Materials Science and Engineering B 174 (2010) 200–204

Contents lists available at ScienceDirect

Materials Science and Engineering B

journal homepage: www.elsevier.com/locate/mseb

Band structure calculations of $Cu(In_{1-x}Ga_x)Se_2$

M. Chandramohan[a,*], S.Velumani[b], T. Venkatachalam[c,1]

[a] Department of Physics, Park college of Engineering and Technology, Kaniyur, Karumatham Patty, Coimbatore 641659, Tamil Nadu, India
[b] Centro de Investigacion y de Estudios Avanzados del I.P.N. (CINVESTAV), Av. Instituto Politecnico Nacional # 2508 Col. San Pedro Zacatenco 07360, Mexico D.F., Mexico
[c] Department of Physics, Coimbatore Institute of Technology, Coimbatore 14, India

ARTICLE INFO

Article history:
Received 1 September 2009
Received in revised form 13 March 2010
Accepted 17 March 2010

Keywords:
Band structure of semiconductors
CIGS
Effective masses
Density of states

ABSTRACT

First principles density calculations of the band structure, and density of states of the $Cu(In_{1-x}Ga_x)Se_2$ in the chalcopyrite type structure have been carried out using the density functional theory. The relationship between the band gap and chemical composition in the structure is discussed. The effective masses of the electrons and holes in the different composition crystals are reported.

1. Introduction

Record conversion efficiencies of CdS/CIGS thin-film solar cells are approaching 20% [1–4]. The major advantages of CIGS are due to its unique combination of properties such as high absorption coefficient, moderate surface recombination velocities and radiation hardness [5,6]. In CIGS solar cells absorber layers are non-uniform Ga/In composition versus absorber depth. The effects of this non-uniformity in $CuIn_{1-x}Ga_xSe_2$ are in the form of (1) back grading, (2) front grading, or (3) double grading. Adding Ga increases the efficiency of the CdS/CIGS thin film solar cells up to a limited value of Ga substitution. Typical high-efficiency CIGS solar cells have minimum band gaps of 1.1–1.2 eV. The CIGS material has variable band gap, which can be changed by varying the Ga/(In + Ga) ratio. In general, high efficiency CIGS films are grown with a Ga/(In + Ga) content ratio of about 0.3 and band gap energy of about 1.15 eV. Many CIGS based solar cells with back grading, front grading and double grading have been fabricated in the last 15 years, but the actual effect of such an in-depth variation of the band gap is still not clear. Numerical modeling is necessary in this to contribute (i) the beneficial effect of grading, (ii) in standardizing thicknesses of the layers, and (iii) increase cell performance. Recently, it has become possible to compute with a great accuracy an important number of electronic and structural properties of solids from first principles calculations. This kind of development in computer simulations has opened up many of interesting and exciting possibilities in condensed matter studies. It is now possible to explain and to predict properties of solids which were previously inaccessible to experiments. Wei and Zunger [7] have theoretically shown that a variation of the Ga/(In + Ga) ratio will mainly affect the level of the conduction band minima. In this paper we report the results of computational studies of the chalcopyrite structures of $CuIn_{1-x}Ga_xSe_2$ especially focusing on structures, density of states, effective masses and band gap of $CuIn_{1-x}Ga_xSe_2$. This quality can be used, not only to optimize the general band gap level, but also to obtain different band gaps at different depths in the CIGS film, so-called band gap profiling.

2. Computational method

The calculations were performed within the framework of the density functional theory (DFT) [8]. The exchange correlation term was treated by using the functional of LDA-CA PZ [9] and GGA-PW91 [10,11]. The ultra-soft pseudo-potential was applied to describe the electron-ion interaction. A plane wave basis set with a 290 eV energy cut-off was used to expand the electronic wave functions. Reciprocal space integration was performed by k-point sampling with sets of special points obtained by using the standard special k points technique of the Monkhorst and Pack. In our case (i.e. for chalcopyrite CIGS) a $4 \times 4 \times 2$ MP meshes were used, yielding ten k points in the irreducible wedge of the Brillouin zone. CIGS chalcopyrite structure belongs to P65 symmetry group, which displays only identity and inversions operations. There are four CIGS groups (31 atoms) per unit cell. The lattice parameters obtained from X-ray diffraction [12] are shown in Table 1.

