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# Two Distinct Phases in $Ga_2Se_3$ Compound Semiconductor

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Crystal structures of low and high temperature $Ga_2Se_3$ which are based on tetrahedral bonding structure are investigated by high resolution electron microscopy and X-ray diffraction. The low temperature $Ga_2Se_3$ is an ordered vacancy phase whereas the high temperature $Ga_2Se_3$ is a mesoscopic phase. The average Ga coordination and the fourfold Ga coordination of Se atoms have top priority for the low and the high temperature $Ga_2Se_3$, respectively, although basic structures are both zincblende type. A remarkable deference in the band gap of the two phases is well explained by the difference in their stabilization mechanisms.

## 1. INTRODUCTION

$Ga_2Se_3$ is a representative of $III_2VI_3$ compound semiconductors which are based on the tetrahedral bonding structure. The ratio of the cation atoms to the anion atoms is less than unity, so that the cation sublattice is occupied by Ga atoms and vacancies [1,2]. These compounds are very interesting semiconductors which satisfy octet rule including the vacancies. Therefore, such vacancies are essential for the $III_2VI_3$ compound semiconductors and named structure vacancies [3,4].

Previous studies have shown the existence of two kinds of phases: low temperature phase and high temperature phase. The former was one of the ordered vacancy compounds (OVC) [5-12] and the latter was a defect zincblende structure in which structure vacancies randomly occupied one third of the cation sites. The phase transition between them was regarded to be order-disorder transition [13].

We have studied the crystal structures of $Ga_2Se_3$ by means of high resolution electron microscopy and X-ray diffraction together with measurements of absorption spectra, and successfully characterized the crystal structures of the two phases. Based on the structure analysis, two distinct stabilization mechanisms of compound semiconductors are proposed and a remarkable difference in band gap of the two phases can be well explained.

## 2. EXPERIMENTAL PROCEDURE

Specimens are prepared by melting of $Ga_2Se_3$ lump (3N, Koujyundo Chemical Lab Co., Ltd., Japan) in evacuated quartz tubes and then air cooled. In order to obtain low temperature $Ga_2Se_3$ crystal with high crystallinity, specimens are annealed at 873 K for 2.6 Ms (about 1 month). For the high temperature $Ga_2Se_3$, annealing at 973 K for 605 ks (about 1 week) is performed. The compositions of these materials are measured by ICP and confirmed by EDS/TEM system. For structure analysis, a JEM-200CX electron microscope is used to take electron diffraction patterns and a JEM-3010 electron microscopy is used for the high resolution electron microscopic study. The X-ray powder diffraction data are collected by a normal $\theta$-$2\theta$ diffractometer with monochrometer.

## 3. CRYSTAL STRUCTURE OF $Ga_2Se_3$

### 3.1 LOW TEMPERATURE PHASE

The low temperature $Ga_2Se_3$ crystals show orange color. Figure 1 shows electron diffraction patterns. The patterns consist of strong spots which indicate that the basic structure is zincblende and extra spots. The extra spots are roughly classified into two groups; the ones are relatively strong and divide fundamental reflections into three parts along a [110]* direction of zincblende in reciprocal space. Their origin is ordered arrangement of the structure vacancies. The others are fairly weak and appear on the midpoint of the fundamental spots along a $[1\bar{1}1]^*$ direction in reciprocal space. Their origin is considered to be systematic atom displacements around the vacancies. Based on such consideration, all the diffraction patterns can be indexed as shown in Figure 1. Two structure models are deduced. However, it cannot be specified which is true at this stage.

In order to establish the final structure model for the low temperature $Ga_2Se_3$, X-ray diffraction - Rietveld analysis is applied [14]. Figure 2 shows the observed X-ray diffraction profile and final calculated profile of the low temperature $Ga_2Se_3$. The calculated diffraction profile can reproduce the observed one and the R-factor becomes sufficiently small. The detailed crystal data are listed in Figure 2. In the crystal, the coordination number for each Se atom is limited to be

