6-80 gwa

Dr. 1486

DSE-4042-T19

CADMIUM SULFIDE/COPPER SULFIDE HETEROJUNCTION CELL RESEARCH

Quarterly Technical Progress Report for June 1—September 30, 1979

By
John A. Thornton

MASTER

November 30, 1979

Work Performed Un

V63E

Telic Corporation
Santa Monica, California

U.S. Department of Energy

Solar Energy

DISCLAIMER

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Paper Copy $6.00
Microfiche $3.50

DSE-4042-T19
Distribution Category UC-63e

CADMIUM SULFIDE / COPPER SULFIDE HETEROJUNCTION CELL RESEARCH

Quarterly Technical Progress Report

Period: June 1, 1979 - September 30, 1979

By John A. Thornton

Telic Corporation
1631 Colorado Ave
Santa Monica, California 90404

November 30, 1979

Work Performed Under Contract No. XJ-9-8033-2

Solar Energy Research Institute
1536 Cole Boulevard
Golden, Colorado 80401

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

RB

TABLE OF CONTENTS

ABSTRACT

Page

ABSTRACT

This report covers the work performed for the approximate period May 31, 1979 to September 30, 1979.

Off-stoiciometry CdS coatings with resistivities of about 10 Ω-cm have been deposited by a cyclic reactive sputtering process where the H_2S injection is periodically switched on and off. Cells with CdS layer fabricated in this way have yielded efficiences of about 0.6% with short circuit currents of about 3.5 mA/cm^2, open circuit voltages of about 0.43V, and fill factors of about 0.40.

CdS resistivity control by In doping has been achieved both by diffusion from a pre-deposited In layer and by using an In-doped Cd sputtering target. Resistivities of about 30 Ω-cm are achieved in CdS coatings about 5 um thick deposited at 250°C over 50 nm thick In layers. A Cd cathode doped with 1 atomic percent In has yielded CdS coatings with resistivities of about 0.1 Ω-cm at substrate temperatures in the 100 to 300°C range. Cells fabricated from the 0.1 Ω-cm CdS with a 0.5 um undoped layer adjacent to the junction have yielded encouraging diode characteristics with a strong photovoltaic effect and will be used in an optimization study.

Cu_xS coatings deposited onto CdS under various conditions have been found to have the same properties as those deposited onto glass substrates in previous studies. The amount of sputtering that is required in order to deposit the Cu_2S heterojunction layer is small compared to that required to achieve steady state conditions in the deposition apparatus. Thus pre-conditioning is required. The results of experiments that examine various conditioning procedures are reported.

1. PROJECT DESCRIPTION

The program objective is to investigate and evaluate the application of cylindrical-post magnetron reactive sputtering for the production of solar cell quality thin films of CdS/Cu_2S for large-scale terrestrial photovoltaic energy conversion. The reactive sputtering process is being investigated at Telic Corporation. The coating and device characterization is being done at the Lockheed Palo Alto Research Laboratory.[1,2]

The Telic portion of the program includes the following tasks.

Task 1: Deposition Process Development

This task calls for modification of the deposition equipment and procedures to overcome the deficiencies identified during the previous program.[3] The modifications include: (1) reconfiguring the cathode shielding to remove foreign surfaces from the proximity of the cathodes and the substrates; (2) installing a vacuum interlock so that substrates can be inserted without exposing cathode and shield surfaces to the atmosphere; and (3) redesigning the substrate holder to provide better substrate temperature control and more rapid substrate cooling. The task also includes an investigation of the use of rf-reactive sputtering as a means for achieving higher deposition rates with the absence of arcing.

Task 2: $Cd_xZn_{1-x}S$, CdS Deposition Studies

This task concentrates on gaining improved control over the deposition of the specific semiconductor layers required for the cells. In the case of the CdS or $Cd_xZn_{1-x}S$ layer, the emphasis is on controlling the coating resistivity, either by In doping or by achieving off-stoichiometry deposits through the use of special deposition techniques or post-deposition heat treatment. In the case of the Cu_2S, the emphasis is on gaining control of the properties of Cu_xS deposited over CdS layers. (In the previous program the specific properties of the Cu_2S had been investigated in detail only for coatings deposited on glass substrates).[3]

Task 3: Device-Material Parameter Optimization

Throughout all stages of the program solar-cell structures will be deposited and their performance evaluated as photovoltaic devices.

This report is organized with respect to the progress made during the second quarter on each of the program tasks.

2. DEPOSITION PROCESS DEVELOPMENT

The emphasis during this quarter was on the apparatus modifications. The specific objectives of the apparatus modifications are to:

1) Reconfigure cathode shielding to reduce the shield surface area adjacent to the sputtering sources and the substrates.
2) Install a vacuum interlock so that substrates can be inserted without exposing the cathode and shield surfaces to the atmosphere.
3) Redesign the substrate holder to permit rapid cooling of the substrates following the CdS and prior to the Cu_2S depositions.
4) Install a movable mask to restrict Cu_2S deposition at the cell edge.

The design of the reconfigured apparatus was described in the first quarterly report.[4] Fabrication of the chamber base plate, vacuum wall, and magnetic field coil system has been completed. Design drawings for the substrate heater, the substrate mounting carrousel, and the substrate loading interlock have been completed. Fabrication is underway. Present plans are to install the modified assembly on our vacuum pumping stand in December, following completion of the present series of cell studies.

It was noted in the first quarterly report that a new dc power supply with an improved arc suppression circuit was being designed and fabricated in an independent Telic - sponsored project for use on the present program. This power supply is presently undergoing its final shakedown tests and should be placed in operation in December.

3. CdS, $Cd_xZn_{1-x}S$, AND Cu_2S DEPOSITION

3.1 Resistivity vs Temperature - Undoped CdS

The solid data points in Fig. 1 show the resistivity versus substrate temperature for CdS coatings deposited using a 99.9999% Cd target with no attempt to obtain an off-stoichiometric state. The coatings were approximately 200 nm thick, and were deposited using the same reactive sputtering conditions that are currently being used for heterojunction fabrication. The resistivity measurements were made by depositing the coatings onto glass substrates having pre-deposited Nb diagnostic electrodes. The coatings were highly photoconductive, undergoing order of magnitude increases in resistivity in the dark. The data in Fig. 1 were obtained under laboratory fluorescent lighting. Data reported by Fraser and Melchior,[5] for coatings deposited by sputtering from a CdS target in an $Ar\text{-}H_2S$ mixture and measured under a microscope lamp, are also shown, along with similar data obtained by Müller et al.[6] At low substrate temperatures ($\sim 50^\circ C$) all the data are in approximate agreement (resistivity 10 to $10^2 \Omega$-cm). However our coatings, which were deposited by reactive sputtering from a metal target, exhibit a less dramatic rise in resistivity with temperature than do the other data.

We have reported previously that CdS coatings deposited under the conditions presently being used exhibit poor adhesion when the coating thickness is greater than a few thousand Angstroms and the substrate temperature is less than about 200 to $250^\circ C$ (probably due to intrinsic stresses). An aspect of this behavior was seen in the resistivity data. Coatings deposited at substrate temperatures of less than 200 to $250^\circ C$ underwent a significant increase in resistivity during storage (over a period of several days). No change in appearance could be seen with an optical microscope. This change in resistivity (in the plane of the film) is indicated in the figure and is believed to have occurred from the development of microcracks too small to observe with an optical microscope.

A CdS resistivity of a few hundred ohm-cm could be tolerated for a thin film solar cell (CdS thickness of a few μm). Referring to Fig. 1, it is seen that such resistivities could be realized for CdS deposited at low substrate temperatures. This approach was used by Müller et al.[6] They achieved efficiencies of 1% for cells with 6μm thick CdS layers formed at a substrate temperature 80°C by sputtering from a CdS target using a working gas of Ar with 1% H_2. (The Cu_xS layers were formed by direct sputtering from a $Cu_{1.98}S$ target.) An attempt by us to use this approach (substrate temperature of 150°C) proved unsuccessful because of cracking in the CdS layer (see Section 4). Coatings deposited at 250°C to 300°C avoid the cracking problem and can be expected to have greater crystalline perfection than those formed at lower temperatures. However, the resistivities of these coatings are 10^4 to 10^5 Ω-cm and therefore too great for direct cell fabrication.

3.2 Resistivity Control by Pulsed Gas Injection

Two general approaches are being examined to achieve resistivity control by off-stoichiometry in coatings deposited at elevated substrate temperatures.[4] One is post-deposition heat treatment in hydrogen (see Section 3.3). The other is to use special deposition techniques such as pulsed reactive gas injection.

The pulsed gas injection method has been the most successful means found thusfar for controlling the resistivity by off-stoichiometry. The basis for the method is as follows. In non-stoichiometric CdS it is difficult to decide whether S vacancies or Cd interstitial atoms are the main ionized donors.[7] In either case it is important that Cd vacancies not be present in large numbers because of their compensating effect. Any environment which minimizes the formation of Cd vacancies can therefore be expected to promote the formation of low resistivity material.

Consider two energy states for atoms in a crystal, as shown schematically in Fig. 2. One is a surface state which could be physisorbed atoms. The second is an internal crystal state, which could be described in terms of vacancies which are annihilated when the sites are filled by atoms from the surface state. At equilibrium the forward and reverse transition rates between these particular levels will balance, as will the rates between these levels and all other levels (state of detailed balance).[8] Thus the rate constants cancel, and the relative populations of the states depend only on their respective energies and the temperature according to the Boltzmann relationship. Finally, the absolute population of the surface state, and thus the other levels as well, is established by the partial pressure of the atomic species in question over the free surface (the pressure establishes the arrival flux of free atoms), as is well known in crystal defect equilibrium calculations.*

The nature of the Cd-H_2S reactive sputtering process is such that under most operating conditions an energetic flux of reactive gas radicals (S and S-bearing species) is believed to be produced at the cathode and to accompany the sputtered Cd flux to the substrates.[3] The excess S is rejected at the high temperature substrate by evaporation (Fig. 2),

---

* In equilibrium calculations the state populations are determined by the relative energy levels. The population of a given state is not influenced by the inclusion or absence of other states. Thus in making equilibrium calculations the surface states are generally neglected. A Cd vacancy, for example, is considered to be formed by the transfer of a normal site to the gaseous state and one writes the defect reaction as

$$\mathrm{Cd}_{\mathrm{Cd}} \rightleftharpoons V^{x}_{\mathrm{Cd}} + \mathrm{Cd} \quad .$$

In terms of the law of mass action the equilibrium constant K is then written as

$$K = \frac{\left[V^{x}_{\mathrm{Cd}}\right] p_{\mathrm{Cd}}}{\left[\mathrm{Cd}_{\mathrm{Cd}}\right]} \quad ,$$

where p_{Cd} is the partial pressure of Cd over the surface, and the bracketed terms are the state populations.

The surface state has been introduced to facilitate discussion of the nonequlibrium deposition case.

so that the resulting coating is nearly stoichiometric and possesses a high resistivity. If the H_2S injection rate is reduced, the excess Cd is rejected, again producing a near-stoichiometric film. The process is similar to "three-temperature evaporation", described previously.

The growing coating is clearly much different from an equilibrium crystal. However, the population of Cd vacancies that survive below the coating surface must be related to the average density of free Cd atoms on the surface during deposition. The Cd surface atom density is determined by a balance between the arrival flux and the rates at which the Cd atoms interact with the crystal and with S surface atoms, or are lost by evaporation. The Cd surface density can therefore be increased by increasing the Cd arrival flux, by decreasing the S arrival flux, or by a combination of the two. Both are achieved in the pulsed reactive gas method by terminating the H_2S injection rate. The presence of H_2S in the sputtering gas causes a modified surface layer to form on the target and thereby to reduce the Cd sputtering rate. Thus, when the H_2S injection flow is terminated, the Cd sputtering rate will, after a short cathode clean-up period (τ_c), reach a value which is larger than the Cd component of the normal CdS reactive sputtering flux. Thus in the pulsed deposition method the H_2S injection rate is periodically disrupted for a time period that is longer than τ_c and the period for pumping the remaining H_2S from the chamber (τ_p), but short compared to the time to deposit a continuous film of Cd. The objective is to increase the time-averaged density of Cd surface atoms during coating growth, not to form a film of discrete alternating CdS and Cd layers. It is important to note in this respect that Cd accumulation much beyond a monolayer is not expected, because of the strong desorption effect at the substrate temperatures of interest, as described above in connection with three-temperature deposition. Thus it is probably not required or desired for the reactive gas termination period to be much longer than $\tau_c + \tau_p$.

For a simple system the mean residence time which an adatom spends on a surface is given by

$$\overline{\tau} = \tau_0 \exp\left(\frac{Ed}{kT}\right) \quad , \qquad (1)$$

where τ_0 is of the order of the Debye frequency (10^{-14} to 10^{-12} sec), T is the temperature,and k the Boltzmann constant.[9] Hudson and Sandejas[10] determined the mean residence time of Cd absorbed on W by using a shutter to interrupt the beam from a Cd evaporator and monitoring the transients in the desorption rate accompanying the opening and closing of the shutter. Their Cd flux was $\sim 10^{15}$ atoms/cm^2-sec, which is very similar to the Cd component of the CdS reactive sputtering flux in our work. Two distinct regions were found. At temperatures below about 750°C Cd atoms could be detected on the W surface when the beam was on. The residence time and associated coverage increased as the temperature was lower until a saturated coverage of a few monolayers occurred at about 600°C. The binding energy implied by the temperature dependence was about 1.77 eV, and the mean residence time at the monolayer coverage was about 1 sec. The resident time and surface coverage then remained constant down to about 150°C, where rapid increases of surface coverage with decreasing temperature began. A binding energy of about 0.9 eV (close to the heat of sublimiation of Cd, 1.16 eV) was determined for the atoms in the thicker layer.

