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LOW-COST PROCESS FOR P-N JUNCTION-TYPE SOLAR CELL

Quarterly Technical Progress Report 2, December 1, 1979—February 29, 1980

By
John B. Mooney
Daniel D. Cubicciotti
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March 1980

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SRI International
Menlo Park, California

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Quarterly Technical Progress Report 2
Covering the Period 1 December 1979 to 29 February 1980

March 1980

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ABSTRACT

In the second quarter of work, we continued to study spray pyrolysis of CuInS_2 . The concentrations of copper and sulfur in the spray solutions were increased so as to increase the copper content of the films to the stoichiometric level. Although Auger analysis indicates that this was successful, X-ray microanalysis has identified the growth of copper-rich crystals on the surfaces of the deposit. Heat treatment in H_2S did not improve the stoichiometry. The copper-rich crystals were also found on a sample sprayed from a solution with no excess copper.

Heterojunctions of glass/ $\text{SnO}_2(\text{Sb})/\text{CdS}/\text{CdTe}/\text{carbon}(\text{Cu})/\text{Ag-In}$ were prepared with a number of methods used to restrict the junction. The various devices failed to exhibit a diode characteristic or a photo-response. Work on this project is being directed toward understanding the type of junction and how it is formed.

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CONCISE DESCRIPTION OF THE PROJECT

The objectives of this project are to fabricate nonsilicon thin-film solar cells of two types on glass substrates:

- A heterojunction CdS/CuInS₂ (and CuInSe₂) deposited by chemical spray pyrolysis.
- A solar cell based on silk screened and sintered CdTe.

This program entails four tasks

- (1) Spray pyrolyze ITO (indium tin oxide) CdS, CuInS₂ and CuInSe₂ with properties necessary for solar cell applications. Determine optimum conditions.
- (2) Prepare chlorine doped CdTe powders, prepare films of these powders on ITO and CdS surfaces by screen printing and sintering, determine optimum conditions, and conduct a thermodynamic and kinetic study of the printing and sintering process.
- (3) Develop photovoltaic devices with a goal of 8 percent efficiency and at least 1 cm² area.
 - Glass/Au/p-CuInS₂/CdS/Al
 - Glass/Au/p-CuInSe₂/CdS/Al
 - Glass/Au/p-CuInSe₂/Cd_{0.84}Zn_{0.16}A/Al
 - Glass/ITO/CdS/n-CdTe/p-CdTe/Cu₂Te or graphite/Au
 - Glass/ITO/CdS/n-CdTe/p-CdTe/Cu₂S/Au
 - Optimize and apply antireflective coatings.
- (4) Evaluate the layers and devices to characterize and optimize the materials and devices including cell stability and degradation mechanisms. Stanford University (Prof. C.W. Bates, Jr.) is a subcontractor in this task.

I INTRODUCTION AND SUMMARY

This program began on 1 September 1979 with two major objectives:

- Preparation of a solar cell using spray pyrolysis for the deposition of all but the contact metalization, and having the structure glass/Au grid/p-CuInSe₂/n-CdS/Al.
- Screen printed and sintered solar cells of the composition glass/ITO/CdS/n-CdTe/p-CdTe/p-Cu₂Te/Au, based on work at Matsushita (Nakayama, 1976)¹* with the modification that the CdS layer is to be deposited by spray pyrolysis.

During this second quarter, SRI has produced a number of CuInS₂ films by spray pyrolysis using conditions intended to improve the stoichiometry of the layer. While Auger and x-ray photoelectron spectroscopy (XPS) analysis of these films indicate that the films were more nearly stoichiometry, X-ray microanalysis indicated the presence of crystallites of high copper content on the surface of the deposit. Heat treatment in H₂S-N₂ atmosphere at 300°C did not change the crystallinity of the films. A spray pyrolyzed device exhibited a photovoltaic response. The efforts on the sintered cell were directed toward an understanding of the type of junction that has been reported by the Matsushita group.¹ Several attempts to restrict the junction-formation process by filling the sintered matrix before applying the graphite/copper suspension failed to produce a photovoltaic junction. The application of a CdTe layer to a spray-pyrolyzed CdS layer resulted in a significant attack upon the CdS layer.

*References are listed at the end of the report.

II PROGRESS DURING THIS QUARTER

A. Spray Pyrolysis

1. Cadmium Sulfide (CdS)

Zanio has shown that CdS films are recrystallized with a significantly reduced resistivity by heat treatment in pure hydrogen.² Similar heat treatment of two spray-pyrolyzed films was undertaken during this reporting period. Table 1 summarizes the experiments. One sample

Table 1

EFFECT OF HYDROGEN HEAT TREATMENT IN TWO SAMPLES
OF SPRAY-PYROLYZED CdS FILMS

Sample *	H ₂ Firing		Sheet Resistance (k Ω /square)
	Temperature (°C)	Time (minutes)	
2-11C	--	0	2000
2-11C-1	300	60	10
2-11C-2	350	90	10
2-11C-3	400	15	5
2-11C-4	400	35	20
2-11C-5	400	60	40
2-56D	--	0	1
2-56B	350	60	0.25
2-56C	400	60	0.25
2-56A	450	60	3

* Sample 2-11C deposited from $\text{Cd}(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{CH}_4\text{N}_2\text{S}$ solution
Sample 2-56 deposited from $\text{CdCl}_2 + \text{CH}_4\text{N}_2\text{S} + 0.3\% \text{InCl}_3$

(2-11C) was sprayed from a $\text{Cd}(\text{CH}_3\text{CO}_2)_2$ solution; the other (2-56) was sprayed from a CdCl_2 solution doped with indium. The acetate film started out 2000 times more resistive than the conductive substrate. The lower resistance of the second film may be due to the chlorine, the indium, or to both. The resistance was subsequently reduced by hydrogen firing at temperatures up to 400°C . Increasing either treatment time or temperature resulted in increased resistance, possibly as a result of reduction of the SnO_2 film, as observed by Zanio.² Future work in this area will attempt to determine the importance of the indium and chlorine dopant on the efficiency of hydrogen firing in reducing resistivity.

2. Copper Indium Sulfide (CuInS_2)

The spray pyrolysis of CuInS_2 continued during this reporting period. The major variables studied were

- Spray rate
- Total volume of solution sprayed
- Ratios of copper to indium and sulfur to indium in the spray solution.

Based on the Auger spectroscopy studies and XPS studies in the preceding quarter, it was determined that an excess of copper in the spray solution improves the stoichiometry of layers; the effects of a excess of sulfur are also being studied. Table 2 summarizes the conditions of preparation and some results for the thin films sprayed during this quarter.