* Corresponding author. Tel.: +91 0421 2334899; fax: +91 0421 2334453.
E-mail addresses: chandramohan59@yahoo.co.in (M. Chandramohan), vels64@yahoo.com (S.Velumani), atvenkatachalam@yahoo.com (T. Venkatachalam).
[1] Tel.: +91 0422 2574071; fax: +91 0422 2575020.

0921-5107/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.mseb.2010.03.043

Table 1
Comparison between experimental and simulated parameters of CIGS chalcopyrite unit cell.

Molecular formula	Experimental data (Å)		Calculated data (Å)	
	a	*c*	*a*	*c*
$CuIn_{0.25}Ga_{0.75}Se_2$	5.72	11.63	5.61	11.39
$CuIn_{0.5}Ga_{0.5}Se_2$	5.73	11.66	5.67	11.54
$CuIn_{0.75}Ga_{0.25}Se_2$	5.75	11.69	5.69	11.57

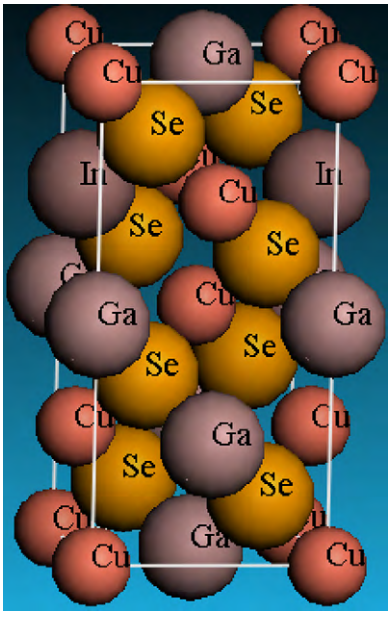

Fig. 1. Chalcopyrite structure of $CuIn_{0.25}Ga_{0.75}Se_2$.

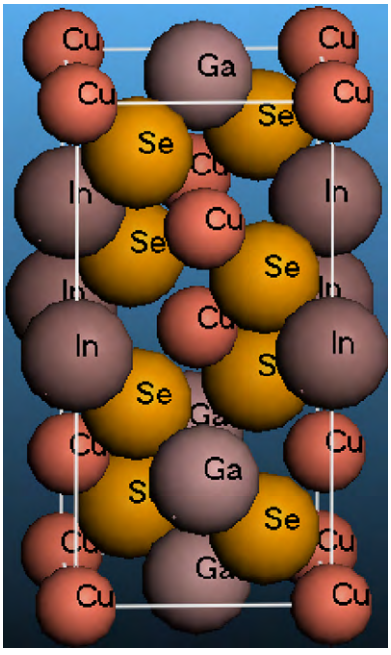

Fig. 2. Chalcopyrite structure of $CuIn_{0.50}Ga_{0.50}Se_2$.

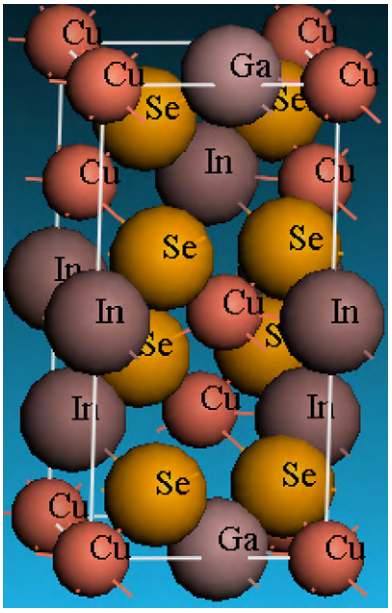

Fig. 3. Chalcopyrite structure of $CuIn_{0.75}Ga_{0.25}Se_2$.

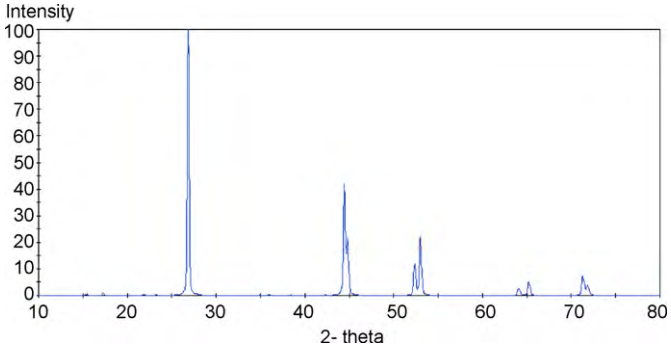

Fig. 4. Simulated XRD pattern of $CuIn_{0.25}Ga_{0.75}Se_2$ structure.

