Mansoura Engineering Journal, (MEJ), Vol. 19, No. 3, September, 1994, E. 62

Chemical-Vapor Deposited Thin Films of Cadmium Sulphide for Photovoltaic Applications

طبقات رقيقة من كبريتيد الكادميوم بواسطة الترسيب الكيميائى البخارى

لتطبيقات الضوء - فولتية

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الخلاصة : تم ترسيب طبقات رقيقة من كبريتيد الكادميوم على حاملات تحتية من الزجاج و السيراميك وذلك باستخدام الترسيب الكيميائى البخارى فى نظام تدفق مفتوح ، وتم تشخيص طبقات كبريتيد الكادميوم المرسبة بالنسبة إلى الشكل الظاهرى ، حجم الحبيبات ، و الخواص التركيبية ، وتم أيضا فحص الخواص الكهربية للطبقات الرقيقة بواسطة قياس المقاومة النوعية فى الظلام وفى الضوء وتحركية هول ، وتم أيضا فحص تأثير بارامترات الترسيب على خصائص الطبقات الرقيقة ، وقد تمنا بإجراء تخمير حرارى لطبقات كبريتيد الكادميوم الرقيقة وذلك فى جو من كبريتيد الهيدروجين و فى جو من الهيدروجين ، وذلك لتحسين الخواص الكهربية للطبقات الرقيقة .

Abstract : *Thin films of cadmium sulphide have been deposited on glass and ceramic substrates using chemical vapor deposition in an open flow system. The deposited CdS films were characterized with respect to morphology, grain size and structural properties. The electrical properties of the films were also checked by measuring the dark- and light resistivity and the Hall mobility. The effect of deposition parameters on the film characteristics was investigated. Annealing of the deposited CdS films in an H_2S atmosphere and in H_2 was done to improve the electrical properties of the film.*

Recieved in 2/6/1994

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INTRODUCTION

Polycrystalline semiconducting thin films are one of the promising candi for low-cost fabrication of large-area solar cells for large-scale terrestrial. Compound II-VI semiconductors have gained much greater importance rec because of their potential as optimum materials for fabricating polycrystalline film photovoltaic cells [1,2]. Compound II-VI semiconducting thin films ar used as absorbers or as windows in pn junction solar cells [3,4] of the hon heterostructure type. CdS is a very promising material because of its intere photovoltaic properties and ease of fabrication [5,6]. Cadmium sulphid characterized by a steep absorption coefficient versus wavelength curve, as sh in figure (1), resulting in the absorption of of solar energy close to the surface o material. It also has short carrier lifetimes, which is a consequence of the d optical transition, and this assures a large α L product (absorption coeffic diffusion length product) even if L is small. Efficient solar converters can b fabricated by suitable surface and geometrical design of the cell, i. e. , sr junction depth with low surface recombination velocity. A further advantage i very thin layers of CdS conductors are required to effectively absorb the inc radiation. Different polycrystalline thin film CdS-based solar cells rep include Cu_2S/CdS, CdTe/CdS, InP/CdS, and $CuInSe_2$ /CdS cells [7]. Se methods have been used for the economic deposition of thin polycrystalline films for photovoltaic application [8], including physical methods, such as va evaporation [9-12], sputtering [13,14], and chemical methods, such as ele spray pyrolysis [15-17], chemical bath deposition (electrodeposition) [1 screen printing and sintering [24,25], close-spaced vapor transport (CSVT 28], chemical vapor deposition (CVD) [29,30], and organometallic chemical deposition (OMCVD) [31].

Heat treatment of the deposited CdS films was reported, in air, in H_2 [14, nitrogen, and in an H_2S atmosphere [11,31] to improve the electrical proper the film, and was found to reduce the resistivity of vacuum-evaporated CdS due to an increase in the free carrier concentration and in the Hall mobility and to improve the CdS/CdTe junction properties and to increase th conductivity in ZnS crystals [33].

In this paper we report the deposition of thin CdS films on conducti insulating substrates using chemical vapor deposition, characterization structural and electrical properties of the film, and investigation of the ef annealing of the CdS film in hydrogen on the properties of the deposited films

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CADMIUM SULPHIDDE FILM DEPOSITION

Substrate Selection And Preparation

The substrate selected for the deposition of CdS must be of low cost and must have certain electrical, chemical, and mechanical properties. It must provide low resistance ohmic contact to the film, must not introduce impurities into the active layer, and must be mechanically and thermally compatible with the deposited layer. The structural properties of the substrate must also be considered, since they greatly affect the microstructure and the crystallographic properties of the CdS film. The substrate must also be chemically inert to the deposition environment of the CdS film.

