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Studies of point defects for annealed $AgInS_2$/GaAs epilayer

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Abstract The $AgInS_2$ epilayers with a chalcopyrite structure grown using a hot-wall epitaxy method have been confirmed to be a high quality crystal. From the optical absorption measurements, a temperature dependence of the energy band gap on $AgInS_2$/GaAs was found to be $Eg(T) = 2.1365\ eV - (9.89\times10^{-3}\ eV)\ T^2/(2930 + T)$. After the as-grown $AgInS_2$/GaAs was annealed in Ag-, S-, and In-atmospheres, the origin of point defects of $AgInS_2$/GaAs has been investigated by using photoluminescence measurements at 10 K. The native defects of V_{Ag}, V_S, Ag_{int}, and S_{int} obtained from photoluminescence measurements were classified as donors or acceptors. It was concluded that the heat-treatment in the S-atmosphere converted $AgInS_2$/GaAs to an optical p-type. Also, It was confirmed that In in $AgInS_2$/GaAs did not form the native defects because In in $AgInS_2$ did exist in the stable form.

Key words Hot wall epitaxy, $AgInS_2$, photoluminescence, Hall effect, Optical absorption, Energy band gap

1. Introduction

Ternary chalcopyrite crystals are currently of technological interest since they show promise for application in the areas of visible and infrared light-emitting diodes, infrared detectors, optical parametric oscillators, upconverters, and far infrared generators. But many of these materials were reported to be difficult to grow in the form of a large and high quality crystal. Also, the fundamental physical properties of these compounds are still not reported.

$AgInS_2$ is a ternary compound semiconductor which has a wide band gap and belongs to the visible region of the spectrum. Its structure was crystallized in the form of chalcopyrite. Thereby, $AgInS_2$ has a uniaxial lattice structure [1]. Also, it can be made a useful n-type [2]. $AgInS_2$ is one of the interesting materials used as optoelectronic devices applicable to the visible region. Many of the fundamental properties of $AgInS_2$ such as photoconductivity [3], heat capacity [4], Hall effect [5], the calculation of the band structure [6], and optical absorption [7] have been carried out. Some attempts have also been made with the object of improving the efficiency of junction devices formed in the ternary compounds. But, for device applications of $AgInS_2$, it is vital to know the electro-optical properties of this material. The electronic and optical properties of $AgInS_2$ crystals are mainly determined by point defects associated with individual atoms forming the ternary compound. However, optical properties and the single layer growth of $AgInS_2$ have not been well understood. Only several researchers 5, 8] have investigated the electrical properties and polycrystalline $AgInS_2$ film growth.

Sulfur has higher vapor pressure compared to those of silver and indium. This is strongly related to native defects generated by non-stoichiometric composition during high temperature growth. These native defects, such as sulfur vacancy (V_S), silver vacancy (V_{Ag}), sulfur interstitial (S_{int}), silver interstitial (Ag_{int}) and complex of these point defects have been known to be produced when the crystal cooled down after the crystal growth. Among the defects, V_S and Ag_{int} are plausible defects because they act as donors. Other defects such as V_{Ag} and S_{int} may form deep levels and/or acceptors. Consequently, low-temperature crystal growth and thin film deposition methods have been recognized as the key technology to reduce native defects in $AgInS_2$. Hot-wall epitaxy (HWE) method is one of the low-temperature crystal growth methods. Although $AgInS_2$ grown by HWE has not been reported in the literature, we tried to grow the $AgInS_2$ epilayers using HWE in this work. HWE has been known to be designed specifically to grow epilayers under the condition close to thermodynamic equilibrium [9].

In this paper, to estimate the predominant point defects of the as-grown $AgInS_2$ through various heat-treat-

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ments, we carried out measurements of the optical absorption and the photoluminescence (PL) spectra. Based on these results, we will discuss the cause of native defects in $AgInS_2$.

