TECHNICAL DEVELOPMENT

J. Sci. Soc. Thailand, **9 (1983)** 257 - 264

INVESTIGATION OF POLYCRYSTALLINE CADMIUM SULPHIDE PHOTOCELLS

T.TUNKASIRI, J.TONTRAKOON, N.SIRIRATWATANAKUL and S.THONGTEM.
Department of Physics, Faculty of Science, Chiang Mai University, Chiang Mai, Thailand

(Received 18 July 1983)

Abstract

Cadmium sulphide photoconductive cells were prepared on clean glass slides by slow precipitation techniques. The doped solution was prepared using various concentrations of cadmium sulphide (CdS), cadmium chloride ($CdCl_2$) and cupric chloride ($CuCl_2$). Amounts of CdS and $CuCl_2$) were fixed at 20 and 0.02 millimoles respectively, but that of $CdCl_2$ varied from 3 to 7 millimoles. Gold leaves were employed as contacts. Annealing was carried out at 600 °C with gradual raising of temperature. The current-voltage characteristic curves of the cells were investigated and compared with those of undoped, evaporated, film of CdS, and laboratary phototube and light dependent resistors (LDR). The cells produced with the $CdCl_2$ concentrations of 3 and 5 millimoles showed good sensitivity and the currents were of the same order as those produced in the phototube and LDR.

Introduction

Cadmium sulphide (CdS) has long been studied for the possibility of producing solar cells. Since the discovery of the photovoltaic effect in single crystal CdS and in thin CdS film in 1954, work concerning (CdS) has been carried out intensively. During the late 1954's, thin layers of semiconductor materials were sought to reduce solar cell material costs and increase the power to weight and weight-per-unit-area ratios for space application. Cadmium sulphide as well as other II-VI compounds were available for producing thin film semiconductor layers on substrates like glass, metal foil or plastic films. The polycrystalline films exhibit higher radiation resistance than silicon cells. By 1961 thin film CdS cells, having 5.2% efficiency and 0.2 cm^2 area, had been developed. Photosensitivity of powder

CdS was also investigated[1]. Its conductive photosensitivity after being doped with copper was highly pronounced post proper annealing. However, the efficiency of the cells are limited due to the instability of CdS[2]. A pilot line production attempt during 1966 and 1967 to improve both efficiency and cell stability was not successful.

The efficiency of the CdS cell achieved so far is in the order of 8 % at room temperature[3]. This limited efficiency, however, does not detract from the potential attractiveness of CdS cells, because their fabrication cost is predicted to be at least one order of magnitude lower than the cost of silicon or gallium arsenide cells. In this paper , an attempt to improve the stability of the CdS cells was carried out. Precipitation techniques[4] and Bube's method[5] of doping were employed.Glass slides on which the contact had already been prepared, were used as substrates. After annealing, the conductive photosensitivity of the samples was studied. The results were comparble to those of Light Dependent Resistor (LDR).

Materials and Methods

A beaker was cleaned with ordinary detergent, rinsed with water , and then left to dry. A slurry of CdS (hexagonal unit cell) was made by placing 20 millimoles of CdS in the bottle and adding 3 millimoles of cadmium chloride ($CdCl_2$) as an aqueous solution in about 20 ml of distilled water from a burette. Further distilled water was then added to make the solution up to 40 ml and the whole shaken well 3 mg (approximately 0.02 millimoles) of cupric chloride ($CuCl_2$) solution was added and the mixture shaken for one hour. The amout of $CuCl_2$ was as discribed by Tunkasiri *et al.*[6]. The solution was then slowly dropped onto a glass substrate (using a pipette). covering the area of about 2x2 cm. Gold leaf was employed as the contact[1]. The cell was dried in the air for 24 hours and then gradually annealed up to 600° C. Current-voltage characteristic curves of the cells were measured in the dark and on irradiation with white light. The circuit used to measure the I-V curves was shown in Figure 1. Forty-watt Philips bulb was employed.

The procedure was repeated using 0.92 g (5 millimoles) of $CdCl_2$ and 1.28 g (7 millimoles) instead of 3 millimoles used originally. The whole procedure was also repeated sothat there were 5 samples to be experimented in each set of cells (ie 5 samples of cell D, F and G). Typical results were shown in Table 1.

The measurement of I-V characteristic was also carried out with an unannealed, undoped evaporated thin CdS film, a laboratory phototube and a Light Dependent Resistor (LDR) for comparison. The results were presented inTable 2. The data of cells D, F and LDR were plotted in Figure 2.

