Study on precipitates in AgGaSe$_2$ single crystal grown by vertical gradient freezing method

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Abstract

In this study, AgGaSe$_2$ single crystal was successful grown by vertical gradient freezing method. Meanwhile, the precipitates on AgGaSe$_2$ single crystal were investigated by x-ray photoelectron spectroscopy (XPS). This technique was recommended as a practicable method to study the precipitates while they are difficult to be detected by other measurements owing to their components and fairly low content. In addition, Energy Disperse Spectroscopy (EDS) and x-ray diffraction (XRD) were employed to characterize the quality of the as-grown AgGaSe$_2$ single crystal. The EDS results indicate a slight deviation from stoichiometric ratio along growth defects. The XRD results manifest that AgGaSe$_2$ crystal has single phase and high purity. The XPS results indicate that precipitates exist on as-grown AgGaSe$_2$ single crystal mainly in the form of Ga$_2$Se$_3$. Ga$_2$O$_3$ and Ag$_2$O were detected by XPS on the polished surface of the as-grown crystal wafer which was regarded as an oxide layer. The study on precipitates may provide important reference for growth process improvement and post-treatment to obtain high quality AgGaSe$_2$ single crystal.

1. Introduction

Silver gallium selenide (AgGaSe$_2$) is an I–III–VI$_2$ ternary semiconductor compound with chalcopyrite structure [1, 2]. It is one of important infrared nonlinear optical semiconductor materials with advantages of large birefringence, large nonlinear optical coefficient ($d_{36} = 43 \times 10^{-12}$ m V$^{-1}$), and wide mid-infrared transmission range (0.7 $\sim$ 21 $\mu$m) [3, 4]. These properties make AgGaSe$_2$ single crystals to be appropriate for applications in difference frequency generation [5–7], second harmonic generation [8] and optical parametric oscillators (OPO) [9–11].

However, it is difficult to obtain high quality large size AgGaSe$_2$ single crystals that may be associate to the growth defects in AgGaSe$_2$ single crystal [12]. It was reported that the existence of such defects as cracks [13], microscopic scattering center [14], intrinsic defects [15, 16], and precipitates [17, 18] may be harmful to AgGaSe$_2$ single crystals optical properties. Therefore, the study of defects may provide important information how to obtain high quality AgGaSe$_2$ single crystals. For generality, it could be mentioned that the precipitate formation was earlier observed and studied in several other chalcogenide crystals [19, 20]. However, there are a few reports concerning AgGaSe$_2$ precipitates because they are hard to be characterized. On the one hand, the content of precipitates is fairly low which is lower than the common XRD measurements allowed error (usually 1%). On the other, precipitates may exist in the form of binary compound such as Ga$_2$Se$_3$ and Ag$_2$Se which may be derived from AgGaSe$_2$ during the growth process. Therefore, it is difficult to characterize the precipitates by the XRD and EDS measurements.

In this study, XPS was employed to characterize the precipitates in AgGaSe$_2$ single crystal grown by vertical gradient freezing method. For the same kind element, the surrounding atoms difference will lead to a binding energy difference which can identify the variety of the precipitates and the intensity of the peak can even calculate the content of them.

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2. Methods

AgGaSe$_2$ polycrystalline materials were synthesized directly from high purity (99.9999%) Ag, Ga and Se element by means of two temperature vapor transport method [21, 22]. AgGaSe$_2$ single crystals were grown using vertical gradient freeze (VGF) method from polycrystalline materials. The AgGaSe$_2$ polycrystalline materials were ground into powder in an agate mortar and then it was insert into the quartz ampoule which was sealed and evacuated under $1 \times 10^{-4}$ Pa. The quartz ampoule was put into the three temperature zone growth furnace, and the seed part was located at the temperature gradient area. The upper zone temperature was slowly increased to 950 °C, the bottom zone to 750 °C, and the temperature gradient was 20 °C cm$^{-1}$, as shown in figure 1. Then the temperature at the setting point was hold for 24 h in order to melt the solid completely. Crystal growth start by the cooling process of the temperature which were decreased gradually from seed part to melt zone until the ingot temperature reaches 750 °C. After growth, the whole furnace was cooled by 30 °C h$^{-1}$ to room temperature. A wafer was cut from the as-grown ingot and polished for XPS measurements.

