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An investigation on 1.62 eV photoluminescence of $CuGaSe_2$ films grown by molecular beam epitaxy

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Cu-rich $CuGaSe_2$ films were grown on [001] oriented GaAs substrates by molecular beam epitaxy. They show frequently a remarkable photoluminescence emission peaked at 1.620 eV at low temperature. The emission can be attributed to donor-to-band recombination accompanying donor-to-acceptor pair recombination. The ionization energies of the bound states were estimated through temperature dependence of the emission.

1. INTRODUCTION

$CuGaSe_2$ is a promising material for optoelectronics[1], nonlinear optics[2] and solar cell active layers[3], and careful investigation of the material is therefore of interest. It is quite difficult to grow stoichiometric bulk crystals of $CuGaSe_2$, due to peritectic melting while the non-equilibrium growth technique such as molecular beam epitaxy (MBE) is useful. Previously we have shown that $CuGaSe_2$ films can be grown epitaxailly on GaAs substrates by MBE when the molecular beam flux ratio of Cu to Ga is controlled precisely[4] and that a photoluminescence (PL) emission at 1.714 eV of the films is attributed to exciton recombinations[5]. In this paper, we discuss a 1.62 eV emission which is frequently dominant in the MBE grown $CuGaSe_2$ films of Cu-rich composition, concluding that the emission can be attributed to donor-to-band recombination accompanying donor-to-acceptor pair recombination of the same donor. The ionization energy of the acceptor and the donor were estimated through temperature dependence of the emission.

2. EXPERIMENTAL

2.1. Sample preparation

The film described in this work was fabricated from elemental sources, Cu(7N), Ga(7N) and Se(6N), which were evaporated using Knudsen's effusion cells. Cu- and Se-cells were held at 1070°C and about 180°C, respectively. The chemical composition of the film was adjusted by changing the cell temperature of Ga source around 880°C. The flux of the Se molecular beam was sufficiently larger than that of the others. The substrate was a [001] oriented GaAs wafer which was degreased with organic solvents then etched with a chemical mixture of NH_4OH, H_2O_2 and H_2O in a ratio of 5:2:10. The film was grown on the substrate held at 490 ℃ for one hour with a growth rate of ~0.8 μm/hour. Reflection high-energy electron diffraction (RHEED) patterns showed spots characteristic of the chalcopyrite structure and its c-axis normal to the substrate surface. X-ray diffraction (XRD) analysis confirmed epitaxial growth of $Cu_xGa_ySe_z$ films on the substrate. The intensity ratios of additional XRD peaks presumably due to formation of second phases were less than 0.3% of (008) reflection. Polycrystalline $Cu_xGa_ySe_z$ films were also fabricated on glass (Corning 7059) substrates under the same molecular beam conditions in order to measure compositions by the electron probe for micro-analysis (EPMA). The composition of the film was determined to be 27.9 % Cu and 27.4 % Ga.

2.2. Photoluminescence measurement

PL measurement was carried out using 514.5 nm line of an Ar^+ ion laser. The sample was cooled ranging from room temperature down to 6.5 K for temperature dependence measurement or fixed at 2 K for excitation power

dependence. The excitation power was 30 mW for temperature dependence measurements or it was changed from 1.3 μW to 148 mW for excitation power dependence measurements. PL emissions were dispersed by a 1 m Czerny-Turner-type monochromator, detected by a Peltier-cooled GaAs-photocathode photomultiplier, amplified using a lock-in technique, and then collected by a computerized system.

3. RESULTS AND DISCUSSION

3.1. Excitation power dependence of PL

Fig.1 shows the PL spectra of excitation power dependence. The dominant emission, which is the typical feature of the spectra for Cu-rich films grown by MBE, reaches the highest at 1.620 eV for weak excitation at low temperature. The optical phonon replica (1LO) of the 1.620 eV emission is observed at 1.587 eV[4,5]. Emission Ex peaked at 1.714 eV is attributed a complex consisting of free exciton and bound exciton recombinations[5].

