Effects of annealing on properties of electrochemically deposited $\text{Cu}_x\text{Zn}_y\text{S}$ thin films

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Zn-rich $\text{Cu}_x\text{Zn}_y\text{S}$ is a transparent p-type semiconductor. In this study, we fabricated $\text{Cu}_x\text{Zn}_y\text{S}$ thin films by electrochemical deposition and investigated changes in properties due to annealing in a sulfur atmosphere. The sample before annealing was amorphous with composition Cu : Zn : S : O = 0.03 : 0.29 : 0.57 : 0.11. After one hour annealing at 400°C, we observed formation of the ZnS phase by X-ray diffraction and Raman measurements. Although the sample exhibited p-type conductivity before the annealing, it did not clearly show p-type conductivity after the annealing at temperatures higher than 300°C. Those results indicate that $\text{Cu}_x\text{Zn}_y\text{S}$ is a metastable phase and is believed to separate into the ZnS phase and a phase including Cu by the annealing at temperatures higher than 300°C.

Key words: electrochemical deposition (ECD), $\text{Cu}_x\text{Zn}_y\text{S}$, transparent semiconductor, annealing

1. INTRODUCTION

For thin film fabrication of semiconductor materials, there are a variety of techniques including evaporation, sputtering, chemical vapor deposition. Many of those techniques require a high-temperature treatment or a vacuum environment, and therefore the manufacturing cost cannot be low. Electrochemical deposition (ECD) is a simple, low-cost technique and now is widely used for metal plating: it does not require vacuum chamber or high-temperature furnace and is able to deposit a large area film. Moreover, the film thickness can be controlled easily by adjusting the deposition time. Thus ECD is advantageous for production of devices having a large area, such as solar cells and displays.

In this study, we prepare $\text{Cu}_x\text{Zn}_y\text{S}$ thin films by the ECD method and examine the variation of properties due to sulfur annealing. $\text{Cu}_x\text{Zn}_y\text{S}$ is considered to be an alloy composed of ZnS and Cu_xS . ZnS is an n-type semiconductor with a band gap of 3.6 eV, and Cu_xS is a p-type semiconductor with its band gap in a range of 1.7~2.5 eV. Thus $\text{Cu}_x\text{Zn}_y\text{S}$ is expected to have a band gap in between those values, and may become both n-type and p-type depending on the composition. Thus, $\text{Cu}_x\text{Zn}_y\text{S}$ can be applied to transparent solar cells (UV solar cells), UV sensors, LED, etc. However, only several groups have investigated properties of $\text{Cu}_x\text{Zn}_y\text{S}$. Yildirim prepared a $\text{Cu}_{0.6}\text{Zn}_{0.4}\text{S}$ thin film having a band gap of 2.1 eV using a chemical solution, but the conduction type has not been reported [1]. Yang et al. prepared a transparent p-type semiconductor $\text{Cu}_x\text{Zn}_y\text{S}$ having a band gap of 3.2 eV using ECD [2,3]. Mandula et al. prepared a p-type $\text{Cu}_x\text{Zn}_y\text{S}$ semiconductor having a band gap of 2.4~3.7 eV [4] by photochemical deposition (PCD). Transparent p-type $\text{Cu}_x\text{Zn}_y\text{S}$ has also been produced by the pulsed laser deposition [5] and chemical solution deposition [6]. Sreejith et al reported fabrication of solar cells based on Cu-rich $\text{Cu}_x\text{Zn}_y\text{S}$ which has a small band gap [7]. It should be noted that Cu_xS is a nonstoichiometric compound, i.e., the Cu/S ratio is not fixed. Consequently, the (Cu+Zn)/S

ratio of $\text{Cu}_x\text{Zn}_y\text{S}$ is not fixed either [2-4].

In ECD and PCD, $\text{Cu}_x\text{Zn}_y\text{S}$ films were deposited at a low temperature (room temperature), and the deposited films were found to be amorphous by X-ray diffraction [2-4]. It has not been confirmed yet whether those $\text{Cu}_x\text{Zn}_y\text{S}$ films are stable even at high temperatures, or present as a metastable phase only at low temperatures. If $\text{Cu}_x\text{Zn}_y\text{S}$ is stable at high temperature, then it should be clarified which crystal structure $\text{Cu}_x\text{Zn}_y\text{S}$ will have, since ZnS and Cu_xS have different crystal structures. The phase stability is important not only as a basic property of the material but also for judging applicability to the devices. In this study, we investigate the stability of ECD- $\text{Cu}_x\text{Zn}_y\text{S}$, by annealing $\text{Cu}_x\text{Zn}_y\text{S}$ thin films in a sulfur atmosphere and examining change in its structural, electrical, and optical properties. On the basis of the previous work [3], we deposit Zn-rich $\text{Cu}_x\text{Zn}_y\text{S}$ films because they are technologically important owing to the large band gap and p-type conductivity.

