Bull. Mater. Sci., Vol. 29, No. 5, October 2006, pp. 529–534. © Indian Academy of Sciences.

Structural, optical and electrical properties of chemically deposited nonstoichiometric copper indium diselenide films

R H BARI, L A PATIL* and P P PATIL†

P.G. Department of Physics, Pratap College, Amalner 425 401, India
†Department of Physical Sciences, North Maharashtra University, Jalgaon 425 001, India

MS received 5 June 2006; revised 31 July 2006

Abstract. Thin films of copper indium diselenide (CIS) were prepared by chemical bath deposition technique onto glass substrate at temperature, 60°C. The studies on composition, morphology, optical absorption, electrical conductivity and structure of the films were carried out and discussed. Characterization included X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), energy dispersive X-ray analysis (EDAX) and absorption spectroscopy. The results are discussed and interpreted.

Keywords. Copper indium diselenide; thin films; chemical bath deposition; non-stoichiometry.

1. Introduction

In recent years, I–III–VI_2 ternary semiconductor compounds ($CuInX_2$, X = S, Se, Te) have received considerable attention because of their possible application in optoelectronic devices. One of these compounds, $CuInSe_2$, with its optical absorption coefficient exceeding 3×10^4 cm^{-1} at wavelengths below 1000 nm, and its direct band gap being between 0·95 and 1·04 eV (Hamakawa and Okamoto 1988), is an excellent solar absorber (Bloss *et al* 1988). Thin film polycrystalline CIS solar cells with a conversion efficiency exceeding 14% have already been achieved (Mitchell *et al* 1988). High absorption coefficient and low cost methods for deposition of thin films make $CuInSe_2$ a promising material for photovoltaic devices. Thin film $CuIn(S, Se)_2$ cells with efficiency of 18·8% have been recorded (Nakada and Mizutani 2002). Various techniques have been employed to prepare $CuInSe_2$ thin films including flash evaporation (Elliot *et al* 1974; Pachori *et al* 1986), single source evaporation (Kazmerski *et al* 1976; Neumann and Nowak 1980), multiple source evaporation (Kazmerski 1979; Nealkanth *et al* 1984), molecular beam epitaxy (Grindle *et al* 1980; Mickelsen and Chen 1980), spray pyrolysis (Agnihotri *et al* 1983; Shirakata *et al* 1996), and electrodeposition (Guillemoles *et al* 1994; Al-Bassam 1999).

It is reported (Bhattacharya 1983; Padam 1987; Garg *et al* 1988; Murali 1988) that the copper indium diselenide films have been prepared by chemical bath deposition technique. Though difficult, they have successfully prepared the $CuInSe_2$ thin films using chemical bath deposition technique. Various characterization techniques such as XRD, optical spectroscopy, scanning electron microscopy, atomic force microscopy etc were employed to study the films.

2. Experimental

The chemical bath deposition technique was used to deposit thin films of copper indium diselenide on glass substrate. The sources used for Cu and In as starting materials were cupric chloride ($CuCl_2 \cdot 2H_2O$, make-sd.fine) and indium trichloride ($InCl_3$, make-Lancaster). All the chemicals used were of AR grade. To obtain films of different compositions of Cu, In and Se, the solutions of different molarity were used. Sodium hydroxide and ammonia solution were used to adjust pH of the reaction mixture and to increase the film adherence. To obtain good quality films time, temperature of deposition and pH of the solution were optimized. The optimum time, temperature and pH were observed to be 2 h, 60°C and 10, respectively.

The process involved the reaction of Cu^+ and In^{3+} ions with Se^{2-} ions in deionized water solution. Elemental selenium (99·95%) was dissolved in aqueous solution of sodium sulphite (pH > 9) at 90°C to form a Na_2SeSO_3 solution. A solution containing complex ions of indium and citrate was added to tetraamine copper. Na_2SeSO_3 solution was then added to the solution bath. In the solution, partially unstable Na_2SeSO_3 yielded Se^{2-} and SO_3^{2-} ions. Sulphite ions reduced tetraamine copper and generated Cu^+ ions.

The structural properties of thin films were investigated by X-ray diffraction (XRD) using CuKα (λ = 1·5418 Å)

*Author for correspondence (lapresearch@rediffmail.com)

Table 1. Elemental composition of CIS films.