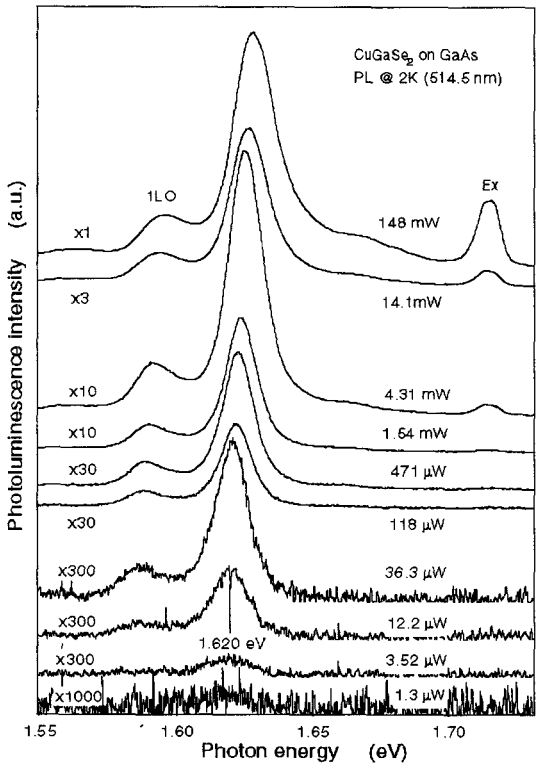

Fig.1 Low temperature photoluminescence spectra of MBE grown $CuGaSe_2$ film as a function of excitation power.

The integrated intensity of the 1.620 eV emission shows under-linear dependence on the excitation power with a factor of 0.79 as is shown in Fig.2. It suggests that the emission is related to recombination processes through states in the band-gap. The peak shifts to high energy with increase of the excitation power, showing that the emission includes a donor-to-acceptor pair recombination process, (D,A).

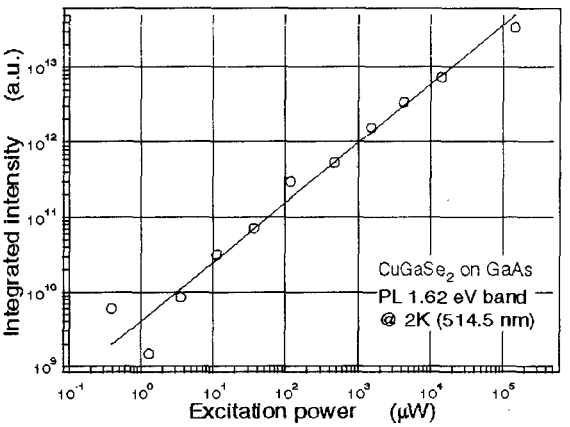

Fig.2 Excitation power dependence of the 1.62 eV photoluminescence intensity.

Photon energies for the half maximum at both flanks of the emission shift to the high energy, while the value of HWHM of the emission has a waist for the excitation power change (see Fig.3). This indicates that the emission is not only from the (D,A) but it includes the process which is independent of the excitation power. The latter can be attributed to a free-to-bound recombination, (F,B). When the (D,A) overlap the (F.B), the (D,A)'s influence is preponderant at the low-energy wing for low excitation and it appears at the high-energy for high excitation. It is reasonable to suppose that one of the two states of the (D,A) is common to that of the (F,B) because no luminescence are observed between the 1.62 eV emission and Ex. Since the energy of the (D,A) is close to that of the (F,B), one of the bound states is considerably shallow and the other one is deep as about 100 meV. The shallow state acts certainly as the acceptor because the film is electrically p-type at room temperature. Therefore the deeper state might act as the donor then the (F.B) can be

attributed to the recombination of electrons at neutral donors with holes on the valence band, (D^0,h).

