Vol 17 No 4, April 2008
1674-1056/2008/17(04)/1454-07

Chinese Physics B

© 2008 Chin. Phys. Soc.
and IOP Publishing Ltd

Comparison between photoluminescence spectroscopy and photoreflectance spectroscopy in $CuGaSe_2$ epilayer*

Zhen Guo-Yong(甄国涌), Jian Ao-Qun(菅傲群), Xu Hong-Yan(徐宏妍), Xue Chen-Yang(薛晨阳)† , and Zhang Wen-Dong(张文栋)

Key Laboratory of Instrumentation Science & Dynamic Measurement (North University of China), Ministry of Education and National Key Laboratory For Electronic Measurement Technology North University of China, Taiyuan 030051, China

(Received 10 July 2007; revised manuscript received 18 October 2007)

Photoluminescence (PL) spectroscopy and photoreflectance (PR) spectroscopy are very useful techniques for studying the properties of materials. In this paper, the same material of Cu-rich metal-organic vapour phase epitaxy (MOVPE) grown $CuGaSe_2$ layer is investigated in a temperature range from 20 to 300 K to compare these two techniques. Both PL and PR spectra appear red shifted, less intense and broadened. The temperature dependence of interband transitions is studied by using the Manoogian–Leclerc equation. The values of the band gap energy at T=0 K and the effective phonon temperature are estimated. The temperature dependences of intensities and broadenings of PL and PR spectral lines are also analysed. Based on the results of the comparison, the features and applications of the PL and PR can be shown in detail.

Keywords: photoluminescence, photoreflectance, comparison, $CuGaSe_2$
PACC: 7860, 7865

1. Introduction

Many optical experimental techniques have been applied to probing either the vibrational or electronic properties of the materials, which include electronic and vibrational Raman scatterings,[1] photoluminescence (PL),[2,3] photoluminescence excitation (PLE) spectroscopy,[4] absorption,[5] photoconductivity, and photoreflectance spectroscopy.[6,7] In order to understand the properties of materials, it is important to have as much information as possible about the band structure. It usually involves interband measurements, such as PLE, absorption, reflectance spectroscopy and modulation spectroscopy. For instance, bulk semiconductor modulation spectroscopy used for obtaining maps of the band structure of various semiconductors is highly successful.[8,9] And PL spectroscopy is frequently used for analysing the structural and optical characterization of chalcopyrite materials.[10−14]In this paper, the structural and optical properties of Cu-rich MOVPE grown $CuGaSe_2$ layer with a [Cu]/[Ga] ratio of 1.13 are studied by using PR spectroscopy and PL spectroscopy in a temperature range of 300–20 K. $CuGaSe_2$, both a wide band gap chalcopyrite and an ideal absorber material, is a promising candidate for high open circuit voltage solar cells. Because of the complexity of the chalcopyrite unit cell (eight atoms per cell with low size symmetry), the electronic structure of ternary Cu–III–VI is more complex than that of binary zinc-blende semiconductors. $CuGaSe_2$ is one typical material of $A^{\rm I}B^{\rm III}X_2^{\rm VI}$ semiconductors, and through the study on such a material, the characteristics of other materials in the group can be derived. In this paper, we focus on a comparison between PR- and PL-spectra by analysing the experimental data, and the features and the applications of these two kinds of measurement methods are completely revealed.

*Project supported by the National Natural Science Foundation of China (Grant Nos 50405025 and 50535030) and the Program for New Century Excellent Talents in University.
†Corresponding author. E-mail: Xuechenyang@nuc.edu.cn

2. Experiment

2.1. Experimental setup for PR-spectra and PL-spectra

The experimental setup for the PR spectrometer consisted of a Xe lamp (XBO,100W), a single diffraction grating monochromator (CVI,1200/grate,1/4 m) located in the path of the incident light beam, several mirrors and lenses to guide the incident and reflected light, and a Si-diode detector. The modulation source was an Ar^+-laser (5 mw) chopped by a mechanical chopper at a frequency of 30 Hz. Laser light scattered on the sample was spectrally separated by a second monochromator (SPEX 1704, 1600/grate, 1 m) situated in the path of reflected light. In the case of photoreflectance, it is important for the apparatus to have a good filtering of the stray laser light, because it has the same frequency (chopped) as the signal of interest and can easily be detected. Furthermore, laser illumination can produce band-gap photoluminescence, which is greater in intensity than the signal of interest under certain conditions. This problem can be eliminated by using long-focal-length optics or by using a second monochromator running in unison with the probe monochromator in this work. And for the low temperature measurements, the samples can be cooled down to 20 K in a closed-He cryostat.

