

CHAPTER - 1.

EXISTING INFORMATION ON COPPER INDIUM DISULFIDE (CuInS_2)

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1.1. INTRODUCTION

As mankind struggles to extract every last bit of energy out of the planet Earth, only to look forward to the negative environmental impact of their use, the technologies of conservation and renewable energy sources continue to make long strides towards economic viability.

Although the estimates vary, it is believed that we will seriously deplete our fossil fuel reserves i.e. natural gas, petroleum, coal etc. within the next two decades. Regardless of its use as energy sources, the negative environmental impact due to excessive carbon dioxide, CO_2 , production is of paramount concern.

Renewable technologies cover an extensive range of disciplines, including bio-fuels, ocean geothermal, hydrogen, wind energy, nuclear energy, and photovoltaic. Of these photovoltaic is relatively cheaper mean of conversion technologies. Photovoltaic is the conversion of radiation power into electrical power through photon absorption by semiconductor materials. The basic elemental and compound material systems most widely used in opto-electronics and photovoltaic applications can be produced in a variety of crystalline and non-crystalline forms. They include, but are not limited to, the following material systems: 1) Single

crystalline bulk and epitaxial multi-layer structures of group IV (Si,Ge) and binary MX (M = II,III & X = VI,V) 2) Poly-and micro-crystalline thin and thick films of elemental, binary MX, and ternary ABX_2 (A = I,II;B = III,IV and X = VI,V) compounds, and 3) Amorphous thin films of Si and Si: (C, Ge, Sn) alloys and the chalcogenide glasses.

The crystalline group of materials have historically exhibited the highest conversion efficiencies, but as a consequence of their substantially higher cost, are presently being considered primarily for space and concentrator applications. The amorphous Si technology has received much attention and study due to its moderate conversion efficiency, low cost, and potential for micro-electronic applications. An intrinsic photo-induced instability problem, however, has stalled progress towards economic viability in photovoltaic applications.

Several candidates in the poly-and micro-crystalline family of materials have recently gained much attention and interest due to their enhanced performance, potential for low cost manufacturability, and exhibited stability and reliability. Included among the success stories are CdTe [1], $CuInSe_2$ [2], $CuIn_{1-x}Ga_xSe_2$ [3] absorber based photovoltaic devices. These materials have exhibited,

respectively, 10.8, 14.1 and 12.4% conversion efficiencies in small area heterojunction thin film devices. Whereas nearly 10% efficiency has been reported for solar cells fabricated with single crystal CuInS_2 [4].

The CuInS_2 is a member of large family of I-III-VI₂ ternary chalcopyrite compounds which have found considerable interest in semiconductor physics. This is particularly well studied for solar cell applications, due to its bandgap of 1.55 eV at 300 K [5], which is close to the ideal value for optimum solar energy conversion. In addition, the application of homojunction has become possible by the fact that both n and p-type CuInS_2 can be prepared. These properties evoked a considerable practical utility of the material in non-linear optical devices or in solar energy conversion systems, both in p-n homo- and hetero-junction and in liquid junction cells. Measurements of various physical, optical and electrical properties have been reported by a number of investigators [6-10].

For many studies of CuInS_2 the availability of single crystals is highly desirable. An effort has therefore been made in the present work to grow CuInS_2 in form of single crystals as well as in thin film form. For any application it is desirable that the grown material must be fully

characterised. Author has therefore used practically all characterisation techniques available with hand to characterise the grown crystals before they are used in the fabrication of devices. This chapter describes in brief the existing information available on CuInS_2 .

1.2. METHODS FOR SYNTHESIS OF CuInS_2

Crystal growth has been a subject of absorbing interest for very many years, much of the recent development in both the understanding and the technology has been stimulated by the increasing commercial importance of the subject. The spectacular growth of modern solid-state electronics, so critically depends on crystal growth and perfection, is a case in point. Much crystal growth is still art and technique rather than science. A number of different methods have been used for the growth of CuInS_2 single crystals. A brief report on growth of these crystals using different growth techniques by several investigators has been presented here.

