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Commercialization of a Thick Film Solar Cell

by

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JOHNSON CONTROLS, INC.
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Abstract

Films of CdS were prepared by screen printing and were sintered using a variety of firing conditions and flux concentrations. At the higher temperatures, longer firing temperatures, and lower flux concentrations crystals of cadmium oxide formed on the surface of the CdS film. Preparation of the copper sulfide barrier via the aqueous solution treatment was found to produce suitable barriers only when the films were pre-etched in HCl and when the dip solution containing Cu_2Cl_2 was hot. CdS films formed on indium oxide coated glass showed no evidence of indium penetration into the CdS layer. Transmission studies of the CdS layer failed because of the opacity of the films relative to the equipment available.

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1. Introduction

This report is the third quarterly report of a program designed to evaluate the use of screen printing as a technique for producing large area solar cells. The attributes of screen printing which make this approach of interest are that it is a well established technique in the electronics industry with well established requirements; it has a demonstrated ability to produce large areas of electronic quality films with good pattern fidelity; it affords means for separating conditions required for film deposition from those required for sintering, which permits better control over microstructure; and it is characterized by high material utilization efficiency. A possible disadvantage of screen printing is that the starting material must be reduced to a powder. The fact that efficient small area solar cells can be prepared by screen printing is documented in the current literature.(1)

In previous reports the comminution of cadmium sulfide and cadmium telluride and the preparation of the first trial films of these materials have been reported. This report covers the improvement made in the preparation of these films and the attempts to produce a complete solar cell.

2. Experimental

2.1. Materials

The sources, purity, and preliminary preparation or purification of the materials used have been described in previous reports. No new materials have been added to this list.

2.2. Equipment

The following equipment has been ordered but not received:

Model 270 GCA Monochromator (8191-1301-0) with scan control (8181-0084-5) and Tungsten halogen light source (8191-0139-0).

Model 5101 PAR Lock-In Amplifier with Model 125A chopper and Model 5101/98 Tuned Amplifier.

Model MP75 Wenking potentiostat.

When received this equipment will be used to characterize the CdS and CdTe films electronically and optically.

A Beckman DB-G grading spectrometer was used to investigate the transmission characteristics of the CdS films.

3. Technical Discussion

3.1. Cadmium Sulfide Films

Films of cadmium sulfide were prepared using various loadings of the cadmium chloride flux and a variety of firing temperatures and times. Table 1 contains a summary of the results obtained along with references to the appropriate SEM photographs for each set of conditions. Films prepared using twenty volume percent cadmium chloride are shown in figures 1 through 8. Sintering at best is minimal. The films appear to be very porous. At the 630°C firing condition larger grains appear on the surface of the film. These features are not present at 552°C or 600°C. At 653°C the surface grains are larger and have well defined facets. The resistance of the film fired at 653°C is higher than that of the films prepared at lower temperatures. The large surface grains are less prominent when the flux content is thirty volume percent, see figures 9 through 16. These films are more continuous even at 552°C and at 600°C. Again by 630°C surface grains appear which by the 653°C firing are very pronounced and which appear to have the effect of lowering the sample conductivity. Parallel features are noted when the flux level is forty volume percent, see figures 17 through 22. All films produced with this quantity of flux are better sintered than the corresponding film produced at lower flux levels. Resistances of the films produced with thirty and forty volume percent cadmium chloride are equivalent, see table one.

Films were also produced with two layers of cadmium sulfide in place of three. Generally, the sintering is not as good as in the corresponding three-layer films, see figures 23 through 28. The thickness of the fired films is almost the same as for the three-layer films even though they contain only two-thirds of the material and the resistance is somewhat higher.

One cadmium sulfide film was fired for 100 minutes to see if the surface grain growth would continue and whether these grains would ultimately sinter together. Figures 29 and 30 show that additional grains formed and that the grains did increase in size (compare with figures 21 and 22). The grains do not appear to be sintering together and the resistance increased during this prolonged firing and surface adhesion was low.

X-ray analysis of some of the films containing large grains on their surface showed the presence of cadmium oxide. SEM work was performed to determine the location of this oxide. Figure 31 is an SEM photograph of a cadmium sulfide film produced at 653°C using 20 volume percent cadmium chloride flux. This sample was chosen for oxygen analysis because of the spacing of the grains on its surface. Figure 32 is an oxygen map of the same area shown in figure 31. Figure 33 is an oxygen line scan (EDAX) across the film. From these results it is apparent that the large crystals on the surface of these films are cadmium oxide.

Reviewing the photographs presented in the September Monthly Status Report shows that the formation of these surface crystals is favored by the following conditions: high firing temperatures, long firing times, and low flux concentrations.

To avoid the formation of oxide on the films, current films are produced at temperatures below 630°C with firing times of less than 50 minutes and flux concentrations of 30 volume percent or greater. Other firing conditions could be used if higher nitrogen flow rates were maintained. Past experience has shown that poor adhesion between the cadmium sulfide layer and the glass is obtained at higher flow rates, presumably due to the premature loss of the cadmium chloride flux.

Samples of cadmium sulfide films were prepared for Hall measurements at S.E.R.I. These one cm^2 samples have been shipped to S.E.R.I. along with state-of-the-art cadmium sulfide films.

3.2. Copper Sulfide Barrier Formation

The films produced above were treated with cuprous chloride to form a cuprous sulfide film. Open circuit voltages obtained under the solar simulator at AM 1 are shown in table one. Some samples were heated to 150°C for one hour in vacuum. In all cases the open circuit voltage increased.

A comparison was made of the techniques used at Westinghouse and Delaware. Only terse information is available on the actual procedures used (2). Suitable results were only obtained using the Delaware procedure. Comparing this procedure with the previous procedures, the following conclusions were obtained:

1. Pre-etching of the cadmium sulfide in hydrochloric acid is required. Hot etching in concentrated HCl resulted in total dissolution of the cadmium sulfide film. Using 55% HCl resulted in satisfactory surface preparation.

2. Hot Cu_2Cl_2 solution (60°C) is required to produce suitable copper sulfide layers.

At this point the best cells are produced using a cadmium sulfide film prepared at 600°C using a 40 minute firing cycle, etched in 55% HCl solution, and dipped in a hot (60°) solution containing 6g Cu_2Cl_2, 2g NaCl per liter for 10 seconds.

Problems were encountered in the preliminary voltage measurements. Multimeters indicated an order of magnitude lower V_{oc} than was found on the curve tracer. This disparity in results is related to the high sweep rate of the curve tracer versus the essentially DC measurements of the multimeter. Receipt of the ordered potentiostat should resolve this problem.

Cadmium sulfide films containing forty volume percent cadmium chloride were fired at 600°C on Nesatron glass (InO_2 coated glass). Sheet resistance of the CdS film on the InO_2 coating was 0.07 kohm. The open circuit voltage of Cu_2S coated films was 0.12 volts. Post-firing thermal treatment at 150°C for one hour in vacuum lowered the open circuit voltage to 0.01 volts. The reason for this voltage drop is under investigation.

Figures 34 and 35 show line scans for indium and cadmium in the CdS films printed on Nesatron glass. The broadness of the indium line is related to the size of the area analyzed ($\sim$ 2 microns). Indium does not seem to have been affected by the CdS film and essentially no interdiffusion has occurred.

3.3. Transmission Characteristics of Cadmium Sulfide Films

An attempt was made to measure the visible and ultraviolet absorption spectra of the CdS films. The CdS films were put into a Beckman DB-G grating spectrophotometer. Without exception all films were too opaque to permit the measurement of the transmission characteristics using this instrument. When the equipment on order is received, this determination will be possible.

4. Future Work

Future work will address improvements in copper sulfide barrier layers, increased grain growth using H_2S post sintering treatment, and characterization of cells produced on indium coated glass.

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Dr. Guy McDonald, Principal Investigator

Approved by:

G. Goodman

Dr. G. Goodman, Project Manager

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References:

1. N. Nakagama, H. Matsumoto, A Nakano, S. Ikagami, H. Uda, and T. Yamashita, Japanese J. of Applied Physics, 19 (4), (1980) pp. 703-712.

2. J. R. Szedon, F. A. Shirland, J. A. Stoll, and H. C. Dickey (Westinghouse), "Development of CuS/CdS Thin Film Solar Cells," 1st. Technical Progress Report, February 1980.

Table One

Performance of CdS Films Relative to Conditions of Preparation

CdS Layers	Firing Temp. °C	Firing Time Min.	Flux Content v/o	Resist. kohms	Thick-ness microns	SEM Photo Figures	V_{oc} volts	Heat-treated V_{oc} volts
3	552	40	20	20	18	1, 2	--	--
3	600	40	20	10	15	3, 4	--	--
3	630	37	20	20	15	5, 6	.02	--
3	653	40	20	150	13	7, 8	.05	--
3	552	35	30	2.5	15	9, 10	.15	--
3	600	40	30	3	15	11, 12	.22	--
3	630	35	30	4	15	13, 14	.05	.12
3	653	40	30	24	13	15, 16	.10	--
3	550	30	40	2.7	10	17, 18	.22	.33
3	600	33	40	3	13	19, 20	.21	--
3	653	40	40	24	10	21, 22	.03	--
2	630	37	20	200	13	23, 24	.02	--
2	630	37	30	50	10	25, 26	.23	--
2	630	37	40	8	10	27, 28	.07	.18
3	653	100	40	498	--	29, 30	--	--