In the semiconductor photoluminescence (PL) spectroscopy, electrons are excited to the conduction band by light absorption (usually using a laser as the light source). The resulting carriers then spontaneously relax to the valence band, emitting light in the process. At low temperatures, phonon-mediated processes which allow an electron to relax to the valence band through defects in the crystal are suppressed. As a result, cryogenic PL is typically much brighter than room-temperature and high-temperature PLs. PL spectrum was excited by the 514.5 nm line of an Ar^+ laser operated at an output power of 300 mW for the study of MOVPE grown sample. The incident laser beam was focused by a cylindrical lens to avoid the local heating of the sample. The emitted light was spectrally analysed by a double grating monochromator (SPEX 1403) with a cooled GaAs photomultiplier detector. For the low temperature measurements, the sample was cooled down to 20 K in a closed-He cryostat. PL spectrum region of 1.4–2.1 eV was corrected according to the spectral sensitivity of the detection system.

2.2. Experimental material

The MOVPE $Cu_xGa_ySe_2$ layers were grown epitaxially on GaAs (001) substrates in a horizontal quartz reactor (AIX200 SC). The precursors were cyclopentadienyl Cu tertiarybutal isocyanide (CpCuCNtB), triethyl Ga, and ditertiarybutyl Se using Pd-diffused hydrogen as a carrier gas. Substrate temperature and reactor pressure were 570°C and 5000 Pa respectively. The substrate was rotated during the growth procedure.

3. Experimental results and discussion

Figure 1(a) shows the typically observed luminescence spectrum recorded on a Cu-rich MOVPE grown $CuGaSe_2$ layer with a [Cu]/[Ga] ratio of 1.13 at 20 K. The peaks at 1.66 eV and 1.63 eV are mainly due to the donor-acceptor-pair transition. The weak peak at 1.60 eV is identified as a phonon replica. The defected-related PL bands are assigned to donor-acceptor-pair recombination (DAP) transitions between a donor level at 12 meV below the lower conduction band and two different acceptor levels at 60 and 100 meV above the upper valence band. Each of the DAP bands is accompanied on its high-energy side by a free-to-bound exciton (FB). The peak ($h\nu$=1.718 eV) can be correlated with free excitonic (FE) and bound excitonic (BE) transitions.[14] With temperature increasing towards room temperature, the FE- and BE-emission peaks cannot be resolved; the overall band is fitted with a Voigt profile dominated by the FE emission. It accords with the observations in Refs.[11,12], that with increasing excitation power and/or temperature, the ratio $I_{\rm BE}/I_{\rm FE}$ diminishes and the peak observed is only dominated by the free exciton. For this reason, the peak gives an indication of FE transition. The last peak at a high energy is close to the E_b gap of $CuGaSe_2$, which is also presented in PR spectrum (shown in Fig.1(b)). $CuGaSe_2$ is a chalcopyrite-type semiconductor characterized by three valence-split bands (Γ_7, Γ_6 and Γ_7), which originate from the spin-orbit interaction (Δ_{so}) and the non-cubic crystal field (Δ_{cf}). The three peaks labelled by E_a, E_b and E_c, which are usually observed in ellipsometry- or PR-measurements, are due to transitions between the conduction band and the three valence split bands. Band energy, width and intensity are obtained by line-shape analysis of the PR-spectra using Aspnes third-derivative functional form (TDFF).[15]

