PREPARATION, STRUCTURE, DIFFUSION AND OPTO-ELECTRONIC STUDIES OF CRISTALLINE CuinSe, FOR SOLAR CELL APPLICATION

by

A. Vahid Shahidi, B.Eng., (McGill Univ.)

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Master of Engineering.

> Department of Electrical Engineering, NcGill University, Montreal, P. Q., Canada. August, 1984

ABSTRACT

Studies have been made on growth characteristics of chalcopyrite CuInSe₂ semiconductor using horizontal and/or vertical Bridgman and Stockbarger methods. The growth procedure and the essential steps required to optimize the growth conditions and to overcome the growth difficulties were established. A comparison of the results obtained using the improved conditions revealed that large monocrystals of CuInSe₂ with better quality could be obtained using the vertical Stockbarger method.

The results of structure analysis (cell dimensions, lattice type and symmetry) for CuInSe₂ based on single crystal x-ray methods , for the first time, were obtained in the present study. Such data were also obtained for CuInTe₂. Powder diffraction pattern of CuInSe₂ has been computed from the single crystal data and was found to be in good agreement with the experimental diffraction results. Compositional uniformity of the ingots was also examined by electron microprobe analysis.

All as-grown samples were p-type as determined by Hall effect measurements, with a typical effective carrier concentration of $10^{17}/\text{cm}^3$ and Hall mobility upto 68 cm²/Vsec at room temperature. The electrical properties of the monocrystalline CuInSe₂ samples after annealing in vacuum and after extrinsic doping by Bi and Te diffusion were investigated. Studies were also made on samples

i

treated in Se atmosphere. It was found that p-type samples were readily converted into n-type under minimum. Se vapor pressure with a carrier concentration of about 1016/cm3 and maximum room temperature Hall mobility of about 1050 cm²/Vsec. The Hall mobility values for both p- and n-type samples obtained in the present work are larger than those reported in the literature. Photoconductivity measurements 77°K for the first time were made at on p-type monocrystalline CuInSe, samples. variation The ∵o£ photoconductivity with wavelength and intensity was also investigated. It was found that the photoconductivity magnitude increased after deep surface etching treatments which appeared to lower the surface recombination velocity.

ii

Å

Des travaux ont été faits sur les caractéristiques de la croissance du semi-conducteur chalcopyrite CuInSe₁, utilisant les méthodes de Bridgman et Stocbarger horizontales et/ou verticales. Les conditions de croissance et les étapes essentielles pour surmonter les problèmes de croissance ont été établies. Une comparaison avec les résultats obtenus , utilisant les conditions optimales, a révélé que de gros mono-crystaux de CuInSe₂ de qualité supérieure pouvaient être obtenus utilisant la méthode de Stockbarger verticale.

読んという い

•

Les résultats de l'analyse structurale(dimension des 'cellules, type de lattice symmétrie et intensités) du CuInSe₂, basés sur les méthodes à rayons X pour des mono-crystaux ont été obtenus pour la première fois par ce travail. De tels résultats ont été aussi produits pour le CuInTe₂.Les patrons de diffraction de poudre de CuInSe₂ ont été calculès se basant sur des données mono-crystallines et ont été comparés avec succés aux résultats expérimentaux de diffractions. L'analyse de l'uniformité de la composition a été effectuée avec une micro-probe électronique.

Tous les échantillons obtenus étaient de type p, tel que déterminé par des mesures d'effet Hall avec concentration effective de porteurs de $10^{17}/cm^3$ et une mobilité Hall de 68 $cm^2v^{-1}sec^{-1}$ à la température du laboratoire. Les propriétés électriques des échantillous

iii

mono-crystallins de CuInSei, après recuit sous vide et aprés dopage extrinsèque par diffusion de Bioute, ont été étudiés.

En plus des travaux ont été effectvés sur des échantillons traités sous atmosphère de Se. Il a été démontré que les échantillons de type p étaient convertis en type n avec une pression de vapeur minimale de Se et une concentration de porteurs d'approximativement 1014/cm³ avec une mobilité Hall à température du laboratoire de 1050 cm²v⁻¹sec⁻¹ Les vateurs de mobilités Hall obtenues pour des échantillons type p ou n, se sont avérées supérieures à ce qui est rapporté dans la littérature. Des mesures de photoconductivité ont été faites à 77° K pour la première fois sur des mono-crystaux de CuInSe, type-p. La variation des paramètres de photoconductivité, à différentes longueurs d'ond et intensités, a été obtenue. Il a été trouvé que l'amplitude de la photoconductivité etait augmentée par l'érosion en profondeur de la surface, ce qui. semblait diminuer la vitesse de recombinasion de surface.

Dedicated to:

「「「

and the state of the

C

()

 $\left(\begin{array}{c} c \\ c \end{array} \right)$

my wife, for her continuous moral support and understanding.

¥

ACKNOWLEDGEMENTS

The author wishes to express his sincere gratitude to Dr. I. Shih for his guidance and assistance throughout this study. Thanks also extended to Dr. C. H. Champness for his helpful advice.

Special thanks are due to Dr. N. V. Quang for helpful discussion , to Dr. T. Araki of the Department of Geological Sciences for assistance on single crystal x-ray measurements, and to Mr. M. Bélonger for translating the abstract into French.

Acknowledgements are also due to the Natural Sciences and Engineering Research Council of Canada for the financial support.

Words can hardly express my sincere appreciation to my mother for her love, encouragement, patience and support throughout my life.

TABLE OF CONTENTS

0

¢ in

1

(!

Ń

		Page
ABSTRACT		i
RESUME		iii
ACKNOWLEDGEME	NTS	v i
TABLE OF CONT	ents	vii
CHAPTER 1	INTRODUCTION	1
CHAPTER 2	HISTORICAL SURVEY	
2.1	Introduction	ູ 5

2.1	Introduction	5
2.2	Crystal Growth	5
2.3	Crystal Structure	7
2.4	Opto-electronic Properties	8
2.5	Summary	9

CHAPTER 3	PREPARATION	AND GROWTH OF	CRYSTALLINE
	Cuinse, AND	Cuinte.	

3.1	Introduction	14
3.2	Phase Diagram and Phase Transition	14
3.3	Melt Growth Systems	16
3.4	Methods of Crystal Growth	17
3.5	Growth Procedure	19
3.5.1	Ampoule preparation	19
3.5.2	Crystal growth	20
3.6	Growth Rate Optimization	22

1

)

CHAPTER	4	EXPERIMENTAL RESULTS OF CRYSTAL GROWTH	
	4.1	Introduction	30
	4.2	Growth Results	30
	4.2.1	Initial growth results	31
•	4.2.2	Improved growth results	33
	4.3	Discussion and Conclusions	36
		· ·	
CHAPTER	5	X-RAY ANALYSIS AND CRYSTAL DATA	
	5.1	Introduction	47
	5.2	Laue Back Reflection Patterns .	47
-	5.3	Single Crystal Crystallography Methods	49
	5.3.1	Buerger precession method	50
	5.3.2	Weisenberg method	54
	5.4	Space Group Determination	55
	5.5	Determination of Unit Cell Parameters	57
	5.6	Crystal Orientation	58
J	5.7	Powder Diffraction	59
•	5.7.1	Sample preparation	60
	5.7.2	X-ray diffraction system	60
	5.7.3	Experimental and calculated results	61
ن <i>ک</i> و	5.8	Conclusions	63
		. •	4
CHAPTER	6	ELECTRICAL AND OPTICAL PROPERTIES	
	6.1	Introduction	83

6.3 🎽 Bulk Hall Measurements

.....

Ohmic Contact

6.2

84 /

84

Ł

	6.4	Annealing Effect of Monocrystalline		
		Samples in Deficient Se	86	
	6.5	Extrinsic Doping Effect of		
		Monocrystalline Samples in Excess Se,		
		Bi and Te	87	
	6.6	Photoconductivity	89	
	6.6.1	Theory	89	
	6.6.2	Experimental method and results	91	
	6.7	Conclusions	94	
CHAPTER	7	DISCUSSION AND CONCLUSIONS		
	7.1	Crystal Growth	107	
	7.2	Crustal Structure Analysis	1.08	

7.2	Crystal Structure Analysis	108
7.3	Opto-electronic Properties	109
REFERENCES		112

ix

.

٦

.

Ň

1

C

17

「「「「「「「」」」」」

1 * *

CHAPTER 1

INTRODUCTION

Ternary chalcopyrite semiconductor compounds of the type A $^{\rm I}$ B $^{\rm III}$ C₂ $^{\rm VI}$ have been shown to be suited for a variety of opto-electronic applications ranging from light detecting and emitting devices to tunable radiation and solar cells. Because of these potential applications, the materials have attracted many researchers. During the last decade, a series of international conferences on the ternary compounds has been held.

Among the ternary compounds studied, the semiconductor CuInSe₂ has received a considerable attention because of its exceptional opto-electronic properties [1.1-1.5]. The energy gap of this material is about 1 eV at room temperature, with direct band gap type [1.6, 1.7]. The band gap value of 1 eV is close to the optimum value required for photovoltaic applications [1.8, 1.9]. This material also has extremely high optical absorption coefficients (of about $4x10^5$ cmg¹ [1.10, 1.11]) for photons with energy above-the band gap. Therefore CuInSe, is an excellent absorber for solar cell applications. In 1975 a monocrystalline cell in the form CuInSe₂ (p)/CdS (n) with an energy conversion efficiency of 12% has been fabricated by Shay et al [1.12]. The lattice mismatch between CuInSe, and CdS (or Cd(zn)S) was found to be small, minimizing interfacial states [1.13]. Recently, CuInSe, thin film

solar cells with an efficiency greater than 10% have been reported [1.14, 1.15] using a three source evaporation technique. These thin film cells have been demonstrated to have a good lifetime stability. Because of these characteristics, CuInSe₂ has been considered to be one of the most promising candidates for terrestral solar cell application.

€.

There are many research experiments required to be done determine and to' control in order to the opto-electronic properties of CuInSe, for high efficiency solar cell or device applications. For these experiments, large and good quality monocrystalline samples are needed. Since the previous work on CuInSe, crystal growth has not been very extensive, therefore a crystal growth program was initiated in the present work using the Bridgman and the Stockbarger methods. The main objectives of the growth experiments were to investigate the growth properties of CuInSe, and to prepare large void- and crack-free crystals for opto-electronic property measurements and for device fabrication.

Since the work on crystal structure and parameter determinations of CuInSe₂ reported in the literatue has been very limited, therefore x-ray diffraction experiments were also performed in the present work. These were done on both single crystal and powdered samples obtained from the grown ingots. Crystal structure and lattice parameters of crystalline CuInSe₂ and CuInTe₂ were determined from the

x-ray experiments.

Information on the effect of doping and annealing (which has not been well known for CuInSe₂) is very important for CuInSe, in device application. Accordingly, annealing and diffusion experiments were performed on monocrystalline CuInSe, samples. These were done specifically to determine the effect of annealing under maximum and minimum selenium vapor pressure. Extrinsic doping experiments were also carried out in an environment containing tellurium or bismuth vapor. Room temperature electrical properties of the treated samples were then determined and compared with those obtained from the as-grown samples.

17

Monesta create the strate

The measurements of photoconductivity on monocrystalline p-type CuInSe₂ samples were made for the first time at liquid nitrogen temperature for wavelengths in the optically sensitive region. An investigation was also made to evaluate the influence of surface treatment and light intensity. The photoconductivity results obtained confirmed the energy gap value of CuInSe₂ reported in the literature.

The structure of the thesis is as follows. A brief historical survey is first given in chapter 2. Chapter 3 then describes the apparatus and the growth procedures while the crystal growth results are given in chapter 4. In chapter 5, results on the structure analysis and the x-ray diffraction data from both single crystal and powdered

samples are presented and discussed. Room temperature electrical properties and the annealing / diffusion effects on the samples are presented in chapter 6, followed by the photoconductivity results at 77° K. Finally, conclusions about the results obtained in the present work are summarized in chapter 7.

()

CHAPTER 2

HISTORICAL SURVEY

2.1 Introduction

The state of the Ander at the states at

ſ

()

In this chapter a brief historical survey of work done on CuInSe₂ semiconducting compound is presented. Previous work on crystalline ingot preparation and crystal structure determination is first described. Work on the opto-electronic properties of CuInSe₂ is then briefly reviewed. The total number of papers published in the last three decades on this compound material is finally given.