Sample no.	Cu (wt%)	In (wt%)	Se (wt%)	Cu (at%)	In (at%)	Se (at%)	Cu (at%)/In (at%)
1	43·15	25·41	31·44	52·29	17·04	30·67	3·07
2	42·37	15·78	41·84	49·98	10·30	39·72	4·85
3	47·63	14·44	37·94	55·29	9·27	35·44	5·96
4	56·86	12·11	31·03	64·22	7·57	28·21	8·48

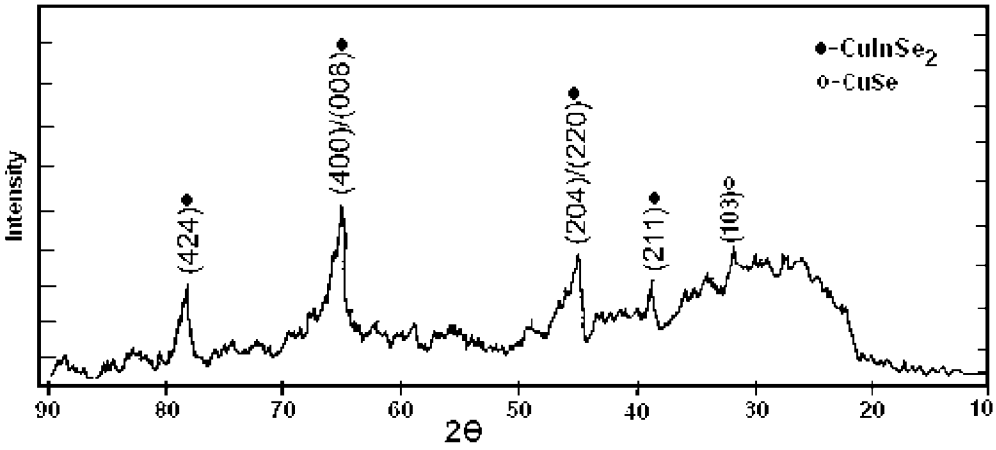

Figure 1. XRD of the sample.

radiation. The optical absorption studies of the films were carried out using Hitachi U-2000 spectrophotometer. The elemental analysis of the films was carried out using an energy dispersive spectrometer (EDS) JEOL, JED-2300, and scanning electron microscopic (SEM) studies were carried out using JEOL 6300 (LA). An AFM nanoscope (model-NSE, Serial no-245) digital instrument with a silicon nitride cantilever was used to probe different portions of the film surface in 'contact mode AFM'.

3. Results and discussion

3.1 *Elemental analysis by EDS*

Table 1 shows the elemental composition of the films determined by EDS.

Theoretically expected stoichiometric composition of CIS in terms of at % is: Cu = 25%, In = 25%, Se = 50%.

It is clear from table 1 that the films are nonstoichiometric in nature.

3.2 *Structural analysis*

Figure 1 shows the diffractogram of sample 4 film scanned in the 2θ range of 10–90°. The XRD peaks approximately matched with standard ASTM data (card no. 23–209) indicating the non-stoichiometric CIS. Additional peak of CuSe is observed. This phase may be present due to higher Cu/In ratio.

3.3 *SEM images representing microstructures*

Figure 2 consists of SEM images representing surface morphology of the as synthesized copper indium diselenide films with different Cu/In ratios. The average grain sizes obtained from the SEM images are tabulated in table 2.

The grains are cubic (except in sample 4) in nature. It is clear from SEM images that the number of grains goes on increasing with the increase in Cu/In ratio. Also, with the increase in at % of Cu there is a decrease in average grain size. It could be attributed to small atomic radii of Cu ions as compared to indium. Smaller the atomic radii, larger would be the nucleation centres and smaller would be the grains. The amount of feed material available in the reaction vessel is constant for a particular reaction. If same material would be divided on the larger nucleation centres, the grain would not grow larger but remain smaller (Sinnott 1958; Patil *et al* 1998; Patil and Wani 2001). This is clearly evidenced from the SEM images.

Figure 3 shows the variation of grain size with Cu/In ratio. Grain size is found to decrease with the amount of copper in $CuInSe_2$.

