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

Metalorganic Vapor Phase Epitaxy of $CuAl_xGa_{1-x}Se_2$ alloys

S.Chichibu[a], K.Yamaya[a], H.Nakanishi[a], S.Shirakata[b], and S.Isomura[b]

[a]Faculty of Science and Technology , Science University of Tokyo , Noda , Chiba 278 , Japan
[b]Faculty of Engineering , Ehime University, Matsuyama , Ehime 790 , Japan

The $CuAl_xGa_{1-x}Se_2$ chalcopyrite alloy epilayers were successfully grown on GaAs(001) substrates by low-pressure metalorganic vapor phase epitaxy (LP-MOVPE). A good controlability of the Al composition, x , in the epilayer was demonstrated, *i.e.*,the distribution coefficient of Al was unity.

A quadratic dependence of the exciton resonance energies associated with the uppermost valence bands, which were determined by means of photoreflectance measurements,on x was confirmed. Spin-orbit splittings of the epilayers were almost comparable to those of bulk alloy single crystals while magnitudes of crystal-filed splittings were larger than those of the bulk crystals, and the results were explained in terms of residual tensile biaxial strain in the epilayers.

1. INTRODUCTION

The $CuAl_xGa_{1-x}Se_2$ quaternary alloys have band gap energies ranging from 1.7 to 2.7 eV[1,2], which cover the visible spectral region from red to blue. It has been very difficult [3,4] to grow high-quality CuAl Ⅵ $_2$ compounds due to an existence of chemically active Al in the matrix. However, metalorganic vapor phase epitaxy (MOVPE) has grown high-quality $CuAlSe_2$ [5,6] and $CuAlS_2$ [7] epilayers, both of which have exhibited excitonic emissions.

The lattice parameter a of $CuAl_xGa_{1-x}Se_2$ is almost constant for all x (0.5612 nm for $CuGaSe_2$ and 0.5607 nm for $CuAlSe_2$) [8,9],and is close to that of GaAs being 0.5642 nm. Therefore this alloy system can be utilized as visible light-emitting devices in the form of the heteroepitaxial layers grown on GaAs (001) substrate. However, only limited information has been available for this alloy system such as optical absorption [10], electrical and PL properties [11] before 1993. We have investigated resonance energies of excitons associated with the uppermost valence bands to the conduction band and PL spectra as a function of Al composition, x, using bulk $CuAl_xGa_{1-x}Se_2$ alloy single crystals grown by the chemical vapor transport (CVT) method [9].

In the present work, heteroepitaxial growth of $CuAl_xGa_{1-x}Se_2$ alloy layers was carried out for the first time by LP-MOVPE. The alloy composition of thin layers was determined using an unique method with an electron-probe microanalyzer (EPMA). Structural, electronic, and optical properties were investigated as a function of x.

2. EXPERIMENT

$CuAl_xGa_{1-x}Se_2$ alloy epilayers were grown using a vertical quartz reactor LP-MOVPE apparatus (BENTEC SCV-2000QR). The source precursors were pentahaptcyclopentadienylcoppertriethylphosphin (CpCuTEP),triisobutylaluminium (TIBAl),normal-tripropylgallium (TPGa),and diethylselenide (DESe).

The growth temperature and reactor pressure were 600 ℃ and 4×10^4Pa,respectively. Pd-purified H_2 was used as a carrier gas. The total H_2 flow rate into the reactor was 3 ℓ /min. and the gas phase Ⅵ / Ⅲ ratio was 200. The growth rate was typically 0.17 μ m/h, and about 0.5 μ m-thick $CuAl_xGa_{1-x}Se_2$ epilayers were grown on GaAs (001) and GaP (001) substrates.

The surface morphology was observed with a Nomarski interference microscope and a scanning electron microscope (SEM) . Lattice images were observed with a transmission electron microscope (TEM) .Orientation of the epilayer was evaluated by the x-ray diffraction (XRD) measurements with the θ -2 θ method using the CuK α line. The solid composition of Cu, Al, Ga, and Se in the epilayers were estimated by EPMA, according to the measurement condition optimized by Kariya *et al* [12].

