Annealing effects of $AgInS_2$/GaAs Epilayer grown by Hot Wall Epitaxy

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Abstract

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

Key Words : hot-wall epitaxy, optical absorption, point defects, annealing effects, photoluminescience

I. 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 generator. 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 limited.

$AgInS_2$ 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, the $AgInS_2$ has uniaxial lattice structure.[1] Also, it can be made usefully n-type.[2] The $AgInS_2$ is one of the interesting materials used as optoelectronic devices applicable to the visible region. Many of the fundamental properties of the $AgInS_2$ 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 single layer growth of $AgInS_2$ have not been well understood. Only, several researchers[8,9] have been investigated the electrical properties and polycrystalline $AgInS_2$ film growth.

Sulfur is the higher vapor pressure compared to these 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 known to be produced when the crystal cooled down after the crystal growth. Among the defects, the V_S and Ag_{int} are an 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 $AgInS_2$. HWE method is one of the low-temperature crystal growth. Although the $AgInS_2$ 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 especially designed to grow epilayers under the condition of a close thermodynamics equilibrium.[10]

In this paper, to estimate the predominant point defects of the as-grown $AgInS_2$ through various heat-treatment, we carried out measurements of the optical absorption and the PL spectra. Based on these results, we will discuss the origin of native defects of the $AgInS_2$.

II. Experiment

Prior to epilayer growth, the polycrystalline $AgInS_2$ used as

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a source material for $AgInS_2$ growth was formed as follows. The starting materials; Ag, In, and S, were the shot forms of 6N purity. After these materials were weighed in stoichiometric proportions, these were sealed in a quartz tube which coated the carbon. The sealed ampoule was placed in the synthesis furnace and successively rotated at rate of 1 revolution per minute. In order to avoid the explosion of the ampoule due to the sulfur vapor pressure, the temperature of ampoule was increased gradually to 1050 ℃. This temperature 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.[11] The grown $AgInS_2$/GaAs were 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 temperature to grow the undoped $AgInS_2$/GaAs were 410 ℃ and 680 ℃, respectively. The minimum value of a full width at half maximum (FWHM) of the grown $AgInS_2$ was 121 arcsec obtained from the x-ray rocking curves. The thickness of the as-grown $AgInS_2$/GaAs measured by a α -step profilometer (Tenco, α -step 200) was 2.6 ㎛. 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 a 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 were sealed in a quartz ampoule at $\sim 10^{-6}$ torr. The samples of $AgInS_2$/GaAs:Ag, $AgInS_2$/GaAs:S, and $AgInS_2$/GaAs: In were annealed for 1 h at 650 ℃, for 30 min at 400 ℃, and for 1 h 550 ℃, 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, 60mW). Then, the emitted light was detected by the photomultiplier tube through the monochromator. The detected signal was amplified by a lock-in amplifier and recorded in a x-y plotter.

III. Results and Discussion

A. As-grown $AgInS_2$/GaAs epilayer

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

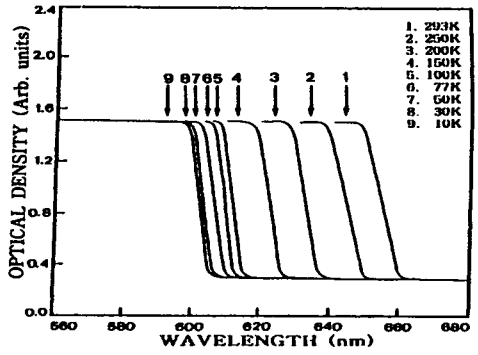

Fig. 1. Optical absorption spectra of the as-grown $AgInS_2$/GaAs epilayer measured at different temperature.

The relation for a direct band gap between the hv and the α is given as

$$(\alpha\ h\nu)^2 \sim (h\nu - Eg). \text{---(1)}$$

Therefore, the temperature dependence of the optical energy band gap of our experimental, as shown in Fig. 2, is well described by the Varshni's equation[12]

$$E_g(T) = E_g(0) - \alpha T^2/(T + \beta) \text{-- (2)}$$

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

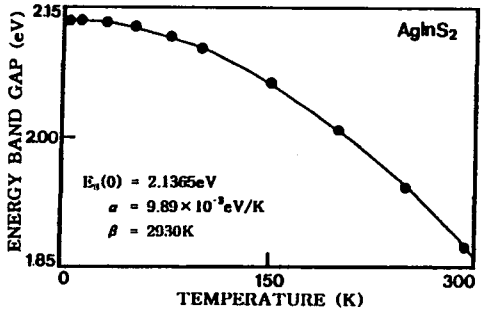

Fig. 2. Experimental values of the optical energy band gap as function of temperature in the range between 10 and 293 K.

