# Temperature variation of nonradiative carrier recombination processes in high-quality CuGaSe_2 thin films grown by molecular beam epitaxy

| メタデータ | 言語: English<br>出版者:<br>公開日: 2020-06-21<br>キーワード (Ja):<br>キーワード (En): Epitaxy, Band gap, Liquid helium, Electric measurements, Electron hole recombination<br>作成者: 吉野, 賢二, 丸岡, 大介, 碇, 哲雄, 仁木, 栄, 山田, 昭政, Maruoka, Daisuke, Fons, Paul J., Niki, Shigeru, Yamada, Akimasa<br>メールアドレス:<br>所属: |
|---|---|
| URL | http://hdl.handle.net/10458/5256 |

# Temperature variation of nonradiative carrier recombination processes in high-quality $CuGaSe_2$ thin films grown by molecular beam epitaxy

Kenji Yoshino,[a] Daisuke Maruoka, and Tetsuo Ikari
*Department of Electrical and Electronic Engineering, Miyazaki University, 1-1 Gakuen Kibanadai-nishi, Miyazaki 889-2192, Japan*

Paul J. Fons, Shigeru Niki, and Akimasa Yamada[b]
*Optoelectronics Division, Electrotechnical Laboratory, MITI, 1-1-4 Umezono, Tsukuba, Ibaraki 305-0045, Japan*

(Received 28 March 2000; accepted for publication 22 May 2000)

The piezoelectric photoacoustic (PPA) measurements for Cu-rich $CuGaSe_2$(CGS)/GaAs(001) epitaxial layer were carried out between liquid helium and room temperatures. The band gap energies of CGS (*A*, *B*, and *C* bands) were measured to be 1.73, 1.83, and 2.04 eV at liquid nitrogen temperature, respectively. The *A* band was clearly obtained from 5 to 300 K, and the temperature dependence of the peak energy was fitted with the modified Manoogian–Woolley equation. PPA signals for CGS/GaAs (001) epitaxial layers were obtained between liquid helium and room temperature. © *2000 American Institute of Physics.* [S0003-6951(00)03128-4]

$CuGaSe_2$(CGS) has attracted much attention for use as a solar cell active layer as well as for nonlinear optical devices similar to the case for $CuInSe_2$(CIS). However, CGS has many as of yet uncharacterized crystalline defects because high quality CGS single crystals are difficult to grow due to the peritectic melting of stoichiometric CGS at 1030 °C. Despite a lack of the accurate material characterization data, conversion efficiencies for polycrystalline CGS based solar cells have significantly improved to values as high as 9.7%.[1] This indicates that CGS is a promising material for high efficiency devices. Although there are reports on growth and characterization of bulk CGS and thin film,[2–6] the volume of literature on CGS is small in comparison to CIS.

We reported in a previous paper[7] that high quality Cu-rich CGS epitaxial layers were successfully grown on semi-insulating (SI) GaAs(001) substrate by a molecular beam epitaxy (MBE) from elemental sources. The chemical composition of the films was adjusted by changing the molecular beam flux of the Cu and Ga sources under a Se overpressure. The obtained Cu-rich samples were of high quality as evidenced by the presence of streaky reflection high-energy electron diffraction patterns and sharp photoluminescence (PL) free-exciton emissions.[8]

In this study, piezoelectric photoacoustic (PPA) measurements are carried out on CGS epitaxial layers between liquid helium and room temperatures. PPA measurements directly monitor nonradiative carrier recombination processes. Another advantage of PPA measurements is their sensitivity in transparent samples with small optical absorption coefficients. Measurements of absorption spectra are very difficult for heterojunction samples. The usefulness of the PPA measurements for heterojunction samples is also discussed.