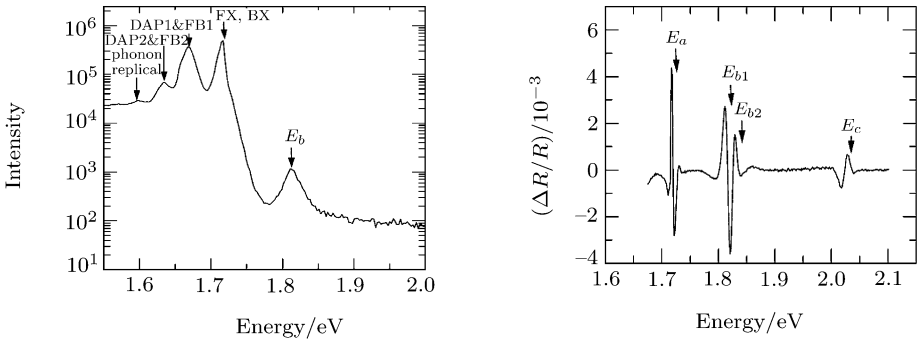


Fig.1. Typical spectra of a MOVPE grown $CuGaSe_2$ layer with a [Cu]/[Ga] ratio of 1.13 at 20 K. (a) PL-spectra, (b) PR-spectra, E_{b1} and E_{b2} are respectively the low energy and the high energy sub-bands of E_b.

Figure 2 demonstrates the temperature dependences of PR-spectra and PL-spectra. With the increase of temperature from 20 to 300 K, the PR spectral bands appear less intense, red shifted and broadened. At the temperatures up to 150 K, this behaviour is mainly due to electron scattering on phonons. Generally, it is attributed to the thermal lattice expansion and the dependence of mismatch strain on temperature. While as the temperature increases from 20 to 300 K, the PL energy and intensity will decrease, but the PL width increases. The PL energy shifting with the temperature accords with the temperature dependence of the material band gap of –0.2 meV/K as estimated in Ref.[11]. The PL bandwidth of the sample exhibits a nonlinear temperature dependence. And

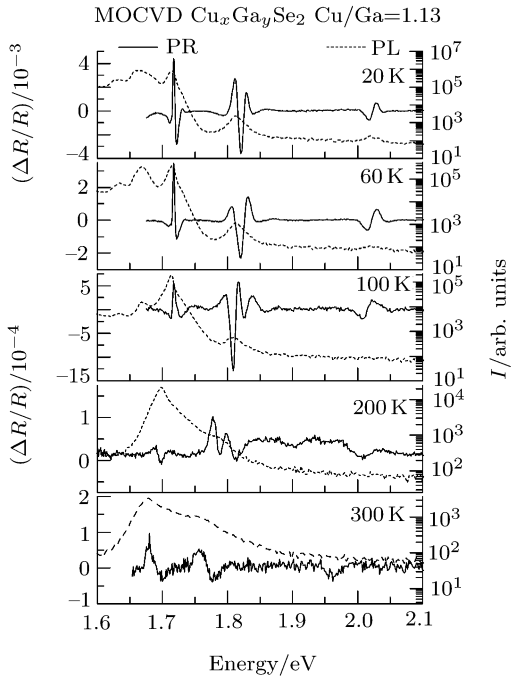


Fig.2. Temperature-dependent PR-spectra and PL-spectra intensity I of the $CuGaSe_2$ layer.

the PL intensity decreases by 3 orders of magnitude with the temperature increasing from 20 to 300 K.

More details are discussed in the following.

1) The temperature dependence of energy peak (E_a)-band is shown in Fig.3, together with the temperature dependence of the free-exciton (FE) transition of a recently performed PL investigation of the same samples, between just 12 meV below the lowest conduction and the upper state of the three valence-split band. The E_a-band (PR) and the FE-peak energy (PL) in dependence of temperature can be fitted with the Manoogian–Leclerc equation:[16]

$$E_g(T) = E_g(0) - C\theta[\coth(\theta/2T) - 1] - \Delta E_g(T)_{th}, \quad (1)$$

where

$$\Delta E_g\,(T)_{th} = -3\alpha a - 22\% * 3.94\ \varepsilon_{xx}\,(T)\,, \quad (2)$$

which is the contribution of thermal expansion to band energy; $E_g(0)$ is the band energy at T=0; the coth terms represent contributions from electron–phonon coupling; θ is the effective phonon temperature; a is