The Kevex X-ray fluorescent system on our scanning electron microscope has a computer and disc storage facility; using this arrangement, the computer can determine (with an accuracy much greater than that obtained by measuring peaks on a CRT display) the total number of counts attributable to a given element. Because standard samples are not yet available to calibrate the X-ray unit, the values in Table 2 are not concentrations in weight or atomic percent.

Table 2

SUMMARY OF SPRAY-PYROLYZED CuInS_2 FILMS

Layer	Moles $\times 10^{-4}$	Spray Conditions		Tir-Bath (°C)	Concentration Ratios		X-ray-Derived Intensity Ratios			Oxygen Content (percent)	Comment
		Rate (ml/min)	Total (ml)		Cu/In	S/In	Ci/In	S/In	Cl/In		
2-43	3.1	120	50	300	1:1	4:1	0.47	1.38	0.29	9.4	$\text{NH}_2\text{OH}\cdot\text{HCL}$
2-44	3.1	85	50	280	1:1	4:1	0.50	1.50	0.37	10	$\text{NH}_2\text{OH}\cdot\text{HCL}$
2-45	6.2	300	100	250	1:1	4:1	--	--	--	-	$\text{NH}_2\text{OH}\cdot\text{HCL}$
2-46	12.4	300	200	280	1:1	4:1	0.79	2.24	0.18	1.4	$\text{NH}_2\text{OH}\cdot\text{HCL}$ (last time)
2-47	12.4	110	200	280	1:1	4:1	0.63	2.35	0.07	1.3	Metering pump introduced
2-48	12.4	130	200	280	1:1	4:1	--	--	--	-	Film flaked
2-49	12.4	40	200	280	1:1	4:1	0.70	2.53	0.07	4.7	Slow metering
2-50	12.4	40	200	280	1.5:1	10:1	0.83	2.30	0.03	6.1	
2-62	12.5	47	200	265	1.5:1	10:1	2.11	3.60	0.00	-	Crystals
							0.74	2.52	0.09	-	Matrix
2-63	12.5	50	200	270	1.5:1	10:1	1.67	3.34	0.00	-	Crystals
							0.75	2.69	0.08	-	Matrix
2.65	27	115	350	285	1.5:1	10:1	0.78	2.37	0.00	-	Average
							4.57	4.05	0.00	-	Crystals
							0.68	2.27	0.00	-	Matrix
2-71	32	135	400	270	1.5:1	8:1	0.91	2.67	0.03	-	Average

Figure 1 shows a scanning electron micrograph of the surface of Sample 2-65, together with a CRT display of the X-ray fluorescence. Figure 1(a) is a SEM photograph at 500X showing clusters of crystalites on a relatively smooth surface. (In the discussion that follows, we refer to these clusters as "crystals" and to the smooth surface as the "matrix".) The CRT display in Figure 1(b) shows the entire area that has been sampled with X-ray fluorescence to produce an "average" analysis for both the crystal and the matrix. Figure 1(c) is a 10,000X magnification of the area indicated in Figure 1(a) by the numeral 1; the square scribed on Figure 1(c) is an area subsequently investigated at 50,000X, reported later in this discussion. Figure 1(d) is the CRT display corresponding to the area in Figure 1(c). In these panels, comparison of the relative heights of the peaks for copper and indium shows that the crystals are relatively rich in copper and deficient in indium.

Table 3 summarizes a similar analysis of spray-pyrolyzed CuInS_2 , including samples that were heat-treated in H_2S . The data in Table 3 are ratios of the X-ray-derived counts for copper-to-indium, sulfur-to-indium, and copper-to-sulfur. Again, these data do not represent concentrations in terms of weight, percent, or atomic percent, but rather the number of counts for copper $k\alpha$ and indium $L\alpha$. Because we have not yet obtained standard samples of CuInS_2 with which to calibrate the apparatus, these data cannot be presented in terms of absolute concentrations. Despite this limitation, it is clear that the matrix has a different composition than the crystals, and that the matrix is similar from sample to sample: The crystals are rich in copper and sulfur and deficient in indium. The matrix was analyzed at 2,000X magnification; the crystals were analyzed at 10,000X and individual crystals at 50,000X. Treating the samples in 20 percent H_2S in nitrogen at 300° for one hour increased the copper and sulfur content of the crystals, and decreased the indium.

Figure 2 shows some of the results of an SEM X-ray fluorescence investigation of Sample 2-65, which had been etched for 75 seconds in concentrated nitric acid. This etching was undertaken to permit a study

(a) 500X VIEW OF SURFACE

(b) X-RAY FLUORESCENCE
READOUT FROM (a)

(c) 10,000X VIEW OF
AREA 1 IN (a)

(d) X-RAY FLUORESCENCE
READOUT FROM (c)

FIGURE 1 SCANNING ELECTRON MICROGRAPH AND X-RAY FLUORESCENCE DATA
FOR SAMPLE 2-65

Table 3

X-RAY MICROANALYSIS OF CuInS_2 , INCLUDING HEAT TREATMENT

Sample Number* and Area	X-ray-Derived Intensity Ratio		
	Cu/In	S/In	Cu/S
49			
Matrix	0.70	2.53	0.28
Matrix	0.63	1.97	0.32
Matrix	0.87	1.32	0.50
Crystals	1.32	3.18	0.42
Crystals	1.10	2.90	0.38
49HT			
Matrix	0.59	1.19	0.49
Crystals/	3.72	6.96	0.53
50			
Average	0.83	2.30	0.36
50HT			
Average	0.92	2.77	0.33
62			
Matrix	0.74	2.52	0.29
Crystals	2.11	3.60	0.59
62HT			
Matrix	0.81	2.71	0.30
Matrix	0.83	2.70	0.31
Crystals	1.54	3.21	0.48

Sample Number* and Area	X-ray-Derived Intensity Ratio		
	Cu/In	S/In	Cu/S
63			
Matrix	0.75	2.69	0.28
Crystal	1.67	3.34	0.45
63HT			
Matrix	0.69	2.32	0.30
Matrix	0.72	2.57	0.28
Crystal	2.55	4.10	0.62
65			
Average	0.78	2.37	0.33
Matrix	0.68	2.27	0.30
Matrix	0.65	2.17	0.30
Crystals	4.57	4.05	1.13
Crystals	2.00	3.61	0.55
Crystals	2.59	3.73	0.69
Crystals	5.89	5.23	1.13
Crystals	5.82	7.09	0.82
71			
Average	0.91	2.67	0.34
71HT			
Average	0.86	2.50	0.35

* HT suffix indicates heat treatment of one hour at 300°C in 20 percent H_2S in N_2 .