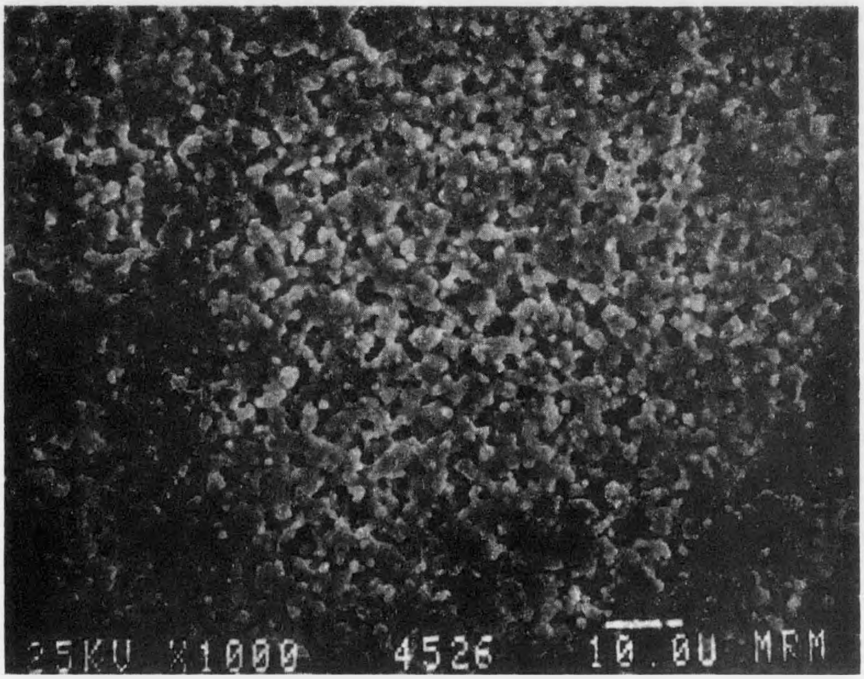

Figure 1. Low magnification SEM photograph of 3-layer CdS film fired at 552°C for 40 minutes, originally containing 20 volume percent $CdCl_2$.

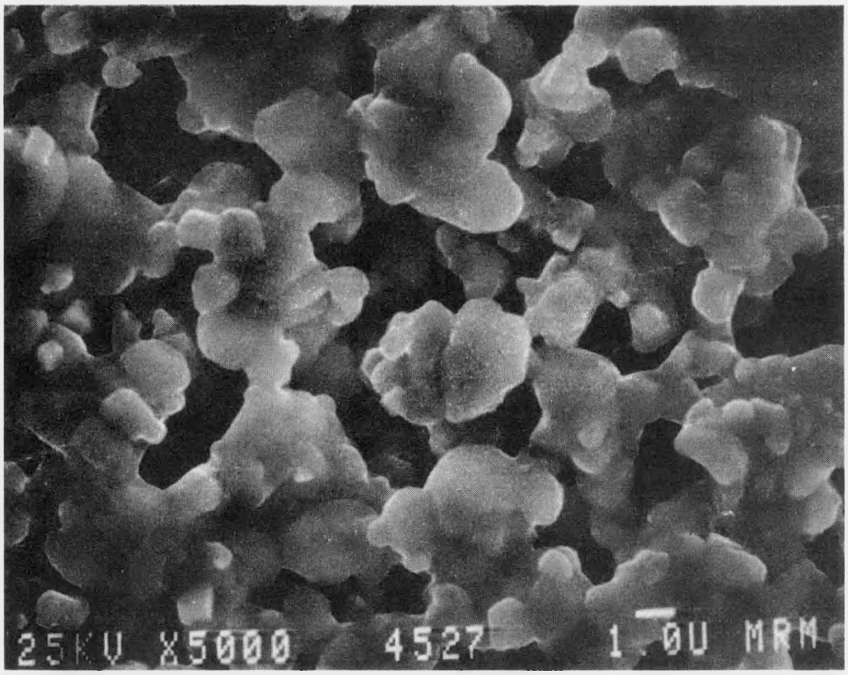

Figure 2. High magnification SEM photograph of 3-layer CdS film fired at 552°C for 40 minutes, originally containing 20 volume percent $CdCl_2$.

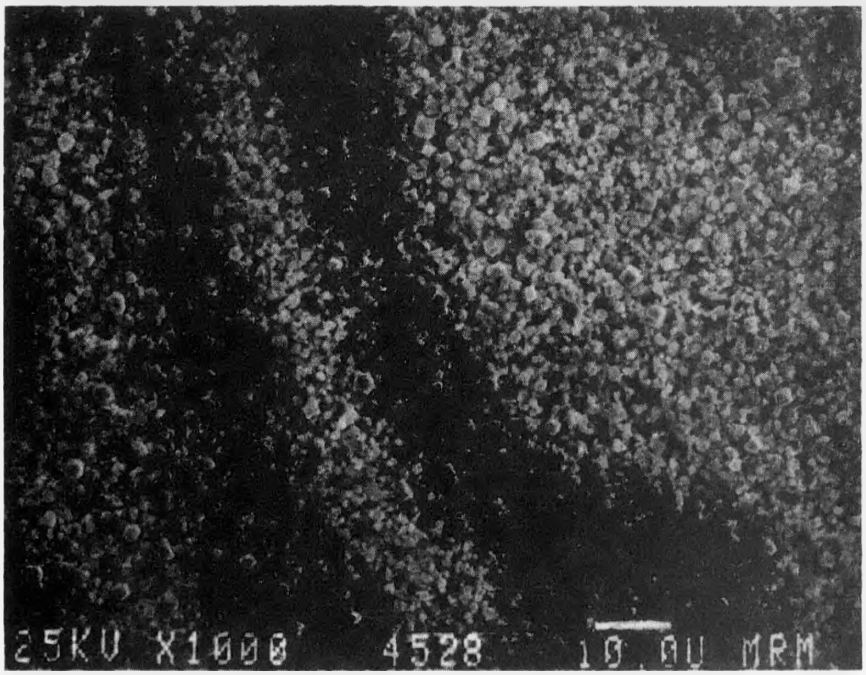

Figure 3. Low magnification SEM photograph of 3-layer CdS film fired at 600°C for 40 minutes, originally containing 20 volume percent $CdCl_2$.

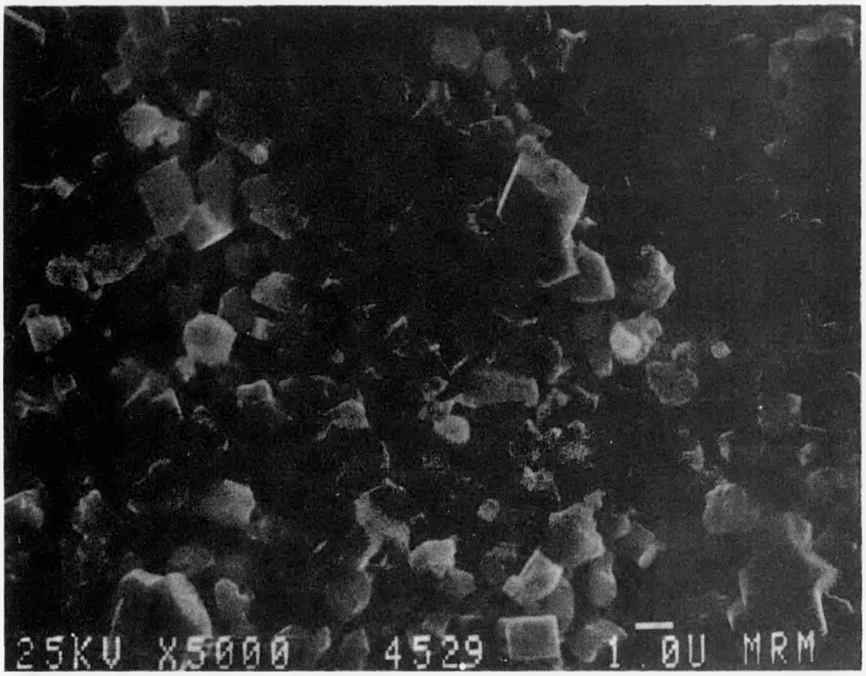

Figure 4. High magnification SEM photograph of 3-layer CdS film fired at 600°C for 40 minutes, originally containing 20 volume percent $CdCl_2$.

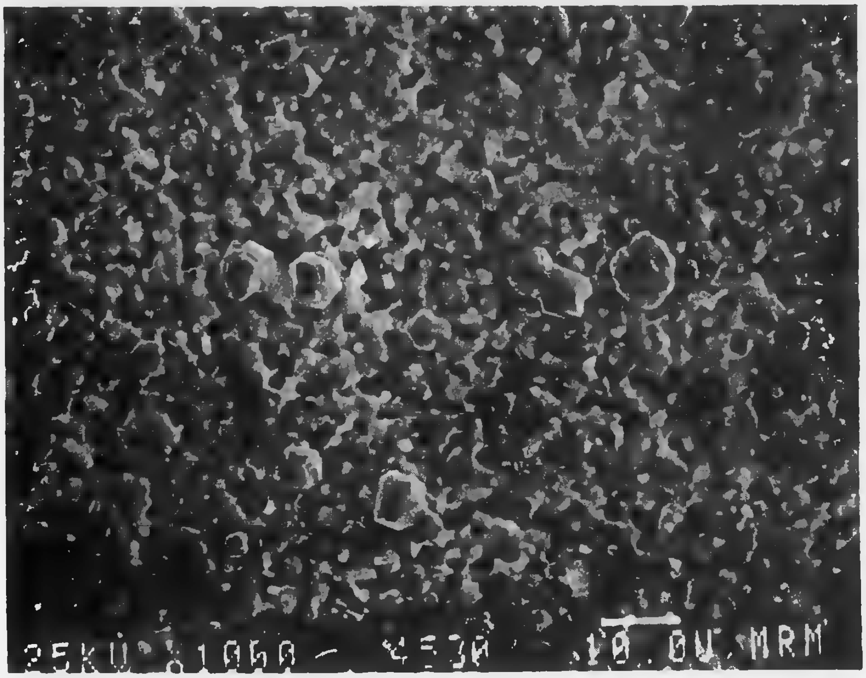

Figure 5. Low magnification SEM photograph of 3-layer CdS film fired at 630°C for 37 minutes, originally containing 20 volume percent $CdCl_2$.

