Transactions of the Materials Research Society of Japan. Vol. 20

Se vapor pressure dependence of the solidifying points of I–III–VI_2 semiconductors (I = Cu, Ag; III = Ga, In)

H. Matsushita,[a] H. Jitsukawa[a] and T. Takizawa[a]*

[a]Department of Physics, College of Humanities and Sciences, Nihon University,
3-25-40 Sakura-Josui, Setagaya-ku, Tokyo 156, Japan

The $CuInSe_2$, $CuGaSe_2$, $AgGaSe_2$ and $AgInSe_2$ compounds have the solidifying points at 996, 1105, 850 and 775°C, respectively, when measured in evacuated ampoules. However, it is found that the solidifying points of $CuInSe_2$ and $CuGaSe_2$ decrease by more than 100° with increasing the Se vapor pressure up to 760 Torr, and that of $AgGaSe_2$ decreases by about 140° with increasing the Se vapor pressure up to 200 Torr and constant above 200 Torr. The solidifying point of $AgInSe_2$ decreases with increasing the Se vapor pressure less than 20 Torr and constant above 20 Torr.

1. INTRODUCTION

I-III-VI_2 group chalcopyrite semiconductors have potential for many kinds of optoelectronic devices. Among these materials, the selenides ($CuInSe_2$, $CuGaSe_2$ and $AgInSe_2$) are ones of the most promising materials for solar cells as absorbers, because they have the band gaps for the optimum conversion efficiency. Actually, to achieve a higher conversion efficiency of photovoltaic cells, high-quality thin films have been prepared by many methods. On the other hand, bulk crystals with high-quality enough to investigate the physical properties of the intrinsic defects have not been grown until now.

Recently, we have prepared bulk crystals, in particular, $CuInSe_2$ by the selenization horizontal Bridgman method under controlling Se vapor pressure.[1,2] Thereby, the Se content in $CuInSe_2$ bulk crystals could be to some extent controlled by Se vapor pressure. In addition, it was found that the solidifying point of $CuInSe_2$ is sensitive to the compositional deviation of Se from stoichiometry.[3] Therefore, it becomes essential to investigate the Se vapor pressure dependence of the solidifying points of those materials to grow high-quality single crystals under controlling Se vapor pressure. In this paper, we have investigated the solidifying points of $CuInSe_2$, $CuGaSe_2$, $AgGaSe_2$ and $AgInSe_2$ compounds by the differential thermal analysis (DTA) measurement with varying Se vapor pressure, using the electric furnace with two temperature zones.

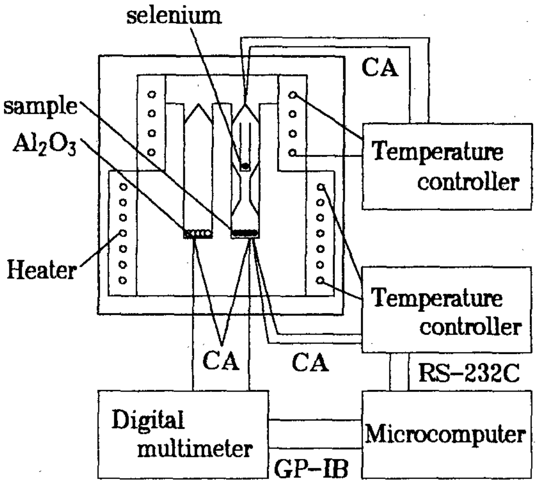

Figure 1. Schematic diagram of the system used for DTA under controlling Se vapor pressure.

2. EXPERIMENTAL PROCEDURE

The DTA system used in a previous work[4] was improved as shown in Fig. 1, to control Se vapor pressure. The electric furnace is controlled by a

---

*E-mail address: takiz@chs.nihon-u.ac.jp temperature controller (Ohkura EC5600). Al_2O_3 powder weighed about 0.3 g is used as a reference. The temperature difference between a sample and the reference material is directly measured by a thermocouple (CA). The DTA signals corrected by the known melting points of In, Sn, Zn, Al, Ag and Cu metals are recorded and processed in a microcomputer.