3.4 *Surface morphology*

A typical copper indium diselenide film was morphologically characterized using atomic force microscopy (AFM). Figure 4 represents AFM pictures of the film (sample 4) having Cu/In ratio, 8·48, which reveals the granular parti-

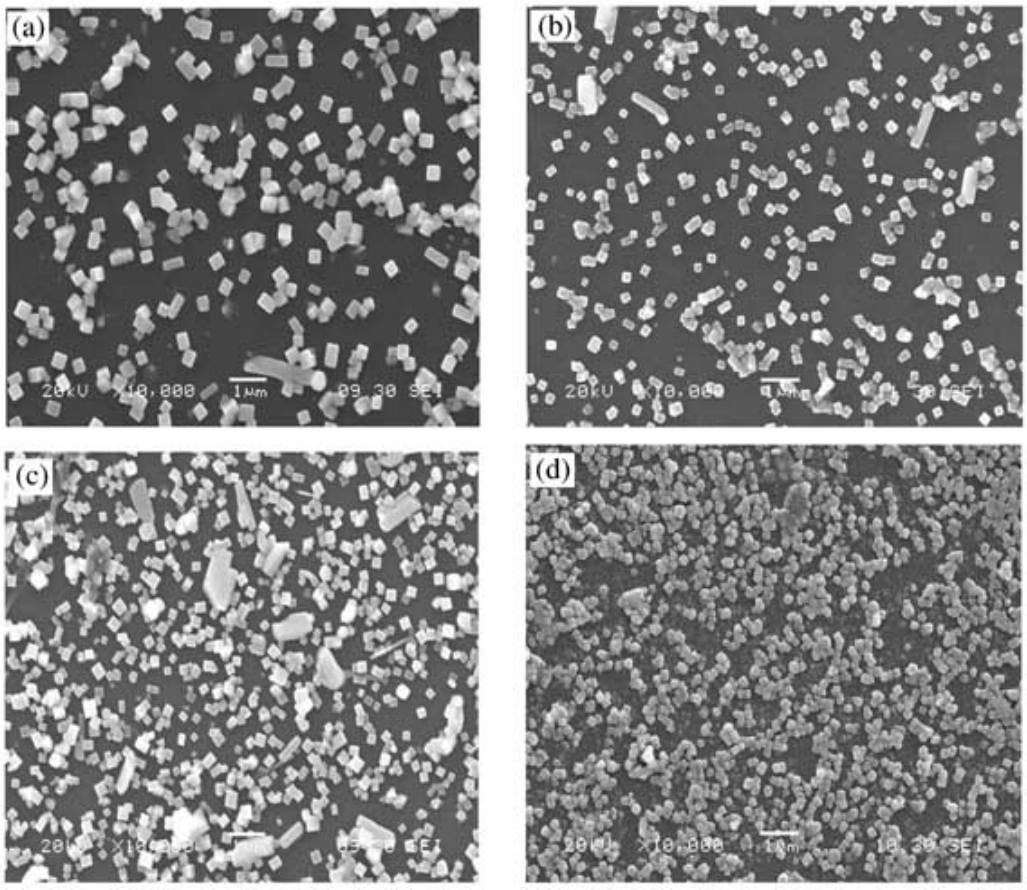

Figure 2. (**a**)–(**d**) SEM images of samples.

Table 2. Dependence of grain size on Cu/In ratio.

Sample no.	Figure 2	Cu (at.%)/In (at.%)	Grain size (nm)	Nature of particles	Shape of grains
1	a	3·07	354	Relatively small number of grains (as compared to sample 2)	Cubic
2	b	4·85	240	Relatively small number of grains (as compared to sample 3)	Cubic
3	c	5·96	204	Relatively small number of grains (as compared to sample 4)	Cubic
4	d	8·48	180	Large number of grains	Spherical

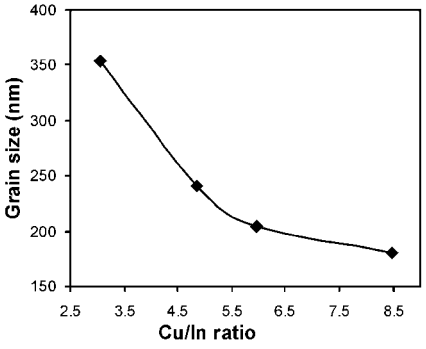

Figure 3. Variation of grain size with Cu (at.%)/In (at.%) ratio.

cles having spherical or elliptical nature. The spherical or elliptical grains could be attributed to faster growth due to higher concentration of copper in the composition. There was agglomeration of particles in most of the cases as evident from the 2D micrographs. The root mean square values of the surface roughness of the film (Rg_{AFM}) from a number of scans from different areas of the film are calculated. It was observed that the surface roughness of the film was 10·91 nm/1 μm*1 μm. The average grain size was observed to be 180 nm. This observation reveals the films to be microcrystalline in nature. The average grain sizes observed from SEM and AFM images are approximately equal.