Paorici et al. [11] used time varying temperature profile CVD method for growing CuInS_2 crystals. In this the temperature of the source and the growth end was oscillated between themselves and large size crystals were obtained.

Sintering method of growth was employed by Takeshi Miyauchi et al. [12] for the growth of perfectly densified and oriented CuInS_2 crystals. Thiel [13] used the method of zone melting for the growth of CuInS_2 crystals.

Hwang et al. [14] theoretically analysed the kinetics involved in the growth of CuInS_2 crystals by Travelling Heater Method (THM). A numeric estimate of the maximum growth rate was obtained and accordingly the speed of the heater was set in practical experiment and large single crystals of CuInS_2 compound were successfully synthesized [15]. Bridgman technique for the growth of CuInS_2 crystal was successfully used by Mittleman et al. [7] and Malsagov et al. [16]. But S. Kobayashi et al. [17] have used horizontal Bridgman method for the growth of CuInS_2 crystals.

Detail flux growth of CuInS_2 from copper indium melt has been reported by Fleming et al. [18]. They reported that by suitably controlling the starting melt, the stoichiometry can be successfully controlled and changed. Solid state growth of some I-III-VI₂ chalcopyrite crystals has been reported using the respective I₂VI and III₂VI₃ binary compounds as the starting material by Yamamoto et al. [19]. They discussed their results with the aid of pseudo-binary phase diagram. Fearheiley et al. [20] have successfully grown

CuInS₂ single crystal by the gradient freeze technique and have studied the effect of sulphur pressure on the growth. But they were unsuccessful in growing perfect stoichiometric crystals using this method.

Binsma et al. [21] studied in detail the growth mechanism of CVT grown CuInS₂ single crystals using iodine transporter. They showed that vapour-liquid-solid (VLS) growth with CuI as liquid phase plays a main role during CVT growth. Prokhorov et al. [22] determined the best technological conditions for obtaining good quality CuInSe₂ crystals by CVT and made recommendation for CuInS₂ growth by this technique. Aksenov et al. [23] have also reported successful growth of perfect stoichiometric CuInS₂ crystals by chemical vapour transport technique. Recently Balakrishnan et al. [24] reported the growth of some indium chalcopyrite semiconductor single crystals by CVT using iodine as the transporting agent.

In the majority of growth methods the crystals always grow in the form of one large single crystal. Thin flakes needed for the physical property measurements are therefore obtained from a large size crystal by the method of cleaving. The process of cleaving can introduce a large number of defects. It is therefore desirable to use a method by which crystals can be grown in the form of thin flakes so that they

bond lengths, $R_{AX} \neq R_{BX}$. Second, the unit cell is tetragonally distorted with a distortion parameter $n = C/2a \neq 1$. Third, the anions are displaced from the ideal tetrahedral site by an amount u . The two near-neighbour bond distances are given by $R_{AX} = a[u^2 + (1+n^2)/16]^{1/2}$ and $R_{BX} = a[(u-1/2)^2 + (1+n^2)/16]^{1/2}$, where a is the cubic lattice constant. The bond length mismatch is hence $\Delta R = R_{BX} - R_{AX} = (u-1/4)a^2$ and vanishes for a zincblende-like undistorted anion sublattice, where $u = 1/4$. Because of the added structural (n,u) and chemical $(A \neq B)$ degrees of freedom relative to their binary analogs, the 36 known ternary ABX_2 semiconductors exhibit a far richer range of physical and chemical properties. The broad range of optical bandgaps and carrier mobilities offered by ternary ABX_2 semiconductors, as well as their ability to form various solid solutions and to accommodate different dopants, has led to their emergence as technologically significant device materials, including applications in photovoltaic solar cells both as single crystal materials (upto 12% efficient [25,26]) and as polycrystalline thin films (at least 9.4% efficient [27]), light-emitting diodes [28], and in various nonlinear optical devices [29]. The $CuInS_2$ compound is one which exhibits this above structure whose details are provided in **Table 1.1**.