2. Experiment

Prior to the epilayer growth, polycrystalline $AgInS_2$ used as a source material for the $AgInS_2$ growth was formed as follows. The starting materials; Ag, In, and S were the shot-types of 6 N purity. After the materials were weighed in stoichiometric proportions, they were sealed in a quartz tube whose lining was coated with carbon. The sealed ampoule was placed in the synthesis furnace and was continually rotated at a rate of 1 revolution per minute. In order to avoid the explosion of the ampoule due to the sulfur vapor pressure, the temperature of the ampoule was increased gradually to 1050°C, which was then maintained for 48 h. After the growth of the polycrystalline $AgInS_2$ ingot, $AgInS_2$ epilayers were grown on semi-insulating (100) GaAs by HWE method using the grown $AgInS_2$ ingot as source materials [10]. The grown $AgInS_2$/GaAs was analyzed by the double crystal x-ray diffraction (Bede Scientific Co. FR 590) to obtain the optimum growth condition. The most suitable substrate and source temperatures to grow undoped $AgInS_2$/GaAs turned out to be 410°C and 680°C, respectively. The minimum value for the full width at half maximum (FWHM) of the grown $AgInS_2$ was 121 arcsec, which was obtained from the x-ray rocking curves. The thickness of the as-grown $AgInS_2$/GaAs measured by an α-step profilometer (Tenco, α-step 200) was 2.6 μm. And the chalcopyrite structure was confirmed by x-ray diffraction study. From the Hall effect on the as-grown $AgInS_2$/GaAs at 293 K measured by the van der Pauw method, we obtained 9.35×10^{17} cm^{-3} and 294 $cm^2/V \cdot s$ for carrier density and mobility, respectively, which confirmed the as-grown epilayer to be an n-type semiconductor. The optical absorption spectra measurement was performed with a UV-VIS-NIR spectrophotometer (Hitachi, U-3501) for a range of 400 nm to 800 nm with the temperature varied from 10 K to 293 K. To prepare samples of $AgInS_2$/GaAs : Ag (annealed in the Ag vapor atmosphere), $AgInS_2$/GaAs : S (annealed in the S vapor atmosphere), and $AgInS_2$/GaAs : In (annealed in the In vapor atmosphere), the as-grown $AgInS_2$/GaAs with each of Ag, S, and In shots was sealed in a quartz ampoule at 10^{-6} torr. The samples of $AgInS_2$/GaAs : Ag, $AgInS_2$/GaAs : S, and $AgInS_2$/GaAs : In were annealed for 1 h at 650°C, for 30 min at 400°C, and for 1 h at 550°C, respectively. The PL measurement at 10 K was carried out using a cryogenic helium refrigerator (AP, CSA-202B). The samples mounted on the cold finger of a cryostat were focused using the 442 nm line of He-Cd laser (Kimmon, 60 mW). The emitted light was then detected by a photomultiplier tube through the monochromator. The detected signal was amplified by a lock-in amplifier and recorded in an x-y plotter.

3. Results and Discussion

3.1. As-grown $AgInS_2$/GaAs epilayer

Figure 1 shows the optical absorption spectra obtained in a temperature range of 10 K to 293 K. In order to identify the energy band gap for $AgInS_2$/GaAs, we carefully examined the relation between the optical absorption coefficient (α) and the incident photon energy (hν)

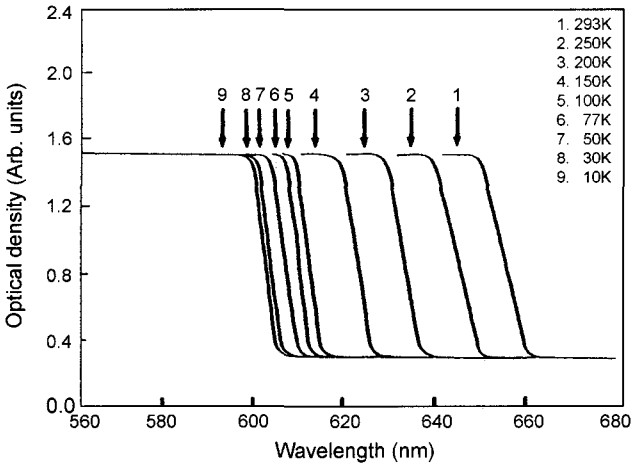

Fig. 1. Optical absorption spectra of the as-grown $AgInS_2$/GaAs epilayer measured at different temperatures.