Results and Discussion

From the Figure 2 we can see that the photosensitivity of the cell D and F are very close to that of LDR. The surface of the cells (examined through an ordinary microscope) showed cracks and small grain boundaries. This may be due to shrinkage of the polycrystallines at the high temperature annealing. However annealing at the temperatures lower than 500 °C did not change the cells from being insensitive[6].

TABLE 1 I-V CHARACTERISTICS OF CELLS D, F AND G AFTER ANNEALING AT 600 ° C.

Cell D				Cell F				Cell G			
Dark		Light		Dark		Light		Dark		Light	
V	μA	V	μA	V	μA	V	μA	V	μA	V	μA
0	0	0	0	0	0	0	0	0	0	0	0
3.95	0.5	0.58	3.2	0.6	0.20	3.5	2.51	2.0	0.54	3.5	
8.43	0.9	0.79	7.1	8.0	2.4	0.40	7.4	3.07	5.5	0.74	7.5
13.18	1.3	0.93	11.0	11.0	4.3	0.56	11.5	3.37	8.0	1.08	11.5
17.70	1.75	1.02	15.0	11.3	4.7	0.71	15.5	3.75	13.0	1.20	15.5
21.8	2.2	1.15	19.0	14.8	8.0	0.86	20.0	3.99	17.0	1.33	19.5
26.4	2.65	1.27	23.5	16.6	9.0	0.98	24.0	4.2	22.0	1.48	23.4
30.9	3.10	1.33	27.5	19.2	11.5	1.14	27.5	4.47	25.0	1.59	27.4
35.5	3.55	1.43	31.5	24.5	12.0	1.20	32.0	4.68	28.0	1.79	31.0
40.05	4.05	1.52	36.0	30.4	12.0	1.33	36.0	4.92	33.0	1.8	35.5
44.3	4.85	1.60	40.0	32.5	13.5	1.54	40.5	5.10	37.0	1.90	40.0

TABLE 2 I-V CHARACTERISTICS OF AN UNDOPED, EVAPORATED FILM OF CdS, A LABORATORY PHOTOTUBE, AND A LDR.

Evaporated Cds				Phototube				LDR			
Dark		Light		Dark		Light		Dark		Light	
V	μA	V	μA	V	μA	V	μA	V	μA	V	μA
0	0	0	0	0	0	0	0	0	0	0	0
3.2	0.56	3.2	0.56	4	0	0.5	2.46	4	0	0	2.82
6.4	1.13	6.4	1.13	8	0	1.6	4.51	7.8	0.14	0	5.63
9.4	1.83	9.4	1.83	12	0	2.9	6.41	11.6	0.28	0	0.45
12.4	2.53	12.4	2.53	16	0	4.8	7.89	15.4	0.42	1	11.27
15.4	3.24	15.4	3.24	20	0	7.3	8.94	19.2	0.56	0	14.08
18.4	3.94	18.4	3.94	24	0	10.4	9.58	23.0	0.70	0	16,90
21.4	4.64	21.4	4.64	28	0	13.8	9.99	26.7	0.92	0	19.72

TABLE III DARK CURRENTS OF THE SAMPLES (20 VOLTS APPLIED)

Sample	Number of cells	Dark current (μA)
Cell D	5	2.0[a]
Cell F	5	14.0[a]
Cell G	5	50
Evaporated CdS	1	4
Phototube	1	0
LDR	10	0.7[a]

[a] average value

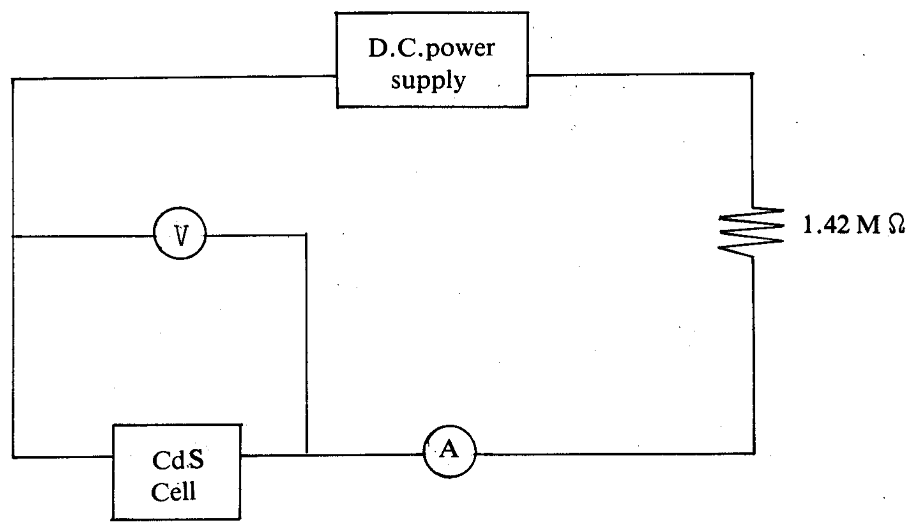

Figure 1 Circuit for the determination of the voltage-current characteristic of the CdS photo-cells.

