# Annealing Effect of Amorphous Gallium Selenide Thin Films

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**Abstract**

Annealing effects of GaSe thin films prepared by flash evaporation were investigated using optical transmission measurement, photoacoustic (PA) spectroscopy, microscopy, and X-ray diffraction technique.

As-deposited films have amorphous structure and their PA signals showed strong absorption in the range from 300 to 800 nm. With the increase of annealing temperature the optical transmission increased abruptly due to the nucleation and growth of spherulites. After further annealing the PA spectra of the crystallized films were resembling the PA spectrum of a single crystal more and more and showed the clear absorption edge near 2.0 eV.

Thus, by the annealing of the as-deposited films a number of the localized levels in the band gap have been removed.

## 1. INTRODUCTION

Gallium selenide, GaSe, is a layered Ⅲ-Ⅵ type semiconductor with a hexagonal crystal structure. The crystal is composed of fourhold layer in the stacking sequence of Se-Ga-Ga-Se[1]. In recent years layered semiconductors, such as GaSe, have been investigated considerably because of the strong anisotropic properties and the intercalating behavior.

So far several studies on GaSe thin films have been reported[2),3),4)]. Thomas[2] studied the structure of the films deposited by the ordinary evaporation method using X-ray diffraction and transmission electron microscopy techniques. Persin et al.[3] made the polycrystalline films by the three-temperature method and reported the structural, electrical and optical properties of the films. Hashimoto and Suzuki observed the dynamical growth of spherulites in the moment when the amorphous films by flash evaporation were subjected to the heating at a constant temperature[4].

In the present paper the annealing effects of the thin films prepared by flash evaporation[5] have been investigated. The behavior from amorphous to crystalline transition at an elevated temperature has been observed by the optical transmission measurement. The growth of spherulites has been visually inspected by microscopical observation. The structure of the as-deposited films and annealed films has been studied by X-ray diffraction technique.

The measurements of the PA spectra in GaSe bulk have been reported by many authors. Baldassarre and Cingolani have measured the PA spectra in GaSe bulk in the region of higher energy than the fundamental energy gap[6]. Todorovic and Nikolic have observed the exciton effect in GaSe with PA spectroscopy[7]. And Ikari et al. have obtained PA spectra of GaSe below room temperature by using piezoelectric transducers[8]. For this thin films, however, the measurement of the PA spectroscopy

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has never been performed.

Hence, we have applied the PA spectroscopy measurements for the thin films and have shown that the PA spectroscopy for the films also is a powerful tool.

## 2. EXPERIMENTAL

Method of flash evaporation was employed for the preparation of GaSe thin films. Substance chipped GaSe single crystal was used as the source material. The GaSe was first synthesized from Ga (5N) and Se (5N) and then grown into a single crystal by the Bridgman method. The thin films were deposited on glass substrates kept at room temperature. After the evaporation the films were annealed in vacuum at a heating rate of 10℃/min from room temperature to 600℃. During the annealing the transmitted light through the film was measured. A mercury lamp is used as the light source and the transmitted light is detected by a photomultiplier. The temperature of the films was monitored by a thermocouple in contact with the substrate. Both the temperature of the film and output of the photomultiplier were recorded by a multi-pen recorder. The pressure in the belljar was kept under $6.7\times10^{-4}$Pa during the experiments. The details of the preparation of GaSe thin films and the arrangement of experimental apparatuses have been described in our previous paper[5].

The films thickness was measured by a multiple-beam interferometer (Mizojiri Type Ⅱ). The structure of the film was analyzed by an X-ray diffractometer (radiation of CuK$\alpha$, Rigaku ROTAFLEX RU-200) and the crystallized film with a spherulite structure was checked by the microscopic observation .

The absorption edge of the films was analyzed by a PA spectrometer. In this apparatus a Xe lamp (Ushio 300 W) was used as the light source. The surface of the films was perpendicularly illuminated with chopped (80Hz) monochromatic light in the range from 300 to 800 nm. The PA signals were detected by a microphone and were calibrated by that of carbon black.

## 3. Results and Discussion

Figure 1 shows a typical optical transmittance curve of the as-deposited films of GaSe annealed at a heating rate of 10℃/min. Measurements were performed on the films of different thicknesses ranging from 220 to 900 nm. The optical transmission behavior, however, was nearly independent of the film thickness except for that the transmission decreased with the increase of thickness. It is seen from the figure that there are three distinct temperature regions for the transmittance in the process of temperature elevation. In the first region the transmittance is low, and almost constant but decreases slightly with increasing temperature. The second region is a part where the transmission increases rapidly around about 350℃. In the third region it is high and increases slowly with temperature and begins to rise again near 550℃.