The CGS thin films reported upon in this work were grown on SI-GaAs(001) substrates by MBE at a substrate temperature of 490 °C. The thickness of the CGS film and the GaAs substrate were about 1.0 and 500 $\mu$m, respectively. The composition of the CGS film used here was determined by means of electron probe microanalysis and is expressed as a Cu/Ga ratio of 1.09 (Cu = 26.9% and Ga = 24.7%). Electrical properties were measured by means of Hall measurements and the Van der Pauw technique. The sample was *p* type. The hole concentration was on the order of $10^{17}$ cm$^{-3}$ and the hole mobility was 5 cm$^2$/(V S) at room temperature.[9]

PPA measurements were carried out for the CGS epitaxial layers between liquid helium and room temperatures with a modulation frequency of 200 Hz. The sample was mounted on the cold finger of a cryostat (Oxford Co. Ltd.: Cryostat DN-V). A W lamp was used as an excitation source. PPA signals were detected by a piezoelectric transducer (PZT) attached directly to the rear surface of the sample with silver paste. The output signals from the PZT were amplified by a digital lock-in amplifier and processed by a personal computer. Details of the experimental procedure have been published elsewhere.[10,11]

A typical PPA spectrum for a CGS epitaxial layer (Cu/Ga = 1.09) at 80 K with a modulation frequency of 200 Hz is shown in Fig. 1. Five distinct peaks are clearly observed. These peaks are indicated by solid lines. The peak at 1.51 eV, which originates from the band gap of GaAs, is in good agreement with those reported in the literature. The peaks at 1.73, 1.83, and 2.04 eV are due to the *A*, *B*, and *C* band transitions of CGS, respectively. The *A*, *B*, and *C* band transitions are the energy gap $E_g$ and crystal-field splitting and spin-orbit splitting bands, respectively. These values are in good agreement with those obtained by polarized photoreflectance (PR) measurements of the same sample as reported in a previous paper.[8] This indicates that the $E_g$ of *A*, *B*, and *C* band transitions can be reliably obtained by PPA measurements as well as PR measurements. Furthermore, the values obtained are similar to those of CGS/GaAs epitaxial layers grown by metalorganic MBE and metalorganic chemi-

[a]Author to whom correspondence should be addressed; electronic mail: yoshino@pem.miyazaki-u.ac.jp
[b]Electronic mail: ayamada@etl.go.jp

 

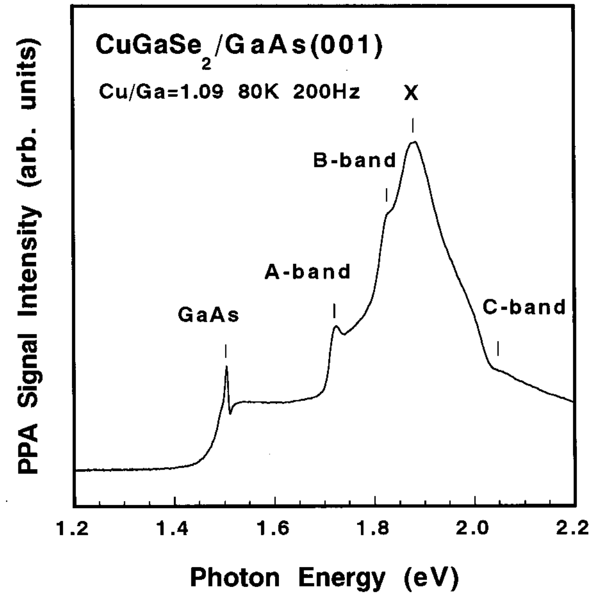


FIG. 1. The PPA spectrum of typical Cu-rich $CuGaSe_2$/GaAs(001) epitaxial layer grown by MBE at 80 K under the modulation frequency of 200 Hz.

cal vapor deposition as reported by Matsumoto *et al.*[4] and Shirakata and Chichibu,[6] respectively. The obtained crystal-field splitting $\Delta_{cf}$ and spin-orbit splitting $\Delta_{so}$ are about $-100$ and 210 meV, respectively, in good agreement with the values for CGS in the literature.[4,6,12] The peak $X$ at 1.87 eV is conjectured to be band transition related to a metastable state (EL2*) in GaAs since the peak intensity decreases with secondary light illumination (photoquenching effect).[13]