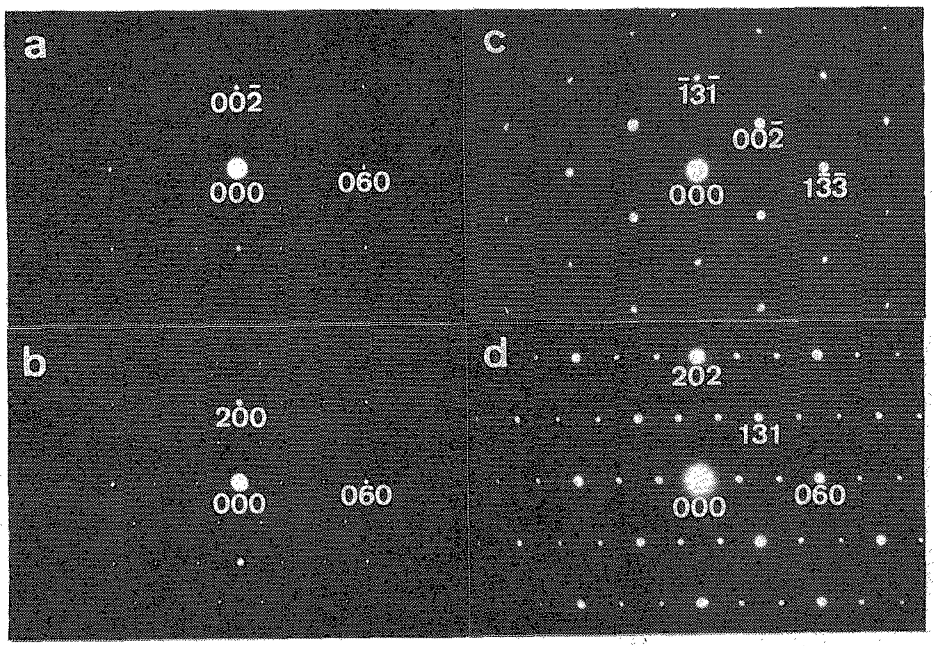

Figure 1. Electron diffraction patterns of low temperature $Ga_2Se_3$. They are indexed by a monoclinic cell. $[1\bar{1}1]$ and [110] direction in zincblende cell are corresponding to [001] and [010] directions in the monoclinic cell respectively. Beam incidents are along the (a)[100], (b)[001], (c)[310] and (d)$[\bar{1}01]$ directions, respectively.

2 or 3 and the existent ratio is 1 : 2. Structure vacancies and twofold Ga coordinated Se atoms form zigzag chains along the [001] direction ( $[1\bar{1}2]$ direction of zincblende structure). Systematic atom displacements of the atoms around the structure vacancies are derived so as to fill up the space corresponding to the structure vacancy. The atomic distances between Ga atoms and twofold Se atoms are about 4% shorter than those between Ga atoms and threefold Se atoms.

### 3.2 HIGH TEMPERATURE PHASE

The high temperature $Ga_2Se_3$ crystals shows dark red color. Figure 3 shows powder X-ray diffraction chart obtained from high temperature $Ga_2Se_3$. It is a typical X-ray chart from zincblende type crystal except for the peak broadening of 111 family. Figure 4 (a) is an electron diffraction pattern. All the diffrac-