2. EXPERIMENTAL

Indium-tin-oxide (ITO) glass sheet was used as the working electrode (substrate), and a platinum sheet as the counter electrode. A saturated calomel electrode (SCE) was used as a reference electrode, and it was brought into contact with the deposition solution using a salt bridge containing saturated KCl agar. The concentrations of the source chemicals CuSO_4 , ZnSO_4 and $\text{Na}_2\text{S}_2\text{O}_3$ were 5 mM, 25 mM, 100 mM respectively, and they were dissolved in deionized water of 50 mL. pH was adjusted to around 2.3 with lactic acid, and the deposition was carried out at 40°C for 20 min.

In an acidic solution, $\text{S}_2\text{O}_3^{2-}$ ions release elemental S according the following reaction.

The metal ions are reduced at the cathode with S thus released, and metal sulfides are formed.

When we deposit $\text{Cu}_x\text{Zn}_y\text{S}$ on ITO directly, indium is sometimes detected in the deposited film. This can be due

to the fact that the ITO substrate is not stable in the deposition solution. In order to suppress the reaction between the substrate and the solution, the ITO substrate was coated with a thin sulfur film. An appropriate amount of sulfur powder was put in a crucible and heated to about 160°C in air, and then sulfur was evaporated and deposited on the substrate placed above the crucible. The thickness of the sulfur coating was about 20 nm. The sulfur coating has negligible resistance and does not seem to affect the ECD process.

The deposited films were annealed at 200°C, 300°C and 400°C. The sample, with sulfur powder of about 10 mg placed on its surface, was sandwiched between glass plates and covered with aluminum foil. Then it was heated in a vacuum furnace [8]. It should be noted that without sulfur powder, sulfur in the films will be preferentially lost during the annealing because of its high vapor pressure. The amount of 10 mg was adopted because we found that further increase in sulfur amount did not cause significant change in properties of the annealed films.

Elemental composition of the thin film was measured by Auger electron spectroscopy (AES) using JAMP-9500F (JEOL). The CuS , ZnS , Cu_2O , and ZnO were used as standard samples to calculate composition ratio by AES. Scanning electron microscope (SEM) observation was carried out using the same equipment. Contamination on the film surface was removed by Ar etching of 15 s prior to the measure. X-ray diffraction (XRD) patterns were obtained using SmartLab (Rigaku) with a $\text{CuK}\alpha$ line. Spectrophotometer U-570 (JASCO) was used for the optical transmittance measurement. Raman spectroscopy was done by utilizing a NRS-3300 (JASCO) laser Raman spectrophotometer. The wavelength of the excitation laser is 524 nm. We examined the photo conductivity and conduction type of the films by a photo-electrochemical (PEC) measurement. The same apparatus as ECD was used with the solution containing 100 mM $\text{Na}_2\text{S}_2\text{O}_3$, and the sample was illuminated with a Xe lamp (about 100 mW/cm^2). The light was turned on/off by a shutter periodically. Under illumination, relative change in the minority carrier concentration is much larger than that in the majority carrier concentration. Therefore, when the electrode reaction is due to minority carriers, the effect of light irradiation is significant. Thus, for an n-type semiconductor electrode, the oxidation reaction is promoted by light irradiation during anodic polarization, whereas for a p-type semiconductor electrode, reduction reaction is promoted by light irradiation during cathodic polarization.

3. RESULTS AND DISCUSSION

Thin films having a thickness of 0.2 μm were deposited. Figure 1 shows the AES measurement results of the as-deposited and annealed films. Oxygen is included in bulk of the thin films, and its origin is considered to be dissolved oxygen molecules rather than OH^- ions since pH of the deposition solution was adjusted to about 2.3.

Figure 2 shows relationship between the composition ratio and annealing temperature. The initial composition ratio of the as-deposited film was $\text{Cu} : \text{Zn} : \text{S} : \text{O} = 0.03 : 0.29 : 0.57 : 0.11$. As shown in Fig. 2, no significant change was observed after the annealing. Figure 3 shows the SEM images of the as-deposited and annealed films. Grains are distributed on the surface of a continuous film,

and the annealing did not cause significant change in surface morphology.

Fig. 1. AES spectra before and after annealing at various temperatures.

Fig. 2. Relationship between the composition ratio and the annealing temperature.

Fig. 3. SEM images of the as-deposited and annealed films.

The XRD results are shown in Fig. 4. All of the peaks observed for the as-deposited, and 200°C and 300°C-annealed samples are the peaks due to ITO. After the annealing at 400°C, a peak appeared around 28.7°. This peak can be attributed to either (002) of wurtzite ZnS or (111) of zincblende ZnS . Since the zincblende structure is stable below about 1000°C [9], this peak is considered to correspond to (111) of zincblende ZnS . The peak is

broad, and therefore the crystal grains are small, or strained. According to those XRD results, the film is amorphous at low temperatures, and the ZnS crystal phase appeared by annealing at 400°C.

Raman results are shown in Fig. 5. For the as-deposited sample, the signal of S appeared at 172, 225, 240, 275, 443, and 491 cm^{-1} , and those are considered to originate from the sulfur coating on the ITO substrate. In addition to them, a very broad peak was observed in a wide wavenumber range 300–400 cm^{-1} . Its relative intensity was increased by the annealing. After the 400°C annealing, a hump was observed clearly at 355 cm^{-1} , and it could be attributed to ZnS LO mode [10]. Origins of the other peaks at 325, 505, 675 cm^{-1} are not understood.

