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Growth of $AgGaTe_2$ Layers by a Closed-Space Sublimation Method

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$AgGaTe_2$ layers were deposited on Si substrates by the closed-space sublimation method. Multiple samples were deposited with various source temperatures and holding times, and constant temperature differential. Variation of the source temperature was used primarily to improve the stoichiometry of the film. Deposited films were evaluated by the θ–2θ method of x-ray diffraction (XRD) and transmission electron microscopy. These results confirmed that the deposited films were stoichiometric (after optimizing the above parameters). From XRD, it was also clear that films deposited on Si (111) have strong preference for (112) orientation.

Key words: Closed-space sublimation method, chalcopyrite compound, $AgGaTe_2$

INTRODUCTION

CdTe is one of the most promising photovoltaic materials available for use in low-cost, high-efficiency solar cells because of its near-optimal bandgap and high absorption coefficient.[1–7] Also, chalcopyrite I–III–VI_2 compounds have recently attracted attention as potential components for semiconductor devices, including applications in solar cells and electrooptic devices.[8–10] In particular, $CuInSe_2$ has already become widely used in making commercial solar cells.[11,12] The bandgap of $AgGaTe_2$ at room temperature is 1.3 eV (close to optimal for absorbing the solar spectrum), and a high optical absorption coefficient is also expected.[13–16] As such, $AgGaTe_2$ is expected to be another ideal candidate novel solar cell material. The lattice constants for the a and c axes of $AgGaTe_2$ are 6.28 Å and 11.94 Å, respectively. Even though the lattice mismatch is fairly large, Si was employed as the substrate in this study owing to its wide use as a substrate material.

This study presents the first deposition of $AgGaTe_2$ thin films by a closed-space sublimation (CSS) method on Si substrates. The CSS method is a vacuum evaporation technique[17,18] and has many advantages for the fabrication of low-cost solar cells; for example, it leads to a rapid growth rate, and the growth system is typically simple. As such, the CSS method is widely used in the fabrication of CdTe thin-film solar cells.

In the CSS method, the stoichiometric powder source and the substrate are placed a very small separation distance apart (a few millimeters) while the source is maintained at a higher temperature than the substrate. Parameters such as the source temperature and temperature differential are crucial for depositing high-quality films. The vapor pressures of Te and Cd are relatively close to each other. As such, control of the stoichiometry during the growth of CdTe by the CSS method is relatively easy. In contrast, the vapor pressures of Te and Ag/Ga are quite different, resulting in some difficulty in controlling the stoichiometry of prepared $AgGaTe_2$ films.

Crystallinity and stoichiometry of the deposited films were studied by x-ray diffraction (XRD) and transmission electron microscopy (TEM). The Cu K_α line was used, and the K_β line was minimized using a nickel K_β filter. In particular, the quality of the film was carefully considered at both macroscopic and microscopic levels. The TEM device (JEM-2100F, JEOL) uses energy-dispersive x-ray (EDX) mapping to resolve images on nanometer scale. This

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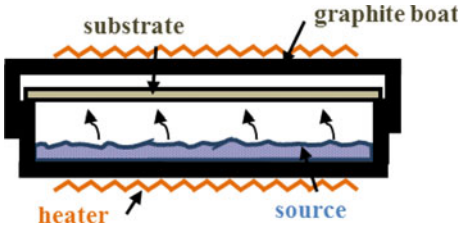

Fig. 1. Schematic of the CSS apparatus used for this study.

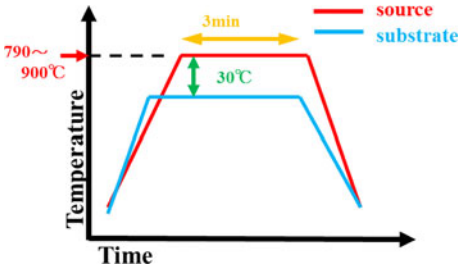

Fig. 2. Temperature schedule employed in this study.

was employed to analyze microscopic characteristics of the layer as well as the uniformity of the mole fraction.

EXPERIMENTAL PROCEDURES

Figure 1 shows a schematic view of the CSS apparatus used for this study. The source was stoichiometric powdered 4 N $AgGaTe_2$, and the substrate was (111)-oriented Si. The distance between the source and the substrate was set to 5 mm. The source material was placed facing the substrate surface, and they were sealed in a graphite boat. During the deposition, the graphite boat was placed in a vacuum furnace, which was pumped down to about 50 Pa. Figure 2 shows the temperature schedule for the source material and the substrate. The substrate was heated in advance to avoid unintentional deposition of material onto the substrate. For this stage of the study, the source temperature was mainly considered, being varied from 750°C to 900°C. The substrate and source temperatures were raised to their target temperatures within 5 min and 6 min, respectively. After the film deposition, both systems were rapidly cooled.