(a) 2000X VIEW OF SURFACE

(b) X-RAY FLUORESCENCE
READOUT FROM (a)

(c) 10,000X VIEW OF
AREA 1 IN (a)

(d) X-RAY FLUORESCENCE
READOUT FROM (c)

FIGURE 2 SCANNING ELECTRON MICROGRAPH AND X-RAY FLUORESCENCE DATA
FOR SAMPLE 2-65 FOLLOWING 75 SECONDS OF ETCHING IN HNO_3

of the bulk of the chemically sprayed layer by XPS. Examination with the SEM revealed that the matrix areas were etched, but that the crystal areas had been attacked selectively only in specific areas, thereby producing what we refer to as a "sponge" material. Figure 2(a) is a 2,000X view of the surface, showing the spongy areas as well as the degree of attack on the matrix. Figure 2(b) is a CRT display of X-ray fluorescence for an area of the matrix; the distribution of copper, indium, and sulfur is similar to what was seen in Figure 1(b) for Sample 2-65. Figure 2(c) is a 10,000X view of one of the sponge areas; the selective attack on the crystals is clearly visible. Figure 2(d), the CRT display corresponding to Figure 2(c), is remarkably similar to Figure 2(b) and demonstrates that the remaining material is of the same composition as the matrix.

In summary, the data in Table 3 and Figures 1 and 2 indicate that, under the conditions of spray in which the copper-to-indium ratio is 1.5:1 and the sulfur-to-indium ratio is of the order of 10:1, there is a tendency for the growth of isolated crystals of Cu_xS (possibly alloyed with an indium compound); however, the data for Sample 2-49 also indicate that the crystals are copper-rich, even when the copper-to-indium ratio in the spray solution is 1:1. The fact that the heat treatment sometimes increases the copper content of the crystals (or decreases the indium) is in agreement with the results in Section II-A-4, wherein thermodynamic studies indicate that the sulfur pressure for In_2S_3 is greater than that for Cu_2S . Thermodynamic studies reported last quarter³ showed that an H_2S atmosphere would be more effective in converting the indium oxide to indium sulfide, but that the vapor pressure considerations also suggested that 300°C was probably the ideal temperature for this kind of heat treatment. Table 4 summarizes the heat treatment for five samples, listing the heat treatment conditions and the measured conductivity for the samples before and after treatment. The heat treatment did not affect the crystallinity of the films; X-ray

Table 4

EFFECT OF HEAT TREATMENT ON THE RESISTANCE OF CuInS_2 FILMS

Sample Number	Heat Treatment Conditions			Sheet Resistance (Ω /square)	
	Temperature ($^{\circ}\text{C}$)	Time (min)	H_2S Concentration (percent)	Before Heat Treatment	After Heat Treatment
2-50	300	60	10	4,000	2,000
2-62	300	60	10	60	50
2-63	300	60	20	150	60
2-65	400	30	20	60	250
2-71	300	60	25	5	15

diffraction patterns taken on one sample after treatment were not different from those taken before. The oxygen analysis has not yet been completed for the heat treatment study.

3. Auger Analysis

Figure 3 is the Auger profile for Sample 2-50, showing the intensities of the various elements normalized to indium and corrected for Auger field on the basis of spectra in the PEI Handbook.⁴ Because of the number of elements included in this chart, these distributions are somewhat difficult to follow. Accordingly, we have replotted the important elements of copper, sulfur, and indium in Figure 4. Even from Figure 3, it is obvious that the oxygen content on the surface is very high and the sulfur content very low. The substrate/glass interface to the CuInS_2 is not well defined; as will be seen elsewhere, these layers are not entirely uniform and some components of the crystalline mixture are sputtered more rapidly and others such that "holes" appear in the deposit area near the interface. Consequently, the signals for the barium and oxygen of the substrate glass appear to rise over a fairly great depth as the holes open, while the copper, indium, and sulfur

FIGURE 3 AUGER PROFILE FOR SAMPLE 2-50

Cu/In = 1.5/1; S/In = 10/1

FIGURE 4 AUGER PEAK RATIOS FOR 2-50

(Solution concentrations: Copper to Indium 1.0:1;
Sulfer to Indium 2.0:1)

intensities drop off relatively slowly as the remaining deposit is removed.

Figure 4 presents the Auger peak ratios for the same sample (2-50) in the form of ratios of copper to indium and sulfur to indium. From these plots it is apparent that, although the surface is low in sulfur, most of the bulk is higher than the theoretical level for CuInS_2 of 2.0. Although the surface is somewhat deficient in copper, after the first 1000 Å the copper concentration exceeds the indium. From this it is clear that the solution's copper-to-indium ratio of 1.5:1 is excessive, as is the sulfur-to-indium ratio of 10:1.

Figure 5 is a similar reduction of data for Sample 14-A, as originally described in Figure 5 of the first quarterly report.³ The solution concentrations for Sample 2-14A were the theoretical values of a 1.0:1 copper-to-indium ratio and a 2.0:1 sulfur-to-indium ratio. Figure 5 of the present report shows that, under those circumstances, sulfur and copper concentrations are both low in the bulk and that the sulfur ratio is still very low to the surface. However, upon sputtering well into the layer near the interface, the copper rises to near the theoretical value of 1.0:1 and the sulfur reaches 1.6:1, which is closer to the theoretical value of 1.0:1.

FIGURE 5 AUGER PEAK RATIOS FOR 2-14A
(Solution concentrations: Sulfur to Indium 2.0:1;
Copper to Indium 1.0:1)

These average values do not represent a uniform homogeneous film, since the SEM analyses show a segregation of the copper and sulfur in surface crystals. However, it remains clear that the composition near the glass interface is closer to theoretical than it is on the surface, and that as the layer grows, the ratios drift off the stoichiometric value. The low sulfur content of almost all surfaces studied to date using both Auger analysis and XPS shows a tendency for the surface to oxidize after it is removed from the nitrogen atmosphere in which it was prepared.

4. Thermodynamic Calculations

In the first quarterly report,³ we presented thermodynamic calculations that simulated the spray pyrolysis of a solution of CuCl , InCl_3 , H_2S (to represent thiourea), and HCl . Those results indicated that the oxides or chlorides of the metals could form instead of the sulfides if the H_2S activity was too small or the H_2O or HCl activities were too large.