We have conducted similar, but much simpler, experiments to obtain an indication of the behavior of the Cd flux on the CdS. The experimental configuration is shown in Fig. 3. In situ contact was made to two predeposited Nb electrodes spaced 1 cm apart on a glass substrate. A 6V potential was applied between the electrodes. The current was determined by measuring the voltage drop across a 600 ohm resister, using a strip chart recorder.

Voltages of about 0.2V could be detected on the chart recording. This corresponds to a current flow through the film of about 0.33 mA. For a film deposited between the electrodes (about 1 cm wide by 1 cm long) such a low current under an applied voltage of 6V (neglecting contact resistance) would imply a film thickness of < 1 Å (projected from bulk resistivity of Cd). Clearly, the resistivity of thin films is much greater than the bulk value. However, such an experimental configuration should be capable of sensing the formation of a continuous film between the electrodes.

In preliminary experiments the condensation of Cd on a glass substrate was investigated by observing the time required for a continuous film to form as a function of substrate temperature for a given sputtered Cd flux. At the conclusion of an experiment the Cd was removed from the plate by evaporation. Typical data are shown in Fig. 4. The Cd flux was about 10^{16} atoms/cm^2-sec. After an incubation period, which was typically about 1 min, the formation of continuous Cd coatings was consistently observed at substrate temperatures of less than 140°C to 170°C. This is consistent with the calculations given in our previous work[3], and with the observations of Hudson and Sandejas concerning the temperature at which coatings greater in average thickness than a few monolayers accumulated on W substrates.[10] Occasionally condensation was observed to occur at higher temperatures ($\sim$190°C), probably because of the presence of residual Cd on the substrate. Substrate contamination is very important in such experiments. Langmuir observed many years ago that small amounts of pre-deposited Cd (surface coverage $\sim$0.03%) greatly increased the critical Cd condensation temperature.[11] A similar effect was reported by Sigsbee while working with Sb.[12] In our case condensation was never observed over the duration of an experiment (7 min) at substrate temperatures above 200°C for the sputtered Cd flux used.

Similar experiments were conducted with pre-deposited CdS layers having thicknesses of about 30 nm or 100 nm forming the substrate for the Cd deposition. The CdS appeared to provide a more consistent substrate than the glass. The formation of continuous Cd coatings was consistently observed to occur at temperatures of 140 to 170°C or below, but not at higher temperatures for the 7 min of deposition (independent of the CdS thickness). The incubation times for the formation of continuous deposits in the 140 to 170°C range were about 1 min and therefore similar to the case of glass substrates.

The gas injection valve pulse sequence is determined by the various relevant time constants. The chamber volume is about 60 liters, and the H_2S pumping speed is about 100 liters/sec. Thus the time constant for removing gas from the bare chamber is only about 0.6 sec. The time for removing gas from the apparatus is greater than that for a simple chamber because of cathodes, substrate holders, and other equipment located in it. Other important time constants relate to the fluid flow within the gas feed system and, as stated previously, to the changing conditions on the cathode surface. Figure 5 shows the variation in gas pressure and discharge voltage during a CdS reactive sputtering experiment in which the H_2S injection was alternated for 23 sec on and 23 sec off. The Ar background pressure was constant at 0.13 Pa (1 mTorr). When the valve was opened the discharge voltage began to drop almost immediately (A in Fig. 5), while the pressure delayed for about 1 sec before rising (B). This could be due to gettering of the injected gas on the freshly coated chamber walls. After this delay, the pressure signal then began to rise as the chamber filled (C). After a period of about 6 sec both the chamber pressure and the discharge voltage had nearly reached steady state values. When the valve was closed, both the pressure and the discharge voltage remained nearly constant for a period of about 1 sec. Then the pressure dropped (D) and the voltage rose (E). This time delay may be related to residual gas in the gas injection system. The subsequent changes in voltage and pressure are very similar and largely completed in a period of about 6 sec. The similarity in temporal behavior of the discharge voltage and pressure during the reactive gas injection and removal suggests that the cathode surface conditioning time constant is short compared to those associated with the reactive gas fluid mechanics.

The data in Fig. 5 indicate that the reactive gas must be pulsed off for a period of at least 6 sec in order for the system to reach a condition where pure Cd is sputtered. Coatings have been deposited with the pulse sequences listed in Table I.

Table I

Valve Closed	Valve Open
6 sec	17 sec
17 sec	17 sec
23 sec	23 sec
30 sec	60 sec

The time periods for deposited Cd are all short compared to the incubation times for forming continuous coatings, even at low substrate temperatures (140 to 170°C as determined by in situ conductance experiments). The Cd-rich deposition should be pictured as producing an increased Cd adsorption on the CdS surface at isolated sites. The rate at which Cd atoms are transferred from a surface state to a crystal state (see Fig. 2) is, of course, a consideration.

A reduction in the resistivity by about an order of magnitude has consistently been obtained for coatings deposited in the 250 - 300°C temperature range when using the pulsed H_2S injection method. The resistivities have been typically about 10^3 Ω-cm in laboratory lighting and are indicated by the shaded region in Fig. 1. Solar-illuminated resistivities of 10^2 Ω-cm and electron mobilities of 20 cm^2/V-sec have been determined for these coatings.[2] An additional reduction in resistivity by a factor of from two to five is desired to provide a suitably low-resistant CdS layer for thin film solar cells. A slight dependence of the resistivity on the gas pulse sequence has been observed. Additional optimization work is required. Cells have been fabricated using CdS layers formed by the pulsed gas injection method. Their performance is superior to that observed previously (see Section 4). Additional work on the pulse method will depend on the promise shown by the In doping technique. A potential problem with the pulsed gas injection method is that the coatings deposited thusfar have undergone an increase in resistivity when heat treated at 250°C (see Section 3.3).

3.3 Resistivity Control by Heat Treatment

Various groups have successfully reduced the resistivity of CdS coatings by post-deposition heating in H_2.[13,14] Our approach has been to begin by exploring different annealing environments in order to determine fruitful avenues for further work. The results thusfar have not been promising. Reactively sputtered CdS coatings deposited at a substrate temperature of 250°C with continuous H_2S injection were annealed immediately following deposition in a 15% H_2 - 85% N_2 gas mixture at atmospheric pressure. Heat treatment under such conditions for 30 min at temperatures of 250°C and 350°C had no effect on the resistivity. Heat treatment of a coating at 430°C caused it to disintegrate over the glass substrate. Coatings deposited with the pulsed gas injection underwent an increase in resistivity when heat treated in the 15% H_2 - 85% N_2 ambient at temperatures of 250°C and 350°C.

Atomic hydrogen is expected to provide a more effective reducing atmosphere for heat treating the CdS coatings.[4] Atomic hydrogen can be provided by a hot tungsten ($T > 1700^\circ K$) surface[15] or by a plasma discharge. We selected the plasma discharge approach. Figure 6 shows the various electrode configurations that have been used. The approach indicated in (6A) was simply to operate the magnetron in H_2 while maintaining the CdS coated substrates at 300°C (above the condensation temperature for Cd). Atomic hydrogen from the plasma discharge and from reflection at the cathode is expected to reach the substrates. Such a treatment for 30 minutes with the discharge operating in 50 mTorr of H_2 did not reduce the coating resistivity. When the plasma discharge was formed, using a stainless steel planar electrode adjacent to the substrates, as shown in 6B, evidence of sputtered stainless steel was seen on the CdS coatings. In the configuration shown in 6C the injected H_2 was passed through a hollow cathode discharge before it reached the substrates. A distinct pattern of low resistivity material was found at the point of impact of the gas stream, possibly due to sputtered stainless steel. When the cathode was mounted parallel to the substrates as shown in 6D, a graded effect was found along the row of substrates. Experiments were conducted at substrate temperatures of 250°C and 300°C with heat treatment times from 5 to 90 min. The H_2 chamber pressure was 500 mTorr. The hollow cathode current was 75 mA. The substrates farthest from the end of the hollow cathode were not affected. Those adjacent to the end of the hollow cathode underwent a loss in thickness. The resistivity was reduced in these samples after a long heat treatment, but this reduction may have been due to the accumulation of sputtered stainless steel from the hollow cathode. Future work on the heat treatment approach will depend on the outcome of the doping studies.

3.4 Resistivity Control by Doping

The objective in the present program is to investigate indium doping of CdS in sufficient detail to determine whether the high doping levels (which previous work indicates are required) compromise the performance of the cells.[4] CdS, rather than $Cd_xZn_{1-x}S$, was selected because of the greater available data base on the performance of CdS solar cells.

Three methods may be used to implement the In doping in the CdS reactive sputtering process:

1) Co-sputtering from Cd and In targets in an H_2S - Ar working gas.
2) Sputtering from an In doped Cd target in an H_2S - Ar working gas.
3) Diffusion of In into a reactive sputtered CdS layer by depositing the CdS over an In coated substrate.

Co-sputtering from Cd and In targets was investigated in previous work.[3] The oblique angles associated with co-deposition tend to develop porous coating structures. Thus this method was used primarily to establish the doping levels required for fabricated In-doped Cd targets. The investigation indicated that one atomic percent of In would provide CdS with a resistivity of about 0.1 Ω-cm when deposited at 300°C. A slightly higher resistivity could be expected for a lower substrate temperature. The work described in the previous quarterly report[4] indicated that the substrate temperature during deposition of the CdS should be less than 250°C in order to avoid the passage of electrically active impurity species from the Nb coated substrate into the coating. Accordingly a 99.9999% Cd target with one atomic percent In was ordered. Work was delayed, because the indium doped target and two replacement targets possessed vacuum leaks, and because the vendor confused one of these targets with an undoped target in labeling.[4] The vacuum leak problem was finally identified by the vendor as resulting from an attempt to use a different casting technique than the one which had been used in the past to produce four targets of good quality. A satisfactory Cd target with one atomic percent In has now been received and placed in operation.

Figure 7 shows the resistivity versus substrate temperature for CdS coatings deposited by reactive sputtering using the Cd target doped with 1 atomic percent In. The coatings were approximately 150 nm thick, and were deposited using the same reactive sputtering conditions and measurement procedures that were used for the undoped target data given in Fig. 1 and that are shown as a dashed curve in Fig. 7. The relatively high doping level is seen to yield a resistivity which is reduced by several orders of magnitude (to about 0.1 Ω-cm) and also has a reduced dependence on substrate temperature. The doped coatings were slightly photosensitive, undergoing a resistivity increase of about 30% in the dark. van der Pauw measurements at Lockheed yielded mobilities of about 10 cm^2/V-sec and carrier concentrations of about 7 x 10^{18} cm^{-3}. This implies a doping efficiency of about 3.5%. This is consistent with the value reported by Partain et al.[16] for single crystal CdS. The resistivity of the doped CdS is also seen to be consistent with the predictions based on the co-deposition doping studies.[17]

The resistivity level of the coatings doped with 1 atomic percent In is in the desired range for making n^+/n cells but too great for making cells with homogeneous CdS layers (see Section 4). Therefore, as part of the continued investigation of the effects of In doping, a 99.9999% Cd sputtering target containing 0.1 atomic percent of In has been ordered.

Figure 8 shows the CdS films resistivity as a function of substrate temperature for coatings doped by the third method—diffusion of In from an In-coated substrate. The coatings were about 5 μm thick and were deposited using the same reactive sputtering conditions as were used for the data shown in Figs. 6 and 7. The target was a 99.9999% Cd cathode. The coatings were deposited over a 50 nm thick layer of In. If this In were to be uniformly distributed within the CdS, it would correspond to a doping level of 2 atomic percent. The method is seen to be reasonably effective in producing doping levels in a desirable range (10 to 100 Ω-cm) over the substrate temperature range of interest. van der Pauw measurements at Lockheed yielded mobilities of about 25 cm^2/V-sec with carrier concentrations in the range from 3×10^{15} cm^{-3} to 5×10^{16} cm^{-3}.

3.5 Cu_2S Deposition Studies

The following five factors are believed to be particularly important in controlling the Cu_xS reactive sputtering process.

1) The H_2S injection rate.
2) The substrate temperature.
3) The chemical state of the cathode (target) surface.
4) The chemical state of the chamber or shield walls surrounding the source.
5) The chemical state of the substrate surface.