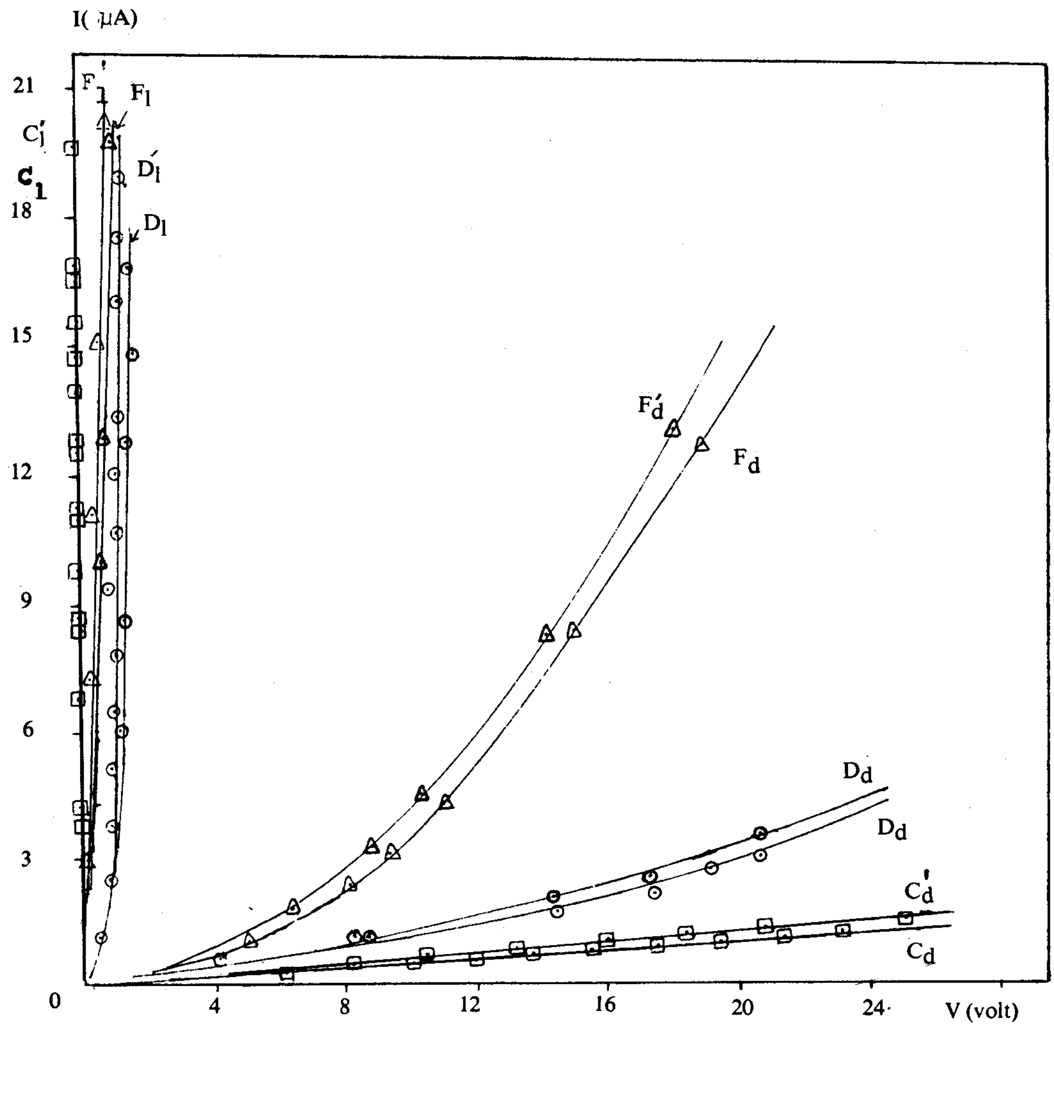

Figure 2 Two sets of the Current-voltage characteristic curves of cells D (D,D′), F (F,F′) and LDR (C,C′). Subscripts l and d stand for light and dark current respectively.