In the second quarter we have made some thermodynamic calculations of the conditions under which, for various reasons, the sulfides become unstable. These calculations can provide some idea of how to change conditions to avoid regions of instability if they are encountered. Unfortunately, the thermodynamic data needed for exact calculations are not available, and we are only able to calculate general trends. Because there are no data for the compound CuInS_2 , we have considered the behaviors of Cu_2S and In_2S_3 separately and assume that they behave similarly in the compound CuInS_2 . Another facet of the problem is the potential formation of solid solutions in which oxygen or chlorine replace sulfur in the compound. The absence of information about such solid solutions prevents a good treatment of those effects.

The results of the calculations are as follows:

Thermal Decomposition--If CuInS_2 is heated in vacuum, or in an inert gas such as nitrogen (which is thermodynamically equivalent to

vacuum), sulfur can evaporate (as gaseous S_2) and leave the solid deficient in sulfur. We have no thermodynamic data for sulfur-deficient $CuInS_2$: accordingly, we have calculated the sulfur pressures generated in the formation of In_5S_6 from In_2S_3 and copper from Cu_2S . (These are the next lower compounds that would form and the calculated sulfur pressures are therefore an indication of the values that might be expected for thermal decomposition.)

For the equilibrium

we calculate the following expression for the pressure of sulfur

$$\log P(S_2, atm) = -14,800/T + 9.51 \quad .$$

For the equilibrium

we find

$$\log P(S_2, atm) = 6.19 - 15000/T \quad .$$

Those equations are shown in Figure 6, from which it is apparent that the sulfur pressure for In_2S_3 decomposition is greater than that for Cu_2S decomposition.

These results indicate that if a mixture of Cu_2S and In_2S_3 were heated under inert conditions (vacuum or N_2 atmosphere), the In_2S_3 would lose sulfur more readily than Cu_2S .

Loss of sulfur from the compound $CuInS_2$ to form a sulfur deficient structure ($CuInS_{2-x}$) would be expected to occur more readily than decomposition of In_2S_3 . Thus, it is anticipated that sulfur pressures for

FIGURE 6 PARTIAL PRESSURE OF SULFUR (S_2) IN EQUILIBRIUM WITH In_2S_3/In_5S_6 AND Cu_2S/Cu AS A FUNCTION OF TEMPERATURE

the compound would be larger than the upper curve of Figure 6. We cannot give a good estimate of how much larger at present because of the lack of good information.

Pressure of H_2S Required to Prevent Thermal Decomposition--The thermal decomposition of sulfides heated in vacuum can be suppressed by imposing a pressure of H_2S . The relevant equations are

for which $\log P(\text{H}_2\text{S}/P(\text{H}_2)) = 2.73 - 2900/T$; and

for which $\log P(\text{H}_2\text{S})/(P\text{H}_2) = 1.07 - 3100/T$.

The reactions involve both H_2S and H_2 ; it is their ratio that determines whether the reaction will go to the right or to the left. The above equations for pressure ratios are plotted in Figure 7. Values of the ratios of H_2S/H_2 above a line in Figure 2 would cause the particular reaction to go to the left as written. The data in Figure 7 show that a higher H_2S/H_2 ratio is required to suppress the decomposition of In_2S_3 than for Cu_2S .

Here again, the existence of a sulfur-deficient compound would influence the interpretation. Loss of sulfur by CuInS_2 to form CuInS_{2-x} would probably occur at higher H_2S/H_2 ratios than those indicated by the upper line in Figure 7; the exact ratios cannot be evaluated at present for want of data.

Substitution of Sulfur by Oxygen--Another possibility is that oxygen can substitute for sulfur in CuInS_2 and alter its electronic properties. Figure 8 shows calculations of the H_2S/H_2O ratio in equilibrium with $\text{In}_2\text{S}_3/\text{In}_2\text{O}_3$ and $\text{Cu}_2\text{S}/\text{Cu}_2\text{O}$. In effect, it gives the ratios of

FIGURE 7 RATIOS OF PRESSURE OF $\text{H}_2\text{S}/\text{H}_2$ IN EQUILIBRIUM WITH $\text{In}_2\text{S}_3/\text{In}_5\text{S}_6$ AND $\text{Cu}_2\text{S}/\text{Cu}$

FIGURE 8 RATIOS OF PRESSURES OF $\text{H}_2\text{S}/\text{H}_2\text{O}$ IN EQUILIBRIUM WITH INDIUM AND COPPER SULFIDES AND OXIDES

H₂S/H₂O in the gas phase needed to prevent conversion of the sulfides to the oxides. For In₂S₃, the ratio is larger than for Cu₂S, which means it is easier to convert the indium sulfide to oxide than copper. The equations are:

$$\text{Log } P(\text{H}_2\text{S})/P(\text{H}_2\text{O}) = -00.07 - 1600/T$$

and

$$\text{log } P(\text{H}_2\text{S})/P(\text{H}_2\text{O}) = -0.56 - 7000/T$$

This calculation is also only a lower limit because we are considering the complete conversion of In₂S₃ and In₂O₃. In the real system, solid solutions of the type CuInS_{2-y}O_y could probably form more easily than the complete conversion. Thus, the incorporation of oxygen impurities in solid solution might occur at H₂S/H₂ ratios that were orders of magnitude larger than the Figure 8 values.

Substitution of Sulfur by Chlorine—There is also the possibility that chlorine can substitute for sulfur in the compound. The equilibrium calculations for the conversion from sulfide to chloride are shown in Figure 9. The relevant equations are:

$$\text{log } P(\text{H}_2\text{S})/P^2(\text{HCl}) = 1970/T - 3.34$$

$$\text{log } P(\text{H}_2\text{S})/P^2(\text{HCl}) = 800/T - 3.03$$

FIGURE 9 RATIOS OF PRESSURES OF H_2S AND HCl IN EQUILIBRIUM WITH INDIUM AND COPPER SULFIDES AND CHLORIDES

The caveat about solid solutions of the type $\text{CuInS}_{2-z}\text{Cl}_{2z}$ applies and for the real system, the values in Figure 9 are again essentially a lower limit.