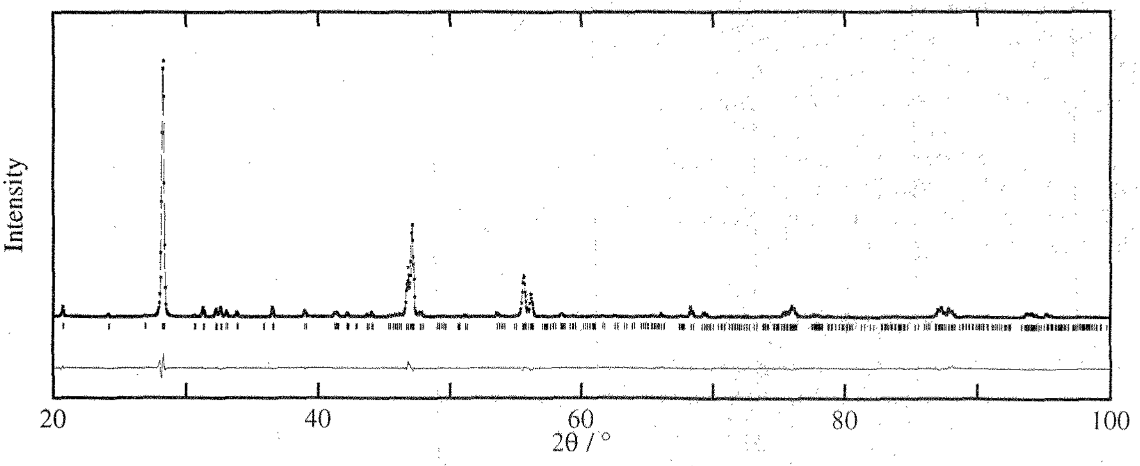

Figure 2. Observed (points) X-ray diffraction pattern, calculated (line) one of Rietveld refinement and their difference of low temperature $Ga_2Se_3$. Monoclinic ($Cc, C_s^4$), a=6.65(8), b=11.64(9), c=6.65(0)Å, ß=108.8(4)° $R_{wp}$=9.85%, S=3.57 $R_F$=2.59%, V=488.148Å$^3$.

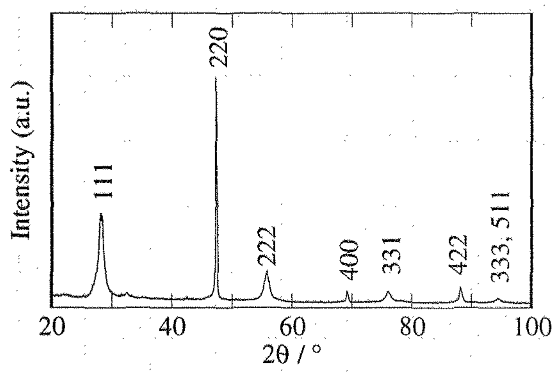

Figure 3. Powder X-ray Diffraction of high temperature Ga$_2$Se$_3$. All the peaks can be indexed by zincblende type structure, but 111 family show the peak broadening.

tion spots are indexed by zincblende structure. However, strong streaks are observed along the <111>* directions in reciprocal space. Corresponding HRTEM image (Fig. 4 (b)) clearly demonstrates unregularly arranged {111} planer defects at intervals of 20 to 100 {111} atomic planes. Such planer defects cannot be removed if specimens are annealed even at higher temperature for a longer time, although the densities of the planer defect are dependent on the annealing temperature. Therefore, the planer defects are essential for the high temperature Ga$_2$Se$_3$. Considering that

1) cleavages are very easy to take place at the planer defects,
2) the planer defects exhibit white contrast in the image,
3) geometrical consideration of Ga$_2$Te$_3$ which shows ordered arrangement of planer defects [15],

the planer defects are concluded to be made of structure vacancies 2-dimensionally aggregated on {111} planes of zincblende structure. Consequently, inside the regions surrounded by such vacancy planes, Se atoms preferentially take fourfold Ga coordination.

