SIXTH QUARTERLY REPORT OF RESEARCH ON $\text{Cu}_x\text{S} - (\text{Cd}, \text{Zn})\text{S}$
PHOTOVOLTAIC SOLAR ENERGY CONVERTERS

B. L. Chin, L. E. Sindelar and J. Washburn

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7/78 - 9/78

B. L. Chin, L. E. Sindelar and J. Washburn

Materials and Molecular Research Division, Lawrence Berkeley Laboratory
and Materials Science and Mineral Engineering, University of California
Berkeley, California 94720

October 1978

ABSTRACT

Progress is reported on the growth of single crystal and polycrystalline CdS and (Cd,Zn)S containing different densities and types of structural defects for use in experimental photovoltaic cells. Hall mobility measurements have been made as a first step towards studying the effects of various structural defects on electrical parameters. Experimental cells have been made by the solid state reaction between (Cd,Zn)S and CuCl in order to permit current-voltage-temperature and spectral response measurements to be made on structurally well characterized material.

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1. LIST OF FIGURES

- Fig. 4.1. SEM micrograph of single crystal CdS grown on (111) Ge substrate in which hexagonal pyramids are the dominant surface feature.
- Fig. 4.2. SEM micrograph of single crystal CdS grown on (111) Ga-face GaAs substrate in which hexagonal flat-tops are dominant.
- Fig. 5.1. Hall mobility vs magnetic field for single crystal CdS film 6208.
- Fig. 5.2. Hall mobility vs magnetic field for polycrystalline CdS film 6218.
- Fig. 6.1. SEM micrograph of the Cu_xS film formed on single crystal (Cd,Zn)S. The cracks are a result of the differences in lattice parameters.

2. SUMMARY

Single crystal CdS and (Cd,Zn)S films were grown on (111) Ga-face GaAs substrates for experimental cells. However, difficulty has been encountered due to a non-ohmic n-CdS/n-GaAs heterojunction. Therefore single crystal films have recently been deposited on (111) Ge for front-wall cells. The different surface morphologies for films grown on GaAs and Ge substrates are discussed. Hall mobility as a function of magnetic field was measured for single and polycrystalline CdS films as a first step towards relating electrical parameters to structural perfection.

3. GROWTH OF SINGLE CRYSTAL CdS AND (Cd,Zn)S

Single crystal CdS and (Cd,Zn)S films were grown on (111) Ga-face GaAs substrates by the hot-wall vacuum method for photovoltaic cell fabrication. However, current-voltage measurement of the n-CdS/n-GaAs heterojunction showed a non-ohmic characteristic. Yoshikawa and Sakai¹ reported that the heterojunction made by the epitaxial growth of CdS on n-GaAs substrates by the close-spaced technique showed Schottky-barrier response (direct comparison cannot be made because their CdS was doped by the diffusion of Ga to carrier concentrations of 10^{19} cm^{-3}). Efforts were made to etch the GaAs from the grown single crystal film for backwall cell construction, but the thickness of the films ($\leq 8 \text{ } \mu\text{m}$, see Table 1) made handling extremely difficult. Further attempts are planned to increase the thickness of the films to greater than $10 \text{ } \mu\text{m}$.

To facilitate front-wall cell construction, preliminary growth experiments have been conducted on (111) Ge substrates to determine if the n-CdS/n-Ge heterojunction would provide a good ohmic back contact. CdS and (Cd,Zn)S films were deposited on Ge substrates purchased from Eagle-Picher under growth conditions similar to those for GaAs substrates. These films, however, were non-adherent. Abdalla, Holt and Wilcox² observed no CdS film growth on Ge substrates heated above 550°C which they attributed to sulfur attack of the Ge resulting in a pitted surface. We have succeeded in growing epitaxial CdS and (Cd,Zn)S film on Ge by lowering the substrate temperature to approximately 320°C at the beginning of the deposition. These results are summarized in Table 1.

Figure 4.1 shows the top surface of a single crystal CdS film grown on (111) Ge in which the surface morphology is dominated by hexagonal

Table 1. Summary of Film Growth Experiments

Run	ZnS Power (watts)	CdS Power (watts)	Run Duration (minutes)	Cylinder Temp. (°C)	Substrate Temp. (°C)	ZnS Rate R_{ZnS} (mmole/hr)	CdS Rate R_{CdS} (mmole/hr)	ZnS Mole Fraction	θ (R_{ZnS}/R_{Total})	Thickness τ (μm)	$d\tau/dt$ ($\text{\AA}/\text{sec}$)	Growth Rate g ($\text{\AA}/\mu\text{mole}$)	Substrate
7258	119	57	60	600	470	0	0.87	0	0	VdP	VdP	VdP	Quartz
7268	135	70	60	600	460	0	1.40	0	0	VdP	VdP	VdP	Quartz
7278	137	70	60	600	470	0.13	1.25	0.03	0.10	VdP	VdP	VdP	Quartz
8018	145	73	60	600	440	0.13	1.20	0.03	0.10	VdP	VdP	VdP	Quartz
8148	164	74	60	600	440	0	1.29	0	0	VdP	VdP	VdP	Corning 7059
8168	148	81	60	600	420	0	1.47	0	0	VdP	VdP	VdP	Corning 7059
8178	202	73	60	600	450	0	1.37	0	0	VdP	VdP	VdP	Corning 7059
8288	130	70	120	500	350	0	--	0	0	VdP	VdP	VdP	Corning 7059
8298	152	74	120	600	480	0	1.03	0	0	6.5	9.03	31.5	(111) Ga
8308	216	93	120	600	420	0.85	1.58	0.08	0.35	8.0	11.11	16.5	(111) Ga
8318	261	93	120	600	420	1.62	0	1.0	1.0	*	*	*	(111) Ga
9078	161	48	60	600	430	0	0.81	0	0	3.5	9.72	43.2	(111) Ga
9148	157	50	60	600	450	0	--	0	0	NA	NA	NA	(111) Ge
9158	144	60	60	600	440	0	0.66	0	0	NA	NA	NA	(111) Ge
9198	165	52	60	600	450	0.13	0.66	--	0.17	NA	NA	NA	(111) Ge
9218	154	51	60	540	420	0	0.17	0	0	*	*	*	(111) Ge
9228	158	65	90	530	420	0	0.24	0	0	*	*	*	(111) Ge
9258	190	73	60	520	410	0.18	0.71	0.08	0.21	1.0	2.78	11.1	(111) Ge
9298	192	84	120	520	410	0.17	0.81	0.08	0.18	2.5	3.47	12.7	(111) Ge