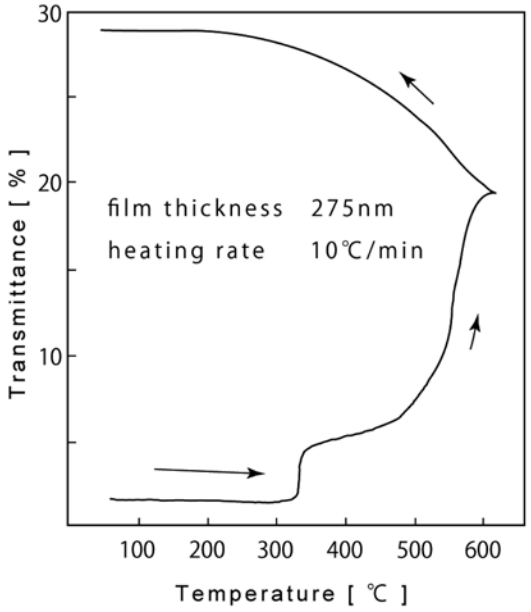


Fig. 1. Typical optical transmittance curve of the as-deposited films of GaSe annealed at a heating rate of 10℃/min.

With decreasing temperature from 600℃ the transmittance of the film gradually increases. This behavior is considered that the transition (from amorphous to crystal) of the film has carried out and reevaporation from the film surface has occured.

Diffraction patterns shown in Fig. 2 show the change of the structure of the films in these three regions. In this figure the diffraction pattern of the powder of GaSe bulk is also shown to be compared with that of the films (Fig. 2(a)). The peaks were indexed based on a hexagonal lattice given by Wyckoff[9]. As shown in Fig. 2(b), no peaks are

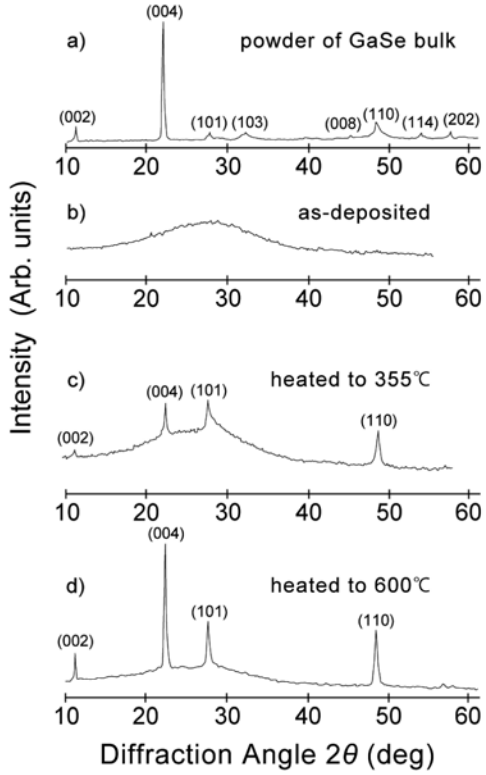


Fig. 2. X-ray diffraction patterns of powder of GaSe bulk and thin films.
a) powder of GaSe bulk, b) as-deposited film, c) film heated to 355℃, d) film heated to 600℃.

observed in the pattern of the as-deposited film suggesting that it has amorphous structure. The diffraction pattern of the film heated up to 355℃ consists of four peaks corresponding to the reflections from the basal planes (0 0 2), (0 0 4), (1 0 1), and (1 1 0). It is superimposed on the amorphous pattern showing the beginning of the crystallization of the film (Fig. 2(c)). Here the film has begun to crystallize.

The pattern of the film heated up to 600℃ also shows four peaks corresponding to the reflections from the same planes as described above. The reflections give sharper and more intense peak than those of the previous film (Fig. 2(d)). Thus, the annealing effect reduces structural defects in the films and improves the crystallinity.