Two types of substrates were used for the deposition of CdS films. An insulating glass substrate (Corning glass 7059) was used to allow the characterization of the electrical properties of the film, such as Hall measurements, and a conducting carbon-coated burnished graphite substrate. The graphite substrate surface was coated with a 2-3 μm carbon layer to make its surface more uniform and reduce its porosity. Thermal decomposition of propane at 1100-1200 °C in an argon atmosphere was used. Before the coating the substrate was thoroughly degreased and ultrasonically cleaned.

Film Deposition

Chemical vapor deposition (CVD) was the method selected for the CdS film deposition because it offered three main advantages. 1) A wide range of film thickness can be easily achieved and controlled, 2) The dopant concentration and distribution in the film can be controlled better than many other techniques, and 3) it is a less expensive technique that is well suited for large-scale mass production. It is necessary that the chemical reaction be predominantly heterogenous, taking place on the substrate surface. Volume reactions, on the other hand, result in the deposition of clusters of random orientaion which will produce a non-adherent deposit. Furthermore, the reaction by-products must be volatile at the processing temperature, to insure high purity of the deposited film.

The reaction used for the deposition of CdS films is:

$$H_2S\,(g) + Cd\,(vapor) \xrightleftharpoons{550\text{-}650\ ^\circ C} CdS\,(s) + H_2\,(g),$$

Figure (2) shows the setup used for the CVD deposition of the CdS film in a gas flow system. A three-zone resistively-heated furnace was used. A cadmium quartz boat (filled with high purity cadmium) and the substrate(s) were placed in the appropriate temperature zones. The cadmium boat was kept at a temperature of about 410 °C, corresponding to cadmium pressure of 2×10^{-2} atm. Graphite substrates 3 x 3 cm and ceramic (Mullite) substrates 1 x 1 cm were used. Typical substrate temperature ranged from 450 to 570 °C. Deposition time was 15 - 45 min. Indium was used for doping some of the samples (an additional indium boat was inserted). Table (1) summarizes some of the parameters of the different CdS depositions performed.

Properties Of The CdS Film

Well adherent, polycrystalline films of CdS were obtained by the CVD deposition. The films were characterized with respect to structure and morphology in addition to characterization of their electrical properties.

Structural Properties - Optical microscope was used to examine the microstructure of the deposted CdS films. The substrate temperature is the most important factor that determines the average grain size in the film. The maximum grain size in each run was measured, and is shown in figure (3) as a function of substrate temperature and film deposition time. The number labels indicate sample number. The maximum grain size ranged from 2 μm to 18 μm. High substrate temperatures resulted in higher deposition rates and large grain films. However, the rate of nucleation is reduced at high substrate temperatures, which could result in discontinuities in the films. Figure (4) shown the CdS film thickness as a function of substrate temperature and film deposition time.

Electrical Properties - The electrical resistivity of the CdS films deposited on glass substrates was measured at room temperature in the dark and under normal room (flourescent) light. Hall measurements at room temperature by the van der Pauw technique was also performed on the same samples to measure the Hall mobility of the carriers in the film and the free carrier concentration. Ohmic contacts to the films were made by the vacuum evaporation of 1.25 Å indium dots of about 1 mm^2 area each at the corners of the substrate through a metal mask followed by contact annealing in hydrogen at 300°C for 40 minutes. The films were $n - n^{++}$ -type having a room-temperature resistivity of 3.27×10^{-2} Ohm.cm, carrier mobility of 8.19 $cm^2/V.sec$, and carrier concentration of 2.3×10^{19} cm^{-3}. Indium doped CdS films had values of $n = 2.8 \times 10^{16} - 1.7 \times 10^{17}$ cm^{-3} and $\mu = 12$ - 4 $cm^2/V.sec$, for the room - temparature free carrier concentration and mobility, respectively. The room-temperature resistivity of some other samples ranged from 160 to about 2,000 Ohm.cm. Table (2) shows the room - temparature free carrier concentration and Hall mobility for some of the In-doped CdS samples, and figure (5) shows the resistivity of the deposited films as a function of deposition temperature and film deposition time. The number labels are resistivity values.