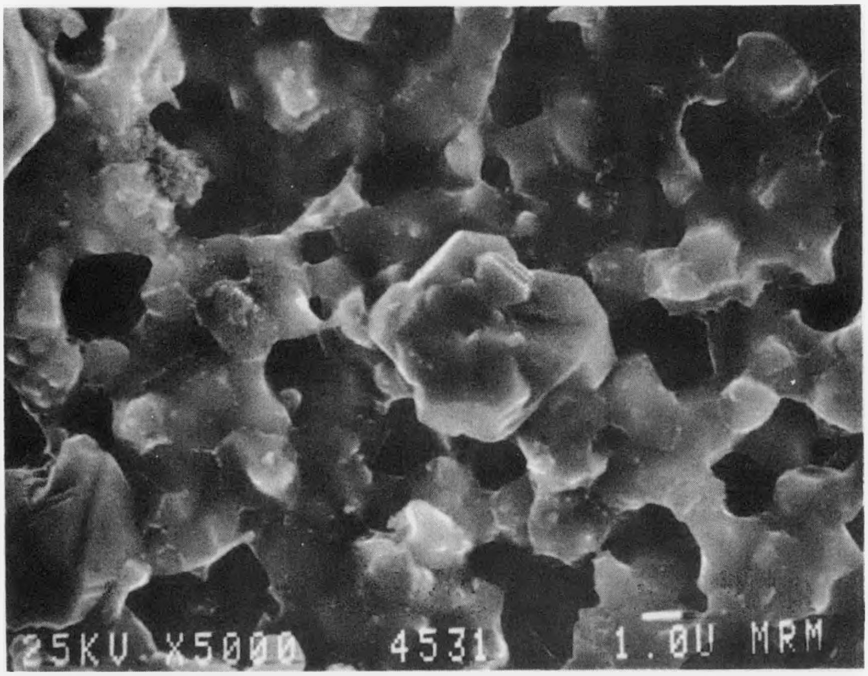

Figure 6. High magnefication SEM photograph of 3-layer CdS film fired at 630°C for 37 minutes, originally containing 20 volume percent $CdCl_2$.

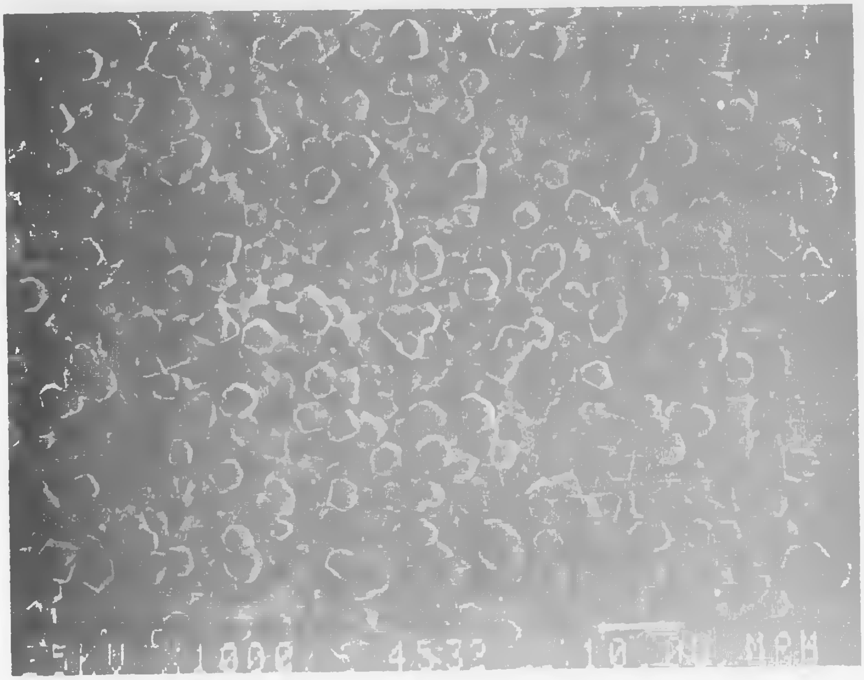

Figure 7. Low magnification SEM photograph of 3-layer CdS film fired at 653°C for 40 minutes, originally containing 20 volume percent $CdCl_2$.

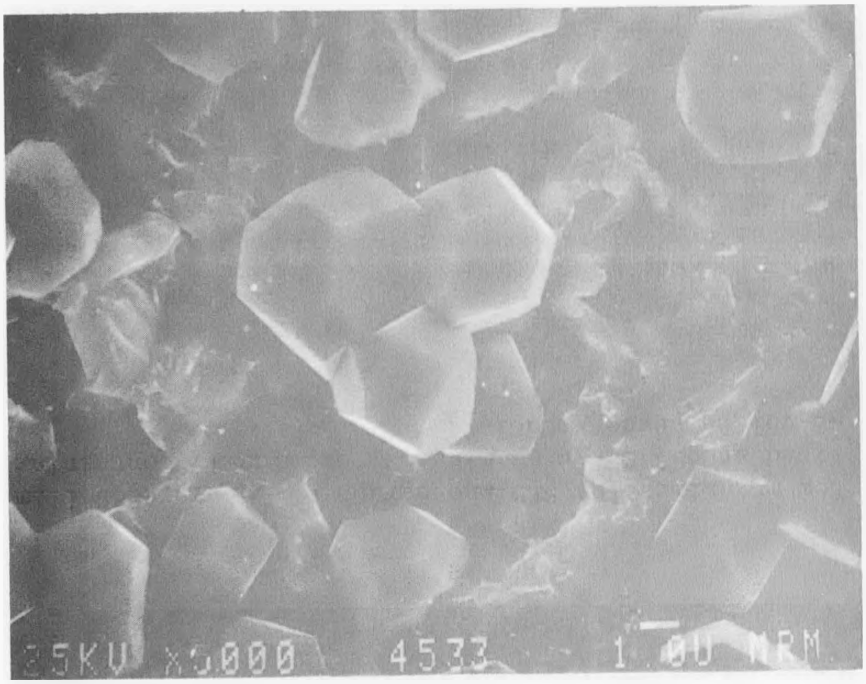

Figure 8. High magnification SEM photograph of 3-layer CdS film fired at 653°C for 40 minutes, originally containing 20 volume percent $CdCl_2$.

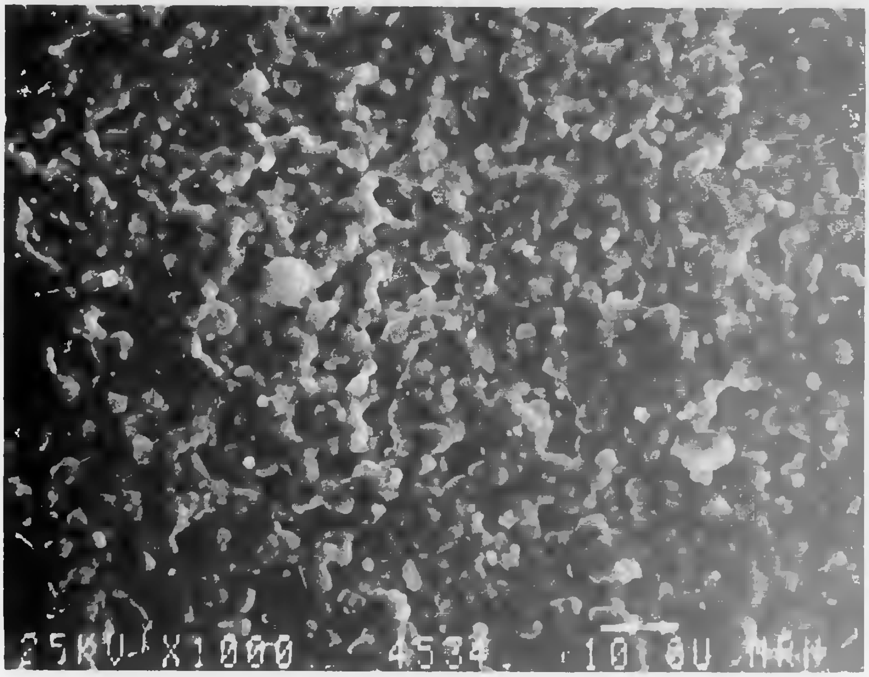

Figure 9. Low magnification SEM photograph of 3-layer CdS film fired at 552°C for 35 minutes, originally containing 30 volume percent $CdCl_2$.

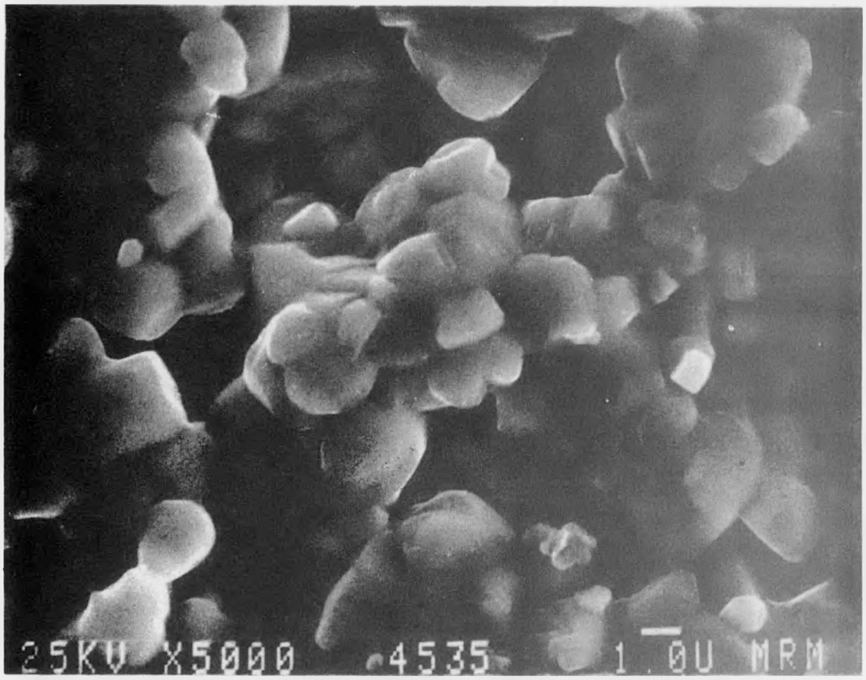

Figure 10. High magnification SEM photograph of 3-layer CdS film fired at 552°C for 35 minutes, originally containing 30 volume percent $CdCl_2$.

