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SPRAY SOLAR CELL RESEARCH: CdS/Cu_2S CELLS BY ION EXCHANGE-CSD

Quarterly Report No. 1, October 1—December 31, 1979

By
H. Paul Maruska
Archie R. Young II

Work Performed Under Contract No. EG-77-C-01-4042

Exxon Research and Engineering Company
Advanced Energy Systems Laboratories
Linden, New Jersey

U.S. Department of Energy

Solar Energy

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ADVANCED ENERGY SYSTEMS LABORATORIES

EXXON RESEARCH AND ENGINEERING COMPANY • LINDEN, NEW JERSEY

SPRAY SOLAR CELL RESEARCH:

CdS/Cu_2S CELLS BY ION EXCHANGE-CSD

Quarterly Report #1
Period: October 1, 1979-December 31, 1979

Contract No. XS-9-8104-1

By
H. Paul Maruska
Archie R. Young II

This work was performed for the
Solar Energy Research Institute
Under Subcontract No. XS-9-8104-1
from Prime Contract No. EG-77-C-01-4042

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AIM OF PROJECT

To develop a novel chemical spray deposition/ion exchange process for the Cu_2S/CdS Solar cell, defining deposition processes and parameters that will lead to conversion efficiencies exceeding 8%.

PREFACE

This is the first quarterly report. During this period much attention was devoted to designing and constructing both a chemical spray deposition apparatus and an ion exchange annealing station. Temporary equipment was used to obtain preliminary results on sprayed and ion exchanged films.

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1. SUMMARY

A study of the applicability on the Chemical Spray Deposition-Ion Exchange Technique to the formation of high efficiency, low cost Cu_2S/CdS solar cells has been undertaken. A Chemical Spray Deposition (CSD) apparatus and an Ion Exchange annealing station have been designed, and construction of these facilities is nearing completion. The object is to form films of CdO and Cu_2O by spraying appropriate solutions onto a heated substrate, and then to convert these oxides into CdS and Cu_2S through ion exchange by annealing in H_2S vapor. Such films will then be the basis for fabricating Cu_2S/CdS solar cells.

Temporary spray and annealing equipment has been used while the permanent facilities are completed. CdO oxide films with thicknesses of 0.1-0.5 microns have been deposited. There is preferred crystal growth in the <111> direction on glass substrates. However, on SnO_2 coated glass, a <200> preferred orientation is obvious. The crystallite size is 5-10 microns, and porous spheres 10-20 microns in diameter are visible on the surface. After annealing in H_2S, the films are converted to CdS, but the reaction is not complete after 2 hours. The optical transmission is now characteristic of CdS. The grain size was found to increase to the 100 micron range, but the surface spheres remain.

A mixture of CuO and Cu_2O was formed in a preliminary spraying. The film converted to the digenite and djurleite phases of copper sulfide.

Much improved control of the deposition process will result when the permanent facilities come on-line.

2. INTRODUCTION

This is the first quarterly report of progress on SERI subcontract XS-9-8104-1, entitled "Spray Solar Cell Research". The period convered is from October 1 through December 31, 1979. The ultimate program objective is to fabricate CdS/Cu_2S thin film cells having conversion efficiencies of 8% or better, by an ion exchange-chemical spray deposition process.

There has been continuing interest in CdS since photovoltaic effects were reported by Reynolds (1) in 1954. These cells used copper contacts, and were later identified as heterojunction CdS/Cu_2S devices by Chamberlin and Skarman (2). Photovoltaic devices have been made from single crystal (3), vacuum deposited polycrystalline (4), chemical spray deposited (5), and sintered (6) cadmium sulfide. Based on studies of these cells, some understanding of the mechanism of cell operation has emerged. One may sketch a simplified band diagram of the heterojunction (6), as shown in Figure 1. The CdS/Cu_2S cell

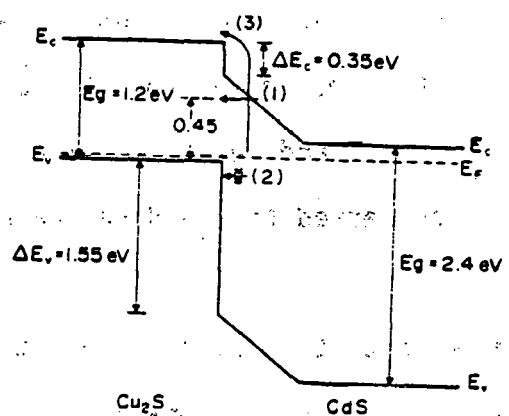


Fig. 1 Band diagram for Cu_2S–CdS junction illustrating possible tunneling paths.

consists of a heterojunction between p-type Cu_2S and n-type CdS. In the front wall version of the device, light is incident on the Cu_2S

layer (E_g =1.2 eV), where most of the photon generated charge carriers are formed. Since however, Cu_2S is a degenerate semiconductor, the depletion region is located primarily in the CdS. The diffusion length for electrons in Cu_2S is low (∿0.3μ), but it is an efficient light absorber, therefore, high electron collection efficiencies can be achieved by using appropriately thin films.

Two approaches to CdS/Cu_2S cell fabrication are being actively studied at present. The principal difference in the two approaches is in the technique used to deposit CdS films. At the Institute for Energy Conversion (University of Delaware), a vacuum deposition method is employed to deposit 20-40μ CdS films on metal substrates. The Cu_2S barrier layer is formed on the CdS film by either wet (7) or dry (8) exchange of Cu^{+1} for Cd^{+2}, during exposure to cuprous chloride and heat. In the case of the dry process, by-product cadmium chloride is rinsed from the surface. In either case the junction is formed by an additional heat treatment in air or nitrogen. Cu_2S layer thicknesses are typically 0.1-0.3μ. Gold grid electrodes are applied to the Cu_2S surface by vacuum evaporation. The highest conversion efficiencies reported for CdS/Cu_2S cells have been achieved with cells fabricated in this manner. The Delaware group have recently reported (9) conversion efficiencies in excess of 9%.

The second fabrication approach has been actively pursued by Photon Power Inc. (10,11). The Photon Power cell is of backwall construction, that is, light is incident on the CdS surface (E_g = 2.4 eV)

and is transmitted through this layer to the absorbing Cu_2S layer. The most significant aspect of the Photon Power fabrication method, however, is the use of chemical spray film deposition techniques. The cell consists of a glass substrate on which are sprayed successively, SnO_2 (a transparent conductor) and CdS films. The spray solution used for CdS film formation contains thiourea as the sulfur source. Proton Power is committed to forming the Cu_2S layer by spray deposition as well, but to date, they have been forming the barrier layer by the hot aqueous cuprous chloride dip method (11). After heat treatment to form the junction, the Cu_2S is covered with copper by vacuum deposition. Conversion efficiencies as high as 5% have been reported (11) for cells containing spray deposited CdS films.

The conversion efficiencies obtained on cells with vacuum deposited CdS films are at present significantly higher than exhibited by cells having spray deposited films. Nevertheless, chemical spray deposition remains an attractive approach to reducing cell fabrication costs and deserves further study.

Since thin films are useful for determining basic optical and electrical properties of new materials, Exxon has been investigating thin film fabrication techniques for several years. Chemical spray deposition is a particularly attractive method of forming thin films. It is an inherently simple procedure, requiring only an efficient substrate heater and a liquid atomizing nozzle. In many instances it provides a simple means of control of film composition via the composition of the spray solution. However, for certain compositions of interest, e.g. $CuFeS_2$ (chalcopyrite) and Cu_5FeS_4 (bornite), we have found it to be extremely difficult to devise solution compositions that will decompose

at a substrate to yield films of desired stoichiometry. To circumvent this difficulty, a variation of the direct spray deposition approach was devised. Specifically, oxide films obtained by spray deposition were converted to desired sulfide compositions by annealing in gaseous H_2S under flow conditions. This process has been named, "ion exchange-chemical spray deposition" (ion exchange-CSD). It has been used successfully to grow thin films of FeS_2, $CuFeS_2$, Cu_5FeS_4, and $Cu_{2-x}S$.

To our knowledge this two-step approach (ion exchange-CSD) has never been applied to grow CdS and Cu_2S films by others. This is understandable, since such films can be obtained directly by spraying solutions containing thiourea or its derivatives (5). However, it is possible that our two-step approach to sulfide film growth may provide better quality films than the direct method. It is well known (12) that film quality is often strongly dependent on the specific chemistry involved in the film growth process. Since improved film quality may lead to higher conversion efficiences in the CdS/Cu_2S system, Exxon has undertaken this investigation of the ion exchange-CSD approach for CdS and Cu_2S film growth.

Specifically, we will determine optimal spray deposition parameters (solution concentration, solution composition, substrate temperature, etc.) and ion exchange process parameters (temperature, flow rate, H_2S concentration, carrier gas, etc.) for obtaining high quality sulfide films from CSD oxide films. Oxide films will be obtained by spraying methanol and methanol-water solutions of nitrates, acetates, or chlorides of cadmium and copper. These oxide films will be converted to the desired sulfide compositions by reaction with H_2S/N_2 or H_2S/H_2 at

temperatures in the range from 300°-500°C. Although under flow conditions equilibrium thermodynamics is not strictly applicable, the two ion exchange reactions of concern to this program (Equations 1 and 2) are favored thermodynamically. This is because of the large negative free energy of formation of H_2O (g) compared to H_2S (g).

(1) $CdO + H_2S \longrightarrow CdS + H_2O$; $\Delta F° = -26.5$ k.cal.

(2) $Cu_2O + H_2S \longrightarrow Cu_2S + H_2O$; $\Delta F° = -32.0$ k.cal.

Sulfide films will be characterized by SEM, X-ray, Optical Spectroscopy, Hall Effect measurements, Photoconductivity measurements, etc., and their properties compared to those reported for films obtained by direct spray deposition and vacuum deposition.

Finally, we shall attempt to fabricate two cell designs (Fig. 2) based on ion exchange-CSD films. In the frontwall design (Fig. 2), the substrates for the initial sulfide film (CdS) will be zinc-coated copper foil (zinc coating for ohmic contact). The backwall design (Fig. 2) will contain commercial SnO_2 coated glass substrates. Electrical characteristics of completed cells will be determined in the dark and under AM-1 illumination.

Work accomplished during the first quarter of this program, in the areas of (1) facilities and apparatus, (2) sprayed oxide films, and (3) H_2S annealed films is discussed in Section 3 of this report.

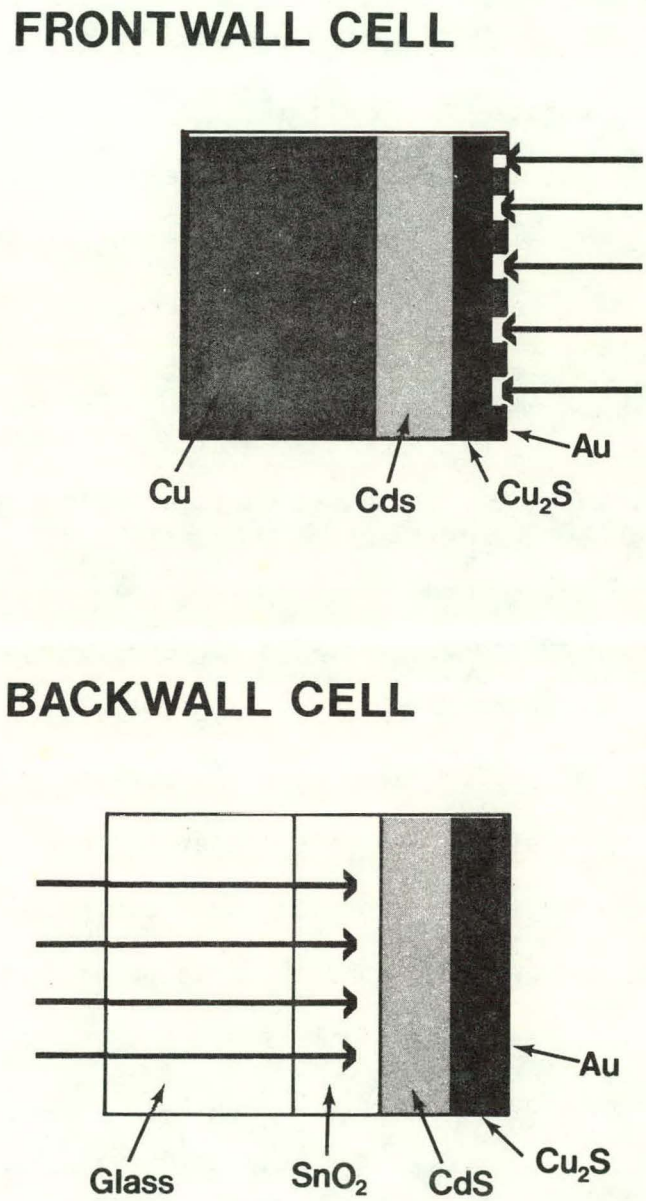


Figure 2. CdS/Cu_2S Thin Film Cell Designs

3. DISCUSSION

3.1 Facilities and Spray Apparatus

3.11 Facilities

This program, as well as a second SERI subcontract (#XS-9-8041-11) involving ion exchange-CSD growth of zinc tin phosphide films, was initiated on October 1, 1979. Unfortunately, the laboratory assigned to these two similar programs did not have sufficient hood space to house the required spray units and tube furnaces. Therefore, a bench top hood was purchased and installed adjacent to an existing hood in the laboratory. The spray units are being installed in the new hood, and at this writing, the installation is nearing completion.