The starting materials, the mixtures of respective compositional elements weighed about 1 g, and additional Se element were sealed and separately set at opposite ends in a quartz tube of $7mm^{\phi} \times 170mm$ under vacuum. The mixtures were first heated to the temperatures above 50~100°C of the melting point of the respective compounds,[5-8] and then solidified. The samples set in the bottom zone were heated and cooled by the rate of 2°/min, and the top zone was held at a temperature corresponding to the desired Se vapor pressure. The temperatures of the phase transitions were determined from the extrapolated onsets of DTA peaks in the heating and cooling process.

The products synthesized after the DTA measurements were confirmed to have the chalcopyrite structure of single phase by the powder X-ray diffraction measurement at room temperature.

3. RESULTS AND DISCUSSION

Figures 2, 3, 4 and 5 show DTA curves of $CuInSe_2$, $CuGaSe_2$, $AgGaSe_2$ and $AgInSe_2$ compounds, respectively, under applying the typical Se vapor pressures in the heating and cooling processes, where those measured in evacuated ampoules (expressed as "vacuum") were also shown. The solidifying points of $CuInSe_2$, $CuGaSe_2$, $AgGaSe_2$ and $AgInSe_2$ compounds without applying the Se vapor pressure are confirmed to be at 996, 1105, 850 and 775°C, respectively.

The extrapolated onset of DTA peaks in the heating process disagreed with that in the cooling process when high Se vapor pressure were applied as shown in Figs. 2 and 4, indicating the effect of suppercooling. Therefore, in the case of high Se vapor pressure, the solidifying points were determined from only the heating process. In contrast to $CuInSe_2$, $CuGaSe_2$ and $AgGaSe_2$, the DTA peak of $AgInSe_2$ for the heating process differs with that for the cooling process above 10

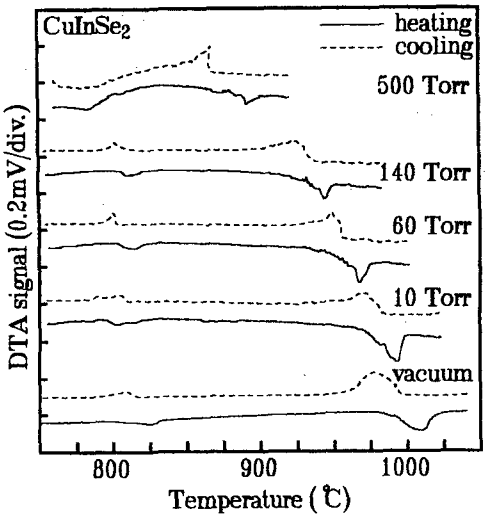

Figure 2. DTA curves of $CuInSe_2$ for the heating and cooling processes with and without Se vapor pressure.

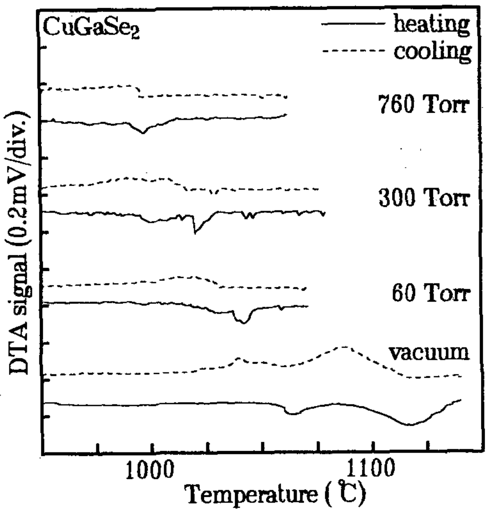

Figure 3. DTA curves of $CuGaSe_2$ for the heating and cooling processes with and without Se vapor pressure.