Brandt et al. [34] also determined the crystallographic parameters of CuInS_2 using X-ray diffraction techniques. They evaluated the lattice parameters a and c using Debye-Scherrer powder data and the computer program package X-RAY SYSTEM. This program package was also used together with intensity data, obtained by conventional Burger precision techniques ($\text{MoK}\alpha$), to evaluate the free parameter X_f . The results are given in Table 1.2.

Using the known values of a , c and X_f , they determined all interatomic bond distances and bond angles for CuInS_2 . The representative data are given in Table 1.3.

1.4. BAND STRUCTURE OF CuInS_2

Poplavnoi et al. [35,36], have used the non-self-consistent empirical pseudopotential method [37] to calculate the electronic structure of group I chalcopyrites, neglecting the noble-atom d orbitals. The pseudopotential form factors of the B- and X-atoms were taken from the II-VI binary analogs, whereas the form factors of Cu were taken from early results of Harrison [38]. The band structure was evaluated at four high-symmetry k points, using a maximum of 150 plane waves. Earlier results of Poplavnoi et al. [35] ignored the anion displacement, leading to indirect bandgaps; in contrast with experimental data of Shay et al. [9], while latter

calculations [36] included this effect ($u \neq 1/4$). The latter results [36] were obtained for CuAlS_2 , CuInS_2 , CuAlSe_2 and CuInSe_2 . Bendt et al. [39] reported the results of first self-consistent study of the electronic structure of CuInSe_2 . They used the potential-variation mixed basis (PVMB) approach which avoids pseudopotential approximations and solves the all electron problem self-consistently within the density functional approach [40]. Jaffe et al. [41] used the PVMB approach to study the chemical trends in the electronic structure of CuInS_2 .

Fig.1.2 displays the self consistent electronic band structures of CuInS_2 calculated with Ceperley's correlation [42]. While Table 1.4 provides the crystal-structure parameters of CuInS_2 .

1.5. PROPERTIES OF CuInS_2

1.5.1. Chemical Properties

In solid state chemistry it is attempted to relate the structure and composition of materials to their physical properties. Not only the overall composition is of importance in this respect, but also the contents of imperfections in the crystal lattice (defects) need to be known usually.

The ternary character opens up new possibilities

for the defect chemistry compared with binary compounds. Because of the three different crystallographic sites, the range of non-stoichiometry is generally greater and the formation of solid solution occurs more easily. As pointed out by Kroger [43] two kinds of non-stoichiometry can be discerned in ternary compounds. The first kind, called "deviation from molecularity", parametrizes the concentration ratio between the both binary compounds of which the ternary compound is made up. The second kind, called "deviation from stoichiometry", parametrizes the concentration ratio between cations and anions and is the only possible kind of non-stoichiometry for binary compounds. A fundamental difference between both kinds of non-stoichiometry is that a deviation from molecularity does not affect the number of valence electrons, while a deviation from stoichiometry results in an excess or a deficiency of valence electrons. Additional native disorder is caused by the cation disorder, leading to A atoms on B sites and vice versa in the ABX_2 chalcopyrite.

Several authors have reported about the defect chemistry of $CuInS_2$. Tell et al. [6] found that annealing in the presence of sulfur yielded p-type conductive $CuInS_2$, while by annealing in the presence of copper, n-type material was obtained. Similar observations were reported by Look et al.

[44], who produced n-type crystals by annealing in the presence of indium. Verheijen et al. [45] studied the photoluminescence and the electrical properties of copper and sulfur annealed material. Masse et al. [46] described the influence of annealing in In, S, In+S or vacuum on the cathodoluminescence.

