta 2\theta$ shows 0.18~0.31°, implying that the crystalline quality of the ZnS films is greatly influenced by the deposition conditions. Therefore, It is considered to be important for the growth of the thin films with higher crystal quality by HW technique to find out optimum deposition conditions.

4. Conclusion

ZnS thin films were prepared on glass substrate at various deposition conditions by a HW apparatus and were systematically investigated the growth characteristics, in terms of deposition rates, absorption edges by a double beam spectrophotometer, and structural analysis by a x-ray diffraction. The deposition rates were increased with increasing the cell temperature and vapor pressure of sulfur, but were decreased with increasing substrate temperature. The optical characteristics of thin films depends on the deposition rates. The band gap energies of 3.46~3.52eV measured at room temperature are smaller than the theoretical value of 3.54eV, indicating that impurities exist in the crystal. All ZnS thin films are oriented in the (111) principal direction of a zincblende structure. By introducing the S vapor, optical and crystalline properties have been improved. $\Delta 2\theta$ of the 111 reflection shows 0.18~0.31°, implying that by finding out optimum deposition conditions, it is considered to obtain the ZnS thin films with higher crystal quality by HW technique.

References

[1] H. Okuyama, K. Nakano, T. Miyajima, K. Akimoto, "Epitaxial growth of ZnMgSSe on GaAs substrate by molecular beam epitaxy", Jpn. J. Appl. Phys., 30, (1991), pp.L1620-L1623.

[2] K. Ohmi, Y. Yamano, S. Lee, T. Ueda, S. Tanaka, H. Kobayashi, "Growth and characterization of SrS/ZnS multilayered electroluminescent thin films grown by hot wall technique", J. Crystal Growth, 138, (1994), pp.1061-1065.

[3] C. Frey, D. Serafin, R. Boudreau,"High-brightness rf-sputtered ZnS:Mn films for TFEL displays", SID 88 Digest, (1988), pp.16-18.

[4] T. Suntola, "Atomic layer epitaxy", Materials Science Report 4, (1989), pp.261-312.

[5] A. Lopez-Otero, "Growth of PbTe films under near-equilibrium condition", J. Appl. Phys., 48, (1977), pp.446-448.

[6] D. Schikora, H.Sitter, J. Humenberger, K. Lischka, "High quality CdTe epilayers on GaAs grown by hot-wall epitaxy", Appl. Phys. Lett., 48, (1986), pp. 1276-1278.

[7] 허성곤, "Hot Wall법에 의한 ZnS 박막의 제작과 특성에 관한 연구", 석사학위논문, (2000).

[8] 日本學術振興會薄膜제31委員會 編, "薄膜ハンドブック", オーム社, (1983), p918.

[9] J.I. Pankove, "Optical process in semiconductors", Dover Pub., Inc., pp.34-60, 1971.

[10] The Electrical Engineering Handbook, Ed.-in-chief R. C. Dorf, CRC Press, Inc., (1993) 2534.

[11] 加藤誠軌, "X線回折分析", 內田老鶴圃, (1990), pp.246-251.

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