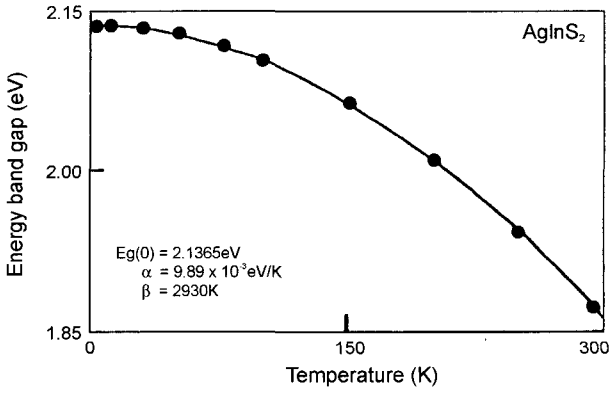

Fig. 2. Experimental values of the optical energy band gap as a function of temperature in the range of 10 to 293 K.

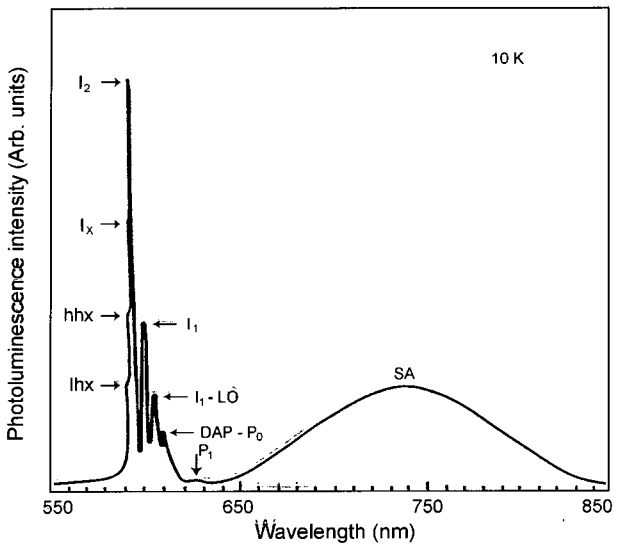

Fig. 3. Photoluminescence spectrum at 10 K for the as-grown $AgInS_2$/GaAs epilayer.

from the optical absorption measurements in Fig. 1. The relation for a direct band gap between hand is given by

$$(\alpha h\nu)^2 \sim (h\nu - Eg). \quad (1)$$

Therefore, the temperature dependence of the optical energy band gap in our experiment, as shown in Fig. 2, is well described by the Varshni's equation [11]

$$Eg(T) = Eg(0) - \alpha T^2/(T + \beta), \quad (2)$$

where Eg(0) is the optical energy gap at absolute zero, α and β are constants. From these experimental measurements, Eg(0), α, and β are determined to be 2.1365 eV, 9.89×10^{-3} eV/K, and 2930 K, respectively.