2.2 Crystal Growth

Although many papers on the compound CuInSe, have been published in the last decades, however, it appears that work on crystal growth to prepare CuInSe, has not been very extensive. Ternary compounds of the A I B III C2 VI type (λ =Cu, λq ; B = $\lambda 1$, Ga, In; C =S, Se, Te) have first been synthesized by Hahn et at [2.1] in 1953. Later in 1956, Austin et al [2.2] reported growth results of CuInSe, using a directional solidification and zone melting method with quartz ampoules. The grown ingots were polycrystalline and contained cracks. Several other ternary compounds were also reported in the same paper. In 1966, Lerner [2.3] reported growth experiments of CuGaSe₁ and AgInSe, employing the zone leveling technique using carbon-coated ampoules. Compounds of CuAlSe, and CuAlS, were grown by

Honeyman [2.4] in 1969 employing chemical vapor deposition using iodine as the transport element. Kasper [2.5] prepared CuInS₂, CuGaS₂ and AgGaS₂ compounds by using the directional solidification with SiO₂ boats. A p more extensive growth study was reported in 1973 by Parkes et al [2.6] who prepared crystalline CuInSe₂ samples also by the zone leveling technique. The as-grown samples were found to be n-type and were converted to p-type by annealing in an environment containing Se vapor. Recently, Haupt and Hess [2.7], Davis et al [2.8], Tomlinson [2.9] and Haworth et al [2.10] have also contributed on these ternary compounds including CuInSe₂ and various techniques have been used to prepare CuInSe₂ thin films [2.11-2.16].

Palatnik et al [2.17] determined the pseudo binary phase diagram of the compounds with reference to the binary compounds λ_2 = C VI and B₂ III C₃ VI and discussed in detail the solid state phase transformation of the materials. It has been shown that there is a range of solid solubility close to stoichiometric composition for this type of structure.

In the present work, a series of crystal growth experiments was made to investigate the growth properties of CuInSe₂ using two growth methods in two growth systems [2.18]. These experiments were made in order to obtain the optimum growth processes to provide monocrystalline samples for electrical, optical, structure analysis and device fabrication experiments.

2.3 Crystal Structure

The ternary compound CuInSe, was among the twenty compounds studied by Hahn et al [2.1] in 1953 using x-ray powder diffraction technique. Crystal data of CuInSe, semiconductor was briefly reported and was found to have a chalcopyrite structure with an international space group notation of $1\overline{4}2d$. The conventional unit cell of the chalcopyrite A I B III C2 VI compounds can be regarded as a zinc-blende type one doubled in height. A prototype form of the chalcopyrite compounds was considered to be the mineral copper iron disulphur. As shown in Fig. 2.1, each A- and B- atom is tetrahedrally coordinated to four C- atoms, while each C- atom is tetrahedrally coordinated to two Aand two B- atoms in an order manner. Powder x-ray data of CuInSe₂ was also reported by Parkes et al [2.19]. Values of the cell constants (a and c) of the compound were determined from the powder x-ray data. Kazmerski et al [2.20] also reported the calculated and the experimental powder diffraction results of thin film samples.

It appears that the above-described papers are the only reported work in the literature [2.21, 2.22] on CuInSe₂ crystal structure determination. Therefore, CuInSe₂ samples in monocrystalline form were studied in the present work using Buerger precession and Weissenberg methods (to be described in chapter 5). This independent experiment was done to confirm the space group and to obtain more precise lattice parameter values for the

crystalline semiconductor CuInSe₂ (and CuInTe₃). Results on growth plane and solidification direction determination will be given [2.23]. Diffraction results obtained from different lattice planes of monocrystalline samples used for structure analysis will be presented. Powder diffraction patterns were also obtained for samples prepared from monocrystalline ingots and compared with the calculated ones obtained in the present work.

2.4 Opto-electronic Properties

Electrical and optical properties of the ternary compounds of the form A I B III C, VI have been reported [2.24-2.27]. In 1972, Tell et al [2.28] reported the room temperature electrical properties of ten A I B III C, VI type (A =Cu, Ag; B =Al, Ga, In; C =S, Se) compounds, and it has been found that all of these compounds, including CuInSe, , have direct band gaps. They also reported that both p- and n-type CuInSe, can be made under a condition with maximum and minimum Se vapor pressure. In 1973, Parkes et al [2.6, 2.29] also reported the conductivity type change under similar conditions. More detailed electrical measurements were reported by Neumann et al in 1978 [2.30] and Irie et al in 1979 [2.31]. From the temperature dependence measurements, they reported the possible scattering mechanisms.

Photoconductivity of CuInSe₂ was first reported by Shuze et al [2.32] using polycrystalline samples. The

photoconductive maximum was found to locate at a wavelength of about 1.3 μ m. Photoconductivity experiments were also made by Abdinov and Mamedov [2.33] on n-type CuInSe₂ samples at temperatures below 260 °K.

Because the reported work in the literature on the electrical properties of CuInSe₂, especially the effect of annealing and doping, has not been very extensive, therefore more studies on CuInSe₂ semiconductor are required [2.34].

Homodiodes of these ternary compounds have been fabricated employing different methods. The diodes were fabricated by diffusion of $\mathcal{L}u$ [2.36], Cd [2.37] and In [2.6] into p-CuInSe₁. Such diodes were also prepared by implantation of Zn, Cl and Br [2.38]. Recently, In-diffused CuInSe₂ homojunctions were also investigated as a function of electrical and photovoltaic properties [2.39].

2.5 Summary

(__)

As a summary, results of the literature search on CuInSe₂ obtained using a computer data-base and from a previous compilation reported by Draper and Miller [2.35] are presented. Fig. 2.2 shows the total number of papers published on CuInSe₂ each year based on the above-mentioned two sources. It is seen that there is a considerable increase from early 1970's. A similar tendency is also shown in Fig. 2.3 which shows the total number of papers published each year on crystal growth, electrical, optical

and luminescent properties as well as solar cells.

Ø)

(

(_)

()





11

C)



C

8

£







()

CHAPTER 3

PREPARATION AND GROWTH OF CRYSTALLINE CUINSe, AND CUINTE,

3.1 Introduction

Large good quality crystalline CuInSe,/CuInTe, ingots are required for reliable measurements of the electrical and optical properties of these materials. Large samples are also needed for substrates in fabrication of devices such as solar cells or detectors. In order to prepare these samples, different crystal growth methods were employed in the present work. In this chapter, information on crystal growth procedure and growth system are briefly described. Phase diagram of the CuInSe, and CuInTe, systems are first given in section 3.2. In section 3.3, two crystal growth systems used in the experiments are described, one for vertical growth and the other for horizontal growth. These systems have been prepared and used in growth experiments for comparison of the results. Crystal growth methods are then briefly described in section 3.4. The growth procedure is finally given in section 3.5.

3.2 Phase Diagram and Phase Transition

The phase relations in the systems $Cu_2C-In_2C_3$ (C=Se, Te) were first investigated and established by Palatnik and Rogacheva [2.17] in 1967 from various methods for

physicochemical analysis, such as thermographic, X-ray diffraction, microstructure and microhardness methods. Later in 1973, Parkes et al. [2.6] reported and confirmed the essential features of the CuInSe₂ phase diagram. The pseudo binary phase diagram of CuInSe₂ and CuInTe₂ with reference to the binary compounds Cu₂C and In₂C, are shown in Fig. 3.1. The melting point is about 986°C [2.17, 3.1] for CuInSe₂ and is 785°C [2.17, 3.1] for CuInTe₂. There are two solid state phase transition temperatures, as shown in Table 3.1, T prite and T ordring , for each compound material. Because of these, the cooling rate after the crystal growth must be slow to allow for an appropriate phase transformation.

Table 3.1 Phase Transition Temperature measured by Differential Thermal Analysis.

Compound	T (m.p.) (°C)	T (prite) T (°C)	(ordring (°C)) Ref.
CuInSe	986		810	[2.17]
	987	665	810	[3.1]
CuInTe	789	- ```	672	[2.17]
	785+2	349*	665+2	[3.1]

* Non-stoichiometric

These pseudo binary phase diagrams show that $CuInC_2$ (C=Se, Te) compounds are associated with a range of solid solubility close to 50 mole % of In_2C_3 . The homogeneity

region is near to the solidus line and with about 2.5 mole of excess In₂Se₃ and 3.5 mole of excess In₂Te₃ for CuInSe₂ and CuInTe₂ compounds respectively [2.17].

3.3 Melt Growth Systems

Two experimental melt growth systems were designed and constructed in the present work. One system was constructed for horizontal growth and the other for vertical growth. Fig. 3.2(a) shows a block diagram of the horizontal growth system which consists of a resistively-heated furnace (Thermco Mini-Brute model MB 71 with water cooling) with a three-action temperature controller, an ampoule driving unit and a temperature control unit. The driving unit is used to drive the ampoule in or out of the furnace at a rate between 0.2 and 3.4 cm/hr and the temperature control unit is used to increase/decrease the furnace temperature at a rate between 1 and 80 °C /hr. For the initial loading of the ampoule, a high speed gear has been added to the drive unit for an efficient operation.

A block diagram of the growth system designed and constructed for the vertical growth is shown in Fig. 3.2(b). This system consists of a transformer, an S.C.R. power unit (LZF2 model, Halmer Electronics, Inc), a digital temperature controller (Leeds and Northrup Ltd., Electromax V Microprocessor model 6001), a remote temperature control unit, a resistively-heated furnace and

a drive unit. The remote temperature control unit provides a stable increase/decrease rate of the temperature setting of the furnace. The performance requirement for this unit is a linear and continuous variation of temperature with respect to time. The driving unit consists of three different dc geared motors to provide three different speed ranges. The combined speed range is from 0.05 to 2 cm/hr. いんちょうちょう ちょうちょうちょう

the ampoule traveling Apart from speed, the temperature gradient is one of the most important parameters for crystal growth. The actual' temperature in the furnaces has been measured for the two systems. The measurements were done using a type K thermocouple (Thermo Electric Ltd.). Fig. 3.3 shows the measured temperature, T, plotted against the distance x (measured from the front end of the furnace, see Fig. 3.5). It is seen from this figure that the temperature gradient of the vertical furnace is greater than that for the horizontal one.

3.4 Nethods of Crystal Growth

In order to minimize thermal decomposition and oxidation at an elevated temperature, it is required to grow CuInSe₂ or CuInTe₂ ingots in a closed tube system. In the present work, both the Bridgman and the Stockbarger methods were used. These two methods were employed in both the horizontal and the vertical systems. For the Bridgman growth, where the ampoule was moving out of the furnace

during the process, the temperature distribution of the furnace was kept unchanged. For the directional freezing growth, the ampoule was kept stationary while the furnace temperature was lowered gradually during the growth. These two methods were found to be useful for the present compound material preparation.

In crystal growth experiments from a melt, it is important to maintain a stable solid-liquid interface. The stable interface can be obtained by a large furnace temperature gradient. If the gradient near the solid-liquid interface is less than the liquidus temperature gradient then there is a super-cooled liquid zone near the interface (arising from a less than unity solute distribution coefficient, see Fig. 3.6). Random nucleation of the material will take place at this unstable interface to result in a polycrystalline ingot. This effect has been studied by Tiller et al. [3.2] and the required condition for a stable interface (i.e. without supercooling) is,

 $\frac{\mathbf{V}_{\mathbf{G}}}{\mathbf{G}_{\mathbf{L}}} < \frac{\mathbf{D}_{\mathbf{1}}}{\mathbf{m}(\mathbf{C}_{\mathbf{s}} - \mathbf{C}_{\mathbf{1}})}$

where V_{G} is the growth rate, G_{L} is the temperature gradient in the liquid at the interface, D_{1} is the solute diffusion coefficient in the liquid, m is the slope of liquidus in the phase diagram, C_{0} and C_{1} are the solute concentration in the solid and the liquid respectively. From this relation, it is required to have either a slow growth rate or a large temperature gradient. In the

present experiments, the maximum temperature gradient achievable in the system is about 40 °C/cm. This gradient value was considered to be large enough for crystal growth at a rate of about 1 cm/hr.

3.5 Growth Procedure

3.5.1 Ampoule preparation

Quartz tubes (one end sealed) with an I.D. of 1.0 cm and an O.D. of 1.3 cm were used to prepare ampoules for the crystal growth experiments. The inner surface of the tubes was first ground using alumina powder solution (diameter 40 ga) by a guartz grinding rod (diameter 6 ma). The grinding rod was attached to an ac motor and rotated at 173 rpm. The ground tube was washed using D.I. water and cleaned in a ultrasonic cleaning bath (D.I. water) for few minutes. After these, the tube was immersed in a cleanser solution for degreasing and then rinsed thoroughly with D.I. water. The tube was then immersed in a saturated solution of KOH in alcohol for 24 hours to remove organic impurities and followed by a mixture of HCl and HNO, (3:1 by volume) for 24 hours to remove inorganic impurities. After the chemical cleaning the tube was washed thoroughly with D.I. water and then evacuated using a diffusion pump unit. The evacuated tube was then inserted into a furnace at a temperature of

about 800 °C. This baking treatment was carried out for a period of at least 5 hours. After the baking, the tube was withdrawn from the furnace and slowly cooled down. Fig. 3.7 shows a photograph of a quartz ampoule under evacuation during the baking process.