RESULTS AND DISCUSSION

θ–2θ profiles of $AgGaTe_2$ films and powders are compared in Fig. 3. The source temperature and the temperature differential for this particular sample were 810°C and 30°C, respectively. The only diffraction peak observed was for 112 $AgGaTe_2$ in the film, whereas various other diffraction peaks were observed from the starting material. From this, it is clear that $AgGaTe_2$ could be deposited on Si substrates by CSS. It should be noted that no strong peaks associated with Ga-Te compounds or Ag-Te

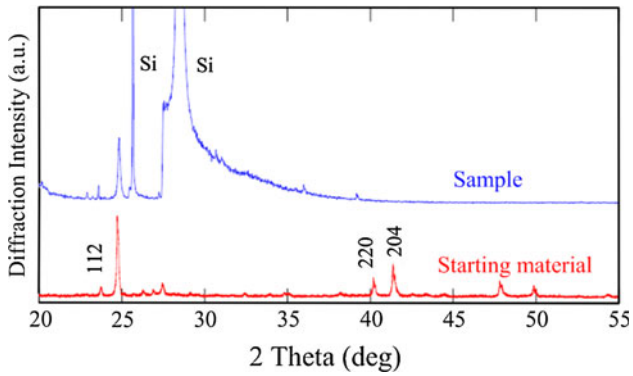

Fig. 3. XRD scans of the $AgGaTe_2$ film and the starting material. The abrupt background level change observed at around 27.5° is due to the absorption edge of Ni used for the K_β filter.

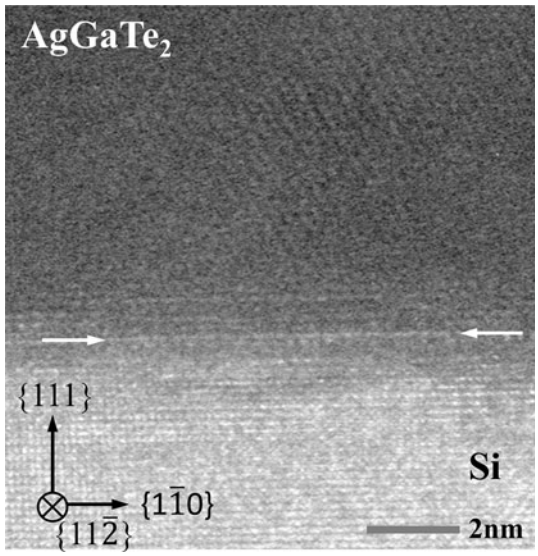

Fig. 4. High-resolution image of the $AgGaTe_2$/Si interface region. The interface is indicated by white arrows.

compounds were observed. Another interesting feature observed from the XRD scans is that films deposited on Si (111) have strong preference for (112) orientation.

A high-resolution image of the Si/$AgGaTe_2$ interface region is shown in Fig. 4. The sample was observed from a ⟨011⟩ direction. As can be seen from the figure, the $AgGaTe_2$ film shows lattice fringes trending in the same direction. Judging from the diffraction pattern at the interface region, the lattice mismatch between Si and $AgGaTe_2$ was about 12%, corresponding closely to the theoretical value. Figure 5 shows TEM–EDS images of the interface region with elemental mapping images. The TEM specimen was prepared using focused ion beam (FIB) etching, and, as such, Ga contamination cannot be ignored. The Ga signal was observed not only from the film but also from other areas. The mapping data were obtained from a relatively wide area of the substrate/epilayer interface to study the

uniformity across the film. Mapping images of elements demonstrate that Ag and Te atoms were homogeneously distributed in the film. Further study is ongoing to characterize the nanoscale segregation and disorder of the material prepared by CSS. Comparing the *Z*-contrast image[19,20] and the Si/Te mapping image, it is clear that the distribution of Si is limited to the substrate, and no Si signal was observed from the film itself. This result suggests that an abrupt interface was formed. The film was deposited for 3 min, and the TEM image indicated that the film thickness was about 120 nm, with surface roughness of about 80 nm. Although a rapid growth rate could be achieved by this method, further adjustment is needed to obtain smooth surfaces.

θ–2θ profiles of $AgGaTe_2$ films formed at different source temperatures are shown in Fig. 6. The peak associated with $AgGaTe_2$ was present only for source temperature between 790°C and 810°C. When the source temperature was below 790°C, congruent sublimation of the source material could not be achieved. The temperature range of 790°C to 810°C was appropriate for Ag and Ga to sublimate, and led to the formation of stoichiometric $AgGaTe_2$ layers. At temperatures above 830°C, Te may have detached from the substrate surface and $AgGaTe_2$ was not formed. The source temperature with the greatest amount of $AgGaTe_2$ formed was around 810°C.

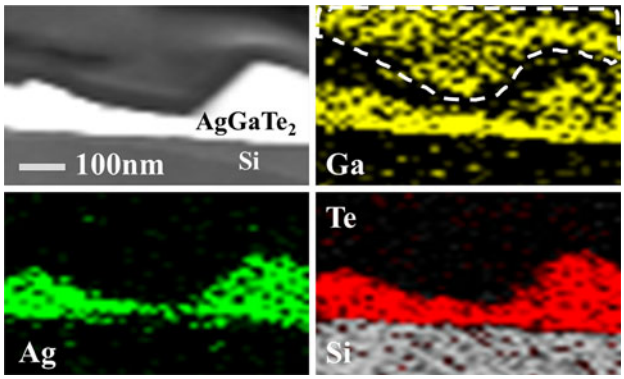

Fig. 5. TEM and elemental mapping images of $AgGaTe_2$: (a) *Z*-contrast image, (b) Ga distribution, (c) Ag distribution, and (d) Te and Si distributions. The bright spot in the elemental mapping image is associated with the location and density of the specific element. The Ga distribution image includes the artifact associated with the FIB (surrounded by the broken line).