Photoluminescence (PL) and photoreflectance (PR) measurements were carried out between 8K to room temperature (300K:RT). For the pump light of the measurements,the 325.0 nm line of a cw He-Cd laser was used for $x \geqq 0.63$. Similarly, the 457.9, 488.0, and 514.5 nm lines of a cw Ar^+ laser were used for $0.34 \leqq x \leqq 0.63$, $0 \leqq x \leqq 0.34$, and x=0, respectively.

3. RESULTS AND DISCUSSION

The Al composition, x, in the alloy layers agrees with $[TIBAl]/([TIBAl]+[TPGa])_{gas}$, which indicates that the distribution coefficient of Al is unity. The same results have been found for CVT growth of bulk $CuAl_xGa_{1-x}Se_2$ [9] and $CuAl_xGa_{1-x}SSe$ [13] alloys. These results imply that MOVPE of $CuAl_xGa_{1-x}Se_2$ is in the cation diffusion-limited regime and the thermal equilibrium between the growing surface and the lowermost boundary layer is mostly held.

The surface morphology of $CuAl_xGa_{1-x}Se_2$ epilayers become rougher with increasing x. For the $CuAl_xGa_{1-x}Se_2$/GaAs (001),a mirrorlike surface with a cross hatches along the [100] and [010] direction is observed for x=0 ($CuGaSe_2$) [14]. Cross hatches are observed for all x owing to the lattice mismatch (Δ a/a ≒ - 0.6% at room temperature) and difference of the thermal expansion coefficients between GaAs and a axis of the alloys [15]. An wavy morphology is seen for $x \geqq 0.43$. The appearance of such a worse morphology implies difficulties in growing alloy layers having higher Al content. The morphology of alloy layers grown on GaP (001) is worse than that of $CuAl_xGa_{1-x}Se_2$/GaAs (001) for all x.

According to the XRD pattern of $CuAl_xGa_{1-x}Se_2$/GaAs (001) ,the diffraction peaks at around 34° and 69° correspond to the (004) and (008) reflection from the epilayer. The XRD results indicate that $CuAl_xGa_{1-x}Se_2$/GaAs(001) have their c axis normal to the substrate plane.

An example of the cross-sectional TEM micrograph of $CuAl_xGa_{1-x}Se_2$/GaAs (001) [x=0.5] is shown in Fig. 1, which is taken with the incident electron beam along the [110] azimuth of the substrate. As is the case with $CuGaSe_2$/GaAs (001) [14] and $CuAlSe_2$/GaAs (001) [4,16], single-domain lattice images without any amorphous phase are recognized.

The exciton energies of $CuAl_xGa_{1-x}Se_2$/GaAs(001) are plotted as a function of x in Fig.2. As is the case with the bulk $CuAl_xGa_{1-x}Se_2$ alloy crystals [9], E_A, E_B, and E_C have nonlinear dependence on x. E_A is approximated by the quadratic dependence on x as:

$$E_A = 2.713x + 1.698\,(1-x) - 0.26x\,(1-x)\ \text{eV}. \qquad (1)$$

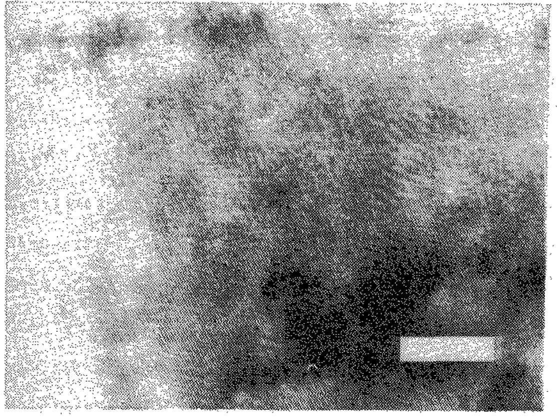

Fig. 1. A cross-sectional TEM micrograph of $CuAl_{0.5}Ga_{0.5}Se_2$/GaAs (001) taken with the incidence along the [110] azimuth of the substrate. Marker represents 10 nm.