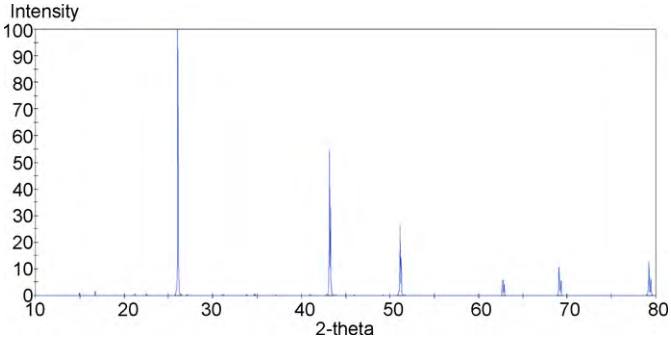

Fig. 5. Simulated XRD pattern of $CuIn_{0.50}Ga_{0.50}Se_2$ structure.

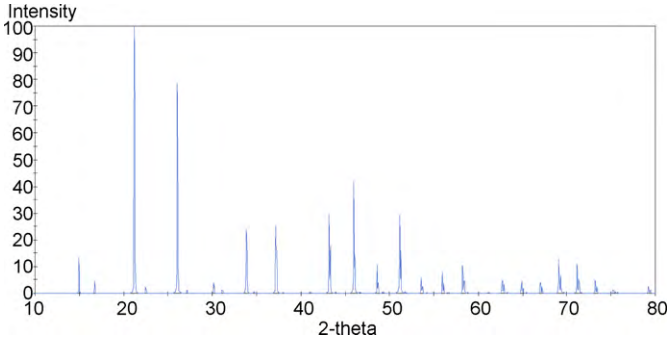

Fig. 6. Simulated XRD pattern of $CuIn_{0.75}Ga_{0.25}Se_2$ structure.

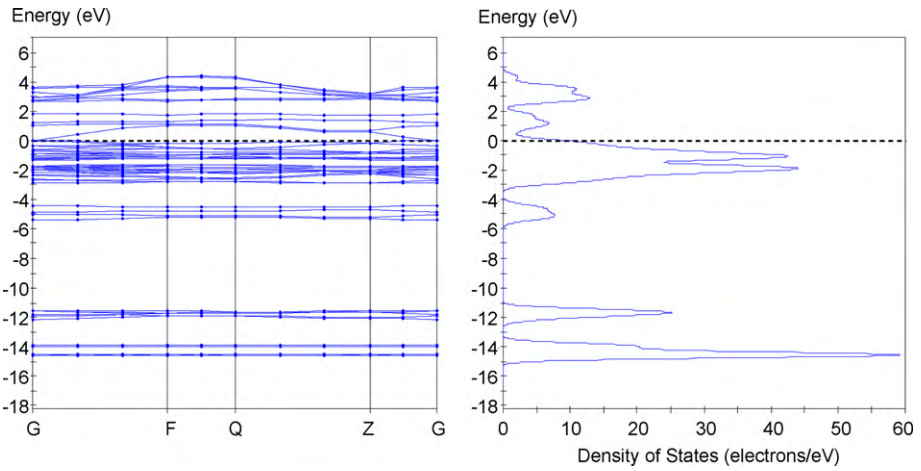

Fig. 7. Band structure and density of states of $CuIn_{0.25}Ga_{0.75}Se_2$ structure (LDA).