3.12 Spray Apparatus

The spray apparatus design is based on a unit (Fig. 3) in use for several years at Exxon to spray SnO_2 films onto silicon substrates. Its main features are (1) vacuum plate substrate holder, (2) high thermal mass-high wattage subsrate heater to facilitate temperature control during spray cycle, and (3) timer controlled liquid flow and shutter valves to precisely control duration of spray.

Detailed drawings of the substrate heater design are shown in the Appendix. The heater block (Appendix, Fig. 1) is a 3" diameter by 1-3/4" copper block with appropriately drilled holes for fastening the top plate and housing, three 1/2" diameter 200 watt rod heaters, and a thermocouple. The top plate (Appendix, Fig. 2) is made of stainless steel. A threaded well is located at the center of the top plate to accept the bottom 3/16" of the threaded fastener (Appendix, Fig. 2).

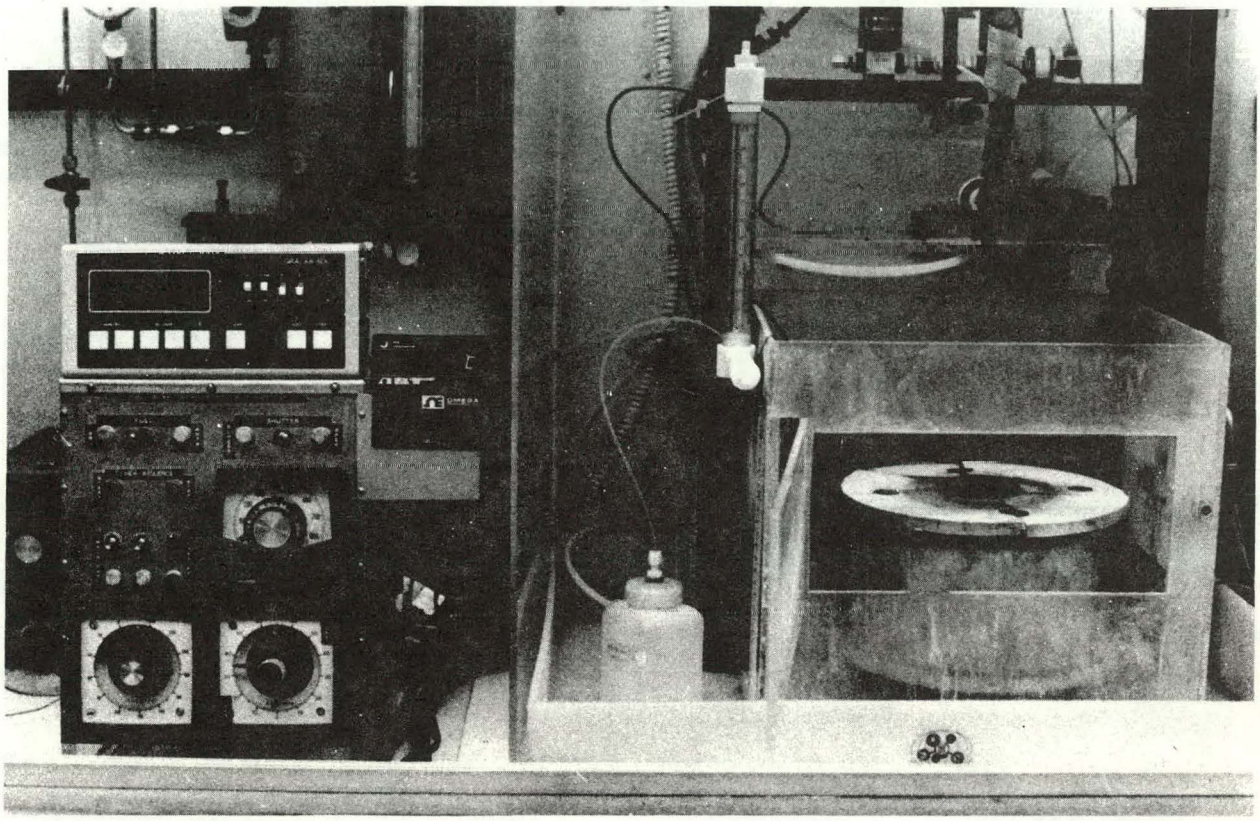


Fig. 3. Spray Apparatus for Depositing Thin Film Oxides

The threaded fastener well reduces to a 1/6" hole that extends to the top surface. A vacuum may be drawn through the fastener from the bottom of the heater assembly in order to firmly fix substrates to the top plate. The thermocouple well (Appendix, Fig. 2) terminates 1/16" from the top surface. A sectional view of the heater assembly is shown in Figure 3 of the Appendix. The heater block is encased in transite and insulated with Pyrex wool.

3.13 Temporary Spray Assembly

In order to get started with our studies of sprayed oxide films while the new hood and sprayer unit were being installed, we set up a temporary spray assembly in the existing laboratory hood. All experimental results to be discussed in this report were obtained with films grown by means of this temporary spray assembly. A diagram of the assembly is shown in Fig. 4. It consists of a stainless steel pneumatic atomizing nozzle (Binks Mfg. Co. #50-175), an air pressure regulator, and an ordinary laboratory hot plate. The spray solution was contained in a 100 ml graduated cylinder. Liquid was fed to the nozzle by means of the partial vacuum created when atomizing air passed through it. Approximate liquid flow rates from the graduated cylinder could be determined by using a timer. During operation, a lucite enclosure was placed around the hot plate to minimize horizontal air currents. Initially the hot plate surface temperature dropped 70-80°C during a three-minute spray interval due to the cooling effects of the spray and atomizing air. This was reduced to about 10-15°C by placing a 1/2" thick steel plate on top of the ceramic hot plate surface. The maximum surface temperature attainable with the spray turned off was 388°C.

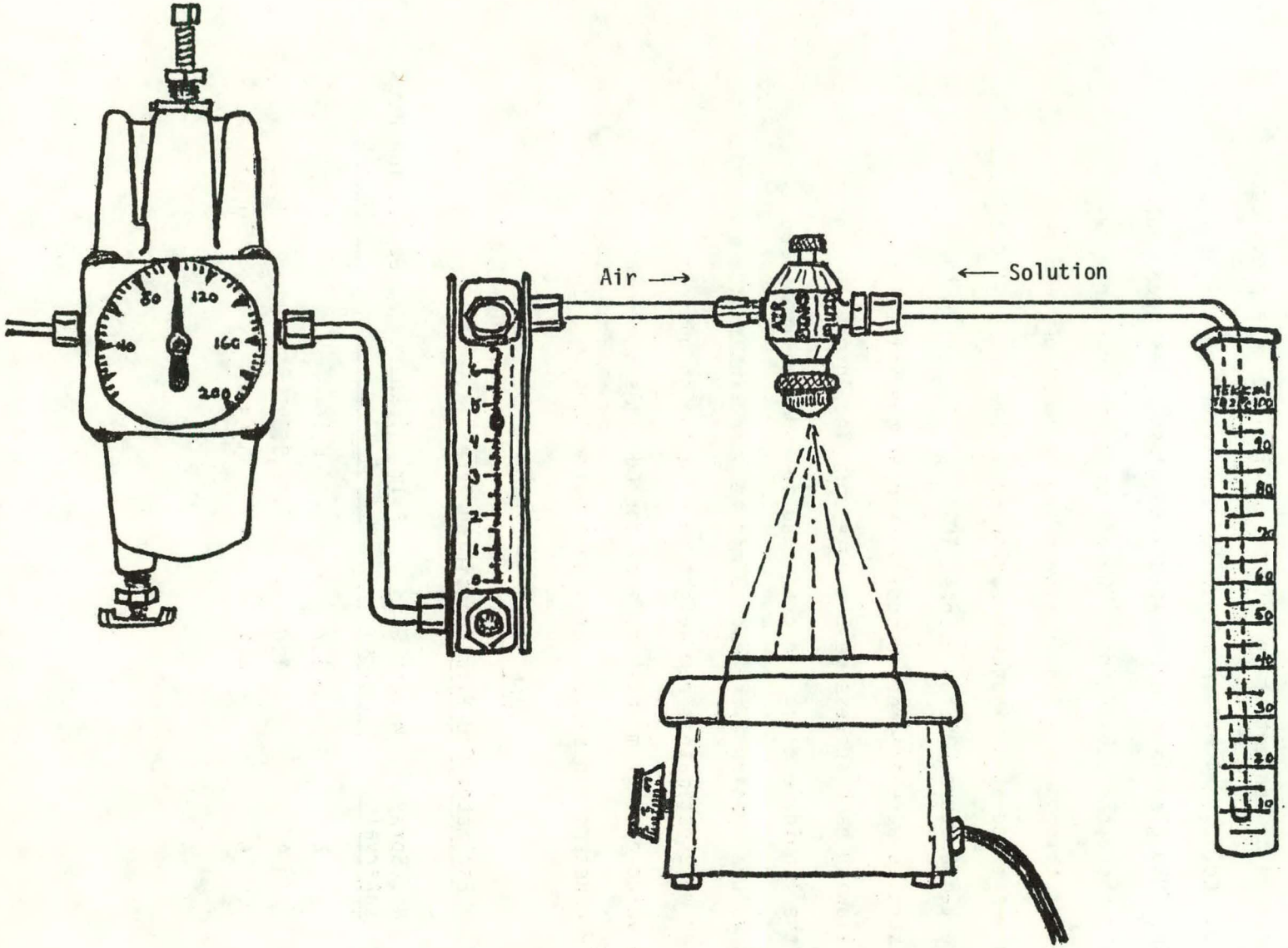


Fig. 4. Temporary Spray Assembly

3.2 Spray Deposition of Cadmium Oxide Films

3.2.1 Experimental Procedures

During this report period, no attempts were made to study solution composition or concentration effects. All films were prepared by spraying 0.05M $Cd(NO_3)_2 \cdot 4\ H_2O$ in methanol. Substrates were 1" x 1.5" x 0.032" Corning 7059 glass and SnO_2 coated 7059 glass. The spray nozzle was centered 12" above the substrates. The air pressure and air flow rotameter were set to produce a liquid flow of about 10 ml per minute. Spray duration was fixed at 3 minutes. During this time interval the initial surface temperature (388°C) dropped 10-15°C. To obtain thicker films, the substrates were allowed to equilibrate at the initial temperature following each successive 3 minute spraying interval. Additionally, the liquid level in the graduated cylinder was restored to the initial volume reading after each 3 minute spray interval. Film thicknesses were estimated from weight gain, assuming uniform coverage and a value of 8 g/cm^3 bulk density for CdO. As shown in Table 1, fairly constant deposition rates were maintained.

TABLE 1

Estimated CdO Film Deposition Rate

Substrate #	No. Spray Intervals	Weight Gain (mg)	Film Thickness (μ)	Deposition Rate (μ/min)
1	2	1.2	0.16	0.027
2	4	3.0	0.39	0.033
3	6	4.1	0.53	0.029

3.22 X-Ray Analyses of CdO Films

X-ray diffraction spectra were obtained on films with a Cu target tube and a Ni filter to absorb K_β radiation. Cadmium oxide has a face-centered cubic crystalline structure (ASTM-5-0640). A powder diffraction pattern from 2θ values of 20° to 40° (Fig. 5) show <111> and <200> maxima of roughly equal intensity at 33.5° and 39.0°, respectively.

The diffraction pattern of a film formed on an amorphous glass substrate after one three-minute spray interval is shown in Fig. 6. It is seen that the film is crystalline and that there is preferred crystallite growth in the <111> direction. That is, the intensities of the <111> and <200> maxima are no longer equal as in the randomly oriented powder sample (Fig. 5).

A single three-minute spray onto the crystalline SnO_2 surface (see Fig. 7) yields a CdO film that is only slightly crystalline (Fig. 8) and appears to have a <200> preferred orientation. After a second three-minute spray interval, the crystallinity of CdO film on the tin oxide surface has increased significantly (Fig. 9), and the <200> preferred orientation is obvious.