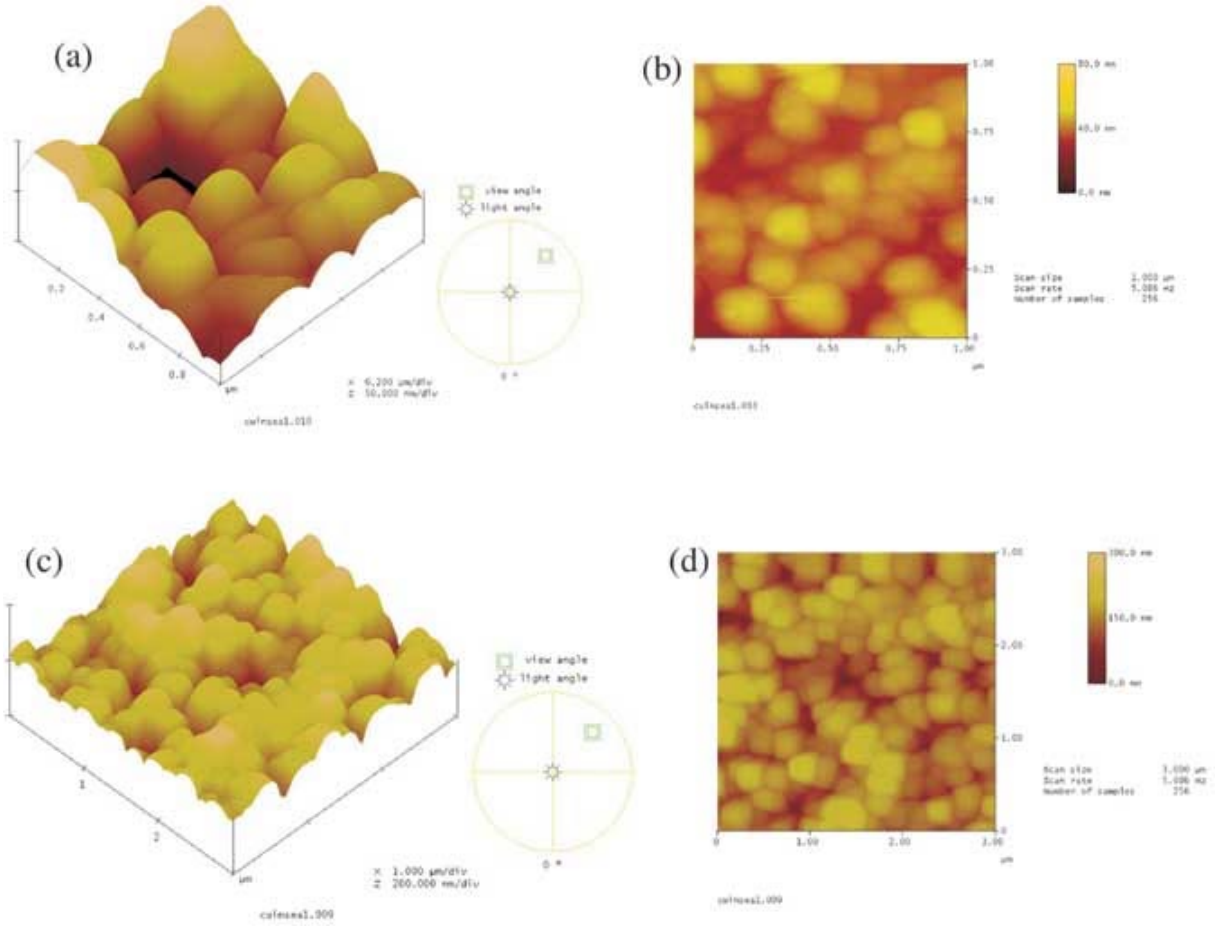

Figure 4. (**a**)–(**d**) AFM pictures of the sample.