Methods for accurate determination of elemental composition of CuInS_2 , CuInSe_2 and related ternary alloys, have been developed by Hwang et al. [47]. These methods virtually eliminate interference effects among the constituent elements which hinder the precise determination. The coulometry method especially developed for CuInS_2 and its ternary alloys, are ideal for single crystal and thin film analysis.

1.5.2. Magnetic Properties

Magnetic properties of n-type CuInS_2 were studied in detail by Jagadeesh et al. [48]. They measured the magnetic susceptibility X , of a polycrystalline n-type CuInS_2 sample in the temperature range 4.2-300K. The temperature dependence of magnetic susceptibility (300 K-78 K) of some polycrystalline I-III-VI₂ semiconductors was determined by Sagredo et al. [49]. They showed that changes in the diamagnetic

susceptibility of CuInS_2 assumed to be due to the presence of a temperature dependent paramagnetic term arose from noninteracting trapped carriers.

1.5.3. Optical Properties

The optical absorption near the band edge has been reported in literature for both crystals and thin films. Makarova et al. [50] measured the optical coefficient in the fundamental absorption edge region of CuInS_2 crystals with natural and preliminarily treated surfaces. The spectrum consisted of a single excitonic peak at 1.53 eV that was shifted to 1.48eV by polishing. Joshi [51] examined lattice dynamical behaviour of CuInS_2 with Fe impurity at 4.2K by using fourier transition spectroscopy. Detailed study of optical absorption spectra in CuInS_2 doped with iron, manganese and chromium was done by Katsuaki Sato et al. [52]. Takahiro Wada et al. [53] studied the effect of annealing temperature on its optical properties for CuInS_2 films. Optical studies were performed on $\text{CuIn}(\text{Se}_{1-x}\text{S}_x)_2$ thin films at room temperature by Aren et al. [54]. CuInS_2 was found to be a direct gap semiconductor with an energy gap E_g in the range 1.524 to 1.54eV.

1.5.4. Electrical Properties

Measurements of various electrical properties have

Zyl'kov et al. [63] have used glass doped with $\text{CuInS}_2(1-x)\text{Se}_{2x}$ as solid state passive switch for neodymium lasers for the first time. Tributsch [64] has shown hope of using CuInS_2 as high temperature superconductor with some modifications.

TABLE 1.1 Lattice parameters of CuInS_2 Compound

Compound	a \AA	c \AA	c/a	Ref.
	5.528	11.08	2.00	[30]
CuInS_2	5.51	11.02	2.00	[31]
	5.524	11.13	2.01	[32]
	5.52279	11.13295	2.0158	[33]

TABLE 1.2 Crystallographic parameters of CuInS_2
determined by X-ray diffraction at 300°K .

$a(\text{Å})$	5.523
$c(\text{Å})$	11.12
X_f	0.214
c/a	2.013

TABLE 1.3 Interatomic bond distances in \AA units and bond angles for CuInS_2 of type ABX_2 , as evaluated from X-ray diffraction data quoted in Table 1.2.

A-X	2.288
B-X	2.517
*X-A-X	$105^\circ 2'$
X-A-X	$111^\circ 6'$
*X-B-X	$112^\circ 9'$
X-B-X	$107^\circ 7'$

* X-X axis perpendicular to c-axis.

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TABLE 1.4 Values of the cubic lattice constant a , the tetragonal distortion parameters $n = c/2a$, and the anion displacement parameter u (in units of a) $1 \text{ a.u} = 0.52917 \text{ \AA}^{\circ}$.

