Growth and Photoconductive Characteristics of $ZnGa_2Se_4$ Epilayers by the Hot Wall Epitaxy

Chang-Sun Park, Kwang-Joon Hong, *

Department of metallurgical and Material Science Engineering, Chosun University, Kwangju, 501-759, Kore

* Department of Physics, Chosun University, Kwangju 501-759, Korea

Abstract

The stochiometric mix of evaporating materials for the $ZnGa_2Se_4$ single crystal thin films were prepared from horizental furnace. The polycrystal structure obtaind from the power x-ray diffraction was defect chalcopyrite. The lattice costants a_0 and c_0 were a_0=5.51 A, c_0=10.98 A. To obtains the single crystal thin films, $ZnGa_2Se_4$ mixed crystal were deposited on throughly etched Si(100) by the Hot Wall Epitaxy (HWE) system. The temperates of the source and the substrate were 590℃ and 450℃, respectively. The crystalline structure of single crystal thin films was investigated by the double crystal X-ray diffraction(DCXD). Hall effect on this sample was measured by the method of van der Pauw and studied on carrier density and mobility dependence on temperature. In order to explore the applicability as a photoconductive cell, we measured the sensitivity (γ), the ratio of photocurrent to dark current (pc/dc), maximum allowable power dissipation (MAPD), spectral response and response time.

1. INTRODUCTION

The ternary semiconducting compound $ZnGa_2Se_4$ single crystal thin film, which is a wide-gap[1] material with an optical energy gap of 2.17eV, has the defect chalcopyrite structure with space group $S^2_4(I\bar{4})$ or $D^{11}_{2d}(I\bar{4}2m)$. $ZnGa_2Se_4$ crystal is a promising optoelectric device material with possibilities for potential applications. Therefore the calculation of the energy-band structure of the $ZnGa_2Se_4$ crystal by the empirical pseudopotential[2], Raman scattering[3], photoconductivity[4], and heat capacity methods[5] have been reported.

But as there have been no reports the growth of $ZnGa_2Se_4$ epilayer by Hot Wall Epitaxy method and their photoconductive characteristics.

In this paper, the stochiometric mix of evaporating materials for the $ZnGa_2Se_4$ single crystal thin films were prepared from horizental furnace. To obtains the single crystal thin films, $ZnGa_2Se_4$ mixed crystal were deposited on throughly etched Si(100) by the Hot Wall Epitaxy (HWE) system. In contrast to other epitaxial growth methods, HWE has been especially designed to grow single crystal thin films under conditions closed to the thermodynamics equilibrium[6-8]. The crystalline structures of single crystal thin films were investigated by double crystal X-ray diffraction (DCRD). Hall effect on this sample was measured by the method of van der Pauw and studied on carrier density and mobility depending on the temperature.

In order to explore the applicability as a photoconductive cell, $ZnGa_2Se_4$ single crystal thin films annealed in a Zn-, Ga-, Se-vapour, vacuum and air atmosphere. We measured the sensitivity (γ), the ratio of photocurrent to dark current (pc/dc), maximum allowable power dissipation (MAPD), spectral response and response time.

2 EXPERIMENTAL

The stochiometric mix of evaporating materials for the $ZnGa_2Se_4$ single crystal thin films used in this experiment were prepared from high-purity (6N) element in shot form. The elements were mixed and sealed in quartz tubes evacuated to 1×10^{-6} Torr. This ampoule was put into the furnace, as shown in Fig. 1 and was first heated up to 500℃ at the rate of 20℃/h followed by 24h of annealing at the same temperature. The next step was heating it up to 1000℃ at the rate of 10℃/h and annealing for 48h. Finally, the ampoule was heated up to 1100℃ at the temperature increase rate of 5℃/h and was annealed for 72h. The $ZnGa_2Se_4$ polycrystal ingot of dark-red color was obtained after the ampoule was cooled

To obtain the thin films, $ZnGa_2Se_4$ mixed crystals were deposited on throughly chemical etched Si(100). Hot wall epitaxy apparatus was used for growing the $ZnGa_2Se_4$ single crystal thin films on the Si(100) substrate, as shown in Fig. 2. During the growth of $ZnGa_2Se_4$, the substrate temperature was maintained at 590℃, and the source temperature was 450℃. The growth rate of the epilayers was about 2 ㎛/h.

The crystal structure and lattice parameter of synthesised $ZnGa_2Se_4$ polycrystal have been determined by the X-ray diffraction technique. The crystalline structure of $ZnGa_2Se_4$ single crystal thin films were investigated by double crystal X-ray diffraction (DCXD).