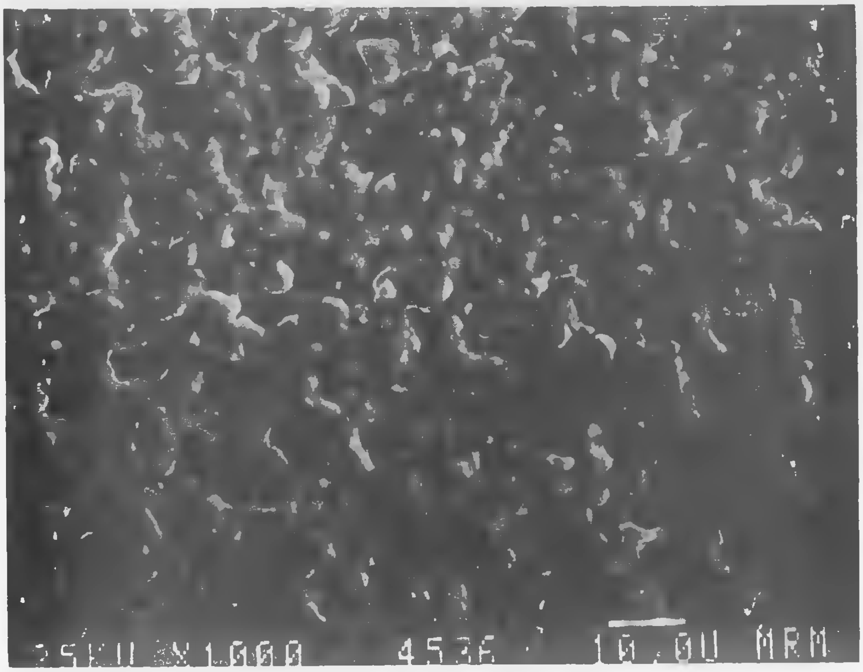

Figure 11. Low magnification SEM photograph of 3-layer CdS film fired at 600°C for 40 minutes, originally containing 30 volume percent $CdCl_2$.

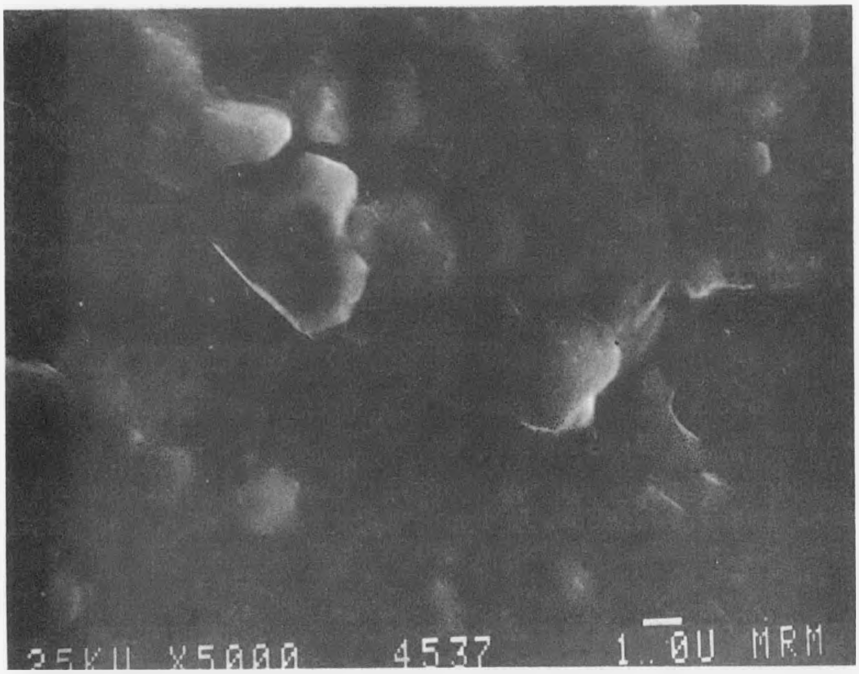

Figure 12. High magnification SEM photograph of 3-layer CdS film fired at 600°C for 40 minutes, originally containing 30 volume percent $CdCl_2$.

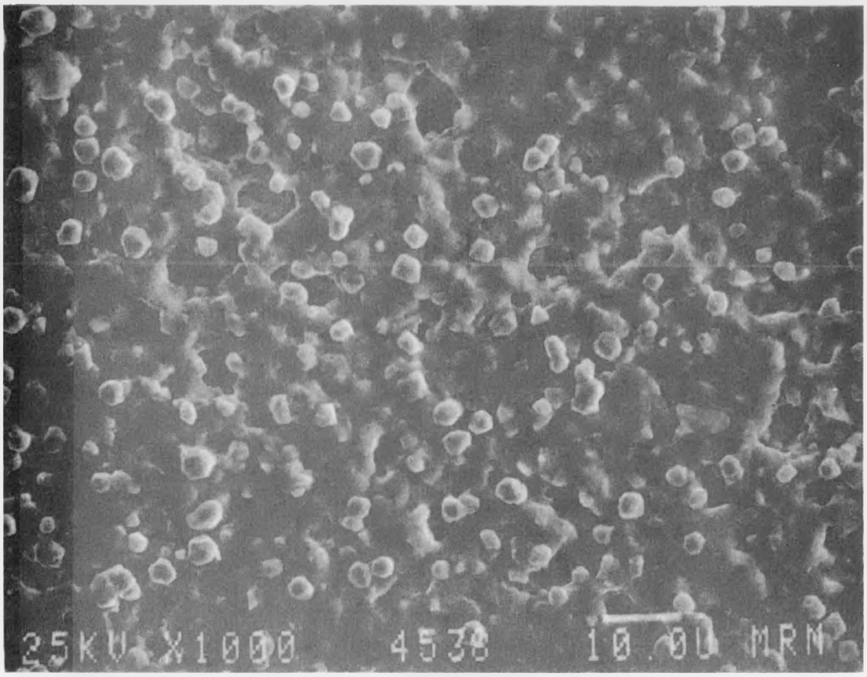

Figure 13. Low magnification SEM photograph of 3-layer CdS film fired at 630°C for 30 minutes, originally containing 30 volume percent $CdCl_2$.

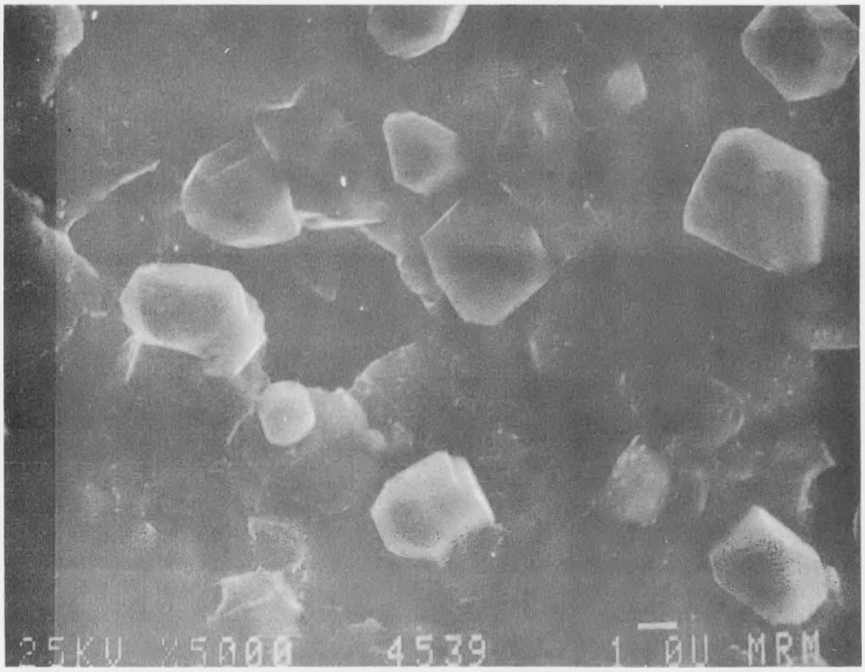

Figure 14. High magnification SEM photograph of 3-layer CdS film fired at 630°C for 30 minutes, originally containing 30 volume percent $CdCl_2$.

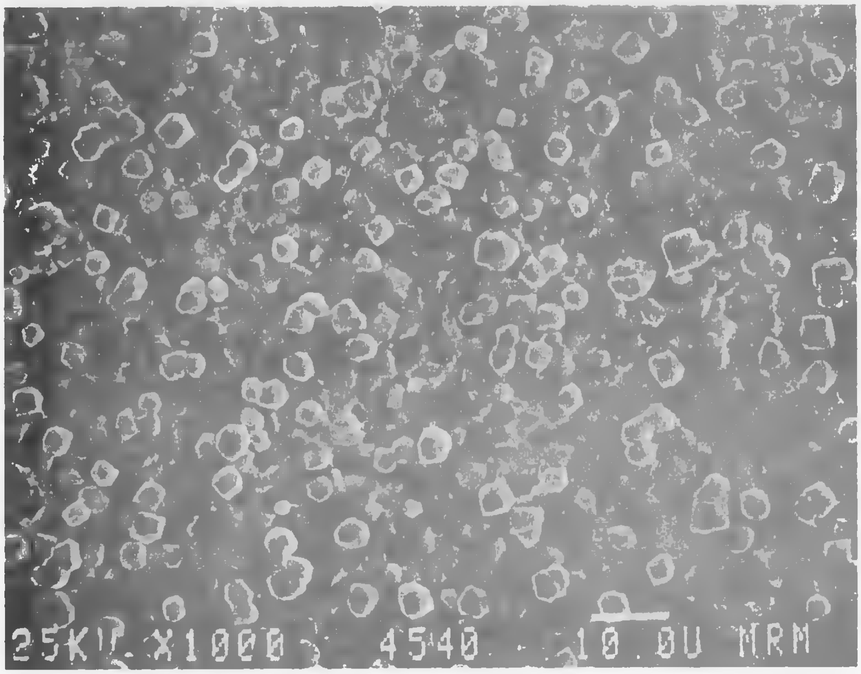

Figure 15. Low magnification SEM photograph of 3-layer CdS film fired at 653°C for 40 minutes, originally containing 30 volume percent $CdCl_2$.