Dependency of chemical spray deposition film crystallinity and orientation on the crystallinity of the substrate as well as on substrate temperature is documented in the literature (13, 14). We will undoubtedly observe substrate temperature effects when we begin using our permanent spray unit, and are able to run at various controlled substrate temperatures. The crystallinity and orientation of initial oxide films may well be important parameters contributing to the quality of sulfide films obtained by H_2S annealing.

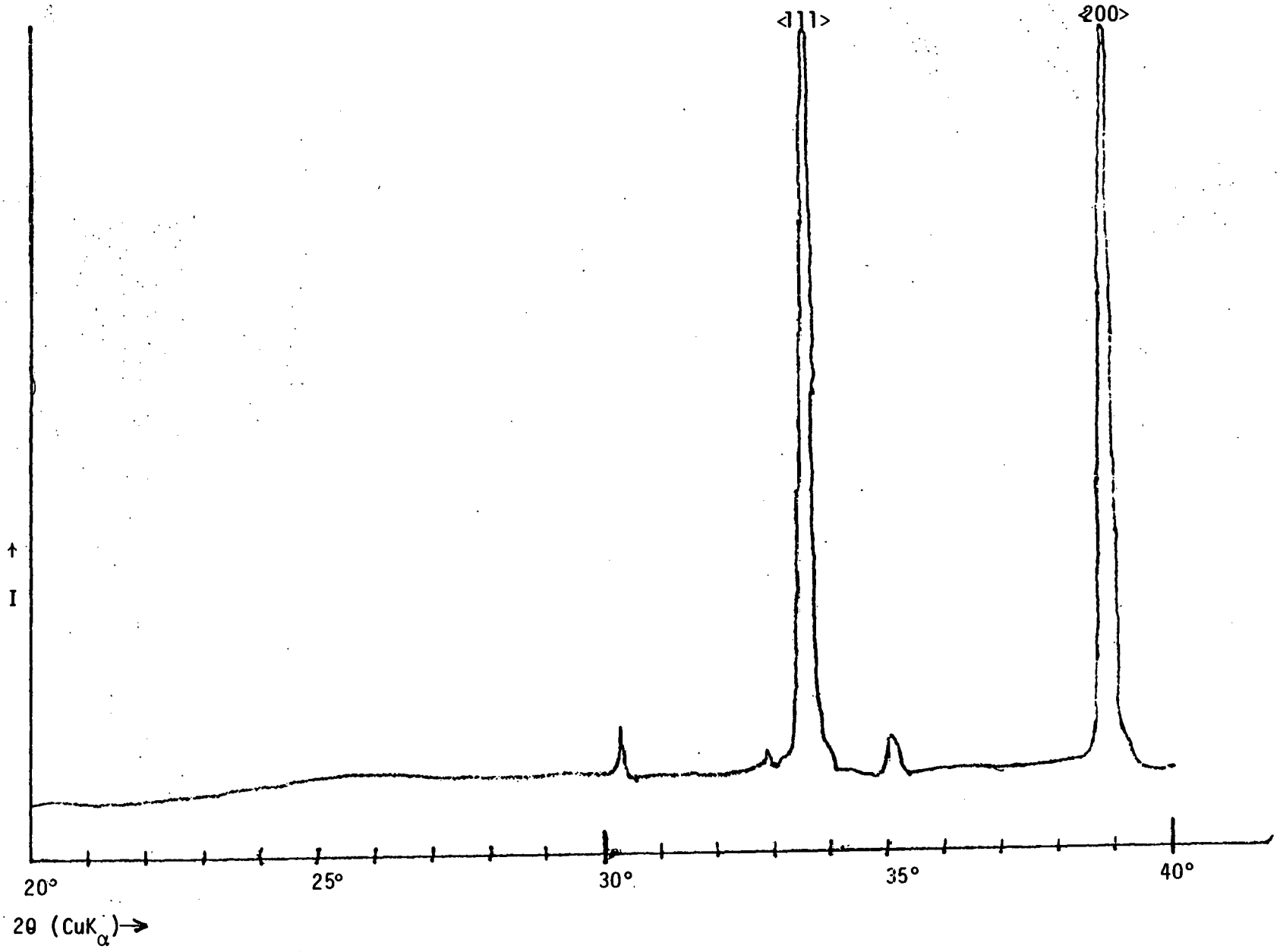


Fig. 5. CdO Powder Diffraction Pattern

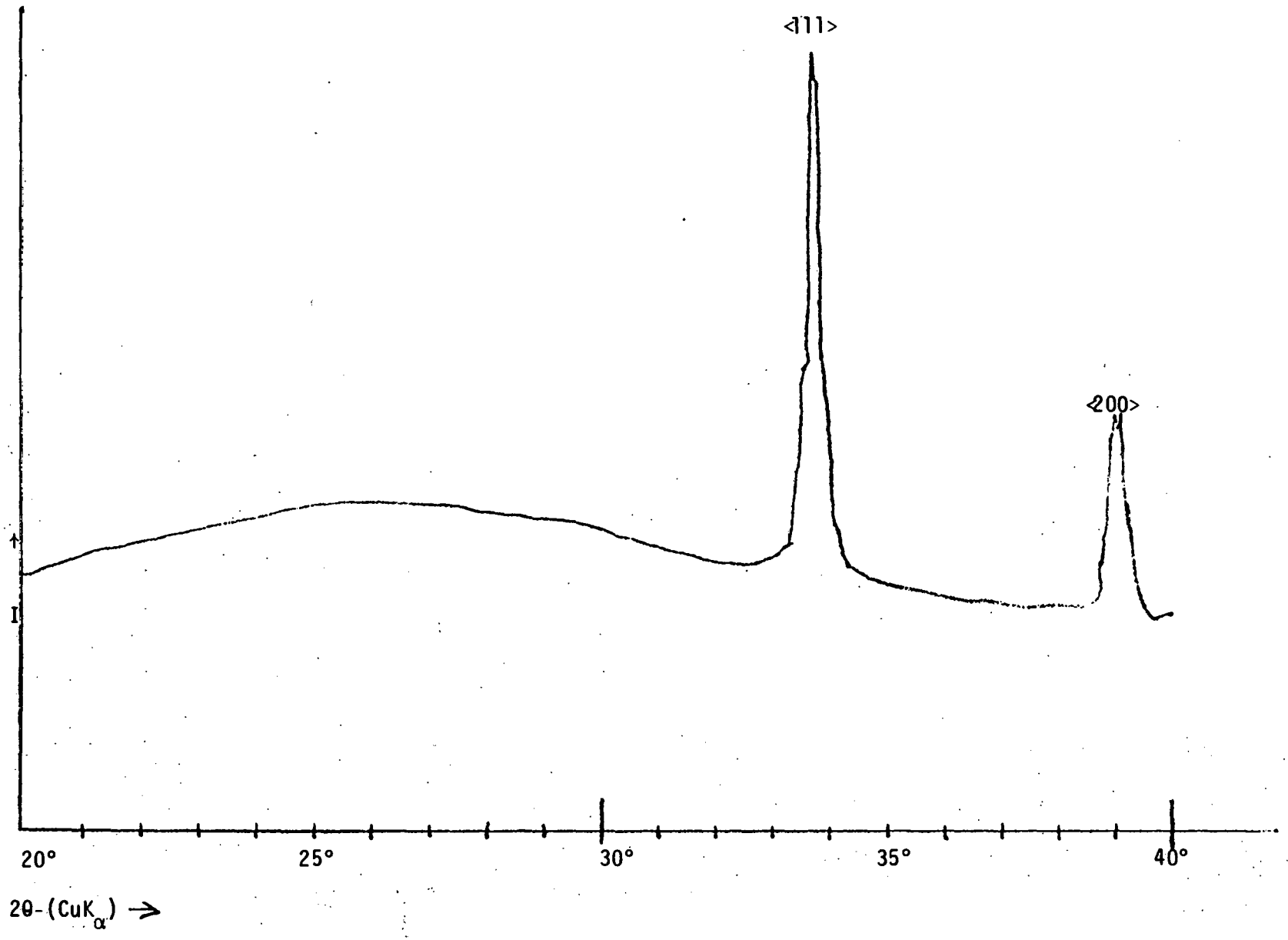


Fig. 6. CdO Film (3 min. Spray) on 7059 Glass

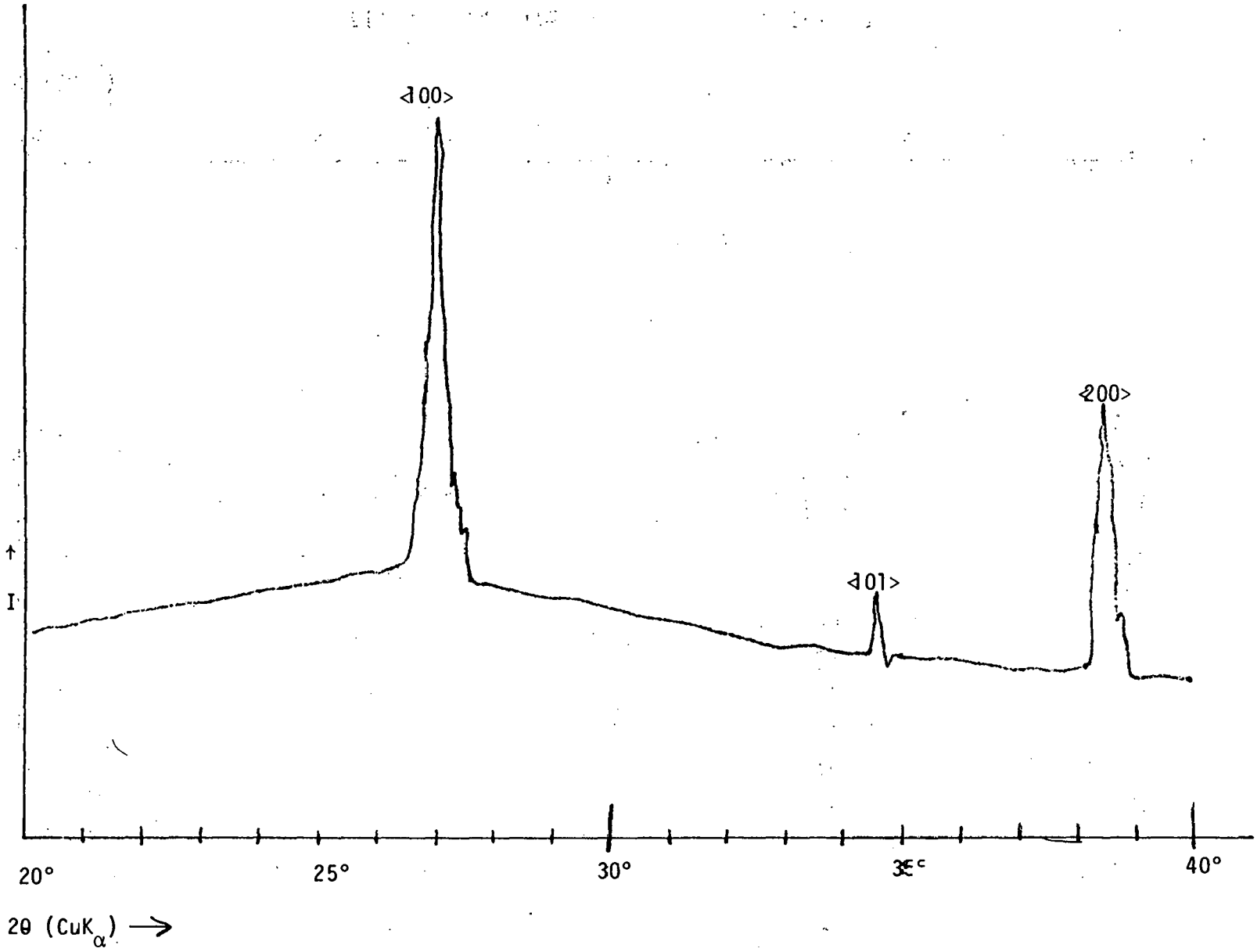


Fig. 7. Tin Oxide Film on Corning 7059 Glass

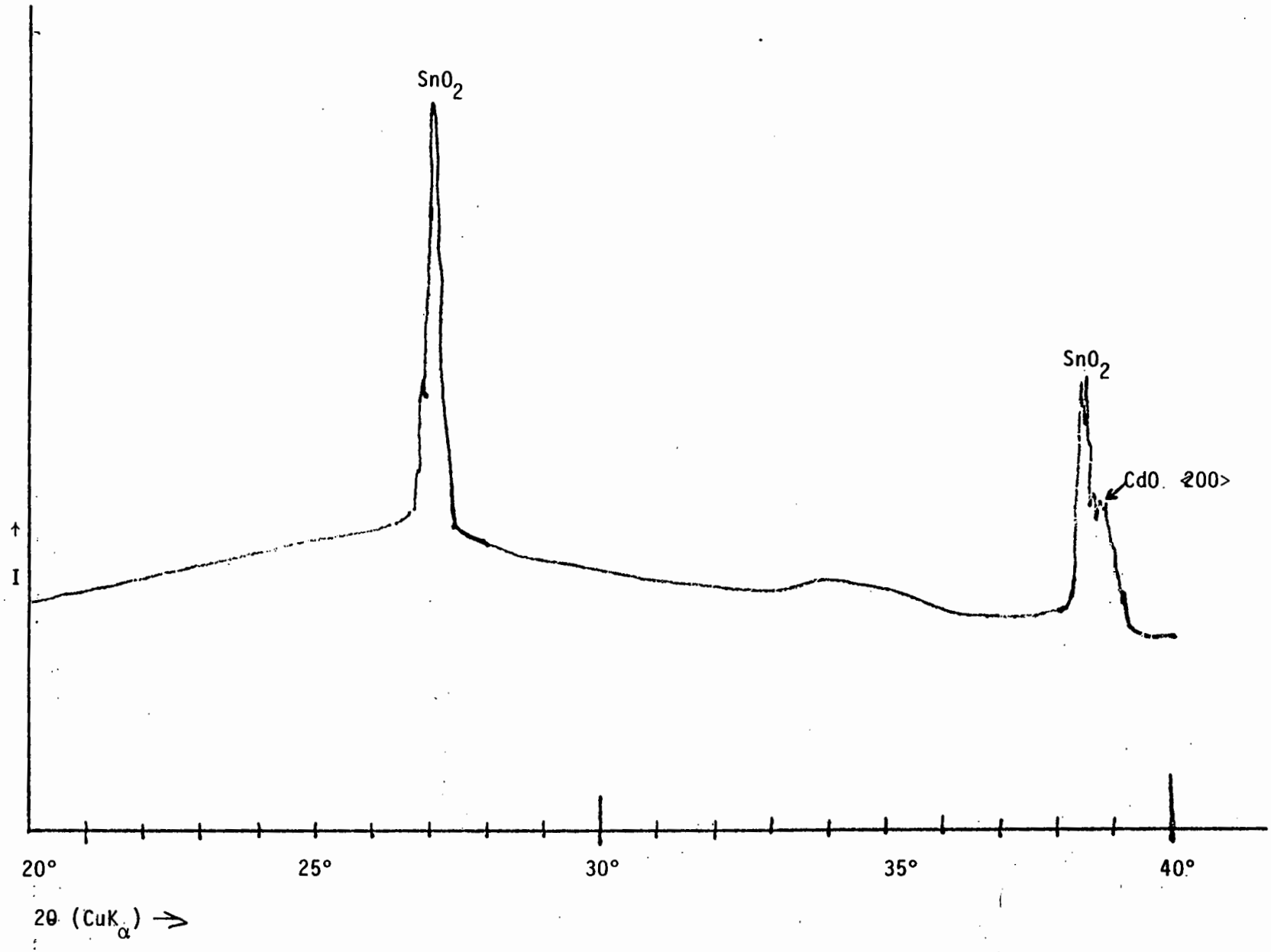


Fig. 8. CdO Film (3 min spray) on Tin Oxide Coating

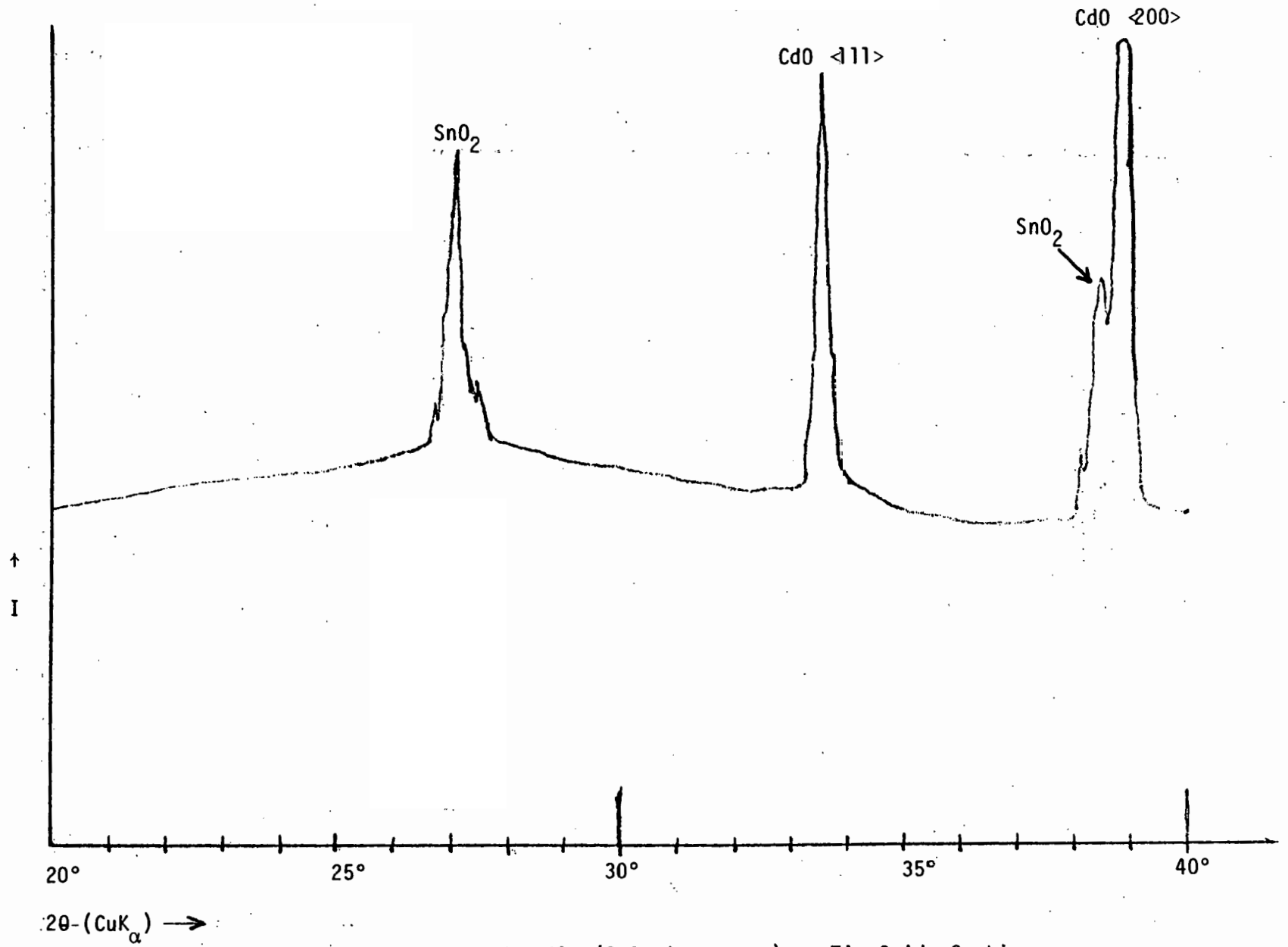
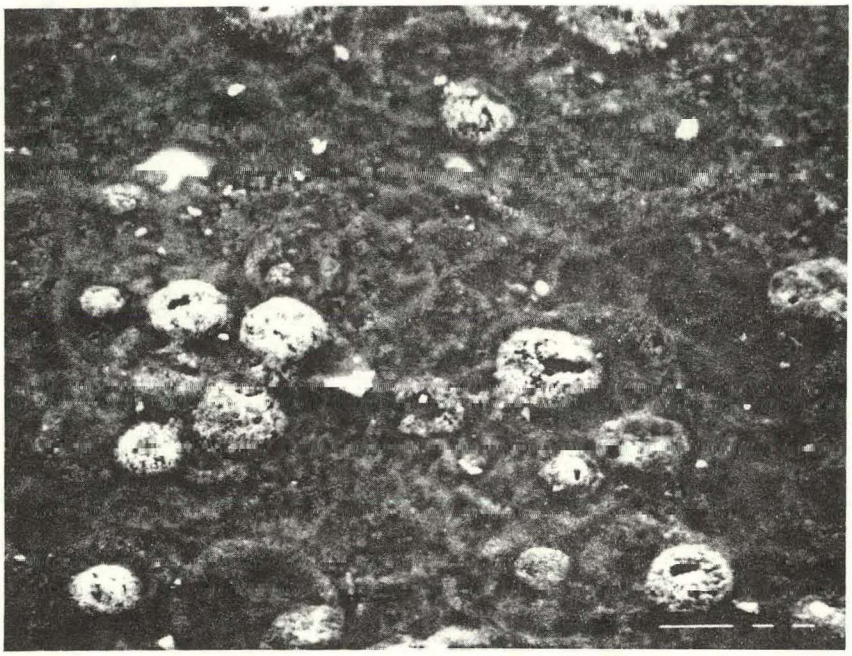


Fig. 9. CdO Film (2-3 min sprays) on Tin Oxide Coating

3.2.3 Scanning Electron Microscopy of CdO Films

SEM photographs were taken of the thinnest (1-3min. spray) cadmium oxide films on glass and on tin oxide substrates. A section of a film on glass is shown in Figure 10 at two magnifications. The most striking features of the photographs are the presence of relatively large ($\sim 10\mu$) porous, spherical growths on the surface, and what appears to be circular droplet impact craters throughout the surface. We believe these surface inhomogeneities were caused by a combination of poor