Figure 3 shows typical PL spectra of the as-grown $AgInS_2$/GaAs measured at 10 K. From the expanded spectrum of Fig. 3, the two peaks at 593.8 nm (2.0880 eV) and 596.9 nm (2.0771 eV) appear on the shoulder toward the shorter wavelength region. These peaks are free excitons associated with a light-hole-exciton (lhx) and heavy-hole-exciton (hhx), respectively. But the lhx and the hhx may be considered as the upper polariton and the lower polariton of the free exciton [12-15]. The energy splitting between the lhx and the hhx is 10.9 meV, which is caused by the strain due to the lattice mismatch between the substrate and the epilayer in the heteroepilayer growth. The equations of the hhx and the lhx are given by

$$hhx = Eg(10) - \delta Ex^{hh} \quad (3)$$

and

$$lhx = Eg(10) - \delta Ex^{lh}, \quad (4)$$

where δEx^{hh} and δEx^{lh} are the hhx and lhx binding energies due to the variance of the strain at $\mathbf{k} = 0$, respectively. The value of Eg(10) was calculated to be 2.1362 eV using eq. (2) and the binding energy of the free exciton, δEx^{lh}, is obtained to be 48.2 meV. And the Ix peak emitted due to the transition from the free exciton to the bound exciton is shown at 597 nm 2.0767 eV. The very strong intensity peak corresponding to the neutral donor bound exciton, I_2, appears at 597.8 nm (2.0741 eV). This exciton is known to be a recombination from bound exciton to neutral donor. Here the binding energy [16] E_D of the donor-impurity can be calculated by

$$I_2(h\nu) = Eg - \delta Ex^{lh} - 0.15E_D, \quad (5)$$

where E_D is determined to be 92.7 meV. This can be ascribed to the donor states of V_S or Ag_{int}, which are located at 92.7 meV below the edge of the conduction band. At the same time, this value is nearly equal to the activation energy obtained by the Hall effect measurement. The sharp intensity peak corresponding to the neutral acceptor bound exciton, I_1, at 600.1 nm (2.0660 eV) and the LO phonon replica at 604.8 nm (2.0500 eV) appear on the right region of I_2 peak. In the PL measurement, the observation of the free and bound excitons indicates that the as-grown $AgInS_2$ epilayer is a high quality because the emission peak of the exciton can be only observed under the condition of a long-range Coulomb coupling between the electron and the hole. And the donor-acceptor pair (DAP) emission at 612.4 nm (2.0246 eV) and its LO phonon replica were observed. Such a DAP emission is caused by an interaction between donors and shallow acceptors. The very intense and broad peak at 732.4 nm (1.6928 eV) in the longer-wavelength region can be attributed to a self-activated (SA) emission.

3.2. Annealing effect of the $AgInS_2$/GaAs epilayer

In order to understand the origins of the several peaks of the as-grown $AgInS_2$/GaAs, we measured the PL spectra for the samples annealed in Ag-, S-, and In-atmospheres. Firstly, to find a role of Ag, we prepared a $AgInS_2$/GaAs : Ag sample which was annealed in Ag-atmosphere for 1 h at 650°C. Therefore, it would saturate $AgInS_2$/GaAs with Ag to anneal the sample in Ag-atmosphere. The PL spectrum of $AgInS_2$/GaAs : Ag measured at 10 K is shown in Fig. 4(a). By comparing the PL spectrum of the as-grown $AgInS_2$/GaAs as shown in Fig. 3 with that of Fig. 4(a), we found that the peaks related to I_1 and its LO phonon replica completely disappeared in $AgInS_2$/GaAs : Ag. This disappearance indi-