Thomas[2] and Persin et al.[3] have reported that the films consisted of the crystallites with their c axes oriented normal to the plane of the substrate. In contrast, Hashimoto and Suzuki have reported that the c axes are formed finely along the radial direction

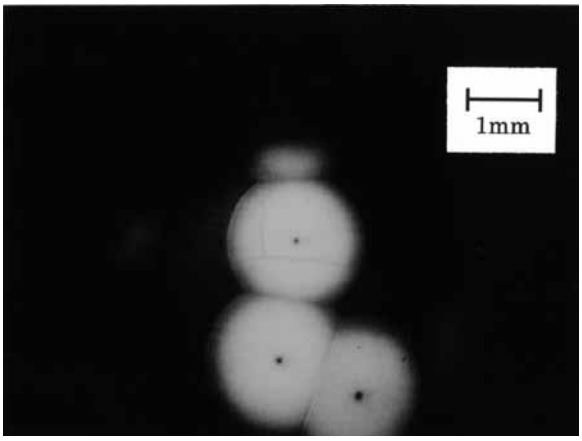


Fig. 3. Micrograph of the GaSe thin film which the spherulites are growing.

of the spherulites[4]. This difference seems to be due to different methods in evaporation and annealing. In crystallized films obtained by us the diffraction patterns do not show as the former reports.

Figure 3 shows a micrograph of the film for which the annealing was stopped on the way the optical transmission started to increase abruptly. Here spherulitic crystallites (in the white part) appear on a homogeneous background of amorphous film (in the dark part). Thus, the start of the increase of the transmission implies the generation of the crystal nucleus. Following this the nucleation and growth of the spherulites caused the transmission to increase rapidly. The end of rapid increasing shows that a whole film has been covered by the spherulites grown.

The nuclei of the spherulite appear at random in the amorphous region. This is homogeneous nucleation. The growth stopped on a common boundary where spherulites touched each other. The boundary lines are nearly straight showing that the growing rate is constant, as reported by Muller[10].

Figure 4 shows the behavior of the optical transmission vs. annealing time at constant temperatures in the region where the transmission increased rapidly. The figure is illustrated as that the substrate temperatures are parameter and the values of the intensity of transmitted light are normalized by that of the saturated intensity of transmitted light. As seen in the figure, the time required for the nuclei generation become short with the increase of the substrate temperature. Assuming that there is no

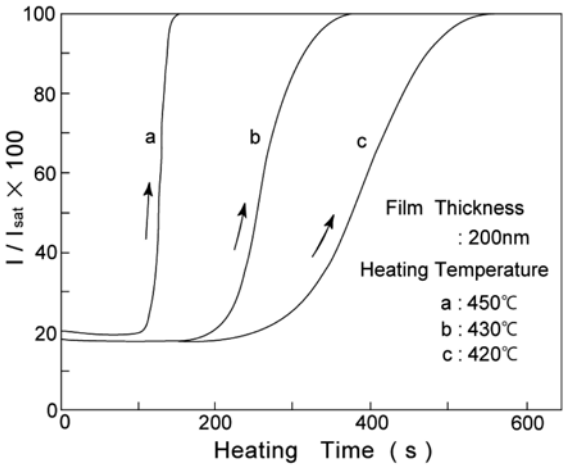


Fig. 4. Heating time dependences of optical transmission. The values of transmission are normalized by that of the saturated intensity of transmitted light .

time lag in formation of nuclei and the transmission is proportional to the area of the spherulites, it increases parabolically in the start as shown in curves of b and c in Fig. 4. At the stage when the whole film is crystallized into the spherulites, once the transmission saturates. The feature described above is in accord with that obtained at a lower annealing temperature. In higher the transmissions show exponential increasing. This seems to be due to continuous nucleation during the annealing and to a large growing rate.

Figure 5 shows the normalized PA spectra of the GaSe films and the single crystal near the absorption edge of GaSe. The absorption edges were deduced from the position of the knees in the PA spectra[11]. In Fig. 5(e) the absorption edge energy of the single crystal was found to be about 2.0 eV, as is in good agreement with the reported value[12]. The PA spectra of the as-deposited films, however, show strong absorption and the band edges do not appear clearly (Fig. 5(a)). The PA spectra of the crystallized films became to show clearly the absorption edge at 2.0 eV and the films became to transmit the light at a lower energy than that of the absorption edge (Fig. 5(c) and (d)).