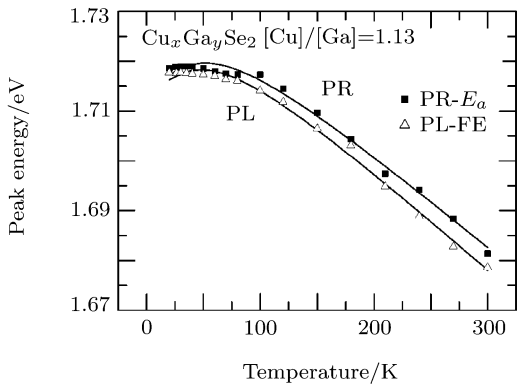


Fig.3. Temperature-dependent energies of the E_a-band (PR) and the FE-peak (PL). The circles and the squares show the PL and the PR experimental data respectively and the solid lines are obtained by fitting to Eq.(1).[17]

the band-gap deformation potential; and $\alpha = (2\alpha_a + \alpha_c)/3$ with α_a and α_c being the linear dilation coefficients along a and c axes respectively, and $\varepsilon_{xx}(T)$ being the temperature dependence of strain between epilayer and substrate; the factor 3.94 is the coefficient of a strain induced shift of the light hole (LH)-like upper valence band. At 20 K the energy-shift induced by strain resulting from the band-gap energy shift of the MOVPE-layer with respect to the band-gap energy of the CVT single crystal is 7meV,[17] and it is just 22% of the theoretically predicted value of 32 meV due to the strain-relaxation in the CuGaSe2-layers with an overcritical thickness. This is because the measured layer has a thickness of (220±20) nm, which is thicker than a critical thickness of 120 nm.[18]

The values of $E_g(0)$, C and θ are listed in Table 1. The values of θ, 167 and 176, for PL and PR respectively, are in good agreement with $\theta = \frac{3}{4}\theta_D \approx 179$ and $\theta_D = 239$ from Rincon's work.[19] The result shows the two different measurements to coincide with each other well.

Table 1. Values of the parameters $E_g(0)$, C and θ obtained by fitting the experimental data peak value vs T of Fig.3 and Fig.4 to Eq.(1).

	Experiment style	$E_g(0)$/eV	$C/10^{-6}$eVK^{-1}	θ/K
E_a	PL	1.7213±4.64×10^{-4}	1.70±3.83	167±11.21
E_a	PR	1.7223±4.84×10^{-4}	1.66±4.28	176±12.67
E_b	PL	1.8162±1.99×10^{-3}	2.4±2.0	233±35.90
E_b(Low energy)	PR	1.8177±7.9×10^{-4}	2.0±6.9	174±17.07
E_b(High energy)	PR	1.8274±1.04×10^{-3}	2.5±20	324±37.30

In the whole temperature range from 300 to 20 K, the PL-energy values are systematically lower than those of the PR-band energy, which results from the local heating of the sample by the incident laser-beam operated for PL-excitation at a power density of 1kW·cm^{-2}, which is 4 orders of magnitude higher than the power-density of the laser used as modulating source for PR-excitation.

2) It is shown in Fig.2 that with the photon energy $E < 1.7$ eV, there are some apparent peaks in the PL spectrum, while the PR spectrum is very smooth. In a spectral range below 1.55 eV, the PL spectrum of the sample has two intensive peaks separately at 1.49 eV and 1.51 eV, which are the peaks of emission from the GaAs substrate.[14] As PR spectrum shows the flat sign in below E_a-band range in Fig.2, PR is not sensitive to detecting Donor or Accepter energy level.

3) It is shown in Fig.2 that while the temperature is 20 K, fine structures of the E_b-band (1.79 eV–1.85 eV) and E_c-band (2.0 eV–2.05 eV) can be observed. The fine structures are attributed to the elastic strains ($CuGaSe_2$ /GaAs and $CuGaSe_2$ /Cu_xSe) induced in Cu-rich $CuGaSe_2$-layers partially covered by Cu_xSe-crystallites, for light can alternately penetrate regions of the bare $CuGaSe_2$ -layer and regions of the $CuGaSe_2-$layer covered by Cu_xSe. This results in lower strains in the former case and higher strains in the latter. Due to the differently strained regions of the chalcopyrite film, the PR-bands observed with the incident light reflected on the crystallites and on the film-surface are differently shifted and the overall band seems to split into two sub-bands. And the temperature dependences of the two peaks of E_b are shown in Fig.4 together with the temperature dependence of E_b-band of PL-spectra. It is shown that all the peak energies are decreasing with the temperature increasing. The three values of peak energies can also be fitted with Eq.(1), and the values of $E_g(0)$, C and θ are listed in the Table 1.