spray atomization and poor control of substrate temperature during the spray run. Control over these two spray parameters will be greatly improved in the permanent spray apparatus. That is, the permanent design will permit independent control of atomizing air flow and of fluid flowrate, so that adequate atomization can be achieved. Additionally, the substrate heater is designed to maintain constant temperatures under spray operations up to 500°C. The irregularly shaped light spots in the upper photograph of Figure 10 are believed to be dust particles.

Figure 11 shows a thin (1-3min. spray) cadmium oxide film on tin oxide at two magnifications. On the basis of the X-ray pattern of the same film (Figure 8), which shows diffraction peaks of SnO_2 but only one weak CdO peak, we believe the light areas to be CdO. That is, there are many crystallites of CdO of size in the 1μ range or less and the SnO_2 substrate is incompletely covered. This interpretation is in essential agreement with results reported by R. Chamberlin (13), namely, that crystalline substrates provide a large number of nucleation sites, so that in the early stages of deposition there is insufficient material available for lateral film growth. The X-ray pattern (Figure 9) of a thicker CdO film (2-3 min. sprays) on tin oxide shows well-defined CdO diffraction peaks. An SEM photograph of the latter film has not been obtained, as yet.



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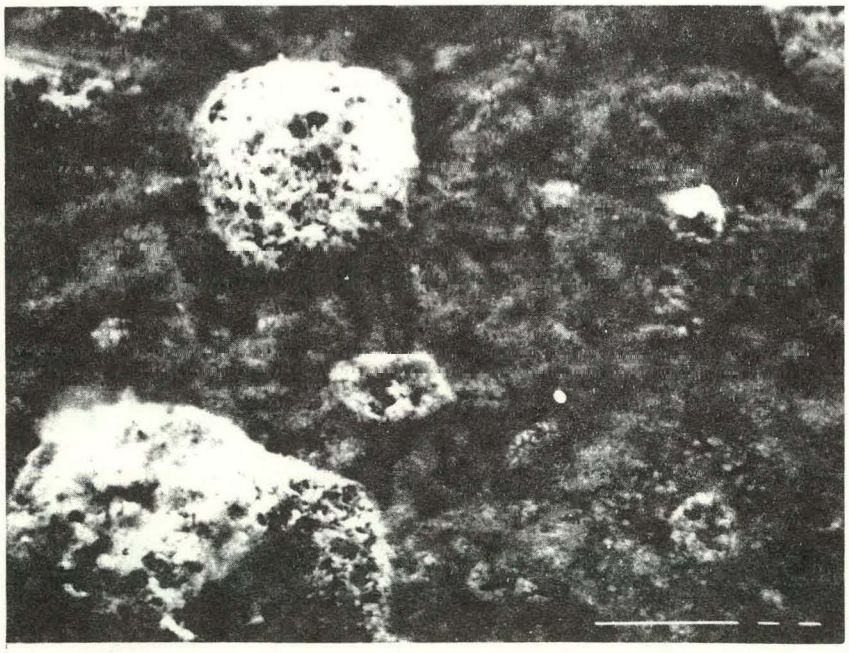
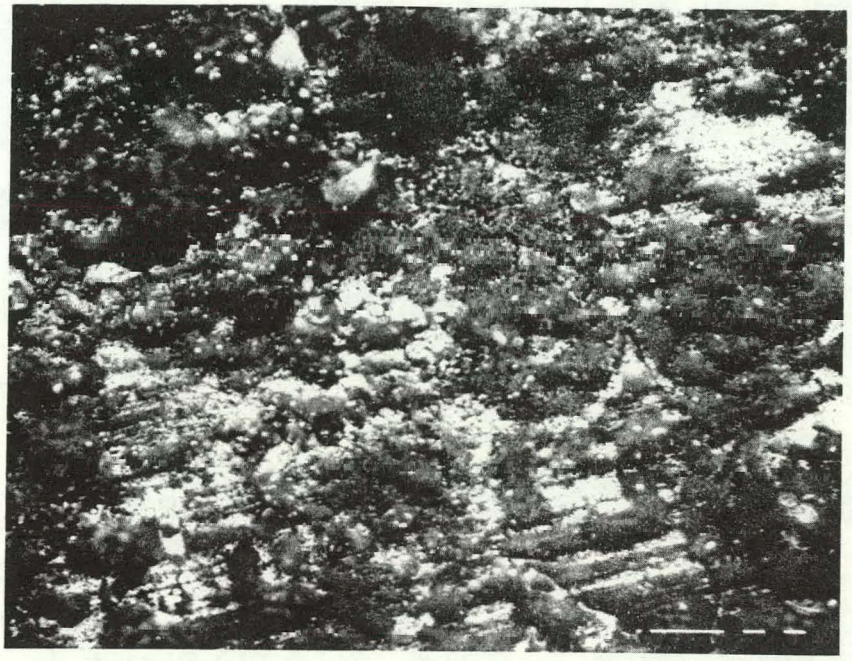
10μ