Compound	$a(\text{a.u})$	n	u
CuInS_2	10.4372	1.0065	0.214

TABLE 1.5 Room temperature electrical properties of CuInS₂ single crystals

Growth Method	Doping material	Heat treatment temperature °C	Heat treatment time hrs.	Type	(ohm.cm)	(cm ² /V.sec)	n or p (cm ⁻³)	Ref.
Melt	None	None	None	p	169	0.4	1 x 10 ¹⁷	[43]
Melt	S	550	60	p	4.8	17	7.9x10 ¹⁶	[43]
Melt	In	700	60	p	2.1x10 ⁴	0.7	4 x 10 ¹⁴	[43]
Melt	In	725	60	n	1.1x10 ⁴	160	3.7x10 ¹²	[43]
Melt	In	745	60	n	1.8x10 ⁴	30	1.2x10 ¹⁴	[43]
Melt	In	755	60	n	24	60	4.4x10 ¹⁵	[43]
Melt	In	775	60	n	15	150	2.9x10 ¹⁵	[43]
Melt	In	800	60	n	0.24	75	3.5x10 ¹⁷	[43]
Bridgman	Cd,Zn	600-650	48	n	0.15	90		[7]
CVT(I ₂)	None	None	--	p	10	15		[8]

CAPTIONS TO THE FIGURES

Fig. 1.1. (a) The chalcopyrite structure compared (b) to two unit cells of the Zinc blende structure (c) crystal structure of the chalcopyrite ABX_2 unit cell. The arrows and the denoted in-plane and out-of-plane directions show the anion displacements relative to the tetrahedral structure.

Fig. 1.2. Electronic band structure of $CuInS_2$ using Ceperley's correlation and the crystal structure parameters of Table 1.4. The principle bandgap is denoted by the shaded area.

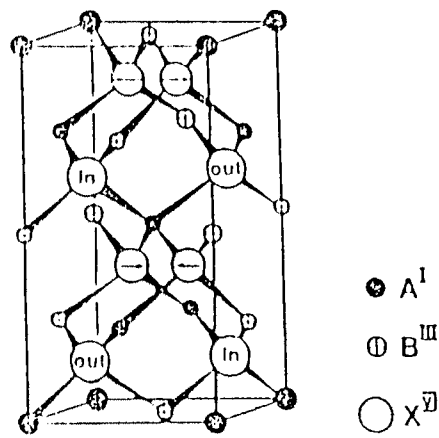
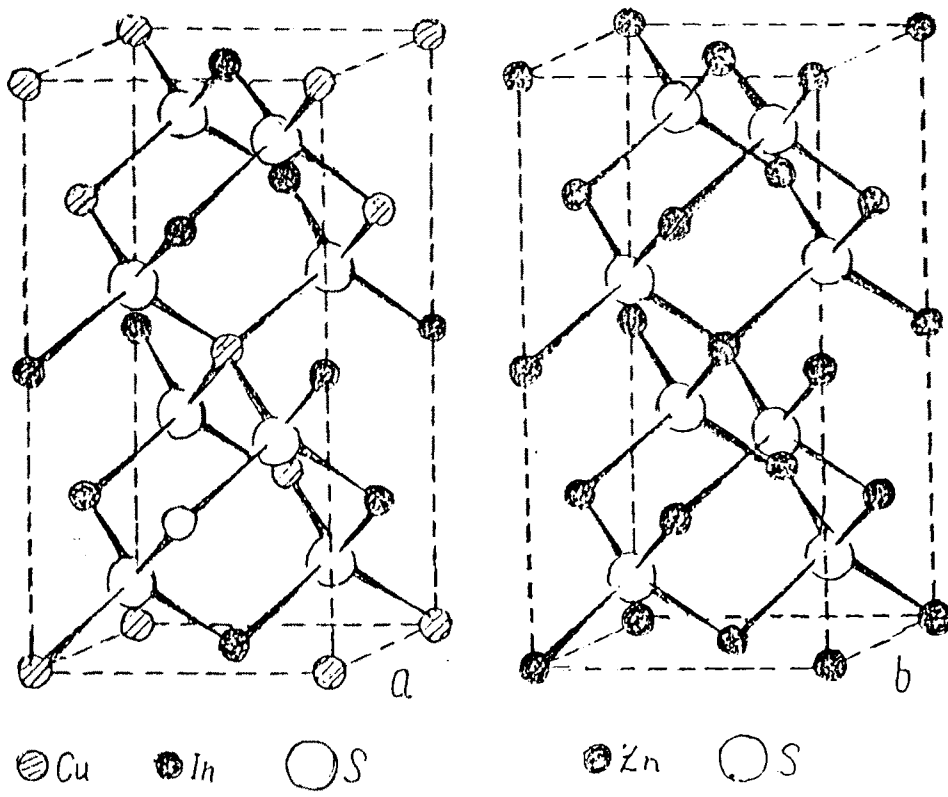