The Hall data were measured from van der Pauw method. The optical absorption spectrum was obatined with a UV-VIS-NIR spectrophotometer(Hitach, U-3501). To study characteristics of $ZnGa_2Se_4$ photoconductive cells, $ZnGa_2Se_4$ single crystal thin film annealed in a Zn-, Ga , Se-vapour, vacuum, and air atmosphere. With the sample so prepared, the following measurements

characterizing of $ZnGa_2Se_4$ photoconductive cells have been carried out : sensitivity, maximum allowable power dissipation (MAPD), spectral response, response time. The annealing conditions are given in table 1.

Table 1. Annealing conditions

samples	annealing condition
$ZnGa_2Se_4$	(unannealed)
$ZnGa_2Se_4$: Zn	Zn 0.0015g, 700℃, 3hr (Zn vapour pressure, $\sim 10^{-1}$torr)
$ZnGa_2Se_4$: Ga	Ga 0.0015g, 550℃, 1hr (Ga vapour pressure, $\sim 10^{-11}$torr)
$ZnGa_2Se_4$: Se	Se 0.0015g, 750℃, 30min (Se vapour pressure, $\sim 10^{1}$torr)
$ZnGa_2Se_4$: Vacuum	vacuum, 650℃, 2hr
$ZnGa_2Se_4$: Air	air, 400℃, 30min

3. RESULTS AND DISCUSSION

3-1 Growth parameters and structural characterization of $ZnGa_2Se_4$ single crystal thin films.

The polycrystal structure of the evaporating materials determined by X-ray diffraction analysis was defect chalcopyrite with lattice constant a_o = 5.48 Å and c_o = 10.96Å, which a good agreement with the lattice constant a_o = 5.49Å and c_o = 10.99Å found by Beun et al[4]. As the compose of starting element, compose rates of growed crystal of $ZnGa_2Se_4$ single crystal thin films was accorded within the error range ±3%, we knew that the composite ratio of stoichiometry was harmonized very well, as shown in table 2.

After the substrate was chemically etched, to make an optimum surface state prior to growth, the substrate was annealed from 700℃ to 800℃ with 20℃ steps and the annealing time was also varied from 10 to 30 min to remove the residual oxide on the surface of the substrate. After the optimum surface heat treatment, to find best growth condition, single crystal thin films were grown while the source temperature was kept at 570℃, 590℃, and 610℃, respectively, and the substrate temperature was changed from 400℃ to 480℃. All of the grown $ZnGa_2Se_4$ single crystal thin films were analyzed by Double Crystal X-ray Rocking Curve (DCRC). DCRC confirmed the good quality to the grown single crystal thin films. During the growth of $ZnGa_2Se_4$, the substrate temperature was maintained at 590℃, and the source temperature was 450℃. We obtained a minimum Full Width at Half Maximum (FWHM) value of 138 arcsec for the optimum grown epilayers with a thickness of 3㎛ in the X-ray rocking curves, as shown in Fig. 3. The electrical transport properties were determined by Hall effect measurement in the van der Pauw geometry. The Hall measurement results show that the carrier density for as-grown $ZnGa_2Se_4$ was 9.36×10^{23} /m^3 and mobility was 2.95×10^{-2} m^2/v.s at the room temperature, as shown Table 3. From Hall data, the mobility was increased in the temperature range 30K to 100K by impurity scattering and decreased in the temperature range 100K to 293K by the lattice scattering[9], as shown in Fig. 4. Activation energy obtained from ln n versus 1/T of carrier density was 0.45eV as shown Fig.5

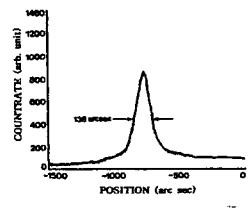

Fig. 3. Double crystal X-ray rocking curve of $ZnGa_2Se_4$ single crystal thin films at substrate temperature of 450 ℃

3.2. The energy gap of $ZnGa_2Se_4$

The optical absorption spectrum in the visible region was measured by a UV-VIS-NIR spectrophotometer at room temperature. Fig. 6 shows the optical absorption spectrum near the fundamental absorption edge of the $ZnGa_2Se_4$. To determine the direct band gap of $ZnGa_2Se_4$, we used the following formula[10]

$$(\alpha \cdot h\nu)^2 \sim (h\nu - E_g) \quad \text{--------(1)}$$

which is the relation betweem the incident photon energy ($h\nu$) and the optical absorption coefficient (α) for a allowed direct transition. This result is shown in Fig. 7 for the $ZnGa_2Se_4$. The direct band gap of the $ZnGa_2Se_4$ obtained by extrapolation to $(\alpha \cdot h\nu)^2$ = 0 in Fig. 7 is found to be 2.16eV at room temperature, which is a good agreement with the fundamental band gap of 2.17eV obtained from the optical absorption spectrum by Beun[4]

Fig. 8. show the temperature dependence of the direct band gaps of the $ZnGa_2Se_4$. The temperature dependence of the direct energy gap is well satisfied with the Varshni equation[11]

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

where, $E_g(0)$ is the band gap at absolute zero, α and $\beta$are constants. We can deduce from Fig. 8 that $E_g(0)$ is 2.38eV for the $ZnGa_2Se_4$. The constants of the Varshni equation are given by $\alpha = 7.83 \times 10^{-4}$ eV/K, and β= 195 K, respectively.