High purity Cu, In, Se and Te (nominal purity 69's, 69's, 59's and 69's respectively) were weighed to a stoichiometric ratio for both $CuInSe_2/CuInTe_2$ to an accuracy of ± 1 mg using a balance. The total weight for each growth run was 12 grams. The weighed high purity materials were introduced into the cleaned ampoule which was then evacuated using the diffusion pump unit to a pressure of less than 10^{-5} torr. After the tube had been evacuated, it was sealed off using an oxygen-acetylene torch to obtain an ampoule with a length of about 12 cm. One end of the ampoule was finally joined to a quartz pull tube with a diameter of 6 mm. Fig. 3.4 shows the arrangement of the ampoule-pull tube assembly in the growth systems.

3.5.2 Crystal growth

Initial reaction of the raw materials was done as follows. The furnace temperature was set to a value between 400-480 °C and the ampoule was brought manually to a position about 6 cm into the furnace. The driving motor was then turned on and the rotation speed was adjusted so that

the ampoule was traveling at a speed of about 1-2 cm/hr into the furnace. A period of about 6-8 hours was required for this initial slow heating for the ampoule temperature to reach about 400-480 °C. This slow heating was very important and was necessary to minimize the excess ampoule heating due to reaction between the constituent elements. The excess heat released during the reaction could lead to a drastic increase in vapor pressure inside the ampoule and Such drastical reaction was result in an explosion. observed in the initial stages of the present experiments. After the initial reaction had completed, the ampoule was brought manually to the central region of furnace and the furnace temperature was further increased at a higher rate between 60-80 °C/hr to a value of about 1100 °C (above the melting point of CuInSe;). The ampoule was then rotated by an ac motor at a rate of 10 rpm for about 2-4 hours for a proper mixing of the starting materials. After the mixing, the rotating ac motor was turned off and the orientation of the ampoule was adjusted so that the tip of the ampoule was pointing downward. The ampoule with the melt in it was kept stationary for 12-24 hours to allow for stabilization. After the stabilization, crystal growth was started either by reducing the furnace temperature with ampoule kept stationary (Stockbarger method), or by withdrawing slowly the ampoule from the central region of the furnace while the temperature profile maintained unchanged (Bridgman For the Stockbarger growth, the temperature method).

decreasing rate was from 4 to 6 °C/hr. The rate Vas increased to 10 °C/hr once the ampoule temperature had been reduced to below the low phase transformation temperature. For the Bridgman growth, the ampoule pulling rate was in a range from 0.1 to 1.0, cm/hr. The furnace temperature was then decreased at a rate of about 10 °C/hr after the ampoule temperature had reached a value below the low phase transformation temperature. For both growth methods, it was arranged so that crystallization started from the tip of In order to obtain ingots with good the ampoule. crystalline quality, all the ampoules used for the growth were specially prepared so that they had a conical-shape tip. The conical tip was found to be useful in obtaining ingots with large monocrystalline grains.

Fig. 3.8 shows photographs of an ampoule containing the starting materials before the growth and two ampoules . containing ingots after the growth runs.

3.6 Growth Rate Optimization

In the initial stages of the present work, most of the growth runs were made using the horizontal Bridgman method. Main difficulties in these stages were the occurrence of surface or bulk voids in the grown ingots and the oxidation of ingot materials resulting from a cracked ampoule. These difficulties were overcome by a number of steps taken during the experiments. The steps included the ampoule

cleaning /preparation procedure described in section 3.5.1 and an additional flame polishing of the ampoules. The ampoule flame polishing was done using the oxygen-acetylene torch before introducing the starting materials. The surface and bulk voids were also observed in the ingots grown using the Stockbarger method in the initial stages of present growth program.

Different growth rates were tried in order to obtain good quality ingots with large grains. The quality and grain size of the grown ingots were examined by visual inspection and by Laue X-ray diffraction. From these results, it was established that the optimum growth rate was about 0.2 cm/hr for both the Bridgman method the Stockbarger methods. It would appear that a growth rate less than the above mentioned value could be beneficial in obtaining good quality ingots. However, these were limited by the stability of the pulling system and the temperature system used in the present experiments.



()

 $O^{(i)}$





(3

 \bigcirc

Ci

٤.

(a)



(b)

Fig. 3.2 Block diagram of (a) the horizontal growth system and (b) the vertical growth system.

المع المراجع . المحافظ المراجع . المحافظ المحافظ المحافظ المحافظ المحافظ .



()

Ċÿ

Ö

Fig. 3.3 Measured temperature profile for both vertical and horizontal furnaces.

J





المريد بي مدين من ا


(

К.

Fig. 3.5 Photograph of (a) the horizontal and (b) the vertical growth systems.



(

(

(

Fig. 3.6 Equilibrium liquidus temperature profile and the super-cooled region in the liquid near the solide-liquid interface.



Fig. 3.7 A photograph showing an ampoule being baked under vacuum.



ないない ない ちょう う

É.

2 Cm

2

Fig. 3.8 Photographs of ampoules containing (a) starting materials, (b) an as-grown CuInSe, ingot and (c) an as-grown CuInTe, ingot.

١.,

(a)

(Ъ)

(c)

, **u**

.

<u>,</u>*

CHAPTER 4

EXPERIMENTAL RESULTS OF CRYSTAL GROWTH

法で「法式に知る」、

4.1 Introduction

As discussed in the last chapter, two methods of crystal growth, the Bridgman and Stockbarger methods were employed using both the vertical and horizontal growth systems. Growth experiments using each system were first started by employing the Bridgman technique. In later stages, the Sockbarger method was added in order to obtain results for comparison. Results from these experiments made it possible to select a better method for large good quality monocrystalline samples. In section 4.2, the crystal growth results of CuInSe, and CuInTe, based on the two methods are presented.

4.2 Growth Results

In this section, crystal growth results of CuInSe₂ using the horizontal and vertical growth systems will be described. Some results on CuInTe₂ using the same system also will be presented. Since the study of ingot growth of CuInSe₁ and CuInTe₂ reported in the literature has not been very extensive, there were several experimental difficulties remained to be solved. The difficulties for the ternary compound growth are :

(a) Homogeneity,

(b) Voids,

- (c) Twins and cracks,
- (d) Oxidation and
- (e) Adhesion of the compound material to the ampoule.

In the present work, a series of investigations has been made to eliminate or to reduce the above difficulties. As a result of these investigations, an improved crystal growth procedure has been established. This procedure was found to be satisfactory in producing good quality monocrystalline samples for X-ray studies, electrical measurements and for device fabrication. Initial growth results are first described in section 4.2.1. In section 4.2.2, the improved results are then given. Conclusions for the growth are finally presented in section 4.3.

4.2.1 Initial growth results

Preliminary growth experiments were carried out using the Bridgman growth technique with a fixed furnace temperature setting. The initial ingots obtained showed several types of defect. The most serious ones were the formation of voids and cracks in the grown ingots and oxidation during the growth. Fig. 4.1 illustrates a crack developed in a guartz ampoule during the growth, leading to

the ingot oxidation. Fig. 4.2 is a photograph showing surface and bulk voids in ingots obtained from initial experiments. The grown ingots with these defects were not useful in reliable electrical measurements and in device fabrication. The above mentioned defects were also found in ingots grown in the initial experiments by the horizontal Stockbarger method. Fig. 4.3 shows two CuInSe, wafers, one cut perpendicular and the other parallel to the growth direction from an ingot grown in the early stages of the work. Both bulk and surface voids are clearly visible in the sample cut perpendicular to the growth direction. The other is an oxidized sample, where it can be seen there are green spots on the sample surface. Photographs of normal samples were also obtained as shown in Fig. 4.6 a and b for comparison.

The sample oxidation was due to a cracked ampoule resulting either from an excess vapor pressure inside the ampoule in the initial heating process or from the thermal expansion coefficient difference (between the ingot and the quartz ampoule) during the ingot cooling process. The ampoule breakage phenomenon, which has been observed in the initial stages of the experiments, was eliminated by adopting the heating procedure described in section 3.5.2. This was done by increasing very slowly the ampoule temperature up to a value above the melting point of selenium/tellerium thus allowing a slow reaction between indium and selenium/telerium to take place during the

heating process. Another cause for the cracked ampoule, as mentioned before, was the thermal expansion coefficient difference between the ingot and the ampoule material. This effect was improved by roughening the inner surface of the ampoule before the growth. The ampoule breakage problem was found to be eliminated for the Stockbarger growth.

Mixing of the starting materials for the horizontal growth was achieved by rotating the ampoule using an ac motor directly connected to one end, of the quartz pull tube. The ampoule was attached to the other end of the pull tube in such a way that the angle between the ampoule axis and the pull tube axis was about 20°. The arrangement enabled the melt to flow back and forth inside the ampoule by the rotational action and ensured a proper mixing of the materials. For the vertical growth system, this mixing action relied only on convection of the melt and inter-diffusion of the materials. The mixing for the vertical growth required longer time and was regarded to be less effective compared to the rotational mixing for the horizontal growth system.

4.2.2 Improved growth results

The initial growth results described in section 4.2.1 were not satisfactory in providing samples for both electrical and optical mesurements. In order to produce large, void- and crack-free monocrystalline samples for the measurements and device fabrication, the improved

preparation conditions described in section 3.6 were used. This procedure was found to be suitable for producing good quality ingots containing grains which were large enough for the measurements and device applications.

As mentioned before, the main difficulties for the growth were the formation of voids and cracks, and the oxidation problems. It was observed in the present work that these difficulties could be eliminated or improved by adopting the improved procedure. Among the various processes in the procedure the ampoule preparation and cleaning process (including the flame polishing and prebaking under vacuum), the ampoule inner surface grinding process and the growth rate control were found to be the most important ones in producing good quality ingots. The chemical cleaning, flame polishing and vacuum prebaking processes were observed to be effective in reducing the void formation problem. The ampoule grinding process adopted appeared to be appropriate in reducing the adhesion between the ingot and ampoule, thus avoiding both ampoule breakage problem (which resulted in the unwanted ingot cracks in the grown ingots. Further oxidation) and improvement in the growth results was achieved by using quartz ampoules with a wall thichness of 1.5 mm (original thichness was 1.0 mm) which essentially completely eliminated the ampoule breakage problem.

It was found from the present work, the lower the growth rate, the better the quality of the grown ingots.

3

1

However, the growth rate limit for the growth systems was found to be about 0.2 cm/hr. Therefore, the improved growth results were obtained for the growth rate range between 0.2 and 0.3 cm/hr. A photograph of one of the grown ingots using the Bridgman method is shown in Fig. 4.4. A typical dimension for single crystal samples cut along the ingot grown by the Stockbarger method was 2x5x15 mm³. These were large enough for the electrical and optical measurements as as device fabrication. Figs. 4.5(a) and (b) vell show respectively several CuInSe, and CuInTe, samples obtained using Stockbarger method. Also, some CuInSe, samples about 2 mm thick cut with a diamond disk from the ingots obtained using the vertical and horizontal Stockbarger methods are shown in Fig. 4.6 (a) and (b) respectively.

(1

Compositional uniformity was also examined by electron microprobe. Quantitative electron microprobe analysis was made on the grown CuInSe, ingots both on the grains and the grain boundaries, (Table 4.1). The composition analysis was also made both along and across the as-grown ingots. The results obtained are shown in Figs. 4.7(a) and (b) respectively. From the phase diagram of CuInSe2, In-rich material is predicted in chalcopyrite solid form. As given in Table 4.1 , Figs 4.7(a) and (b), compositional results show an In/Cu ratio of greater than one. This fact suggests that In has a larger segregation coefficient than copper. These results are similar to the one reported for zone grown CuGaSe, [4.1].

4.3 Discussion and Conclusions

Crystal growth of a compound involving several elements usually is more difficult than that for the elemental growth. In the present study for CuInSe₂ and CuInTe₂, several difficulties such as the initial reaction between elements, the ampoule breakage and oxidation problem have been encountered. These difficulties have been overcome in the present work by adopting the improved growth procedure developed for these materials. Crack- and void-free ingots containing large size monocrystalline grains were successfully prepared. These samples were used in the electrical measurements and X-ray studies and device fabrication (see Fig. 4.8).

From the supercooling criteria described in section 3.4, it is expected that the higher the temperature gradient at the solid-liquid interface the better the growth results wi11 be. Therefore, in the present experiments, it was attempted to apply the highest temperature gradient possible for both horizontal and vertical growth systems. The temperature gradient was 25 and 37 °C/cm for the horizontal and the vertical system respectively. Beside the large temperature gradient values, the growth rate was maintained to be about 0.2 cm/hr. This value was obtained from the ampoule pulling rate (with a fixed temperature profile) or the furnace temperature decressing rate (with the ampoule stationary) for the Bridgman method or the Stockbarger method.