Fig. 1.1

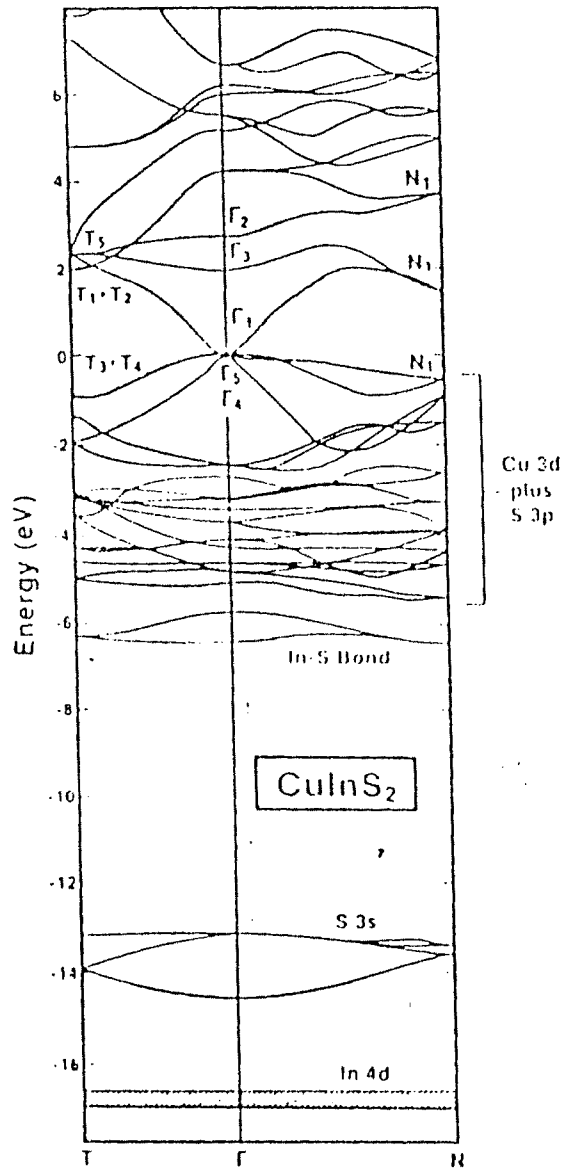


Fig. 1.2

REFERENCES

1. S. P. Albright, J. F. Jordon, B. Ackerman and R. C. Chamberlain; *Solar Cells* **27**,77 (1989).
2. K. W. Mitchell, C. Eberspacher, J. Ermer, K.Pauls, D. Pier and D. Tanner; *Solar Cells* **27**,69 (1989).
3. W. E. Devaney, W. S. Chen, J. M. Stewart and R. Mickelson; *IEEE Trans. Elec. Devices* **37**, 428 (1990).
4. H. J. Lewerenz, H. Goslowsky, K. D. Husemann and S. Fiechter; *Nature* **321**, 687 (1986).
5. J. M. Meese, J. C. Manthuruthil and D. R. Locker; *Bull. Amer. Phys. Soc.* **20**,696 (1975).
6. B. Tell, J. L. Shay and K. W. Kasper; *J.Appl. Phys.* **43**, 2469 (1972).
7. S. D. Mittleman and R. Singh; *Solid State Commun.* **22**,659 (1977).
8. S. Mora, N. Romeo and L. Tarricone; *Solid State Commun.* **29**,155 (1979).
9. J. L. Shay and J. H. Wernick; *Ternary Chalcopyrite Semiconductors :Growth, Electronic Properties and Applications* [New York : Pergamon] (1975).
10. H. Neumann, W.Horig, V.Savelev, L.Lagzdonis, B. Schumann and G. Kuhn; *Thin Solid Films* **79**,167 (1981).

