Transactions of the Materials Research Society of Japan. Vol. 20

Photoluminescence spectra and electrical properties of $CuAlSe_2$ grown on GaAs substrate by molecular beam epitaxy

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$CuAlSe_2$, one of the wide gap members in chalcopyrite-type compounds, were grown on GaAs substrate by molecular beam epitaxy. High quality $CuAlSe_2$ with a smooth surface morphology could be obtained when the substrate temperature was set to 600°C and the growth rate was about 0.1μm·h^{-1} though the optical and electrical properties of grown layers strongly depended on their thickness. The excitonic emission was observed in PL spectra at 5 K when the layer thickness was about 1 μm, and the epilayers thicker than 0.5 μm showed p-type conductivity with the low electrical resistivity.

1. INTRODUCTION

$CuAlSe_2$, one of the chalcopyrite-type compounds, is promising material for blue laser diodes because it has a direct band gap of 2.7 eV at room temperature [1]. But it has been difficult to prepare the wide gap chalcopyrite-type compounds containing aluminum as a constituent element because of its high reactivity. Molecular beam epitaxy (MBE) may be one of the solution to obtain high quality epitaxial $CuAlSe_2$ since it is one of the crystal growth technique in the ultra high vacuum environment. In this study, the optimum growth conditions to obtain high quality $CuAlSe_2$ layers were examined by MBE at first, and their optical and electrical properties were characterized by photoluminescence (PL) and Hall measurements. It was shown that the optical and electrical properties of $CuAlSe_2$ strongly depended on the layer thickness. The excitonic emissions or near band-edge emissions were observed in the PL spectra at 2 K only when $CuAlSe_2$ layers were thicker than 0.8μm. The electrical resistivity of epitaxial layers thinner than 0.5 μm were too high to measure the Hall voltage while thicker epilayers showed the low resistivity p-type conductivity.

2. EXPERIMENTAL PROCEDURES

Elemental Cu (7N), Al (6N) and Se (6N up) were used as source materials. Cu and Al ingots in pBN crucibles were melted and well degassed at 1250°C for 2 hours in the growth chamber of the MBE system previously. Undoped semi-insulating GaAs (100) was used as a substrate. It was etched in the H_2SO_4:H_2O_2:H_2O=5:1:1 solution before loading to the sample exchange chamber where the substrate was heated to desorb H_2O at 250°C for more than 8 hours. Then it was transferred to the growth chamber to remove the oxidation layer of the surface by the thermal etching. The growth conditions were as follows; the substrate temperature, 300-700°C, the beam equivalent pressure of Cu, $P_{Cu}=2.7\times10^{-9}$ Torr, and $P_{Al}=2.2\times10^{-9}$-4.5×10^{-10} Torr, $P_{Se}=5\times10^{-6}$-1×10^{-5} Torr. The growth rate was about 0.11 μm under these conditions. The thermal etching and the growth process was monitored by the reflection high energy electron diffraction (RHEED).

The quality of the grown layers were characterized by x-ray diffraction measurements used Cu*K*α line as a x-ray source. The optical properties were characterized by PL measurements at 2 K using He-Cd (325 nm, 2 mW) or Ti-doped Sapphire (400 nm, 20 mW) laser as the excitation source. Hall measurements were carried out to characterize the electrical properties by the van der Pauw technique. High purity (6N) indium was used as the electrode metal. Each sample was sealed at 5×10^{-6} Torr in a quartz tube and annealed at 200°C for 5 minuets to make a ohm contact. It was supposed that the serious desorption of Se atoms from the surface did not occur since the PL spectra did not show any change before and after annealing. The magnetic field applied to samples was 7.0×10^3 G.