The ampoule wall thichness of 1.5 mm was found experimentally to be sufficient to overcome the ampoule breakage problem. A smaller thickness of 1.0 mm, however, was found to be not sufficient to stand the vapor pressure in the ampoule. Rotational mixing of the melt appeared to be efficient in obtaining homogeneous materials. The 24 hours inter-diffusion process at a temperature above the melting point further ensured the homogeneity of the compound. This inter-diffusion process was believed to be important and necessary in obtaining good quality semiconductor compouds.

Special attentation was given to the effect of growth rate on the quality of the ingots. It has been found that the quality of the ingots grown by the Stockbarger method was better than that by the Bridgman method. The effect was considered to be due to the excess ampoule vibration resulting from the instability of the pulling system.

The occurrence of micro-cracks in the grown ingots in the initial stages of the experiments was found to be due to the adhesion of the compound material to the inner surface of the ampoule. Exessive strain could be induced in ingots during the cooling process which resulted in micro-cracks. The ingot quality was further improved by using the ground ampoule.

The formation of voids also appeared to be due to an incomplete mixing of the constituent elements in the melt. The incomplete mixing led to bubble nucleation. The

37 .

undesired voids finally formed in the grown ingots. Strel'chenko et al. [4.2, 4.3] have studied the CuInSe₂ and CuInTe₂ systems and reported the existence of considerable vapor pressure for $InSe_2(InTe_2)$ and $Se_2(Te_2)$ in these compounds. The ingots grown using the improved procedure did not show any voids. It was therefore believed that the combination of the rotational mixing, inter-diffusion and the growth rate used was adequate to avoid these voids.

In summary, the conditions for good quality CuInSe₂ and CuInTe₂ ingot growth using the Stockbarger method are given below :

- (a) Application of the cylindrical guartz ampoule with a conical tip,
- (b) Grinding the inner surface of the ampoule,
- (c) Appropriate cleaning of the ampoule,
- (d) Mixing and inter-diffusion of the melt at a high temperature, and
- (e) Cooling very slowly to a temperature below the solid phase transition points.

The average dimension of the monocrystalline grains grown by the Stockbarger method was larger than that by the Bridgman method. These grains were found to be large enough to prepare samples for the electrical and optical measurements, and for device fabrication. Monocrystalline

samples with a typical size of 2x5x15 mm³ were readily obtained from the ingots grown in the present experiments.

(__;

١

Sample No.	Cu	In	Se	Location	
	(at. %)				
	<u></u>				
83-VP10-ES/1	24.84	25.30	49.87	Grain	
83-VP16-ES/1	22.74	24.87	52.38	Grain	
84-HF65-ES/1	23.81	25.16	51.04	Grain	
84-HF65-ES/2	23.39	25.32	51.28	Grain	
84-HF72-ES/1	22.65	26.38	50.88	Grain	
83-VP10-ES/2	29.16	20.70	5 0.14	Grain	Boundary
83-VP16-ES/2	22.11	25.32	52.57	Grain	Boundary
84-HF65-ES/2	25.83	25.02	49.15	Grain	Boundary
84-HF72-ES/2	22.06	26.38	51.56	Grain	Boundary

(

Table 4.1 Quantitative electron microprobe results for different CuInSe₂ growth runs.

· 0

÷



Fig. 4.1 A photograph showing a cracked quartz ampoule



Fig. 4.2 A photograph showing surface and bulk voids in the initial grown results.

 \mathbf{C}



Fig. 4.3 A photograph showing a circular sample (cut perpendicular to the growth direction) with voids and sample a (cut parallel to growth direction) with both voids and oxidation.

1

いい しょうちょうかい いいろう



Fig. 4.4 A photograph showing a complete as-grown ingot in the ampoule.



ť

1

ه و سور ر

,



; , ,

,

ì

このであるとのないになっていたいできたのであるとうであるとう いっているとう

(a)





Fig. 4.5 Photographs of void- and crack-free samples of (a) CuInSe, and (b) CuInTe, (obtained using Stockbarger method).

COLOURED PICTURES Images en couleur - ----

•

(

.



(a)



 (b)
 Fig. 4.6 Photographs showing unpolished CuInSe₂ slices obtained using (a) vertical and
 (b) horizontal Stockbarger methods.

COLOURED PICTURES Images en couleur

(

гÇ.

(

44

×.

1

•

مكندان ج

•



٢

Ţ

(

Luinder States





Fig. 4.8 A photograph of CuInSe; single crystal samples used for carrier transport studies.

COLOURED PICTURES Images en couleur

(

(

Ţ

CHAPTER 5

X-RAY AMALYSIS AMD CRYSTAL DATA

5.1 Introducton

a study on crystal structure of In compound semiconductor using powder x-ray method, Hahn et al. [2.1] reported in 1953 that the ternary compound CuInSe, crystalized in a chalcopyrite form. Later in 1973, Parkes et al. [2.19] presented data on crystalline CuInSe, based diffraction results using on x-ray powder the Debye-Scherrer technique. They also reported unit cell parameters obtained from an approximation method involving the Nelson and Riley's extrapolation function [5.1]. However, the unit cell parameters and structure analysis for CuInSe₂ based on single crystal data have not been reported in the literature. Accordingly, in the present work, x-ray experiments were performed on monocrystalline CuInSe, samples using Laue back reflection method, Buerger precession method and Weissenberg method. The results were determine the cell parameters and crystal used to structure. The cell parameters were then used to compute the theoretical powder pattern and finally compared with the experimental powder diffraction results obtained from powder CuInSe, samples.

5.2 Laue Back Reflection Patterns

One of the most convenient methods to examine the

quality of a grown ingot is the Laue back reflection technique. Patterns obtained from this technique also can be used for crystal orientation determination. Fig. 5.1 shows a schematic diagram of the experimental arrangement. The x-ray beam (Cu or Ag radiation) from a source is collimated and directed onto a CuInSe₂ sample mounted in a sample holder. Diameter of the beam is about 1 mm. The reflected beams are detected by a Polaroid film inserted in the film casette. The sample under the test is stationary, therefore the orientation of each lattice plane is fixed with respect to the x-ray beam and the reflection beam from lattice plane in accordance with the Bragg condition is given by, 「「「「「「「「「」」」」」

$$n\lambda = 2d_{hkl} \sin \theta \qquad (5.1)$$

where the reflection angle θ is fixed for each set of planes so that the plane spacing d_{kk1} is determined for a given hkl and the only variables are n and k. Here n is an integer and k is the x-ray wavelength. Both Cu and Ag white radiation were used in the present experiments.

In the initial stage of the present experiments, most of the grown ingots were polycrystalline with many grains. Diameters of these grains were usually small and the Laue reflection patterns were not single. Fig. 5.2 shows a Laue back reflection photograph taken from one of the early ingots, indicating the fine grain polycrystalline nature.

(1

Using this method, samples prepared under different conditions were examined until a procedure for large grain growth was established (described in chapter 4).

Fig. 5.3 shows a Laue back reflection photograph obtained from an ingot prepared using the improved procedure. In order to determine the grain size, large grains were selected from the grown ingots and mounted in the sample holder. A multiple-exposure experiment was then performed on the selected samples. This was done by first taking a Laue reflection pattern from one spot and the sample was then moved along the plane perpendicular to the x-ray beam to a new position. A second pattern was then taken on the same photographic film. Monocrystallinity of determined examining the sample Vas by the multiple-exposure patterns. Fig. 5.4 shows the results obtained from a monocrystalline sample before and after moving the sample.

The Laue back reflection method is a convenient way in obtaining the crystallinity information. However, in the present work, attempts have not been made to determine lattice parameters and sample orientation using this technique. These were done using more sophisticated x-ray methods involving single crystal and powder samples to be described in the following sections.

.5.3 Single Crystal Crystallography Methods

Two commonly used x-ray methods for single crystal

2

structural and lattice parameters determination are the Buerger precession method [5.2] and the Weisenberg method [5.3]. These methods provide complementary information of lattice type, lattice parameters and structural symmetry for a single crystal sample. The data for CuInSe,, taken using the single crystal techniques, have not been reported before in the literature. In this section, a brief description of the two methods is first given. Results obtained from several monocrystalline CuInSe₂ samples prepared in the present work are then described. Lattice structural results are and the parameters finally presented.

5.3.1 Buerger precession method

The Buerger precession method is a moving crystalmoving film technique which can record an undistorted reciprocal lattice level onto a photographic film. Fig. 5.5 shows a schematic diagram of the precession camera used in the present work. The crystal is oriented on the device with a desired reciprocal plane normal to the incident x-ray beam. The motion of the crystal is arranged so that it oscillates simultaneously about mutually two perpendicular zone axes, and the direction of the x-ray being is normal to the vertical axis. When these two oscillations, which are symmetrical with respect to the x-ray beam, are combined, having the same magnitude but 90 out of phase, then the crystal axis sweeps out a cone which

50

Ì

is coaxial with the beam and makes a constant angle $\overline{\mu}$ to the x-ray beam throughout its motion. The rotations of the film holder and reciprocal level are synchronized by a linkage connecting L to L' and U to U' for vertical and horizontal oscillations and the crystal-to-film distance remains unchanged. Insertion of the layer line screen between crystal and film allows the reflections from only one reciprocal plane to reach the film. By a proper setting of the layer line screen, it is possible to have the diffracted beams from the different reciprocal lattice levels.

To prepare for a photograph, various settings are required for the Buerger precession camera. These are the inclination of crystal translation to x-ray beam, $\overline{\mu}$, the radius of the reciprocal level screen, r $_{\pm}$, the screen-to-crystal distance, s, the crystal-to-film distance, F, and the upper level height, d*. These are consistent with international notation and are related by the expression

 $\mathbf{s} = \mathbf{r}_{\pm} \operatorname{cotcos}^{-1}(\cos \overline{\mu} - d^{\pm}) \tag{5.2}$

for the case of zero-level photography where d* is equal to zero, equation (5.2) becomes,

s = r , cotā

(5.3)

There are tables available from "International Tables for x-ray crystallography" which gives the trigonometric part of equation (5.2) and the screen settings for zero-level photographs as given by equation (5.3). Another useful equation which relates d^* to $\overline{\mu}$ and $\overline{\nu}$, the half-apex angle of the first level reflection cone is given by,

 $d^* = \cos \vec{\mu} - \cos \vec{\nu} \qquad (5.4)$ where, $\tan \vec{\nu} = r_* / s$

therefore equation (5.4) becomes,

 $d^{\pm} = \cos \bar{\mu} - \cot ^{-1}r$. /s

From equation (5.2) all the setting values can be determined from a nomogram given in ref.[5.4].

A Zr-filtered MoKg radiation source ($\lambda = 0.71069$ Å) operated at 40 KV and 12 mA was used. The required exposure time varied from several to 30 hours.

Sample preparation

Since the x-ray absorption coefficient for Se is high, therefore a small sample diameter of 0.2 mm was adopted to minimize the absorption effect. Four monocrystalline samples were first selected from four different as-grown ingots. The crystal specimen was glued to a fine glass fiber and then attached to a goniometer head, having two perpendicular sets of arcs for rotating and two perpendicular slides for lateral motion of the crystal. Adjustments of the arcs and slides enabled one to set a desired reciprocal plane perpendicular to the incident x-ray beam with the principal axis parallel to the horizontal rotation axis of the precession camera.

Results

Several preliminary diffraction photographs were taken for crystal orientation. Zero level diffraction patterns were obtained from the (h01), (0k1), (hh1) and (hh1) reciprocal planes, as illustrated in Figs. 5.6 and 5.7. For some of these planes higher level photographs were also taken.

A zero- level photograph in a certain direction taken from the sample No. 83-HF43-X/2 is shown in Fig. 5.8(a) where a hexagonal characteristic appears to be present. To determine the symmetry nature of crystalline CuInSe, a higher level photograph was taken and shown in Fig. 5.8(b). The results suggest that the structure of CuInSe, is pseudo cubic and pseudo hexagonal rather than hexagonal. Precession photographs were also taken from the 83-HF42-X/1, 83-HF43-X/1 and 83-VP14-X/2 samples. These results showed the same symmetry nature for CuInSe₂. Similar experiments were also performed for CuInTe₂ and the zero level pattern from the (h01) and (hk2h) are presented in Figs. 5.9(a) and 5.9(b) respectively.

5.3.2 Weisenberg method

In order to avoid ambiguity in the structural determination, photographs were also taken using the Weisenberg method from the set of samples used in the previous Buerger experiments. The Weisenberg method provides a distorted projection of the reciprocal level on a film which, although not very convenient, can be used in the structural determination. This method was used in order to get diffraction patterns from (hk0) level. The result is shown in Fig. 5.10.