A detailed study of the influence of the H_2S injection rate, and to some extent the substrate temperature, for Cu_xS coatings deposited onto glass substrates was conducted during the previous program.[18]

Coatings about 150 nm thick were deposited at substrate temperatures of about 35°C and 130°C using various H_2S injection rates at a fixed Ar partial pressure and discharge current. Prior to each deposition the cathode was operated for 10 min at the H_2S injection rate of interest to condition the state of the cathode, wall and shield surfaces. Figure 9, from this work, summarizes (1) the working pressure change during discharge ignition, (2) the discharge voltage, and (3) the coating resistivity, as functions of the H_2S injection rate. The pressure change is a measure of the consumption of H_2S in the chemical reaction. Discharge voltage variations at a fixed discharge current provide an indication of the change of state of the cathode surface (changes in the electron secondary emission coefficient). Three operating ranges were identified. At low H_2S injection rates (Region I) the pressure change corresponded closely to that assocciated with complete consumption of H_2S. The coatings were of a mixed metal-sulfide type and exhibited a resistivity which increased with increasing H_2S injection rate. The discharge voltage also increased. At intermediate rates (region II) the pressure change was less, the voltage began decreasing, and the resistivities peaked at values characteristic of chalcocite ($\sim 10^2$ Ω-cm). Beyond this critical range of injection rates two distinct materials were observed. One material, which formed primarily on the substrates at 130°C, exhibited a resistivity of about 10^2 Ω-cm and a relatively high density of Cu nodules (several μm in size) on the surface. X-ray diffraction indicated that the material was primarily chalcocite with a small djurleite content which increased with increased H_2S injection rate. The Cu nodule density decreased with increasing H_2S injection rate. The second material, which formed primarily on the low temperature (35°C) substrates, exhibited a resistivity of about 10^{-2} Ω-cm and a much lower density of nodules, which virtually disappeared with increasing H_2S injection rate. X-ray diffraction showed this material to be a mixture of chalcocite and djurleite, becoming primarily djurleite with increasing injection rate. The absorption coefficients of the high resistivity material, and the low resistivity material deposited at low H_2S injection rates, were found to be in excellent agreement with those previously reported for chalcocite.[18] The net absorption coefficient of the high resistivity material was decreased, however, by the shadowing effect to the copper nodules. The absorption coefficient of the low resistivity material that was deposited at high H_2S injection rates appears to correspond to a mixture of the chalcocite and djuleite. At high H_2S injection rates (region III) the pressure change and discharge voltage are seen in Fig. 9 to be nearly independent of injection rate.

Deposition conditions for Cu_xS layers deposited during most of our heterojunction studies using the multi-source deposition apparatus have differed from those used in the preliminary study in the following ways:

1) The coatings were deposited onto CdS rather than glass substrates.
2) The substrate temperature was 150°C (the higher substrate temperature was used to minimize the time delay between the CdS and Cu_xS depositions and to assist in formation of the junction).
3) Extensive conditioning of the cathode was not used between the CdS and Cu_xS depositions.

Several inconsistencies have been encountered between the resistivities of Cu_xS coatings deposited in the heterojunction work and the trends shown in Fig. 9. Thus at the start of the present program a procedure was adopted whereby the Cu cathode was operated in Ar for 5 min to clean the surface and then in H_2S for 3 min to condition the surface before opening the chamber and loading the substrates. During cell fabrication, following the CdS deposition, the Cu cathode was again conditioned by operating in H_2S for 4 min with the substrates shielded. The resulting coatings were found to have low resistivities over injection rates ranging from 0.07 to 0.175 Torr-liters/sec, even though the deposition temperature was 150°C, at odds with Fig. 9. When the <u>in situ</u> conditioning step was discontinued, the expected high resistivity coatings were deposited. The cause of the low resistivity coatings was tentatively attributed to heating of the cathode shield and the release of sulfur-bearing species which effectively increased the H_2S injection rate.[4]

Additional work was conducted during the present reporting period with particular emphasis on the role of the CdS substrate and those aspects of the Cu_xS deposition procedure that can be expected to be applicable to the modified apparatus (see Section 2). Thus coatings have been deposited onto pre-deposited CdS layers, 500 nm thick, at substrate temperatures of 50°C and 150°C. The circular shield was removed from the Cu source (see Fig. 2 of Ref. 4) to approximate the modified apparatus, and particular attention has been given to the effects of cathode sputter cleaning and conditioning, since the modified apparatus will permit effective incorporation of these procedures. The following has been observed.

1) The basic resistivity versus H_2S injection rate relationship shown in Fig. 9 for glass substrates has been confirmed for coatings deposited onto CdS. Thus at moderate H_2S injection rates coatings with high resistivities were obtained at substrates temperatures of 50°C and 150°C. Above a critical injection rate of about 0.14 Torr-liters/sec, coatings with low resistivities were obtained at 50°C. At high injection rates low resistivities were also found for the 150°C coatings. The data is summarized schematically in Fig. 10. In all cases the cathode was sputter-cleaned in Ar and pre-conditioned just prior to depositing the Cu_xS coating, by operating for several minutes at the prescribed H_2S injection rate with the substrates shielded.

2) With one exception (see item 4 below), regardless of the deposition conditions, those Cu_xS coatings with high resistivities possessed a relatively high density of the Cu surface nodules, while those with low resistivities did not. The nodule diameter was typically about 2 μm. The nodule surface density was typically about $5 \times 10^6/cm^2$, decreasing slightly with increased H_2S injection rate. See Fig. 11.

3) The required Cu_xS coatings are sufficiently thin so that the amount of sputtering required to deposit the coatings is small compared to that amount which is required to reach a state of equilibrium on the cathode and shield or chamber wall surfaces. Consequently the system can have a memory of previous deposition conditions, or can undergo a drift when an attempt is made to operate under fixed conditions. This is believed

to be the cause of two departures which were seen from the data shown in Fig. 10. In one case a series of Cu_xS coatings were deposited at 150° with the cathode surface in the state which existed following a previous set of cell depositions. The resistivities were low over H_2S injection rates of from 0.05 to 0.2 Torr-liters/sec, even though the cathode was preconditioned by sputtering in the desired Ar-H_2S mixture for 4 min prior to exposing the substrates. Consistent results were obtained in subsequent work after the cathode was extensively sputter-cleaned in Ar. In a second case, a high rather than the expected low resistivity was obtained in a 50°C coating deposited at a high H_2S injection rate just following work at low injection rates, even though the cathode was pre-sputtered in Ar for 3 min and preconditioned in H_2S for 4 min. The solution to these unwanted variations is to suitably sputter-clean and condition the cathode for a sufficient length of time before each deposition. It will be possible to conveniently perform this operation in the modified apparatus.

4) The dependence of the Cu_xS coating properties on the state of the cathode and wall surfaces at the start of deposition raises the possiblity of forming coatings under combinations of conditions not shown in Fig. 10, by conditioning the cathode under one set of conditions and depositing the coating under another. In one case this procedure provided a high resistivity coating with an almost negligible density of Cu nodules. Additional work is required to explore the feasibility of this approach.

5) The Cu_xS coating appears to produce a high state of stress in the Cu_xS/CdS composite, at least after exposure to the atmosphere. Thus the bare 50 nm thick CdS coatings exhibited reasonably good adhesion on the glass substrates. However, the CdS coatings which were over-coated with 150 nm of Cu_xS often exhibited poor adhesion, particularly after exposure to the atmosphere. Internal stress levels in representative CdS and Cu_xS coatings were reported in Ref. 17.

The cylindrical symmetry and the uniformity of the deposition flux in cylindrical magnetron sputtering sources often permit a useful comparison to be made between experimental observations and calculations. Such is the case with Cu_xS reactive sputtering where order-of-magnitude calculations provide an indication of the mechanisms that may lead to the copper nodule formation. A common observation during reactive sputtering with cylindrical magnetrons is that at low reactive gas injection rates virtually all of the injected gas is consumed in the reaction (gettered by the metal component of the coating which is deposited over a sufficiently large area to make the getter pumping speed large compared to that of the physical pump). At a critical injection rate the reactive gas consumption stops increasing abruptly and may actually decrease (for a fixed discharge current). This point generally corresponds to the formation of a stoichiometric compound.

Consider the particular case of Cu_xS shown in Fig. 9. An abrupt cessation in the rate of increase of the reactive gas consumption (pressure change) occurs at an injection rate of about 0.10 Torr-liter/sec and corresponds to a peak in resistivity of the resultant coatings at a value ($\sim 10^2$ Ω-cm) consistent with the formation of chalcocite. X-ray diffraction confirms that the coatings are primarily chalcocite. The coatings are covered with surface cones (Fig. 11) which are found by microprobe analysis to be elemental copper. The cones are typically about 2 μm in diameter with a density between 10^6 and $10^7/cm^2$ (Fig. 11A). They often, but not always, have a general conical shape (Fig. 11B and are poorly bonded to the substrate (Fig. 11C) A measurement of the coating thickness at the wall of the cavity left by a departed nodule (Fig.11D) suggests that the base of the nodule is at the CdS/Cu_xS interface.

The discharge voltage is in the range 1100 to 1300V (Fig. 9). The sputtering yield for copper bombarded with 1000 eV Ar ions is a little over 3.[19] We pick a value of 3, since some of the ions are H_2S rather than Ar, and since the cathode surface is slightly modified (voltage increase with H_2S injection seen in Fig. 9). The discharge current is 1A. For a secondary emission coefficient of 0.10 (this is a typical value for Ar bombardment of a metal) the total ion flux to the cathode is 5.7×10^{18} ions/sec. For a sputtering yield of 3 the sputtered flux is therefore 0.49 Torr-liter/sec (1 Torr-liter = 3.5×10^{19} atoms). The injected H_2S flux is about 0.10 Torr-liter/sec. This ratio of the Cu/S flux entering the reaction is about 4.9. One would expect a ratio of 2 for the formation of Cu_2S. The larger value is consistent with the presence of the Cu nodules. The density of nodules is about $5 \times 10^6/\text{cm}^2$. The volume of a nodule with the shape of a right circular cone, a base diameter of 2 μm and a height of 2 μm, is $2.1 \times 10^{-12}\ \text{cm}^3$. Thus if an average nodule volume of $2 \times 10^{-12}\ \text{cm}^3$ is assumed, the volume of Cu per cm^2 in the nodules is $10^{-5}\ \text{cm}^3$. This corresponds to Cu density per unit surface area of film of 1.4×10^{-6} moles/cm^3. The coatings such as those shown in Fig. 11 were typically 150 nm thick. The surface density of Cu and sulfur in a 150 nm thick coating of Cu_2S is: Cu = 1.1×10^{-6} moles/cm^2 and S = 0.54×10^{-6} moles/cm^2 (the volume loss in the base of the cones can be neglected). Thus the Cu/S ratio for a Cu_2S film containing a surface density of $5 \times 10^6/\text{cm}^2$ of 2 μm diameter conical nodules is 4.6. This is in reasonable agreement with the value of 4.9 predicted from the sputtered Cu and injected reactive gas fluxes.

There is reason to believe that stoichiometric high resistivity Cu_2S may be unstable in the absence of excess Cu.[18] The shape and spacing of the nodules suggests that they may form at discontinuities or other imperfections on the substrate and become repositories for excess Cu which arrives in the coating flux when Cu/S >2 and is rejected by the Cu_2S coating. See Figs. 11 and 12. Thus a large area surrounding a nodule becomes a collection region for feeding Cu to a given cone by lateral diffusion, as indicated in Fig. 13. At elevated substrate temperatures (130 to 150°C) the formation of high resistivity material (Cu_2S) with nodules continues as the H_2S injection rate is increased. This could be due to a high Cu diffusion rate, instability of the Cu_2S, or a reduced S sticking coefficient. At low substrate temperatures (30 to 50°C) a low resistivity material is formed at H_2S injection rates that are larger, but not large enough to convert all the Cu to Cu_2S. The nodule density in this material is much reduced and in many cases totally absent. This suggests that the excess copper may be trapped in solution, the host being a mixture of chalcocite and djurleite. When the H_2S injection reaches a value of 2.5 Torr-liters/sec, the ratio of the sputtered Cu to the injected S is two, and the simple considerations described above would suggest that copper nodules would no longer form. High nodule densities were not observed at high H_2S injection rates.[3,18] It is interesting to note that this injection rate corresponds to the boundary between Regions II and III in Fig. 9 and approximately to the occurrence of low resistivity, nodular free deposits, even at 150°C, in Fig. 10.

4. DEVICE-MATERIAL PARAMETER OPTIMIZATION

The following four types of cells were fabricated during the present reported period.

1) Cells with CdS deposited at low temperatures (150°C).
2) Cells with CdS resistivity control by pulsed gas injection.
3) Cells with CdS doped with 1 atomic percent In.
4) Cells with composite n^+/n CdS structure consisting of n^+ region doped with 1 atomic percent In adjacent to rear electrode and undoped region adjacent to junction.

All cells were fabricated onto 7059 glass plates, 25 mm x 25 mm x 1.2 mm. The basic cell configuration is shown in Fig. 4 of Ref. 3. A Nb rear electrode 100 nm thick was deposited onto the glass substrates in a separate pumpdown. These precoated substrates were then stored and used as required in the multi-source deposition chamber where sets of three cells were formed at one time. Predeposition pumping was typically to a pressure of 10^{-4} to 10^{-3} Pa. The substrates were generally heated at a temperature of 250°C or higher for at least one hour prior to deposition to assist the outgassing. The CdS layers were typically 3 to 6 μm thick. The Cu_2S layers were 150 nm thick. The Au top grid electrodes were applied in a separate chamber by sputter deposition using a mechanical mask. The grid consists of 31 lines 0.05 mm wide and 1 μm thick, spaced on 0.75 mm centers. The bus bars that connect the lines are not being deposited at the present time. An antireflective layer is also not being used at this time.

Low Temperatures CdS. Referring to Fig. 1, one sees that resistivities of a few hundred ohm-cm can be obtained in undoped CdS by depositing at a low substrate temperature. This is in a range suitable for forming thin film solar cells. This approach was used by Muller et al.[6] to fabricate all sputter-deposited cells having efficiencies of about 1%. An attempt was made to form cells using a CdS layer deposited at 150°C. The approach proved unsuccessful because of cracking in the CdS layer. See Section 3.1.