VdP = Van der Pauw samples

* = Thickness less than 1 μm and difficult to analyze

NA = Non-adherent film

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Fig. 4.1

pyramids. Christmann, Jones and Olsen (CJO)³ found for CdS grown epitaxially on SrF₂ substrates that the hexagonal pyramids were associated with an excess amount of cadmium, and that they could be formed by growth around a cadmium droplet. Cadmium droplets formed when conditions existed which did not allow the cadmium adatoms sufficient time to diffuse to their equilibrium positions. Figure 4.2 is a SEM micrograph of a single crystal CdS film grown on a (111) Ga surface of GaAs in which the supersaturation was lower than on the Ge substrates (approximately 100°C higher substrate temperature at the beginning of the deposition with relatively equivalent CdS evaporation rates). Hexagonal flat-tops are dominant which is in agreement with CJO who showed that this morphology was the equilibrium growth form produced by two-dimensional nucleation. TEM studies are planned to determine the effects of substrate temperature on the defect nature and populations in these grown films.

A difficulty encountered in growing single crystal (Cd,Zn)S films has been cracking which occurs for layers greater than several microns thick. CJO also reported that CdS films thicker than 2.5 μm on SrF₂ could not be grown because either the films or the substrates would be cracked by the stresses generated by the difference in thermal expansion coefficients. Possible solutions to this thickness-dependent cracking problem are presently being investigated.

Ohmic contacts have been made to uncracked (Cd,Zn)S and the Ge substrate using alloyed In and a Ga-In eutectic respectively. The current-voltage characteristics of the (Cd,Zn)S-Ge junction were found to be ohmic, thus allowing for front-wall cell construction.

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Fig. 4.2

4. HALL MEASUREMENTS

Yoshikawa and Sakai⁴ reported that CdS films grown on GaAs substrates in H₂ gas by the close-spaced technique resulted in films with low resistivity and carrier concentrations as high as $5 \times 10^{19} \text{ cm}^{-3}$. They found for films grown at substrate temperatures of 750°C for 10 min that the dominant donor species was Ga which had diffused from the GaAs substrate. Our Hall measurements made on single crystal and polycrystalline films grown on GaAs substrates showed carrier concentrations in the 10^{16} cm^{-3} range. This data along with the fact that the films were grown at substrate temperatures 300°C lower than that used by Yoshikawa and Sakai led us to believe that autodoping was not a problem.

Hall mobility measurements of two samples at room temperature have been made at different magnetic fields to determine the effects of magnetoresistance. Physically, magnetoresistance is due to the deflection of charge carriers by a magnetic field in a direction normal to the current vector. The resulting trajectories are curved rather than straight, and the average drift distance along the current flow direction between successive collisions is thereby reduced. Figures 5.1 and 5.2 show the change in Hall mobility with magnetic field for samples 6208 (single crystal CdS) and 6218 (polycrystalline CdS), respectively. The error bars represent the greatest deviation from the average of two readings taken on different days. Note that the curves take the same form for both single crystal and polycrystalline samples. Beer and Willardson,⁵ by taking into account mixed scattering from acoustic phonons and ionized impurities, have reported this same type of behavior

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Fig. 5.1

Fig. 5.2

for single crystal Ge. Since our measurements were taken at room temperature, scattering from both of these processes are probably present. Future measurements will be directed toward studying the effects of high dislocation densities and grain boundaries on carrier mobility.

5. DEVICE MEASUREMENTS

Cu_xS has been formed on single crystal CdS and (Cd,Zn)S films by vacuum evaporation of CuCl and subsequent solid state reaction. CuCl powder (5N pure, Apache Chemicals Inc.) was washed in 10% HCl (by volume) to reduce any Cu^{2+} to Cu^+ ions. This powder was evaporated from an alumina-coated tungsten boat in which the pressure during deposition was maintained at less than 1×10^{-5} torr. The CuCl film on CdS or (Cd,Zn)S was heated in argon gas at 135°C for 1 hr. The reaction products were removed with methanol and the surface blown dry.

The I-V measurements of the junctions fabricated by this dry process showed shorted cells and SEM investigation of the top surfaces revealed cracking (see Fig. 6.1) after the Cu_xS formation. The cracks are due to the difference in lattice parameter as reported by Singer and Faeth⁶ and Cook, Shiozawa and Augustine.⁷ It is believed that these cracks provide a diffusion path for Cu resulting in short-circuits through the cell. Use of thicker (Cd,Zn)S films are being planned and also other stress-relief mechanisms are being investigated.

Fig. 6.1

ACKNOWLEDGEMENTS

Very helpful discussions with Dr. Terry M. Peterson are greatly appreciated. We would like to thank Scott Hubbard and Eugene Haller of the Semiconductor Materials and Devices Group for the use of the Hall effect measurement apparatus and for Ge sample preparation.

This work was performed for the Division of Solar Technology, U. S. Department of Energy.

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This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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