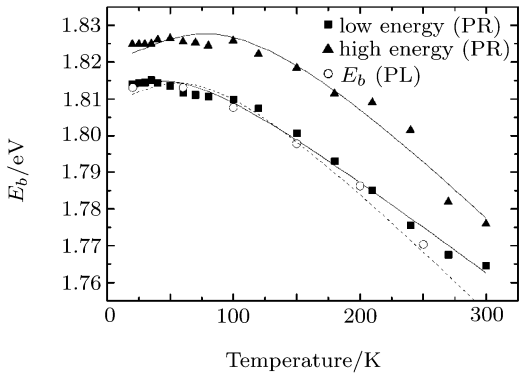


Fig.4. Temperature-dependent values of E_b for PR-spectra (solid line) and PL-spectra (doted line). The triangles and squares show the high energy and the low energy experimental data respectively and the lines are obtained by fitting to Eq.(1).

With the temperature increasing, the two peak intensity amplitudes of E_b are decreasing consistently,

while the two broadening values of E_b are increasing consistently. The PL-intensity of E_a is almost three orders of magnitude higher than that of E_b, which, in its turn, is one order of magnitude higher than that of E_c (I_{E_a}:I_{E_b}:I_{E_c}:=3000:12:1). Furthermore, the PR emission is governed by the polarization state of the light through the Fresnel equations. But the PL emission does not depend directly on light polarization, and the E_a transition is expected to be most probable and efficient, while the E_c transition should be the less efficient one. Thus, the almost equal PR-intensities of the E_a- and E_b-transitions and the lower intensity of the E_c-transition observed in the PR-spectra under illumination with light polarized in the direction normal to the c-axis can be explained as being due to a weak E_a, a strong E_b and a strong but less probable E_c transition respectively. In the PR-spectra of $CuGaSe_2$ epilayer, the three valence-split bands, i.e. E_a, E_b and E_c, which are only weakly present in the PL-spectrum, are clearly observed and can be evaluated by using a third derivative functional.

In Papadimitriou *et al*'s[20] research, a linear dependence of the band gap energy on Ga content is found to accord with the results of PR studies on $CuIn_{1-x}Ga_xS_2$.PR spectroscopy has been proved to be the most accurate and reliable method of obtaining the band gap energies directly, when applied to the band structure studies.

So the PL spectrum exhibits the strong excitonic emission to the upper valence band and the weak emissions to the deep level valence bands; the PR is a more sensitive tool for studying the band structure and is also applicable to the study of deep level bands.

4) An overall decrease of the luminescence intensity with increasing temperature can be attributed to a change in the dominant recombination mechanism, namely, from radiative to non-radiative recombinations. Alterations in the near-band-edge luminescence peak structure must be considered in terms of different radiative recombination paths. No new luminescence signal appears in the high-temperature spectra. Instead, the near-band-edge luminescence signal, identified at 20 K as free-excitonic luminescence, shifts linearly with increasing temperature towards lower energies. So the opinion is ruled out that the luminescence changes from excitonic to band-band with increasing temperature, and the transition energies of the free-exciton and the band-band luminescences would be separated by $E_{\mathrm{FX}} + k_{\mathrm{B}}T/2$, which causes the new luminescence peak in the PL spectrum.[21] The interpretation of near-band-edge luminescence dominated by excitonic states at high temperatures is supported. This interpretation accords with piezoelectric photoacoustic PPA measurement.[22]

The PL intensity of the sample decreases by 3 orders of magnitude with temperature increasing from 20 to 300 K, which is shown in Fig.5. At the same temperature, PVD films show that the intensity changes by only a factor of 5. The reason for the difference in decrease of PL intensity with temperature between PVD and MOVPE films could be the carrier localization associated with surface states at the grain boundaries of the polycrystalline PVD film or with confinement effects in crystallites of sampler size (5 nm).[14] This behaviour can be understood on the assumption that excitons are trapped in a number of defect states increased, and located at the grain boundaries of the polycrystalline-films. It is the dominance of exciton trapping over trap-ionization with increasing temperature. This is consistent with excitonic lifetime that is inversely proportional to PL-peak widths and the peak-broadening with increasing temperature. PL band intensities are found to be strongly dependent on temperature and growth mechanism.

For PR spectra, the spectral lines appear less intense and red shifted with temperature increasing from 20 K to 300 K, which is due to carrier scattering on phonons and thermal-strain effects.