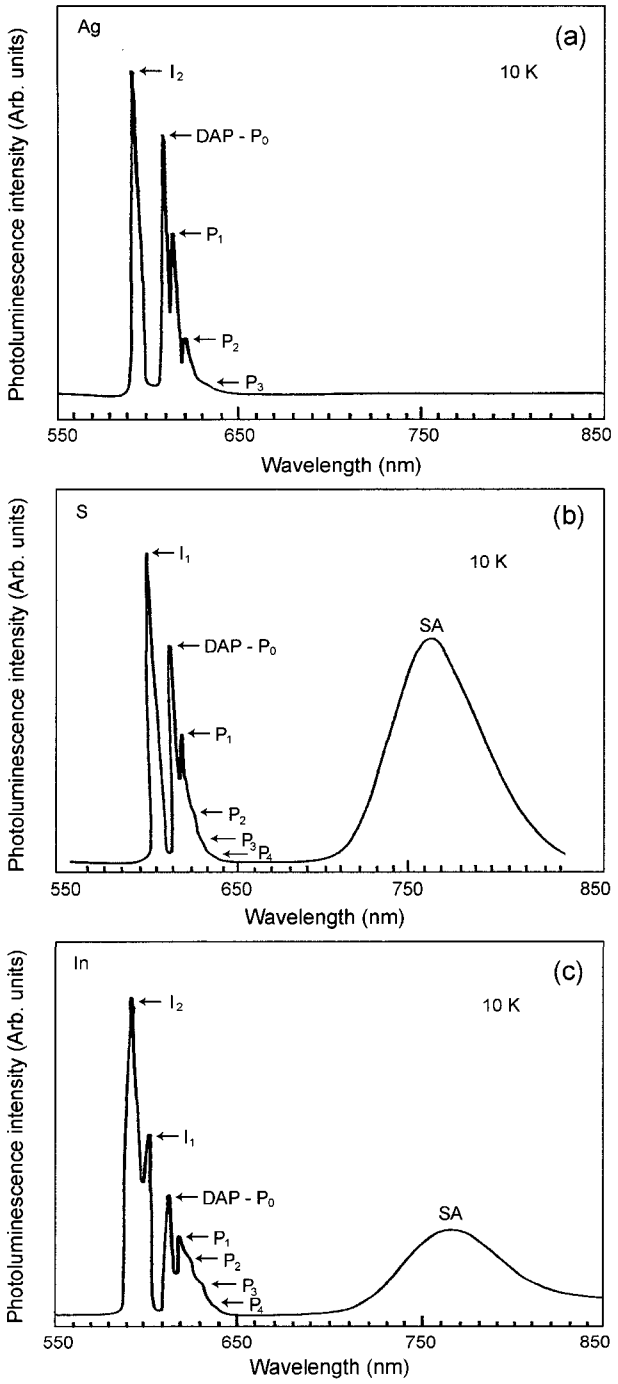

Fig. 4. (a) Photoluminescence spectrum at 10 K for the $AgInS_2$/GaAs : Ag epilayer, (b) Photoluminescence spectrum at 10 K for the $AgInS_2$/GaAs : S epilayer, (c) Photoluminescence spectrum at 10 K for the $AgInS_2$/GaAs : In epilayer.

cates that I_1 and its LO phonon replica are certainly associated with an acceptor level of V_{Ag} or levels of antisite native defects such as In_{Ag} and Ag_{In}. On the other hand, the I_2 emission became the dominant peak in the PL spectrum of the $AgInS_2$/GaAs : Ag. This peak is known to be observed in typical n-type $AgInS_2$/GaAs. The full width at half maximum of the I_2 peak for PL is taken to be 8 meV. However, the I_2 peak is not related to Ag because the sites of V_{Ag} should be substituted with the saturated Ag. Therefore, I_2 may be related to V_S or Ag_{int}. Also, the complete disappearance of the SA emission in the sample means that $AgInS_2$/GaAs : Ag is refined by annealing in the Ag-atmosphere and the SA emission is related to V_{Ag}. Among the samples prepared in this experiment, the DAP emission and its LO phonon replicas were dominantly observed only in the sample which had been annealed in the Ag-atmosphere. The origin of these DAP emissions may be associated with the point defects of V_S, Ag_{int}, or the complex of these. Also, the peaks of hhx, lhx, and Ix completely disappeared in $AgInS_2$/GaAs : Ag.

