Thin film CdZnS/CuInSe₂ solar cells by spray pyrolysis

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Abstract. Cd₁₋₉ZnₓS/CuInSe₂ solar cells having efficiencies in the range of 2.3 % were fabricated by spray pyrolysis. The best cell had the following parameters: $V_{oc} = 305$ mV, $J_{sc} = 32$ mA/cm², FF = 0.32 area = 0.4 cm² and efficiency = 3.149 %. $V_{oc}$ versus temperature measurements showed that the electron affinity difference was 0.22 eV. Forward dark current versus voltage curves were plotted and a possible current mechanism occurring in these cells has been proposed.

Keywords. CuInSe₂ solar cells; thin film solar cells; CdZnS/CuInSe₂; spray pyrolysis.

1. Introduction

CuInSe₂ is a I-III-VI₂ ternary chalcopyrite semiconductor which has recently excited considerable interest as a photovoltaic material. It has a direct band gap of 1.02 eV and falls in the optimum range for terrestrial photovoltaic applications (Kazmerski et al 1976, 1977). Owing to its high absorption coefficient, it requires at the most a few microns of thickness to make devices. Besides, inexpensive thin film deposition techniques can be used in the fabrication. CuInSe₂ when paired with CdS, has a compatible lattice structure with a lattice mismatch of only 1.2 % and a favourable electron affinity difference (0.1 eV) (Tell et al 1972; Shay et al 1975; Chen and Mickelsen 1980). The CdS/CuInSe₂ solar cell has been modelled by Ireland et al (1979) and has been analysed as one of the highest efficiency photovoltaic heterojunctions available. A 11 % thin film CdZnS/CuInSe₂ cell prepared by an elemental three-source evaporation has already been demonstrated by the Boeing Aerospace Co., Washington (Hermann et al 1984). The Boeing cells have been found to have excellent stability owing to the tetragonal structure of CuInSe₂ (Mickelsen and Chen 1982).

2. Experimental procedure

2.1 CuInSe₂ films

Aqueous solutions of cupric chloride, indium trichloride and seleno-urea were mixed together in the Cu:In:Se ratio of 1:1:4 and sprayed onto glass substrates heated to 300°C to obtain CuInSe₂ films about 1 µ thick. The films were characterized by x-ray diffraction, optical transmission spectra, transmission electron microscopy (TEM), scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS) and electrical measurements. The properties of these sprayed films have been reported elsewhere (Agnihotri et al 1983; Raja Ram et al 1985).
2.2 Fabrication of cells

A number of Cd$_{0.85}$Zn$_{0.15}$S/CuInSe$_2$ solar cells having efficiencies in the 2–3% range were prepared by spray pyrolysis. Indium tin oxide films of high transmission and low sheet resistance (1–5 Ω/□) were used as the substrates for the junctions.

The ITO substrates were placed on a hot plate, partially covered and heated to 350°C. A 1.5 μ thick layer of Cd$_{1-x}$Zn$_x$S (x = 0.15) was grown on the uncovered portion of the ITO by spraying a mixture of aqueous solutions of CdCl$_2$, ZnCl$_2$ and thiourea. Indium (5–10%) in the form of InCl$_3$ solution was also added to reduce the resistivity of the CdZnS layer. The substrates were further covered and about 2 μ of CuInSe$_2$ were grown at 300°C. The junctions were then removed from the hot plate and fitted inside a vacuum coating chamber to deposit the gold contact on the CuInSe$_2$ back layer. Thus junctions of the type ITO/CdZnS/CuInSe$_2$/Au were formed.

2.3 Characterisation of the cells

The cells were illuminated at 100 mW/cm$^2$ through the glass, ITO and CdZnS, and the I-V characteristics were plotted on an automatic I-V plotter. The values of $V_{oc}$ versus

![Image of I-V characteristics](image-url)

Figure 1. I-V characteristics of a CdZnS/CuInSe$_2$ solar cell illuminated at 100 mW/cm$^2$. 