2000X

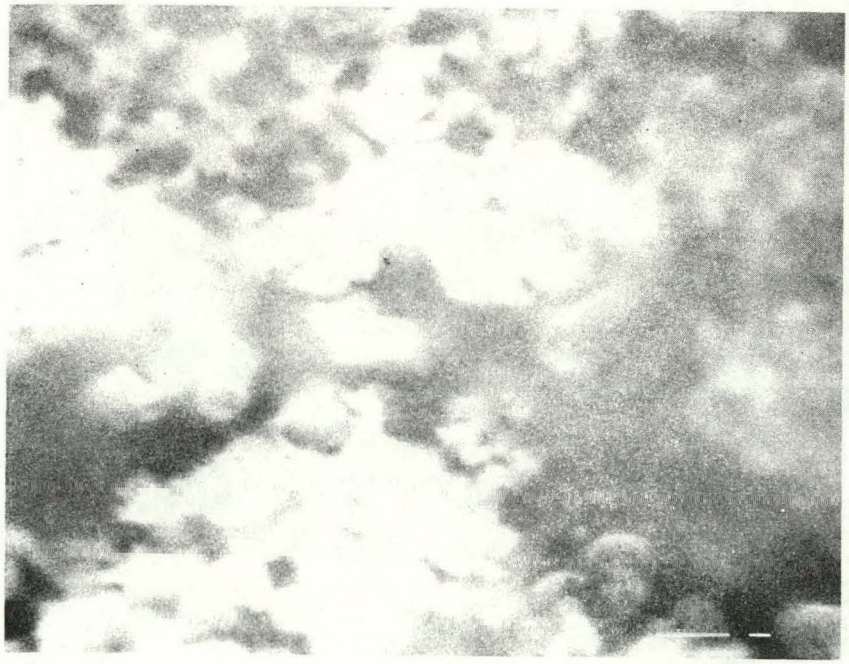
10μ

Figure 10. CdO Film on Glass (3 Min. Spray)



1000X

'10μ'



10000X

'1μ'

Figure 11. CdO Film on Tin Oxide (3 Min. Spray)

3.3 H_2S Annealing Experiments

3.3.1 Experimental Procedures

. Some attempts were made to convert spray-deposited cadmium oxide films to the hexagonal sulfide during this quarter. Because of ongoing construction and installation of a gas manifold system in the hood that houses our tube furnace, the number of conversion runs was limited. There was little opportunity under these conditions to investigate effects of varying experimental parameters on conversion rates. In the few runs attempted H_2S was generated in a Pyrex flask by dropping 6M HCl at a constant rate ($\sim$ 0.5 ml/min) onto lead sulfide powder. The H_2S was carried from the generator flask into the tube furnace by flowing nitrogen. To terminate a run, acid flow was stopped and nitrogen flow was allowed to by-pass the H_2S generator flask. Runs were carried out at 400°C for periods up to two hours. Obviously, with this experimental set up, H_2S concentrations in the gas stream are an unknown quantity. Upon completion of installation of the gas manifold system, we shall be able to use commercial H_2S cylinders and to accurately meter reactant (H_2S or H_2S/H_2) and carrier gases into the tube furnace. Thus, it will be possible to determine concentration, composition, and flow rate effects on conversion rates, as well as the effect of temperature.

3.3.2 X-Ray Analyses of Annealed Films

X-ray diffraction patterns were obtained after CdO films on tin oxide and on glass substrates were annealed in H_2S/N_2 as described in Section 3.3.1. It was ascertained by X-ray analyses, optical transmission measurements, and sheet resistance measurements, that tin oxide films are not affected by H_2S, under the conditions of these runs.

Figure 13 shows the diffraction pattern of a CdO on tin oxide film after annealing for two hours in H_2S/N_2 at 400°C. The oxide films was obtained by two 3 minute spray depositions, and its estimated thickness was 0.15μ. Four characteristic diffraction maxima of hexagonal CdS (see Figure 12) are clearly present in the pattern (Figure 13). However, two small peaks at 2θ values of 33.8° and 39.1°, respectively, are due to the presence of unconverted CdO. Comparison of relative intensities of CdS maxima in the pattern obtained for the film (Figure 13) with those for a random powder sample (Figure 12), indicates a preferred < 002> orientation of crystallites in the film. That is, the hexagonal "C"-axes of most of the CdS crystallites are perpendicular to the substrate. Two characteristic diffraction maxima of the underlying SnO_2 substrate are also apparent in Figure 13. One tin oxide peak (see Figure 7) coincides with the < 002 > peak of CdS at 2θ equal to 27°. Figure 14 shows the pattern obtained for a thicker CdO film on tin oxide (estimated to be 0.38μ), annealed in H_2S/N_2 for two hours at 400°C. The relatively strong CdO peaks at 2θ values of 33.8° and 39.1° are indicative of a lower degree of conversion to sulfide in the thicker film. These results suggest that the sulfide-oxide ion exchange rate may be severely limited by diffusion rates within the bulk of the films. As soon as we have completed installation of our gas manifold, a concerted effort will be undertaken to define the seriousness of this apparent problem.

Figure 15 is the diffraction pattern of a converted CdO film (2-3 min. sprays) on glass after 2 hours under H_2S/N_2 at 400°C. There is only one small CdO peak at 39.1°(2θ), so this is the most completely converted film obtained to date. Like the films on SnO_2, it shows strong < 002 > preferred orientation of CdS crystallites.