CdS Resistivity Control by Pulsed Gas Injection. Several cells were fabricated using undoped CdS in which the resistivity was controlled by pulsed gas injection. See Section 2.3. The CdS layers were nominally 4 μm thick and were deposited with a valve-pulse sequence in which the H_2S injector valve was open for 23 sec and closed for 23 sec, as shown in Fig. 5. The deposition temperature was 250°C. This is a change from the 300°C substrate temperature that had been used in earlier cell fabrication.[4] As reported on Ref. 4, a substrate temperature of 300°C was found to result in a spurious diffusion from the rear electrode. The Cu_xS layers were deposited at a substrate temperature of 150°C using an H_2S injection rate of 0.1 Torr-liters/sec. No in situ cathode conditioning was used. The substrate cooling delay time between the CdS and Cu_2S deposition was about 15 minutes.

These cells have provided the best performance achieved thusfar. Evaluation and heat treatment studies were conducted at Lockheed. The as-deposited cells exhibited short circuit currents of about 1 mA/cm^2 and open circuit voltages of about 0.27V under a solar simulator at an incident power of 107 mw/cm^2. Annealing in H_2 at 200°C for 2 minutes raised the open circuit voltage to about 0.43V and the short circuit current to about 3 mA/cm^2. The IV characteristic for a cell in this group (#653) with an efficiency of about 0.6% is shown in Fig. 14. Additional annealing for 2 min at 200°C caused a drop in short circuit current to about 2.5 mA/cm^2.

CdS doped with 1% In. Two sets of cells were fabricated with CdS layers deposited using a cathode doped with 1 atomic percent of In. The substrate temperature was 250°C. The CdS resistivities were not measured but are projected from Fig. 7 to be about 0.15 Ω-cm. The Cu_xS layers were deposited at a substrate temperature of 150°C using an H_2S injection rate of 0.1 Torr-liters/sec. The Cu cathode was sputter cleaned in Ar for 1 min and pre-conditioned in H_2S just prior to depositing the Cu_xS layer.

No barrier developed between the Cu_xS and CdS in these cells. This may have been the result of electron tunneling. The calculated depletion layer thickness, based on carrier concentrations measured in similar CdS, was only about 10 nm.[20] Annealing in H_2 at 200°C did not develop the barrier by, for example, causing Cu to diffuse into the CdS and widen the depletion layer by compensating the In.

Composite n^+/n CdS Structure. Several cells were fabricated with a composite CdS structure consisting of a 0.5 μm thick layer of undoped CdS deposited over a thicker (4 to 6 μm) CdS layer doped with 1 atomic percent In. The substrate temperature was 250°C for both layers. The Cu_xS was deposited at a substrate temperature of 150°C using H_2S injection rates of from 0.1 to 0.3 Torr-liters/sec. The copper cathode was preconditioned in H_2S for from 4 to 10 minutes prior to depositing the CdS layer.

All of the cells fabricated by this technique possessed rectifying junctions that exhibited a photovoltaic effect in the as-deposited state. Open circuit voltages were in the range 0.10 to 0.15V. Preliminary annealing studies indicate some improvement in both the open circuit voltage and the short circuit current.[20] Meaningful short circuit current and efficiency data are not available at the present time, since the cells were examined only with respect to the individual grid bars. This was done to assess the cell uniformity. About 75% of the grids gave good diode characteristics, about 15% had soft reverse bias characteristics, and about 10% were shorted. The frequency of shorting appeared to vary with the width of the gold grid lines (i.e., the probability of the gold covering a flaw in the CdS). Additional work is required to improve the mask contact and therefore the width of the grid lines as well as the integrity of the CdS. One cell had no shorts and only one soft diode characteristic. Therefore the prospect for improving these cells appears good.

The structure of the composite CdS layer has been studied at Lockheed[20] by capacitance-voltage measurements. The measurements show a carrier concentration of about 5×10^{13} cm^{3} in the undoped region and verify a large increase in carrier concentration ($>10^{17}$ cm^{-3}) at a distance of 0.48 μm below the junction.

The overall structure of the CdS layer is columnar, as shown in Fig. 12 A and C. Many of the cells exhibited a high density of the Cu nodules, as can be seen in Fig. 12. (See Section 3.5.) An important observation was that Cu nodules under a Au contact grid did not result in a cell short, even though the nodules extend through the Cu_xS layer as shown in Fig. 11.

<u>Controlled Atmosphere Containers</u>. A set of shipping containers which permit cells to be shipped from Telic to Lockheed under vacuum or in a controlled atmosphere has now been put into service. Cells and other samples are stored under vacuum at Telic prior to shipment to Lockheed.

5. SUMMARY STATUS

Considerable progress has been made on all three Research tasks during this reporting period. Design of the modified apparatus (Task 1) was delayed to take advantage of the experimental observations during the early part of the present program, but has now been completed. Parts fabrication is nearing completion and assembly onto the vacuum pumping stand is scheduled for mid-December.

Progress has been made in controlling the resistivity of reactively sputtered CdS coatings by achieving off-stoichiometry through the use of special deposition methods (Task 2). An order of magnitude reduction in the resistivity of coatings deposited at a substrate temperature of 250°C has been achieved by using a cyclic reactive sputtering process where the H_2S injection is periodically switched on and off. Typical resistivities are about $10^3\,\Omega$-cm. Carrier mobilities are about 20 cm^2/V-sec. Cells fabricated using this method have yielded efficiencies of about 0.6% with short circuit currents of about 3.5 mA/cm^2, open circuit voltages of about 0.43 V, and fill factors of about 0.4 (Task 3). These are the highest efficiencies achieved thusfar.

Progress has also been made in controlling the resistivity of reactively sputtered CdS coatings through the use of In doping. Resistivities in the range 10 to 100 Ω-cm has been achieved for 5 um thick CdS coatings deposited of 50 nm thick pre-deposited In layers at substrate temperatures in the range from 300 to 300°C. Carrier mobilities are about 25 cm^2/V-sec. Resistivities in the range from about 0.05 to 0.15 Ω-cm have been achieved by depositing coatings at substrate temperatures in the range 150 to 300°C, using a Cd target doped with 1 atomic percent of In. Carrier mobilities are typically about 10 cm^2/V-sec. Cells with an n^+/n design, using a 0.5 um thick undoped CdS layer adjacent to the junction, and a 0.1 Ω-cm base layer deposited from the doped cathode, have consistently yielded encouraging diode characteristics with a strong photo-voltaic effect. It is planned that cells of this design will be used in an optimization study.

CdS deposition temperatures for cell fabrication have been decreased from 300°C to 250°C following the recommendations of the rear electrode interaction studies reported in Ref. 4. This change in fabrication procedure has eliminated the occurrence of non-ohmic rear electrode contacts.

Considerable progress has been made in reducing the number of pinhole shorts which are present in Au gridded cells.

The modified apparatus with its interlock substrate insertion system and improved inter-source shielding will permit much better control over the Cu_xS deposition process. The Cu_xS deposition is particularly vulnerable to process drifts, because the deposition time is short compared to the typical times required to condition the cathode and the deposition surfaces. Preliminary experiments have examined these influrences from the point of view of the control that will be available in the modified apparatus.

Major activities during the next reporting period will concentrate on the studies of CdS resistivity control, using In-doped sputtering sources, and on assembly of the modified apparatus.

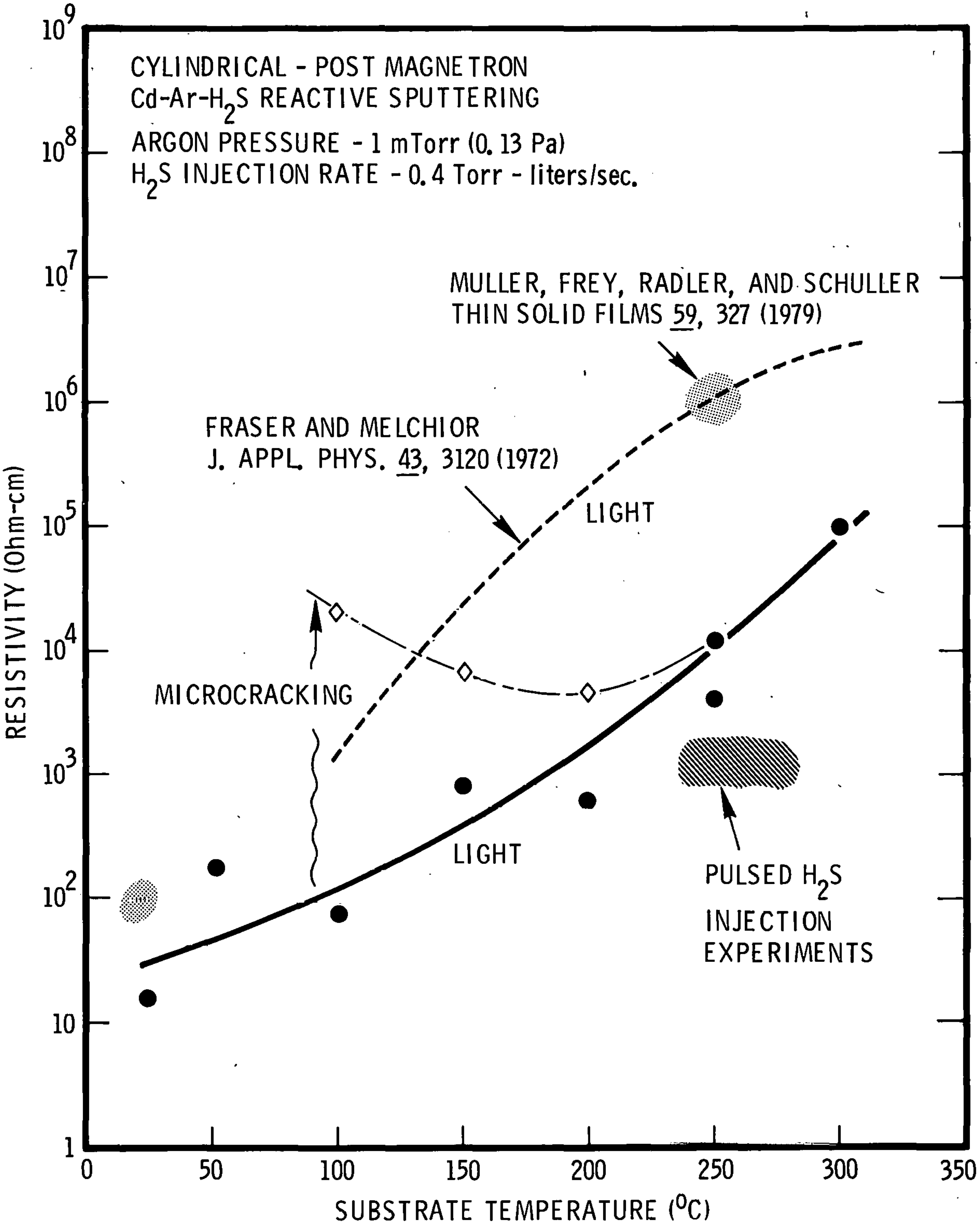


Fig. 1 Resistivity versus substrate temperature for CdS coatings deposited with a 99.9999% Cd target. Data points refer to restivities measured in the plane of the film. The data by Fraser and Melchior are for measurements through the thickness of the film.

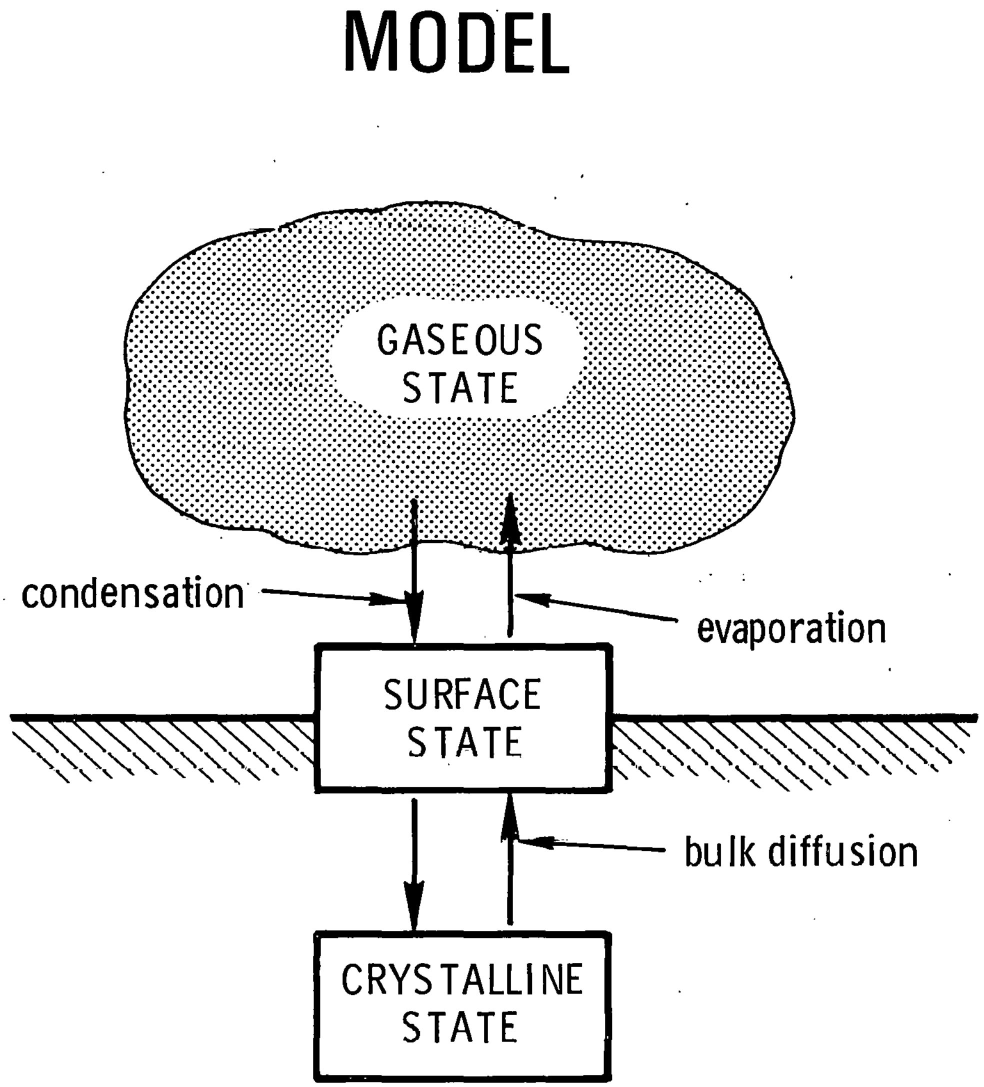


Fig. 2 Schematic representation showing energy states at surface and within crystal to illustrate the model that was used as basis for pulsed reactive gas injection method.