3. RESULTS AND DISCUSSION

3.1. Optimizing of the growth conditions

Figure 1 shows the x-ray diffraction profiles of $CuAlSe_2$ grown on GaAs substrate under the five different beam equivalent pressure of Al. That of Cu was kept at 2.71×10^{-9} Torr through the experiments. The thickness of epilayers was about 0.3 μm. The profiles of $CuAlSe_2$ (008) reflections in Fig. 1 (a), (d) and (e) were broad and accompanied by the shoulder peaks, which means the poor quality of the grown layers. On the contrary, in figure 1 (b) and (c), no shoulder was observed around the (008) reflection of $CuAlSe_2$ in addition that the peaks from epilayers split into the doublet due to $CuK\alpha_1$ and $CuK\alpha_2$ lines as well as GaAs substrates, which indicates the good crystalline quality of the epitaxial $CuAlSe_2$. As the surface morphology of epilayer (c) was smoother than that of (d), the beam equivalent pressure of Al was set to 1.05×10^{-9} Torr in following experiments. The epitaxial $CuAlSe_2$ layers were obtained when the substrate temperature (T_S) was between 500°C and 600°C. The grown layers became polycrystals at T_S=300-450°C and 700°C. The RHEED pattern during the growth showed sharp streaks with Kikuchi lines at T_S=550°C and 600°C, but it became diffused spots at T_S=500°C. The PL spectra of $CuAlSe_2$ grown at T_S=550°C and 600°C are shown in Fig. 2 (a) and (b), respectively. The thickness of each layer was about 1.0 μm. The very intense near band-edge emissions were observed for the layer grown at T_S=600°C as shown in Fig. 2 (b) while no edge emission was detected in Fig. 2 (a). The optimum growth conditions of $CuAlSe_2$ were as follows; $P_{Cu}=2.71\times10^{-9}$ Torr, $P_{Al}=1.05\times10^{-9}$ Torr, $P_{Se}=5\times10^{-6}$-1×10^{-5} Torr and T_S=600°C for the reasons mentioned above. The epitaxial $CuAlSe_2$ layers discussed their optical and electrical properties in following sections were grown under these conditions.

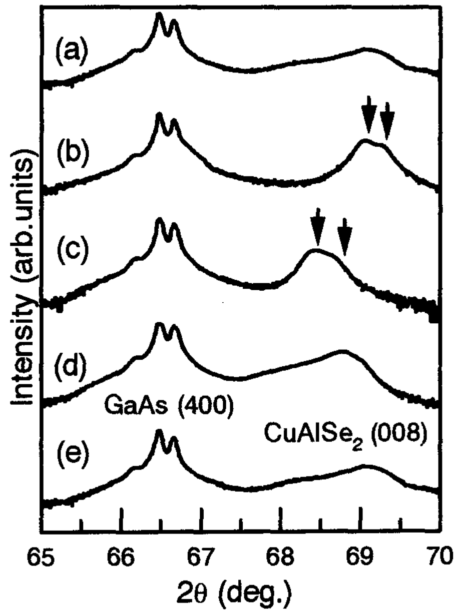

Fig. 1 X-ray diffraction profiles of $CuAlSe_2$ grown on GaAs under various beam equivalent pressures of Al. (a) $P_{Al}=2.22\times10^{-9}$ Torr, (b) 1.51×10^{-9} Torr, (c) 1.05×10^{-9} Torr, (d) 6.93×10^{-10} Torr and (e) 4.64×10^{-10}Torr.

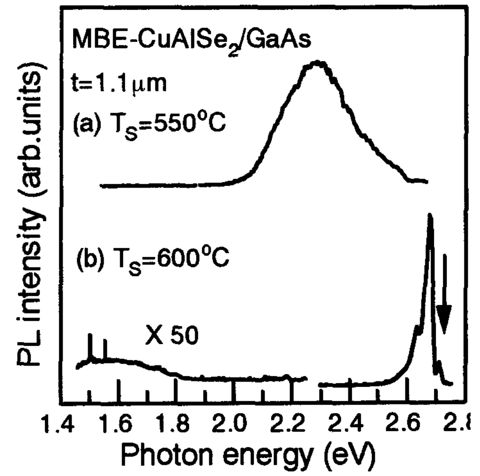

Fig. 2 Photoluminescence spectra of CuAlse$_2$ grown on GaAs at the substrate temperature 500°C (a) and 600°C (b).