Therefore the absorption in the lower energy side of the amorphous films is considered to be due to a number of the locallized levels in the band gap formed by the structural defects and these levels are removed by annealing. In the first region of the

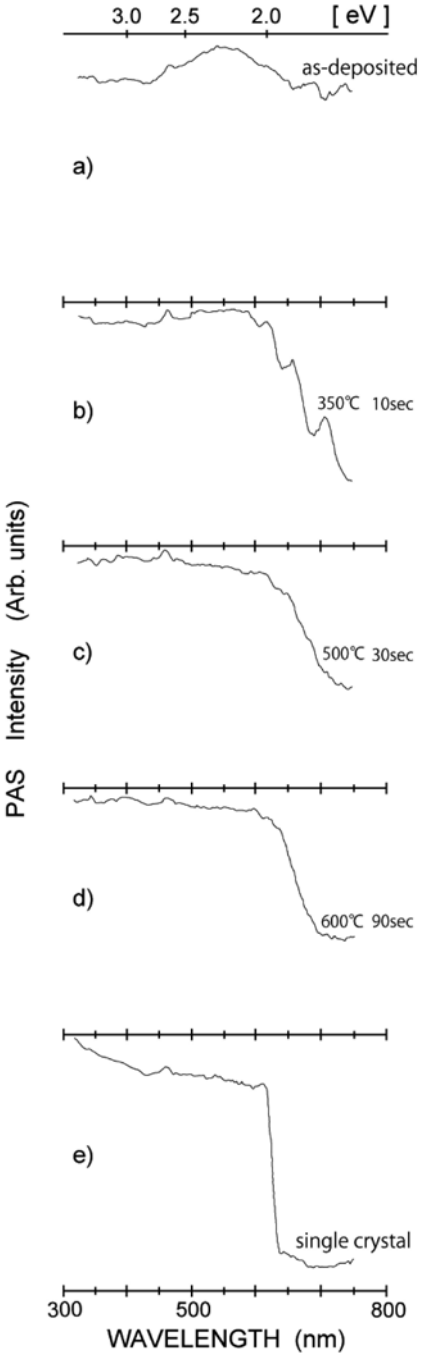


Fig. 5. PA spectra of GaSe thin films and the single crystal.
a) as-deposited film, b) film annealed at 350℃, c) film annealed at 500℃, d) film annealed at 600℃, e) single crystal.

transmission measurements, the slow decreasing seems to be related to the temperature dependence of the optical gap energy in an amorphous inherence but the structural imperfections are not reduced. In the third region the PA signals rise steaply in near the absorption edge with annealing. The PA spectra

tend to be like that of the single crystal. It was found that the crystallinity of the films still improved in this region since the transmission increased slowly with annealing temperature. The transmission rise at nearly 600℃ is considered to be due to the reevaporation from the film surface.

In addition, we note that the PA spectrum of a film annealed at 350℃ has been observed to increase in a step-like manner with a few local maxima in the lower energy region (Fig. 5(b)). This appears to be due to multiple reflection interference effects[13]. It is necessary to further examine the reflection measurement for the sample in the future.

## 4. Conclusion

Annealing effects of amorphous GaSe thin films prepared by flash evaporation were investigated. By thermal annealing the films have reduced structural defects and have improved the crystallinity. And a number of the localized levels in the band gap have been removed.

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## References

1) A. Kuhn, A. Chevy and R. chevaller: phys. stat. sol. (a) 31 (1975) 469.
2) M. B. Thomas: Thin Solid Films 8 (1971) 273.
3) M. Persin, A. Persin, S. Popovic and B. Celustka: Thin Solid Films 20 (1974) 75.
4) H. Hashimoto and H. Suzuki: Jpn. J. Appl. Phys. 21 (1982) L783.
5) H. Nishimura, T. Okada, H. Suzuki, K. Nagata, Y. Miyamoto, and T. Ikari: Fukuoka Univ. Sci. Rep. 19 (1989) 93.
6) L. Baldassarre and A. Cingolani: Solid State Commun. 44 (1982) 705.
7) D. M. Todorovic and P. M. Nikolic: Applied Optics 24 (1985) 2252.
8) T. Ikari, S. Shigetomi, Y. Koga, S. Shigetomi, H. Nishimura and H. Suzuki: J. Phys. C: Solid State Phys. 19 (1986) 2633.
9) R. W. G. Wyckoff: Crystal Structures (Interscience Publishers, New York, London and Sydney, 1965) p.145.
10) H. Muller: phys. stat. sol. (a) 66 (1981) 199.
11) A. Rosencwaig: Phys. Today 28 (1975) 23.
12) R. H. Bube and E. L. Lind: Phys. Rev. 115 (1959) 1159.
13) A. Conde-Gallardo, A. Cruz-Orea and S. A. Tomas: Appl. Spectroscopy 58 (2004) 917.