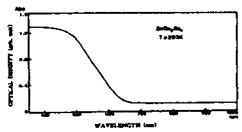

Fig. 6. Optical absorption spectra of $ZnGa_2Se_4$ single crystal thin films

3.3. The characteristic of $ZnGa_2Se_4$ photoconductive cell

3.3.1 sensitivity

Sensitivity of photoconductive cell is a relation

between intensity of incident illumination to photoconductive surface and out put of cell. Sensitivity can be expressed by current and resistance of cell, and it is common to denote sensitivity as resistance of cell. We used tungsten lamp as light source, and then measured the resistance of cell by adjusting illumination gradually from 10lx to 1000lx. We named γ characteristic as linear gradient at the relation of intensity of illumination and resistance, and it is

$$\gamma_{10}^{1000} = \tan\theta = \frac{\log R_{10} - \log R_{1000}}{\log 1000 - \log 10}$$

where, R_{10} and R_{1000} are resistance of one each, when intensity of illumination is lighted with 10lx and 1000lx. We illuminated the relation between resistances of cell what was measured by changing lighted intensity of illumination from 10lx to 1000lx, as shown Fig. 9. They, (a)Zn, (b)Ga, (c)Se, (d)vacuum, and (e)air in Fig.9 are components of cell change according to illumination of the annealled $ZnGa_2Se_4$ sample. At this time, the values of γ are (a) 0.88, (b)0.75, (c) 0.99, (d)0.27, and (e) 0.90 when it is annealed under the condition of Zn-, Ga-, Se-vapor, vacuum, and air atmosphere. The sample annealed in Se vapour the sensitivity characteristics was best. From this results, it could be practical use when γ value is over 0.8[11].

3.3.2 Maximum Allowable Power Dissipation (MAPD)

This is maintained linear to relation with illumination current as long as we irradiated constant intensity of light on photoconductive cell and changed D.C input voltage. When the in-put voltage is increased gradually from 1V, it is lineared, then it is deviated. We are defined its phenomenon as MAPD and denote mW. We illuminated the relation between in-put voltage and current by irradiation of light of annealed $ZnGa_2Se_4$ thin films at Se vapour, as shown Fig. 10. When we fixed intensity of illumination at 300lx, 500lx, and 800lx and increase gradually in-put voltage from 1V, it is kept linear within 100V, 77V and 58V at 300lx, 500lx, and 800lx, and then MAPD measured 343mW. The annealed sample at Zn, Ga vapour, air and vacuum atmosphere measured by this methed, MAPD of annealed sample are 193mW, 117mW, 251mW, and 28mW respectively, and MAPD of the annealed sample is the biggest value in the sample annealed Se vapour.When MAPD is big, it means appling fields are extensive, though the in-put voltage is increased as connecting circuit and it is because of the maintained range as linear.

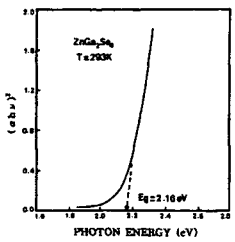

Fig. 7. Plots $(\alpha h\nu)^2$ versus the incident photon energy hν for $ZnGa_2Se_4$ single crystal thin films

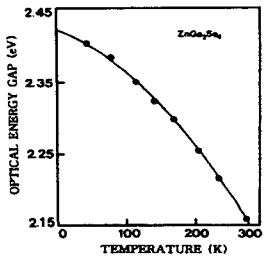

Fig. 8. Temperature dependence of the energy gaps in $ZnGa_2Se_4$ single crystal thin films. The solid line represents the fit to the varshni equation

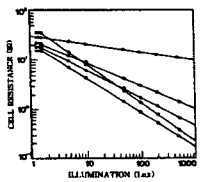

Fig. 9. Cell resistance vs illumination characteristics for $ZnGa_2Se_4$ single crystal thin films

3.3.3 pc/dc

We measured the value of ratio by dark current (dc) measuring in-put voltage (1.5V), and photocurrent (pc) measuring illuminated white light (3000lx) on an annealed sample in Zn-, Ga-, Se-vapour, vacuum and air atmosphere, as shown in table 4. The biggest rate value of photocurrent versus darkcurrent is the case of annealed in Se vapour, it is expected the possibility as a good photoconductor because its value of rate (pc/dc) is 9.83×10^6. it could be practical use at last ratio is 10^5[12].

