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CONTROLLED CADMIUM TELLURIDE THIN FILMS FOR SOLAR CELL APPLICATIONS

Final Technical Report for April 9, 1979—April 8, 1980

By
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June 1980

Work Performed Under Contract No. AC02-79ET23013

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U.S. Department of Energy

Solar Energy

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FINAL TECHNICAL REPORT

for the Period

April 9, 1979 to April 8, 1980

Controlled Cadmium Telluride Thin Films for Solar Cell
Applications

(Emerging Materials Systems for Solar Cell Applications)

to

U.S. Department of Energy
Division of Solar Energy

Under Contract No. DE-AC02-79ET23013

June 1980

by

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ABSTRACT

This report summarizes the work accomplished under this project during the contract period April 9, 1979 to April 8, 1980. After a brief review of the work done during the first three quarters, the report discusses in some detail the work done during the last quarter. In brief, CdTe sputtered self-doped and indium-doped n-type layers on Ni-film on glass have been investigated for film resistivity, contact resistance, Hall mobility and Schottky barrier diode characteristics. Ni has been found to provide satisfactory ohmic contacts and self-doped samples have indicated Hall mobility of approximately $8\text{cm}^2/\text{Vsec}$ when the effective doping concentration is approximately 10^{18}cm^{-3} . Use of indium doped sputtered films, when properly surface treated prior to metallization, appear to yield the best kind of Schottky barrier diode with approximate barrier height of 0.77 volt and Richardson constant $A^* \approx 60\text{ A/cm}^2\text{K}^2$. In spite of these attractive parameter values, these devices showed low V_{OC} and the capacitance showed unexpected frequency dependence that require further investigation. Finally suggestions for future work is presented.

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1. Introduction

Cadmium Telluride fits admirably as an emerging material since solar cell efficiencies greater than 10% have been achieved⁽¹⁾ with CdTe single crystal wafers. Furthermore, Cadmium telluride is the only II-VI compound which can be doped to have both useful p- and n-type conductivity. It has an energy gap of about 1.5 eV close to the optimum value derived from theoretical considerations for photovoltaic solar energy conversion at room temperature⁽²⁾ and also for operation at elevated temperatures⁽³⁾. It has a direct band gap and consequently high optical absorption coefficient so that the carrier lifetime requirements are considerably relaxed. This material can also be prepared as thin films rather easily by relatively simple vapor deposition techniques. Further, its components (Cd and Te) are relatively inexpensive, even though they are rare by-product metals, because they can easily be refined to semiconductor grade purity.

In spite of all these extremely favorable properties of cadmium telluride suitable for photovoltaic cells, the number of studies reported in the literature on the successful fabrication of CdTe solar cells are rather few, and further the efficiency attained is not particularly high. Both p-n homo and heterojunction solar cell structures have been fabricated with CdTe. These investigations include the $\text{Cu}_2\text{Te}/\text{CdTe}$ and the p-CdTe/CdS systems⁽⁴⁻¹⁹⁾, as well as the Schottky-barrier-like junctions on CdTe⁽²⁰⁻²¹⁾. Efficiencies as high as 10.5% have been achieved⁽¹⁾ in these investigations which is certainly competitive with CdS solar cell results. However, there is no fundamental reason why CdTe solar cells cannot come closer to the theoretically predicted⁽²⁾ efficiencies of about 25%. The answer⁽²²⁾ to the question of what is holding back CdTe is three fold: (1) erratic and non-reproducible performance of thin films, (2) bulk lifetime problems, and (3) lack of good contacts to low resistivity p-type material.

This report describes the results obtained on a new research project entitled, "Controlled Cadmium Telluride Thin Films for Solar Cell Applications," started a year ago at The Pennsylvania State University under the sponsorship of the U.S. Department of Energy as part of its overall Photovoltaic Program to investigate emerging material systems.

This research program is aimed at carrying out a systematic study on the preparation and characterization of rf-sputtered CdTe thin films with a view to understand their properties and evaluate their usefulness in photovoltaic applications and finally optimize the efficiency of the resulting solar cell structures. Our extensive past experience in rf-sputtering in general and some experience of sputtering CdTe, in particular, provide the background for this research. From our earlier studies, we find that the nature and properties of the sputtered CdTe are strongly dependant on the sputtering conditions, such as rf power, Ar pressure and physical geometry and arrangement of the target substrate temperature etc.

In the next section we summarize the results obtained during the first 3 quarters of this contract. The following section (Section 3) then describes the results obtained during the last quarter.

2. Work Accomplished During the First Three Quarters

The major objectives of this research project can be grouped into three categories; namely (i) preparation of CdTe thin films, (ii) characterization of the films, and (iii) fabrication and evaluation of solar cells. During the first nine months of the period, substantial progress has been achieved in the first two objectives, and work on the third objective, namely the fabrication of solar cells, is in progress. A number of Schottky barrier cells have been fabricated and are currently being evaluated. In what follows we describe in detail some of the major milestones achieved during the last eight months.