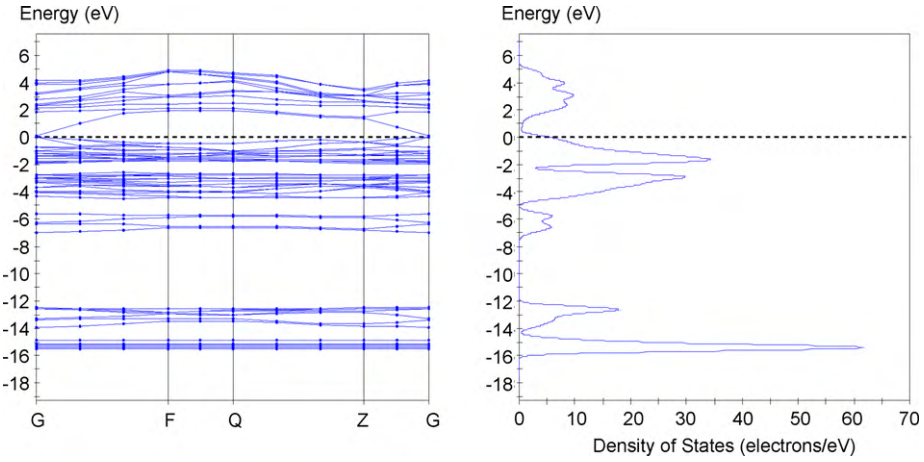

Fig. 8. Band structure and density of states of $CuIn_{0.25}Ga_{0.75}Se_2$ structure (GGA).

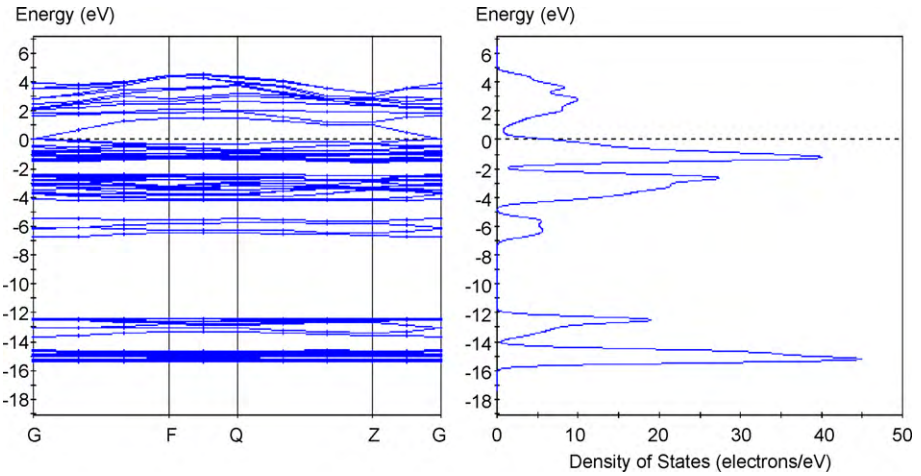

Fig. 9. Band structure and density of states of $CuIn_{0.5}Ga_{0.5}Se_2$ structure (LDA).

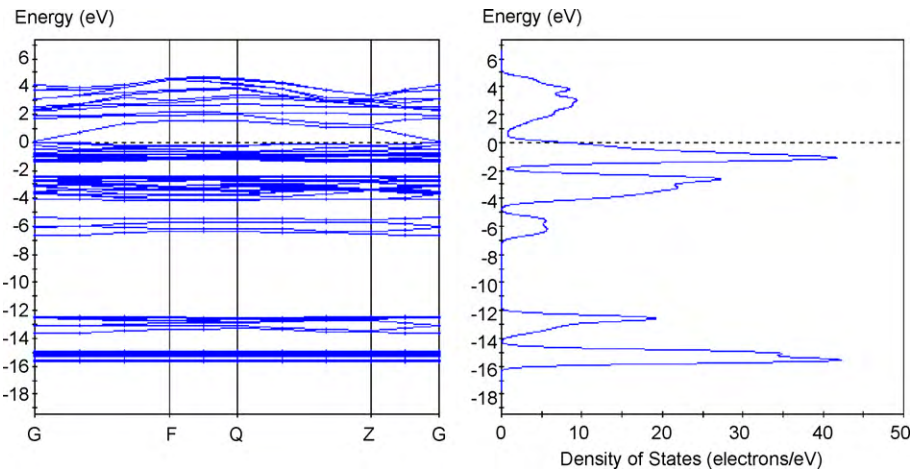

Fig. 10. Band structure and density of states of $CuIn_{0.5}Ga_{0.5}Se_2$ structure (GGA).

