Investigation of CuGaSe$_2$/CuInSe$_2$ double heterojunction interfaces grown by molecular beam epitaxy

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In-situ reflection high-energy electron diffraction (RHEED) observation and X-ray diffraction measurements were performed on heterojunction interfaces of CuGaSe$_2$/CuInSe$_2$/CuGaSe$_2$ grown on GaAs (001) using migration-enhanced epitaxy. The streaky RHEED pattern and persistent RHEED intensity oscillations caused by the alternate deposition of migration-enhanced epitaxy sequence are observed and the growths of smooth surfaces are confirmed. RHEED observation results also confirmed constituent material interdiffusion at the heterointerface. Cross-sectional transmission electron microscopy showed a flat and abrupt heterointerface when the substrate temperature is as low as 400°C. These have been confirmed even by X-ray diffraction and photoluminescence measurements. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4908229]

Chalcopyrite materials such as CuInSe$_2$ (CIS), CuGaSe$_2$ (CGS) and their mixed compounds CuIn$_{1-x}$Ga$_x$Se$_2$ (CIGS) have been of technological interest as thin film solar cell absorber layers.$^{1–3}$ However, their optical and electrical characteristics are quite unique and attractive. Therefore, this material system could be applied to variety of semiconductor devices other than solar cells. Characteristic features of this system include a wide range of band gap energies in CIGS (1.04 ~ 1.68 eV). Since these materials have direct band gap, they can be applied to light-emitting devices and photodetectors. At the CGS/CIS interface, almost all the band gap energy difference $\Delta E_g$ is distributed to the conduction band-edge discontinuity $\Delta E_C$. The value of $\Delta E_C$ is as large as 540 meV, while the valence band-edge discontinuity $\Delta E_V$ is only 100 meV (Ref. 4). Such a large difference in band-edge discontinuity provides interesting applications of quantum wells, such as resonant tunneling devices and quantum cascade lasers. An attempt of CGS/CIS quantum well growth on GaAs (001) has been reported using metal-organic vapor phase epitaxy (MOVPE),$^5$ where an appreciable interdiffusion between In and Ga at the CGS/CIS interface were detected. Because of the interdiffusion, the bandgap energy of the quantum well increased to over 1.2 eV. On the other hand, CGS shows high excitonic binding energy of approximately 20 meV because of its relatively large electron effective mass of 0.14 $m_0$ and low refractive index of 2.14.$^6,7$ In addition, high hole mobility has been reported in these material.$^8$

In order to explore new applications of CIS, CGS and CIGS, we have investigated fundamental characteristics of these materials and their heterostructures. Even though chalcopyrite material has a high density of defects and being classified as ordered defect compound (ODC), we employed migration-enhanced epitaxy (MEE) method to control the defect formation process. The most
serious problem of this material system in developing new devices such as those done in III-V compound semiconductors, is the difficulty in growing n-type materials.

One of our research objectives was to fabricate n-type chalcopyrite materials. Although we have obtained high resistive material, n-type conductivity has never been achieved. Thus, we propose a new approach which is modulation-doped structure using CGS/CIGS heterojunctions or superlattices (SLs), where sample growth was performed using non-equilibrium method MBE/MEE. In the SL structure, quantum well and barrier would be CIS and CGS, respectively. Considering the large $\Delta E_C$ in CGS/CIS quantum wells as shown in Fig. 1, electrons in the deep donors of barriers are expected to be activated into the conduction band of CIS, which would contribute to n-type conductivity. In our previous study of doping in CGS, Si and Zn produce donor levels with depths of 30-50 meV (Ref. 9) as shown in Fig. 1. If the modulation doped structure mentioned above works successfully, and n-type conductivity is achieved, new application field will be opened in the chalcopyrite materials. It can be also applicable to solar cells. In this case, pn junction solar cells without lattice mismatch at the interface unlike CGS/CdS can be achieved. If interface issues are eliminated, dramatic increase in the solar cell efficiency can be achieved.