2.1 Preparation:

From our earlier studies (made prior to this contract)⁽²³⁾ we know that the value of deposited film is found to be strongly dependent on the sputtering conditions. In fact, we can produce either crystalline (cubic and/or hexagonal) or amorphous films of CdTe purely by controlling the Ar pressure, rf voltage and power and the physical geometry of the target, substrate, etc. CdTe films were deposited using two MRL rf-sputtering systems. The present sputtering system (MRC 8520) totally dedicated to CdTe work, is similar to the earlier one and has such capabilities as sputtering up, sputtering down, substrate etching, etc. Preliminary runs were carried out at lower power levels to see that properties of films prepared are indeed system independent. This in fact, established one of our objectives of obtaining films with reproducible physical properties.

The CdTe target is of MARZ grade quality from Materials Research Corporation, with no impurity concentration greater than 1 ppm. Although 5" CdTe target was used most of the time, 3" CdTe target was used on selected cases. The sputtering chamber was routinely pumped down to less than 1×10^{-6} torr before purified (Ti gettered) Ar sputtering gas was admitted to the chamber.

The main sputtering parameters that were varied in the course of preparation were Ar pressure and rf power. The gas pressure was varied from 5mTorr to 30mTorr while the rf power was varied from 50W to 400W. The substrate-to-target distance was maintained at about 35mm. Table 1 summarizes the details of preparation conditions. Most of the CdTe films were deposited onto Ni substrates (both Ni foil as well as 1 μ m Ni sputtered on glass cover slips were used) for electrical characterization purposes. Films on glass slides were used for X-ray and SEM inspection and the ones on Mo were used for chemical compositional analysis. Doping the film is one of the most important aspects of material preparation and to a very large measure is the reason for the very slow development of CdTe solar cells until now. We have been successful in self-doping CdTe films with

Table 1

Sample No.	P_{Ar} (mTorr)	Power (watts)	rf voltage	Time (min)	Dopants	Substrate	Remarks
PSCD 001	20	50	500	80	Cd	Glass	
002	20	100	550	45	Cd	Glass	
003	20	150	750	32	Cd	Glass	
PSCD 004	20	50	525	80	Te	Glass	
005	20	100	575	45	Te	Glass	
006	20	150	750	32	Te	Glass	
PSCD 007	20	50	480	120	Te	Glass & Mo	
008	20	100	575	70	Te	Glass & Mo	
009	20	150	625	45	Te	Glass & Mo	
PSCD 010	20	50	475	123	Cd	Glass & Mo	
011	20	100	550	70	Cd	Glass & Mo	
012	20	150	610	45	Cd	Glass & Mo	
PSCD 020	25	150	550	50	Cd	Ni foil (chem. etch)	Sys. A; n/n^+ obtained by relative motion of the Substrate
021	25	200	650	40	Cd	Ni foil (chem. etch)	
022	25	200	650	45	Te	Ni foil (chem. etch)	
023-027	23	200	900	53	Cd	Ni*	Sys. E n/n^+ (new sputtering system)
PSCD 028	23	200	900	50	Cd	evaporated In*	
031	23	200	550	30	Cd	Ni*	Too thin film
032-035	23	200	800	60			
036	25	200	750	60	Cd	Ni (no sputter etch)	
038	23	200	1050	90	Cd	Ni, Ni/glass, glass	System overhauled, Plasma easy to tune and extremely stable
PSCD 039-041	23	200	1050	90	Cd	Mo glass*	
042	23	200	1050	90	Cd	ITO (nesaglass)*	
044-045	23	400	1650	55-90	Cd	Ni, Mo & glass*	
046	23	300	1425	75	Cd	Ni glass*	
048	23	200	1025	95	Cd	Mo and glass*	For X-ray and ISS and SEM work
PSCD 050	23	300	1400	75	Cd	Mo and glass*	
PSCD 051	23	400	1650	55	Cd	Mo and glass*	
PSCD 052	23	200	1025	95	Te	Mo and glass*	For X-ray and ISS and SEM work
PSCD 053	23	300	1400	75	Te	Mo and glass*	
PSCD 054	23	400	1650	55	Te	Mo and glass*	

*Substrate sputter-etching carried out

both Cd and Te with the Cd rich films appearing n type whereas the Te rich films the p type. Most of the first three quarters of the contract were spent in preparation, characterization and device fabrication using Cd and Te doped CdTe films.

2.2. Characterization:

(a) Chemical: An ion scattering (ISS) and an Auger electron spectrometer (AES) combined in the same ultrahigh vacuum system, designed at the Materials Research Laboratory, were used for the compositional analysis of CdTe films on molybdenum substrates.