The temperature variations of the PPA spectra for the CGS epitaxial layer (Cu/Ga=1.09) between liquid helium and room temperatures is shown in Fig. 2. The GaAs peak shifts to lower energy in comparison the CGS peak with increasing temperatures. The shift for GaAs and CGS are about 90 and 35 meV, respectively, over the range from 5 to 300 K. The value of 35 meV is in good agreement with the values derived from PL measurements as reported by Chichibu *et al.*[5] and similar to those obtained for the CIS/GaAs epitaxial layer by PPA measurements.[14] This implies that the temperature dependence of the band gap energy in chalcopyrite semiconductors is very small in comparison with III–V and II–VI compound semiconductors.

The temperature variation of the $E_g$ ($A$ band) of the CGS is shown in Fig. 3. We have also plotted the temperature variation of the $E_g$ ($A$ band) of CGS as estimated by the PL measurements. The data were fit to the modified Manoogian–Wolley equation[15]

$$E_g(T)=E_g(0)+UT^x+V/[\exp(\hbar\omega/kT)-1], \qquad (1)$$

where, $a$, $b$, $U$, $V$, and $x$ are fitting parameters and $\hbar\omega$ represents the energy of phonons that interact with electrons. The $E_g(0)$ of CGS used was 1.731 eV as estimated by extrapolation and $\hbar\omega$ was set to 26 meV. The other parameters, $a$, $b$, $U$, $V$, and $x$, are the same as reported earlier.[8] The temperature variation of the $E_g$ ($A$ band) obtained from the PPA measurements is well fit by the Manoogian–Woolley relation, in excellent agreement with the results of PL measurements. However, while PL emissions were only observable up to about 200 K, PPA signals are clearly observed up

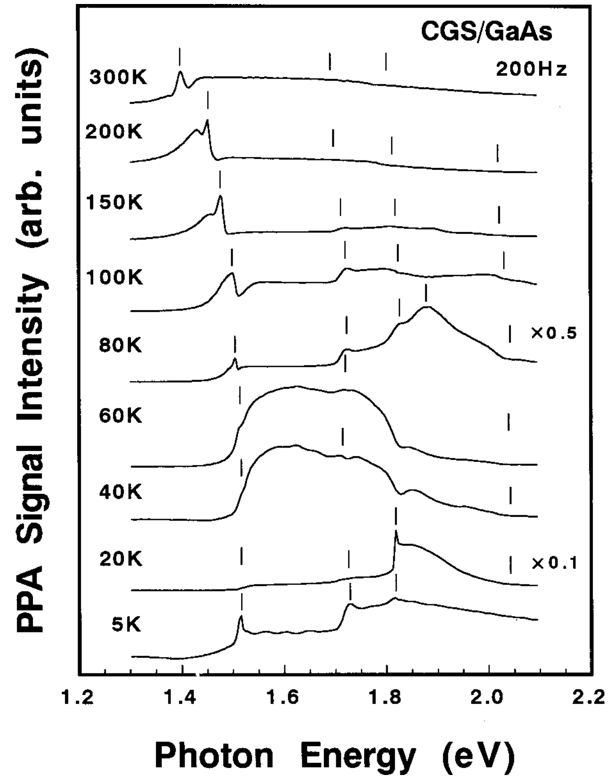


FIG. 2. The temperature variation of the PPA spectra of typical Cu-rich $CuGaSe_2$/GaAs(001) epitaxial layers grown by MBE under the modulation frequency of 200 Hz.

to 300 K. This indicates that the PPA measurements are effective in measuring the temperature variation of $E_g$ in the CGS as has been done for CIS.[14] The temperature variations of the $E_g$ ($B$ and $C$ bands) of CGS and the fitted curve, Eq. (1) are shown in Fig. 4. The values used for $E_g(0)$ of the $B$