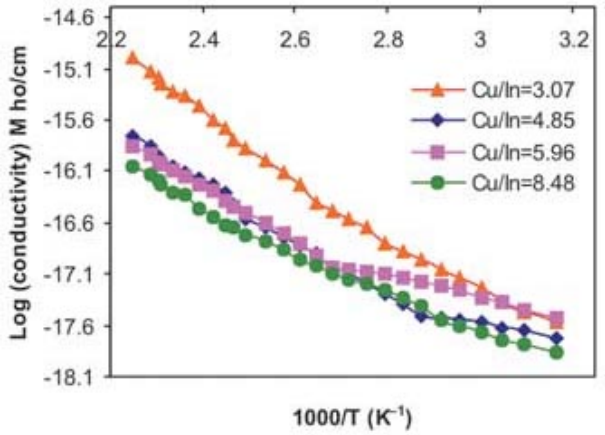

Figure 5. Variation of electrical conductivity with temperature.

3.5 *Electrical conductivity and activation energy*

Electrical conductivity of $CuInSe_2$ thin films were measured by using d.c. two-probe method in the temperature range 313–423°K. Figure 5 shows the temperature dependence of d.c. electrical conductivity for various compositions of $CuInSe_2$. The activation energies were calculated by using the slopes of the graph and are given in table 3. It is observed that activation energy goes on decreasing with the increase in Cu/In ratio. Lower activation energy in case of the sample having higher atomic percent of copper, could be attributed to high reactivity of copper ions with available anions. Due to high reactivity, larger at.% of copper ions would be incorporated in the compositions, which lead to higher conductivity, and in turn, lower activation energy.

3.6 *Optical absorption studies*

Optical absorption studies of $CuInSe_2$ films were carried out in the wavelength (λ) range 800–1500 nm at room temperature. The variation of absorbance with wavelength (λ) is shown in figure 6(a). The band gap energies of the samples were calculated from the absorption edges of the spectra. The slope drawn from the start of an absorption

Table 3. Dependence of band gap energies and activation energy on Cu/In.

Sample no.	Cu/In (at.%)	Grain size (nm)	Activation energy (eV)	Band energy (eV)
1	3·07	354	0·62	0·92
2	4·85	240	0·55	1·08
3	5·96	204	0·53	1·20
4	8·48	180	0·44	1·30

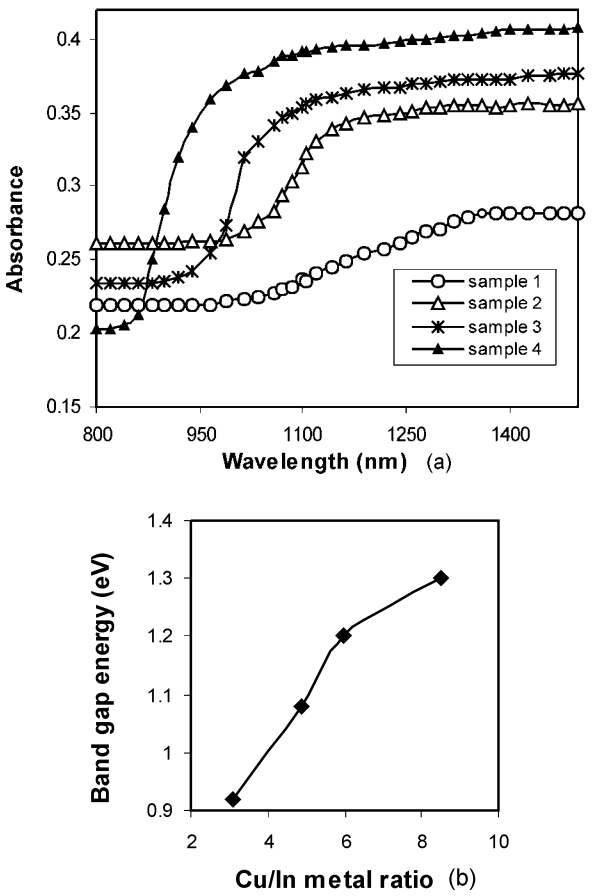

Figure 6. (**a**) Plot of optical absorbance vs wavelength (λ) and (**b**) the variations of energy gap vs Cu/In metal ratio.

edge (the onset of absorbance) and horizontal tangent had drawn on absorption minimum and intercepted each other at some point. The vertical line drawn from this point on wavelength axis gave the absorption edge wavelength. This value of λ(nm) was then used in the following relation to know band gap energy, *Eg*.

$$Eg = hv = hc/\lambda = 1240/\lambda \text{ (nm) eV}.$$

The values of band gap energies are matching approximately with the reported band gap energy [1·04] of $CuInSe_2$ (Wanger and Holah 1977; Horig *et al* 1978; Fray and Lloyd 1979).