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The electrical properties of CdS films on conducting substrates were evaluated by measuring the current-voltage characteristics from dot-to-dot and through the indium dots, which were separated by about 2.2 mm.. Figure (6) shows the dot-to-dot measurement, giving R_D = 10 M.ohm and R_L = 4 M.ohm. Figure (7) shows the current-voltage characteristics for two of the CdS samples, measured through the Indium dots. Rectification is a problem, and also the rapid diffusion of indium through the polycrystalline film grain boundaries, patricularly at high temperatures, is a problem that can cause shunting of the comleted devices. Table (3) shows the typical dark and light resistance, and the photosensitivity of the CdS film, defined by the equation :

$$\text{Photosensitivity} = \frac{\sigma_L - \sigma_D}{\sigma_D}$$

EFFECT OF ANNEALING

The effect of annealing of the deposited CdS film in H_2 atmospheres was studied. Typical annealing conditions were 500 °C for 20-30 minutes. Annealing did not have much effect on the grain size but affected the resistivity of the CdS film. Figure (8) shows the the electrical resistance measured between the indium dots, at different locations on different glass substrates. It is noticed that annealing reduced the resistance by several orders of magnitude. Table (4) lists the parameters of some of the sanles before and alter annealing in hydrogen.

CONCLUSIONS

Thin films of CdS have been deposited on glass and graphite substrates by the chemical vapor deposition technique. The structural and electrical properties of the polycrystalline films were measured. The technique offers a very good potential for the fabrication of CdS-based thin film solar cells of large area. The properties of the film need to be optimized, and the interface problems solved for the fabrication of large-area high efficiency heterojunction solar cells

ACKNOWLEDGEMENTS

The author wishes to express his sincere gratefulness to Drs. T. L. Chu and E. D. Stokes, for their valuable discussions and comments, and for help with the measurements.

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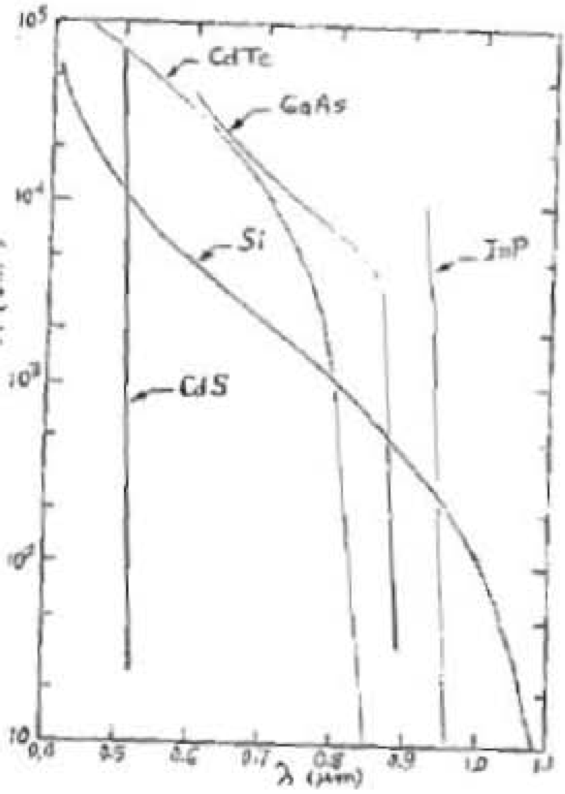


Figure (1) Absorption coefficient of Cadmium Sulphide versus wavelength.

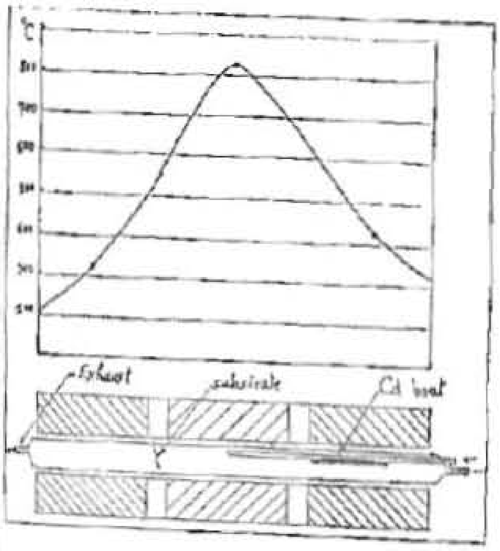


Figure (2) Cadmium sulphide deposition system.

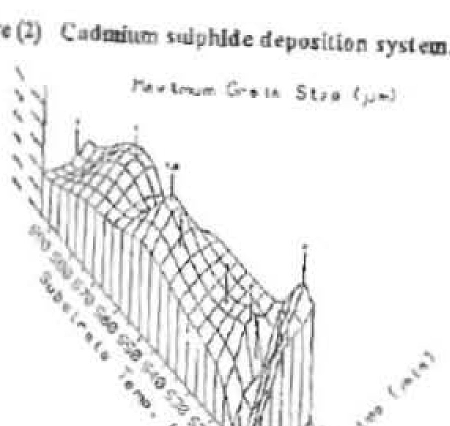


Figure (3) Maximum grain size in the CdS film as a function of substrate temperature and deposition time.