Fig. 5.11 shows a schematic diagram of the Weisenberg camera used in the present experiments. The filtered and collimated Cu Kg radiation is incident on a crystal (incident beam normal to the rotational axis of the crystal) mounted on a goniometer head. The diffracted x-ray beams are collected by a film held against the inner surface of the cylindrical film casette. A cylindrical layer line screen, which is concentric with the crystal rotational axis, is used for "level selection. During the exposure, the crystal oscillation and the film movement are achieved by a motor in a synchronized mechanism so that the angle of oscillation is linearly proportional to the distance traveled by the film casette. Diffraction beams are received wherever a reciprocal lattice point passes through the sphere of reflection. 5.4 Space Group Determination

Space group of the semiconducting compound CuInSe₂ prepared in the present experiments was determined using the diffracted patterns taken by the Buerger precession and the Weisenberg methods. With the aid of these x-ray diffraction patterns, systematic absences due to lattice centering and the presence of space group symmetry elements were determined and classified systematically. The information led to a choice from a limited number of space groups, and finally taking geometrical structure factor into consideration, the correct space group was found. 「ないない」

To perform the space group determination, a knowledge of the number of formula weight per unit cell of the CuInSe₂ crystal is needed. This number, z, can be found using the following expression,

$$z = \frac{G V}{1.660 M}$$

where M is the total mass of a unit of $CuInSe_2$, V is the volume of the unit cell and G is the density (measured value is 5.73 ± 0.01 and calculated value is 5.75 gmcm⁻³ [2.19]). The calculated values of V and M are determined from the cell dimensions and the atomic weights respectively. From the cell dimension values obtained in the present study (see section 5.5), the value of k was found to be 4.

From the photographs obtained for (h01) and (0k1)

planes, Figs. 5.6 (a) and (b), the following condition was found to satisfy,

h+k+1 = 2n

where n is an integer. This condition suggests that the CuInSe₂ lattice is body-centered (I) with the centering point lies midway on the body diagonal. From the absence due to space group symmetry elements using the (hhl) plane, as shown in Fig. 5.7(a), it has been deduced and found that,

2h+1 = 4n, l=2n

is the possible condition. It follows then there exist a diamond glide (d) for this structure. Results from the deduced presence and orientation of space group symmetry elements in turn leads to three choices of space groups for this tetragonal system, namely, $I4_1/amd$, $I\overline{4}2d$ and $I4_1md$. Another projection of reciprocal lattice plane, (hk0), obtained by the Weisenberg method, as shown in Fig. 5.9(a) was examined for possible condition of indices, where both h and k are even,

h = 2n, k = 2n only

(h = 2n+1 and k = 2n+1 all missing)

It leads to perfectly missing if the space group would be $I4_1/amd$, and possibility of $I\overline{4}2d$ and $I4_1md$ if these are missing due to accidentally weak intensities. Also, we can have from atom position assignment for z = 4, or,

こうちょうちょうないとうないとうないないないないないないないない ちょうちょう ちょう

4Cu $\overline{4}2m$, 4In $\overline{4}2m$ and 8Se at 2/m or mm

in $I4_1$ /amd. This does not explain the intesities of (200), and (600) planes. The possibility of $I4_1$ md is also eliminated. In other words, in general for space groups $I4_1$ /amd and $I4_1$ md the following conditions exist,

> 200 4 f + 4 f 600 Cu In 400 4f + 4 f + 8 f 800 Cu In Se

It shows at least medium intensities but from the Precession films there exist very weak intensities, therefore, the space group $I4_1/amd$ and $I4_1md$ are rejected. Then it is evident that the space group of CuInSe₂ semiconducting compound is $I\overline{4}2d$ with a principal axis of four fold inversion and a two fold axis perpendicular to the principal axis.

5.5 Determination of Unit Cell Parameters

The unit cell parameters of the semiconducting CuInSe₂ were obtained from the precession photographs taken from two single crystal samples. Four independent measurements were made for each of the unit cell of each single crystal sample using the photographs taken for (hol) and (Okl) planes. Similar measurements were carried out for CuInTe₂. To improve the parameter accuracy, measurements were made for 16 and 32 lattice spacings for both a- and c-axis. After these measurements, the direct lattice parameters

were determined using the following expression,

$$d = \frac{\lambda(K\alpha_1)60}{t}$$

where d is the direct lattice parameter in \tilde{A} , λ is the x-ray wavelength (0.70926 Å, MoR α), t is the measured spacing in mm, and the number 60 is the magnification factor. The average lattice parameter results for two samples were finally obtained and these are shown in Table 5.1. Parameter values reported in the literature using powder x-ray data are also included in the table for comparison. A lattice distortion value, which is defined as 2 - c/a, was found to be equal to - 0.006 for CuInSe₂ from the present work.

5.6 Crystal Orientation

The orientation of a crystalline sample can be determined from the Buerger precession photograph. This method therefore was used to examine the crystal solidification direction and growth plane of CuInSe₂ ingots prepared in the present experiments. The information is useful for further growth experiments and for device fabrications.

Eight samples were prepared for the orientation examination. Six of these were cut with their large surface perpendicular to the solidification direction and the other two with the large surface parallel to the solidification direction. Among the eight samples six of them were cut

from ingots grown by the horizontal method and the rest two samples from those by the vertical method. The cut samples were then polished using Al_2O_3 powder to a final thickness of about 0.1 mm. This thickness was chosen to minimize the absorption of the x-ray radiaton.

Diffraction patterns were obtained using the precession camera with the Mo Kg radiation. All the films were then indexed through the interplanar spacing in order to identify the plane. Zone direction was obtained using the perpendicularity condition which is given by,

$$\frac{a^2}{-u} = \frac{a^2}{-v} = \frac{c^2}{-w}$$

$$h \quad k \quad 1$$

for this tetragonal system, where plane (hkl) is perpendicular to line [uvw] and is related to the cell parameters a and c. The results obtained for the solidification direction and growth plane are shown in Table 5.2.

5.7 Powder Diffraction

To examine the phase of a material, the powder diffraction method is frequently used. In the present work, powder diffraction patterns were obtained for powder samples prepared from crystalline CuInSe₃. The measured powder diffraction results were then compared to the results calculated from the lattice parameter values obtained in the previous sections. The single phase nature

of the semiconducting CuInSe₂ prepared in the present work was finally confirmed from these results.

. .

5.7.1 Sample preparation

A fine powder material, with an average size of about 20 μ m, was first prepared from the grown CuInSe, ingots. A mixture was then made by mixing the powder material in a solution containing a plastic cement and acetone (1:20 by volume). CuInSe, powder sample (randomly oriented) was then prepared by spraying the mixture onto a glass slide. The plastic cement is an ideal binder for the powder sample because it does not absorb x-rays, does not produce diffraction pattern, dries rapidly and produce a flat powder layer.

Three CuInSe, powder samples were prepared using the above-described procedure. Two of the samples were prepared using crystalline ingot material obtained from the horizontal growth method and the other from the vertical growth method. It is seen that the solidification direction and gowth plane are random. This is considered to be due to the fact there was no seed involved during growth.

5.7.2 X-ray diffraction system

The x-ray diffractometer system used in the present experiments consisted of a SIEMENS model.805 x-ray source, a D500 diffractometer and an M73922 graph unit. A nickel

filtered Cu K σ x-ray radiation, having the mean wavelength value of 1.54178 Å was used. The Cu K σ radiation source was selected because the wavelength was different from the K absorption edge of Cu, In and Se.

Typical settings of the system during the measurements are listed below : -Applied voltage and current : 40 KV and 20 mA -Aperture of Divergence 0 Scatter Slits (I0II) : 1 -Aperture of Receiving Slit (III) : 1 -Aperture of Detector Slit (IV) : 0.15 -Speed (scanning), 2 : 2 /min -Chart speed : 2cm/min -Detector type, KV : 1.200 -Base line : 2.0

-Gain : 16

Several preliminary runs were made to determine the required time constant and the rate meter sensitivity values. For the present experiments, the values of 2 seconds and 10 counts/sec were found to be appropriate. The scanning 20 range was between 10° and 144°.

5.7.3 Experimental and calculated results

X-ray diffraction patterns were obtained from the three samples. All of the results showed the same characteristics which were similar to those reported by Parkes et al. [2.19], who reported their results for a scanning range upto 90°. In the present work, the scanning

range is between 10° and 144°. Table 5.3 gives the observed relative intensities, the corresponding interplanar spacing d_{hk1} and 20 values. the relative intensities were taken from the normalized average value of the three readings (determined by the enclosed area of each peak).

According to the Bragg law, the reflection angle θ is dependent on the incident x-ray wavelength and the interplanar spacing d . The relative intensity of the reflected beam is determined by the crystal structure, geometrical factors and the multiplicity due to the symmetry of the planes. Therefore, a set of theoretical diffraction intensities (versus 2 θ) can be calculated if the crystal structure and the lattice parameters are known.

The crystal structure and parameter results obtained in sections 5.4 and 5.5 were used for the present calculation. This calculation was done by using a computer program CALPOW [5.5]. Values of hkl and d were determined based on a relation for the tetragonal system which is given by,

$$\frac{1}{d} = \sqrt{\left(\frac{h^2 + k^2}{a^2} + \frac{1^2}{c^2}\right)}$$

where a and c are the measured unit cell parameters.

Table 5.4 shows the calculated and measured relative intensities. X-ray diffraction patterns of the present measured and calculated results are shown in Figs. 5.12 and 5.13 respectively for the scanning range from 10° to 144°.
Any contribution of `other phases in the x-ray diffraction data was not found. These results thus confirmed the single-phase quality of the as-grown ingots.

5.8 Conclusions

1

Work has been, succesfully performed on X-ray diffraction experiments for CuInSe,, which have not been very extensive as reported in literature. Laue back reflection method was used to determine the crystalline quality of the ingot in order to establish the best growth conditions for CuInSe₂. From the results obtained for single crystal Weisenberg and Precession methods, both CuInSe, and CuInTe, have been confirmed to have a space group of 142d. Unit cell parameters for CuInSe, were also determined from these single crystal data. For the ingots prepared in the present study, the growth plane and solidification direction appeared to be random, as revealed by the X-ray diffraction results. The random plane and direction were believed to be due the growth method used in the present study, where a seed has not been employed for the growth experiments.

Powder diffraction data of CuInSe₁ also have been computed from the single crystal diffraction results. These have been found to be in very good agreement with the experimental powder diffraction data obtained for CuInSe₁. These results thus confirmed that the prepared ingots were single phase with the chalcopyrite structure.

Compound	a (Å)	с (Å)	2-c∕a	Ref.
CuInSe'	5.789	11.612	-0.006	Present study
CuInSe;	5.782	11.620	0.01	[2.19]
CuinTe ₂	6.180	12.366	0.001	Present study
CuinTe;	6.179	12.36	0.00	[2.1]

Table 5.1 (a) Chalcopyrite lattice parameters.

(b) Calculated lattice constant and atomic distances.

Compound	1 X	[A-C] (A)	3 [B-C] (Å)
CuinSe ₂	0.2485	2.5043	2.5141
CuInTe ₂	0.2498	2.6756	2.6773

$$\frac{1/2}{11 \ x = 1/2 - (c^3/32a^2 - 1/16)}$$

$$\frac{1/2}{21 \ [A-C] = [a^2x^2 + (4a^2 + c^2)/64]}$$

$$\frac{1/2}{21 \ [B-C] = [a^2(1/2 - x) + (4a^2 + c^2)/64]}$$

Table 5.2. The growth plane and the solidification direction.

Sample	No.	Zone	Solid.	Growth	Real Angle	Rem.
		Direct.	Direct.	Plane	betw. Solid. and	
		[uvw]		(hkl)	Growth Plane	
83-HF26	5- x /1	[221]	[122]	(128)	89.86	1
83-HF55	5-1/2	[221]	[122]	(128)	89.86	1
83-H P 55	5-X/1	[221]	[221]	(112)	89.84	2
83-VP11	- X /1	[021]	[021]	(024)	89.83	2
83-HF62	? −,x /1	[111]	[111]	(114)	89.84	2
83-HF62	2-X/2	[112]	[112]	(118)	89.89	2
83-VP14	-1/2	[111]	[111]	(114)	89.84	2
83-HF63	I-X/1	[112]	[112]	(118)	89.89	2

l: Large face (slice) parallel to solidification
 direction.

.

l

2: Large face (slice) perpendicular to solidification direction.

65

Table 5.3 X-ray diffraction data using Cu Kg radiation for a single-crystal CuInSe, powder sample.

hkl	20 (degree)	d (Å)	Measured I/I*
101	17.04	5.2033	4.5
112	26.61	3.3497	100
103	27.67	3.2238	2.2
211	35.56	2.5245	3.7
105	41.91	2.1555	1.4
213			
204	44.19	2.0495	69.1
220			
301	47.81	1.9024	1.1
116	52.39	1.7464	40.3
312	, ,		
305	62.65	1.4828	1.0
323			
008 [,]	64.41	1.4465	7.8
400			1
217	67.12	1.3945	0.9
411			

ĺ

hkl	20 (degree)	d (A)	Measured I/I*
316	70.95	1.3283	11.5
332			
325	71.40	1.3211	0.7
413			
228	81.34	1.1829	11.8
424			•
327	83.95	1.1526	0.9
431			
501			
11,10	87.30	1.1168	1.2
336	87.58	1.1140	5.5 /
512			
417 5	92.16	1.0702	0.7
521	4		
408	97.56	1.0249	3.5
440			
31,10	103.50	0.9806	2.2
516	103.87	0.9791	4.6
532			
419	10 8. 78	0.9482	0.6
507)
437	~~		\langle
611			
604	114.71	0.9155	4.8
620	1		14

67 🕓

hkl	20 (degree)	d (A)	Measured I/I*
33.10	121.54	0.8834	3.3
536	/		
21,13	132.41	0.8425	0.7
41,11			~
545			
633			
448			
712	144.12	0.8103	3.5
552			

ţ

68

1

\$

- .