Figure 6(b) shows the variation of optical band gap energy with Cu/In metal ratio. It is clear from the graphs that the values of band gap energy go on increasing with the increase in Cu/In ratio.

Table 3 summarizes the effect of at.% of Cu (in CIS) on grain size, activation energy and band gap energy.

4. Conclusions

Copper indium diselenide films were deposited onto glass substrate by simple chemical bath deposition technique. The films obtained were uniform and had good adherence to the substrate. The EDAX of the film indicated that the films were nonstoichiometric. The values of band gap energy and numbers of grains were observed to be increasing, activation energy and grain sizes were decreasing with the increase of Cu/In ratio.

Acknowledgements

The authors are thankful to the Head, Department of Physics and Principal, Pratap College, Amalner, for providing laboratory facilities. The authors are thankful to Dr Ajay Gupta, Centre Director, IUC, Indore, for giving consent for completing a part of this work at the consortium. One of the authors (RHB) acknowledges the University Grants Commission, Western Region, Pune, for the award of a teacher fellowship under the 10th plan.

References

Agnihotri O P, Rajaram P, Thangaraj R, Sharma A K and Raturi A 1983 *Thin Solid Films* **102** 291
Al-Bassam A A I 1999 *Physica* **B266** 192
ASTM card number 23-209
Bhattacharya R N 1983 *J. Electrochem. Soc.* **130** 2040
Bloss W H, Pfisterer F and Schock H W 1988 *Adv. Solar Ener.* **5** 1
Elliot E, Tomlinson R D, Parkes J and Hampshire M J 1974 *Thin Solid Films* **20** S25
Fray A F and Lloyd P 1979 *Thin Solid Films* **58** 29
Garg J C, Sharma R P and Sharma K C 1988 *Thin Solid Films* **164** 269
Grindle S P, Clark A H, Falconer E, Neily M and Kazmerski L L 1980 *J. Appl. Phys.* **51** 5664

Guillemoles J F, Cowache P, Massaccesi S, Thouin L, Sanchez Lincot D and Vedel J 1994 *Adv. Mater.* **6** 379
Hamakawa Y and Okamoto H 1988 *Adv. Solar Ener.* **5** 201
Horig W, Neumann H, Scbotta H, Schumann B and Kuhn G 1978 *Thin Solid Films* **48** 67
Kazmerski L L 1979 *Thin Solid Films* **58** 29
Kazmerski L L, Ayyagari M S, Sanborn G A, White F R and Merril A J 1976 *Thin Solid Films* **37** 323
Mickelsen R A and Chen W S 1980 *Appl. Phys. Lett.* **36** 5
Mitchell K, Eberspacher C, Ermer J and Pier D 1988 *Proc. 20th IEEE PV spec. conf., Las Vegas, New York,* p. 1384
Murali K R 1988 *Thin Solid Films* **167** L19
Nakada T and Mizutani M 2002 *Jpn J. Appl. Phys.* **41** L165
Nealkanth G, Dhere M, Lourence C, Ramesh G, Dhere G and Kazmerski L L 1984 *Solar Cells* **13** 59
Neumann H and Nowak E 1980 *Thin Solid Films* **74** 197
Pachori R D, Banerjee A and Chopra K L 1986 *Bull. Mater. Sci.* **8** 291
Padam G K 1987 *Mater. Res. Bull.* **22** 789
Patil L A and Wani P A 2001 *Cryst. Res. Technol.* **36** 371
Patil L A, Wani P A, Saraf K B and Wagh M S 1998 *Cryst. Res. Technol.* **33** 233
Shirakata S, Tomonori M, Kariya Tetsuya and Shigehiro I 1996 *J. Appl. Phys.* **35** 1991
Sinnott M J 1958 *The solid states for engineers* (New York: John Wiley and Sons) pp 97–103
Wanger S and Holah G D (eds) 1977 *Ternary Compounds, Inst. Phys. Conf. Ser.* **35** 207