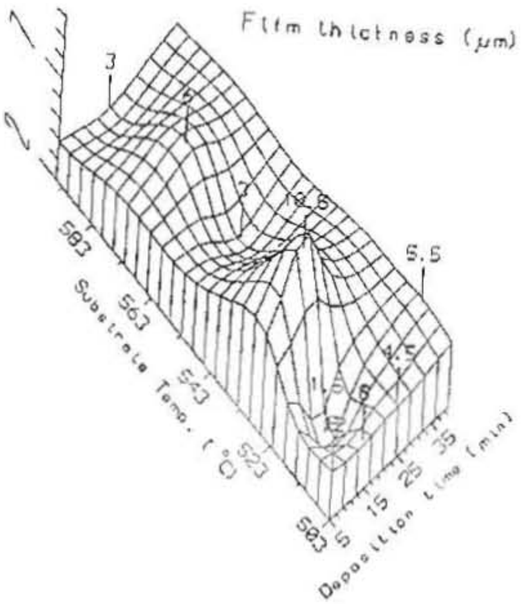


Figure (4) CdS film thickness as a function of substrate temperature and deposition time.

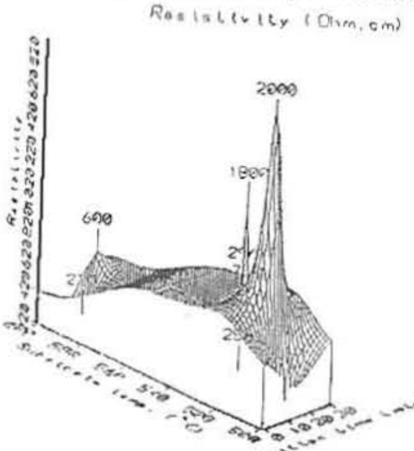


Figure (5) The resistivity of the deposited films as a function of deposition temperature.

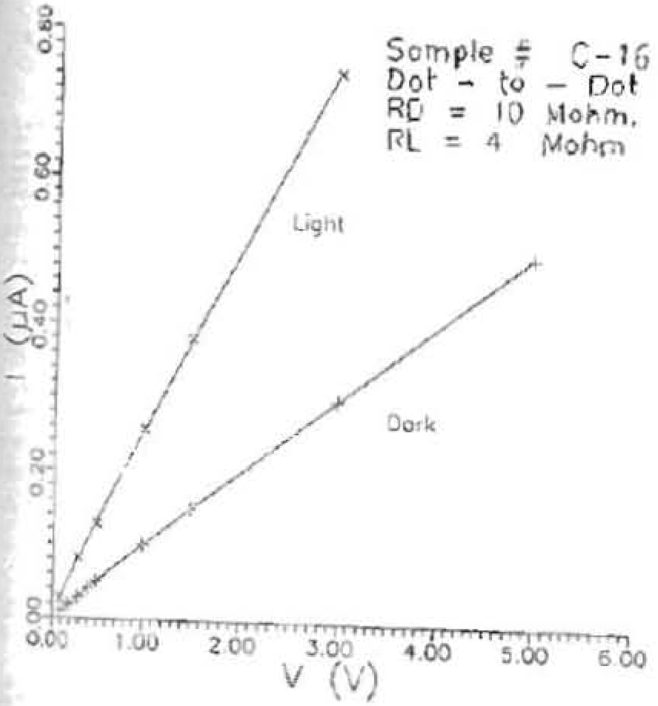


Figure (6) Current-voltage characteristics between Indium dots on CdS samples.