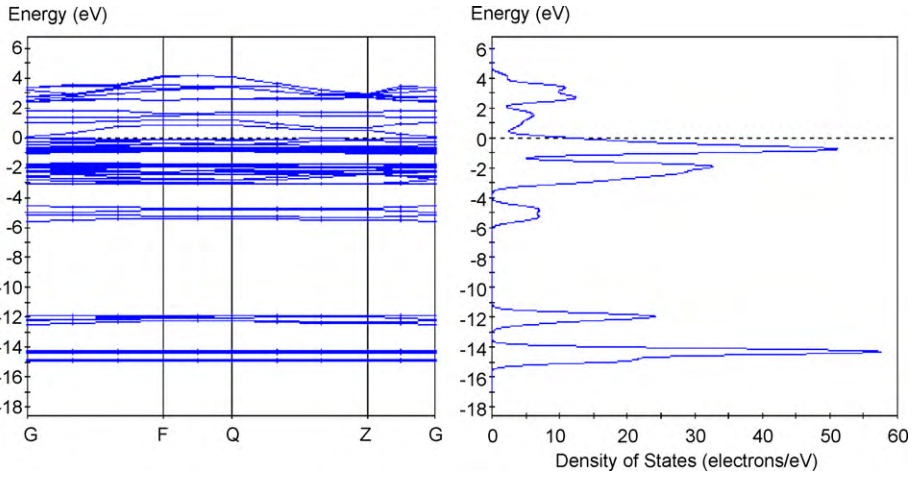

Fig. 11. Band structure and density of states of $CuIn_{0.75}Ga_{0.25}Se_2$ structure (LDA).

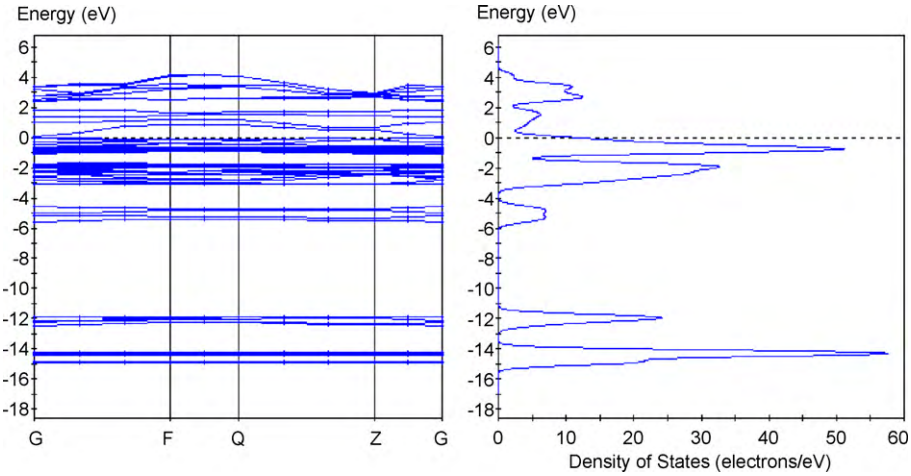

Fig. 12. Band structure and density of states of $CuIn_{0.75}Ga_{0.25}Se_2$ structure (GGA).

Table 2
Band energy gap of CIGS.

Molecular formula	Band gap		Effective mass (m_e)			
	LDA (eV)	GGA (eV)	Electrons		Holes	
			LDA	GGA	LDA	GGA
$CuIn_{0.25}Ga_{0.75}Se_2$	1.2	0.8	0.089	0.089	0.69	0.68
$CuIn_{0.5}Ga_{0.5}Se_2$	0.9	0.8	0.088	0.087	0.68	0.67
$CuIn_{0.75}Ga_{0.25}Se_2$	0.8	0.7	0.086	0.085	0.67	0.66

3. Results and discussion

3.1. Structural optimization

The crystal structure and locations of the particular atoms of the CIGS chalcopyrite structure have been determined from X-ray diffraction data [12–14] as a starting point for total energy minimization. The chalcopyrite structure of CIGS of three combinations such as $CuIn_{0.25}Ga_{0.75}Se_2$, $CuIn_{0.50}Ga_{0.50}Se_2$, and $CuIn_{0.75}Ga_{0.25}Se_2$ with the lattice parameters (Table 1) are constructed as shown in Figs. 1–3. After obtaining convergence, the final lattice parameters were obtained and tabulated as shown in Table 1. The cut off energy was assumed in the plane wave basis set. Optimization (relaxation) of the atomic positions and crystal cell parameters was performed before the main calculations of the electronic characteristics; total electronic energy, band energy dispersion, density of electronic states and optical properties. The lattice parameters obtained in the LDA and GGA calculations are 3% smaller than the experimental values. The simulated XRD spectra of the CIGS unit cell of different combinations are as shown in Figs. 4–6.