3.2. Optical properties of epitaxial $CuAlSe_2$

Figure 3 shows the PL spectra at 2 K of $CuAlSe_2$ with different layer thicknesses. The PL spectra were dominated by the deep emissions around 1.8 eVand the near band-edge emission could not be observed when the thickness was less than 0.55 μm. On the other hand, the very intense near band-edge emissions were observed for layers thicker than 0.55 μm and the deep emissions almost vanished. The emission at 2.72 eV in Fig.3 (e) was assigned as the free excitonic emission from the results of the photoreflectance measurements [2]. Figure 4 (a) and

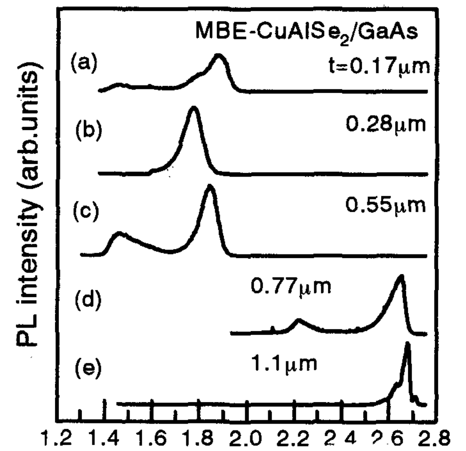

Fig. 3 Dependence of the photoluminescence spectra of $CuAlSe_2$ on the layer thickness. (a) 0.17μm, (b) 0.28μm, (c) 0.55μm, (d) 0.77μm, (e) 1.1μm.

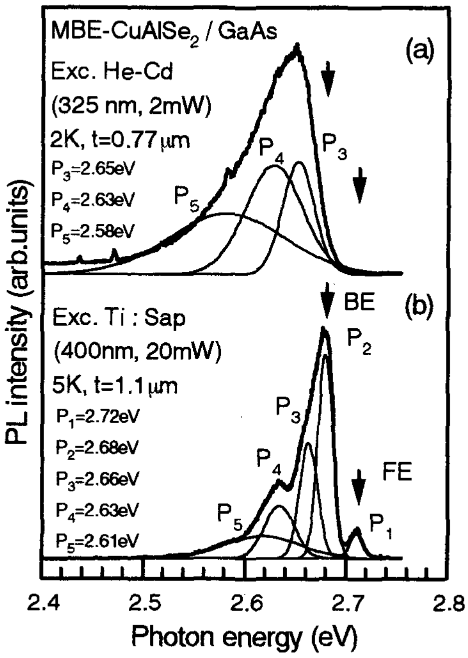

Fig. 4 Near band-edge photoluminescence spectra of $CuAlSe_2$. Thicknesses of (a) and (b) are 0.77 μm and 1.1μm, respectively.

(b) shows the detailed PL spectra near band-edge of the samples shown in Fig.3 (d) and (e), respectively. It was reported that five peeks were observed in the PL spectra near band-edge of $CuAlSe_2$ grown by metalorganic chemical vapor deposition (MOCVD) [3]. The peak fitting calculations were carried out assuming that those were also observed in the MBE-grown $CuAlSe_2$. The peak energies of the emissions shown in Fig. 4 (b) were determined as follows; P_1=2.72 eV, P_2=2.68 eV, P_3=2.66 eV, P_4=2.63 eV and P_5=2.61 eV. These values were consistent with those reported in ref. [3]. Since the free excitonic emission (P_1) and P_2 in Fig. 4 (a) was vanished simultaneously, the P_2 was considered a bound excitonic emission. The origins of P_3, P_4 and P_5 peaks which were identical in both Fig. 4 (a) and (b) will be discussed in the next section taking the results of the Hall measurements into consideration. The PL spectra at 77 K and 300 K of MBE-grown $CuAlSe_2$ are shown in Fig. 5 with those of the bulk $CuAlSe_2$ single crystal grown by chemical vapor transport [4]. The spectra were dominated by the deep emissions in both crystals above 77 K. The origin of the deep emissions in the epitaxial $CuAlSe_2$ was different from that of the bulk crystal because the deep emissions of the bulk showed the blue shift as the temperature decreased while those of the epilayer did not.

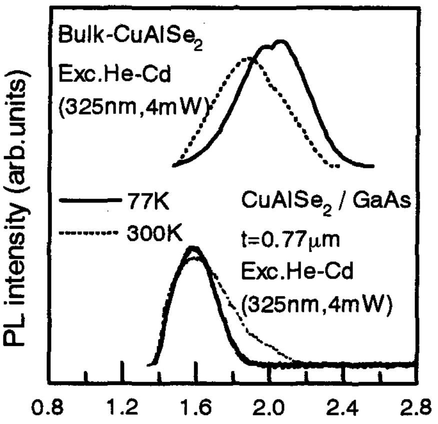

Fig. 5 Photoluminescence spactra at 77 K and 300 K of bulk $CuAlSe_2$ grown by chemical vapor transport and MBE-grown epilayer.