11. (i) C. Paorici, L. Zanotti and G. Zuccalli; *J. Cryst. Growth* **43**, 705 (1978).
(ii) C. Paorici, L. Zanotti and M. Curti; *Cryst. Res & Technol.* **17**, 917 (1982).
12. Takeshi Miyauchi, Nobuyuki Yamamoto and Hideaki Higuchi; *Jpn. J. Appl. Phys.* **27**, L1178 (1988).
13. F. A. Thiel; *J. Electrochem. Soc.* **129**, 1570 (1982).
14. H. L. Hwang, Y. L. Yen, K. J. Hsu, D. C. Liu and C. Y. Sun; *Nuovo Cimento* **2D**, 1762 (1983).
15. H. J. Hsu, C. Y. Sun and H. L. Hwang; *Electron Lett.* **20**, 376 (1984).
16. A. U. Malsagov; *Neorg Mater*; **25**, 25 (1989).
17. S. Kobayashi, S. Ota and N. Saito; *Jpn. J. Appl. Phys.* **20**, 1973(1981).
18. J. G. Fleming, M. L. Fearheiley and H. L. Lewerenz; *J. Electrochem. Soc.* **136**, 1506 (1989).
19. N. Yamamoto, K. Yokota and H. Horinaka; *J. Cryst. Growth* **99**, 747 (1990).
20. M. L. Fearheiley, M. Kanis and S. Fiechter; *J. Electrochem. Soc.* **140**, 1396 (1993).
21. J. J. M. Binsma, W.J.P. Van Enckevort and G. W. M. Staornik; *J. Cryst. Growth* **61**, 138 (1983).
22. V. A. Prokhorov, E. N. Kholina, A. V. Klymkiv and V. A. Voronim; *Inorg. Mater* **15**, 1512 (1979).

23. I. A. Aksenov, N. A. Sobolev and V. A. Sherauklov; *Phys. Status Solidi (a)* **123**, L171 (1991).
24. K. Balakrishnan, B. Vengatesan, N. Kanniah and P. Ramaswamy; *Cryst. Res. Technol.* **25**, 633 (1990).
25. S. Wagner, J. L. Shay, P. Migliorata and H. M. Kasper; *Appl. Phys. Lett.* **25**, 434 (1974).
26. L. L. Kazmerski and Y. J. Juang; *J. Vac. Sci. Technol.* **14**, 769 (1977).
27. R. A. Mickelsen and W. S. Chen; *Fifteenth IEEE Photovoltaic Specialists Conf.*, p 800 (1981).
28. N. Yamamoto; *Proc. Fourth International Conf. on Ternary and Multinary Compounds*, Ref.11, p 45.
29. B. R. Pamplin, T. Kiyosawa and K. Masumoto; *Prog. Cryst. Growth Character.* **1**, 331 (1979).
30. H. Hahn, G. Frank, W. Klinger, Ad. Meyer and G. Storger; *Z. anorg. Chem.* **271**, 153 (1953).
31. N. A. Goryunova; *The Chemistry of Diamond-like Semiconductors*, Ed. J.C.Anderson [MIT Press, Cambridge, Mass] p.142 (1965).
32. H. M. Kasper; *NBS Special Publication No.364, Solid State Chemistry, Proceedings of the 5th Materials Research Symposium*, p.671 (1972).
33. S. C. Abrahams and J. L. Bernstein; *J.Chem.Phys.* **59**, 5415 (1973).