IN SITU RESISTIVITY-APPARATUS

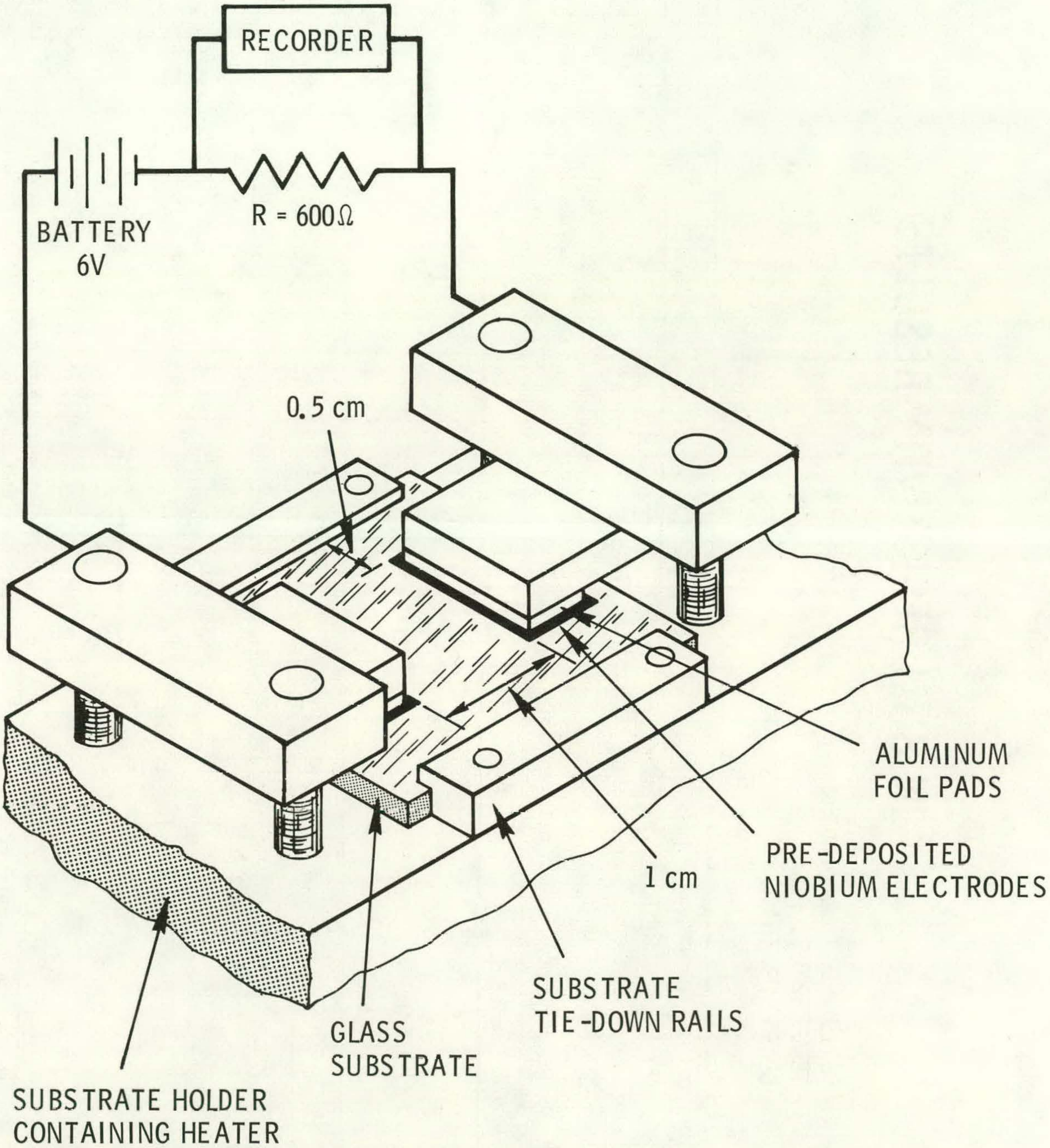


Fig. 3 Electrode configuration that was used in making in-situ resistivity measurements. Electrode assembly attached to same substrate holder that was used in depositing solar cell coatings.

IN SITU RESISTIVITY-RESULTS

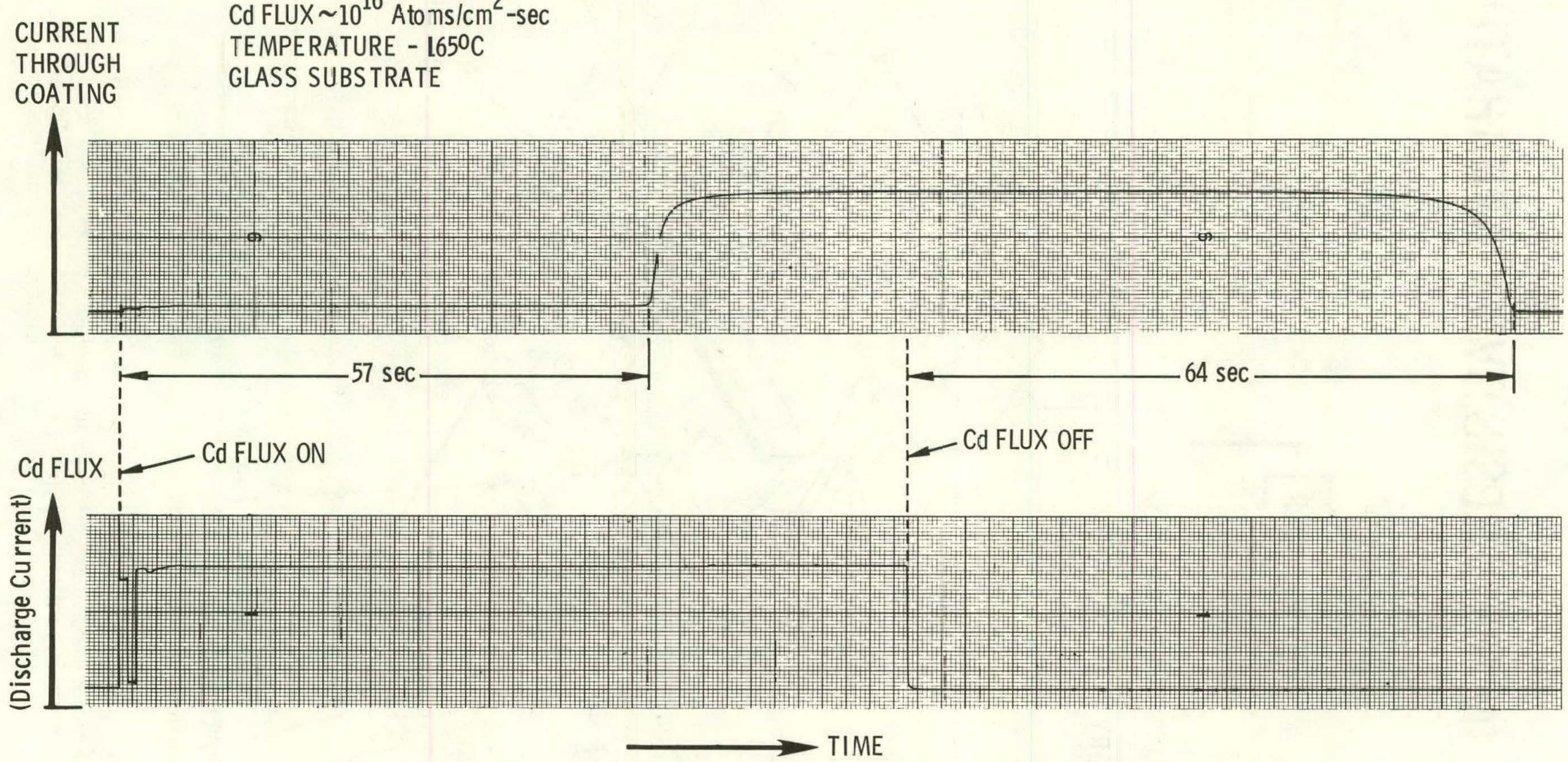


Fig. 4 Typical result from in-situ resistivity measurements. Continuous coating forms 57 sec. after supttered Cd flux is initiated and is removed by evaporation 64 sec. after sputtered flux is terminated.

PULSED H_2S INJECTION

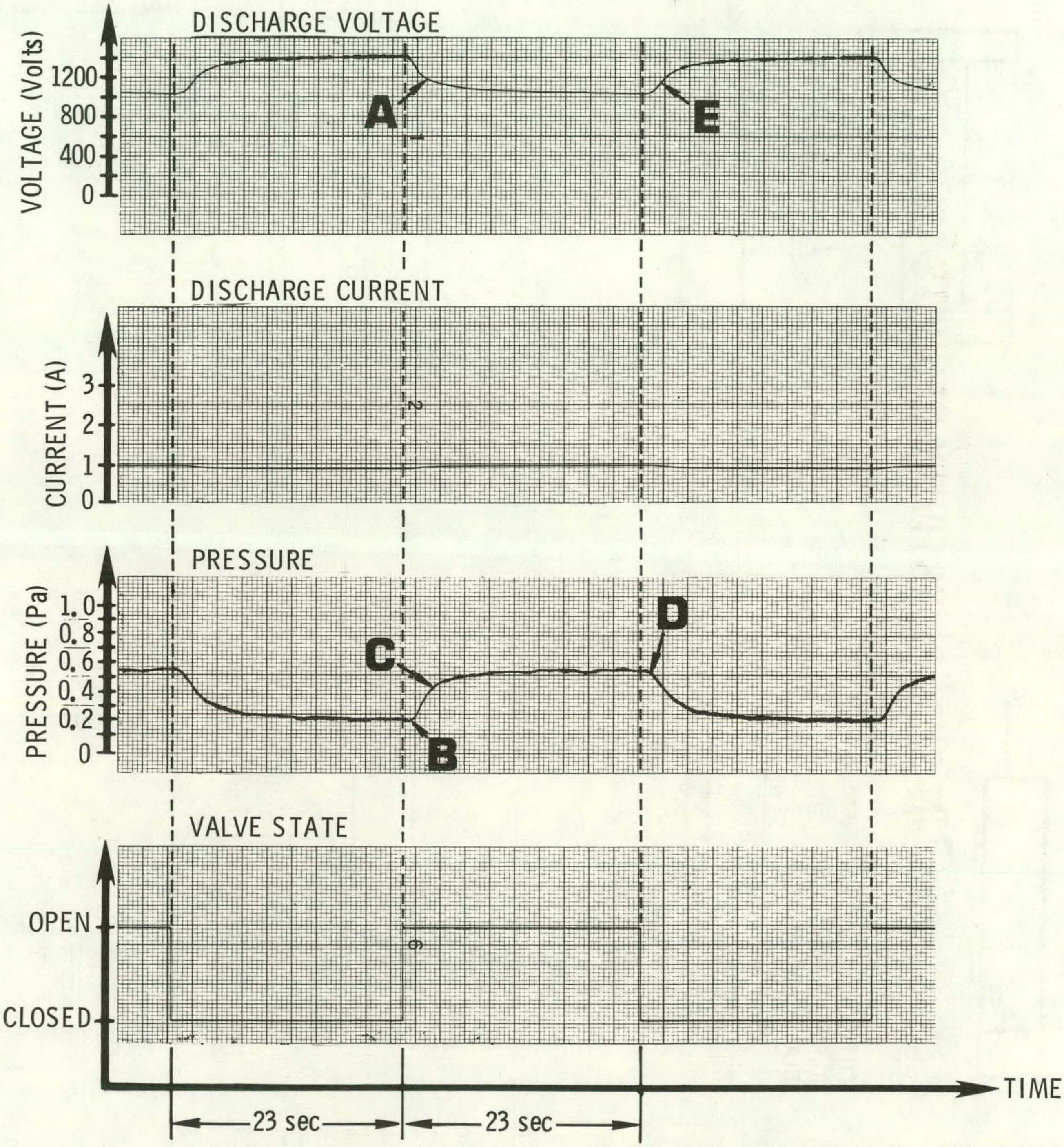


Fig. 5 Strip chart recording of valve state, total system pressure, discharge current, and discharge voltage during deposition using pulsed reactive gas injection method for reactive sputtering Cd in Ar - H_2S mixture. Ar pressure 0.13 Pa. See text for explanation of A, B, C, D and E.