Doping Conditions--We can approximate the conditions for doping materials from thermodynamic considerations, however, the data needed for accurate evaluations are generally not available. For doping CdS with chlorine we make the following calculations. For the equilibrium

we calculate for the equilibrium constant, K,

$$\log K = 4000/T - 6.32 \quad .$$

The equilibrium constant expression is

$$K = \frac{a(\text{CdCl}_2) \cdot P(\text{H}_2\text{S})}{a(\text{CdS}) \cdot P^2(\text{HCl})} \quad .$$

For a CdS, crystal $a(\text{CdS})$ is unity. We shall assume that the activity of CdCl_2 is given by the following expression:

$$a_{\text{CdCl}_2} = S_{\text{Cd}} \cdot Y_{\text{Cl}}^2$$

where X_{Cd} is the atom fraction of Cd in the metal sublattice ($X_{\text{Cd}} = 1$ for chlorine doping) and Y_{Cl} is the atom fraction of Cl on the anion sublattice. Thus, the equilibrium constant becomes

$$K = \frac{Y_{\text{Cl}}^2 P(\text{H}_2\text{S})}{P^2(\text{HCl})} \quad .$$

For 0.1 percent chlorine doping $Y = 10^{-3}$ and $K^{-1} = 10^{-6} \frac{P(\text{H}_2\text{S})}{P^2(\text{HCl})}$.

So that

$$\log \frac{P(\text{H}_2\text{S})}{P^2(\text{HCl})} = 4000/T - 0.32$$

for chlorine doping at the 0.1-percent level according to this treatment. For larger ratios of $P(\text{H}_2\text{S})/P^2(\text{HCl})$, the amount of chlorine would be smaller and vice versa.

For doping CdTe with indium using InCl_3 vapor, the following equilibrium can be considered:

for which $\log K = 10.36 - 12700/T$.

For this equilibrium to hold, the pressure of InCl_3 must not exceed its vapor pressures. Other equilibria must be considered for those cases. Those vapor pressures are given by

$$\log P(\text{InCl}_3, \text{atm}) = 10.74 - 8270/T$$

The equilibrium constant for the above equilibrium is given by

$$K = \frac{a(\text{InTe}) a(\text{Cd}) P^2(\text{HCl})}{a(\text{CdTe}) P(\text{InCl}_3) P^{3/2}(\text{H}_2)}$$

We shall assume that:

$$a(\text{CdTe}) = 1 \text{ (i.e., host crystal)}$$

$$a(\text{Cd}) = \text{(i.e., cadmium leaves the crystal to form a separate phase)}$$

$$a(\text{InTe}) = X_{\text{In}} Y_{\text{Te}} = X_{\text{In}} .$$

Then for 0.1 percent In in CdTe, $X_{\text{In}} = 10^{-3}$ and $K^1 = 10^{-3} \frac{P^3(\text{HCl})}{P(\text{InCl}_3)P^{3/2}(\text{H}_2)}$, which becomes

$$\log \frac{P^3(\text{InCl})}{P(\text{InCl}_3)P^{3/2}(\text{H}_2)} = 13.36 - 12700/T$$

This relation gives the conditions under which we anticipate 0.1 percent In doping in CdTe, based on the assumptions made.

In both cases of doping treated, the expressions derived depend on activity coefficients that we have assumed to be unity. Therefore, the expressions are inaccurate numerically but give the form of the relationships of applied gas pressures.

5. X-ray Photoelectron Spectra (XPS) Studies

In the first quarter, CuInS_2 films were prepared by spray pyrolysis on glass substrates in air at temperatures between 200°C and 230°C. The ratios of the starting components were varied in attempt to produce a film of stoichiometric CuInS_2 . The copper-to-indium ratio was held constant at 1:1 molar, while the sulfur-to-indium and sulfur-to-copper ratios were varied from 2:1 to 6:1. Examination of the core level spectra suggested that the copper and indium were bound up in oxides within 20 Å of the surface and that the ratios of copper and indium to sulfur were about one-fourth to one-sixth of what would be expected. A large amount of oxygen existed in these films.

In an attempt to decrease the oxygen content and improve the stoichiometry of the sprayed films, we have in this quarter sprayed films in nitrogen and have used sulfur-to-indium ratios greater than 6:1. All surfaces have been heat-treated in ultrahigh vacuum (10^{-10} torr) at temperatures between 100°C and 400°C for periods ranging from

one to twenty-four hours. The results of these experiments can be summarized as follows:

- The amount of oxygen was decreased by an order of magnitude from that found in films sprayed in air. A fair amount of oxygen persists throughout the bulk of these films, although the major amount is in the surface region ($\sim 20 \text{ \AA}$).
- Films sprayed with sulfur-to-indium ratios of 10:1 and greater show phase-separated regions of Cu_2S .
- Heat treatment in ultrahigh vacuum between 100°C and 400°C does not appear to result in compositional or structural changes.
- Regardless of the starting ratios of copper to sulfur and indium to sulfur, the bulk ($> 100 \text{ \AA}$) is very near stoichiometric CuInS_2 , although the surface is never close.

We have also etched sprayed films of CuInS_2 in concentrated HNO_3 for periods of up to about 75 seconds. Preliminary results show that the expected improvement in stoichiometry was achieved, but the surface resistivity increased to an unacceptable level. A solar cell made entirely by the spray pyrolysis technique, consisting of CdS/CuInS , was made with a measured efficiency of 0.5 percent. The large lattice mismatch is a contributing factor to the low efficiency.

Future efforts are expected to proceed along the following lines:

- CuInSe_2 films will be prepared. Our previous work has indicated that the large lattice mismatch between CuInS_2 and CdS will result in low-efficiency cells when spray pyrolysis fabrication techniques are used.
- Films with nonstoichiometric surfaces and stoichiometric bulks will be treated by heating in H_2S atmospheres to remove the oxygen and restore the desired resistivity.
- Films prepared in this fashion will be measured for optical absorption throughout the visible spectrum. Resistivity and Hall effect measurements will also be made.

B. Sintered Layers

The resistance of our sintered CdS has been high despite its being doped with chlorine and gallium. Zanio² has reported success in reducing the resistivity several orders of magnitude by annealing in pure H_2

at 45°C, but the ITO was converted to very high resistance. We have reduced our sintered layers from $10^6 \Omega/\text{square}$ to $10^4 \Omega/\text{square}$ by a similar treatment at 400°C. Under these conditions, the $\text{SnO}_2(\text{Sb})$ conductivity is maintained, but the mechanical strength of the layer is greatly reduced by the grain growth process. When this layer was coated with a CdTe suspension, the processing resulted in the cracking and lifting of the sintered CdS layer.