The infrared micrograph of as-grown AgGaSe$_2$ single crystal wafer is shown in figure 2 and growth defect can be obviously seen, as shown by marking red line a. The EDS test along lines a (shown in red) and b (blue) were carried out. The optical microscope photograph of the polished wafer surface is displayed in figure 3.
3. Results and discussion

3.1. XRD analysis

A small piece of as-grown AgGaSe$_2$ single crystal was ground into powders for XRD test use. Then, the powders were measured by XRD using Cu radiation ($\lambda = 0.154184$ nm). The x-ray generator run at 40 kV, 20 mA in recording the x-ray diffraction patterns, the scanning rate was 0.06° s$^{-1}$, and the 20 range was from 10° to 90°. The obtained pattern is shown in figure 4. The XRD analysis indicates that no other precipitate phases such as Ag$_2$Se and Ga$_2$Se$_3$ are detected and the pattern of AgGaSe$_2$ single crystal sample is in good agreement with the standard XRD pattern (PDF No. 31-1240).

3.2. Composition analysis

The elemental composition was measured by EDS on the polished wafer surface along lines a and b, as shown in figure 2. The test allowed error is 1% and the results are shown in table 1. According to the results, it can be seen that line b has a good stoichiometric ratio which are close to the ideal stoichiometric ratio (1:1:2).

However, comparing with line b, line a has a slight deviation from stoichiometric ratio. The Ag content at line a is lower by 2.71% than that at line b, and the Ga and Se contents at line a are higher by 1.38 and 1.33%, respectively, than those at line b. In addition, in AgGaSe$_2$ single crystal, the content of Se can not higher than 50% because it is easy to volatile at high temperature during polycrystalline synthesis and single crystal growth.

Figure 3. Optical microscope photograph of the polished wafer.

Figure 4. XRD pattern of the AgGaSe$_2$ powder in comparison with several other standard XRD patterns. (From top to bottom: AgGaSe$_2$ sample, AgGaSe$_2$, Ag$_9$GaSe$_6$, Ga$_2$Se$_3$, Ag$_2$Se, GaO$_2$, and Ag$_2$O standard XRD patterns.)
progress. The reason for the deviation of line a may be the existence of Ga₂Se₃ which may lead to a higher content of Ga and Se in AgGaSe₂ single crystal.

3.3. XPS analysis

The XPS test were carried out on the outside surface of polished AgGaSe₂ wafer. The XPS measurements were carried out with an ESCALAB 250Xi spectrometer with the use of monochromatic Al-Kα source, vacuum lower than $5 \times 10^{-10}$ mbar and the optimal energy resolution of 0.43 eV. The energy scale was calibrated in reference to C 1s core level assigned at 284.8 eV.

The recorded Ag 3d, Ga 3d, Se 3d and O 1s XPS spectra are displayed in figures 5–8, and the fitting curves are given by color. The results manifest that the obtained ingot consist of several components including AgGaSe₂,

| Sample element | Line a (at%) | Line b (at%) |
|----------------|-------------|-------------|
| Ag             | 22.25       | 24.96       |
| Ga             | 26.63       | 25.25       |
| Se             | 51.12       | 49.79       |
| Ratio (Ag:Ga:Se) | 1.00:1.20:1.92 | 1.00:1.01:1.99 |

Table 1. Composition of line a and b on the wafer.
precipitates and oxides and it is in disagreement with the XRD results. The comparison of binding energies of the sample and references manifest that binding energy of all detected components are generally in agreement with references, except gallium compounds of Se 3d5/2 (Ga2Se3) and Ga 3d, O1s (Ga2O3), as shown in table 2.

The fitting curves of high resolution Ag 3d doublet acquired on the surface of AgGaSe2 wafer are displayed in figure 5. As seen, the spectrum can be fitted to three components with different intensities. The most intense components at 374.5 and 368.5 eV are attributed to the Ag 3d5/2 and Ag 3d3/2 lines of AgGaSe2 single crystal and they are shown in red color. The components at 374.0 and 367.9 eV are attributed to the presence of Ag2O and they are shown in blue color. The third set of component at 375.2 and 369.0 eV, as shown in green, is assigned to of Ag2Se appeared during the AgGaSe2 single crystal growth. In addition, the measured binding energy of Ag 3d5/2 is close to the references value, as shown in table 2. The little difference in binding energies of Ag 3d lines between our measurements and references may be owing to that atoms around Ag are different in different compounds measured in the experiments.

In figure 6, the fitting curves for high resolution Ga 3d XPS spectrum acquired on the polished outer surface of AgGaSe2 single crystal sample are displayed.