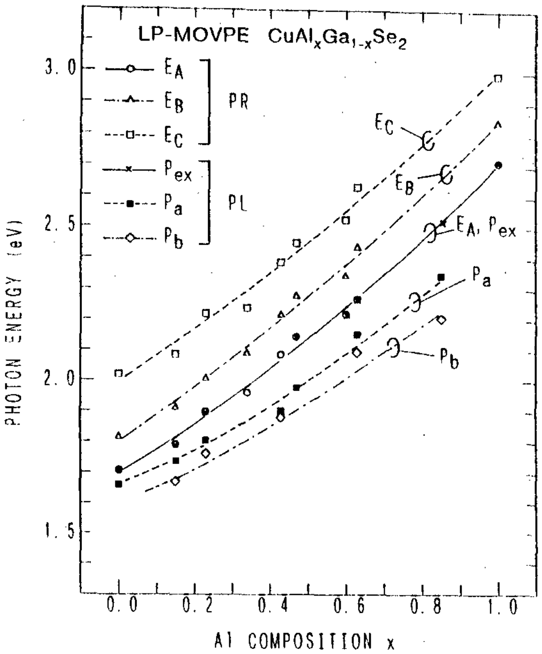

Fig. 2. Exciton energies (E_A , E_B , and E_C) in $CuAl_xGa_{1-x}Se_2$/GaAs(001) as a function of x at 77 K obtained by the analysis of the PR spectra. PL peak energies (P_{ex} , P_a , and P_b) at 30 K are also plotted.

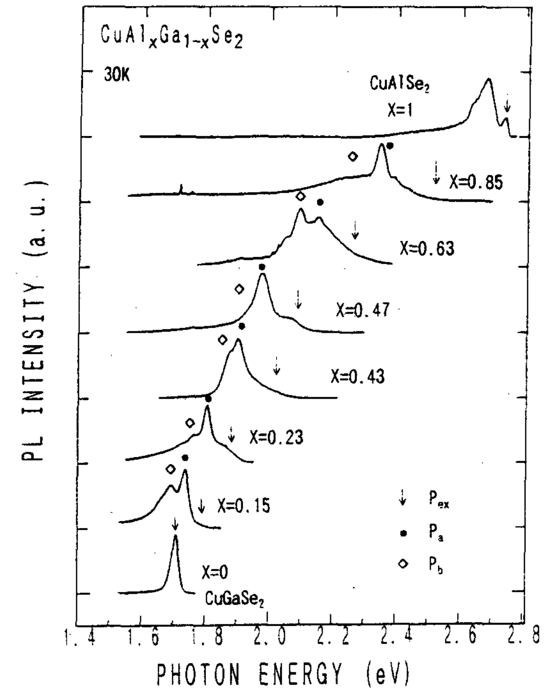

Fig. 3. PL spectra in $CuAl_xGa_{1-x}Se_2$/GaAs(001) at 30 K. Arrows , closed circles , and open rombuses indicate P_{ex} , P_a , and P_b peaks , respectively.

The constants of the first and second terms are smaller by $17\sim23$meV than those of the bulk alloys[9], as stated above. On the other hand, approximation equations for E_B, and E_C almost agree with those of bulk crystals within the error of ± 3meV. A bowing parameter obtained from Eq. (1) for E_A is -0.26 eV, the value being comparable with that of the bulk alloy crystals (-0.28 eV) [9].

PL spectra of $CuAl_xGa_{1-x}Se_2$/GaAs(001) measured at 30 K are shown in Fig. 3. Color of the PL changes from red to crimson, orange, yellow, green, and bluish-purple with increasing x from 0 to 1. PL peaks are classified into three types. They are labeled P_{ex}, P_a, and P_b in order from high to low energy,as shown in Fig. 3. It is recognized from Fig.2 that the energy of P_{ex} agrees well with the A exciton energy,indicating that P_{ex} is related to an exciton emission [5,14]. The PL peak at 2.680 eV in $CuAlSe_2$ has been assigned as a bound exciton emission [5,6]. Relative P_{ex} intensity against other PL peak intensities in the PL spectra of alloy layers ($x \neq 0,1$) is weaker than those in the spectra of terminate compounds. This result suggests poor quality of alloy layers,especially for those having higher Al content.