3.2. ab initio studies of electronic properties

The calculations of electronic characteristics; total electronic energy, band energy dispersion, density of states of CIGS structures are simulated for the optimized crystal structures. For $CuIn_{0.25}Ga_{0.75}Se_2$, 144 electrons (72 up spins and 72 down spins) and 76 bands are as chosen as electronic parameters. The total energy per atom convergence, eigen energy convergence tolerance, smearing width and Fermi energy convergence tolerance are taken as 0.2×10^{-5} eV, 0.4×10^{-6} eV, 0.1 eV and 0.4×10^{-7} eV, respectively, are taken as electronic minimization parameters. Band structure of the crystal is calculated of 76 bands of the Brillouin zone with band convergence tolerance of 0.1×10^{-4} eV and 4 k-points are considered for Brillouin zone sampling. The obtained band structures and density of states are displayed as shown in the Figs. 7 and 8. The same procedure is repeated for the other two structures and their band structures and density of states are similar to each other as shown in Figs. 9–12s. Band energy gap and effective mass of the electrons and holes of the different structures are determined from the graphs and the values are as shown in Table 2.

4. Conclusions

Our present paper reports a systematic study of the structural and electronic properties of $CuIn_{0.25}Ga_{0.75}Se_2$, $CuIn_{0.50}Ga_{0.50}Se_2$, and $CuIn_{0.75}Ga_{0.25}Se_2$ structures using LDA and GGA. The ground state properties like equilibrium lattice constants obtained from our calculation agree with the available experimental values. For the electronic properties the calculations provides an excellent description of the band structures for all the CIGS where we found they have direct band gap. The band structure details presented could be useful for further experimental investigations.

Acknowledgment

We are grateful to Dr. Hongbo Liu (Mexico) for the discussion and computational works in this paper.

References

[1] K. Ramanathan, M.A. Contreras, C.L. Perkins, S. Asher, F.S. Hasoon, J. Keane, D. Young, M. Romero, W. Metzger, R. Noufi, J. Ward, A. Duda, Prog. Photovolt. 11 (2003) 225.
[2] M.A. Contreras, B. Egaas, K. Ramanathan, J. Hiltner, A. Swartzlander, F. Hasson, R. Noufi, Prog. Photovolt. 7 (4) (1999) 311.
[3] Y. Hagiwara, T. Nakada, A. Kunioka, Technical Digest of 11th International Photovoltaic Science and Engineering Conference, Sapporo, 1999, pp. 83–84.
[4] T. Negami, Y. Hashimoto, S. Nishiwaki, Technical Digest of 11th International Photovoltaic Science and Engineering Conference, Sapporo, 1999, p. 993.
[5] H.W. Schock, Proceedings of the International Symposium on Polycrystalline Semiconductors and Grain Boundaries, 1989, p. 2461.
[6] G.A. Landis, A.F. Hepp, Proc. Eur. Space Power Conf., vol. 99, Florence, 1991, p. 517.
[7] S.H. Wei, A. Zunger, J. Appl. Phys. 78 (1995) 3846.
[8] M.D. Segall, P.J.D. Lindan, M.J. Probert, C.J. Pickard, P.J. Hasnip, S.J. Clark, M.C. Payne, J. Phys.: Condens. Mat. 14 (11) (2002) 2717–2743.
[9] D.M. Ceperley, B.J. Alder, Phys. Rev. Lett. 45 (1980) 566.
[10] J.P. Perdew, A. Zunger, Phys. Rev. B 23 (1981) 5048.
[11] J.P. Perdew, S. Burke, M.E. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
[12] M. Venkatachalam, M.D. Kannan, S. Jayakumar, R. Balasundaraprabhu, N. Muthukumarasamy, A.K. Nandakumar, Solar Energy Mater. Solar Cells 92 (2008) 517–575.
[13] F. Long, W. Wang, J. Du, Z. Zou, J. Phys.: Conf. Ser. 152 (2009) 012074–12077.
[14] I.M. Dharmadasa, Semicond. Sci. Technol. 24 (2009) 055016–55025.