From the fitting curves, the spectrum may be fitted by three components of different intensities. The most intense component at 20.1 eV corresponds to the Ga 3d signal from the AgGaSe2 bulk, as shown in red. At 19.1 eV, other component of Ga2Se3 appears as shown in blue, which may be formed as precipitates during the process of AgGaSe2 single crystal growth. It can be note that at 21.3 eV, a third component appears as shown in green, which is attribute to the existence of Ga2O3. Beside, according to NIST database (table 2), it can be note that there is a significant difference in binding energy value for Ga 3d of Ga2O3 between references.
(20.2–20.9 eV) and measured value (21.3 eV). The reason for the disagreement may be that the difference of atoms around Ga would result in different electronegativity (O > Se > Ga > Ag). For one element measured by XPS method, value of binding energy is in reference to electronegativity that result from atoms around, the less electronegative it is, the smaller the binding energy values is. Therefore, for Ga 3d in Ga2O3, a binding energy value shifted to 21.3 eV occurred.

The fitting curves for high resolution Se 3d XPS spectrum are displayed in figure 7. As seen, the Se 3d spectrum might be fitted to three components of different intensities. The most intense component located at 54.4 eV corresponds to the signal owing to the existence of the AgGaSe2 bulk, as shown in red. The other component located at 55.6 eV, as shown in green, is attributed to the existence of the Ga2Se3 precipitates which is consistent with the analysis of Ga 3d spectrum. At 52.9 eV, a third component arises, as shown in blue, that is due to the existence of AgSe which is in agreement with the results of analysis of Ag 3d spectra. In addition, the high intensity fitting curves of Ga2Se3 indicate a high content of precipitate which is not in agreement with XRD result. The reason for the disagreement may be that the measuring depth of the XPS can reach no more than 10 nanometer on the outer surface of the wafer while the XRD can reach to the micron scale. It indicate that XRD results can reflect the whole ingot phase information, and the XPS method can only provide a partial information of the wafer layer. Therefore, Ga2Se3 and AgSe may exist on the AgGaSe2 local region as precipitates produced during growth progress. And the content of precipitates analyzed by XPS may only reflect partial information of the wafer, not the whole AgGaSe2 ingot.

The high resolution O 1s XPS spectrum with fitting curves is displayed in figure 8. The O 1s spectrum might be fitted to three components of different intensities. The most intense component at 531.4 eV corresponds to the signal owing to the adsorbed oxygen on the outer-surface of AgGaSe2 wafer. The component located at 530.4 eV and shown in blue is attributed to the existence of the Ag2O which is consistent with the analysis of Ag 3d spectrum. At 52.9 eV, a third component arises, as shown in green, that is due to the existence of Ga2O3 which is in agreement with the results analysis of Ga 3d component. In addition, the intensity of fitting curves corresponding to Ga2O3 and Ag2O are fairly low indicating an extremely low content of oxides. In general, the oxides observed on the outer-surface of the sample are considered to be an oxide layer which could be removed by mechanical polishing.

### 4. Conclusions

The XRD results indicate that single phase AgGaSe2 crystal was successfully obtained using VGF method. The EDS manifest a slight deviation from stoichiometric ratio along growth defects which may due to Ga2Se3 precipitates. According to XPS analyses, the precipitates mainly present in the forms of Ga2Se3 and a much lower content of AgSe which have not been detected by XRD because of its fairly low content. Ga2O3 and Ag2O oxides were detected on the outer-surface of the sample as an oxide layer. This study provides a targeted reference to reduce or even eliminate precipitates in the as-grown AgGaSe2 single crystal by post-processing treatment.

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| Table 2. Values from measurements and literature (eV) [23–30]. |
|-----------------|-----------------|-----------------|
| Binding energy components | Obtained values (eV) | References (eV) |
| Ag 3d | Ag2O | 367.9 | 367.7, 368.2 |
| | Ag2Se | 369.0 | 369.0, 367.8 |
| | AgGaSe2 | 368.5 | 368.4 |
| Ga 3d | Ga2O3 | 21.3 | 20.2, 20.9 |
| | Ga2Se3 | 19.1 | 19.7, 19.9 |
| | AgGaSe2 | 20.1 | — |
| Se 3d | Ga2Se3 | 55.6 | 54.5, 54.9 |
| | AgSe | 52.9 | 53.8 |
| | AgGaSe2 | 54.4 | 54.7 |
| O 1s | Ag2O | 530.4 | 529.2–530.9 |
| | Ga2O3 | 532.3 | 529.8–531.3 |
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