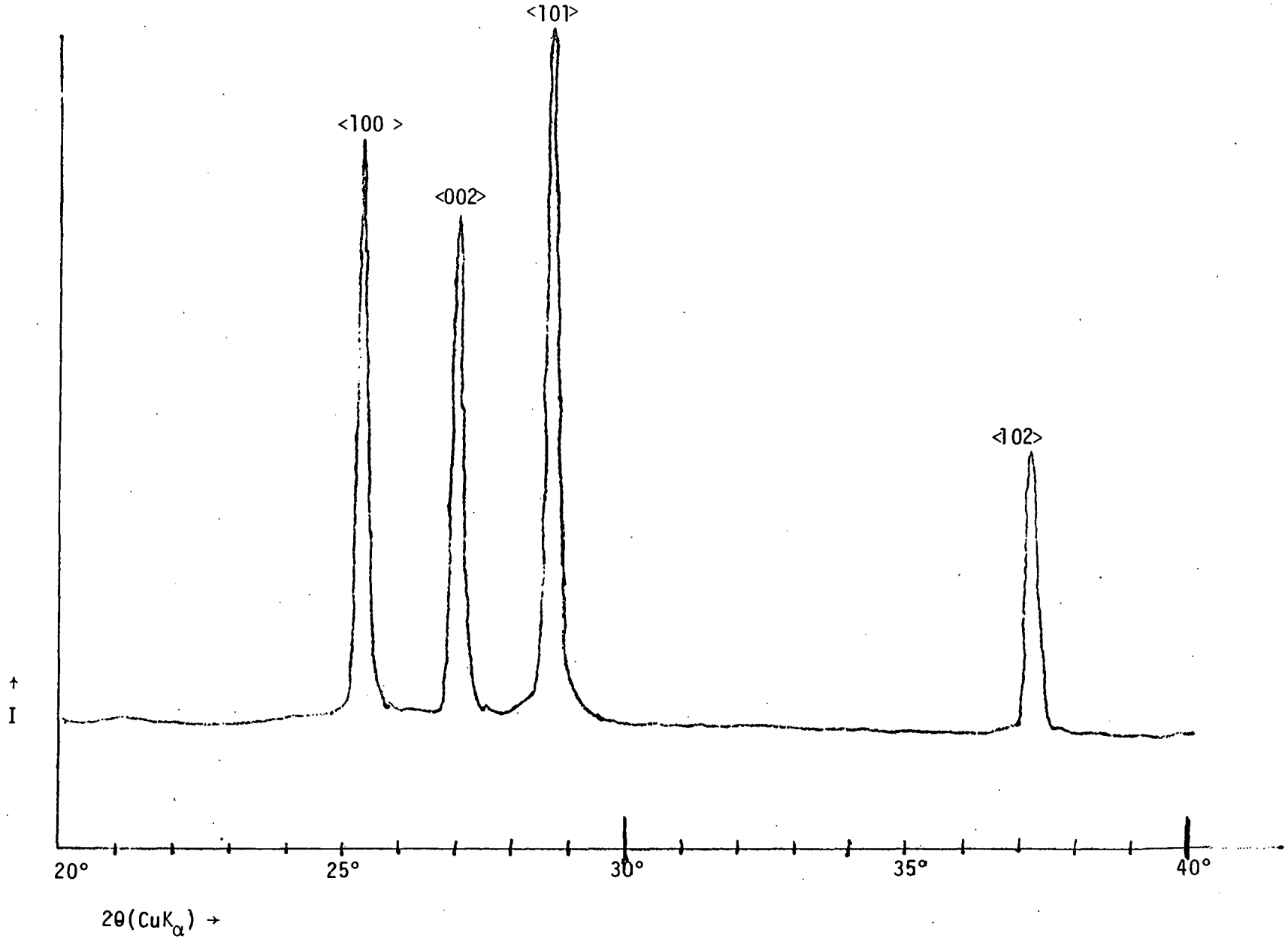


Figure 12. CdS Powder Diffraction Pattern

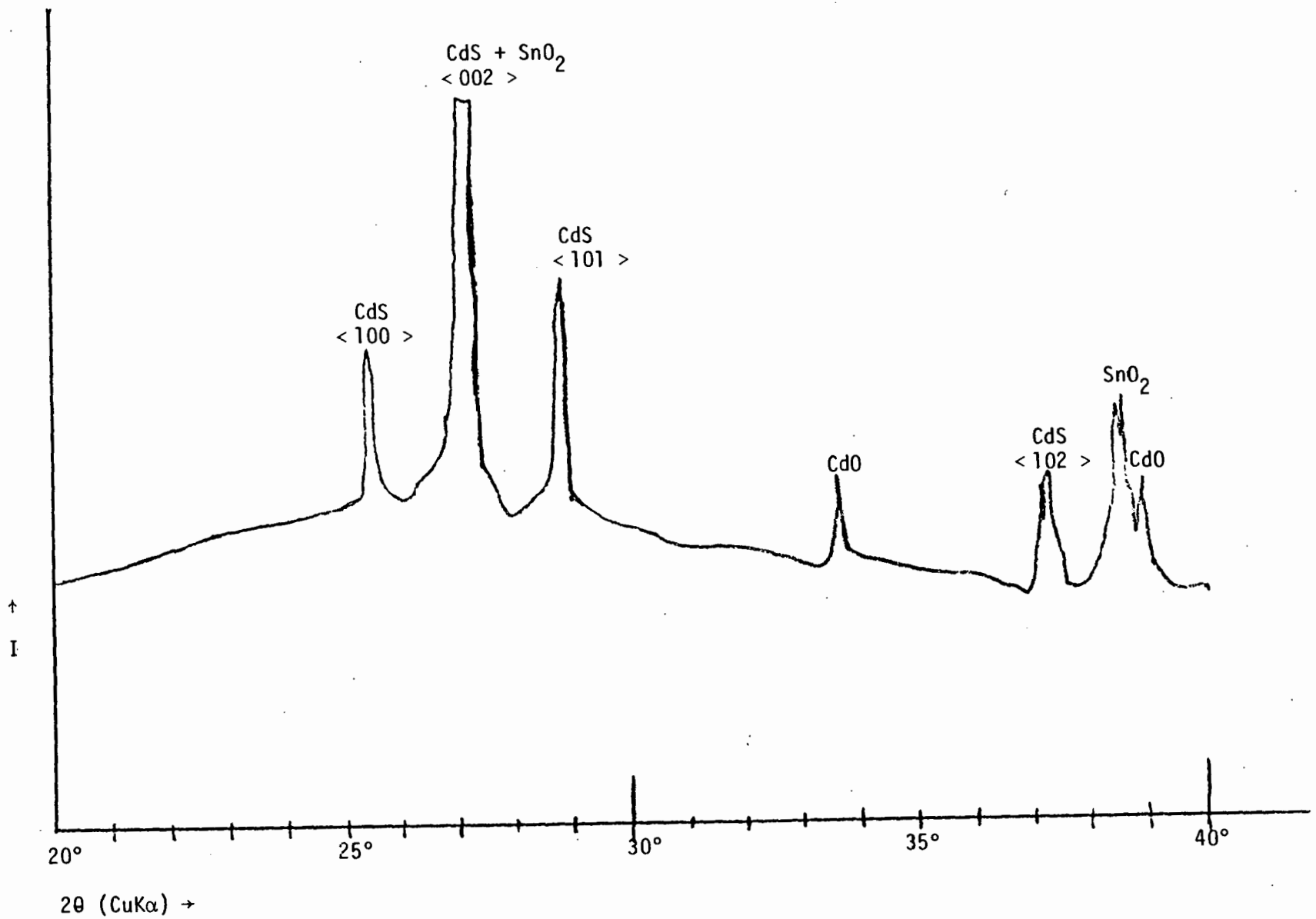


Figure 13. Converted CdO Film (2-3 Min. Sprays) on Tin Oxide Coating

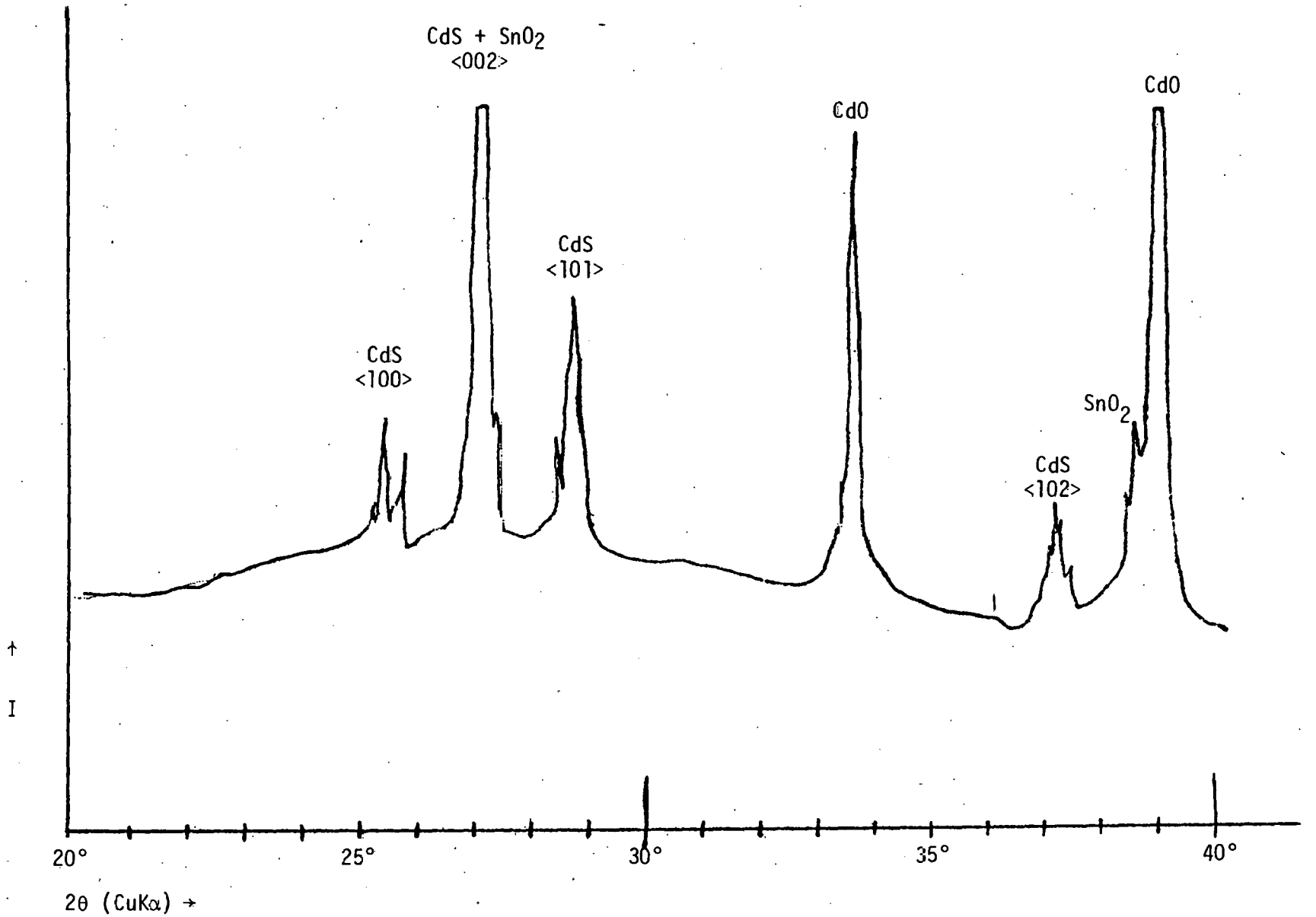


Figure 14. Converted CdO Film (4-3 Min. Sprays) on Tin Oxide

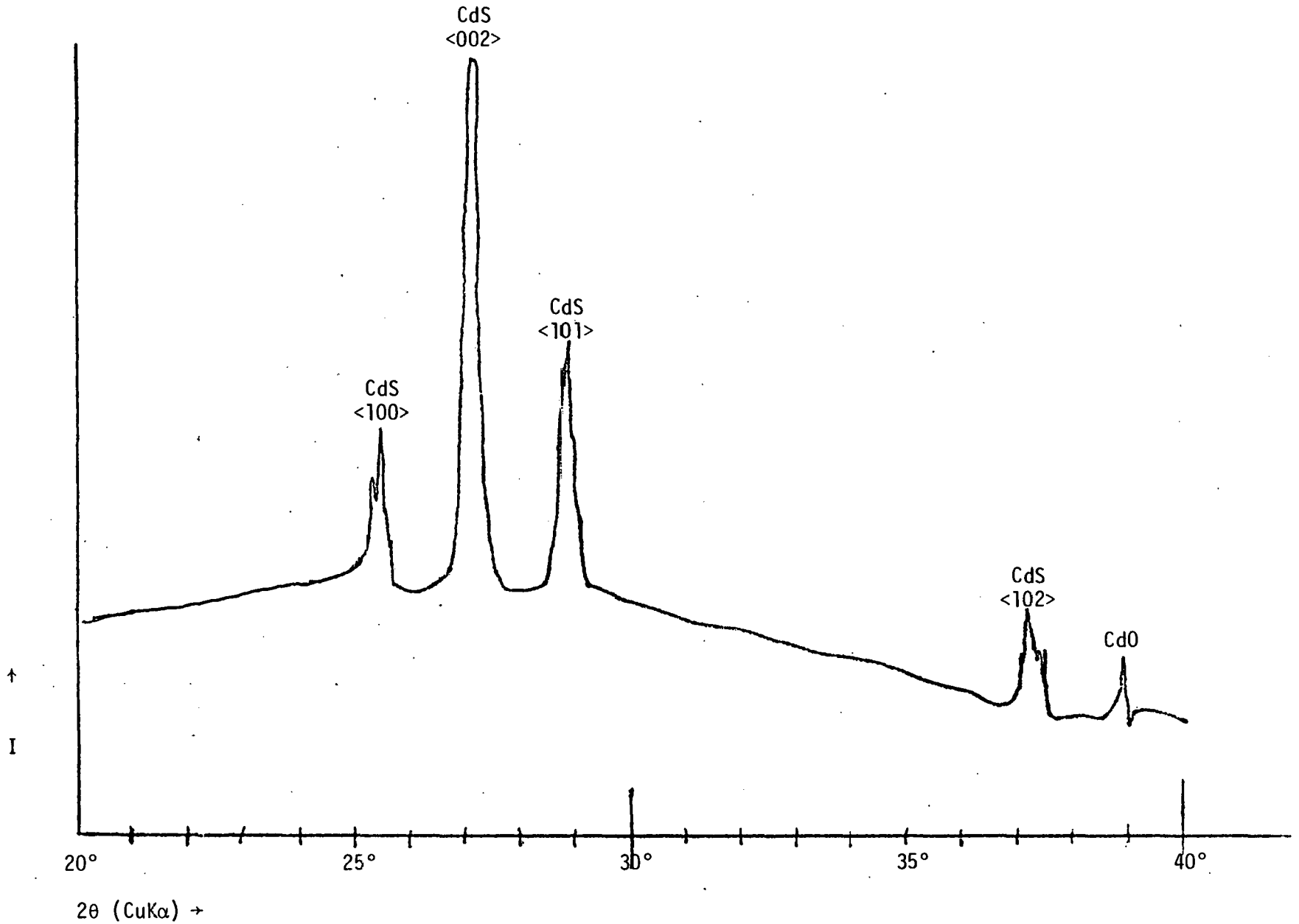


Figure 15. Converted CdO Film (2-3 Min. Sprays) on Glass

At this point it is well to consider whether any other chemical species in addition to CdS may form during the ion exchange. Specifically, we may question whether $CdSO_4$ could be produced during the reaction according to

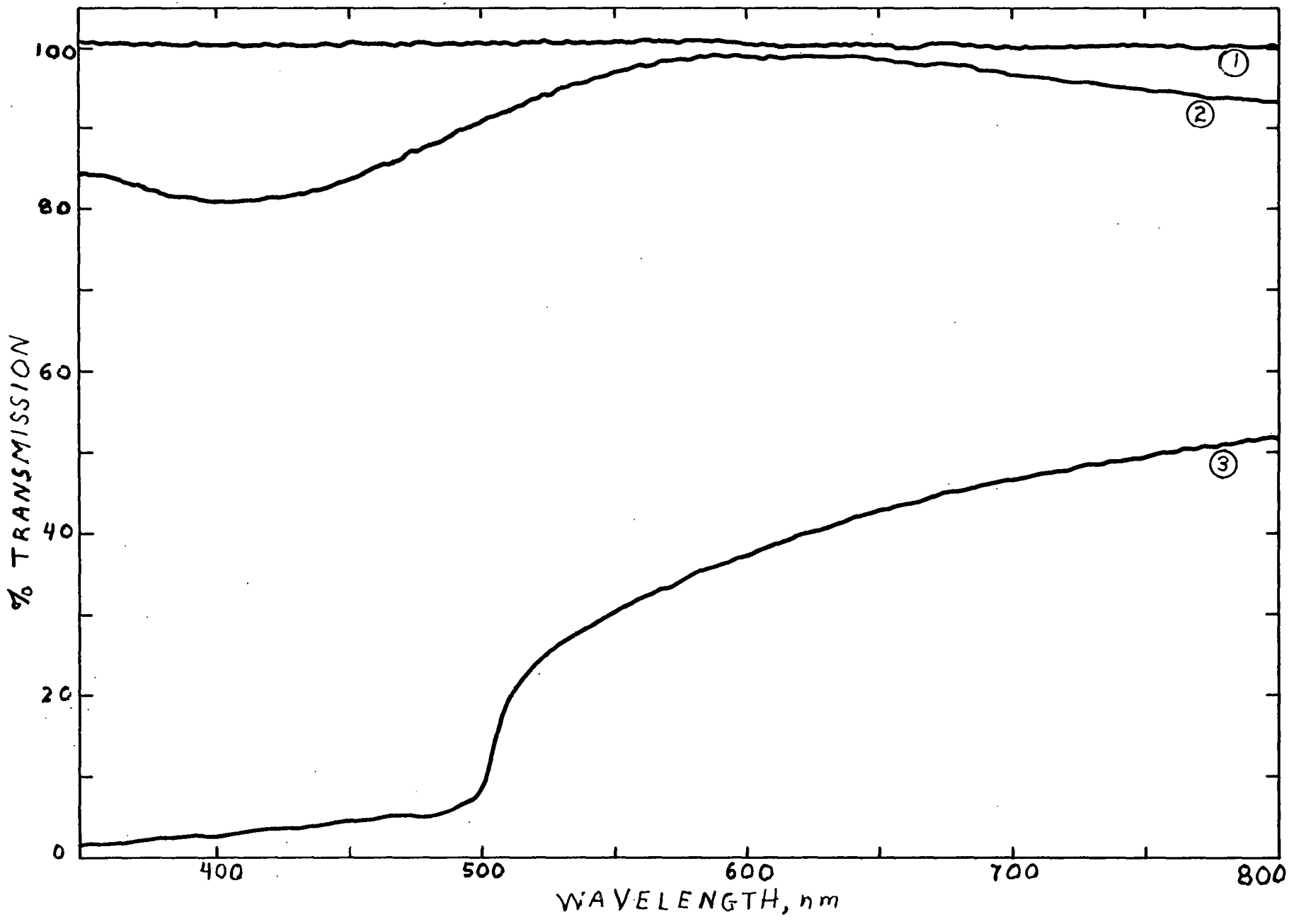
$$4CdO + 4H_2S \rightarrow 3CdS + CdSO_4 + 4H_2.$$

The standard free energy change for this reaction is -58Kcal, and therefore the formation of $CdSO_4$ is thermodynamically possible. On the other hand, this reaction requires the oxidation of sulfur from the -2 state to the +6 state, which involves the transfer of 8 electrons. Thus the reaction should suffer severe kinetic limitations. Furthermore, the intermediate reaction whereby sulfur substitutes for cadmium bonded to oxygen would yield gaseous sulfur dioxide, which would diffuse away. Finally, no evidence for sulfate formation was determined by the X-ray diffraction studies.