The chemical compositions of the Cd-doped films are plotted in Figure 1. The resulting compositions were Cd rich depending upon the distance of each sample from the location of the dopant on the target. That is, the Cd concentrations of samples 010-5 and 010-7 were the same to within experimental error. These results were not unexpected inasmuch as both samples were underneath the Cd island. For samples situated more than ~80mm radially from the Cd island (i.e. 010-12 to 010-16) the film compositions approached the 50% level.

The variation of composition as a function of radial distance from the Te dopant, Figure 2 showed similar type behavior. As the rf power level increases from 50 watts to 150 watts, the gradient in composition between samples located directly below the Cd or Te dopant and those situated greater than 84mm from it decreases. This shows that in addition to the effect of radial distance of the substrate from the dopant, the rf power levels provide additional control in the tailormaking of these films with the desired doping levels.

As the power level was increased to 300 and 400W, however, more abrupt changes in the doping levels as a function of radial distance from the Cd pellet were noted. For example, a Cd concentration of ~52 atomic % was measured

Figure 1 Variation of Cd concentration (at %) vs. sample number for Cd-doped CdTe films sputter-deposited at 50 watts (O), 100 watts (+), and 150 watts (•) rf power levels.

Figure 2 Te concentration (at %) vs. sample number for Te-doped CdTe films sputter-deposited at 50 watts (0), 100 watts (⊗), and 150 watts (+) rf power levels.

for the 300W sample 050-3 situated 30mm from the dopant, while the Cd concentration of sample 051-3 which was deposited at 400W approached the 50% level. This sharper decrease in the composition may arise from a higher CdTe:Cd sputter-deposition-rate ratio at the higher rf-power levels as compared to the lower powers so that the films at large r are nearly stoichiometric, or differential sputtering mechanisms between different types of materials (eg. metals and semiconductors) or thermal effects at both the sputtering target and the growing film. We have been able to obtain up to 30% Cd rich films and 36% Te rich films.

(b) Structure: X-ray diffraction patterns of selected films prepared under various sputtering conditions were obtained. Figure 3 shows a composite of X-ray patterns of the samples prepared at 150W power at four different radial distances measured from the Cd-rich end of the substrate holder. Similar composites for films prepared at 50W and 150W rf power were also obtained. These show that the CdTe films exhibit both cubic and hexagonal phases. This is in agreement with the results of our earlier studies carried out with an older undoped CdTe (and not high purity) target. A closer inspection of Figures 3a, b, c and d reveals that while the hexagonal phase is predominant at small values of r , the cubic phase increases with increasing r . In conjunction with the data shown in Figure 3, the above results mean that the amount of cubic phase increases as stoichiometry is approached. Also, the (002) peak at 23.7° predominates. Thus, the preferential orientation of the hexagonal phase of the films changes with the composition at the three different power levels. Furthermore, at the near-stoichiometric compositions where the cubic phase becomes a more significant portion of the hexagonal/cubic diphasic mixture, the cubic phase is preferentially oriented with (220) planes parallel to the film surface. Similar variations were seen for films deposited at higher powers. With Te pellet replacing the Cd the film again show mixed

Figure 3 X-ray diffraction patterns obtained on CdTe samples #PSCD 012, as a function of distance from the cadmium pellet end of the substrate holder.

cubic and hexagonal phases. However, the Te-rich films exhibit non-crystalline solid (NCS) formation with increasing Te concentration, with the hexagonal phase starting to increase as nonstoichiometry is increased. Optical absorption for selected samples were studied. It is seen that the optical absorption edge is near 850nm for Cd rich as well as Te rich samples. Surface morphology of selected CdTe:Cd films on various substrates were investigated using SEM. Films on both Ni foil as well as sputtered Ni film were similar with grain size ranging from 0.1 to 0.3 μ m. While the films in general are smooth, substrate surface structure has strong influence in the film growth particularly with respect to nodular (or defect) growths. Sputter etching the substrate, at least in case of glass substrates, appear to reduce the size and number such nodules on these films.

2.3. Electrical Characterization

2.3.1. Test Device Structures and Measurement Systems. For electrical characterization of the sputtered CdTe films several test device patterns were used. They included (a) a Schockley ladder pattern for sheet resistance and contact resistance measurement, (b) a solar cell structure with metal grid pattern, and (c) an array of circular (dot) electrodes Schottky barrier diode metallization pattern.

For the ladder pattern Ni ohmic contacts were deposited by shadow masking within the sputtering chamber. For the solar cells a thick grid metal pattern was used after an initial deposition of a transparent metal layer. The circular electrode Schottky diodes were fabricated using p-type sputtered layer on Ni and either Al or Au electrodes and n-type sputtered layer on Ni and either Au or Ag electrodes.

For the measurement of solar cell performance a variable intensity solar simulator was designed and built that used four ELH Sylvania 300W (120V) lamps and SCR control circuits. Specialized circuits were also built for short-circuit

and open-circuit cell measurements. For I/V and C/V measurements a shielded probe box with a sample holding stage having high insulation and low parasitic capacitance was designed and built for measurements at room temperature in absence of illumination. Specialized jigs for capacitance and conductance measurements were fabricated for the B601 Wayne Kerr R.F. Bridge that covered the frequency range of 100KHz to 2.5MHz. These jigs allow d.c. bias to be applied to the device and two coaxial cables couple the testing probes. With this arrangement capacitance with respect to the ground can be fully balanced before the probe makes the contact with the top electrode.