Figure 4(b) displays the PL spectrum of $AgInS_2$/GaAs : S which was annealed in the S-atmosphere for 30 min at 400°C. The figure shows that the I_1 peak is very sharp and its PL intensity is high. However, the hhx, lhx, Ix, and I_2 are not observed. As is well known, small deviations from stoichiometry in the crystal can be adjusted by changes in the concentration of vacancies in the appropriate sublattice. Probably V_{Ag} and V_{In} are present in $AgInS_2$/GaAs which includes excess S atoms. But, in the starting material to form a $AgInS_2$ epilayer, the concentration of the In atoms is equal to that of Ag atoms. However, the concentration of V_{In} will be little compared with that of V_{Ag}. Because the group I atoms participate only weakly in the covalent bonding, most of the covalent bonding occurred between the group III and group VI atoms [2]. Therefore, V_{Ag} is a more likely candidate than V_{In} and S_{int}. The origin of I_1 can be ascribed to the deep acceptor level originated from V_{Ag} due to stoichiometric deviation. And that means that the conversion from the n-type to the optical p-type occurs when V_S disappears. From the results of the I_1 emission, the binding energy of the acceptor-impurity [16], E_A, is obtained by

$$I_1(h\nu) = Eg - \delta Ex^{lh} - 0.08E_A, \quad (6)$$

where E_A is calculated to be 275 meV. The optical transitions of E_A may be associated with a deep level of S_{int} or V_{Ag} point defects. The intensity of the I_2 peak was enhanced after the Ag-atmosphere treatment, however, it disappeared completely after the S-atmosphere treatment. Therefore, the origin of the I_2 emission is believed to be related to V_S. The I_1 peak disappeared in the Ag-atmosphere treatment, but it became the dominant peak after the S-atmosphere treatment. This indicates that the origin of the I_1 emission is related to V_{Ag} or S_{int}. And the DAP emission and its LO phonon replicas were domi-

nantly observed in the sample annealed in the S-atmosphere. Therefore, those peaks are related to V_{Ag}, S_{int}, or the complex of them, which acted as acceptors. Also, the excess S atoms were contained in $AgInS_2$/GaAs : S, so that V_S was hardly contained in $AgInS_2$/GaAs : S. Ag atoms can be expected to readily move between interstitial positions since they participate only weakly in the covalent bonding. Therefore, the most probable intrinsic donors are believed to be Ag_{int}. Ag_{int} is related to the DAP emission, which acted as donors. Also, the intensity of the SA emission increased after the S-atmosphere treatment. This means that the origin of the SA emission is related to S_{int}.

Figure 4(c) shows the PL spectrum of $AgInS_2$/GaAs : In annealed in the In-atmosphere for 1 h at 550°C. It shows a close spectrum with Fig. 3. This means that In is not related to the formation of the native defect in the sample because In forms more covalent bonds than Ag and S in chalcopyrite structure semiconductors, i.e., In participates in the formation of pre-covalent and less-ionic chalcopyrite compounds than Ag and S. Therefore, the above evidences indicate that In is a stable element in $AgInS_2$.

4. Conclusions

The absorption and PL spectra of $AgInS_2$/GaAs epilayers grown in the HWE method were investigated. The energy band gap obtained from the absorption spectra was well described by the Varshni's relation, $Eg(T) = 2.1365\ eV - (9.89\times10^{-3}\ eV)T^2/(2930 + T)$. The free excitons of lhx and hhx have been found in the as-grown $AgInS_2$/GaAs and its energy gap splitting between lhx and hhx was determined to be 10.9 meV. This free exciton peak is associated with the strain due to lattice mismatch between the substrate and the epilayer. Also, the binding energy of the free exciton was estimated to be 48.2 meV. The I_2 emission was confirmed to be related to V_S or Ag_{int} generated by non-stoichiometric composition. These defects were proved to act as donors. Therefore, these defects indicate one of the reasons why $AgInS_2$ grown is generally an n-type. At the same time, the binding energy of the donor-impurity calculated was found to be 92.7 meV.