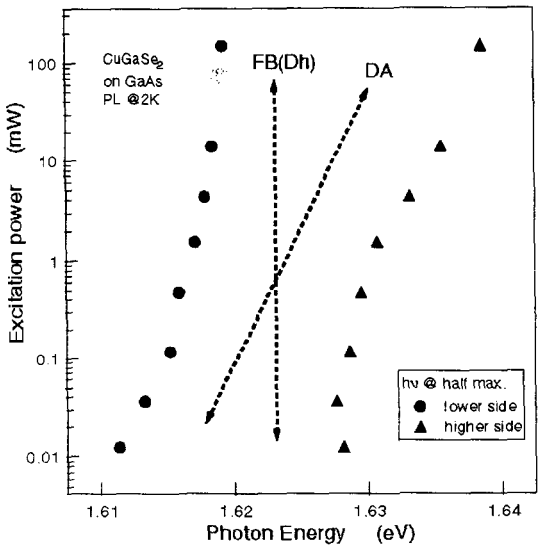

Fig.3 Excitation power dependence of photon energies at half maximum on both flanks of the 1.62 eV photoluminescence.

3.2. Temperature dependence of PL

The photon energy, $\hbar\nu_p$ at the peak of the (F,B) is given by the following equation as a function of temperature after Eagles' hydrogen model[7] ;

$$\hbar\nu_p = E_g - E_D + 0.5kT, \qquad (1)$$

where E_g is the band-gap energy, k is Boltzmann's constant, T is temperature and E_D is the donor ionization energy. However, $\hbar\nu_p$ cannot always be decided distinctly or it is influenced by neighboring emissions if exist. Since the 1.62 eV emission has the close (D,A) at the low energy wing, it is reasonable to measure the photon energy shift of the high energy flank of the emission. The same model brings that the photon energies at the half maximum for low energy flank and for the high energy, respectively $\hbar\nu_l$ and $\hbar\nu_u$, change linearly, too, with temperature;

$$\hbar\nu_l = E_g - E_D + 0.0509kT \qquad (2)$$

$$\hbar\nu_u = E_g - E_D + 1.8464kT. \qquad (3)$$

$\hbar\nu_u$ is generally favorable for characterizing (F,B)s because the factor is larger comparing to $\hbar\nu_p$.

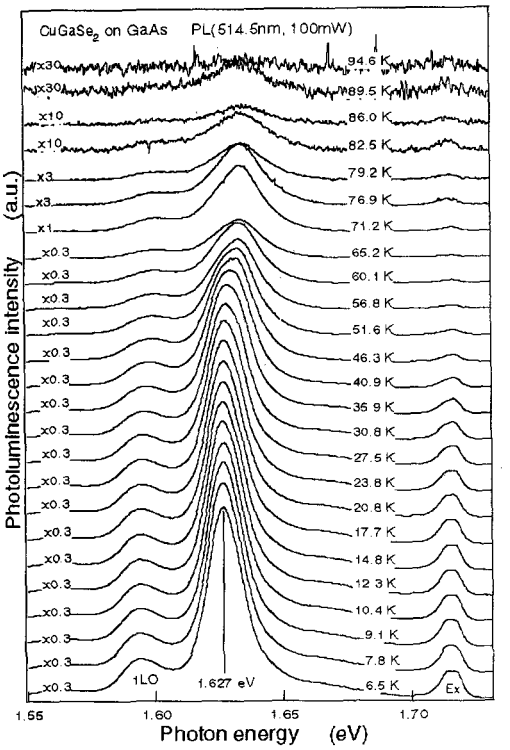

Fig.4 Temperature variation of photoluminescence spectra of MBE grown $CuGaSe_2$ film.