CIS, CGS and CIS/CGS, CGS/CIS heterostructures have been grown by a solid source molecular beam epitaxy (MBE). Since the lattice constants of CIS and CGS (5.784 Å and 5.614 Å, respectively) are very close to that of GaAs (5.653 Å), we employed GaAs (001) substrates. The migration enhanced epitaxy (MEE) deposition sequence often yields better quality epitaxial layers rather than conventional MBE deposition. In the growth of CIS, MEE deposition sequence is composed of alternate deposition of Cu+In and Se, while Cu+Ga and Se are alternately deposited for CGS growth. When only cations (Cu+Ga/In) are supplied, group I and III adatoms have enough time to find the preferable nucleation sites and able to produce well-ordered and smooth surface layer. This directly suppresses the defect formation. There was a report about CGS growth using MBE method, however, the grown samples exhibited very low hole mobility. In the MEE growth, Cu+In (Cu+Ga) deposition period, the RHEED specular beam intensity increased and reached its maximum at the end of the deposition period. In contrast, the specular beam intensity dropped in the Se deposition period. Therefore, during MEE growth, RHEED specular beam intensity showed oscillation with constant amplitude according to the deposition sequence. However, continuous RHEED intensity oscillation appeared only when the deposition conditions, such as molecular beam intensity and deposition duration for each component are optimized. Otherwise, RHEED oscillation quickly disappears after starting the growth.
Optimized beam equivalent pressures of Cu, In, Ga and Se are $1 \times 10^{-7}$ Torr, $3 \times 10^{-7}$ Torr, $3 \times 10^{-7}$ Torr and $1 \times 10^{-5}$ Torr, respectively. The durations of deposition are 2 sec for both Cu+In(Ga) and Se deposition as shown in Fig. 2. Background pressure of the growth chamber was as low as $5.0 \times 10^{-10}$ Torr. After removing the native oxide from the GaAs (001) substrate at 590 °C, we have confirmed (2×4) reconstruction. First, 500nm-thick CGS layer is grown at 580 °C. Then the subsequent CIS and CGS layers are successively grown at 580, 500 and 400 °C.

For structural studies, X-ray diffraction (XRD) measurements and transmission electron microscope (TEM) observations are performed for grown CGS/CIS/CGS heterostructures. We have measured and analyzed the photoluminescence (PL) of this double heterostructure, together with an undoped CGS bulk layer as a reference. In the present PL study, we employed cooled InGaAs-CCD detector and the excitation laser energy of 2.33 eV. Hall measurements are also performed at room temperature.

A conventional MBE tool equipped with a RHEED gun having an acceleration voltage of 20 kV and an incident angle of 1.5° is used for the in-situ observation. The RHEED specular beam intensity oscillation caused by the MEE deposition sequence is demonstrated in Fig. 3. Here, the RHEED intensity variation during growth of CIS on CGS at 580 °C is demonstrated. One cycle of RHEED intensity oscillation corresponds to the growth of 2.5 ML chalcopyrite structure. During CGS growth, the highest peaks occur at Se deposition period, while lowest valleys correspond to the deposition of metallic components. The constant amplitude oscillation implies the optimized deposition condition. In the CIS growth, persistent oscillation with constant amplitude also appears. The amplitude observed in CGS growth, however, is a little higher than in the CIS growth. In addition, the intensity level decreases after several MLs from the interface, while the amplitude remains constant. This transient is probably caused by the strain relaxation between CGS and CIS. The
thickness of this transient is approximately equal to the critical thickness predicted by using People’s estimation. Similar behavior of the RHEED oscillation has been reported in heterostructures of III-V compound semiconductors.

The growth of CGS on CIS exhibits a very different feature compared with the deposition of CIS on CGS described above. Figure 4 shows the RHEED specular beam intensity trace during MEE deposition process of CGS on CIS at 580 °C. In the growth of CIS, RHEED oscillation with constant amplitude is observed. On the other hand, when the growth is switched from CIS to CGS, higher oscillation amplitude is observed as expected. The amplitude increased gradually for first 70 MLs from the heterointerface. This phenomenon is probably caused not only by the strain relaxation but also by the intermixing between the constituent elements of CIS and CGS. Since In and Ga has different bonding energy in CIS and CGS, respectively, In atoms in CIS can be easily replaced by Ga atoms during CGS growth. Not limited to growth sequence, substrate temperature is also a vital parameter of this atom-exchange process, the result in Fig. 4 clearly indicates that the substrate temperature of 580 °C is too high to grow abrupt CGS/CIS interfaces. Thus, low-temperature growth is essential for this material system.