Q

Table 5.4 Calculated and measured x-ray powder diffraction of CuInSe₂ using Cu Kg radiation.

. مربع

۶

hkl	,	Calculat			Measured		
	F ² x10 ³	d (Å)	20(degree)	I∕I≭	I/I*		
101	6.35	5.1809	17.11	6.9	4.5 ,	. 0	
112	2.31x10 ²	3.3455	26.64	. 100	100		
103	5.83	3.2 ¹⁷⁷	27.72	2.3	2.2		
211	5.15	2.5269	35.55	2.4	3.7	*	
105	4.64	2.1554	41.93	1.7	1.4		
213	4.31	2.1519	42.01	1.7	1.4		
204	2.20x10 ²	2.0497	44.20	69.0	69.1		
220	2.19x102	2.0467	44.27	•			
301	4.53	1.9036	47.80 *	0.6	1.1	\mathbf{i}	
176	1.36x10 ²	1.7496	52.31	39.8	40.3)	
312	1.36x10 ²	1.7459	52.43		\sim	•	;
305	2.93	1.4842	62.61	0.7	1.0.		3 1 1
323	3.62	1.4831	62.66				•
008	2.]1x10 ²	1.4515	64.19	9.7	7.8		נ ני איני איני
400	2.10x10 ²	1.4473	64.40				
217	3.18	1.3967	67.03	0.7	0.9		
411	2,97	1.3939	67.19				
316	9.26x10	1.3299	70.88	14.0	11.5		19 19 19
325	3.19	1,3207	71.45	0.6	0.7		
413	3.00	1.3199	71.50				

Ъ	Ŀ,	1	
11	л	⊥.	

ı.

(.

ı,

,

Calculated

3

	F ² x10 ³	d (Å)	20 (degree)	I∕I*	1/1*
109	2.64	1.2593	75.49	0.3	<u> </u>
307	3.02	1.2579	75.62		
415	2.69	1.2015	79.86	0.3	-
228	1.50x10 ² 5	1.1840	81.29	17.6	11.8
424	1.49x10 ²	1.1823	81.44		
327	2.23	1.1537	83.91	0.5	0.9
431	2.72	1.1521	84.03		
501	2.07	1.1521	84.03	6	
11,10	6.70x10	1.1171	87.32	2.4	1.2
336	6.68x10	1.1152	87.51	7.2	5.5
512	6.66x10	1.1142	87.61	-	
417	2.17	1.0717	92.04	0.4	0.7
521	2.61	1.0704	92.19		
505	2.49	1.0362	96.20	0.2	-
435	1.95	1.0362	96.20		
408	1.12x10 ²	1.0249	97.62	5.6	3.5
440	1.10x10 ²	1.0234	97.81		
31,10	5.01x10	0.9806	103.72	3.3	3.2
516	4.99x10	0.9793	103.88	6.8	4. 6 -
532	4.98 x10	0.9786	104.04		

'n'

hkl		Calcula	Measured		
	F ² x10 ³	d (Å)	20 (degree)	I∕I *	I/I *
419	1.84	0.9500	108.54	0.5	0.6
507	1.61	0.9494	108.64		
# 43 7	2.07	0.9494	108.64		
611	1.96	0.9485	108.79		
20,12	8.44x10	0.9177	114.35	3.2	1.7
604	8.38x10	0.9156	114.77	6.4	4.8
620	8.38x10	0.9153	114.82		
33,10	3.84x10	0.8843	121.41	4.8	3.3
536	3.82x10	0.8834	121.63		
32,11	1.83	0.8821	121.94	0.2	-
453	1.94	0.8804	122.32	0.2	-
509	1.39	0.8617	127.01	0.2	-
439	1.77	0.8617	127.32		
21,13	1.52	0.8444	131.94	0.7	0.7
41,11	1.61	0.8438	132.13		
545	1.79	0.8425	132.52		
633	1.71	0.8423	132.59		
448	6.52x10 `	0.8364	134.47	3.7	3.6
529	1.73	0.8259	138.07	0.2	_

ł

hkl		Calculated				
F ² x10	F ² x10 ³	a (Å)	20 (degree)	I/I*	I/I *	
617	1.56	0.8255	1 38.2 1	0.3	_	
701	1.81	0.8244	138.43			
11,14	3.01x10	0.8129	143.04	2.1	1.6	
51,10	3.00x10	0.8118	143.62	4.3	3.2	
71 2	2.98x10	0.8107	144.10	6.6	4.7	
635	1.59	0.8089	144.87	0.2	-	

l

72

ą



4

ť

Fig. 5.1 A schematic diagram of the Laue back reflection apparatus.



Fig. 5.2 A back-reflection Laue photograph taken from a randomly oriented CuInSe₂ ingot, showing multiple spots.

(

0

ø

٠,



Fig. 5.3 A back-reflection Laue photograph taken from a randomly oriented CuInSe, ingot.

60

(

.



Fig. 5.4 A back-reflection Laue pattern, taken from a monocrystalline sample for a two-spot expoure.

ı

7

.

٥

t

.



¢€

¢

`

Fig. 5.5 A schematic diagram of the Buerger precession cammera.

C

(

 (\cdot)

75

.

ĩ







 (\cdot)



atterations on an automatic designed

(b) Fig. 5.8 Diffraction pattern of (a) zero level and (b) first level of a plane for single crystal CuInSe₁ sample.



(a)



(b) Fig. 5.9 Diffraction pattern of (a), (h01) and (b), (hk2h) reciprocal planes of a single crystal CuInTe, sample.

C

۰.

Q.



Fig. 5.10 Diffraction pattern of (hk0) reciprocal plane of a single crystal CuInSe₂ sample.

Ф-

 ζ







Fig. 5.12 Measured diffraction intensity plotted versus 20.



CHAPTER 6

ELECTRICAL AND OPTICAL PROPERTIES

6.1 Introduction

One of the main requirements for a material to be used in device applications is the ability to control its basic parameters. Specifically, the improvement and control of electrical properties of a semiconducting material are necessary for opto-electronic devices. Because the reported experiments in the literature on electrical properties of CuInSe, especially the effect of annealing and extrinsic doping have not been very extensive, therefore more studies on annealing and doping are required in order to improve and control the electrical properties of this material.

In this chapter, after introducing a suitable low resistance ohmic contact material found for p-type CuInSe, , Hall effect results are presented. Results obtained from annealing and extrinsic doping experiments of the monocrystalline CuInSe₂ samples are then followed. Finally, photoconductivity results obtained as-growng on monocrystalline CuInSe, samples at 77°K will be presented. The photoconductive response has been determined as function of optical wavelength, light intensity and applied bias voltage. All of the measurement results to be presented and discussed in this chapter were made on single crystalline samples taken either from ingots by the

horizontal or vertical directional solidification method.

6.2 Ohmic Contact

In the initial stages of this work, investigation was carried out in order to find an ohmic contact material for p-type CuInSe₂. Various metals, Au, Ag, In, Al, Mo, Bi, Sn, Ag epoxy and alloys Sn, Pb and In, Wood's alloy were either sputtered, evaporated or soldered onto p-type samples. All of them were found to show a rectifying effect. However, a silver paint (EPO-TEK H20E, Epoxy Technology Inc.) was found to produce an ohmic contact for p-type CuInSe₂, as shown in Fig. 6.1. For n-type CuInSe₂ samples, evaporated In was used as the contact material [2.6].

6.3 Bulk Hall Measurements

Thermal-probe testing indicated that all of the as-grown crystalline ingots were p-type. This was confirmed later by Hall effect measurements on the monocrystalline samples cut from as-grown CuInSe₂ ingots. The typical dimensions of the samples for these experiments were about $10x2.5x1 \text{ mm}^3$. The samples were polished by alumina powder with a diameter of about $0.05 \ \mu\text{m}$. Current contacts were then made using the silver paint on the two ends of the samples, then heated at $100 \ ^\circ$ C for one hour. Finally, fine metallic wires were soldered to the end contacts using. Wood's alloy. Wood's alloy was selected because of its low

melting point. Side contacts were made with four spring-shaped gold wires (two on each side of the sample). Soldered-contacts were also tried for voltage contacts, but the pressure contacts was found to give more accurate results because of the needle like tip.

As a try run, Hall effect measurements were made on n-type Si (with known resistivity and mobility) prior to the actual Hall effect measurements of the CuInSe, samples. The measured mobility and resistivity values of the Si sample were consistent with the nominal values.

The Hall voltage values observed during experiments on CuInSe, samples were very small. Accordingly, a check on the linearity of the Hall voltage versus magnetic field and the current passing througth the sample were necessary. This was carried out on the samples and the experimental results obtained for one of the samples are shown in Figs. 6.2 and 6.3. As expected, Hall voltage varies linearly with the magnetic field and the current changes which confirms the measured values to be Hall voltages. All the as-grown samples for Hall measurements were p-type. The hole concentration, p, and Hall mobility, μ , were obtained . The results of Hall mobility, specific resistivity and effective concentration obtained for the single crystalline samples obtained from different growth runs are given in Table 6.1.

6.4 Annealing Effect of Monocrystalline Samples in Defficient Se

The starting p-type single crystal samples and powderered CuInSe, were vacuum sealed (better than 10⁻¹ torr) in a quartz ampoule. The purpose of the powder material in the ampoule was to prevent excess sample decomposition during the annealing. Two sets of annealing experiment were carried out. The first set was made at different temperatures for a fixed period of time. After the annealing, the sample was cooled slowly to room temperature. An automatic unit was used for driving the ampoule in or out of the furnace (Fig. 6.4), in order to minimize stresses in the sample during the cooling process. The second set of experiment was made fixed at а temperature but for different time and again cooled the sample slowly to room temperature. As a result of Se out diffusion under minimum Se vapor pressure, resistivity of the samples varied. Figs. 6.5 and 6.6 show the normalized resistivity measured using a four-point probe versus temperature and time respectively. Normalized resistivity is defined as ρ/ρ_{\bullet} , where ρ is the resistivity after each testing experiment and p_{\bullet} is defined to be 5 and 10 ohm-cm respectively in Figs. 6.5 and 6.6. Room temperature results without intentional heating are included in the figures for comparison.

Hall measurements were also made on some of the annealed samples and the results are given in Table 6.2.

Results obtained show that the conductivity type of the samples was converted from p to n (with the effective concentration from 1015 cm-3 to 1014 cm⁻³) after the annealing under minimum Se vapor pressure at 600°C for about 10 minutes. This change of concentration is due to out diffusion of Se. This further suggests that there is a compensation region near the peak for the conductivity type changes, see Figs. 6.5 and 6.6. The nature of the electronic properties can be affected by the concentration of the diffused element in this ternary compound. The tendency of the variation of the resistivity curves shown are the same under each experimental condition. The order of the variation changes with respect to high temperature more rapidly than it does versus time at relatively low temperature (160° C).

6.5 Extrinsic Doping Effect of Monocrystalline Samples in Excess Se, Bi and Te

P-type monocrystalline CuInSe, samples were selected from as-grown ingots and the sample preparation process was carried out in the same manner as explained in the last section for the annealing experiments. Diffusion experiments under excess Se, Bi and Te vapor pressure were made using methods described in the papers reported by Parkes et al [2.6] and Migliorato [6.1]. The p-type single crystal samples, powdered CuInSe, and the high purity material were vacuum sealed in a guartz ampoule. Weighed

amount of each elemental dopant was used in order to provide sufficient vapor pressure in the ampoule. As shown in Fig. 6.7 Se has a high vapor pressure at relatively high temperature [6.2]. This pressure value is expected to be greater than that for the CuInSe₂ compoud. This will then allow diffusion to take place in the samples under the maximum Se vapor pressure with minimum loss of the compound material at a relatively high temperature. All the samples in this experiment were etched in a solution of HCl: HNO₃: H₂O (3: 3: 1 by volume) for about 12 minutes after each diffusion.

