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# Visible and Ultraviolet Photoluminescence from Cu-III-$VI_2$ Chalcopyrite Semiconductors Grown by Metalorganic Vapor Phase Epitaxy

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Photoluminescence (PL) properties of heteroepitaxial layers of $Cu(Al,Ga)(S,Se)_2$ ternary chalcopyrite semiconductors were studied. The metalorganic vapor phase epitaxy technique enabled us to grow high-quality heteroepitaxial layers. PL peaks due to free and bound exciton recombinations were found in all ternaty compounds. The energy of the exciton peak shifted to lower energy with increasing the tensile biaxial lattice strain. A noticable excitonic feature was found in the PL spectra of $CuAlS_2$ up to room temperature. Time-resolved and excitation intensity dependent PL measurements revealed the exsistence of free-to-bound (FB) recombination emission centers in some compounds and alloys. The activation energy of the thermal quenching of those FB emissions increased with increasing the band gap, which implied an increase of the hole effective mass. The chalcopyrite semiconductors were shown to have a potential as new light emitting materials.

## 1. Introduction

The I-III-$VI_2$ (III=Al,Ga and VI=S,Se) ternary chalcopyrite (Ch) semiconductors[1)] are interesting materials as possible candidates for light emitters operating in the visible to ultraviolet (UV) spectral ranges because the band gap energy of them ranges from 1.67 eV for $CuGaSe_2$ to 3.49 eV for $CuAlS_2$. The melt growth of some of the bulk single crystals is difficult due to the complex phase diagram and/or phase transition during postgrowth cooling. Therefore several heteroepitaxial growth of them on III-V substrates has been reported[2)] in recent ten years. The optically pumped stimulated emission from the $CuGa(S_ySe_{1-y})_2$ active layer has been demonstrated.[3)] However, the growth of high-quality $CuAlS_2$ and $CuAlSe_2$ has long been difficult because they contain chemically active Al in the matrices, and no exciton emission has been found from the epilayers grown by metalorganic vapor phase epitaxy (MOVPE)[4)] or molecular beam epitaxy[5)] before 1993.

Since Ch compounds have the tetragonal distortion along their *c*-axis, it is interesting to study the heteroepitaxy of them on the zincblende III-V substrates in terms of lattice orientation[6)] and residual strain[7)] as well as studying the luminescence properties.[8-11)]

In this work, results of the photoluminescence (PL) measurements were reviewed for the heteroepitaxial layers of $CuGaSe_2$, $CuGaS_2$, $CuAlSe_2$, $CuAlS_2$ and $CuAl_xGa_{1-x}Se_2$ alloys grown by low-pressure MOVPE. Strong UV, bluish-purple, green and red emissions were observed. Effects of strian on the exciton energy was discussed.

## 2. Experiments

The epitaxial growth was carried out using a MOVPE reactor[8)] operated at $4\times10^4$ Pa. The growth temperature was 600 ℃. The source precursors were cyclopentadienyl-coppertriethylphosphine (CpCuTEP), triisobutylaluminium (TIBAl), normal-tripropylgallium (TPGa), ditertiarybutyl-sulfide (DTBS) and diethylselenide (DESe). Dimethylzinc (DMZn), ethyliodide (EI) or octamethyldialuminiummono-magnesium (OMDAMg)[8)] was used as a doping source gas for $CuAlSe_2$. The growth rate was 0.14-0.23 $\mu$ m/h, and about 0.2-0.9 $\mu$ m-thick epilayers were grown on GaAs or GaP (001) substrates. Prior to the optical measurements, the epilayers were confirmed to be the single crystal by X-ray diffraction (XRD) and transmission electron microscope (TEM). The surface morphology was observed with scanning electron microscope (SEM), atomic-force microscope (AFM) and Normalski interference microscope. To determine exciton energies, photoreflectance (PR) measurements were carried out in connection with the PL measurements. PL was excited by the appropriate line of He-Cd or $Ar^+$ laser.

## 3. Results and Discussion

The measured samples were *c*[001]-oriented epitaxial layers. The surface roughness of $CuGaSe_2$/GaAs(001) is about 0.14 nm, which is comparable to the monolayer thickness of c[001]-oriented $CuGaSe_2$. The surface condition of $CuAlSe_2$ is worse than $CuGaSe_2$. However, the roughness is smaller than 3 nm. The surface roughness of good-quality $CuGaS_2$ and $CuAlS_2$ is smaller than 2 nm. TEM observation reveals the exsistence of stacking faults and dislocations in $CuGaS_2$ and $CuAlS_2$ grown on GaAs(001), whose lattice mismatches are about 5%. Conversely, no stacking faults were found in $CuGaSe_2$ and $CuAlSe_2$ grown on GaAs(001). In this case, the epilayers are nearly lattice matched to the substrate at the growth temperature. These results confirm good quality of c[001]-oriented epilayers.