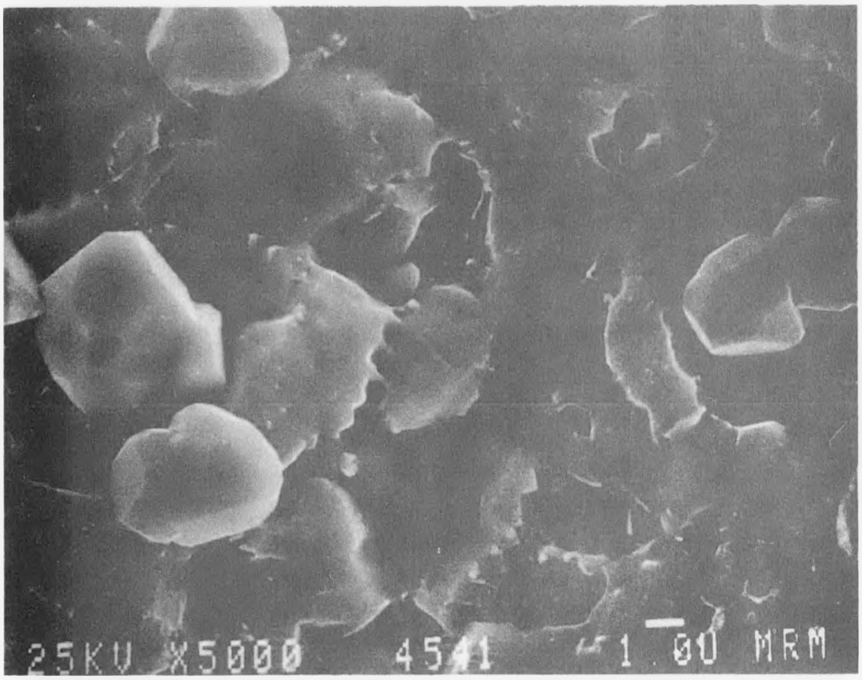

Figure 16. High magnification SEM photograph of 3-layer CdS film fired at 653°C for 40 minutes, originally containing 30 volume percent $CdCl_2$.

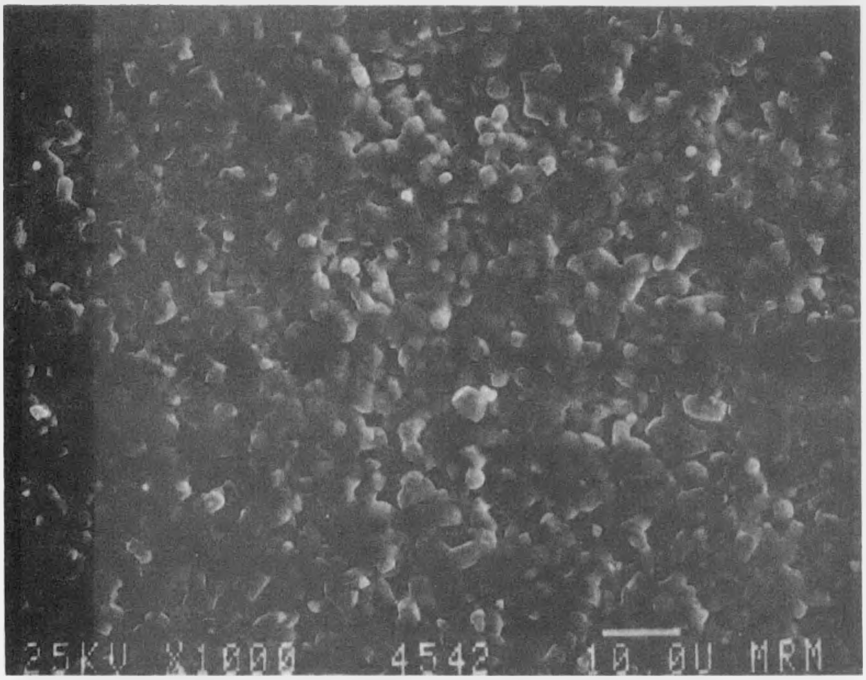

Figure 17. Low magnification SEM photograph of 3-layer CdS film fired at 550°C for 30 minutes, originally containing 40 volume percent $CdCl_2$.

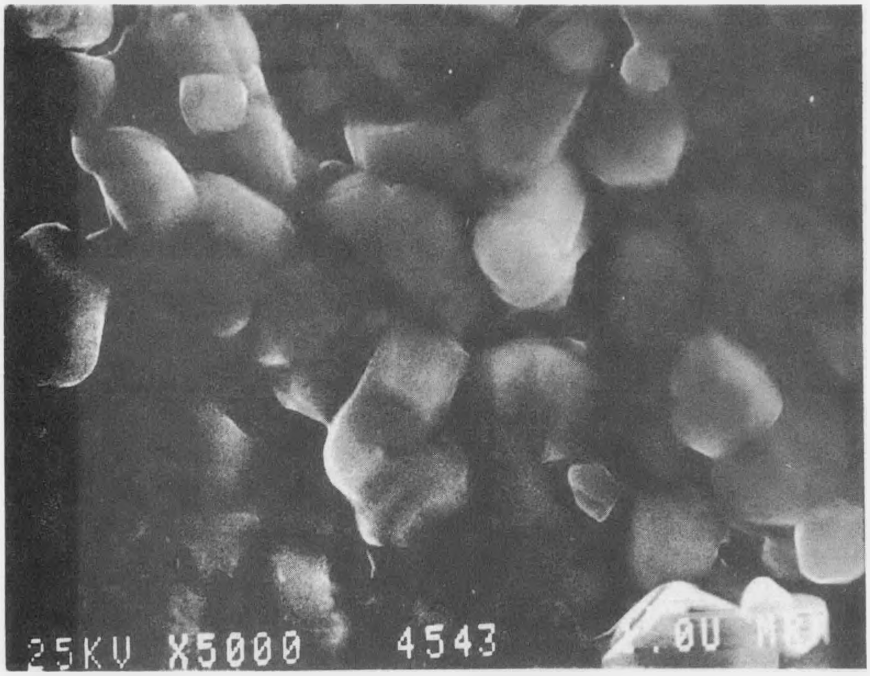

Figure 18. High magnification SEM photograph of 3-layer CdS film fired at 550°C for 30 minutes, originally containing 40 volume percent $CdCl_2$.

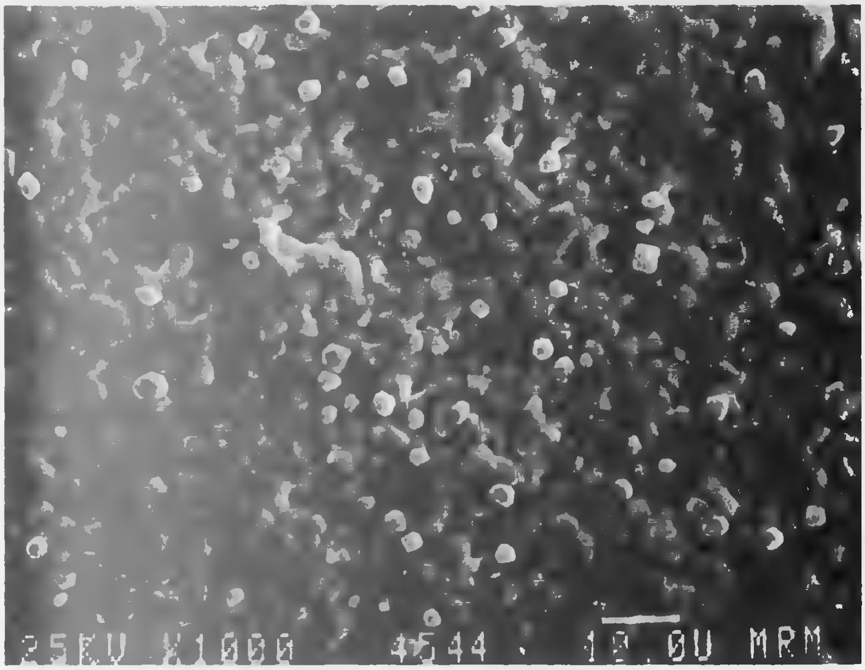

Figure 19. Low magnification SEM photograph of 3-layer CdS film fired at 600°C for 33 minutes, originally containing 40 volume percent $CdCl_2$.