Figure 3 shows the typical PL spectra of the as-grown $AgInS_2$/GaAs measured at 10 K.

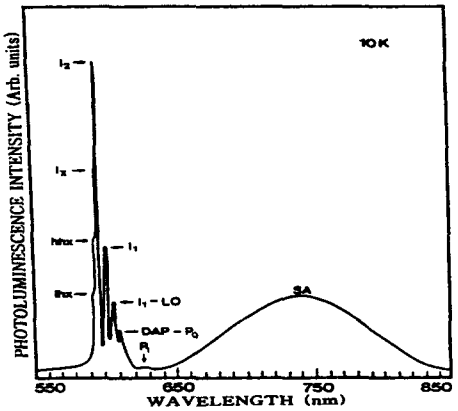

Fig. 3. Photoluminescence spectrum at 10K for the as-grown $AgInS_2$/GaAs epilayer.

From the expanded spectrum of the 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 short-wavelength region. These peaks are free excitons associated with 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 free exciton.[13-16] The splitting energy between the lhx and the hhx is 10.9 meV, which is caused by the strain due to the lattice mismatch between substrate and epilayer in the heteroepilayer growth. The equations of the hhx and the lhx are given by

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

and

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

where δEx^{hh} and δEx^{lh} are the binding energy of the hhx and the lhx due to the variance of the strain at $\vec{k} = 0$, respectively. The value of Eg(10) was calculated to be 2.1362 eV using the 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 between free exciton to 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,[17] E_D, of the donor-impurity can be calculated by

$$I_2(hv) = Eg - \delta Ex^{lh} - 0.15E_D \text{ -(5)}$$

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 Hall effect measurement. A neutral acceptor bound exciton, I_1, of the sharp intensity peak at 600.1 nm (2.0660 eV) and LO phonon replica at 604.8 nm (2.0500 eV) appear on the right region of the wavelength. 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 DAP emission is caused by an interaction between donors and shallow acceptors. The very strong intensity and broad peak at 732.4 nm (1.6928 eV) in the longer-wavelength region can be attributed to a self-activated (SA) emission.

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

In order to know the origins of the several peaks of the as-grown $AgInS_2$/GaAs, we measured the PL spectra for samples annealed in Ag-, S-, and In-atmosphere. Firstly, to know a role of Ag, we prepared $AgInS_2$/GaAs:Ag sample which were annealed in Ag-atmosphere for 1 h at 650 ℃. Therefore, it would be saturated the $AgInS_2$/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.

By comparing the PL spectrum of the as-grown $AgInS_2$/GaAs as shown in Fig. 3 with that of Fig. 4, we found that the peaks related to the I_1 and its LO phonon replica completely disappeared in the $AgInS_2$/GaAs:Ag. This disappearance indicates that the 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 the typical n-type $AgInS_2$/GaAs. The FWHM value of the I_2 peak 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, the I_2 may be related to the V_S or Ag_{int}. Also, the SA emission completely disappeared in the sample, this means that the $AgInS_2$/GaAs:Ag is refined by annealing in 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 was dominantly observed only in the sample which was annealed in the Ag-atmosphere. The origin of these DAP emission may be associated with point defects of V_S, Ag_{int}, or these complex. Also, the peaks of hhx, lhx, and Ix completely disappeared in the $AgInS_2$/GaAs:Ag.

Figure 5 displays the PL spectrum of the $AgInS_2$/GaAs:S which was annealed in the S-atmosphere for 30 min at 400 ℃.

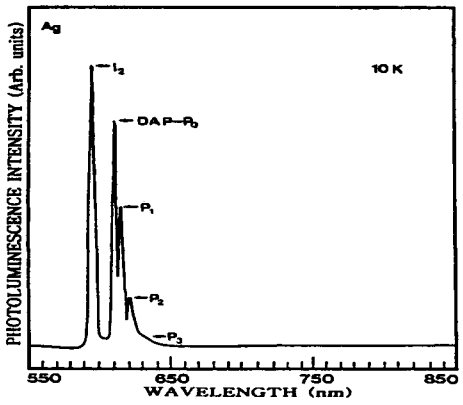

Fig. 4. Photoluminescence spectrum at 10K for the $AgInS_2$/GaAs:Ag epilayer.