Parkes et [2.6] have carried al out diffusion experiments to convert n-type samples to p-type. In the present work, similar diffusion was done but on p-type samples to reduce the resistivity. It was found that the resistivity of all samples used in these experiments was changed. The normalized resistivity, p/p. (🌶 is the measured resistivity by four-point probe after each **diffusion experiment run and** p is defined to be 10 ohm-cm) versus tempereture and time is shown in Fig. 6.8. The final measured resistivity value of each diffused sample was found to be lower than the initial resistivity value measured at room temperature. Apart from Se, Bi (group V) and Te (group VI) were also used as extrinsic dopants for the in-diffusion experiments. Prior to Hall measurement, a check on linearity of the Hall voltage versus the current passing through the sample was carried out for n-type

(* *

samples and the results are shown in Fig. 6.9. The Hall voltage obtained for n-type samples were found to be greater than that for p-type sample. The effective concentrations of all the samples after the diffusion experiments under maximum vapor pressure of either Se, Bi or Te were found to be different from the original values, as determined by Hall effect measurements. The measured values of mobility, μ , and concentration, p/n, after the diffusion experiments are given in Table 6.3. As seen in the table, all of the samples after the Se and Te diffusion remained p-type. However, after the Bi extrinsic diffusion, samples converted to n-type. In the case of such. in-diffusion under excess Se and Te vapor pressure, the acceptor state density is increased (or the donor state density is reduced), resulting in an increase in the effective carrier concentration. And vice versa for the case of Bi in-diffusion.

6.6 Photoconductivity

6.6.1 Theory

Start French

()

When light is incident on the surface of an infinite slab of p-type semiconductor with a thichness of d and an equilibrium hole concentration of p_{θ} , the relative conductivity variation with a photon flux density D _{ph} is given by [6.3],

 $\frac{\Delta \sigma}{\sigma_{0} D} = \frac{(1+b)\tau}{p_{0} d (1-K^{2}L^{2})} \left[1-e^{-\kappa d} + KL \frac{(KL-\sigma)e^{-\kappa d} - (KL+\sigma)}{1+\sigma \coth(d/2L)} \right]_{(6.1)}$

where τ is lifetime, b is the electron-to-hole mobility ratio, K is the absorption coefficient and L is the diffusion length, α is defined as $sL/D=s\tau^{-1/2} D^{-1/2}$, where D is diffusion coefficient of electrons and s is the surface recombination velocity. Examining equation (6.1), as the absorption coefficient K is increased, then $\Delta \alpha / \alpha_0 D$ ph increases to a maximum value between Kd=1 and 10, the values decrease as Kd further increased,

$$\left(\frac{\Delta \sigma}{\sigma_{0} D}\right)_{\text{Rd}=\infty} = \frac{1+b}{p_{0} d} \frac{\tau}{1+\operatorname{ccoth}(d/2L)}$$
(6.2)

()

In the case of a thick sample, where the thickness of the sample is much greater than 1/K and L, equation (6.1) will reduce to [6.4]



and for a thin sample, where the thichness is much less than both 1/K and L, equation (6.1) will reduce to,

$$\frac{\Delta \sigma}{\Delta_{\bullet} D_{\rm pb}} = \frac{(1+b)K^3 d\tau'^2}{2p_{\bullet}(1-K^2L^2)\sigma}$$
(6.4)

It is noted from equations (6.3) and (6.4) the photoconductivity is proportional to 1/d and d respectively.

6.6.2 Experimental method and results Sample preparation

The monocrystalline CuInSe, samples prepared for this measurements were first abrasively polished using alumina powder paste of diameter $0.05 \ \mu m$, and then chemically polished using a solution of H_2SO_4 : $K_2Cr_2O_7$ [2.33] in a ratio of 9:1 by volume. The final dimensions of the samples were about 8 mm in length, 2 mm in width and 0.2 to 2 mm in thickness. All the ohmic contacts (two for current and two for voltage) were made using silver paint, fine copper wires were soldered to the contacts by Wood's alloy (melting point about 74 °C which allows the low temperature soldering). Finally a thick rectangular black paper with a window in the center was used to cover all the contacts from incident light.

a construction of the state of the state

Measurement procedure

()

The prepared sample was mounted in the cooled finger of a cryostat with a Kodak IRTRAN 2 window (ZnS). Steady current from a battery was applied to the sample and controlled by a potentiameter. Monochromatic radiation was obtained from a Beckman model 2400 monochromator (chopped at 89 Hz) and focused onto the sample through an aperture. The incident light intensity was measured by placing a calibrated InSb photovoltaic detector operating at 77 °K at the position of the sample and measuring its output. The photoconductive changes were obtained from the side-probes

and were fed to a lock-in amplifier (Princeton Applied Research model 124A) set at the chopped frequency. Finally a digital voltmeter was used to measure the dark steady voltage between the probes.

Results

At room temperature, the photoconductivity voltage changes were very small, in the range of few μV , but relatively large signal with better stability was observed as the sample was cooled to 77°K. Prior to the photoconductivity measurements of each sample, the linearity of the photoconductivity voltage versus the applied bias voltage was established (at 77 •K) at different fixed wavelengths, as shown in Fig. 6.10. The value of the current passing through the sample was then selected from the linear region.

Let R, and R be respectively the dark and illuminated resistance of uncovered portion of the sample and R , be the series resistance including the covered portion of the samples and the two side contacts. Due to ligh illumination the lalative conductivity change is given by,

$$\frac{\Delta \sigma}{\sigma_{0}} = \frac{(V_{0} - V)(R_{+} + R)R_{0}}{VR_{+}R}$$
(6.5)

where V and V, are the voltages obtained for the uncovered portion of the sample for the dark and iluminated respectively. In the case for the low levels of light

illumination where the value of $\Delta V/V_{\odot}$ is small, the relation is reduced to,

$$\frac{\Delta \sigma}{\sigma_{\bullet}} = \frac{\Delta V}{V_{\bullet}} \left(1 + \frac{R_{\bullet}}{R_{\bullet}}\right) \frac{\Delta V}{V_{\bullet}}$$
(6.6)

Photocondutivity response, $\Delta e/e_0 D_{ph}$, (here Δe is the conductivity change, e_0 is the dc conductivity in darkness) versus optical wavelength between 0.4 and 1.6 µm at 77 °K was measured. Results obtained for four bulk monocrystalline CuInSe₂ samples are shown in Fig. 6.11. These are the first photoconductivity results measured and reported for p-type monocrystalline CuInSe₂ sample at 77°K.

1

The photoconductive voltage versus the intensity of the monochromatic light was also determined using a set of calibrated filters. Such results at different wavelengths are shown in Fig. 6.12. The plots illustrate the linearity relation between the photoconductivity voltage and the light intensity. It was found that the photoconductivity was increased after the surface deep etching treatments. It is believed that the deep etching also gives better surface stability and as a result lowers the surface recombination velocity [2.33]. The photoconductivity results obtained roonfirmed the energy gap value of CuInSe₂ reported in the literature.

6.7 Conclusions

()

In the present work, annealing experiments of CuInSe, under maximum and minimum selenium vapour pressure have been carried out. Extrinsic diffusion experiments of bismuth and tellurium into crystalline CuInSe, were also performed. Results obtained from four-point probe and Hall effect measurments indicated that all the as-grown ingots were p-type. The results also showed that the electronic properties of the samples were very semisitive to the annealing and diffusion treatments. The originally P-type as-grown CuInSe, samples were converted into n-type after the treatment under minimum selenium pressure and after the bismuth diffusion.

The room temperature Hall mobility values measured in the present work for both p- and n-type samples are greater than those reported in the literature, suggesting that the grown ingots have a better microscopic quality. The low resistance silver point contacts to p-type CuInSe, were found to be ohmic. This contact material is believed to be useful for future studies of the compound CuInSe,.

Table 6.1 Room temperature electrical results on monocrystalline CuInSe₂.

0

đ

(_;

('

Sample No.	Cond.	Resist.	Hall Mobility	Carrier Conc.	
	Туре	ρ ,(Ω-cm)	μ , (cm ² /Vsec)	p, (1/cm ³)	
83-HF3 2-H/1	P	4.6	12.7	1.1x1017	
83-HF46-H/1	p	0.4	44.9	3.7x1017	
83-HF39-H/1	P	4.1	69.4	2.2x1014	
83-HF 39-H/2	₽	4.7	68.1	2.0x1014	
83-HF 39-H/3	P	4.8	66.4	2.1x1014	
83-VF13-H/1	p	1.5	57.7	7.1x1014	
83-VP10-H/2	L P	3.8	67.6	2.4x1014	
83-VP10-H/2	r p	999.8	73.9	8.8x1013	

1: Measured at room temperature
2: Measured at 77°C

7

95

43⁸

Table 6.2 Room temperature electrical results of annealed monocrystalline CuInSe₂ samples.

Sample	No.	Cond.	Resist.	Hall Mobility	Carrier Conc.
		Туре	ρ,(Ω-cm)	μ ,(cm ² /Vsec)	p/n,(l/cm³)

Ì

83-HF32-AS/72	n	1.8	1050	3.3x1015
83-HF37-AS/4 ²	n	0.8	645.7	12.5x10 ¹⁵
83-HF39-AS/4 ²	p	8.9	64.7	1.1x1016
83-VP10-AS/11	р	13.3	33.3	1.4x1016
83-VP10-AS/12	р	1.6	65.9	59.0x10 ¹⁵
83-HF56-AS/11	p	6.8	47.2	1.9x1016
83-HF56-AS/2 ²	р	15.8	36.9	1.1x1014

(

()

1: Measured before annealing in minimum Se vapor pressure 2: Measured after annealing in minimum Se vapor pressure

96

~

Table 6.3 Room temperature electrical results of Se-, Te- and Bi- diffused monocrystalline CuInSe₂ samples.

Sample	No.	Cond.	Resist.	Hall Mobility	Carrier Conc.
		Туре	₽ ,(Ω-cm)	μ , (cm ² /Vsec)	p/n,(l/cm³)

84-HF71-DS/21	р	0.4	48. 0	3.6x1017
83-HF39-DS/4 ¹	р	1.6	64.2	5.9x1016
83-HF56-DS/32	n	3.6	975.4	1.8x1015
84-HF72-DS/4 ²	n	4.2	774.1	1.9x10 ¹⁵
84-VF20-DS/13	P	3.8	24.9	6.6x10 ¹⁶
84-HF83-DS/23	p	1.8	45.7	7.8x1014

1: After Se in-diffusion
2: After Bi in-diffusion
3: After Te in-diffusion

1

C

97

ŧ



(

((

(

Fig. 6.1 Neasured I-V results between the Ag epoxy contact and p-type CuInSe₂ showing ohmic characteristics.



Fig. 6.2 Hall voltage plotted versus magnetic field under constant applied current condition.

98 *e*


(

(

()

Fig. 6.3 Hall voltage plotted versus applied current at a constant magnetic field.



Fig. 6.4 A photograph showing the annealing/doping apparatus including the automatic unit used for driving the sample.





S.

Fig. 6.6 Normalized resistivity of monocrystalline CuInSe₂ samples versus annealing time under minimum vapor pressure at a fixed temperature.

ð

C,

9



Fig. 6.7 Vapor pressure of Se, Te and Bi plotted versus temperature (data taken from ref. [6.4]).

۰ :



£

1.9

 $\boldsymbol{\zeta}$

Fig. 6.8 Normalized resistivity versus diffusion temperature under excess Se vapor pressure.



Fig. 6.9 Variation of Hall voltage versus applied current at a constant magnetic field for an n-type CuInSe, sample.

Ì



きんちょう ちょうちょう

Ģ

S

Fig. 6.10 Photoconductivity response versus applied voltage at 77 °K at different wavelengths.



ないのであると

(0)

(

Fig. 6.11 Relative photon photoconductivity versus optical wavelength for p-type monocrystalline CuInSe samples at 77 °K.



「「「「「「

C

 \mathcal{O}

()



CHAPTER 7

DISCUSSION AND CONCLUSIONS

In this chapter, final conclusions of crystal growth, structural analysis, diffusion and Hall effect measurements of CuInSe₂ are given.

7.1 Crystal Growth

Two methods of crystal growth, the Bridgman and the Stockbarger methods have been employed using two growth systems for both horizontal and vertical growth. Several difficulties such as voids, cracks, oxidation and adhesion of the compound to the ampoule have been encountered in the initial stages of the program. These difficulties have been overcome in the present work by adopting the improved growth procedure developed for this compound, as described in section 4.3. Although it has been a general belief that crystal growth of a compound material involving several elements is more dificult than that for elemental materials, however, good quality CuInSe, ingots containing large monocrystalline grains were successfully grown. Monocrystalline CuInSe, and CuInTe, with a typical dimensions of 2x5x15 mm³ were readily obtained from the ingots grown in the present work. These samples were used in the present study.

A comparison of the results obtained using the improved conditions (from the Bridgman and Stockbarger

methods), revealed that large monocrystalline grains of the compound with better guality can be obtained using the Stockbarger method. These results further showed that better results (in terms of size and quality) can be obtained using the vertical system. The formation of voids appeared to be due to incomplete mixing of the constituent elements in the melt. The combination of rotational mixing, inter-diffusion and the slow growth rate used was found to be adequate to overcome these growth problems. From the phase diagram of CuInSe₂ system, In-rich material is predicted in the solid state form. Analysis has been made using a micro probe on the as-grown ingots to confirm this prediction and in addition, to determine the compositional uniformity of the material. Experimental results obtained from the micro probe analysis showed an In/Cu ratio which was greater than one.