2.3.2. Results of Electrical Measurements. Using the Schockley ladder pattern, test devices were fabricated on glass substrates. These were used to measure the sheet resistance and contact resistance of both p- and n-type sputtered layers. Effective bulk resistance was calculated from a knowledge of the film thickness. Typical results are presented in Figs. 4 and 5 showing the characteristics of two different n-type samples as a function of radial distance from the Cd dopant pellet. The contact resistance values are not too low but low enough for solar cell applications.

After establishing the reproducibility of Ni-CdTe ohmic contacts we began to fabricate metal-semiconductor Schottky barrier solar cells and test diodes. Preliminary examination of cell structures indicated that some devices on n-type substrates were capable of generating 200mV open circuit voltage and small short-circuit currents. Diodes were tested for I-V and C-V characteristics. Some of these were fabricated on n-type layers on Nickel substrates using either Au or Ag electrodes and others were on p-type layers on Ni substrates. We were not able to produce Schottky barriers with good I/V characteristics. However, Al on p-type layers showed Schottky barrier like I/V characteristics.

Figure 4 Resistivity of sputter deposited CdTe films as a function of distance from Cd pellet end of the substrate holder.

Figure 5 Potential distribution measured along the rungs of the ladder test device. Sample #PSCD 001.

The p-type devices with Au electrode showed unexpected C/V characteristics (with little frequency dependence) indicative of the presence of interfacial layers and surface states. The n-type device with Au electrode appeared to show rather symmetrical square-law low current and high voltage characteristics. These devices showed nearly constant capacitance vs. bias voltage.

These results convince us that either without a proper surface treatment or in situ metal deposition in vacuum no Schottky barrier diodes with expected behavior can be fabricated.

3. Progress During the Last Quarter

3.1 Preparation:

During this quarter Indium doped CdTe films were prepared by rf sputtering onto Ni substrates. Both Ni foil as well as Ni films sputtered on glass were used as substrates. In addition ITO films sputtered on glass cover slips, In evaporated on glass, In on ITO and glass and metallic glass were also used as substrates for a few selected CdTe:In films. The In dopant pellets were so placed on the CdTe target and the substrates radially placed as to obtain films with different doping levels and hence different physical and electrical characteristics. The range of In doping was augmented by using three different (1/4", 3/8" and 1/2") size pellets. Table 2 summarizes the preparation conditions employed for various samples.

The films were sputtered at 5mTorr Ar pressure with the rf power ranging from 100 to 400W. the sputtering procedure was the same as in the past. In a number of runs 100Å thick Au layers were deposited onto the CdTe:In films by 'insitu' evaporation. For these films no Bromine-Methanol chemical etching was carried out. In addition to the Au and Ag dots on chem-etched CdTe:In films for the purpose of device characterization, ladder patterns using Ni were also laid for measurements on contact resistance as well as sheet and bulk resistivity.

Table 2

Sample No.	P _{ac} (mTorr)	Power (watts)	rf voltage	Time (min)	Dopants	Substrate	Remarks
PSCD 055-057	23	200	1000		Te	glass	Hall & SEM samples
058-059	23	200	1000		Cd	glass	Hall & SEM samples
060-063	30	200	1000		Cd	p type CdTe crystal	Hall & SEM samples
064-067	30	200	1000		Cd	ITO/glass	Hall & SEM samples
068-069	30	200	1000		Cd	ITO/glass & Ni/glass	Hall & SEM samples
070-071	5	200	1200		Cd	In/ITO/glass & ITO/glass	Hall & SEM samples
PSCD 072	5	100	550		1/4" In	Ni/glass	Old 5" CDTE target
073	5	100	550		1/4" In	Ni/glass	Old 5" CDTE target
074	10	100	550		1/4" In	Ni/glass	Old 5" CDTE target
075	5	100	600	120	1/2" In	Ni/glass	Old 5" CDTE target
076	5	100	600	120	1/4" In	Ni/glass + In/ITO/glass	Old 5" CDTE target
077	5	100	600	120	1/4" In	Ni/glass + ITO/glass	Old 5" CDTE target
PSCD 078	5	200	1400	90	1/4" In	Ni/glass	New 3" target
079	5	200	1400	90	1/4" In	Ni/glass	New 3" target
080	5	200	1430	105	1/4" In	Ni/glass	New 3" target
081	5	100	825	120	1/4" In	Ni/glass	New 3" target
PSCD 082	10	100	675	120	1/4" In	In/ITO/glass	New 5" target
083	5	100	700	120	3/8" In	In/ITO/glass	New 5" target
084	10	100	675	120	3/8" In	In/ITO/glass	New 5" target
085	5	100	700	120	3/8" In	In/ITO/glass	New 5" target
086	10	100	675	180	3/8" In	In/ITO/glass	New 5" target
087	5	100	700	180	3/8" In	In/ITO/glass	New 5" target
088	5	100	750	150	3/8" In	In/ITO/glass	New 5" target
089	5	100	725	180	3/8" In	In/ITO/glass	New 5" target
090	5	100	650	120	3/8" In	In/ITO/glass	New 5" target
091	5	100	650	210	3/8" In	In/ITO/glass	New 5" target
092	5	100	750	180	3/8" In	In/ITO/glass	New 5" target
PSCD 093	5	100	650	200	3/8" In	Ni/glass	Old 5" CdTe target
094	5	100	650	100	3/8" In	Ni/glass	Old 5" CdTe target
095	5	100	675	210	3/8" In	Ni	Old 5" CdTe target
096	5	100	700	180	3/8" In, 1/4" CdI ₂	Ni/glass	Old 5" CdTe target
097	5	100	650	180	3/8" In, 1/4" CdI ₂		Old 5" CdTe target
PSCD 098	5	200	1300	90	3/8" In	Ni/glass	Old 5" CdTe target
100	5	200	1300	90	3/8" In	Ni/glass	Old 5" CdTe target
101	5	200	1300	90	3/8" In	Ni/glass	Old 5" CdTe target
102	5	100	750	150	3/8" In	Ni/glass	Old 5" CdTe target
103	5	400	1650		3/8" In	Ni/glass	Old 5" CdTe target