The peak P_a located below P_{ex} dominates the PL spectra of $CuAl_xGa_{1-x}Se_2$/GaAs (001) ($x \neq 0,1$), as can be seen in Fig. 3. Occasionally,P_a was found in $CuAl_xGa_{1-x}Se_2$/GaAs (001) at low temperatures [17]. P_a has been assigned to the radiative transition of a free electron with a bound hole (F-B emission) [17]. Excitation intensity dependence of PL peak energy is examined for all x. An absence of the energy shift of P_a indicates that P_a is not a donor-acceptor (D-A) pair emission. Therefore P_a in $CuAl_xGa_{1-x}Se_2$/GaAs(001) is assigned to a F-B transition , similar to the case of $CuGaSe_2$, because the plots of the P_a peak energy can smoothly be connected with increasing x (data not shown).

4. CONCLUSIONS

$CuAl_xGa_{1-x}Se_2$ alloy epilayers were grown on GaAs (001) by LP-MOVPE. All alloy epilayers had their c axis normal to the substrate plane. A combination of TIBAl and TPGa allowed us to control the alloy composition by adjusting the gas phase input molar fraction; the distribution coefficient of Al was found to be unity.

A quadratic dependence of exciton energies on x was confirmed. Spin-orbit splittings of $CuAl_xGa_{1-x}Se_2$/GaAs (001) were almost the same as those of the bulk alloy crystals while magnitudes of crystal-field splittings were larger than those for the bulk crystals. The increase of the magnitude of $-\Delta\ cf$ was attributed to the residual tensile biaxial strain in the epilayers.

Color of the low-temperature PL changed from red to bluish-purple with increasing x. A peak due to free-to-acceptor transition dominated the PL spectra of $CuAl_xGa_{1-x}Se_2$/GaAs (001).

This work was supported in part by the Foundation of Ando Laboratory.

REFERENCES

[1] J.L.Shay and J.H.Wernick, *Ternary Chalcopyrite Semiconductors: Growth, Electronic Properties, and Applications*, (Pergamon, Oxford, 1975).

[2] M.Bettini, Solids State Commun. **13**, 599 (1973).

[3] K.Hara,T.Shinozawa, J.Yoshino, and H.Kukimoto, J. Cryst. Growth **93**, 771 (1988).

[4] S.Chichibu, A.Iwai, S.Matsumoto, and H.Higuchi, J. Cryst. Growth **126**, 635 (1993).

[5] S.Chichibu, S.Shirakata, S.Matsumoto, H.Higuchi, and S.Isomura, J. Appl. Phys. **74**, 6446 (1993).

[6] S.Chichibu, S.Shirakata, R.Sudo, M.Uchida, Y.Harada, S.Matsumoto, H.Higuchi, and S.Isomura, Jpn. J. Appl. Phys. **32-3**, 139 (1993).

[7] S.Chichibu, S.Shirakata, S.Isomura, Y.Harada, M.Uchida, S.Matsumoto, and H.Higuchi, J. Appl. Phys. **77**, 1225 (1995).

[8] JCPDS card File-Set.44($CuAlSe_2$ diffraction data).

[9] S.Shirakata, S.Chichibu, R.Sudo, A.Ogawa, S.Matsumoto, and S.Isomura, Jpn. J. Appl. Phys. **32**, L1304 (1993).

[10] I.V.Bodnar, N.L.Gil, and A.I.Lukomskii, Sov. Phys. Semicond. **17**, 333 (1983).

[11] K.Sugiyama, S.Iwasaki, T.Endo, and H.Miyake, J. Appl.Phys. **65**, 5212 (1989).

[12] T.Kariya, S.Shirakata, and S.Isomura, Adv. X-ray Chem. Anal. Jpn. **26**, 273 (1995). [in Japanese]

[13] S.Chichibu, S .Shirakata, A.Ogawa, R.Sudo, M.Uchida, Y.Harada,T.Wakiyama, S.Matsumoto, and S.Isomura, J. Cryst. Growth **140**, 388 (1994).

[14] S.Chichibu, Y.Harada, M.Uchida, T.Wakiyama, S.Matsumoto, S.Shirakata, S.Isomura, and H.Higuchi, J. Appl. Phys. **76**, 3009 (1994).

[15] H-G.Bruhl, N.Neumann, and G.Kuhn, Solid State Commun. **34**, 225 (1980).

[16] S.Chichibu, S.Shirakata, A.Iwai, S.Matsumoto, H.Higuchi, and S.Isomura, J. Cryst. Growth **131**, 551 (1993).

[17] H.Miyake, M.Yamada, and K.Sugiyama, J. Cryst. Growth **153**, 180 (1995).