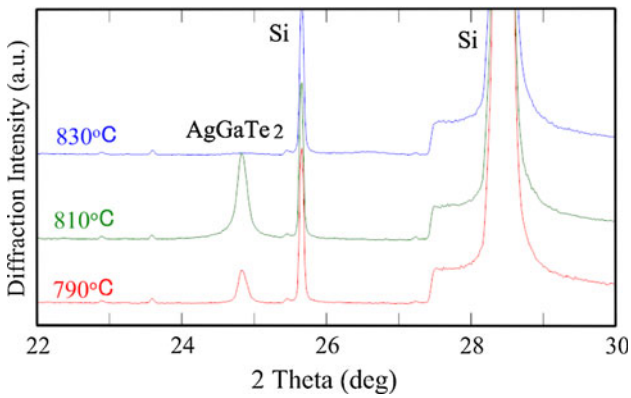

Fig. 6. XRD scans of $AgGaTe_2$ films grown at 790°C, 810°C, and 830°C.

CONCLUSIONS

It was found that $AgGaTe_2$ can be deposited on (111) Si substrates by using the CSS method. The optimal condition to grow $AgGaTe_2$ was source temperature of around 810°C. Deposited films were shown to have preferred orientation in the (112) plane. The quality of the deposited $AgGaTe_2$ layer was confirmed by XRD and TEM–EDX. In particular, The XRD data indicated that stoichiometric material was deposited, and the TEM–EDX data indicated reasonable film uniformity.

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REFERENCES

1. J. Li, Y.F. Zheng, J.B. Xu, and K. Dai, *Semicond. Sci. Technol.* 18, 611 (2003).
2. H.R. Moutinho, F.S. Hasoon, F. Abulfotuh, and L.L. Kazmerski, *J. Vac. Sci. Technol. A* 13, 2877 (1995).
3. T. Okamoto, Y. Harada, A. Yamada, and M. Konagai, *Sol. Energy Mater. Sol. Cells* 67, 187 (2001).
4. N. Romeo, A. Bosio, R. Tedeschi, A. Romeo, and V. Canevari, *Sol. Energy Mater. Sol. Cells* 58, 209 (1999).
5. C.S. Ferekides, D. Marinskiy, V. Viswanathan, B. Tetali, V. Palekis, P. Selvaral, and D.L. Morel, *Thin Solid Films* 361, 520 (2000).
6. J. Schaffner, M. Motzko, A. Tueschen, A. Swirschuk, H.J. Schimper, A. Klein, T. Modes, O. Zywitzki, and W. Jaegermann, *J. Appl. Phys.* 110, 064508 (2011).
7. M. Tsuji, T. Aramoto, H. Ohyama, T. Hibino, and K. Okura, *Jpn. J. Appl. Phys.* 39, 3902 (2002).
8. M.A. Contreras, B. Egaas, K. Ramanathan, J. Hiltner, A. Swartzlander, F. Hasoon, and R. Noufi, *Proc. Photovolt.* 7, 311 (1999).
9. S. Nishiwaki, T. Satoh, Y. Hashimoto, S. Shimakawa, S. Hayashi, T. Negami, and T. Wada, *Sol. Energy Mater. Sol. Cells* 77, 359 (2003).
10. J.M. Raulot, C. Domain, and J.F. Guillemoles, *J. Phys. Chem. Solids* 66, 2019 (2005).
11. T. Nakada, K. Migita, and A. Kunioka, *Jpn. J. Appl. Phys.* 32, L1169 (1993).
12. T. Nakada, R. Onishi, and A. Kunioka, *Sol. Energy Mater. Sol. Cells* 35, 209 (1994).
13. S.N. Rashkeev and W.R.L. Lambrecht, *Phys. Rev.* B63, 165212 (2001).
14. S. Arai, S. Ozaki, and S. Adachi, *Appl. Opt.* 49, 829 (2010).
15. R. Kumar and R.K. Bedi, *J. Mater. Sci.* 40, 455 (2005).
16. B.H. Patel and S.S. Patel, *Cryst. Res. Technol.* 41, 117 (2006).

17. Y.S. Tyan and E.A. Perez-Albuerne, *Proc. 16th IEEE Photovoltaic Specialists Conf.* (New York: IEEE, 1982), p. 794.
18. T.M. Ratcheva and I.D. Dragieva, *Phys. Stat. Sol.* 29, 579 (1975).
19. S.J. Pennycook and D.E. Jesson, *Acta Metall. Mater.* 40, S149 (1992).
20. E. Abe, Y. Kawamura, K. Hayashi, and A. Inoue, *Acta Mater.* 50, 3845 (2002).