STRUCTURAL AND ELECTRONIC PROPERTIES OF CuInSe₂

A. Vahid Shahidi, I. Shih, T. Araki* and C.H. Champness

Department of Electrical Engineering, McGill University
3480 University Street, Montreal, P.Q., H3A 2A7, Canada.
*Department of Geological Sciences, McGill University.

(Received October 18, 1984; revised February 5, 1985)

Structural investigation on monocrystalline CuInSe₂ samples has been made. From the single crystal results, the space group of CuInSe₂ was confirmed to be I₄₂d and the crystal solidification direction was investigated. Compositional uniformity of the ingots was established by EPMA and it was found that the indium concentration was greater than that for copper. Systematic annealing experiments were carried out in vacuum at different temperatures (as low as 160°C) and for different times. Large variation in resistivity was observed after the annealing treatment. P-type samples were found to convert to n-type after the heat-treatments.

Key words: Copper indium diselenide, structural and electrical properties, annealing effects.

Introduction

The ternary semiconductor CuInSe₂ is a member of I-III-VI₂ compounds, which is an analog of the sphalerite modifications of binary II-VI compounds [1] with a direct energy gap of about 1 eV [2]. Due to its opto-electronic properties this material has received increasing attention.
as a candidate for opto-electronic devices, in particular for photovoltaic cells. Recently, thin film solar cells with an energy conversion efficiency greater than 10% [3] with good stability and a single crystal cell with an efficiency of 12% [4] have been reported.

The phase diagram based on the pseudo-binary Cu$_2$Se and In$_2$Se$_3$ has been determined [5] and the phase relations for this system with further improvements have been reported recently by Bachmann et al. [6]. Various methods have been attempted and reported for the preparation of thin film and bulk CuInSe$_2$ [7-10]. Recently, growth experiments were performed in our laboratory to prepare monocrystalline samples with improved electrical properties [11].

In a study on crystal structure using the powder x-ray method, Hahn et al. [12] reported that the compound CuInSe$_2$ crystallizes in a chalcopyrite form. Later in 1973, Parkes et al. [13] reported data on CuInSe$_2$ material based on x-ray powder diffraction results. They also reported unit cell parameters, which were obtained from an approximation method (involving the Nelson and Riley's extrapolation function [14]).

P- and n-type CuInSe$_2$ samples have been made and the conductivity type could be altered by heating the samples under minimum and maximum Se vapor pressure [15]. Parkes et al. [9] reported the conversion of n-type CuInSe$_2$ to p-type under maximum Se vapor pressure. Diffusion coefficients of Se in CuInSe$_2$ as a function of Se partial pressure was reported [16]. Attempts have also been made with regard to extrinsic doping experiments of CuInSe$_2$ using various dopants [17-19]. Temperature dependence of the electrical properties and possible scattering mechanisms for both p- and n-type samples have been reported and discussed [20,21]. Because the reported work in the literature on the electrical properties of CuInSe$_2$, especially the effect of annealing, has not been very extensive, more studies on annealing/doping are required in order to improve and to control the electrical properties of the material for device applications. In the present paper, the effect of annealing on as-grown p-type single crystal samples is presented and discussed. Also, unit cell parameters and structure analysis for CuInSe$_2$ based on single crystal x-ray experiments are given.