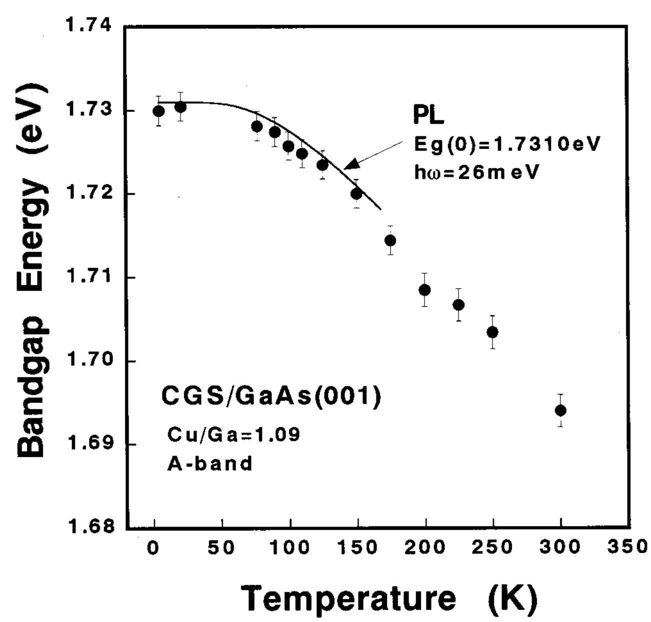


FIG. 3. The variation of the band gap energy ($A$ band) of $CuGaSe_2$/GaAs (001) epitaxial layers grown by MBE as a function of temperature. The band gap energies are estimated by means of the PPA and PL measurements. The fitting curves are also plotted by modified Manoogian–Woolley equation.

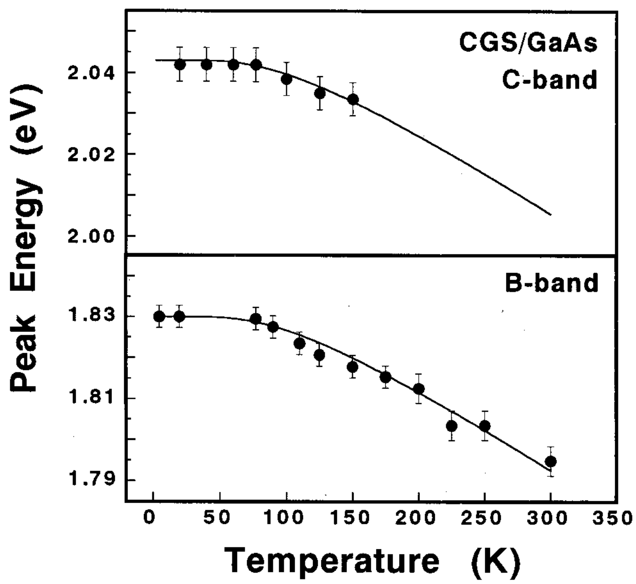


FIG. 4. The variation of the *B* band (lower) and *C* band (upper) of $CuGaSe_2$/GaAs(001) epitaxial layers grown by MBE as a function of temperature. The fitting curves are also plotted by modified Manoogian–Woolley equation.

and *C* bands were 1.831 and 2.042 eV, respectively. The other parameters used are the same as those used in Fig. 3. The temperature variation of the $E_g$ (*B* and *C* bands) of CGS are also in good agreement with the relationship predicted by Eq. (1).

The PPA spectra for CGS at 40 and 60 K is shown in Fig. 2. These spectra are dramatically different from those of other temperatures (less than 40 K and more than 60 K); peak intensities increase from 20 K, especially between about 1.5 and 1.8 eV. These peaks are interpreted as being due to nonradiative carrier recombination centers in the CGS layer since the peak energies are larger than the GaAs band gap energy. The peak intensities then decrease from 60 to 80 K. The overall temperature dependence of the PPA signal intensities is thus paraboliclike with a peak at about 60 K. It is well known that the PPA signals are sensitive to strain and thermal conduction, thus it is speculated that the thermal conductivity strongly enhances PPA signals at low temperatures since the thermal conductivity in the semiconductor generally changes in a parabolic manner with a peak at low temperatures.[16] Furthermore, the PPA signals of the *A*, *B*, and *C* bands are clearly observable around 80 K. One of the reasons that it is assumed here that carrier recombinations related to the GaAs metastable state (EL2*) are present is that PPA signals from the EL2* state are large around 80 K.[17]