Fig. 4. XRD patterns of the ITO substrate and the $\text{Cu}_x\text{Zn}_y\text{S}$ samples before and after annealing.

Fig. 5. Raman measurement results for the as-deposited and annealed films.

Figure 6 shows the results of the optical transmission measurement. The transmission in the visible region is not high, about 25%, and this is thought to be due to scattering by surface roughness and absorption by the sulfur film on the ITO substrate. The absorption edge near 500 nm is due to elemental sulfur [12]. The absorption edge due to the films is not clear but seems to be around 350 nm, and the change in transmission due to the annealing is not large. Thus the band gap would not be changed significantly by the annealing.

Fig. 6. Transmission measurement results for the as-deposited and annealed films.

The results of the PEC measurement are shown in Fig. 7. For the as-deposited and 200°C-annealed samples, under the negative bias, negative photo-current was clearly observed. Therefore, those two samples have p-type conductivity. However, for the samples after the annealing at 300°C and 400°C, photo-response in the negative direction is weak and comparable to the positive photo-response under the positive bias. This indicates that the conduction type approaches intrinsic by the annealing above 300°C.

As shown above, formation of the ZnS crystal phase was observed after the annealing at 400°C by XRD and Raman measurements. In addition, p-type conductivity of as-deposited $\text{Cu}_x\text{Zn}_y\text{S}$ was no longer clearly observed after the annealing at temperatures above 300°C. This can be because of formation of the n-type ZnS phase. Therefore, one may consider that p-type $\text{Cu}_x\text{Zn}_y\text{S}$ is a metastable phase present in an amorphous state, and that it is separated into the ZnS phase and other unknown phases when it is crystallized by the heat treatment. The other unknown phases should include Cu, but any Cu compound phases were not observed in the XRD and Raman measurements, probably because the Cu composition ratio is much smaller than that of Zn. On the other hand, since p-type conductivity is clearly observed even after the 200°C annealing, amorphous p-type $\text{Cu}_x\text{Zn}_y\text{S}$ is considered to be sufficiently stable for the device application.

Fig. 7. PEC measurement results for the as-deposited and annealed films.

4. CONCLUSION

We have prepared $\text{Cu}_x\text{Zn}_y\text{S}$ thin films by ECD, and

examined the effects of sulfur annealing on the structural, electrical, and optical properties. P-type thin films having about 0.2 μm thickness and the composition ratio Cu : Zn : S : O = 0.03 : 0.29 : 0.57 : 0.11 were obtained by ECD. By the XRD and Raman measurements, it was confirmed that the as-deposited film was amorphous, and that the ZnS crystal phase was formed by the annealing at 400°C. From the PEC results, p-type conductivity was clearly observed for the as-deposited and 200°C-annealed films, while the film became almost intrinsic after the annealing at 300 and 400°C annealing. Therefore, $\text{Cu}_x\text{Zn}_y\text{S}$ is thought to be separated to the n-type ZnS phase and some phase including Cu by the annealing at temperatures above 300°C.

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REFERENCES

- [1] M. A. Yildirim, A. Aytunc, A. Aykut, *Physica E*, **41**, 1365-1372 (2009).
- [2] K. Yang, M. Ichimura, *Jpn. J. Appl. Phys.*, **50**, 040202 (2011).
- [3] K. Yang, Y. Nakashima, M. Ichimura, *J. Electrochem. Soc.* **159**, H250-H254 (2012).
- [4] Mandula, K. Yang, M. Ichimura, *Sci. Technol.* **27**, 125007 (2012).
- [5] M. Diamond, L. Corbellini, K. R. Balasubramaniam, S. Chen, S. Wang, T. S. Matthews, L.-W. Wang, R. Ramesh, J. W. Ager, *Phys. Status Solidi A*, **209**, 2101-2107 (2012).
- [6] D. E. Ortíz-Ramos, L. A. González, R. Ramirez-Bon, *Mater. Lett.* **124**, 267-270 (2014).
- [7] M. S. Sreejith, D. R. Deepu, C. Sudha Kartha, K. Rajeevkumar, and K. P. Vijayakumar, *Appl. Phys. Lett.*, **105**, 202107 (2014).
- [8] D. A. Maz'on-Montijo, M. T. S. Nair, and P. K. Nair, *ECS J. Solid St. Sci. Technol.*, **2**, P465-P470 (2013).
- [9] G. C. Trigunyat and G. K. Chadha, *Phys. Status Solidi A*, **4**, 9-42 (1971).
- [10] J. Schneider, K. D. Roger, *Phys. Rev. B*, **6**, 1290-1294 (1972).
- [11] M. Ichimura, M. Yosuke. *Thin Solid Films*, **594**, 277-281 (2015).
- [12] A. K. Abass, A. K. Hasen, R. H. Misho, *J. Appl. Phys.*, **58**, 1640-1642. (1985).

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