34. G. Brandt, A. Rauber and J. Schreider; Solid State Commun. **12**, 481 (1972).
35. A. S. Poplavnoi and Yu. J. Polygalov; Neorg. Mater. **7**, 1706 (1971).
36. A. S. Poplavnoi, Yu. J. Polygalov and A. M. Ratner; Sov. Phys. J. **19**, 689 (1976).
37. K. L. Cohen and T. K. Bergstresser; Phys. Rev. **141**, 799 (1965).
38. W. A. Harrison; Phys. Rev. **131**, 2433 (1963).
39. P. Bendt and A. Zunger; Phys. Rev. **B26**, 3114 (1982).
40. W. Kohn and L. J. Sham; Phys. Rev. **B 140**, A1130 (1965).
41. J. E. Jaffe and Alex Zunger; Phys. Rev. **B 28**, 5822 (1983).
42. D. M. Ceperley and B. J. Alder; Phys. Rev. Lett. **45**, 566 (1980).
43. F.A.Kroger; Chemistry of Imperfect Crystals [North-Holland Publ.Co., Amsterdam] p.826 (1973).
44. D. C. Look and J. C. Manthurithil; J.Phys.Chem.Solids **37**, 173 (1976).
45. A. W. Verheijen, L. J. Giling and J. Bloem; Mater. Res. Bull. **14**, 237(1979).
46. G. Masse, N. Lohlou and C. Butti; J.Phys. Chem. Solids **42**, 449 (1981).

47. H. L. Hwang, M. H. Yang, C. S. Sen and L. M. Liu; Sixteenth IEEE Photovoltaic Specialists Conf. [San Diego,USA] p.867 (1982).
48. M. S. Jagadeesh and M. S. Seehra, Solid State Commun. **34**, 257 (1980).
49. V. Sagredo, A. Aristimuno and A. Lopez Rivera; Nuovo Cimento **2D**, 1900 (1983).
50. T. L. Makarova, G. A. Medvedkin and Yu. V. Rud; Zh. Tekh. Fiz **58**, 1612 (1988).
51. N. V. Joshi; Jpn. J.Appl.Phys. **20**, L 733 (1981). 52. Katsuaki Sato, Mikio Isawa and Nobumitsu Takahashi; Jpn. J.Appl. Phys. **27**, 1359 (1988).
53. Takahiro Wada, Takayuki Negami and Mikihiko Nishitani; Appl. Phys. Lett. **62**, 1943 (1993).
54. G. Aren and O. P. Agnihotri; J. Mater. Sci. Lett. **12**, 1176 (1993).
55. A. M. A. ElSoud, H. A. Zayed and L. I. Soliman; Thin Solid Films **229**, 232 (1993).
56. J. J. M. Binsma, L. J. Giling and J. Bloem; J.Cryst. Growth **50**, 429 (1980).
57. H. Neuman, G. Kuehn and W. Moeller; Phys.Status Solidi B **144**, 565 (1987).
58. I. V. Bodnar, and N. S. Orlova; Phys. Stat. Solidi A. **78**, K59 (1983).

59. G. Kuehn, H. Neuman and E. Nowak; J. Therm. Anal. 33, 197 (1987).
60. P. Deus, V. Frei, O. Bilek and W. Cordts; Phys. Status Solidi B 112, 269 (1982).
61. M. Brussler, H. Metzner, K. D. Huseman and H. J. Lewerenz; Hyperfine Interact. 60, 805 (1990).
62. J. Herrero and J. Ortega; Solar Energy Mater. 20, 53 (1990).
63. V. A. Zyl'Kov, A. E. Kazachenko, S. G. Kotov, D. V. Kovalav and A. A. Stavrov; Sov. J. Quantum Electron 22, 579 (1992).
64. H. Tributsch; J. Appl. Phys. 65, 252 (1989).