In summary, PPA measurements have been carried out for Cu-rich CGS/GaAs epitaxial layers between liquid helium and room temperature. The peaks at 1.73, 1.83, and 2.04 eV are due to the *A*, *B*, and *C* band transitions of CGS, respectively. These values are in good agreement with those obtained by the polarized photoreflectance measurements of the same sample. The crystal-field splitting $\Delta_{cf}$ and spin-orbit splitting $\Delta_{so}$ values obtained are about $-100$ and 210 meV, respectively. The *A* band of CGS was clearly obtained from 5 to 300 K, on the other hand, free-exciton emission is observed up to 200 K in the PL spectra. The temperature variation of the *A* band in the PPA spectra is well fit by a modified Manoogian–Woolley equation and is also in good agreement with the results obtained by PL measurements. This indicates that the PPA measurements are effective in estimating the band gap energy over a wide temperature range in comparison with PL measurements.


[1] M. Saad, H. Riaze, E. Bucher, and M. Ch. Lus-Steiner, Appl. Phys. A: Mater. Sci. Process. **62**, 181 (1996).
[2] L. Mandel, R. D. Tomlinson, and M. J. Hampshire, J. Cryst. Growth **36**, 152 (1976).
[3] K. Sugiyama, A. Sawada, K. Ito, S. Iwasaki, and T. Endo, J. Cryst. Growth **84**, 673 (1987).
[4] T. Matsumoto, K. Kiuchi, and T. Kato, Cryst. Res. Technol. **31**, 325 (1996).
[5] S. Chichibu, Y. Harada, M. Uchida, T. Wakiyama, S. Matsumoto, S. Shirakata, S. Isomura, and H. Higuchi, J. Appl. Phys. **76**, 3009 (1994).
[6] S. Shirakata and S. Chichibu, J. Appl. Phys. **79**, 2043 (1996).
[7] A. Yamada, Y. Makita, S. Niki, A. Obara, P. J. Fons, and H. Shibata, Microelectron. J. **27**, 53 (1996).
[8] A. Yamada, Y. Makita, S. Niki, A. Obara, P. J. Fons, H. Shibata, M. Kawai, S. Chichibu, and H. Nakanishi, J. Appl. Phys. **79**, 4318 (1996).
[9] A. Yamada, P. Fons, S. Niki, H. Shibata, A. Obara, Y. Makita, and H. Oyanagi, J. Appl. Phys. **81**, 2794 (1997).
[10] T. Ikari, S. Shigetomi, Y. Koga, H. Nishimura, H. Yayama, and A. Tomokiyo, Phys. Rev. B **37**, 886 (1988).
[11] K. Yoshino, M. Kawahara, D. Maruoka, A. Fukuyama, K. Maeda, H. Miyake, K. Sugiyama, and T. Ikari, Inst. Phys. Conf. Ser. **152**, 609 (1998).
[12] B. Tell and P. M. Bridenbaugh, Phys. Rev. B **12**, 3330 (1975).
[13] A. Fukuyama, Y. Morooka, Y. Akashi, K. Yoshino, K. Maeda, and T. Ikari, J. Appl. Phys. **81**, 7567 (1997).
[14] K. Yoshino, T. Shimizu, A. Fukuyama, K. Maeda, P. J. Fons, A. Yamada, and S. Niki, Sol. Energy Mater. Sol. Cells **50**, 127 (1998).
[15] A. Monoogian and J. C. Woolley, Can. J. Phys. **62**, 285 (1984).
[16] H. Neumann, Sol. Cells **16**, 399 (1986).
[17] A. Fukuyama, M. Iwamoto, Y. Akashi, K. Yoshino, K. Maeda, and T. Ikari (unpublished).