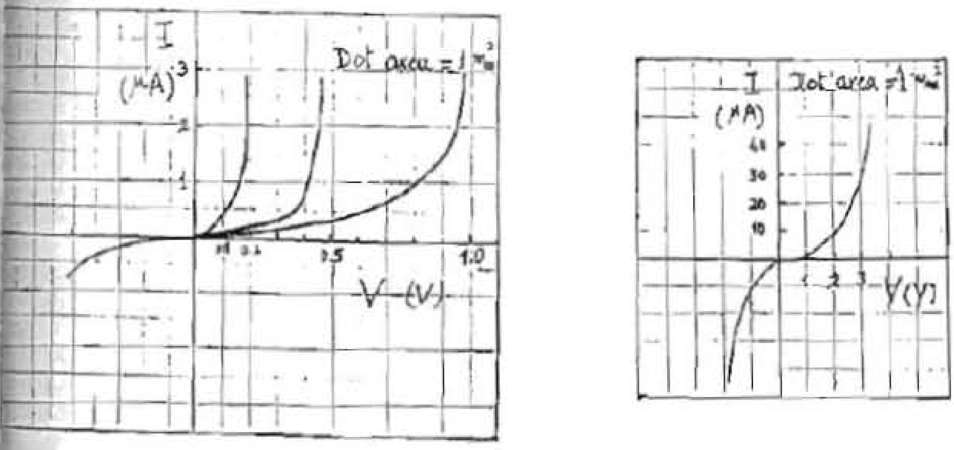
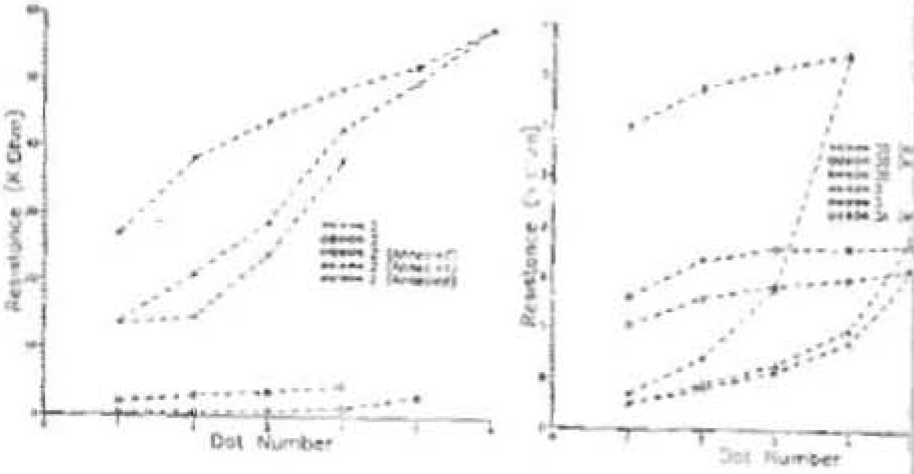


Figure (7) Current-voltage characteristics through the Indium dots for two CdS samples.



(a) Sample # 2 (b) Sample # 3

Figure (8) Resistance measured between indium dots for two different samples.

Table (1) Summary of CdS Depositions

Sample #	Substrate	Substrate Temperature (°C)	Deposition Time (min)	Maximum Grain size (μm)	Film Thickness (μm)	Annealing Time (min)	Annealing Temp. (°C)
1	Corning Glass (7059)	516	30	--	--	3	516
2	" "	509	5	2	--	No	
3	" "	503	5	15	12	2	527
4	Graphite	504	15	8	8	2	504
5	" "	500	15	--	--	30	505
6	Corning Glass (7059)	500	15	7	7	2	509
7	Burnished graphite	516	15	7	1.5	2	520
8	" "	504	25	8	4.5	No	--
9	" "	513	40	3	5.5	30	506
10	Molibdemum	526	5	3	--	--	--
11	Not good						
12	Graphite	550	15	7.5	--	--	--
13	Burnished graphite	526	15	7	10.5	--	--
14	Graphite	595	20	3	5	No	--
15	" "	595	15	—	--	No	--
16	" "	570	20	6	6	30	597
17	" "	556	25	3	2	15	579

Table (2) free carrier concentration and Hall mobility for In-doped CdS samples.

Sample #	2-0	2-2	2-4
Free-carrier conc. (cm^{-3})	1.7×10^{17}	4.6×10^{16}	2×10^{16}
Hall mobility ($cm^2/V.sec$)	12	17	39

Table (3) Dark and light resistance of CdS films.

Sample #	94B	94C	16
R_D (Ohms)	2.25×10^4	3.289×10^4	1×10^7
R_L (Ohms)	5.919×10^4	7.964×10^3	4×10^6
R_D/R_L	0.381	4.130	2.500
Photosensitivity	-0.620	3.130	1.500

Table (4) Summary of Results of CdS Annealing in H_2

Sample #	Substrate Temperature (°C)	Deposition Time (min)	Maximum Grain size (μm)	Film Thickness (μm)	Resistivity (Ohm.cm)
3	527	5	11	12	
3 annealed	527	5	2	8	
4	504	15	8	8	160-500
4 annealed	504	15	6	6	320-350
15	595	15	--	--	1500-3000
15 annealed	595	15	--	--	220-600