Fig.4 shows the PL spectra of temperature dependence. The behavior of the measured $\hbar\nu_u$ confirms that the high energy part of the emission is attributable to the (F,B). The measured $\hbar\nu_l$ shows a bowing at low temperature suggesting existence of the (D,A) in consistent with the results of the excitation power dependence. Although $\hbar\nu_p$, $\hbar\nu_l$ and $\hbar\nu_u$ should be theoretically the same at T=0 K to be E_g-E_D, some discrepancy between them is observed even after the contribution of the (D,A) is subtracted. The discrepancy is presumably due to the band filling by rather high excitation power applied for the temperature dependence measurement; the theoretical model is basic and does not include such a correction in the

equation. The fluctuation of the bound state level may also be considered as the origin of the discrepancy.

Ionization energies of the bound states can be estimated by the temperature dependence of the PL emission intensity. Since the emissions of the (F,B) and the (D,A) are too close to be separated, we set up an peculiar equation including both the acceptor and donor ionization energies on the basis of transition probability of carriers. The detailed discussion for the equation will be presented elsewhere. The ionization energy of these defect levels are found to be 3.4 meV and 108 meV by parameter fitting of the equation to the integrated intensity. The 3.4 meV state and the 108 meV state are certainly the acceptor and the donor, respectively, as mentioned above. Formerly, an emission at 1.63 eV has been observed and attributed to the (F,B) of the donor due to the Se vacancy[8]. The emission is believed to be the same as the 1.62 eV emission. The ionization energy has been estimated to be 80 meV which is smaller by about 20 meV than our result because a wrong value was used for the band gap energy at that time. Since the 1.62 eV emission is characteristic of Cu-rich films which is deficient in Se, the 108 meV state can be consistently attributed to Se vacancies. This is confirmed by the fact that the emission is quenched by anneal in Se pressure environment. The 3.4 meV state is presumably attributed to anti-site defects, Cu atoms at Ga sites, because the film is Cu rich and the anti-site defect may have smaller formation energy than the other defects by the analogy of the case of $CuInSe_2$[9].

4. CONCLUSIONS

Nearly stoichiometric or Cu-rich $CuGaSe_2$ films grown by molecular beam epitaxy on GaAs substrates show a dominant photoluminescence emission at 1.62 eV. The emission can be attributed to donor-to-band recombination accompanying donor-to-acceptor pair recombination. Ionization energies of the states are found to be 3.4 meV and 108 meV by temperature dependence of the photoluminescence intensity. The 3.4 meV state is certainly the acceptor and the 108 meV state can be attributed to Se vacancies which act as the donor.

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REFERENCES

1. J.L.Say and J.H.Wernik, Ternary Chalcopyrite Semiconductors: Growth, Electronic Properties and Application (Pergamon Press, New York, 1975).
2. D.J.Bottomley, A.Mito, S.Niki, and A.Yamada, Optics Letters, **21**, 799 (1996).
3. W.H.Bloss, J.Kimmerle, F.Pfisterer, and H.W.Schock, Proc. 17th IEEE Photovoltaics Specialists Conf., 715 (1984).
4. A.Yamada, Y.Makita, S.Niki, A.Obara, P.Fons, and H.Shibata, Microelectronics Journal **27**, 53 (1996).
5. A.Yamada, Y.Makita, S.Niki, A.Obara, P.Fons, H.Shibata, M.Kawai, S.Chichibu, and H.Nakanishi, J. Appl. Phys. **79**, 4318 (1996).
6.I.V.Bodnar and N.S.Orlova, Inorganic Materials **21**, 967 (1986).
7.D.M.Eagles, J. Phys. Chem. Solids **16**, 76 (1960).
8. e.g. M.Susaki, T.Miyauchi, H.Horinaka, and N,Yamamoto, Jpn. J. Appl. Phys. **17**, 1555 (1978), G.Masse and E.Redjai, J. Phys. Chem. Solids **47**, 99 (1986).
9. H.Neumann, Seminar; Centro de Estudio de Semiconductores. Universidat de los Andes, Benezurela, Nov. 1984.