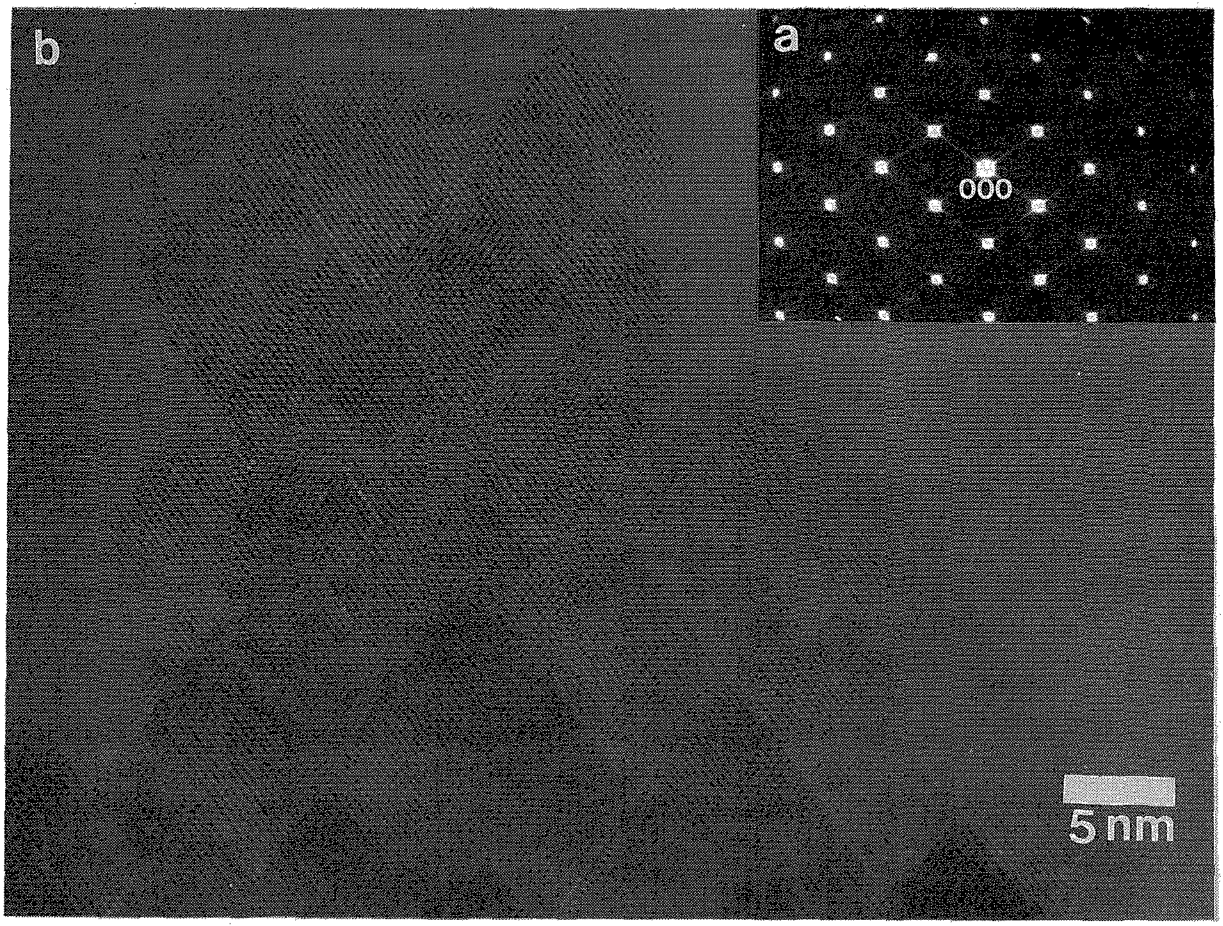

Figure 4. (a) Electron diffraction pattern and (b) HRTEM image of high temperature Ga$_2$Se$_3$ taken along the <110> direction of zincblende cell. The blight dots lines correspond to the vacancy planes formed on {111} planes of zincblende structure.

### 3.3 ABSORPTION SPECTRA OF $Ga_2Se_3$

Figure 5 shows absorption spectra of the two phases. The absorption edge of the high temperature phase is around 635 nm and that of the low temperature phase is 540 nm. The corresponding band gaps are estimated to be 1.95 eV and 2.28 eV, respectively. By measuring the absorption spectra, both phases are confirmed to be semiconductors. The observed colors of the crystals are well corresponding to the measured band gaps, respectively.

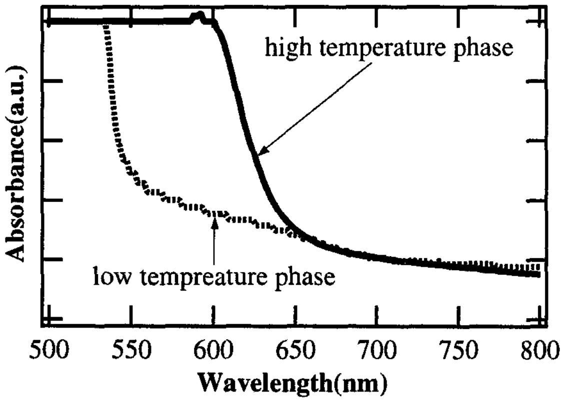

Figure 5. Absorption spectra of two $Ga_2Se_3$ phase. The absorption edge of the high temperature phase is at 635nm and that of low temperature is 540nm.