This figure shows that the I_1 peak is a 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 of the concentration of vacancies in the appropriate sublattice.

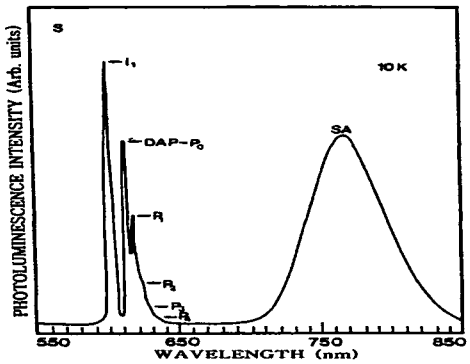

Fig. 5. Photoluminescence spectrum at 10K for the $AgInS_2$/GaAs:S epilayer.

Probably V_{Ag} and V_{In} are present in the $AgInS_2$/GaAs which include excess S atoms. But, in the starting material to form $AgInS_2$ epilayer, the concentration of 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 and most of the covalent bonding occurred between the group III and group VI atoms.[2] Therefore, V_{Ag} are more likely than V_{In} and S_{int}. The origin of I_1 can be ascribed to the deep acceptor level originated from the V_{Ag} due to stoichiometric deviation. And it means that the conversion from n-type to optical p-type occurs when V_S disappear. From results of the I_1 emission, the binding energy of acceptor-impurity,[17] E_A, is obtained by

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

E_A is calculated to be 275 meV. The optical transitions of the E_A may be associated with a deep level of S_{int} or V_{Ag} point defects. The intensity of the I_2 peak 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, 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 dominantly observed in the sample annealed in the S-atmosphere. Therefore, these peaks are related to V_{Ag}, S_{int}, or these complex, which acted as acceptors. Also, the excess S atoms were contained in the $AgInS_2$/GaAs:S, so that the V_S were hardly contained in the $AgInS_2$/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 possible intrinsic donors are believed to be Ag_{int}. The 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 6. shows the PL spectrum at 10K of the $AgInS_2$/GaAs:In annealed in the In-atmosphere for 1h at 550℃.

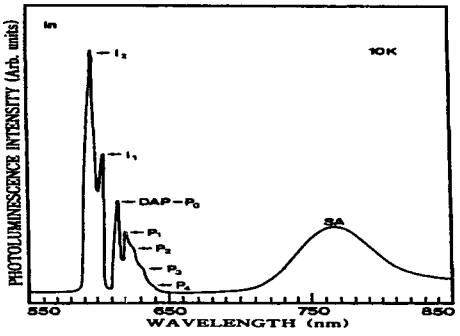

Fig. 6. photoluminescence spectrum at 10K for the $AgInS_2$/GaAs:In epilayer.

With comparison of the peaks of Fig. 3, there is a similarity to respective peak positions and intensities of PL spectrum. This means that In is not related to form the native defect in the sample, because In forms more covalent bonds than Ag and S in chalcopyrite structure semiconductors, i.e., In is closer to the axis of the Periodic Table and participates in the formation of pre-covalent and less-ionic chalcopyrite compounds than Ag and S. Therefore, the above evidences indicates that In is the stable element in the $AgInS_2$.

IV. Conclusion

The absorption and PL spectra of $AgInS_2$/GaAs epilayers grown by using HWE method were investigated. The energy band gap obtained from the absorption spectra was well described by the Varshni's relation of $Eg(T) = 2.1365\ eV - (9.89 \times 10^{-3}\ eV)T^2/(2930 + T)$. The free excitons of the lhx and hhx have found in the as-grown $AgInS_2$/GaAs and its splitting energy gap between the lhx and the hhx was determined to be 109 meV. This free exciton peak is associated with the strain due to lattice mismatch between substrate and 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 the V_S or Ag_{int} generated by non-stoichiometric composition. These defects were proved to be acted as donors. Therefore, these defects indicates one of the reasons why the $AgInS_2$ grown is generally the n-type. At the same time, the binding energy of the donor-impurity was calculated to be 92.7 meV.

The I_1 emission became the dominant peak in the $AgInS_2$/GaAs:S after the S-atmosphere treatment. We confirmed that the $AgInS_2$/GaAs:S is converted into the optical p-type by using the PL measurement and that the origin of the I_1 emission is related to V_{Ag} or S_{int}. The DAP emission is caused by 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 the $AgInS_2$/GaAs is not related to forming the native defects because the In is the stable ingredient of the $AgInS_2$.

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