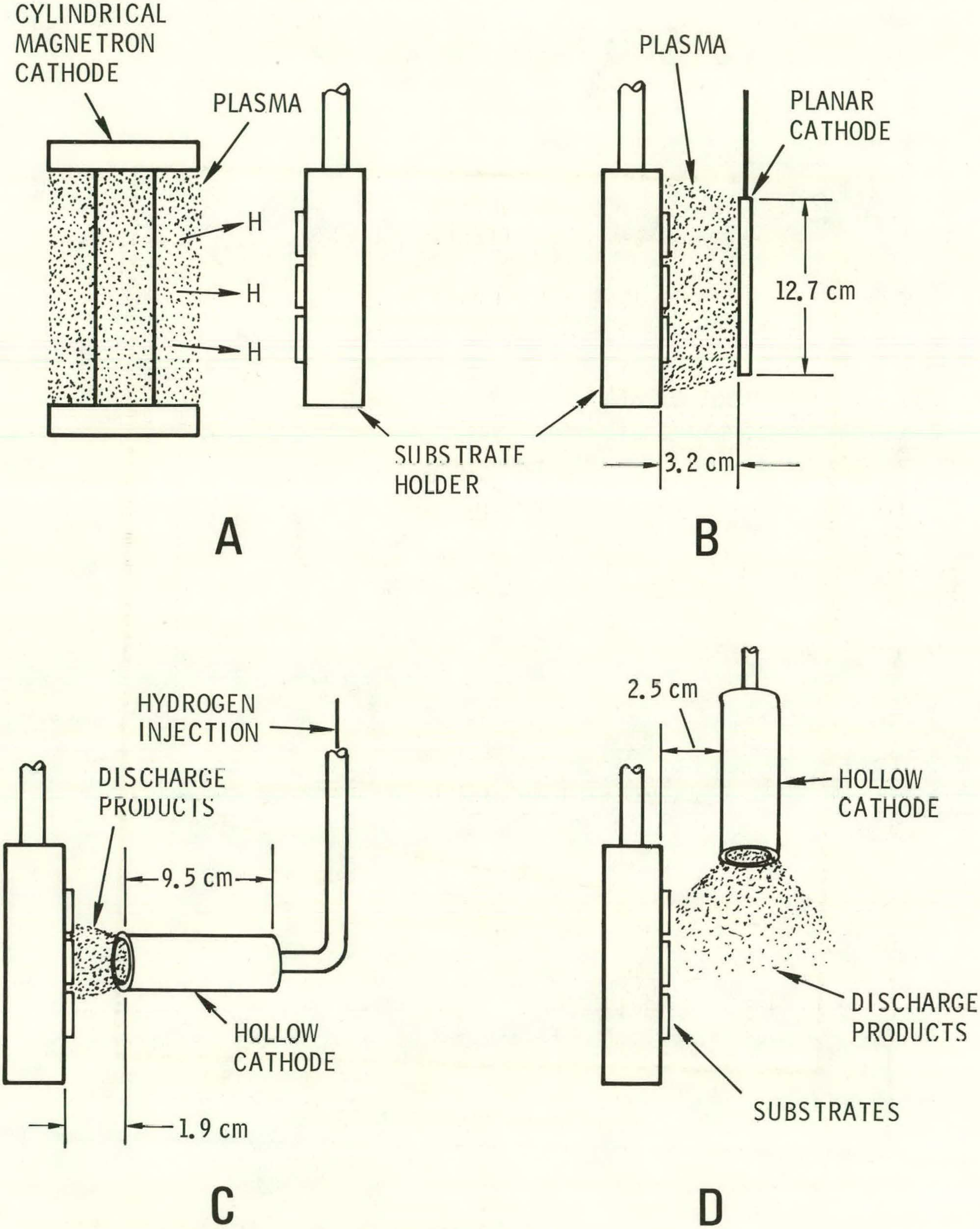


Fig. 6 Schematic illustration of various electrode configurations that were used to permit CdS coatings to be heat-treated in the presence of a H_2 plasma discharge or the products of such a discharge.

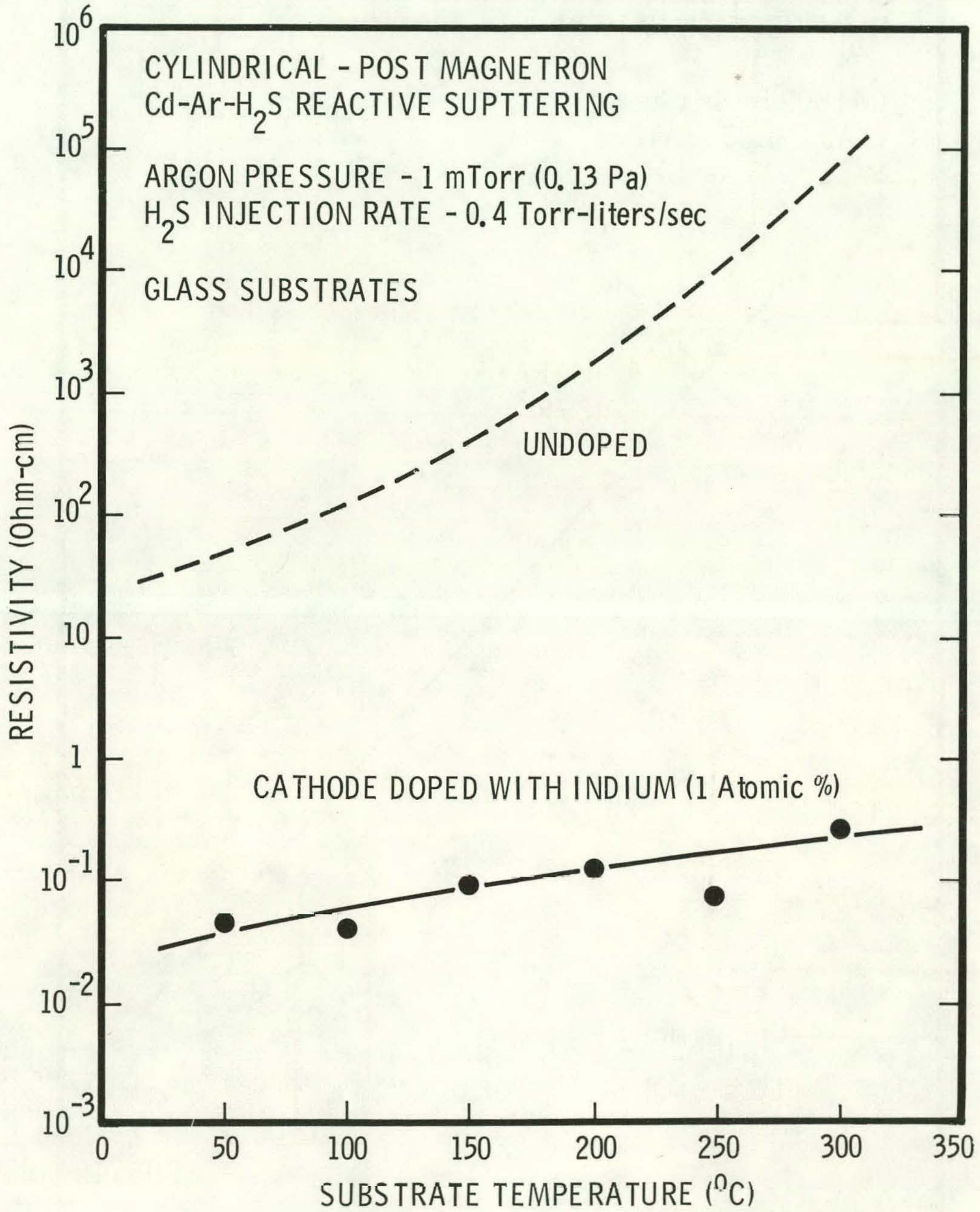


Fig. 7 Resistivity versus substrate temperature for CdS coatings deposited using Cd target doped with 1 atomic percent In. Restivities were measured in the plane of the film under fluorescent lighting. Dashed curve refers to undoped coating data from Fig. 1.

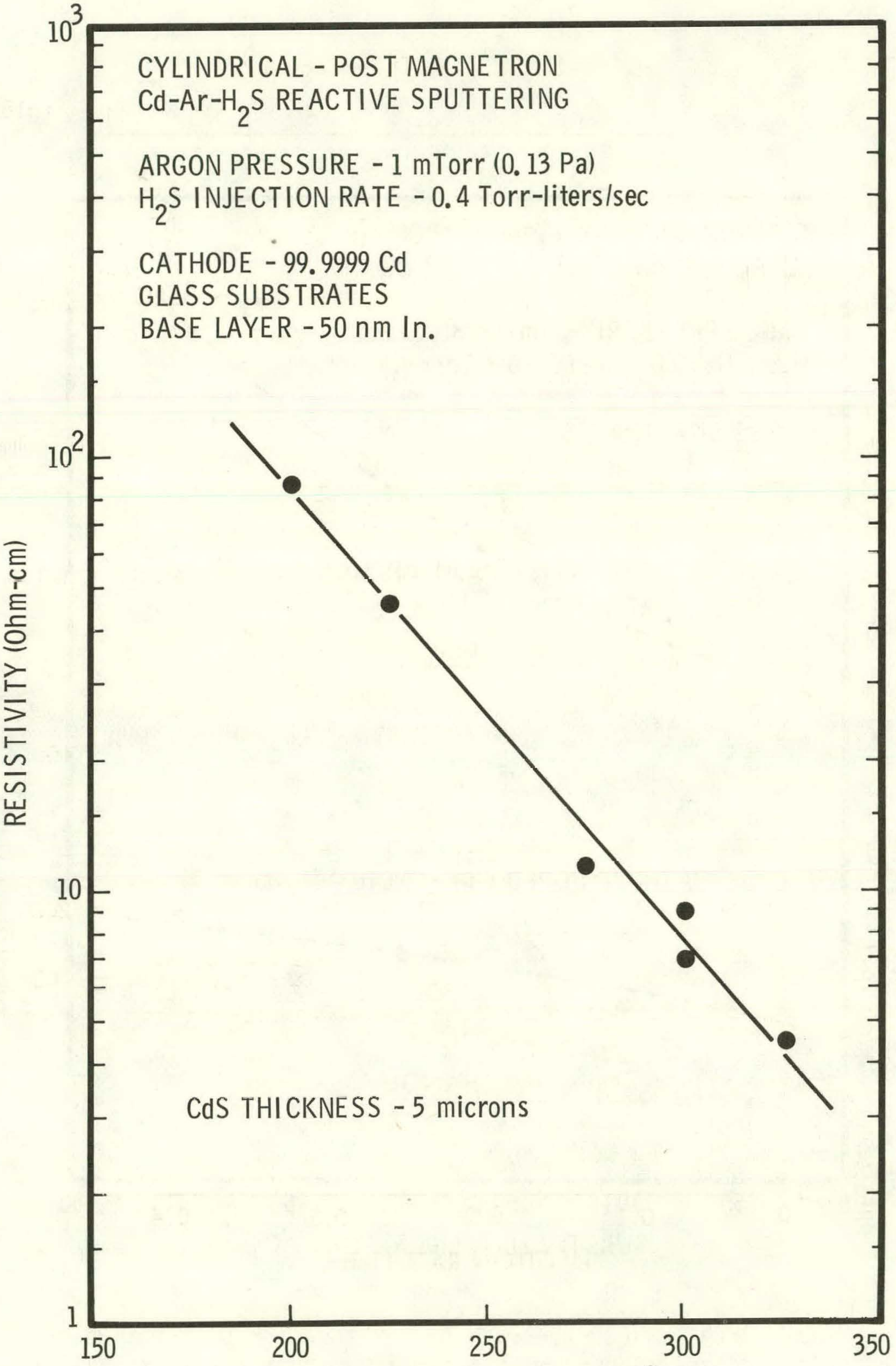


Fig. 8 Resistivity versus substrate temperature for CdS coatings doped by diffusion from a predeposited In layer.