## 4. DISCUSSION

The low temperature $Ga_2Se_3$ is constructed by only 2 and 3 Ga coordinated Se atoms. The numbers 2 and 3 are the closest two integers to the average Ga coordination number 2.67 (= 4 × (2/3)) in the $III_2VI_3$ compound semiconductors. As far as $Ga_2Se_3$ crystal is based on tetrahedral bonding structure, it is impossible to realize all the Se atoms have the identical coordination. Therefore, it is concluded that deviation from the average coordination number is minimized as much as possible. In other words, the structure of low temperature $Ga_2Se_3$ is one of the most uniform structures for the Ga atom and the structure vacancy. On the other hand, the structure of the high temperature $Ga_2Se_3$ is characterized by the {111} planer defects and fourfold Ga coordinated Se atoms. Since the structure vacancies are not distributed uniformly, local specimen compositions on a unit cell scale never coincide with the composition of the crystal. Only the mesoscopic regions can do. Therefore, the high temperature $Ga_2Se_3$ should be recognized as a mesocsopic phase. Fourfold Ga coordinated Se atoms have disadvantage on the chemical bonding because the bondings are of electron excess. Fourfold Ga coordinated Se atoms, however, are preferentially formed because they have advantage on the symmetry of the tetrahedral bonding. It is concluded that effective formation of fourfold Ga coordination for Se atom has the top priority in the mesoscopic phase.

In the $Ga_{0.5}In_{0.5}P$, change in band gap with development of ordering has been reported [16]. However, the difference of the band gap in $Ga_{0.5}In_{0.5}P$ is only 50 meV and is considerably smaller than that of $Ga_2Se_3$. In the case of $Ga_2Se_3$, the difference of the band gap is derived not from ordering of structure vacancy but from the difference in chemical bonding manner or stabilization mechanism although basic structures are both zincblende type.

In conclusion, crystal structures of the low and the high temperature $Ga_2Se_3$ are well established and the stabilization mechanisms are found to be quite distinct from each other. The phase transition between two phases is no longer order-disorder transition. It is order - mesoscopic transition.

## REFERENCES

1) P. C. Newman, J. Phys. Chem. Solids, 23 (1962) 19
2) P. C. Newman, J. Phys. Chem. Solids, 24 (1963) 45
3) J. Ye, T. Yoshida, Y. Nakamura, and O. Nittono, Appl. Phys. Lett., 67 (21) (1995) 20
4) J. Ye, Y. Nakamura, and O. Nittono, Philos. Mag., A73 (1996) 169
5) D. Lubbers and V. Leute, J. Solid State Chem., 43 (1982) 339
6) G. Ghemard, S. Jaulmes, J. Etienne, and J. Flahaut, Acta Cryst., C39 (1983) 968
7) M. Y. Khan, J. Appl. Cryst., 10 (1977) 70
8) M. Y. Khan, Indian J. Phys., 68A(2) (1994) 159
9) A. C. Wright, J. O. Williams, A. Krost, W. Richter and D. R. T. Zahn, J. Crystal Growth, 121 (1992) 111
10) T. Okamoto, N. Kojima, A. Yamada, M. Konagai, K. Takahasi, Y. Nakamura, O. Nittono, J. J. Appl. Phys., 31 (1992) L143
11) N. Teraguti, M. Konagai, F. Kato, K.Takahashi, J. Crystal Growth, 115 (1991) 798
12) N. Teraguch, F. Kato, M. Konagai, K. Takahashi, Y. Nakamura, N. Ostuka, Appl. Phys. Lett., 59 (1991) 567
13) L. S. Palatnik and E. K. Belova, Inorg. Mater., 1 (1965) 1703
14) F. Izumi, "The Rietveld Method," ed. by R.A. Young, Oxford University Press, Oxford (1993), Chap. 13; Y. I. Kim and F. Izumi, J. Ceram. Soc. Jpn. 102 (1994) 401.
15) Y. Watanabe, Y. Nakamura and O. Nittono, to be published
16) A. Gomyo, T. Suzuki and S. Iijima, Phys. Rev. Lett., 60 (1988) 2645