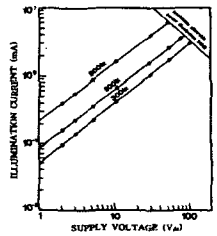

Fig. 10. Illumination current vs voltage characteristics of $ZnGa_2Se_4$ single crystal thin films annealed in Se vapour.

Table 4. Comparison of darkcurrent with photocurrent of $ZnGa_2Se_4$ single crystal thin films grown by HWE method annealed in Zn, Ga, Se, atmosphere and air, vaccum (light intensity : 3,000 lx)

sample	darkcurrent (A)	photocurrent (A)	ratio (pc/dc)
$ZnGa_2Se_4$	1.93×10^{-3}	2.52×10^{-3}	1.31×10^{0}
$ZnGa_2Se_4$: Air	8.24×10^{-6}	5.98×10^{-1}	7.25×10^{4}
$ZnGa_2Se_4$: vaccum	7.39×10^{-3}	2.42×10^{-1}	3.27×10^{1}
$ZnGa_2Se_4$: Ga	6.38×10^{-5}	2.41×10^{-2}	3.77×10^{2}
$ZnGa_2Se_4$: Zn	6.36×10^{-6}	1.35×10^{-1}	2.12×10^{4}
$ZnGa_2Se_4$: Se	1.74×10^{-7}	1.71×10^{0}	9.83×10^{6}

3.3.4 Response Time

The response time can defined into two things, 'rise time' required till a peak value of current become 63% after being illuminated light to photoconductive cell and 'decay time' required till the peak value become 37% after being removed light. This 'decay time' is called carrier life.

When light (10 lx) illuminated on $ZnGa_2Se_4$ photoconductive cell made by HWE, the response time was the best for the sample annealed in Se vapour compare with the sample annealed in Zn-, Ga-, Se-vapour air and vacuum atmosphere, as shown in table 5. Then we obtained the rise and decay time of 9ms and 9.3ms, respectively. Response time can be practical used within 20ms of rise time, and decay time[12]. This response time depends on intensity of light, load resistance, condition of crystal deposition, temperature, and so on.

Table 5. Response time of $ZnGa_2Se_4$ single crystal thin films epilayer

sample	10 lx	
	rise time (ms)	decay time (ms)
$ZnGa_2Se_4$: Ga	20.3	20.1
$ZnGa_2Se_4$: Zn	14.3	12.2
$ZnGa_2Se_4$: Se	9	9.3
$ZnGa_2Se_4$: air	12.5	10.2
$ZnGa_2Se_4$: vaccum	32.4	29.6

4. CONCLUSIONS

We grown $ZnGa_2Se_4$ single crystal thin film by HWE method, and it is annealed in Zn-, Ga-, Se vapour, vacuum, and air atmosphere. After that, we worked the characteristic of photoconductive cell and physical characteristic.

The result was following

1) From X-ray diffraction of synthesized $ZnGa_2Se_4$ polycrystal, lattice constant is obtained a_0 = 5.48Å, c_0 = 10.96Å by extrapolation method.

When the temperature of substrate is 450℃, and temperature of evaporation source is 590℃, full width at half maximum(FWHM) is 138arcsec, and it is the best growth condition because it is the smallest value.

2) As result of measuring Hall effect of $ZnGa_2Se_4$ single crystal thin film, we determined it was the p-type semiconductor. Activation energy obtained from ln n of carrier density versus 1/T was 0.45eV. Hall mobility was caused from piezoelectric scattering between 30K and 200K and decreased according to polar optical scattering betweem 200K and 293K

3) According to characteristic of photoabsorption, energy gap was 2.16eV at room temperature

4) Application device of $ZnGa_2Se_4$ single crystal thin film could be used as photocell, only when the rate value (pc/dc) of dc and pc is the biggest, and that is annealed cell in Se vapour. The value is 9.83 $\times10^6$ and 7.25 $\times$ 10^4 in air atmosphere, 2.12 $\times$ 10^4 in Zn vapour atmosphere, 3.77 $\times$ 10^2 in Ga vapour atmosphere, and 3.27 $\times$ 10^1 in vacuum atmosphere.

Also, in case of sensitivity, the best value of annealed cell was 0.99 in Se vapour, and 0.88 in Zn vapour atmosphere, 0.75 in Ga vapour atmosphere, 0.90 in air atmosphere, and 0.27 in vacuum atmosphere.

5) In case of MAPD, the best value of annealed cells was 343mW in Se vapour, and 193mW in Zn vapour atmosphere, 117mW in Ga vapour atmosphere, 251mW in air atmosphere, and 28mW in vacuum atmosphere.

Also, in case of response time, the fastest value of annealed cell was rise time 9ms, decay time 9.3ms in Se vapour atmosphere.

6) We grown $ZnGa_2Se_4$ single crystal thin film by HWE method and its annealed cell in Se vapour, air atmosphere obtained photoconductive chatacteristic better than Hamamatsu's made by sinter method.