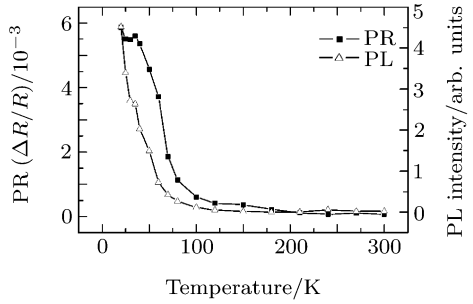


Fig.5. Temperature-dependent peak intensities of PR-spectra and PL-spectra.

5) Figure 6 demonstrates that the bandwidths of the PL- and PR-spectra of the sample exhibit a nonlinear temperature dependence, and the line widths become broader with temperature increasing from 20 K to 300 K. The line broadenings of the PR- and PL-spectra are mainly due to the mismatch strain and the size distribution of crystallites within the film. Because the strain is distributed across the layer, the broadening introduced by the mismatch strain is inhomogeneous.

The temperature dependence of the linewidth of the direct gaps of $CuGaSe_2$ can be expressed as follows:[23]

$$\Gamma_0(T) = \Gamma_0(0) + \gamma_{AC}T + \Gamma_{LO}/[\exp(\theta_{LO}/T) - 1], \quad (3)$$

where the first term on the right-hand side of Eq.(3) is due to intrinsic effects (electron–electron interaction, impurity, dislocation, and alloy scattering) at T=0; the second term corresponds to lifetime broadening due to the electron (exciton)–acoustic phonon interaction; γ_{AC} is the acoustical phonon coupling constant; the third term is caused by the electron (exciton)–longitudinal-optical (LO) phonon (Fröhlich) interaction; the quantity Γ_{LO} represents the strength of the electron (exciton)–LO phonon coupling; θ_{LO} is the LO phonon temperature.[24]

As the temperature is raised, the linewidth first increases from its zero-temperature value because of acoustical phonon scattering. Above 60–70 K, the LO phonon contribution becomes important and eventually dominant in the linewidth. By means of a least-square fit, the values of $\Gamma_0(0)$, Γ_{LO}, γ_{AC}, θ_{LO} are obtained and listed in Table 2. The differences in Γ_{LO} and θ_{LO} between the PR and PL experiments are also mainly due to the local heating of the sample by the incident laser-beam operated as mentioned above.

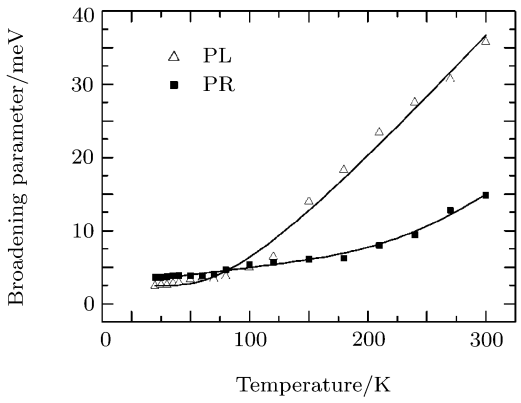


Fig.6. Temperature-dependent broadening parameters of PR-spectra and PL-spectra. The circles and squares show the PL and PR experimental data respectively and the solid lines are obtained by fitting to Eq.(3).

Table 2. Values of the parameters that describe the temperature dependence of Γ (in terms of HWHM) for the energy gap of $CuGaSe_2$.

Experimental style	$\Gamma_0(0)$/meV	Γ_{LO}/meV	θ_{LO}/K	γ_{AC} /10^{-6}eV/K
PR	2.97±0.09	579.45±27.99	1365.55	20.00
PL	2.40±0.32	46.96±1.08	262.61	2.72

6) The excitation source of the PL-spectra is Ar^+ laser, which is easy to be assembled into a point of light source through lens, and its radiation can be focused into a spot size of approximately 10 μm, and even 0.8 μm with a microprobe. So it is possible for PL-spectra to do mapping of the material.[14] The light of PR-spectra is generated by a Xe-lamp, and the light is difficult to assemble, so it is usually used to make the surface-analysis of samples.