3.3.3 Optical Transmission of a Converted Film

An optical transmission curve of the annealed film of Figure 13 (2-3 min. sprays on tin oxide) is shown in Figure 16. This film is roughly 95% CdS. Transmission curves for 7059 glass and a tin oxide film on 7059 glass are shown for purposes of comparison. The transmission of the sulfide film is 40-50% in the 600 to 800 nm region, and a fairly sharp absorption edge appears at 505 nm. The transmission of this film is roughly the same as that reported by J. Bougnot et al. (15) for a much thicker sprayed CdS film. This discrepancy may be due to surface inhomogeneities in our film.

Figure 16. Optical Transmission of ① Glass Substrate, ② SnO_2 on Glass Substrate, and ③ Ion-exchanged CdS on SnO_2/Glass

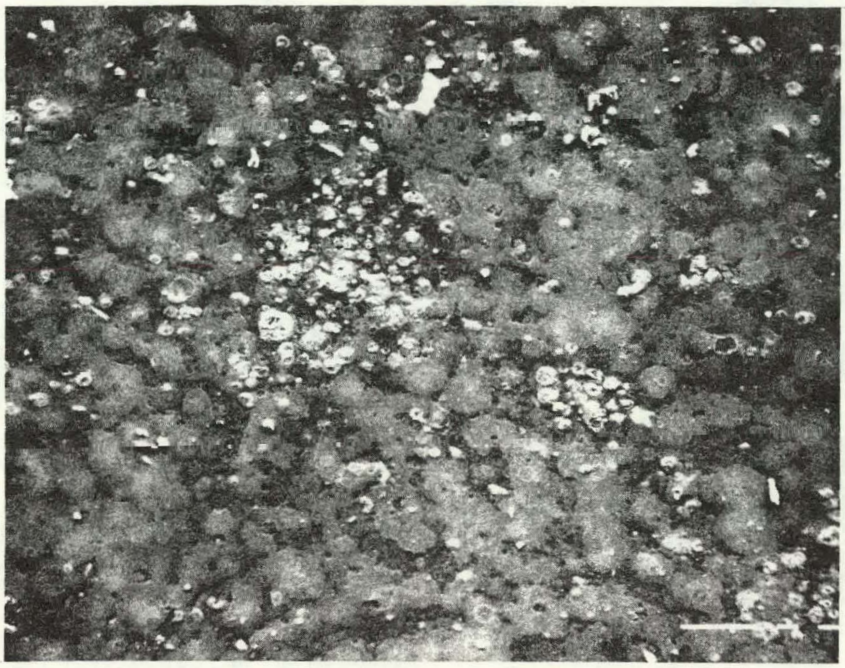


3.3.4 Scanning Electron Microscopy of Annealed Films

We have observed significant changes in the appearance of the films that have been converted to the sulfide. The grain sizes are much larger, as shown in Figure 17. Many of the grains are 100 microns in diameter. Our x-ray analysis (Section 3.3.2) has shown that these grains have the c-axis oriented perpendicular to the substrate. The surfaces of these grains also exhibit structure, as shown in Figure 18. The features appear to be microvoids with approximately 0.1 micron diameter. It should be noticed from Figure 17 that the little spheres that were present in the oxide film of Figure 10 continue to be evident after the anneal. One of these spheres was studied in detail in Figure 19. It appears that the spheres may not be affected by the annealing procedure in the way that the bulk of the film transforms.

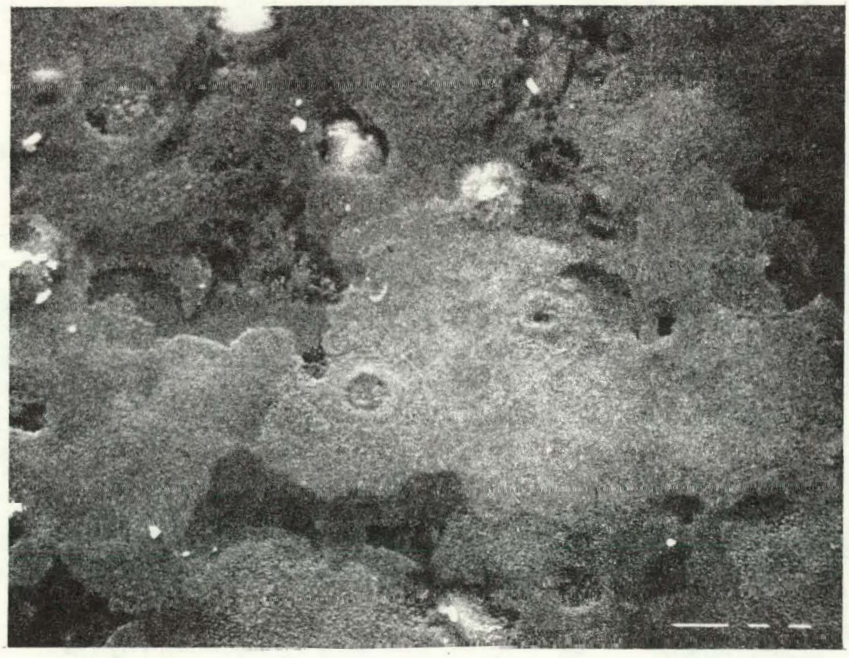
3.4 Copper Sulfide Experiments

A few preliminary experiments with the copper oxide-copper sulfide system were performed. Initial copper oxide films formed by spraying copper nitrate solutions consist of CuO and Cu_2O, depending on water/methanol ratio. After ion exchange in H_2S, a film then exhibited three phases with compositions $Cu_{1.75}S$ and $Cu_{1.8}S$ (digenite), and $Cu_{1.96}S$ (djurleite), as determined by x-ray diffraction. We anticipate that altered annealing conditions will yield chalcocite.



100X

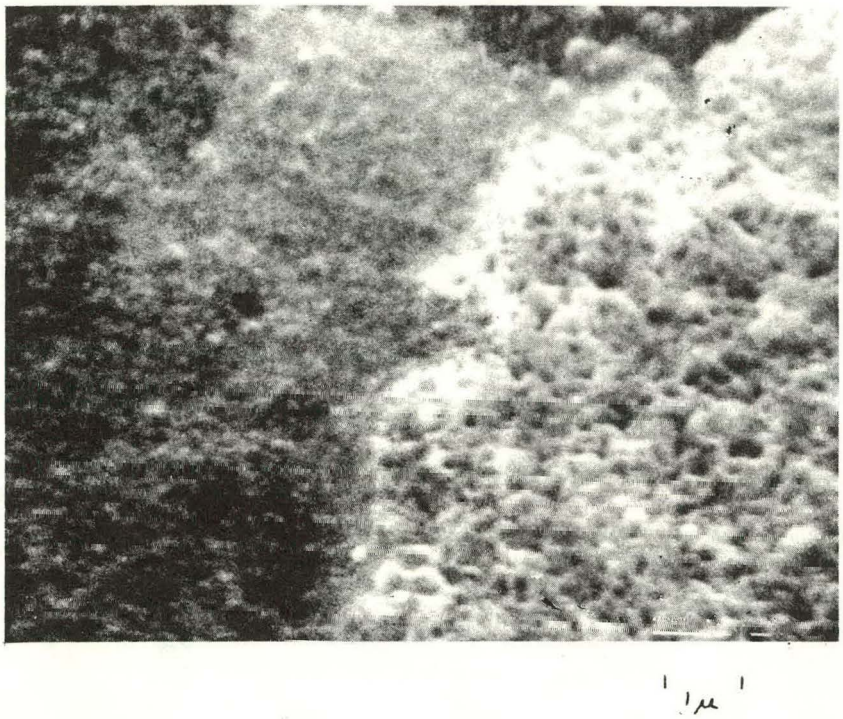
100μ



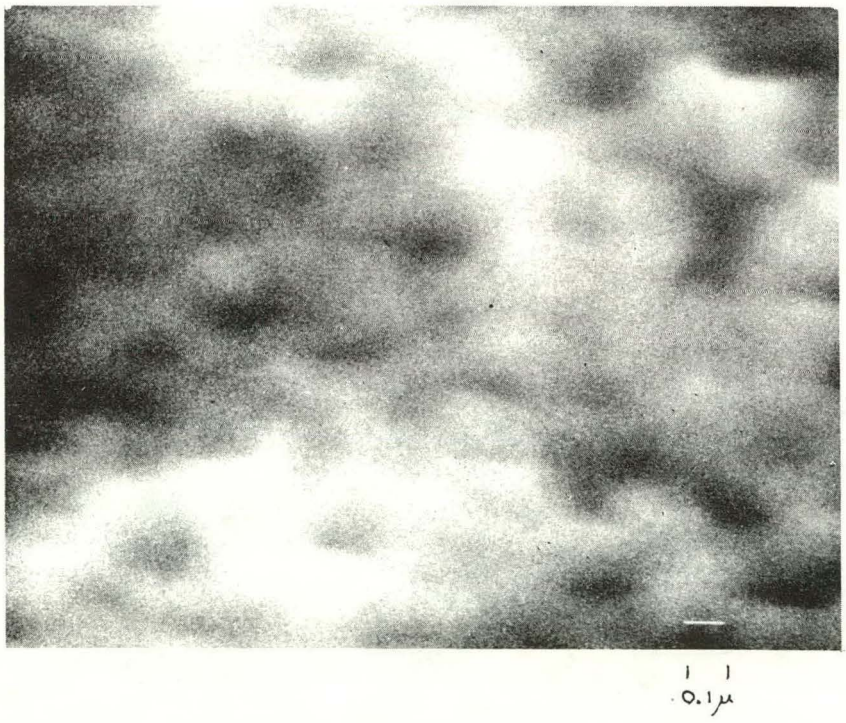
700X

10μ

Figure 17. Ion-Exchanged CdS Film

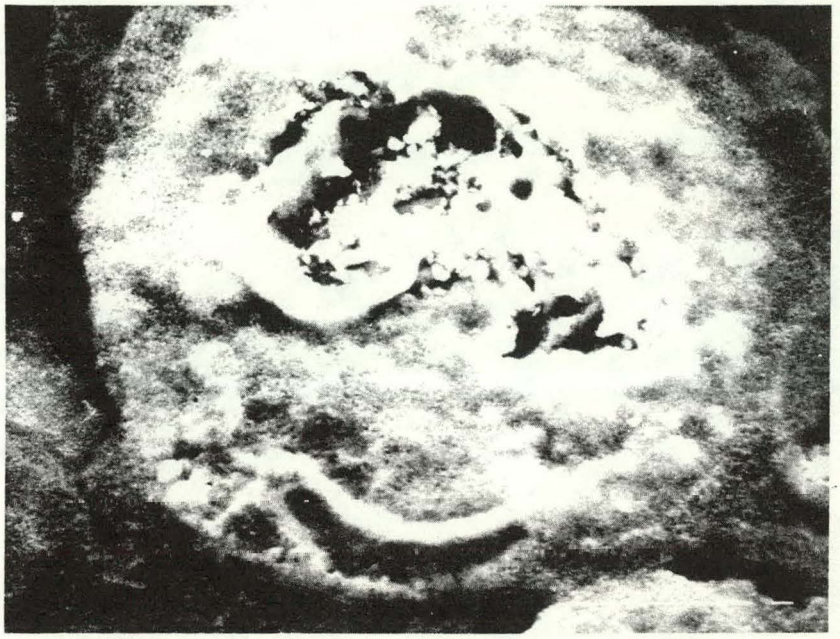


10000X



50000X

Figure 18. Detailed Micrographs of Ion-Exchanged CdS Film



20000X

1 micron

Figure 19. Micrograph of a Sphere Present After the Ion-Exchange

4. PLANS FOR FUTURE WORK

Access to the permanent spray and ion exchange equipment will allow us to vary deposition conditions in a systematic way. We will investigate the necessary conditions to achieve complete conversion of CdO to CdS. The deposition and ion exchange of the copper system will be more closely studied. Solar cells will be fabricated and analyzed.