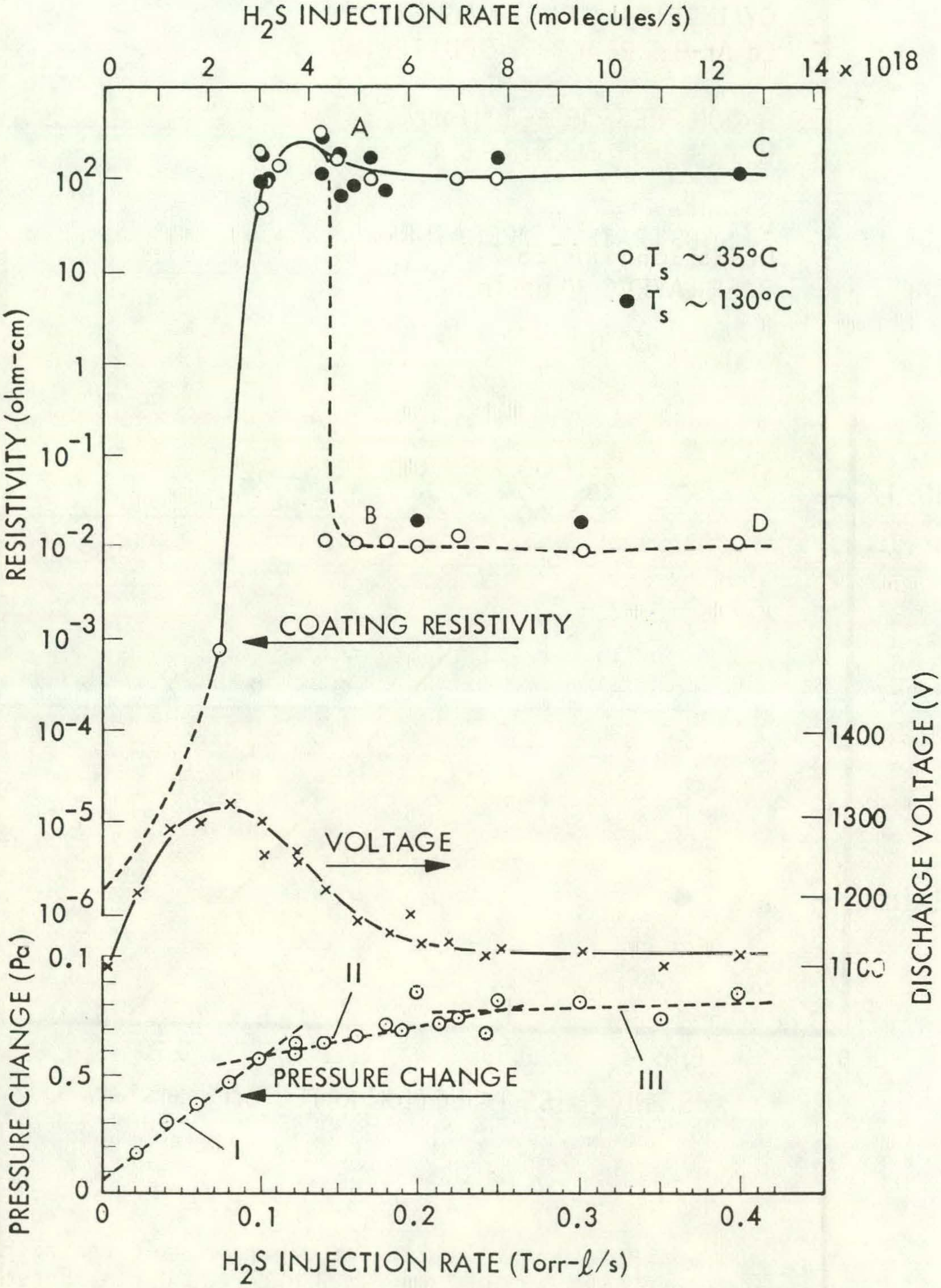


Fig. 9 Reactive sputtering of Cu in Ar-H_2 gas mixture. From Ref. 18.

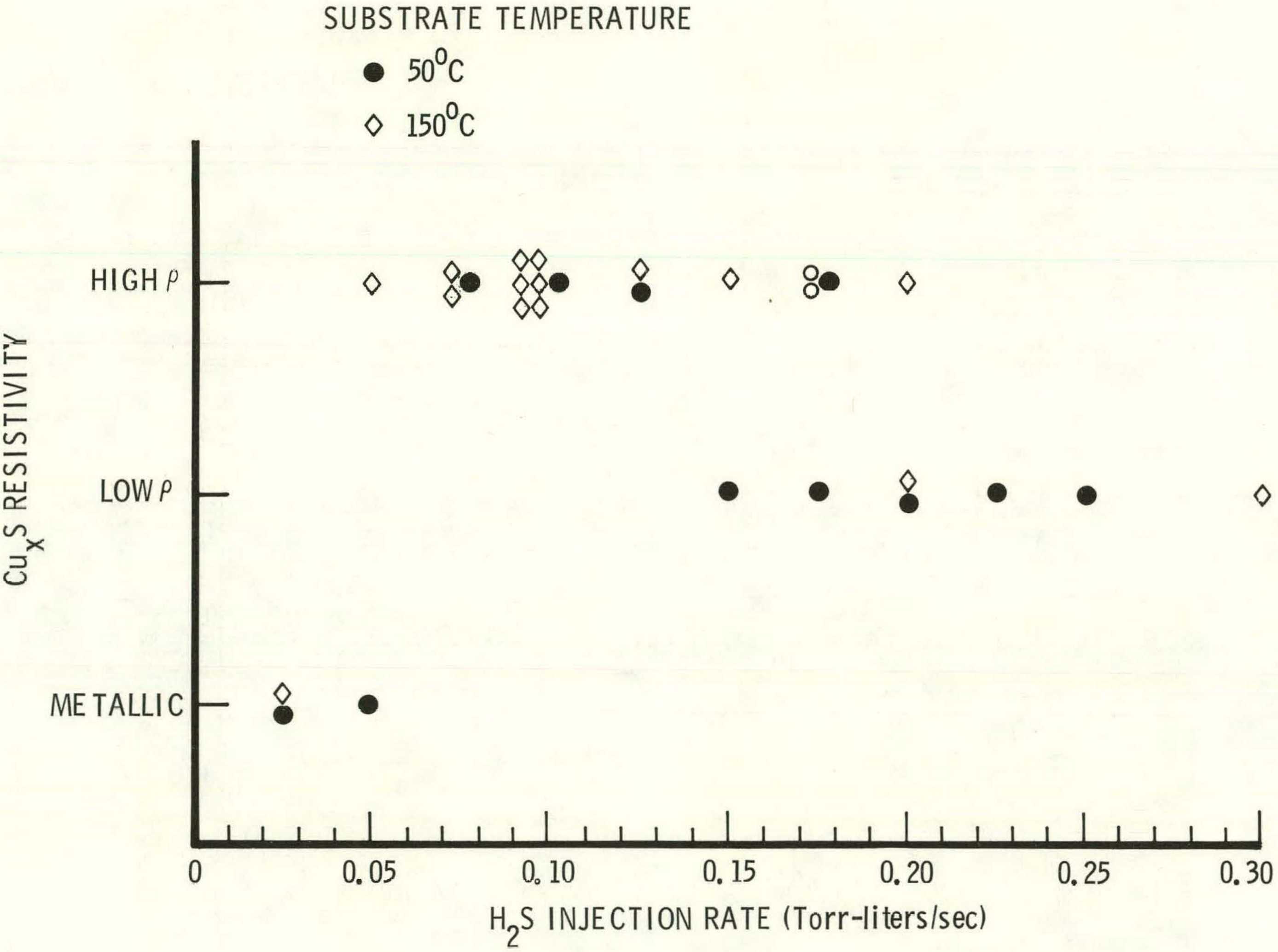


Fig. 10 Schematic representation of dependence of resistivity on H_2S injection rate for coatings deposited onto CdS during present program.

COPPER NODULES

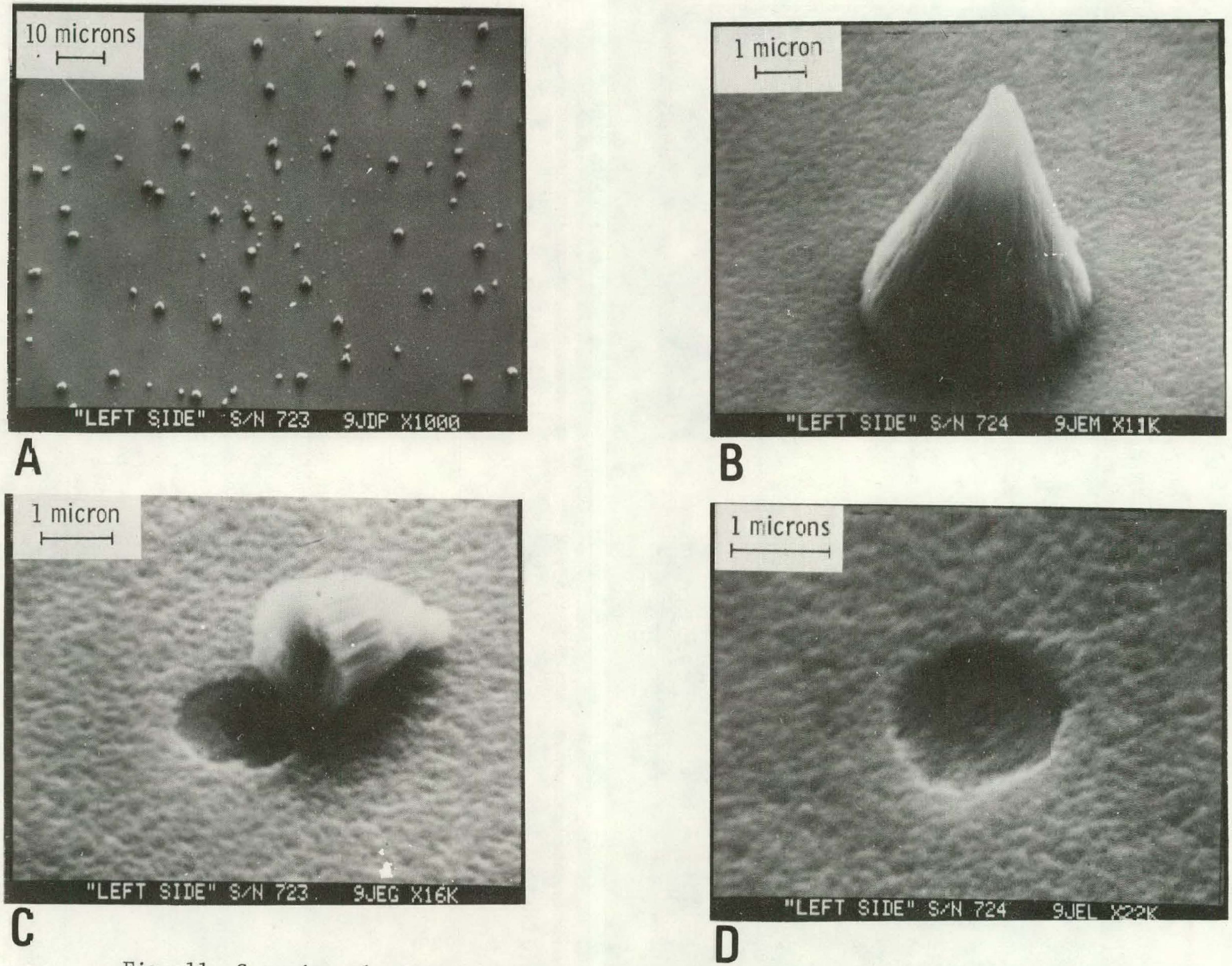


Fig. 11 Scanning electron microscopy photomicrographs showing copper nodules that form under certain conditions during Cu_xS deposition.

CdS CELL STRUCTURE

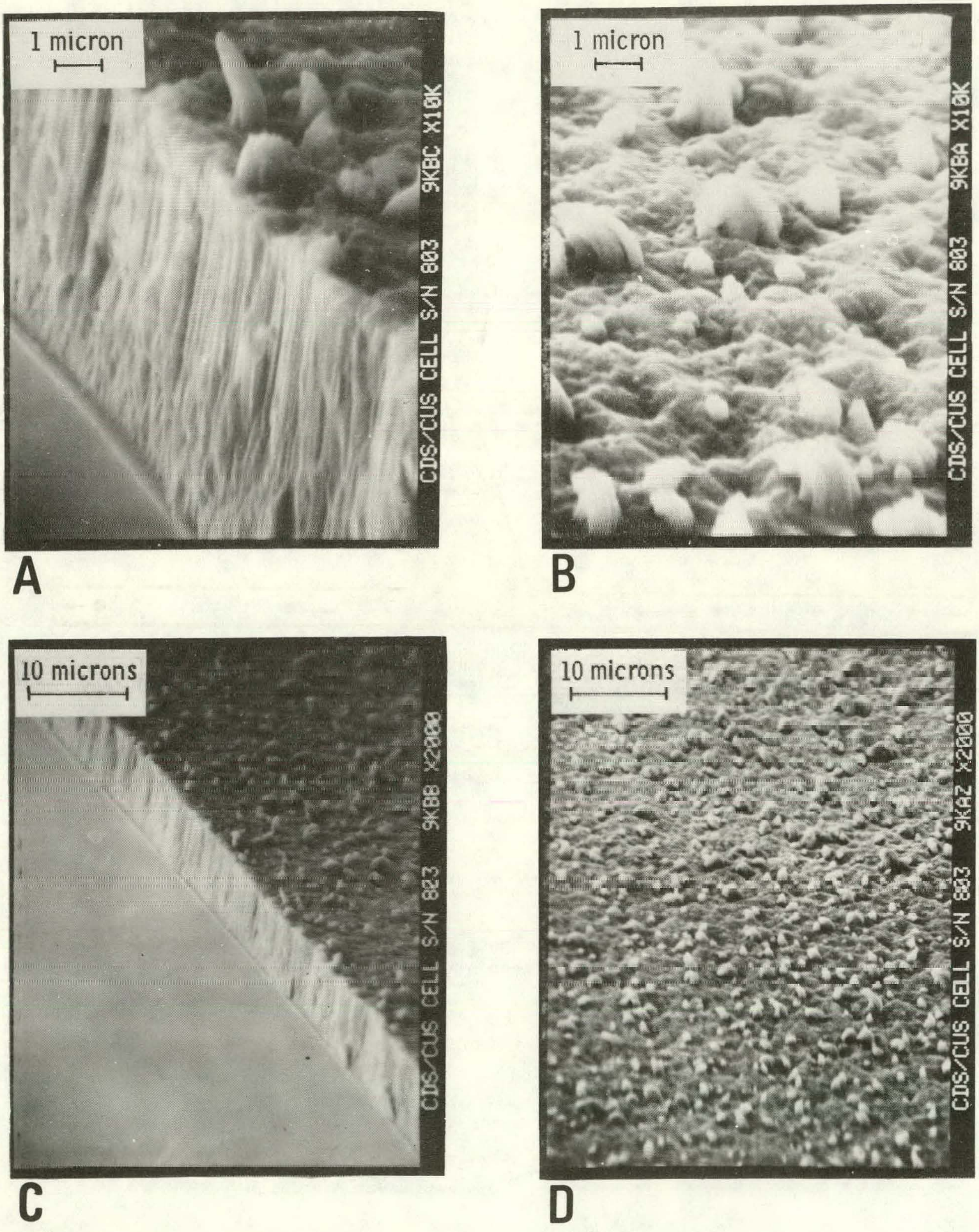


Fig. 12 Scanning electron microscopy photomicrograph of fracture cross section and surface of solar cell showing columnar structure of CdS layer and copper nodules on the surface.