Light currents of the cells D and F were very close together while the dark currents of the cells show some differences. This may be due to the different amounts of $CdCl_2$ Similar results were also obtained with other samples of cells D and F (not shown). Therefore we may conclude that the higher the concention of $CdCl_2$ used the higher the dark currents of the cells were.

From Table 2, we can see that, the unannealed, undoped, evaporated thin CdS films showed very low photo-sensitivity whilst the low temperature annealed film showed no photo-sensitivity. The dark currents values were all summarized in Table 3, including that of the laboratory phototube. Apparently cells D and F showed very good sensitivity when compared to that of LDR and the phototube. The dark currented of cells F were highest nevertheless (see Table 3). This may be due to the concentration of $CdCl_2$ as mentioned earlier.

Work has been pursued to give reproducible results for cells D and F. Twenty of cells D and F were then prepared under the same conditions as before. I-V characteristic was measured on each cell. The results showed similarity to those presented in Table 1 with discrepancy in the range of 5 %. Dark currents of cells D were less than 3 uA but that of cells F varied from 12 to 15 /µA. when 20 volts were applied. However, 4 and 5 of cells D and F respectively, broke down after firing at 600°C. Therefore, othee substrates such as fireclay[7] must be studied to replace glass slides.

With slow precipitation techniques[4] and gradual annealing methods applied, the polycrystalline CdS photocells were still unstable. This may be due to shrinkage of the the polycrystalline CdS photocells were still unstable. This may be due to shrinkage of the grains after annealing and degradation (due to moisture absorption) of the CdS crystal. Thin CdS films can also be prepared by spraying methods[8,9] which could have avoided the shrinkage of CdS films. The surface of CdS could also be prevented from degradation by applying encapsulation techniques like those of implanted GaAs. Polycrystalline CdS cells could then be further developed, and which could have better stability and higher effeciency.

Acknowledgement

The authors would like to thank the National Research Council for a grant and Dr.P. Thavornyutikarn for his help in preparation of chemical solutions.

References

1. National Research Council (1977-1979) Reports on 'Change of Semiconductors due to High Temperature Annealing', NRC, Bangkok.
2. Spear W.E., and Anderson D.A. 1977 Phil. Mag., **36**, 695.
3. Michels T.(1981) *Solar Utilization,* Van Nostrand Reinhold, New York.
4. Kaelble E.F. (1967) Handbook of X-Rays McGraw-Hill, New York, p. 25.
5. Bube R.H., and Themsen S.M. (1955) J.Chem. Phys 23, 15.
6. Tunkasiri T., Tontrakoon, J., Siriratwatanakul, N., and Anantachai S. (1980) *J.Fac. Sci. Chiangmai University* **7**, 1.
7. Smith E.V. (1970) *Manual of Experiments in Applied Physics,* Butterworths, London.

8. Brewster R.Q. and McEwen W.E. (1968) *Organic Chemistry,* Prentice-Hall of India Private Limited.
9. Jittagawe Y. (1982) Master Thesis,Faculty of Science, Chiangmai University Chiangmai, Thailand.

บทคัดย่อ

เซลล์ไวแสงแอุดเมียมซัลไฟด์สร้างขึ้นจากการเตรียมสารบนแผ่นแก้วสไลด์ด้วยวิธีตกตะกอนอย่างช้า ๆ สารละลายเตรียมจากส่วนผสมของแคดเมียมซัลไฟด์, แคดเมียมคลอไรด์และคิวปริคคลอไรด์ต่าง ๆ กัน ความเข้มข้นของแคดเมียม–ซัลไฟด์และคิวปริคคลอไรด์ คงที่คือ 20 และ 0.02 มิลลิโมลตามลำดับ แต่จำนวนแคดเมียมคลอไรด์แปรจาก 3 ถึง 7 มิลลิโมล ขั้วไฟฟ้าใช้แผ่นทองคำเปลว หลังจากนั้นเผาที่อุณหภูมิ 600°ซ โดยค่อย ๆ เพิ่มอุณหภูมิ การตรวจสอบเซลล์กระทำโดยการวัดค่ากระแส–ความต่างศักย์ของเซลล์เปรียบเทียบกับหลอดโฟโต แผ่นฟิล์มแคดเมียมซัลไฟด์ที่เกิดจากการระเหยในสูญญากาศและตัวความต้านทานที่แปรค่ากับแสง (LDR) ผลจากการวัดแสดงให้เห็นว่าเซลล์ที่สร้างจากแคดเมียมคลอไรด์ 3 และ 5 มิลลิโมล จะมีความไวต่อแสงมากค่ากระแสพอจะเทียบกับหลอดโฟโตและความต้านทานที่แปรกับแสง