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APPENDIX

SUBSTRATE HEATER DRAWINGS

Figure 1. Substrate Heater - Copper Block

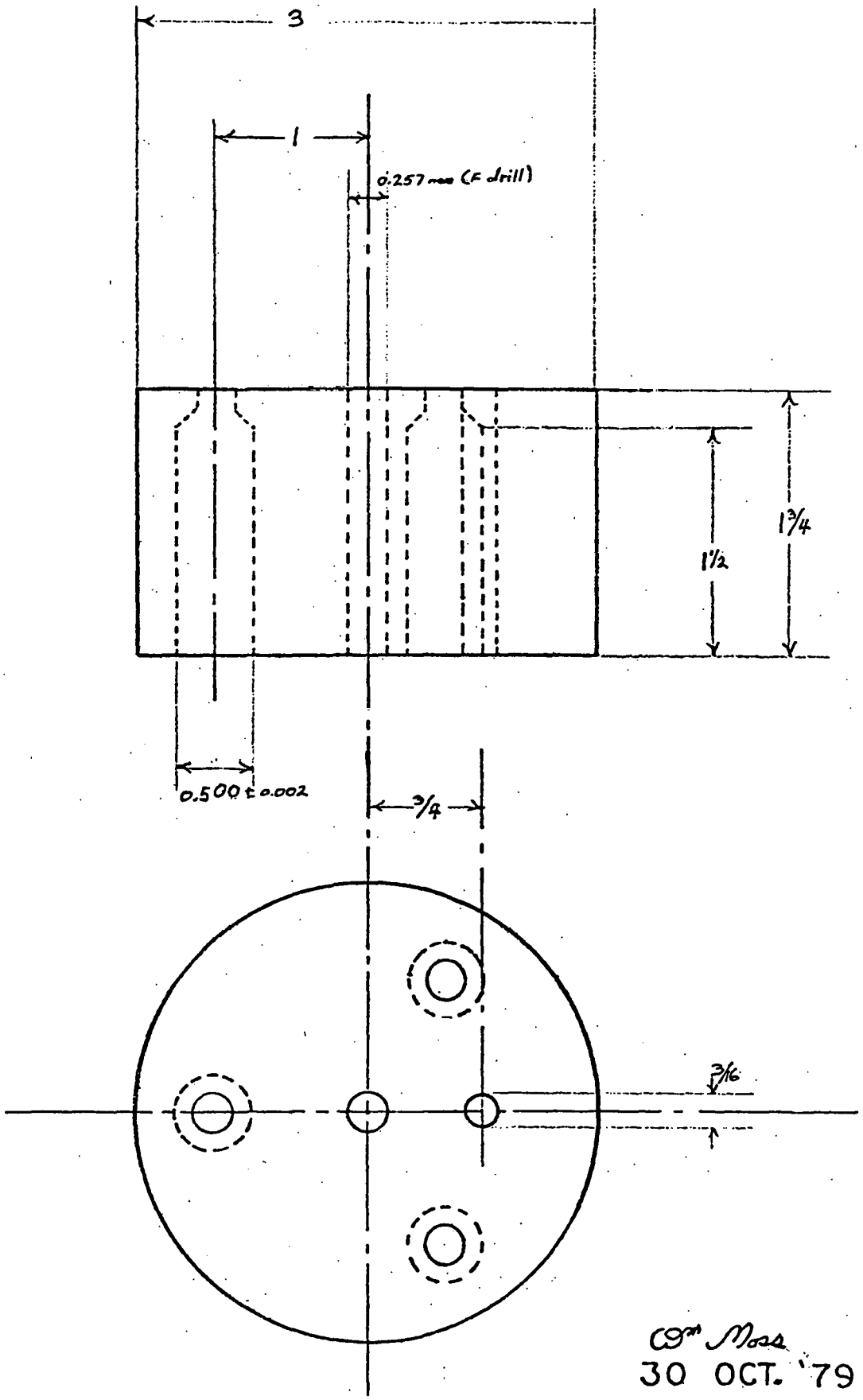


Figure 2. Substrate Heater - Stainless Steel Top

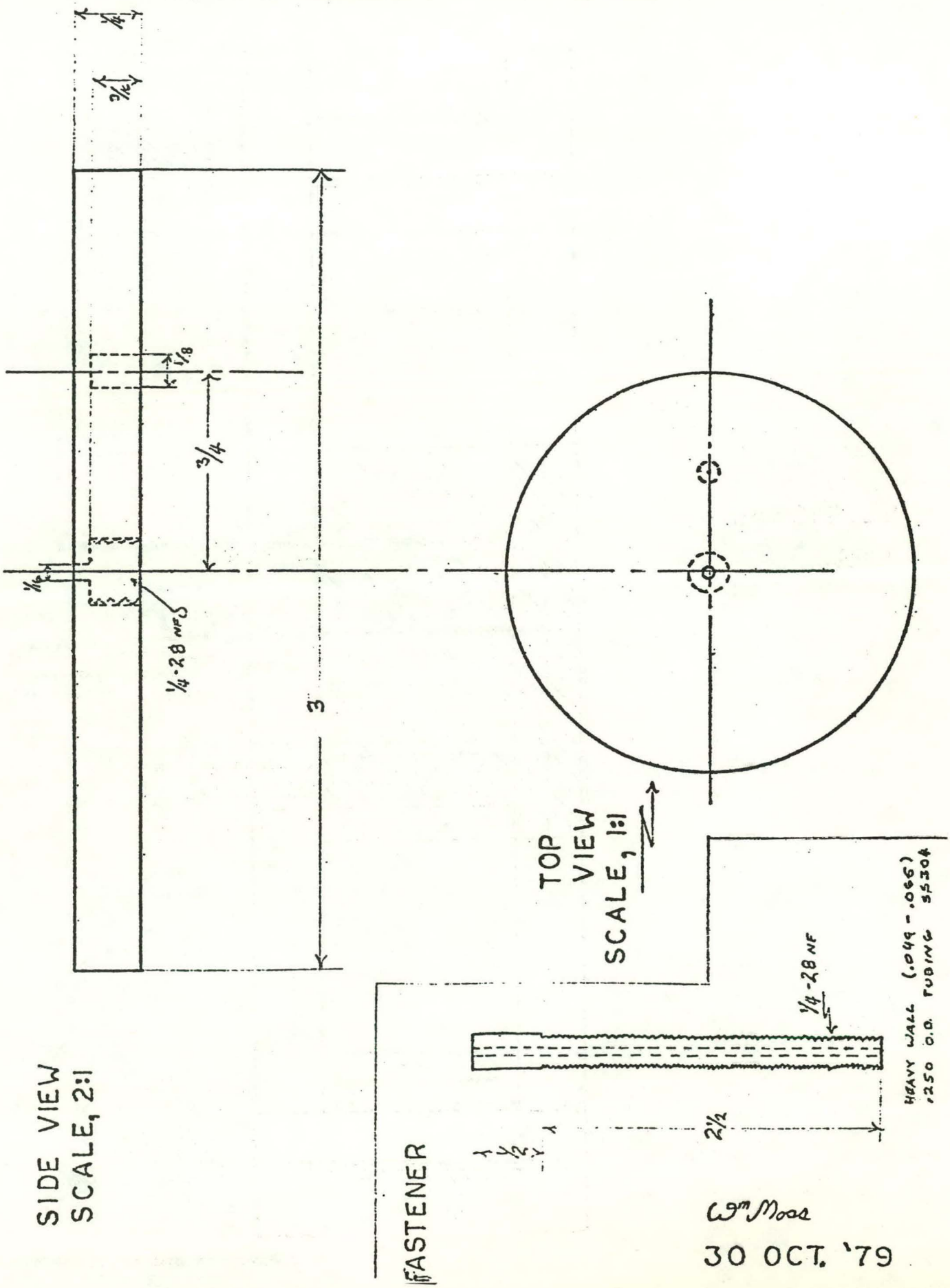
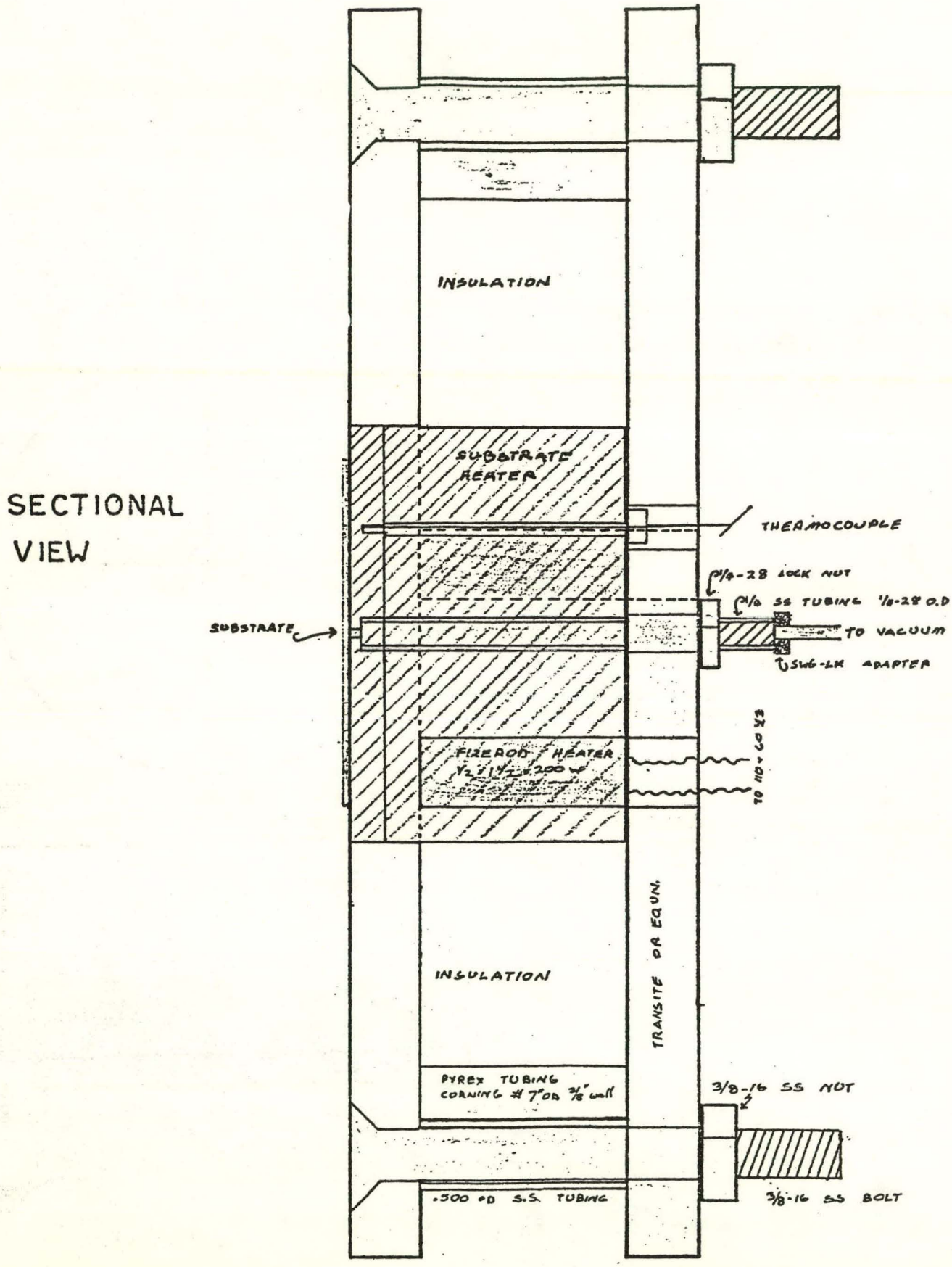


Figure 3. Substrate Heater - Sectional View



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