Representatives of the PL spectra of $Cu(Al,Ga)(S,Se)_2$ measured at room temperature (RT) and low temperature (LT) are shown in Fig.1. All compounds exhibit edge emissions at LT. The PL peak indicated by the arrow in each spectrum is due to exciton recombinations, because the peak energy agrees with the exciton resonance energy obtained

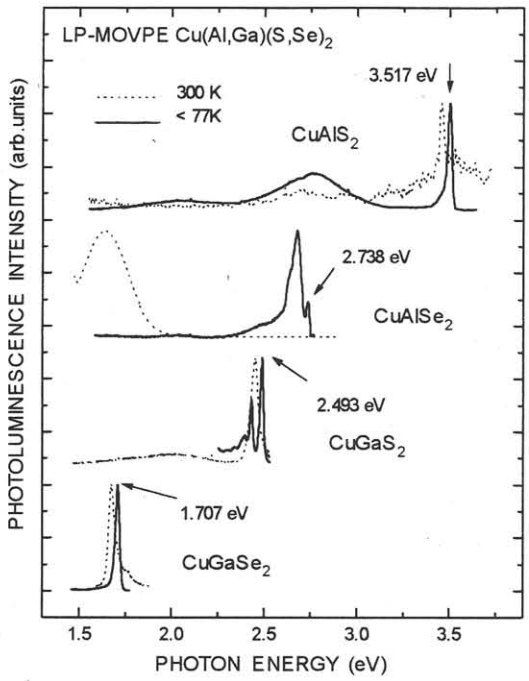


Fig.1 PL spectra of Cu(Al,Ga)(S,Se)$_2$ epilayers at 300 K and 30-77K.

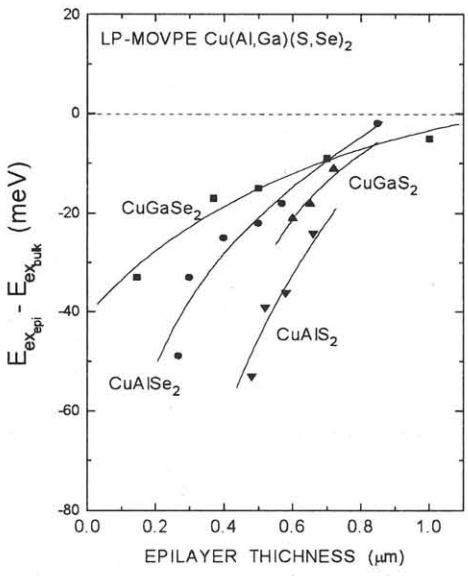


Fig.2 Energy difference between the free exciton in the bulk crystal and that in the epilayer of Cu(Al,Ga)(S,Se)$_2$ at 30-77 K.

from the analysis[12] of the PR spectra.[7]

The value of the free exciton energy in the epilayers is smaller than that in the bulk crystals.[7-11] In addition, the full width at half maximum (FWHM) of these exciton emissions is about 11-34 meV, which is remarkably large for the exciton emission. These features are explained by the residual tensile biaxial strain in the epilayers as follows. In Fig.2, difference in energies between the free exciton in the unstrained bulk crystal ($E_{ex,bulk}$) and that in the epilayers grown on GaAs(001) substrate ($E_{ex,epi}$) are plotted as a function of the layer thickness. It is found that the exciton eneregy decreases with decreasing the epilayer thickness for all compounds. The lattice parameter *c* of the epilayers also decreases with decreasing the thickness, which indicates the increase of the tensile biaxial strain. The lattice parameter *a* of $CuAlSe_2$ and $CuGaSe_2$ is very close to that of GaAs ($\Delta a/a$=-0.2%) at the growth temperature. Therefore the epilayers grow coherently for the thickness smaller than the critical thickness (about 80-100nm), and relaxes gradually with increasing the thickness. Conversely, the lattice parameter *a* of $CuGaS_2$ and $CuAlS_2$ is about 5% smaller than that of GaAs. Therefore, the epilayers grow under fully lattice-relaxed condition due to the large lattice mismatch. In both cases, the residual strain in the epilayer is predominantly determined by the thermal stress, which is introduced by the difference in the thermal expansion coefficients between the epilayer and the substrate. The thermal expansion coefficient of Cu(Al,Ga)(S,Se)$_2$ is about 11-13$\times 10^{-6}$, which is twice larger than that of GaAs (6.8$\times 10^{-6}$). This large difference introduces the tensile biaxial strain in the epilayers, leading to the decrease of the lowest exciton energy shown in Fig.2 and the increase of the crystal-field splittings in the valence bands.[7] Such strain-induced variation on the valence band energy is also found in $CuAl_xGa_{1-x}Se_2$ alloy epitaxial layers. One of the reasons for the large FWHM value may attributable to the partial relaxation of the thermal stress. Nevertheless, the epilayers exhibit predominant band-edge emission at RT except for $CuAlSe_2$. The growth of high-quality $CuAlSe_2$ is the most difficult among these compounds.