3.2 Chemical Composition:

A few selected diodes that showed desirable electrical characteristics were analyzed for chemical composition using Ion Scattering and Auger Electron Spectroscopy. The presence of Br in the near surface region of the CdTe film which has been chemically etched in 1% Bromine methanol solution (Sample #PSCD 075-1-R) was looked for by Auger Electron Spectrometry (AES). Special care was employed during scanning the Br Auger peaks first because the halide could be desorbed by electron bombardment. No Br was indicated in the scans. The detected pre-sputtering peaks were Cd, Te, Cl, C and O. Relative to other CdTe sputter-deposited films, the oxygen level was substantial at the surface. This could be due to the formation of a surface oxide inasmuch as the sample was exposed to the atmosphere for 25 days before the Auger analysis was made.

Figure 6 shows the depth profile of the chemically etched area of the CdTe sample. The profile of this reveals that the Cl impurity resided only to within $\sim 40\text{\AA}$ from the surface. After a sputtering time, $t = \sim 4$ min., the Cd, Te and O signals became stable.

Figure 7 is a plot of the Cd/Te AES signal ratio vs Ne-20 ion sputtering time. The data point at $t = 25$ min. corresponds to the Cd/Te AES signal ratio of undoped CdTe samples whose compositions were close to the stoichiometric value. As can be seen from this figure, a region of about $20\text{\AA}$ from the surface was depleted of Cd.

Some indications of In in the Auger data for this film was noted. The major Auger peaks of In are observed at 404 and 410 eV. The present analog mode of recording the Auger data inhibits an estimate of the In doping level to be made because Te has an Auger peak at ~ 413 . We are currently interfacing the Auger unit to a microprocessor so that the Auger spectra can be stored digitally. The signal from Te at 413eV can then be subtracted from the raw data to retrieve the In 410 eV signal.

CdTe Film No. PSCD 075-IR

Figure 6 AES signal vs. Ne-20 ion bombardment time for sample PSCD 075-IR

Figure 7 Variation of the Cd/Te AES signals ratio vs. Ne-20 ion bombardment time for sample PSCD 075-IR.

3.3 Electrical Characterization

3.3.1. Hall Mobility in Sputtered CdTe Layers. Hall-effect test samples were prepared using self-doped films on glass and mounted on insulating perspex sheet and silver epoxy bonded with gold wires. Both the current carrying terminals and the voltage probing terminals were coupled with 50 Ω coaxial cables into a shielded box. The Hall sample was inserted in the magnetic field after an initial balance outside the magnetic field and the magnitude of Hall voltage was noted. The magnetic field strength was measured at 4K-Gauss. Because of low observed Hall voltage magnitudes (50 μ V-2mV), measurement with both voltage contact points were taken separately with reference to the ground potential and an average was taken. Typical values of mobility and effective doping concentration calculated from these measurements on 0.2 Ω -cm films are: $\mu_n = 9\text{cm}^2/\text{Vsec}$ and $n_0 \approx 10^{18}\text{cm}^{-3}$. Measurements with p-type samples proved to be very difficult because of high resistivity and low mobility. In measuring n-type films we observed current dependence of the noise content across the Hall output terminals and therefore operating current was varied from 50 μ A to 400 μ A and an average of the repeatable values of Hall voltage was taken. The dimensions of the test samples were 1.8cm x 0.45cm.