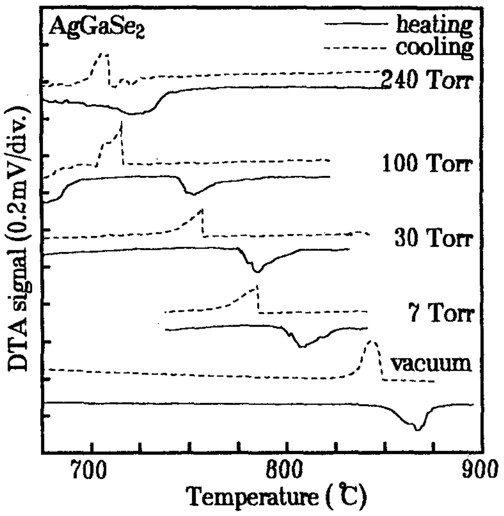

Figure 4. DTA curves of $AgGaSe_2$ for the heating and cooling processes with and without Se vapor pressure.

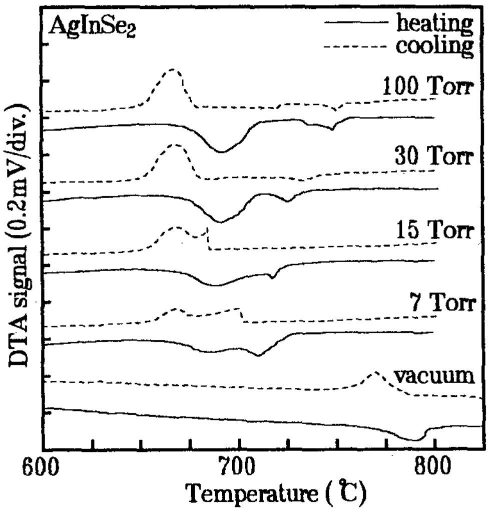

Figure 5. DTA curves of $AgInSe_2$ for the heating and cooling processes with and without Se vapor pressure.

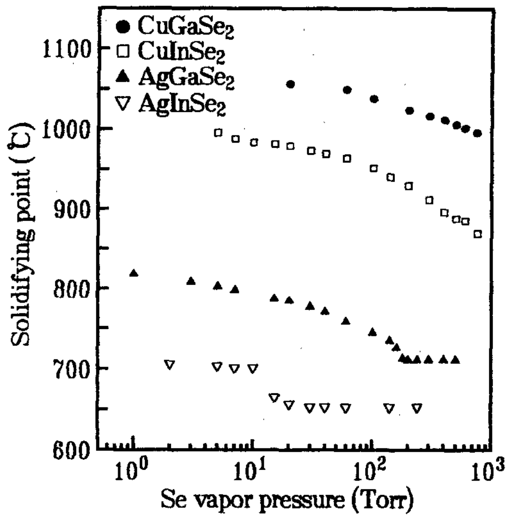

Figure 6. The solidifying points of $CuInSe_2$, $CuGaSe_2$, $AgGaSe_2$ and $AgInSe_2$ compounds as a function of Se vapor pressure.

Torr, so that the solidifying points were determined from only the cooling process in this work. Figure 6 shows the Se vapor pressure dependence of the solidifying points of $CuInSe_2$, $CuGaSe_2$, $AgGaSe_2$ and $AgInSe_2$ compounds.

The solidifying point of $CuInSe_2$ (at 996°C without Se vapor pressure) decreases by about 130° with increasing the Se vapor pressure up to 760 Torr. The melting points reported by other authors[3,5-10] were scattered between 986 and 1000°C. This might be caused by the facts that the respective measurements were performed under the different conditions, in particular, under different Se vapor pressures. The phase transition point from chalcopyrite to sphalerite structure has known to decrease down to about 750°C with increasing the Se composition.[3] However, the transition point is seen to be almost fixed at about 820°C with varying the Se vapor pressure, as shown in Fig. 2. Thus, the compositional deviation from stoichiometry is not so great as to produce the heterogeneous phases in the $CuInSe_2$ phase. That is, the variation of the solidifying point is mostly due to the Se vapor pressure. The $CuInSe_2$ crystals grown under applying a Se vapor pressure more than 50 Torr could not be measured by the Hall effect at low temperature owing to noisy signals.[1] The reason is that the temperature width of the temperature gradient zones of our growing furnace missed the solidifying point when a Se vapor pressure more than 50 Torr was applied.

