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STUDIES ON VACUUM ANNEALED CADMIUM SULPHIDE SINTERED PHOTO-CONDUCTIVE LAYERS

MRS MARY JULIANA CHOCKALINGAM, R MAHALINGAM, K NAGARAJA RAO, I RADHAKRISHNA, N RANGARAJAN AND C V SURYANARAYANA

Central Electrochemical Research Institute, Karaikudi 623 006

ABSTRACT

The effects of heat-treatments in vacuum on the electrical and photoconductive properties of screen printed and sintered layers of cadmium sulphide have been studied. The dark conductivity of the sintered layers is found to increase by several orders of magnitude. These layers are useful for making solar cells.

INTRODUCTION

Thin film photovoltaic cells based on heterojunctions have been considered for many years as interesting alternatives to single crystal solar cells. Thin film technology is highly suitable for making cheap and viable photovoltaic cells useful for solar energy conversion. The most promising thin film photovoltaic generator which has been widely investigated and where much progress in research and technology has been obtained during the last few years is the CdS/Cu_2S solar cell. It is expected that this type of solar cell can reach the price goal which has been defined for economical operation competitive to conventional power plants.

Thin film solar cells require a minimum of material and energy input. This is an important advantage in view of the availability of materials and pay-back time of solar cells.

CdS films required for solar cell fabrication may be obtained by (1) vacuum vapour deposition (2) sputtering (3) spray deposition and (4) sintering. Certain advantages are noticed in the sintering technique : a) large area cells can easily be made b) incorporation of impurity is easy c) good bonding to substrate is obtained and d) the method is less expensive. The only disadvantage with the method is that the dark resistivity of the CdS layers sintered in air is very high of the order of 10^8 ohm-cm. In this paper, the sintered layers have been annealed in vacuum to obtain the desired resistivity of 1 ohm-cm to 100 ohm-cm. The effects of vacuum annealing studies on CdS have been studied previously [1, 2]. Recently an efficiency of 12.8% has been reported on screen printed and sintered CdS/CdTe solar cells [3].

EXPERIMENTAL

High purity CdS powder is obtained by the interaction of cadmium acetate with thiourea under optimum pH conditions. A slurry is prepared using the powder, a fluxing material and a non-aqueous solvent, and then painted on ceramic substrates by the screen printing technique. The layers are sintered in an atmosphere of air in the temperature range between 500°C and 600°C for about 30 minutes. Ohmic contacts of indium with an inter-electrode spacing of 1 mm are applied on the CdS layers by employing Hind Hivac Vacuum coating unit Model 12A4.

The resistance values have been measured using Keithley Solid State Electrometer, Model 610C. The thickness values of the sintered CdS layers as measured with the TESA Digital micrometer have been found to be 25 microns. For vacuum annealing studies, the sintered layers have been introduced into the Vacutherm Microfurnace. Vacuum heat-treatments have been carried out at various temperatures for a period of 30 minutes in a vacuum of 10^{-5} torr.

RESULTS AND DISCUSSION

From the present investigation, the values of resistance of the CdS cells and the photosensitivity obtained by dividing dark resistance by light resistance are given in Table I. The sintered cell before vacuum annealing possesses dark resistance value of 500 MΩ and light resistance value of 50 KΩ at 100 lux. The photosensitivity before vacuum annealing is equal to 10^4. On vacuum annealing, the dark resistance of these cells changes considerably and so also the light resistance.

Table I : Relationship between vacuum annealing temperature and resistance

Temperature in °C	Dark resistance in ohms ($\times 10^3$)	Resistance at 100 lux in ohms ($\times 10^3$)	Photo-sensitivity
250	250	30	8.3
300	13	9	1.4
350	4	4	1.0
400	45	30	1.5
450	70	40	1.8
500	350	45	7.8
550	100×10^3	150	667
700	300×10^3	1.4×10^3	215

It is observed that the dark resistance decreases from 500 MΩ (as sintered in air) to 250 KΩ when heat-treated in vacuum at 250°C reaching a minimum of 4×10^3 ohms at 350°C. This reduction in resistance is due to the desorption of oxygen states. Above 350°C, again the resistance values increase as the temperature is increased upto 700°C. Thus we notice that the dark resistance value decreases by 5 orders of magnitude at 350°C. Photo-sensitivity also is the least at 350°C. Oxygen centres act as sensitizing centres in CdS. They immobilize holes. When all the oxygen states are desorbed, holes are made free which recombine with photoexcited electrons thereby destroying photosensitivity.

The effects of heat-treatments in vacuum and in air at relatively low temperatures (120°C) have been reported [4]. In those experiments vacuum heat-treatments have not altered the conductivity markedly while air treatments decrease it by two orders of magnitude. However, a decrease in resistivity by four orders of magnitude is reported when samples were subjected to annealing at 260° ± 20°C at a high vacuum [5]. This is attributable to oxygen desorption. The present experiments also behave in a similar fashion.

The sintered cadmium sulphide layers possess very high resistance values. This is due to the compensation caused by the acceptor-like oxygen states. Oxygen chemisorption phenomenon on cadmium sulphide crystals both as to its kinetics and energetics has been studied [6]. It has been established that oxygen forms deep acceptor-like states in cadmium sulphide with a level at 0.91 eV below the conduction band. The present investigation confirms this behaviour.

The adsorbed oxygen acts like an acceptor impurity. On the one hand, this causes a decrease in electron density and on the other hand acts as a trap for the carriers that increase the potential barrier at the grain boundaries. This in turn affects the mobility according to the relation [7, 8].

$$\mu = \mu_0 \exp\left(\frac{-q\phi}{kT}\right)$$

where μ represents the mobility, μ_0 the mobility at absolute zero, q represents the number of charge carriers, and ϕ represents the potential barrier between the grains.

The reduction in resistivity observed when samples were annealed in vacuum upto 350°C indicates the loss of oxygen and chlorine from grain boundaries with a consequent reduction in ϕ.

The increase in dark resistance that we have observed when the temperature of heat-treatment is above 350°C might be due to the secondary recrystallization occuring at this temperature as a change in preferential orientation. A recrystallization temperature at 350°C is low compared with the value of 600°C reported earlier [9] for pure CdS deposited in vacuum. However, the presence of impurities other than oxygen, which are known as inhibitors of recrystallization, may produce this effect. During recrystallization, the grain boundary movement due to crystallite growth would incorporate the impurities into the boundaries. These impurities seem to act like sensitizing centres with the result that photosensitivity increases above 350°C. At 700°C, some of the acceptor-like impurities will be removed. Hence, photosensitivity decreases.

It has been noticed earlier that the minimum resistance occurs at 500° C vaccum annealing [1]. In this case, the starting material was cadmium chloride instead of cadmium acetate. When cadmium chloride is the starting material, it is likely that more chloride ions might have entered the lattice during sintering. This has been confirmed and the dark resistance value is found to be 2 MΩ for these samples [1]. When vacuum annealing was carried out with this sample upto the temperature of 500°C, oxygen and chlorine might have come out of the lattice giving rise to increased donor concentrations. In the present case, since cadmium acetate is the starting material oxygen alone will disappear and this happens at a lower temperature of 350°C. From the dark resistance value, the dark sensitivity of the CdS layer after vacuum annealing at 350°C works out to be 100 ohm-cm. Such layers are useful for CdS heterojunction solar cells.

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