3.3.2. Results of Solar Cell Tests on Schottky Diodes. Many attempts were made to produce Schottky barrier diodes using different substrates and metal combinations and a careful record was maintained to see the trend of performance of these diodes as solar cells. Results of these tests are tabulated in Table III.

3.3.3. A Temperature Controlled Probe Box. A leak-proof positive pressure dry nitrogen filled probe box was designed and built for temperature dependent measurements of I/V and C/V characteristics. A schematic of this is shown in Fig. 8. The system can be cooled by allowing a flow of liquid nitrogen and

TABLE III

SAMPLE NO.	DEPOSITION	V _{oc} (mV)	I-V CHARACTERISTICS	SAMPLE NO.	DEPOSITION	V _{oc} (mV)	I-V CHARACTERISTICS
018A-1*	Au	Poor	H.R.	032-1	Au	None	L.R., Ohmic
B-2*	Al	99	H.R.	-2	Ag	Poor	H.R., Unstable
C-2*	Al	200	H.R.	033-1*	Au	None	L.R., Ohmic
020-1&2*	Au	Poor	H.R., Unstable, Struct. Damage	-2	Ag	None	L.R., Ohmic
-3*	Au	Poor	H.R., Unstable	035-1	Au	Poor	H.R., Unstable
-4*	Au	192	H.R.	-2	Ag	15mV	H.R., Unstable
-5*	Au	55	H.R.	038-1	Au	30mV	H.R., Unstable
021-1*	Au	Poor	H.R., Unstable	-2	Au	Poor	H.R.
-3*	Au	125	H.R.	039-1	Au	Poor	H.R.
-6*	Au	Poor(-)	H.R., Unstable	040-1	Au	Poor	H.R.
022-1*	Au	Poor(-)	L.R., S.N.O.	-2	Ag	Poor(-)	H.R.
-2	Au	Poor	L.R., S.N.O.	041-1	Au/SiO ₂	Poor	H.R.
-3*	Al	None	H.R., Unstable	042-1	Au	20mV	H.R.
-5*	Al	Poor(-)	H.R., Unstable	043-1	Au, Al/SiO ₂	33/Poor(-)	H.R.
-6*	Al	200	H.R., Unstable	044-1	Au	151	H.R.
023-1*	Au	Poor	L.R., Ohmic	-2	Au/SiO ₂	Poor	H.R.
-2*	Au	None	L.R., Ohmic	045-1	Au/CdTe	Poor	H.R.
024-1*	Au	None	L.R., Unstable	046-1	Au/SiO ₂	Poor	H.R.
026-1*	Au	None	L.R., Ohmic	048-1	Au	Poor	L.R., S.N.O.
027-1*	Au	None	L.R., Ohmic	065*	Au	Poor	H.R.
028-1*	Au	Poor	L.R., Ohmic	068A	Au, Al	None/Poor(-)	I.R., Ohmic/Unstable H.R., S.N.O.
030-1*	Ag	None	L.R., Unstable- Ohmic	069A	Au	None	M.R., S.N.O., Unstable
-2*	Au	Poor	L.R., Unstable	070	In, Aqu	None/Poor	L.R., Ohmic/H.R., S.N.O.

TABLE III (cont'd)

SAMPLE	DEPOSITION	V _{oc} (mV)	I-V CHARACTERISTICS	SAMPLE	DEPOSITION	V _{oc} (mV)	I-V CHARACTERISTICS
071	In,Aqu	Poor/Poor	Unstable, L.R./ H.R., S.N.O.	078-1*	Au	Poor(-)	H.R., Unstable
072-A	In	None	L.R., Ohmic	-2	Au	Poor(-)	H.R., Unstable
-B	In,Au	None	L.R., Ohmic	079-N-2*	Au	Poor	H.R., S.N.O.
073-A	In,Au	None	L.R., Ohmic	N-1*	Au	Poor	H.R., S.N.O.
-B	In	None	L.R., Ohmic	E-1	Au	Poor(-)	H.R., S.N.O.
-C	In,Au	None	L.R., Ohmic	080 E-1	Au	Poor	H.R., S.N.O.
074-3L	In,Aqu	None/Too Thick	L.R., Ohmic/(Thick Dot) Diodes & S.N.O.	N-1*	Au	None	H.R., S.N.O.
-2L	In,Au	None	L.R., Ohmic	081 S-1	Au	Poor(-)	H.R., S.N.O.
-1L	In	None	L.R., Ohmic	N-1*	Au	Poor(-)	H.R., S.N.O.
-0	In,Au	None/None	L.R., Ohmic/Mostly Ohmic, 1 Diode	082 C*	Au	None	L.R., Ohmic
-1R	In	None	L.R., Ohmic	S-1	Au	47	H.R., S.N.O.
-2R	In,Au	None	L.R., Ohmic	N-1	Au	None	L.R., Ohmic
-3R	In	None	L.R., Ohmic	E-1	Au	20	H.R., S.N.O., Unstable
075-3R	Aqu,Ag,Au	117/100/60	Unstable, H.R., S.N.O. Diode/S.N.O.	083 C	Aqu,Au	14/10	Diode, S.N.O./ Unstable Diode
-2R	Ag	177	Unstable Diodes	N-2	Au	Poor(-)	H.R., S.N.O./ Unstable
-1R	Aqu,Ag,Au	21/153/120	Diode(M.R.)/Unstable Diode/Diode(M.R.)	N-1	Au	12	H.R., S.N.O.
-2L	Au	77	Stable Diodes	084 N-1	Au	Poor	M.R., S.N.O.
-1L	Au	104	Stable Diodes	E-1	Au	Poor	M.R., S.N.O., Unstable
076-1R	Aqu,Ag,Au	76/126/0	M.R., S.N.O./Unstable Diodes/L.R., Ohmic	W-1	Au	Poor	L.R., S.N.O., Unstable