4. Conclusion

In this paper, we have presented a review of the photoluminescence spectroscopy (PL) and photoreflectance spectroscopy (PR) in experimental, theoretical and instrumental aspects. The photoreflectance is extremely useful, for it is contactless and has no requirements for the special mounting of samples. Moreover, photoreflectance can be carried out even at room temperature, providing as much information as that obtained from the optical methods of PL, PLE spectroscopy at very low temperatures. The two techniques of PR spectroscopy and PL spectroscopy are used to study the same MOVPE grown $Cu_xGa_ySe_2$, and the results can be summarized as follows:

1) PL spectroscopy has been frequently used for structural and optical characterization of chalcopyrite materials. However, the PL spectra exhibit the strong excitonic emission to the upper valence band and the weak emissions to the deep level valence bands.

2) The temperature-dependent PR-spectra, the E_b- and the E_c- bands show a fine structure, so photoreflectance (PR) is a more sensitive tool for studying the band structure and is also applicable to the study of deep level bands.

Acknowledgments

The authors wish to thank Professor D. Papadimitriou for fruitful discussions. And they are also grateful to Professor M. Ch. Lux-Steiner for providing the samples.

References

[1] Zhang X, Wan S M, Zhang Q L, Yin S T, You J L, Chen H and Wang A H 2007 *Acta Phys. Sin.* **56** 1152 (in Chinese)

[2] Liu C M, Fang L M, Zu X T and Zhou W L 2007 *Chin. Phys.* **16** 95

[3] Cao L, Liu R B, Pan A L, Wang F F and Zou B S 2007 *Chin. Phys.* **16** 1791

[4] Miller R C, Kleinman D A, Tsang W T and Gossard A C 1981 *Phys. Rev.* B **24** 1134

[5] Masselink W T, Pearah P J, Kelm J, Peng C K, Morkoc H, Sanders G D and Chang Y C 1985 *Phys. Rev.* B **32** 8027

[6] Miao Z L, Chen P P, Lu W, Xu W L, Li Z F, Cai W Y, Shi G L and Shen X C 2001 *Acta Phys. Sin.* **50** 111 (in Chinese)

[7] Yuan X Z and Miao Z L 2004 *Acta Phys. Sin.* **53** 3521 (in Chinese)

[8] Cardona M 1969 *Modulation Spectroscopy* (New York: Academic) p15

[9] Seraphin B O 1972 Semiconductors and Semimetals (New York: Academic) p1

[10] Bauknecht A, Siebentritt S, Albert J and Lux-Steiner M Ch 2001 *J. Appl. Phys.* **89** 4391

[11] Bauknecht A, Siebentritt S, Albert J, Tomm Y and Lux-Steiner M Ch 2000 *Jpn. J. Appl. Phys.* **39** 332

[12] Yamada A, Makita Y, Niki S, Obara A, Fons P, Shibata H, Kawai M, Chichibu S and Nakanishi H 1996 *J. Appl. Phys.* **79** 4318

[13] Yamada A, Fons P, Niki S, Shibata H, Obara A, Makita Y and Oyanagi H 1997 *J. Appl. Phys.* **81** 2794

[14] Xue C, Papadimitriou D, Raptis Y S, Esser N, Richter W, Siebentritt S and Lux-Steiner M Ch 2003 *J. Appl. Phys.* **94** 4341

[15] Blossey D and Handler P 1972 Semiconductors and Semimetals (New York: Academic) p257

[16] Manoogian A and Leclerc A 1979 *Phys. Sat. Sol.* (b) **92** 23

[17] Xue C, Papadimitriou D and Esser N 2004 *Thin Solid Films* **451–452** 189

[18] Bauknecht A 1999 *Ph.D. thesis* (Berlin: Freie Universität) p10

[19] Rincon C and Gonzalez J 1989 *Phys. Rev.* B **40** 8552

[20] Papadimitriou D, Theodoropolou S, Xu H Y and Xue C 2005 *6th International Symposium on Test and Measurement* ISTM/2005 **1** 994

[21] Meeder A, jager-Waldau A, Tezlevan V, Arushanov E, Schedel-Niedrig T and Lux-Steiner M Ch 2003 *J. Phys.: Condens Matter* **15** 6221

[22] Yoshino K, Maruoka D, Ikari T, Fons P J, Niki S and Yamada A 2000 *Appl. Phys. Lett.* **77** 259

[23] Rudin S, Reinecke T L and Segall B 1990 *Phys. Rev.* B **42** 11218

[24] Malikova L, Krystek Wojciech, Pollak Fred H, Dai N, Cavus A and Tamargo M C 1996 *Phys. Rev.* B **54** 1280