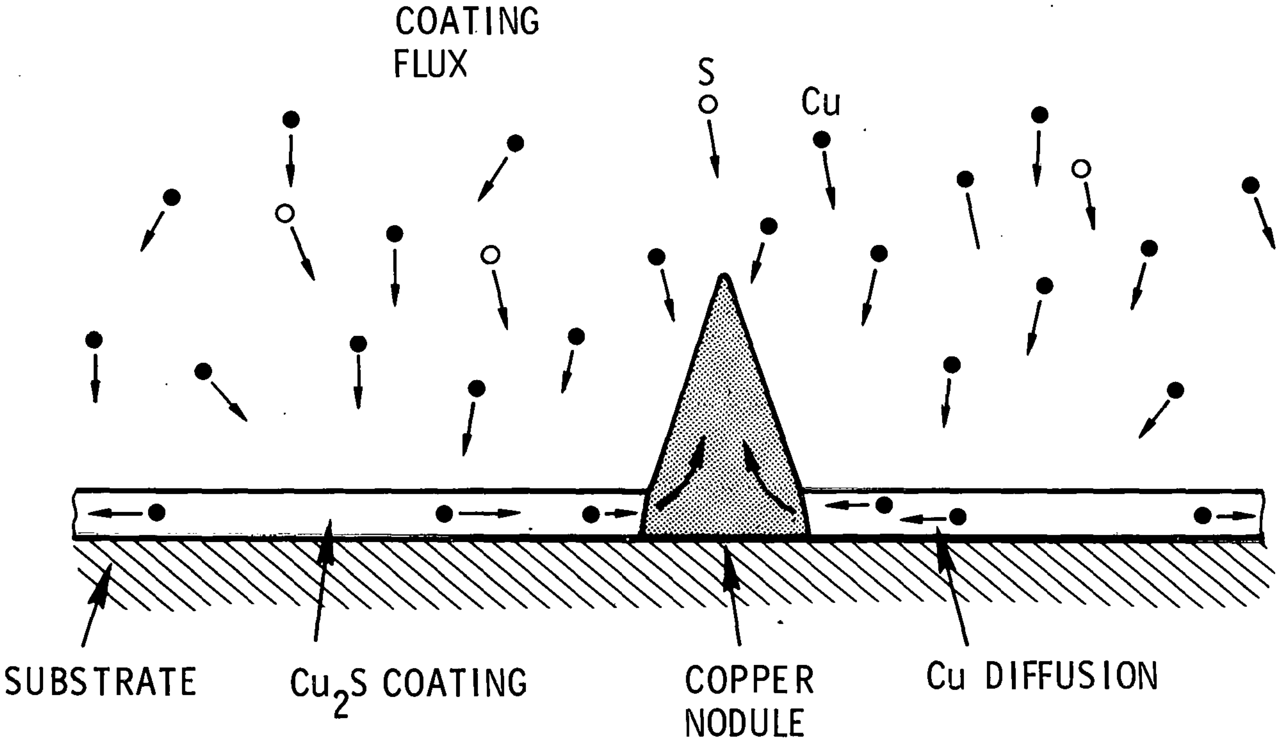
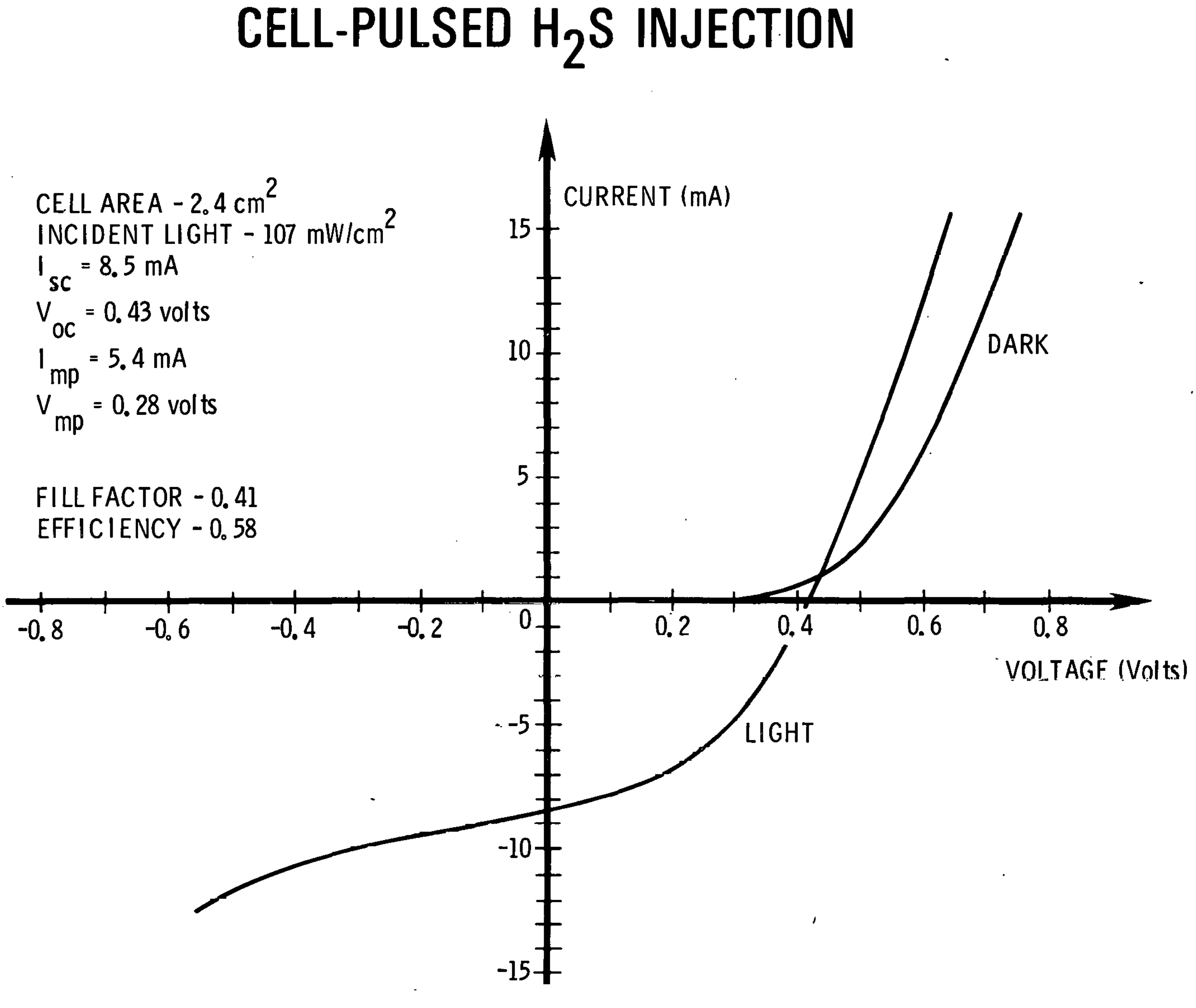


Fig. 13 Schematic illustration of possible mechanism for formation of copper nodules during Cu_xS deposition.



CELL-PULSED H_2S INJECTION

CELL AREA - 2.4 cm^2
INCIDENT LIGHT - 107 mW/cm^2
I_{sc} = 8.5 mA
V_{oc} = 0.43 volts
I_{mp} = 5.4 mA
V_{mp} = 0.28 volts

FILL FACTOR - 0.41
EFFICIENCY - 0.58

Fig. 14 Current-voltage characteristic for solar cell of type that has yielded the best efficiencies obtained during the present reporting period.

REFERENCES

1) W. W. Anderson, "Cadmium Sulfide/Copper Sulfide Heterojunction Cell Research". Tech. Progress Rpt. Feb. 26, 1979 - May 31, 1979, SERI Contract XJ-9-8033-1, Lockheed Palo Alto Research Laboratory (June 1979).

2) W. W. Anderson and A. D. Jonath, "Cadmium Sulfide/Copper Sulfide Heterojunction Cell Research", Tech. Progress Rpt. June 1, 1979 - Aug. 31, 1979, SERI Contract XJ-9-8033-1, Lockheed Palo Alto Research Laboratory (Oct. 1979).

3) W. W. Anderson, A. D. Jonath and J. A. Thornton, "Cadmium Sulfide/Copper Sulfide Heterojunction Cell Research", SAN-1459-5, U. S. Dept. of Energy, Final Report DOE Contract EG-77-C-03-1459, Lockheed Palo Alto Research Laboratory (November 1978).

4) J. A. Thornton, "Cadmium Sulfide/Copper Sulfide Heterojunction Cell Research", Tech. Progress Rpt. Feb. 26, 1979 - May 31, 1979, SERI Contract XJ-9-8033-2, Telic Corporation, Santa Monica, Ca. (July 1979).

5) D. B. Fraser and H. Melchior, "Sputter-Deposited CdS Films with High Photoconductivity through Film Thickness", J. Appl. Phys. 43, 3120 (1972).

6) W. Müller, H. Frey, K. Radler and K. H. Schuller, Thin Solid Films 59, 327 (1979).

7) R. H. Bube, Electronic Properties of Crystalline Solids, Academic Press New York (1974) p. 310.

8) D. ter Haar, Elements of Statistical Mechanics, Holt Rinehart and Winston, New York (1960) p. 391.

9) R. Glang, R. A. Holmwood, and J. A. Kurtz, "High Vacuum Technology" in Handbook of Thin Film Technology, ed. by L. I. Maissel and R. Glang, McGraw-Hill, New York (1970) p. 2-41.

10) J. B. Hudson and J. S. Sandejas, see C. A. Neugebauer" Condensation, Nuecleation and Growth of Thin Films", in Handbook of Thin Film Technology, ed. by L. J. Maissel and R. Glang, McGraw-Hill, New York (1970) p. 8-26.

11) L. Holland, Vacuum Deposition of Thin Films, Chapman and Hall Ltd., London (1966) p. 203.

12) R. A. Sigsbee, see C. A. Neugebauer "Condensation, Nucleation and Growth of Thin Films", in Handbook of Thin Film Technology, ed. by L. I. Maissel and R. Glang, McGraw-Hill, New York (1970) p. 8-26.

13) K. Mitchell, A. L. Fahrenbruch, and R. H. Bube, "Structure and Electrical Properties of CdS and CdTe Thick Films for Solar Applications", *J. Vac. Sci. Technol.*, Vol. 12 p. 909 (1975).

14) Y. Y. Ma and R. H. Bube, "Properties of CdS Films Prepared by Spray Pyrolysis", J. Electrochem. Soc., *124* 1430 (1977).

15) W. W. Anderson, Lockheed Palo Alto Research Laboratory, private communication, Oct. 1979.

16) L. D. Partain, G. J. Sullivan, and C. E. Birchenall, "Effects of Indium on the Electrical Properties of n-type CdS", *J. Appl. Phys.*, Vol. 50, p. 551 (1979).

17) J. A. Thornton, "Cadmium Sulfide/Copper Sulfide Heterojunction Cell Research - Review of Telic Work, summary presented at SERI CdS/Cu$_2$S and CdS/Cu Ternary Compound Review Mtg., Univ. of Delaware, Feb. 28 - March 2, 1979.

18) A. D. Jonath, W. W. Anderson, J. A. Thornton and D. G. Cornog, "Copper Sulfide Films Deposited by Cylindrical Magnetron Reactive Sputtering", *J. Vac. Sci. Technol.*, Vol. 16, p. 200 (1979).

19) L. Maissel, "Application of Sputtering to the Deposition of Films", in *Handbook of Thin Film Technology* ed. by L. J. Maissel and R. Glang, McGraw-Hill, New York (1970) p. 4-40.

20) W. W. Anderson, "Cadmium Sulfide/Copper Sulfide Heterojunction Cell Research", Technical Status Report No. 8, SERI Contract XJ-9-8033-1, October 1979, Lockheed Palo Alto Research Laboratory.

☆ U.S. GOVERNMENT PRINTING OFFICE: 1980-640-258/2314