3.3. Electrical properties of epitaxial $CuAlSe_2$

Table1 shows the results of the Hall measurements for the same samples shown in Fig. 4 (a) and (b). The Hall measurement did not succeed for $CuAlSe_2$ epilayers thinner than 0.55 μm because their resistivities were too high to make ohmic contacts. The $CuAlSe_2$ layers thicker than 0.55 μm showed the p-type conductivity. The resistivity of each sample was between 10^{-3} Ω·cm and 10^{-2} Ω·cm. Similar

Table 1. The resistivities, hole concentrations and Hall mobilities of $CuAlSe_2$ layers grown on GaAs by MBE.

Thickness (μm)	ρ ($\Omega \cdot cm$)		p (cm^{-3})		μ ($cm^2 \cdot V^{-1} \cdot s^{-1}$)	
	77 K	300 K	77 K	300 K	77 K	300 K
<0.55	—		—		—	
0.77	1.0×10^{-2}	1.1×10^{-3}	1.2×10^{20}	2.5×10^{19}	11	120
1.1	4.2×10^{-2}	3.5×10^{-3}	4.3×10^{17}	3.9×10^{18}	110	230

results were also obtained for MOCVD-grown $CuAlSe_2$ [5]. As the acceptor levels in epitaxial $CuAlSe_2$ were supposed relatively shallow, the emissions P_3, P_4 and P_5 in Fig. 4 were considered due to the optical transitions between the conduction band and the acceptor levels (free-to-bound emissions). The acceptor levels were estimated as 75 meV, 105 meV and 145 meV for P_3, P_4 and P_5, respectively assuming 25 meV as the binding energy of the free exciton of $CuAlSe_2$ (this value is almost equal to that of ZnSe, the analogous compound of $CuAlSe_2$). As it was reported that the activation energy of acceptors in bulk $CuAlSe_2$ was 65 meV and its origin was assigned to Cu vacancy [6], P_3 may be the emission relative to the Cu vacancy. The PL and Hall measurements for $CuAlSe_2$ grown under slightly Cu-rich condition compared with the optimum beam pressure ratio (P_{Cu}/P_{Al}) are under study for the assignment. The increase of the hole concentration for the 0.77 μm-thick sample at low temperature side was considered due to the formation of an acceptor impurity band as observed in Ge and Si [7]. The measurement of the temperature dependence of the Hall coefficient is required to verify this presumption. High quality epitaxial $CuAlSe_2$ with enough thickness showed the low resistivity and p-type conductivity while the resistivity of thin layers made a ohmic contact impossible. This was supposed as follows; the p-type conduction was proper to $CuAlSe_2$. When Ga and As atoms were incorporated into $CuAlSe_2$ by the interdiffusion at the $CuAlSe_2$ /GaAs interface during the growth, they compensated acceptors by forming defects such as dislocations acting as a deep carrier trap or broke epilayers near the interface. In fact, many pits or voids were observed at the interface by the scanning electron microscope. Similar defects were also observed in GaN/GaAs (100) interface when the thickness of the buffer layer was improper [8]. Composition analysis across the $CuAlSe_2$/GaAs interface by the secondary ion mass spectroscopy (SIMS) is now under progress.

4. CONCLUSION

Epitaxial $CuAlSe_2$ layers were grown on GaAs substrate by molecular beam epitaxy. High quality $CuAlSe_2$ were obtained under following growth conditions; $P_{Cu}=2.71 \times 10^{-9}$ Torr, $P_{Al}=1.05 \times 10^{-9}$ Torr, $P_{Se}=5 \times 10^{-6}$-1×10^{-5} Torr and $T_S=600°C$. The excitonic and near band-edge emissions related to the acceptor levels were observed in the PL spectra at 2 K when the layer was thicker than 0.55 μm. The deep emissions around 1.8 eV were dominant in the PL spectra of thin layers. It was shown that the optical properties depended on the layer thickness. $CuAlSe_2$ with superior optical properties showed the low resistivity p-type conductivity while the resistivity of thin layers (< 0.55 μm) was too high to measure the Hall effect, which suggested that the interdiffusion at the $CuAlSe_2$/GaAs interface degraded the optical and electrical properties of thin layers. The composition analysis across the interface using SIMS is required to verify the diffusion of Ga and As atoms.

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