TABLE III (cont'd)

Abbreviations

- H.R. - High resistance; usually greater than $100k\Omega$.
- M.R. - Moderate resistance; usually between $10k\Omega$ and $100k\Omega$.
- L.R. - Low resistance; usually between essentially "short circuit" and $10k\Omega$.
- S.N.O. - "symmetric non-ohmic"; approximately symmetric character of I-V indicating field emission.
- Unstable - Non-ohmic conduction; a generally unstable device which may show several I-V schemes depending on bias treatment, occasionally forming rectification effects and breakdown recovery effects. Also the device may be unstable under biasing conditions such that switching and/or oscillations occur; temporary or permanent breakdown may occur.
- Poor(-) - Negative V_{oc} , below 10mV.
- Au - Gold.
- Al - Aluminum.
- Aqu - Aquadag (Aquadag Colloidal graphite from Ted Pella, Inc., Tustin, CA 92680)
- Ag - Silver.
- ITO - Indium tin oxide.
- Ni - Nickel.
- All V_{oc} 's are referenced with Ni, ITO, etc. as "ground".
- * - Indicates large area metallization ($A \approx .8cm^2$); no asterisk indicates small area, typically $1.5 \times 10^{-2}cm^2$.

Figure 8 An enclosed temperature controlled probe box.

heated by a variac controlled heater built-in under the sample holding stage. A digital thermometer was used to indicate the sample temperature and I/V characteristics were measured using an x-y recorder. At present this arrangement is satisfactory for above the room temperature measurements and being tested for low temperature work.

3.3.4. I/V Characteristics of Improved Schottky Barrier Diodes. Use of an appropriate surface treatment prior to the metal deposition for Schottky barrier contacts has improved the quality of the device characteristics. The best characteristics were obtained on Indium doped sputtered layers as shown in the curve tracer plot of Fig. 9(a). Among the many diodes examined for I/V characteristics two distinct shapes appeared to prevail, one is the symmetrical square-law type and the other the Schottky barrier exponential type as shown in Fig. 9(b) at room temperature. However, at low temperatures the Schottky barrier type I/V characteristic has been observed to degenerate into the symmetrical square-law type ($I \propto V^2$). In order to understand this fully, an in-depth study has been planned for a wide temperature range using the temperature controlled probe box mentioned above. Some Indium doped diodes showed more high currents than that of others for the same forward voltage indicating that either the device had a small effective SB contact area due to poor surface preparation or a large series resistance or both. An example is presented in Figs. 10. This contrasts with a higher emission device as depicted in Fig. 11 showing characteristics at four different temperatures. These characteristics indicate a varying diode ideality factor ϵ in the well-known I/V equation,

$$I = AA^*T^2 \exp\left(-\frac{q\phi_B}{kT}\right) \left\{ \exp \frac{qV}{\epsilon kT} - 1 \right\}$$

where A is the metal electrode area, A^* is the effective Richardson constant, T is the temperature in the Kelvin scale, ϕ_B is the modified

Figure 9(a) Typical diode I/V characteristic for 075-1L #5.

Figure 9(b) Typical current-voltage characteristics of two types of diodes.

Figure 10 Typical I/V characteristics of indium-doped low-current Schottky barrier diodes.

Figure 11 Typical I/V characteristics of high-current type Schottky barrier diodes at different temperatures.

barrier height, ϵ is the ideality factor, kT is the thermal energy and q is the electronic charge.

Taking I_0/T^2 and I_f/T^2 vs. $1/T$ Richardson plots were generated from data of Figure 11, (where I_0 is the extrapolated current at $V = 0$ and I_f is the forward current at $V_f = 130\text{mV}$). These plots for a limited range of temperatures produced quite acceptable results for ϕ_B and A^* (see Table IV). Further measurements over a wider temperature range will be needed to justify the validity of these data.