7.2 Crystal Structure Analysis

()

Laue back reflection technique was used to examine the quality of the grown ingots in order to establish the procedure for large grain growth. The structure analysis has been carried out to determine cell dimensions, lattice type, solidification direction and the growth plane for CuInSe, compound based on single crystal x-ray methods (Buerger precession and Weisenberg). These single crystal results have not been reported in the literature. Similar analysis was also made for CuInTe,. These X-ray methods

also enabled one to determine the precise cell parameters. The ratio of c/a was found to be 2.006 and 2.001 for CuInSe, and CuInTe, respectively. The results further confirmed that the height of the unit cell was almost double of its base axes. The crystal orientation results showed that the solidification direction was random, although some ingots were found to have a growth direction of [221] which was normal to the (112) plane. This was considered to be due to the fact that there was no seed involved during the growth. To determine more precisely the growth direction, further X-ray experiments using complete monocrystalline ingots are needed.

Powder x-ray analysis has been made and the results showed that the grown crystals were single phase with the chalcopyrite structure. From the observed relative intensities, the corresponding interplanar d $_{hk1}$ were obtained for the scanning 20 range between 10° and 144°. Powder diffraction pattern of CuInSe₂ has been computed from the single crystal diffraction data and was found to be in very good agreement with the experimental diffraction results.

7.3 Opto-elctronic Properties

The studies have been made prior to experimental measurements in order to develop ohmic contacts for p-type CuInSe₂. As a result of these studies silver paint was found to produce very good ohmic contacts with p-type CuInSe₂. The main advantage of the silver point contacts was the simplicity in processing.

Room temperature specific resistivity and Hall effect measurements have been carried out on single crystal Cuinse, samples prepared from the as-grown ingots. The results showed that all of these samples were p-type with a typical Hall mobility value of about 68 cm²V⁻¹sec⁻¹ and an effective carrier concentration of about 1017/cm-3. Studies were made on samples after the annealing and in-diffusion treatments under minimum and maximum Se vapor - pressure and the extrinsic doping by Bi and Te diffusion. These were performed on as-grown monocrsytalline CuInSe, samples and the results obtained have been given in this thesis.

It has been shown that p-type CuInSe, samples were converted into n-type by the annealing treatment under minimum Se vapor pressure. It appeared that there w wa's a compensation region separating the p- and n-type samples. The typical value of carrier concentration was 101 cm⁻³ and the maximum Hall mobility was 1050 cm²V⁻¹sec⁻¹ for the n-type samples. For the annealed samples both resistivity concentration varied, suggesting that selenium and out-diffusion did occur during the process. The selenium out-diffusion led to a decrease in acceptor state density so that the resistivity of the samples increased before the compensation region and decreased after. For in-diffusion experiments under Se, Te and Bi vapor pressure, the

resistivity and the concentration of all the samples were found to vary as determined by Hall effect measurements. The samples used in the Bi extrinsic doping investigation were also found to convert from p- to n-type. This effect was considered to be the result of Se out-diffusion which was believed to be dominant during the process. The carrier concentrations of n-type samples after the annealing or Bi-diffusion process were found to be lower than their original p-type values.

Photoconductivity response results versus wavelength in the optically sensitive region at 77°C were measured and these are the first results to be reported for p-type monocrystalline CuInSe₂ samples. The photoconductive voltage variation as a function of light intensity and applied voltage were also investigated. It was found that the photoconductivity magnitude was increased after the surface deep etching treatments which appeared to lower the surface recombination velocity.

REFERENCES

[1.1] S. Wagner, J.L. Shay, P. Migliorato and H.M. Kasper, Appl. Phys. Lett., 25, (1974) 434.

Q.

[1.2] S. Wagner, Inst. Phys. Conf. Ser., 35, (1977) 205.

[1.3] L. L. Kazmerski, Inst. Phys. Ser., 35, (1977) 217.

[1.4] E. Bucher, Appl. Phys., 17, (1978) 1.

- [1.5] L. L. Kazmerski, Proc. 16th IEEE Photovoltaic Spec. Conf., San Diego U.S.A. (1982).
- [1.6] J. N. Gan, J. Tauc, V. G. Lambrecdt Jr. and M. Robbins, Phys. Rev., B12, (1975) 5799.
- [1.7] C. Ricon, J. Gonzalez and G. S. Perez, Phys. Stat. Sol. (b) 108, (1981) K19.
- [1.8] J. L. Shay and J. H. Wernik, Ternary Chalcopyrite Semiconductors: Growth, Electronic Properties and Applications (Pergamon, New York, 1975).
- [1.9] J. J. Loferski, J. Appl. Phys., 27, (1956) 1956.
- [1.10] W. Horig. H. Neumann, H. Sobotta, B. Schumann \rangle

ł.

and G. Kuhn, Thin Solid Films, 48, (1978) 67.

٦)

t

- [1.11] L. Y. Sun, L. L. Kazmerski, A. H. Clark, P. J. Ireland and D. W. Morton, J. Vac. Sci. Technol. 15, (1978) 265.
- [1.12] J. L. Shay, S. Wagner and H. M. Kasper, Appl. Phys. Lett., 27, (1975) 89.
- [1.13] L. L. Kazmerski, in Ternary Compounds, 1977 (Institute of physics, London; 1977) pp. 217-228.
- [1.14] R. A. Mickelsen and W. S. Chen, Proc. of the l6th IEEE Photovoltaic Spec. Conf., (1982) 781.
- [1.15] A. M. Hermann, L. Fabic, K. Zweibl and R. Hardy, Proc. of the 16th IEEE Photovoltaic Spec. Conf., (1982) 840.
- [2.1] H. Hahn, G. Frank, W. Klinger, A. D. Meyer and G. Storger, Z. anorg. allgem Chem., 271, (1953) 153.
- [2.2] I. G. Austin, C. H. L. Goodman and A. E. Pengelly, J. Electrochem. Soc., 103, (1956) 609.

[2.3] L. S. Lerner, J. Phys. Chem. Solids, 27, (1966) 1.

- [2.4] W. N. Honeyman, J. Phys. Chem. Solids, 30 (1969) 1935.
- [2.5] H. M. Kasper, Solid State Chem., Proc. of the 5th y Materials Research Symp., (1972) 671.
- [2.6] J. Parkes, R. D. Tomlinson and M. J. Hampshire, J. Cryst. Growth, 20, (1973) 315.
- [2.7] H. Haupt and K. Hess, Inst. Phys. Conf. Ser., 35, (1977) 5.
- [2.8] J. G. Davis, P. M. Bridenbaugh and S. Wagner, J. Elect. Mate., 7, (1978) 39.
- [2.9] R. D. Tomlison, E. Elliot, L. Haworth and M. J. Hampshire, J. Cryst. Growth, 49, (1980) 115.
- [2.10] L. Haworth, R. D. Tomlinson and I. S. Al Safar, Proc. of the 4th Int. Con. on Ternary and Multinary Compounds, Jpn. J. Appl. Phys., 19 (1980) 77.
- [2.11] L. L. Kazmerski, M. S. Ayyagari and G. A. Sanborn, J. Appl. Phys., 46, (1975) 4865.

[2.12] L. L. Kazmerski, D. L. Sprague and R. B. Cooper,

J. Vac. Sci. Technol., 15, (1978) 249.

- [2.13] F. R. White, A. H. Clark, M. C. Graf, S. P. Grindle and L. L. Kazmerski, J. Vac. Sci. Techn., 16, (1979) 287.
- [2.14] R. A. Mickelson and W. S. Chen, Appl. Phys. Lett., 36, (1980) 371.
- [2.15] R. Durny, A. E. Hill and R. D. Tomlinson, Thin Solid Films, 69, (1980) L11.

(→

- [2.16] S. P. Grindle, A. H. Clark, S. Rezaie, E. Falconer J. McNeily and L. L. Kazmersi, J. Appl. Phys., 5, (1980) 5464.
- [2.17] L. S. Palatnik and E. J. Rogacheva, Sov. Phys. Dokl. Akad. Nauk., 12, (1967) 503.
- [2.18] I. Shih, A. Vahid Shahidi and C. H. Champness, J. Cryst. Growth, in press.
- [2.19] J. Parkes, R. D. Tomlinson and M. J. Hampshire, J. Appl. Cryst., 6, (1973) 414.

[2.20] L. L. Kazmerski, M. S. Ayyagari, G. A. Sanborn,F. R. White and A. J. Merrill, Thin Solid Films,

115

•

- [2.21] J. Troller, Int. Union of Crytall., Met. and Inorg. Index, 47, (1980) 63.
- [2.22] J. Troller and L. D. Calvert, Int. Union of Crystall., Met. and Inorg. Index, 39A, (1973) 51.
- [2.23] A. Vahid Shahidi, I. Shih and C. H. Champness, J. Elect. Mate., to be submitted.
- [2.24] S. M. Zalar and I. B. Cadoff, Trans. AIME, 224, (1962) 436.
- [2.25] W. N. Honeyman, J. Phys. Chem. Solids, 30, (1969) 1935.
- [2.26] B. Tell, J. L. Shay and H. M. Kasper, Phys Rev. B 4, (1971) 2463.
- [2.28] B. Tell and J. L. Shay, J. Appl. Phys., 43, (1972) 4485.

[2.29] J. Parkes, R. D. Tomlison and M. J. Hampshire, Solid State Elect., 16, (1973) 773.

- [2.30] H. Neumann, N. Van Nam, H. J. Hobler and G. Kuhn, Solid State Comm., 25, (1978) 899.
- [2.31] T. Irie, S. Endo and S. Kimura, Jpn. J. Appl. Phys., 18, (1979) 1303.
- [2.32] V. P. Zhuze, V. M. Sergeeva and E. L. Shtrum, Sov. Phys. Tech., 3, (1958) 1925.
- [2.33] A. S. Abdinov and V. K. Mamedov, Sov. Phys. Semicond., 14, (1980) 526.
- [2.34] A. Vahid Shahidi, I. Shih and C. H. Champness, Can. J. Phys., submitted.
- [2.35] R. C. J. Draper and A. Miller, Inst. Phys. Conf. Ser., 35, (1977) 265.
- [2.36] R. D. Tomlinson, E. Elloit, J. Parkes and N. J. Hampshire, Appl. Phys. Lett., 26, (1975) 383.
- [2.37] P. W. Yu, S. P. Faile and Y. S. Park, Appl. Phys. Lett., 26, (1975) 384.

[2.38] P. W. Yu, Y. S. Park and J. T. Grant, Appl. Phys. Lett., 28, (1976) 214.

ł

ł

- [2.39] I. Shih, A. Vahid Shahidi and C. H. Champness, J. Appl. Phys., 56, (1984) 421.
- [3.1] K. D. Becker and S. Wagner, Phys. Rev., B 27, (1983) 5240.
- [3.2] W. A. Tiller, K. A. Jackson, J. W. Rutter and B. Chalmers, Acta Met., 1 (1953) 428.
- [4.1] L. Mandel, R. D. Tomlinson and M. J. Hampshire J. Cryst. Growth, 36 (1976) 152.
- [4.2] S. S. Strelchenko, S. A. Bondar, A. D. Molodyk, L. I. Berger and A. E. Balanevskaya, Izv. Akad. Nauk SSSR, Neorg. Mat., 5 (1969) 593.
- [4.3] S. S. Strelchenko, S. A. Mondar, A. D. Molodyk,
 A. E. Balanevskaya and L. I. Berger, Russ. J.
 Phys. Chem., 41 (1967) 1679.
- [5.1] J. B. Nelson and D. P. Riley, Proc. Phys. Soc. 57, (1954) 160.

[5.2] M. J. Buerger, 'The Precession Method', John

Wiley and Sons Inc., (1964).

(🔿

÷

Ì

- [5.3] J. W. Jeffery, 'Methods in X-ray Crystallography' Academic Press, (1971).
- [5.4] J. S. Kasper and K. Lonsdale, 'International Tables for X-ray Crystallography', Vol. II Mathematical tables, Kyroch Press, (1959).
- [5.5] T. Araki, Department of Geological Sciences, McGill University, private communication.
- [6.1] P. Migliorato, J. L. Shay and H. M. Kasper, J. Elect. Mat., 4 (1975) 209.
- [6.2] R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelley and D. D. Wagman, Selected values of the Thermodynamic Properties of the Elements (Americ. Soc. Met., 1973), P.77, P.462, P.509.
- [6.3] N. G. Shyamprasad, 'Study of Photoconductivity in undoped Tellurium', McGill University thesis (1979).
- [6.4] N. G. Shyamprasad, C. H. Champness and I. Shih, Infrared Phys., 21, (1981) 45.

119