We have used GaCl_3 as a dopant source; however, as discussed in Section II-D, the Matsushita group uses GaCl_2 because of its lower vapor pressure. We have ordered GaCl_2 and will use it for doping studies. At the same time, we will investigate the conditions of film preparation and firing that will not only produce low resistivity, but will also provide the necessary physical strength for the layer.

C. Spray Device Development

A heterojunction was spray deposited with the structure

The film was cracked after deposition of the CuInS_2 layer, presumably because of a thermal-expansion mismatch between the CdS and the CuInS_2 . An array of 0.02 cm^2 dots was deposited by vacuum evaporation. The position of a few of the gold dots corresponded with a section inside the cracking pattern. One of these areas produced the dark/light I-V characteristic shown in Figure 10. This is the as-deposited material, and may have improved upon appropriate heat treatment. This device, which unfortunately did not survive processing and testing, had a high series resistance and low efficiency. However, compared to the first sprayed $\text{CuInS}_2/\text{CdS}$ devices reported in the literature for sprayed $\text{CuInS}_2/\text{CdS}$ cell,⁵ it is a good beginning.

FIGURE 10 PHOTORESPONSE OF SPRAYED CELL

Structure is glass/SnO₂(Sb)/n-CdS/p-CuInS₂/gold.

$P_o = 150 \text{ mW/cm}^2$, $A = 0.20 \text{ cm}^2$, $V_{oc} = 0.28 \text{ V}$, $I_{sc} = 0.095 \text{ mA}$,

$FF = 0.5$, $\eta = (V_{oc} \times I_{sc} \times FF \times 100)/(P_o \times A) = 0.4 \%$

D. Sintered Device Development

1. Literature Survey

We have five papers on the screen-printed and sintered cells developed by Matsushita. Table 5 tabulates the significant variables in methods of preparation and reported photovoltaic measurements and includes the data on the various SRI experiments for comparison. The various aspects of the device are discussed in the following paragraphs, after which the results of the experimental program is presented in the light of that discussion.

The most important questions in this program are, Where is the junction and what is its nature? The classical wet CuCl process of Cu₂Te formation was used at first.¹ Later papers^{6,8,9} all refer to a carbon electrode. Prince¹⁰ reports that copper impurities are added to the carbon paste.

Table 5
SUMMARY OF CELLS REPORTED BY MATSUSHITA AND SRI
All Devices on ITO-Coated Glass

Cell Characteristics	Reference					
	Nakayama ¹	Ikegami ⁶	Nakano ⁷	Nakayama ⁸	Prince ⁹	SRI
CdS Layer						
Composition	CdS + ?	CdS + (0.3-1%)GaCl ₂ + (3-5%) CdCl ₂ + Propylene glycol	CdS + GaCl ₂ + CdCl ₂	Unknown	CdS + (0.2-1%)GaCl ₂ + (3-5%)CdCl ₂ + Propylene glycol	CdS + GaCl ₃ + CdCl ₂ + N ₂ -HCl
Thickness (μm)	20 [*]	25	Unknown	Unknown	25	50
Heat treatment	?	630°C in N ₂	630°C in N ₂	630°C in N ₂	Dry at 120°C; 650°C in N ₂	650°C in N ₂
CdTe Layer						
Composition	n-CdTe(In) + CdCl ₂	CdTe + CdCl ₂ + <1% Propylene glycol	Unknown	Cd + Te "No CdCl ₂ "	CdTe (pure) + <1% CdCl ₂	CdTe (pure) + CdTe(In) + <1% CdCl ₂
Thickness (μm)	10 [†]	15	Unknown	Unknown	15	20
Heat treatment	500-800°C in N ₂	Unknown	Unknown	600°C in N ₂ for 60 min	720°C	720°C
Contact						
p-Region	Cu ₂ S (wet)	Carbon	Unknown	Unknown	Carbon (Cu)	CuCl and Carbon
p-Contract	Ag paint	Ag paint	Unknown	Unknown	Ag paint	Ag paint
n-Contact	In-Ga	In-Ga	In-Ag paint	Unknown	In-Ag paint	In-Ag paint
Heat treatment	200°C for 10 min	300°C in N ₂	Unknown	Unknown	300°C	300°C
Performance						
V _{oc} (V)	0.68	Unknown	0.64	0.68	3.43 [‡]	0
I _{sc} (mA)	31	Unknown	10.8	12.7	711 [‡]	0
FF (%)	Unknown	Unknown	Unknown	38	50.8 [‡]	0
AM1 Efficiency (%)	8.1	8.1	4.3	4.7	5.5 [§]	0

* Bulk resistivity was 0.2 Ω-cm.

† Bulk resistivity was 0.1 to 10 Ω-cm.

‡ For five-cell array.

§ For active area; overall module efficiency was 3%.

The contacts have also varied. Nakayama¹ used a silver paint on the p-type layer and an In-Ga electrode on the CdS. Ikegami⁶ indicates the same electrode. The subject of Nakano's⁷ paper is a screen-printable electrode made by adding indium powder to a commercial silver paint; this electrode was included in the presentation reported by Prince.⁹

The CdS layer preparation process is the same in all reports: CdCl₂ is used as a flux, and the three references that report on gallium doping refer to GaCl₂ as the source of gallium. The boiling points of GaCl₂ is shown in the CRC Handbook¹⁰ as being higher than that of GaCl₃: 535°C against 201°C. Because Ga III functions as a donor in CdS, oxidation must occur at some point in the process. We assume that the Ga II compound is used because of its low volatility.

The CdTe layer is made from indium-doped n-type CdTe. Nakayama and coworkers¹ report that the sintered CdTe layer is 10⁻¹ to 10 Ω-cm and that the resistivity of the bulk that was used to make the paste was 0.2 Ω-cm. Therefore, they must have pulverized a larger crystal to produce their powder. More recently, Prince⁹ reported that Matsushita used 99.99-percent CdTe and does not mention indium doping. Nakano⁷ reported that a borosilicate substrate was used, Nakayama⁸ mentioned a high-quality glass, and Prince⁹ said that one remaining problem is a low-cost glass substrate. The softening point of borosilicate glass (Pyrex, Corning No. 7740) is 821°C, and that of PPG float glass is 725°C. The highest processing temperature in Table 5 is 720°C; however, 600°C is the maximum temperature in the new Cd + Te → CdTe reported by Nakayama.⁸ Our experience¹¹ in processing photoconductors on glass substrates for electrophotography has been that soft glass can be routinely processed at 550°C if the rate of temperature rise and fall is compatible with the thermal shock of the glass. These CdS layers, which have a bulk resistivity of 10¹² Ω-cm or better for the photoconductor plus binder, are so heavily compensated by copper that they are unaffected by impurities emanating from the glass substrate. If soda lime substrates are processed at 600°C, the softening and deformation of the glass is

apparent despite the 725°C rating, and diffusion of impurities (such as sodium) into the CdS is probable.