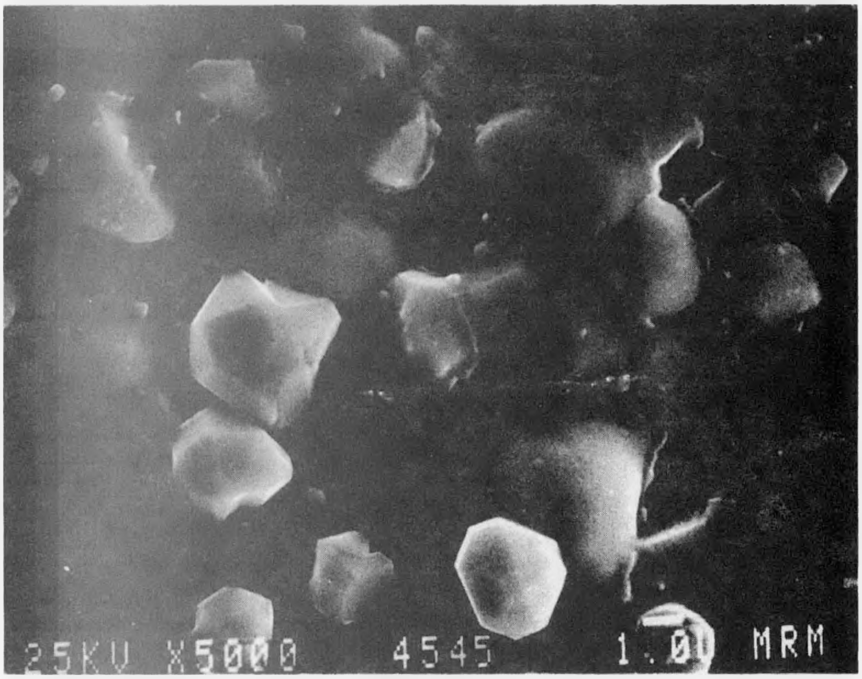

Figure 20. High magnification SEM photograph of 3-layer CdS film fired at 600°C for 33 minutes, originally containing 40 volume percent $CdCl_2$.

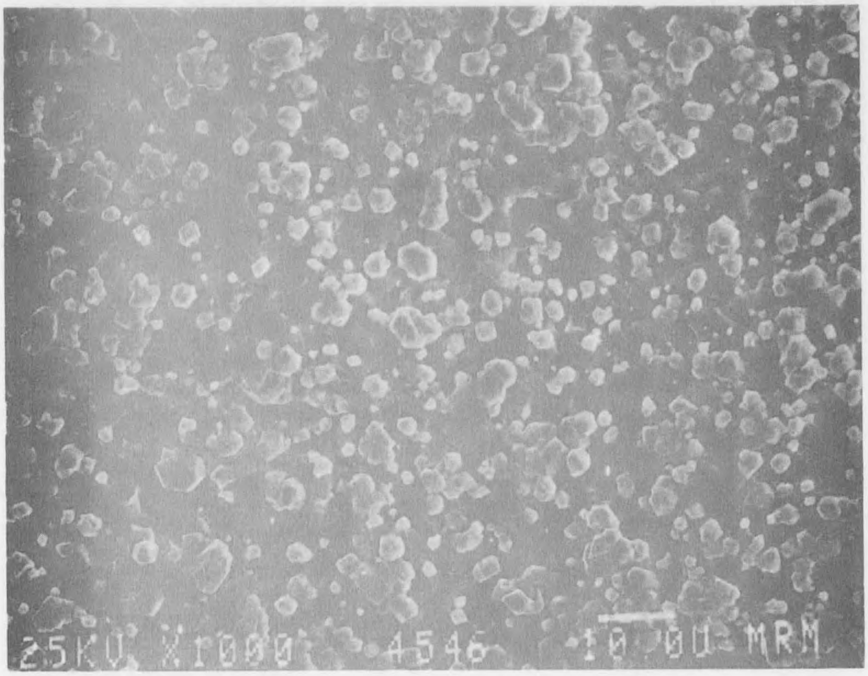

Figure 21. Low magnification SEM photograph of 3-layer CdS film fired at 653°C for 40 minutes, originally containing 40 volume percent $CdCl_2$.

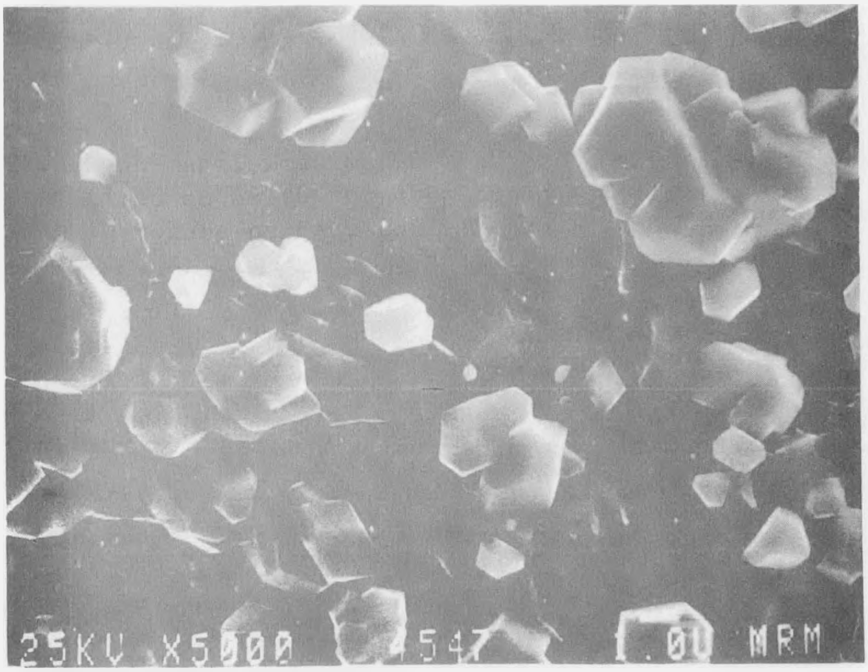

Figure 22. High magnification SEM photograph of 3-layer CdS film fired at 653°C for 40 minutes, originally containing 40 volume percent $CdCl_2$.

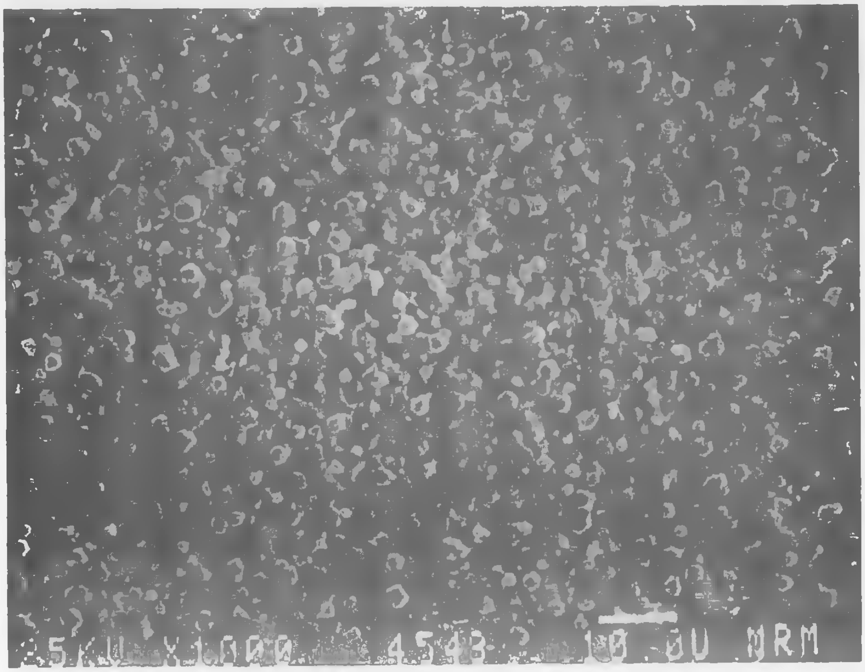

Figure 23. Low magnification SEM photograph of 2-layer CdS film fired at 630°C for 37 minutes, originally containing 20 volume percent $CdCl_2$.

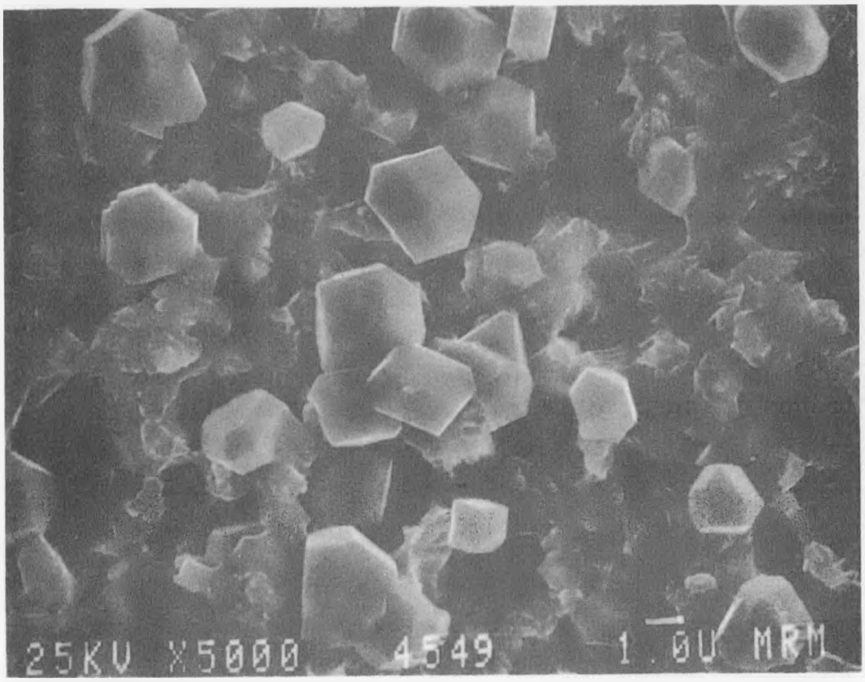

Figure 24. High magnification SEM photograph of 2-layer CdS film fired at 630°C for 37 minutes, originally containing 20 volume percent $CdCl_2$.