It seems that there is certain contribution of excitons in the near-band-edge emission of $CuGaS_2$ and $CuAlS_2$ up to RT. The exciton binding energy of $CuGaS_2$ is 28 meV.[13] We cannot calculate exactly the exciton binding energy and Bohr radius of $CuAlS_2$ due to the lack of the data for the effective masses and dielectric constant. However, using the values of $CuGaS_2$,[13] ZnSe, ZnS, and related I-III-VI$_2$ compounds,[14] the exciton binding energy of $CuAlS_2$ is estimated to be about 70 meV. The charge density to screen free excitons at RT is also estimated to be about $1\times 10^{18}$ cm$^{-3}$ and $4\times 10^{18}$ cm$^{-3}$ for $CuGaS_2$ and $CuAlS_2$, respectively. Therefore, though we have to consider the exciton-phonon coupling, it is not odd to observe excitonic emissions from these compounds at RT because the epilayers are of the highest purity to our knowledge. The emission lifetime of the exciton peak in $CuAlS_2$ is shorter than the system response (300 ps) at 77 K, which may reflect the large oscillator strength of excitons having the small Bohr radius. Conversely, the lifetime of the free-to-bound (FB) emission at 2.76 eV in $CuAlS_2$ is anout 3 ns.

A series of the PL spectra for $CuAl_xGa_{1-x}Se_2$ alloys at 30 K are shown in Fig.3. The color of the emission changes from red, crimson, orange, yellow, green and bluish-purple with increasing x. The PL spectra of alloys are dominated by a band-to-acceptor transition rather than excitons. The

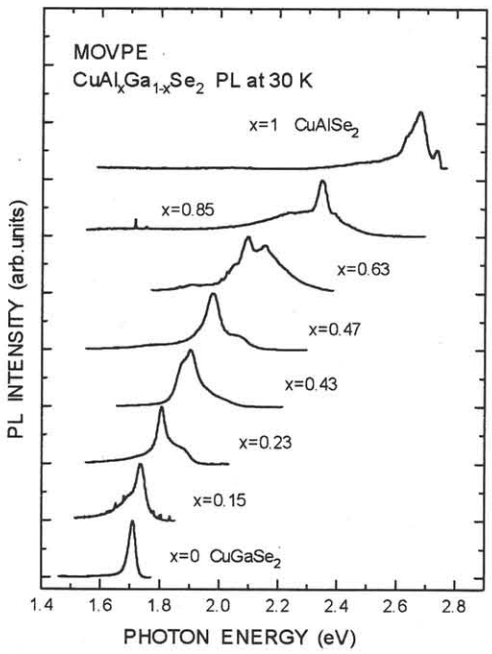


Fig.3 PL spectra of $CuAl_xGa_{1-x}Se_2$ alloys at 30 K grown by MOVPE

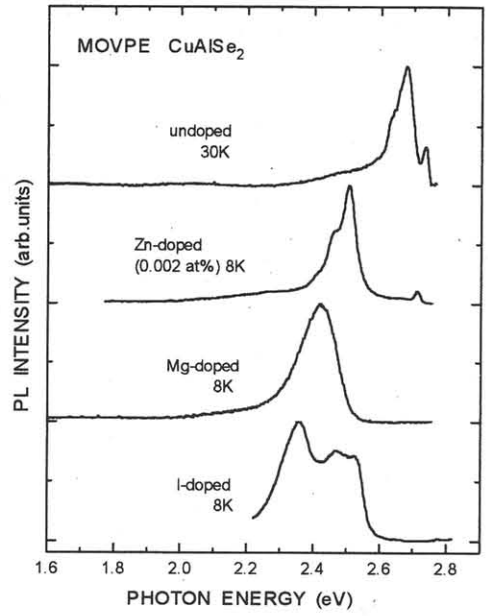


Fig.4 PL spectra of undoped and impurity-doped $CuAlSe_2$ epilayers grown by MOVPE

ionization energy of the acceptor increases with increasing x, which may be due to the increase of the hole effective mass. Similar increase of the activation energy for the thermal quenching of the excitonic emission with the increase of the band gap is observed for the ternary compounds, i.e. the activation energy increases from about 40meV for $CuGaSe_2$, 50 meV for $CuGaS_2$, 60 meV for $CuAlSe_2$ and 110 meV for $CuAlS_2$.

The PL spectra of undoped and Zn, Mg, or I-doped $CuAlSe_2$ are shown in Fig.4. New PL peaks are found between 2.3 and 2.5 eV. These emissions have been assigned to donor-acceptor pair (DAP) recombinations based on the time-resolved PL measurements.[8] Though excitonic and FB emissions in undoped samples quench at about 70 K due to exsistence of nonradiative recombination centers, these DAP emissions are obserbable up to 170K. This result suggests that these impurites would act as effective luminescence centers.

## 4. Conclusion

In summary, visible and UV emissions were observed in high-quality heteroepitaxial layers of $Cu(Al,Ga)(S,Se)_2$ chalcopyrite semiconductors grown by MOVPE. All terminate compounds, namely $CuGaSe_2$, $CuGaS_2$, $CuAlSe_2$ and $CuAlS_2$, exhibited excitonic emissions. The room temperature PL spectra were dominated by near-band-edge emissions except for $CuAlSe_2$. A noticable excitonic feature was observed for the PL spectra of $CuGaS_2$ and $CuAlS_2$ even at room temperature. Though there still remain problems for the controllability of conductivity and cunductivity-type, the chalcopyrite semiconductors were shown to have a potential as new light emitting materials.

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