2. Experimental Work

Our experimental program has investigated a number of variations in the form of the sintered device. The original proposal envisioned a device in which the spray-pyrolyzed CdS layer would be substituted for the sintered CdS layer. The rationale for this design was that a semi-transparent sprayed film of a few micrometers thickness would constitute a better window than would 20 to 25 μm of sintered powder. As noted in the previous report,³ the sintering CdTe layer or its flux reacted with the CdS layer except in the middle of broad areas. It appeared that the attack occurred from the edges of the delineated CdTe layer, and it may be that the actual structure is:

glass/In-Ga/ITO/n-CdS/n-CdS_xTe_(1-x)/n-CdTe/p-CdTe/carbon/silver.

If this is in fact true of the spray-deposited surface, then it must also enter into the sintered device, although probably in a still more complex geometry.

Our proposal also contemplated producing n-type CdTe powder by doping 99.999-percent CdTe with chlorine and indium under conditions that, from our experience with CdS, were expected to recrystallize the CdTe and result in a fairly narrow range of crystal sizes. The advantages of this approach were that, by starting with micrometer-sized particles and growing them in an atmosphere containing the dopants, the resulting regrown crystals would have uniform dopant distributions. If the growth process could be controlled so as to produce crystals of 5 to 10 μm diameter, it would not be necessary to grind them to a reduced crystal size. Grinding is a damaging process, in that it introduces impurities from the grinding media and in that it can damage the crystal lattice. As reported last quarter,³ we have been unable to find a set of conditions under which we can control the size distribution of CdTe. During this quarter, we have proceeded with chlorine- or indium/chlorine-doped

CdTe that was ground after doping in a tube furnace. We have found no significant difference in the chlorine- or chlorine/indium-doped CdTe as far as the resistance of the layer is concerned. It is difficult to measure resistivity of a sintered layer with precision because of the problem of applying and defining the contact. We did measure the resistance between a pair of silver paint dots and calculated a bulk resistivity of 0.1 to 0.2 Ω -cm. Normally, CdTe layers are prepared on CdS layers, and we measure the resistivity with a pair of conducting rubber probes that have dimensions and spacings appropriate for an Ω /square measurement. Because the resistivity of the CdTe is usually lower than that of the CdS, we believe that this is a reasonable measurement. At this point, our primary interest is in the junction and how it is formed; hence, our principal efforts are directed toward these questions.

Reference 3 described our first efforts at producing sintered devices. We had succeeded in producing device structures on sprayed CdS as described above, and on sintered CdS layers that were doped with gallium and chlorine. We also tried (without success) a modified wet CuCl process, and a carbon paste and carbon paste mixed with CuCl solution. We were not successful in producing a device, although a diode characteristic was observed in the one in which an undoped carbon electrode was applied. Because none of these approaches was successful, we have attempted in this second quarter to restrict the junction by partially filling the porous structure with a solvent. The concept is to fill the porous sintered mass with a fluid that will prevent penetration by the suspension of carbon and dopant film; the hope was that the resulting junction would be in the upper portion of the CdTe layer.

In the first experiment (Sample 3-22), we used chloroform to define the junction because chloroform is heavier than water (which is the vehicle for Graphilm, a carbon suspension marketed by Asburg Graphite Films, Inc.). Copper, in the form of 1 ml of 0.625 mol CuCl, was added to 10 ml of graphite and painted on 1-cm² areas delineated in the CdTe layers. The substrate was SnO₂-coated glass with a sintered gallium-

doped CdS layer and an indium-doped CdTe layer. The CdTe layer was formed at 720°C for 30 minutes in nitrogen. The Graphilm was painted on the 1-cm² areas with care to avoid going outside the CdTe and thereby shorting the junction. The bare CdS areas were not treated to prevent capillary migration of the copper dopant into these regions. The contacts were baked at 300°C in nitrogen for 30 minutes. The contact to the CdS was silver-indium paint; silver paint was used for the p-type contact.⁷ This device was tested and found to be ohmic.

3. Microscopic Studies

The device was broken and the edge examined under the microscope and with the scanning electron microscope. Figure 11 is a photomicrograph taken at 170X; the various layers are indicated in the associated line drawing. Figure 12 are SEM representations of the same sample. Figure 12(a) is a 200X view of the broken edge, showing the glass, the sintered CdS, the sintered CdTe, and the carbon. This area did not have a silver contact. Figure 12(b) shows that a distinct difference is still visible at 500X. Figure 12(c) is the same area viewed with the

FIGURE 11 PHOTOMICROGRAPH OF SINTERED DEVICE No. 3-32 AT 170X

**(a) BROKEN EDGE AT 200X
SHOWING STRUCTURE**

**(b) SAME AREA AS (a),
BUT AT 500X**

**(c) TELLURIUM DISTRIBUTION
AT 500X**

FIGURE 12 SCANNING ELECTRON MICROGRAPHS OF SINTERED DEVICE No. 3-32

(d) CdS LAYER AT 500X

(e) CdTe LAYER AT 500X

FIGURE 12 SCANNING ELECTRON MICROGRAPHS OF SINTFRED DEVICE No. 3-32 (Concluded)

X-ray fluorescence system and using a window adjusted for tellurium radiation; the CdTe layer is clearly defined. The signal outside this area could as easily be noise as tellurium that has diffused into the other layers, as discussed earlier.

Figures 12(d) and 12(e) are 500X views of the CdS and CdTe layers, respectively, showing the good sintering that occurred during the processing and the resulting porosity. These layers appear to be less dense than the 80 percent of theoretical that was reported last quarter,³ although the preparation was essentially the same.