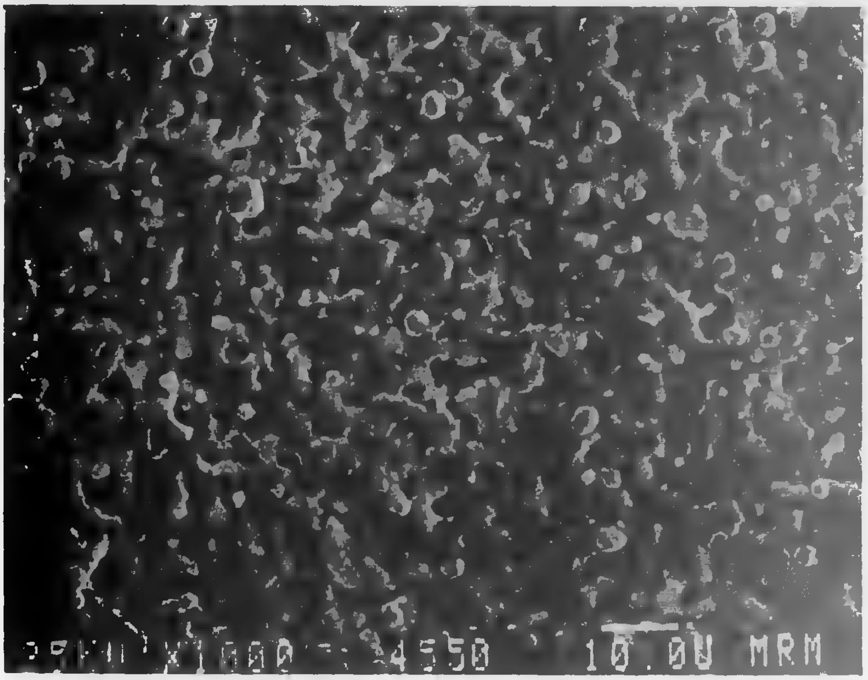

Figure 25. Low magnification SEM photograph of 2-layer CdS film fired at 630°C for 37 minutes, originally containing 30 volume percent $CdCl_2$.

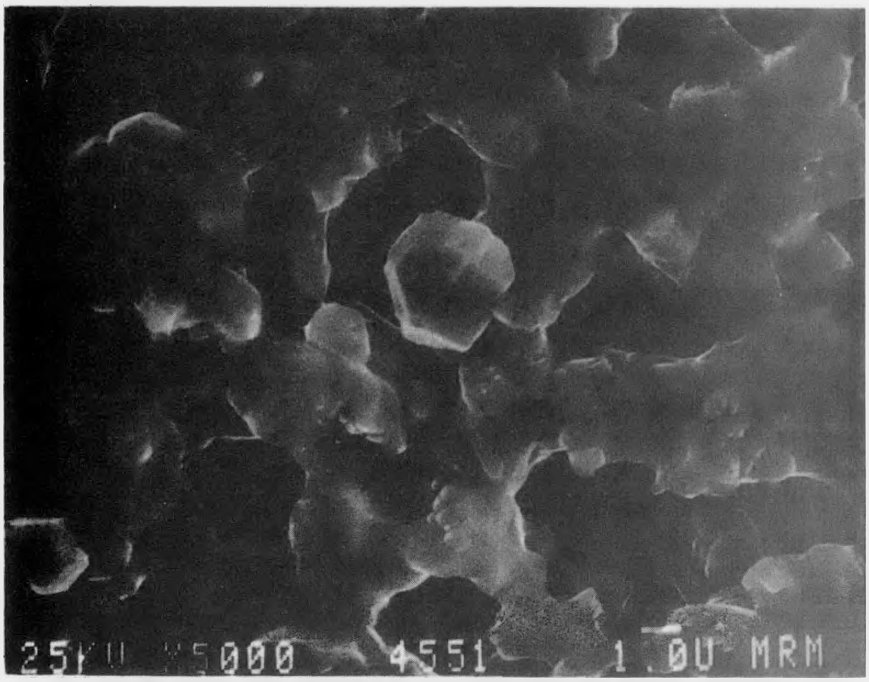

Figure 26. High magnification SEM photograph of 2-layer CdS film fired at 630°C for 37 minutes, originally containing 30 volume percent $CdCl_2$.

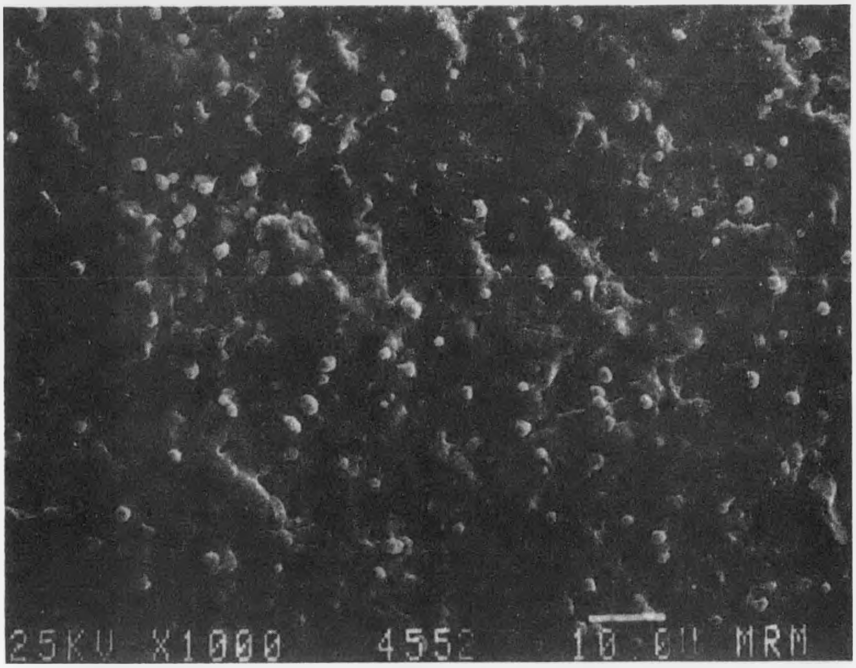

Figure 27. Low magnification SEM photograph of 2-layer CdS film fired at 630°C for 37 minutes, originally containing 40 volume percent $CdCl_2$.

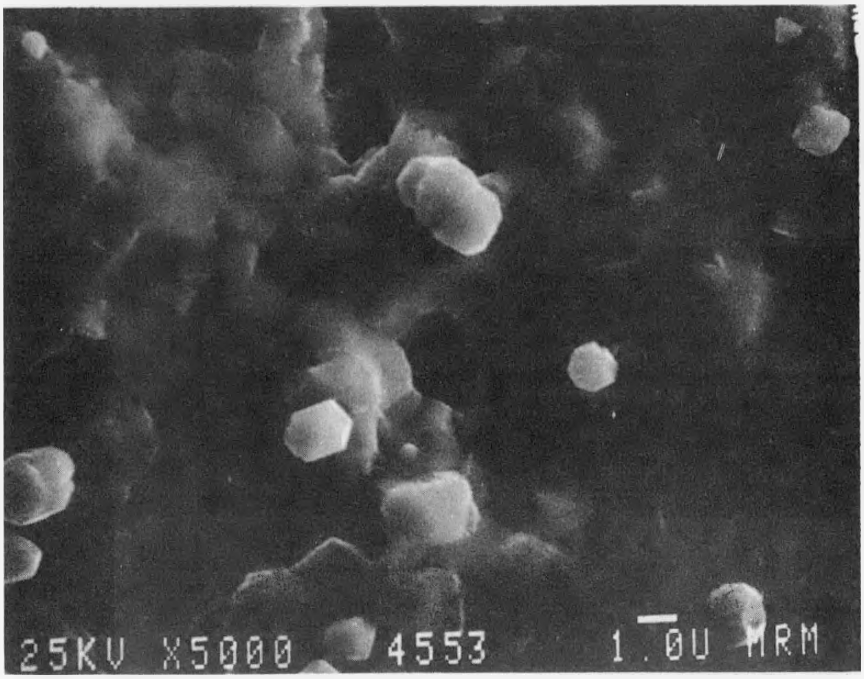

Figure 28. High magnification SEM photograph of 2-layer CdS film fired at 630°C for 37 minutes, originally containing 40 volume percent $CdCl_2$.

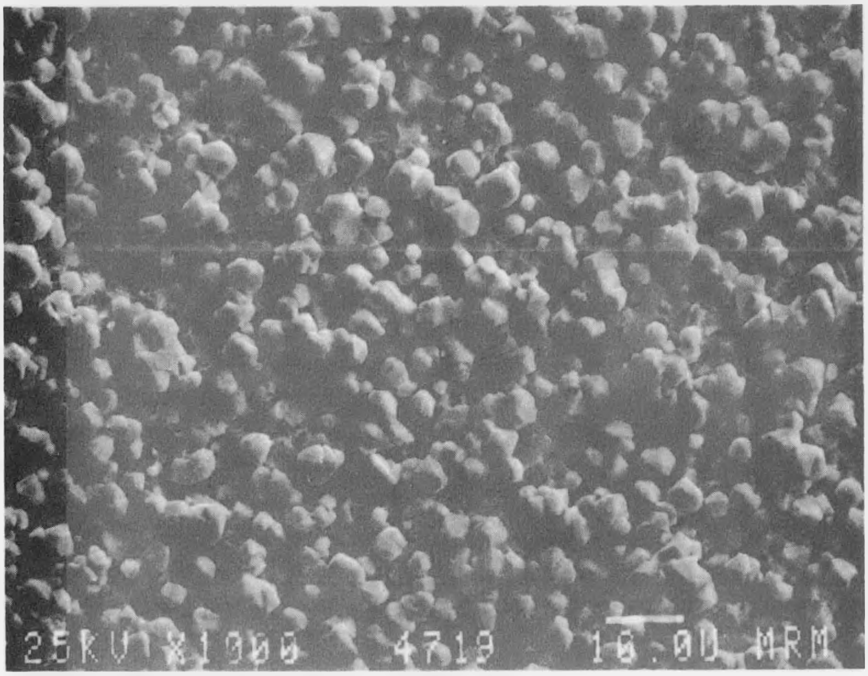

Figure 29. Low magnification SEM photograph of 3-layer CdS film fired at 653°C for 100 minutes, originally containing 40 volume percent $CdCl_2$.