The I_1 emission became the dominant peak in $AgInS_2$/GaAs : S after the S-atmosphere treatment. By using the PL measurement, we confirmed that $AgInS_2$/GaAs : S was converted into the optical p-type and that the origin of the I_1 emission was related to V_{Ag} or S_{int}. The DAP emission is caused by the interaction between donors such as V_S or Ag_{int}, and shallow acceptors such as V_{Ag} or S_{int}. Finally, the role of In in $AgInS_2$/GaAs is not related to the formation of the native defects because In is the stable ingredient of $AgInS_2$.

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References

[1] J.L. Shay, B. Tell, L.M. Schiavone, H.M. Kasper and F. Thiel, "Energy Band of $AgInS_2$ in the Chalcopyrite and Othorhomic Sturcture", Phys. Rev. B9 (1974) 1719.

[2] B. Tell, J.L. Shay and H.M. Kasper, "Room-Temperature Electrical Properties of I-III-VI_2 Semiconductors", J. Appl. Phys. 43 (1972) 2369.

[3] N.V. Joshi, L. Martinez and R. Echevrria, "An Experimental Investigation of the Photoconductivity Spectrum of a Monocrystal of $AgInS_2$ Grown by Bridgman and Chemical Transport Techniques", J. Phys. Chem. Solids 42 (1981) 281.

[4] I.V. Bodnar and N.S. Orlova, "X-ray Study of the Thermal Expansion Anisotropy in $AgInS_2$ Compounds over the Temperature Range from 80 to 610 K", Phys. Stat. Sol. (a) 91 (1985) 503.

[5] K. Hattori, K. Akamatsu and N. Kamegashira, "Electrical Properties of Polycrystalline Chalcopyrite $AgInS_2$ Films", J. Appl. Phys. 71 (1992) 3414.

[6] J.L. Shay, B. Tell, H.M. Kasper and L.M. Schiavone, "Electronic Structure of $AgInS_2$ and $CuInS_2$", Phys. Rev. B7 (1973) 4485.

[7] L. Martinez Z., S.A. Lopez-Rivera and V. Sagred, "Prepartion and Properties of $AgInS_2$ Single Crystal", Il Nuovo Cimento 2 (1983) 1687.

[8] M. Gorska, R. Reaulieu, J.J. Loferski and B. Roessler, "Spray Pgrolysis of Silver Indium Sulfides", Thin Solid Films 67 (1980) 341.

[9] A. Lopez-Otero, "Trends in the Crystal Growth and Chemical Compounds of $AgInS_2$", Thin Solid Films 49 (1987) 3.

[10] H.S. Kim, "The Study of Growth and Opto-electrical Characterization of $AgInS_2$ Single Crystal Thin Film by Hot Wall Epifaxy", Thesis, Chosun University (1992).

[11] Y.P. Varshni, "Far-infrared Optical Absorption of Fe^{2+} in ZnSe", Physica 34 (1967) 149.

[12] B. Tell, J.L. Shay and H.M. Kasper, "The Anomalous Photovoltalic Effect Polycrystalline $AgInS_2$ Thin Films", Phys. Rev. B4 (1971) 2465.

[13] J.J. Hopfield and D.G. Thomas, "Pressure Dependence of the Energy Gap in Some I-III-VI_2 Compound Semiconductors", Phys. Rev. 132 (1963) 563.

[14] J.J. Hopfield, "Theory of the Band Gap Anomaly in

ABC_2 Chalcopyrite Semiconductors", Phys. Rev. 112 (1958) 1555.

[15] D.D. Sell, S.E. Stokowski, R. Dingle and J.V. Dilorenzo, "Effects of p-d Hybridization on the Valance of I-III-VI_2 Chalcopyrite Semiconductors", Phys. Rev. B7 (1973) 4568.

[16] R.R. Sharma and S. Rodriguez, "Optical Properties of the Chalcopyrite Semiconductors $AgInS_2$", Phys. Rev. 159 (1967) 649.