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# Fabrication of vacuum-evaporated SnS/CdS heterojunction for PV applications

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# ABSTRACT

SnS/CdS heterojunction is a promising system for the fabrication of thin film solar cells. In our work, thin film SnS/CdS heterojunction was prepared by evaporating CdS and SnS films. The photovoltaic properties of the heterojunction were investigated with posttreatment of the window material treatment by CdCl<sub>2</sub> for grain size enlargement. *I–V* characteristics in dark and at light were taken and figures of merit were evaluated. The efficiency with and without window layer treatment were about 0.08% and 0.05%, respectively, under 100 mW/cm<sup>2</sup> intensity. To the best of our knowledge so far there has been no report on vacuum-evaporated SnS-based heterojunction with window material treatment by CdCl<sub>2</sub>.

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# 1. Introduction

Recent interest in thin film photovoltaics is primarily due to improvements in conversion efficiency of cells and effective lowering of the manufacturing costs compared to expensive crystalline and polycrystalline silicon technology. Attempts have been made for searching non-toxic, cost-effective new materials which are tailor-made for that purpose.

Tin sulfide is a IV–VI compound semiconductor with layered orthorhombic structure, where each layers of S and Sn atoms are bonded by weak van der Waals forces [1,2]. It is a promising material for low-cost photovoltaic conversion of solar energy because it usually exhibits p-type conductivity and room temperature band gap reported to be 1.30 eV [3], lying midway between that of Si (1.12 eV) and GaAs (1.43). It has a high absorption coefficient ( $\alpha > 10^4 \text{ cm}^{-1}$ ) in the solar spectrum comparable to that of CdTe. Both Sn and S are cheap and nontoxic in nature. Thus SnS is a material of great importance in solid-state device fabrication like photoconductors [4], photovoltaic conversion [5–8], holographic recording media [9], solar control device [10], near-infrared detector [11] etc.

For photovoltaic applications p-SnS being the absorber material requires an n-type wide bandgap transparent semiconductor (TS) as the heterojunction partner. Essentially among all known TS, non-stoichiometric or doped oxides and sulfides such as SnO<sub>2</sub>,

ZnO, CdS and ZnS may be the best choice for n-type material as the heterojunction partner for p-type SnS. Previous workers fabricated SnS/CdS heterojunction by chemical methods [5-8]. They mainly focused their attention to fabricate low-resistive CdS window material by introducing different dopants (Ag, In) but at the same time paid little attention to the substantial amount of impurity phase present in the absorber layer. Tin sulfide thin films fabricated by chemical methods were usually accompanied by unintentional and uncontrollable doping and thereby were highly susceptible to form defects due to inherent nature of the postformation process. Moreover, in wet chemical method of fabrication possibility of phase mixture (SnS, SnS<sub>2</sub>) could not be ruled out owing to the stability of Sn<sup>2+</sup>, Sn<sup>4+</sup> system. However, no such amount of phase mixture was present in the films fabricated by evaporating high-purity tin sulfide powder. The mechanism of evaporation of tin sulfide takes place according to the equation  $(SnS)_{Solid} \leftrightarrow (SnS)_{Vapor}$  with trace amount of  $SnS_2$  present in the vapor [4,12,13]. Using pure CdS or that doped with Ag as the heterojunction partner with SnS, researchers reported the photovoltaic conversion efficiency, which is far below than the theoretically expected level [12,13]. Noguchi et al. studied CdS/ SnS heterojunction by successive deposition of n-CdS, p-SnS and Ag on ITO coated glass substrate [14]. In this context, the present paper has intended to study the following:

- (a) The photovoltaic properties of SnS/CdS heterojunction after post deposition annealing and the effect of heat treatment on the crystallinity and composition of the absorber layer (SnS).
- (b) The effect of CdCl<sub>2</sub> treatment on the window layer (CdS) and its manifestation on the cell performance.





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# 2. Experimental techniques

Fabrication of thin film vacuum-evaporated SnS/CdS solar cell comprised of four distinct steps. These were

- (a) low resistive and high transmittive CdS film preparation,
- (b) fabrication of SnS layer onto CdS,
- (c) SnS/CdS junction formation,
- (d) Back contact fabrication.

These are at seriatim shown in Fig. 1.

# 2.1. CdS film fabrication

Polycrystalline CdS films of 0.3 µm thickness were grown through standard high vacuum evaporation technique by evaporating high-purity CdS powder (99%) at 180 °C substrate temperature onto previously cleaned ITO coated glass substrate having typical transmission in the range of 80-85% in the visible-nearinfrared range and a sheet resistance in the range of 12-15  $\Omega$ /square. The as-deposited films were free of pinholes and strongly adherent to the substrate with a typical carrier concentration in the range of  $10^{14}$ – $10^{16}$  cm<sup>-3</sup> and had a mobility of 300 cm<sup>2</sup>/V s. Absorption studies indicated that the deposited films had band gap in the range of 2.4-2.45 eV. It was observed previously that the resistivity of the CdS thin films grown chemically remain lower compared to that deposited using physical vapor deposition, probably due to the unintentional and uncontrolled chlorine doping [15]. The basic requirements of these CdS films for optoelectronic applications are high optical transparency, low dark electrical resistivity, high photoconductivity and better crystallinity. CdS film grown by vacuum evaporation method renders poor electro-optic properties. To combat the problem, various dopants like Cu, Ag, In, Cl can be incorporated for lowering the dark resistivity of pure CdS thin film but simultaneously there is a decrease in the photoconducting response of the doped CdS thin film.

#### 2.1.1. Cadmium chloride treatment: chlorine doped CdS

Doping by chlorine has some significant effect on structural, optical and electrical properties of CdS thin films. It attributed improved transmission and grain size enlargement resulting in lower shunt resistance and resistivity [16].

The as-deposited vacuum-evaporated CdS films were dipped into 0.01 M  $CdCl_2$  solution for some time, followed by backing in



Fig. 1. Configuration of SnS/CdS thin film solar cell.

presence of air at 550 °C for 4-6 min. Such processing caused appreciable grain size enlargement and the significant reduction of lattice defect states. This in turn lowered the number of highresistance paths of CdS thin films [17] and thus lowering the series resistance of CdS/ITO structure by an order of magnitude. Thus, cadmium chloride treatment contributed to the smaller series resistance of the whole solar cell through the overall improvement of optical properties of CdS thin films [18]. With higher doping concentration there was decrease in resistivity and marked improvement of carrier concentration and mobility [15,16]. So the higher grain size would allow the carriers freely in the lattice resulting in reduction in the resistivity. The CdS films obtained after CdCl<sub>2</sub> treatment were etched with dilute HCl to get a cone and valley structure. Fig. 2a and b shows the XRD spectra of untreated and CdCl<sub>2</sub>-treated CdS films, respectively, of 0.3 µm thickness (evaporated on ITO coated glass). As a result of CdCl<sub>2</sub> treatment, prominent cubic phases appeared in the film besides the weak hexagonal phases in the untreated film. The grain sizes,



Fig. 2. (a) XRD spectra of untreated CdS film. (b) XRD spectra of CdCl<sub>2</sub>-treated CdS film.

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