In the heating and cooling processes without applying Se vapor pressure, two DTA onset points of $CuGaSe_2$ were observed at 1105°C and 1055°C. These are ascribed to the melting, i.e., $CuGaSe_2$ (sphalerite): solid $\rightarrow$ liquid and phase transition, i.e., $CuGaSe_2$ (chalcopyrite) $\rightarrow$ $CuGaSe_2$ (sphalerite) + liquid. It is seen that the solidifying point decreases by about 100°C with increasing the Se vapor pressure up to 760 Torr. As already stated in the case of $CuInSe_2$, this is why the data of the melting and phase transition points so far reported by other authors[5,7,8,11,12] differed with each other. On the other hand, the transition point was found to disappear above 300 Torr. Consequently, it might be possible to precipitate the $CuGaSe_2$ chalcopyrite single phase under the higher Se vapor pressure.

The $AgGaSe_2$ compound has the solidifying point at 850°C but no phase transition point was observed in this work, which are in agreement with the data reported by other authors.[6–8,12] The solidifying point of $AgGaSe_2$ decreases by about 140° with increasing the Se vapor pressure up to 200 Torr but keeps a constant value of about 710°C above 200 Torr. Based on the phase diagram of the Ag_2Se–Ga_2Se_3 system,[12] it is expected that the DTA peak of about 710°C is due to the precipitation of the Ag_2Se phase from liquid phase. Therefore, it is necessary to apply a Se vapor pressure less than 200 Torr to form the $AgGaSe_2$ single phase.

The solidifying point of $AgInSe_2$ decreases with increasing the Se vapor pressure less than 20 Torr but keeps a constant value of about 655°C above 20 Torr. In contrast to $CuInSe_2$, $CuGaSe_2$ and $AgGaSe_2$, the difference in the DTA curves for the heating and cooling process above 10 Torr may be due to the decomposition of the liquid phase. However, the origin is not clear at this stage. For the time being, it might be recommended to apply a Se vapor pressure less than 10 Torr to form the $AgInSe_2$ single phase.

4. CONCLUSION

We have investigated the Se vapor pressure dependence of the solidifying points of $CuInSe_2$, $CuGaSe_2$, $AgInSe_2$ and $AgGaSe_2$ compounds. It is found that the solidifying points of $CuInSe_2$ and $CuGaSe_2$ decrease by more than 100° with increasing the Se vapor pressure up to 760 Torr, and that of $AgGaSe_2$ decreases by about 140° with increasing the Se vapor pressure up to about 200 Torr but is constant above 200 Torr. The solidifying point of $AgInSe_2$ decreases with increasing the Se vapor pressure less than 20 Torr and keeps a constant value above 20 Torr.

In conclusion, in the case of growing the bulk crystals by the selenization horizontal Bridgman method where the temperature profile is moved electrically, it is necessary to determine the optimum temperature width of the temperature gradient zones under the respective Se vapor pressures to grow high-quality single crystals.

REFERENCES

1. H. Matsushita, T. Suzuki, S. Endo and T. Irie, Jpn. J. Appl. Phys., 34 (1995) 3774.
2. H. Matsushita and T. Takizawa, J. Cryst. Growth, 160 (1996) 71.
3. M. L. Fearheiley, Sol. Cell, 16 (1986) 91.
4. H. Matsushita and T. Takizawa, Jpn. J. Appl. Phys., 34 (1995) 4699.
5. H. Matsushita, S. Endo and T. Irie, Jpn. J. Appl. Phys., 30 (1991) 1181.
6. A. Zunger, Appl. Phys. Lett., 50 (1987) 164.
7. I. V. Bodnar, B. V. Korzun and A. P. Chernyakova, Phys. Status Solidi A, 101 (1987) 409.
8. L. A. Mechkovski, S. A. Alfer, I. V. Bodnar and A. P. Bologa, Thermochimica Acta, 93 (1985) 729.
9. K. J. Bachmann, H. Goslowsky and S.Fiechter, J. Cryst. Growth, 89 (1988) 160.
10. L. S. Palatnik and E. I. Rogacheva, Sov. Phys. -Doklady, 12 (1967) 503.
11. J. C. Mikkelsen, Jr, J. Electron. Mater. 10 (1981) 541.
12. L. S. Palatnik and E. K. Belova, Sov. Phys. -Inorg. Mater., 3 (1967) 1914.