Figure 5 shows double-crystal X-ray 2θ - ω scans of the samples of CGS/CIS/CGS heterostructures in the vicinity of (004) GaAs Bragg angle. Each layer has a thickness of 500 nm. The first CGS layer in each sample is grown at 580 °C, while the other layers are grown at 400, 500
and 580 °C. The sample grown at 400 °C exhibits well-distinguished diffraction peaks close to the angle\textsuperscript{15} for CIS (008), CGS (008) and GaAs (004) indicating that high crystalline and interfacial quality of the heterostructure. Relaxation of lattice distortion in vertical and horizontal strain lattice mismatch between GaAs and CGS is only 0.7%, however it is 2.3% between GaAs and CIS. Hence, we have chosen to grow CGS on GaAs, subsequently followed by CIS. Lattice mismatch \( | \Delta a/a | \) is proportional to the reciprocal of critical thickness \( h_c \). Literature\textsuperscript{16} reveals that \( h_c \) is at maximum when \( | \Delta a/a | \) is only \(-0.08\%\). Plausible reason for this contradiction is due to the difference of thermal expansion coefficient between the GaAs substrate and coherently grown epitaxial layer. As shown in Fig. 5, the sample grown at 580 °C has no CIS peak, however, obvious CIGS peak with 40% of Ga incorporation is detected, instead. On the other hand, the sample grown at 500 °C confirms a mixed phase, CIGS peak appears at 15% of Ga incorporation. This implies that even the growth temperature of 500 °C is enough to induce In-Ga intermixing by Ga atomic replacement.  

Transmission electron microscopy (TEM) measurement is performed by using Hitachi HF2200 with 200 kV acceleration voltage to analyze the heterostructure in details. Cross-sectional scanning TEM images of CGS/CIS heterointerfaces grown at 400 and 500 °C are demonstrated in Fig. 6. The
sample grown at 400 °C exhibits flat and abrupt interface, while the sample grown at 500 °C shows rough and diffused interface. TEM also confirms the nominal thickness of the grown layers which is approximately equal as calibrated monolayer/cycle.

PL measurements are carried out on the CGS/CIS/CGS double heterostructures to identify the energy levels associated with various compositions of the samples. PL measurements are performed between 10 and 300 K using 532 nm excitation source with 2–30 mW and InGaAs CCD detector. The PL spectra at room temperature observed from CIS of the heterostructures grown at 400 and 500 °C are shown in Fig. 7. The peaks of these spectra appear at 1.01 and 1.06 eV, respectively, which are probably caused by the transition between bands or band to impurity levels. The latter is caused by Ga intermixing at 500 °C. Intense and sharp spectra are obtained when the structure is grown at 400 °C. Figure 8 demonstrates the PL result at 10 K. Although intense and sharp spectra are observed in both 400 and 500 °C grown samples, they exhibit dominant emission peaks at 0.96 and 1.01 eV, respectively. These energies are in the lower energy side of the room temperature spectra. Hence, the detected peaks at low temperatures are attributed to radiative recombination of CIS defect levels, such as $V_{Cu}$, $V_{In}$, $V_{Ga}$ and $V_{Se}$. Further investigations such as temperature dependence and excitation power dependence are required in order to clarify these PL peaks.

Electrical properties are also investigated for these three CGS/CIS double heterostructure samples by selectively (modulated) doping with Ge in CGS barrier layers by Hall effect measurements. Although the samples grown at 400 and 500 °C exhibit high sheet resistivity and low hole concentration; i.e. $10^4 \sim 10^5 \Omega /sq$ and $4 \sim 5 \times 10^{16} /\text{cm}^2$, no n-type conductivity has been obtained. The hole mobility of both the samples were about 200 cm$^2$/Vs at room temperature and $>1500$ cm$^2$/Vs at 100 °C. To achieve efficient modulation doping, much shorter periods, such as SL structures may be needed.

In conclusion, we have successfully grown CGS/CIS double heterostructures on GaAs (001) substrates using MEE growth sequence. Study on RHEED specular beam intensity oscillation during MEE growth at 580 °C revealed that the interface of CGS on CIS shows diffused structure compared with CIS on CGS interface because of the In-Ga intermixing. Indeed XRD results confirmed that CGS growth on CIS produces no signal of CIS but only mixed CIGS phase. Although intermixing of CGS on CIS occurred to some extent at 500 °C, the effect is not so serious and double heterojunction of CGS/CIGS/CGS can be grown. When the growth temperature is reduced to 400 °C, flat and abrupt interfaces are obtained as confirmed by XRD and TEM image.
observation. Hence, the essential growth temperature for CGS/CIS heterostructures should be below 400°C. This low temperature growth condition has been proved beneficial also by PL characteristics. The CGS/CIS double heterostructure grown at 400°C showed an efficient PL emission with sharp spectrum. The PL emission can be attributed to transition between bands or band to impurity levels. Even though n-type CGS/CIS was not achieved through modulation doping with Ge as a dopant, high sheet resistivity and low hole concentration of the samples motivates this research.

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