3.3.5. Capacitance Characteristics of Schottky Barrier Diodes. Schottky barrier diode capacitance is usually frequency independent but varies as $(\phi_B - V)^{-1/2}$. For the two types of diodes we have examined, the symmetrical square-law type indicates only small variations of capacitance with voltage and frequency. The type with exponential I/V characteristics showed some voltage dependence and large frequency dependence to capacitance. To illustrate this we present the zero-bias capacitance and shunt resistance of both types in Figure 12, for a wide frequency range (500Hz to 1MHz). The two types are distinctly different in their frequency response. The near inverse frequency dependence of shunt resistance for the type 075L makes it difficult to model this by a simple series RC type of network. Further examination of these properties are planned using more samples and different temperatures of measurement. The frequency dependence behavior of the SB diode capacitance and shunt resistance implies that C/V measurements need to be performed over a wide frequency range including low frequencies. The Wayne Kerr B221 admittance bridge can be used for this purpose in conjunction with an appropriately fabricated termination jig that will allow d.c. biasing for the device without affecting the bridge measurement. This work will be done during the second year of this program, and hopefully, these results will enable us to determine whether it is the quality of the sputtered layer or the interfaces that is responsible for this capacitance behavior.

Table IV. Calculations of Barrier Height ϕ_B

T	$\frac{1000}{T}$	I_0	ξ	$I_f(V_f=130\text{mV})$	I_0/AT^2	I_f/AT^2
$^{\circ}\text{K}$	$^{\circ}\text{K}^{-1}$	A	--	A	$\text{A/cm}^2\text{K}^2$	$\text{A/cm}^2\text{K}^2$
318	3.14	6.81×10^{-3}	1.60	1.49×10^{-6}	3.85×10^{-11}	8.40×10^{-10}
328	3.05	1.67×10^{-7}	1.60	3.11×10^{-6}	8.85×10^{-11}	1.63×10^{-9}
344	2.90	1.69×10^{-6}	1.62	1.12×10^{-5}	3.35×10^{-10}	5.37×10^{-9}
357	2.76	2.58×10^{-6}	1.61	3.82×10^{-5}	1.15×10^{-9}	1.70×10^{-8}

From $\frac{I_0}{T^2}$ vs. $\frac{1}{T}$: $\phi_B \approx 0.757\text{V}$; $A^* \approx 60\text{A/cm}^2\text{K}^2$

From $\frac{I_f}{T^2}$ vs. $\frac{1}{T}$: $\phi_B - \frac{V_f}{\xi} = 0.694$; $\phi_B \approx 0.774\text{V}$

Figure 12 Frequency dependence of capacitance and shunt resistance of diodes under zero bias condition.

4. Summary and Future Plans

CdTe sputtered self-doped and indium-doped n-type layers on Ni-film on glass have been investigated for film resistivity, contact resistance, Hall mobility and Schottky barrier diode characteristics. Ni has been found to provide satisfactory ohmic contacts and self-doped samples have indicated Hall mobility of approximately $8\text{cm}^2/\text{Vsec}$ when the effective doping concentration is approximately 10^{18}cm^{-3} . Use of indium doped sputtered films, when properly surface treated prior to metallization, appear to yield the best kind of Schottky barrier diode with approximate barrier height of 0.83 volt and Richardson constant $A^* \approx 100\text{ A/cm}^2\text{K}^2$. In spite of these attractive parameter values the diode capacitance appears to show unexpected frequency dependence that require further investigation.

We plan to investigate the structure, using x-ray diffraction, of CdTe:In and CdTe:I₂ films prepared over a wide range of sputtering conditions. SEM will be used to examine the surface morphology of the above films. Efforts will be made to optimize the preparation conditions so as to obtain void-free films and then to use them in making the devices.

The vacuum chamber of the present AES/ISS instrument is also being modified so that the sample can be positioned more accurately with respect to the electron beam of the AES unit. After the modifications have been made, more extensive usage of AES will be undertaken on the CdTe solar cell structures during the various processing steps in making the cell. In addition to AES and ISS we plan to use SIPS (sputter Induced Photon Emission Spectroscopy) and SIMS for chemical analysis of the cell structures at various stages of their fabrication.

In the immediate future we plan to examine the In-doped layers for contact resistance, film resistivity and Hall mobility properties. The I/V characteristics of ~~working~~ samples will be examined for a wide temperature range using the

newly-built temperature controlled chamber. The results of these measurements will be helpful in understanding the physical mechanisms involved in the current/voltage relationship. The reverse bias characteristics and also the observed forward bias non-exponential type characteristics will be fully examined.

The C/V characteristics need a thorough examination as a function of frequency along with the shunt resistance of the device. Perhaps the key to an understanding of the interfacial layer and surface charge both at the top and bottom of the sputtered layer lies in these characteristics. If possible, we would also carry out temperature dependence behavior of capacitance. Once the results of I/V and C/V measurements are fully appreciated we plan to carry out thermally stimulated current and capacitance measurements for the characterization of deep levels in the sputtered films.

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