In Sample 3-29, the glass substrate had a chromium grid of 0.25-mm lines on 2.5-mm centers, and $\text{SnO}_2(\text{Sb})$ had been spray deposited over this grid. The sheet resistance was about 300 Ω /square. (We have ordered an ITO sputtering target; pending its arrival, we are working with antimony-doped SnO_2 .) The CdS layer was prepared from a suspension of 20 g of 99.999-percent CdS, 0.13 g GaCl_3 , and 0.40 g $\text{CdCl}_2 \cdot 2.5 \text{H}_2\text{O}$ in 15 ml propylene glycol. The GaCl_3 and $\text{CdCl}_2 \cdot 2.5 \text{H}_2\text{O}$ were heated with the propylene glycol to saturate the propylene glycol and dehydrate the CdCl_2 , as discussed in the first quarterly report.³ After drying at 120°C in nitrogen for 60 minutes and sintering at 650°C for 60 minutes in nitrogen, the sheet resistivity of the sintered layer was 10 to 100 Ω -cm. The CdTe layer was prepared from a mixture of 10 g of CdTe with 0.075 g $\text{CdCl}_2 \cdot 2.5 \text{H}_2\text{O}$ and 6 ml of propylene glycol. The suspension was applied with a doctor blade with a 0.125-mm gap, dried at room temperature for 72 hours and at 120°C for 24 hours, then fired at 650°C for 25 minutes. The resistivity was then approximately 1 Ω -cm.

The CdTe film had been patterned into seven 1-cm² squares before the heat treatment. The areas between these squares where the CdS was exposed were first saturated with glycerine by impregnation to prevent the capillary diffusion of the contact material around the CdTe. Three pretreatment conditions were applied to the CdTe areas in an attempt to limit the location of the junction. These pretreatments and the three levels of contact dopant are summarized in Table 6. The sample was heat

Table 6

SUMMARY OF PREPARATION OF SAMPLE 3-29

Area	Pretreatment	Carbon Suspension
1a	None	10 ml Graphilm, 0.5 ml 3.1 molar CuCl in HCl, 0.05 g tellurium powder; water added until fluid
1b	None	10 ml Graphilm, 5 ml 3.1 molar CuCl in HCl, 0.05 g tellurium powder; water added until fluid
2a	Glycerine	10 ml Graphilm, 0.5 ml 3.1 molar CuCl in HCl, 0.05 g tellurium powder; water added until fluid
2b	Glycerine	10 ml Graphilm, 5 ml 3.1 molar CuCl in HCl, 0.05 g tellurium powder; water added until fluid
3a	Isopar M	10 ml Graphilm, 0.5 ml 3.1 molar CuCl in HCl, 0.05 g tellurium powder; water added until fluid
3b	Isopar M	10 ml Graphilm, 5 ml 3.1 molar CuCl in HCl, 0.05 g tellurium powder; water added until fluid
3c	Isopar M	10 ml Graphilm, 0.5 ml 3.1 molar CuCl in HCl

* Pretreatment consisted of saturating the porous CdTe layer with glycerine or Isopar M [alserosene hydrocarbon, Exxon trademark], then blotting the surface dry and leaving the bulk saturated.

treated at 300°C in nitrogen for 20 minutes. Contacts were evaporated indium on the CdS and evaporated gold on the CdTe/carbon. Silver paint was added to the gold because of the fragile nature of the sintered material. All areas were ohmic and none exhibited a diode characteristic. Scribing the 1-cm² areas into smaller squares in an attempt to avoid any area in which there might be shorting around a junction did not result in any improvement.

Despite the fact that a spray-pyrolyzed CdS layer is heavily attacked by the CdTe layer-formation process, our modest success in reducing the resistivity of spray-deposited CdS by hydrogen firing (Section II-A-1) led us to attempt to form a junction on a particularly

heavy spray-pyrolyzed CdS deposit that had been heat treated for 35 minutes at 400°C in H₂. A CdTe layer from the same source as the preceding sample was applied, dried, and heat-treated in nitrogen at 650°C for 25 minutes. A large section of the CdTe layer vaporized or had reacted alloyed with the CdS. The area where the CdTe remained covered about half of the total substrate. Two small areas were coated with Graphilm and two with a mixture of 10 ml Graphilm and 0.5 ml 3 molar CuCl. After drying overnight, the device was fired at 300°C in nitrogen for 20 minutes. Silver and silver-indium contacts were applied immediately upon removal of the sample from the nitrogen atmosphere. Copper wire leads were attached with the paint, and the sample heated to 180°C in nitrogen to set the contact. The whole area was immediately sealed with Q-dope as an encapsulant. Tests indicate that all four areas were ohmic. This was designated Sample 3-31. The resistivity of the CdTe layer after device processing was 1 to 10 Ω -cm, assuming that the measured resistivity was unaffected by the higher resistivity CdS (10 to 100 Ω -cm).

Up to now in this program, we have studied the preparation of n-CdTe powders with controlled crystal size, and have found that the distribution of crystal size is not as easily controlled as in CdS powders treated in a similar manner. In the future, we will work with sintered CdS. The sintered CdS layers used to date have been about 50 μ m thick when prepared with our methods and using a doctor blade with a 0.125-mm gap. We will next use a 75- μ m gap to approach more closely the 20- to 25- μ m thick layer reported by Prince.⁹

In the coming quarter, we will try a copper-free carbon film that exhibited a diode response (all of the CuCl-treated carbon films have been ohmic.) We will also look into a mixture of carbon and finely divided copper metal. We will look again at the use of the wet process to form Cu₂Te as reported by Nakayama.¹ We will develop a process for Cu_xS spray pyrolysis to apply to a CdS/CdTe structure.

III PLANS FOR THE COMING QUARTER

In the next quarter, the spray pyrolysis program will be directed toward CuInSe_2 . The experience gained to date with CuInS_2 will serve as a starting point. Solution composition, spray rates, and temperature will be the significant variables. Sprayed devices will also be studied. In our original proposal we planned a front-wall cell:

glass/gold grid/ CuInSe_2 /CdS/aluminum.

Since we have found that the first deposited material is more stoichiometric and free of the Cu_xS crystals, we also plan to investigate the back-wall device in which the best material is deposited at the interface.

We will continue heat-treatment studies on spray-deposited CdS layers. It is possible that the use of a metallic grid on the glass of the back-wall cell will make possible a broader range of hydrogen heat treatment to reduce the CdS resistivity, since there will be no problem with reduction of the transparent conductor. CdS films will be deposited on chromium grids and heat treated. It is important to complete heat treatment before CuInSe_2 is deposited, as diffusion of the cadmium into the CuInSe_2 and copper into the CdS will be damaging to the device.

The study of the sintered device will include a reinvestigation of the wet CuCl process, and spray pyrolysis of a Cu_xS layer on the CdS/CdTe. A supply of GaCl_2 has been obtained for CdS doping. Indium-doped CdTe crystals will be obtained and pulverized to provide a starting material of known conductivity. We will also precipitate CdTe from an aqueous solution to obtain starting material of very small particle size.

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