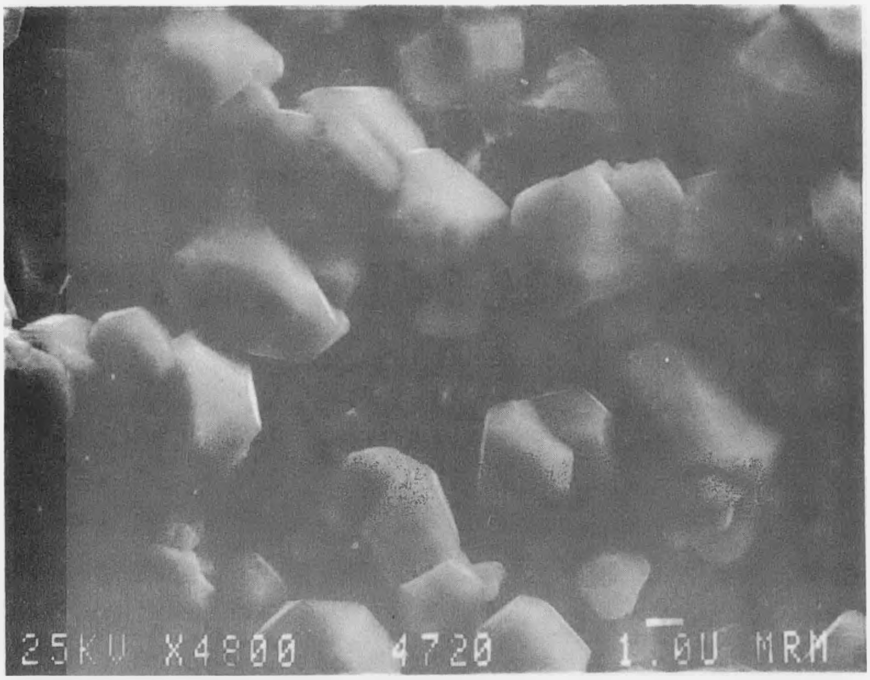

Figure 30. High magnification SEM photograph of 3-layer CdS film fired at 653°C for 100 minutes, originally containing 40 volume percent $CdCl_2$.

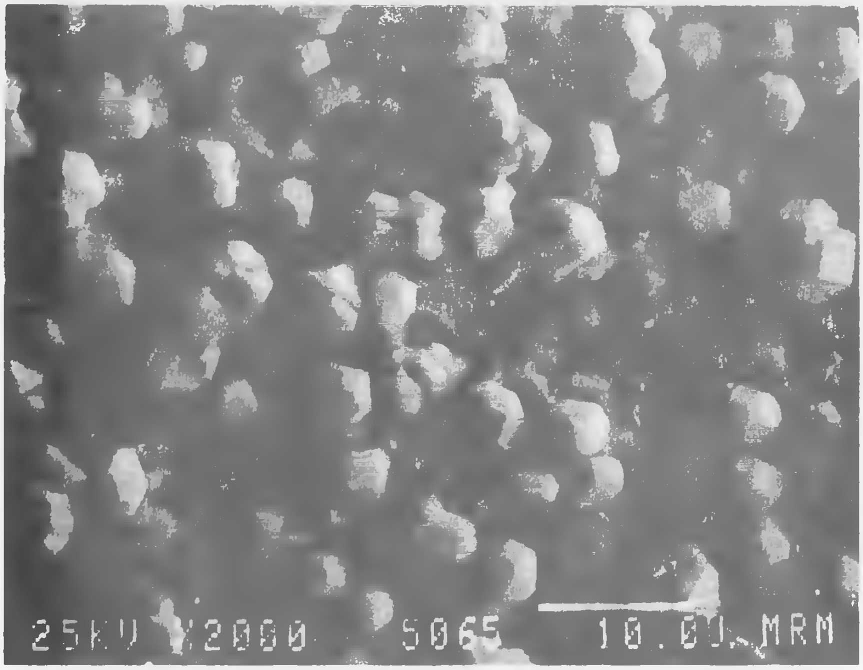

Figure 31. SEM photograph of 3-layer CdS film fired at 653°C for 40 minutes, originally containing 20 v/o $CdCl_2$.

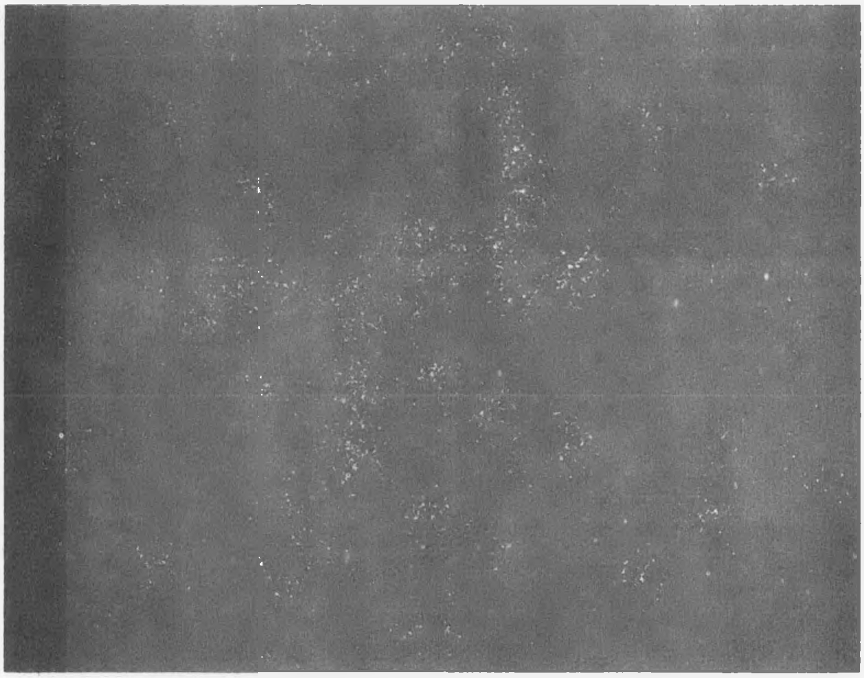

Figure 32. Oxygen map of same film shown in figure 31.

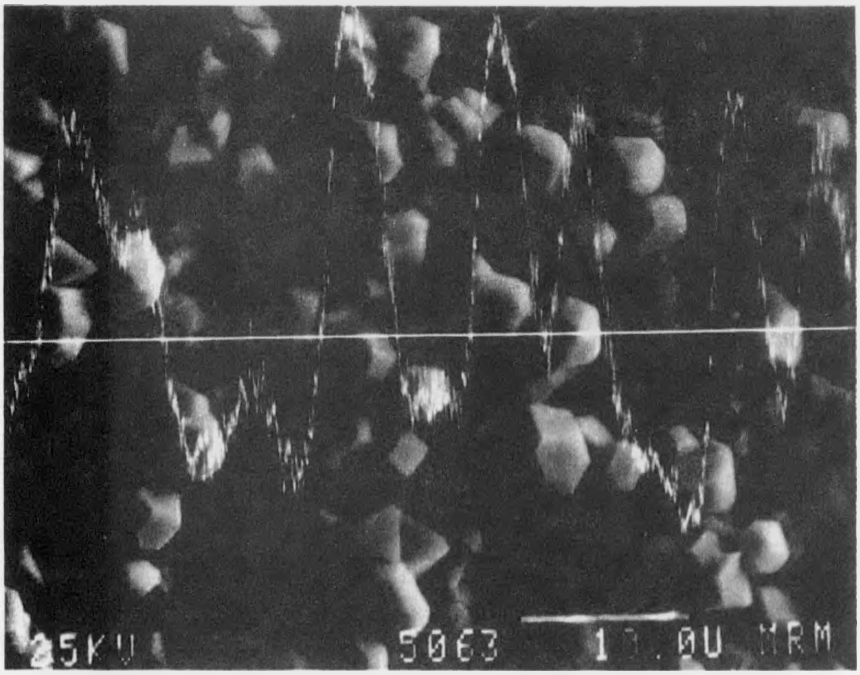

Figure 33. Oxygen scan of 3-layer CdS film fired at 653°C for 40 minutes, originally containing 20 v/o $CdCl_2$.

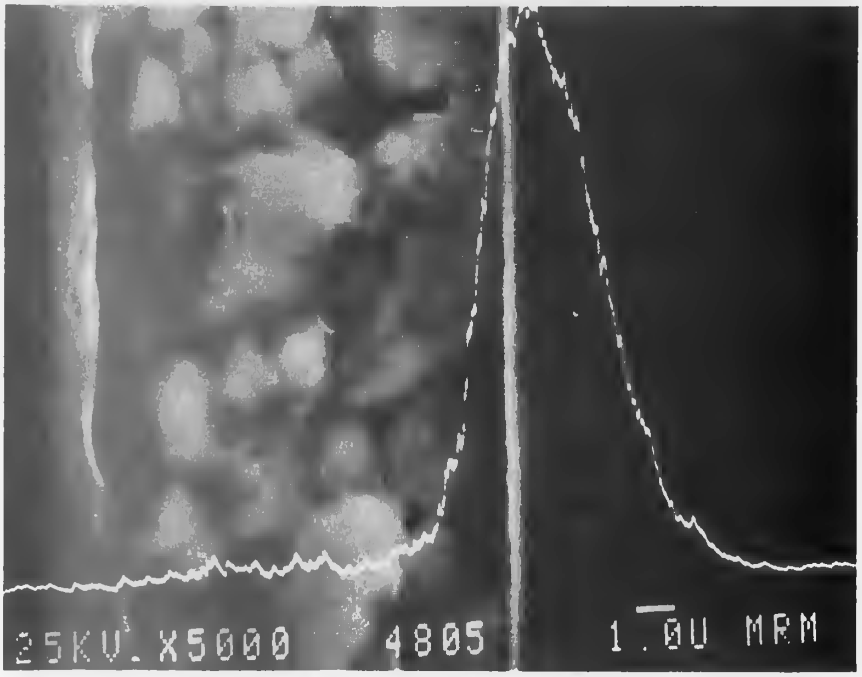

Figure 34. Indium line scan of CdS film on indium oxide coated glass.

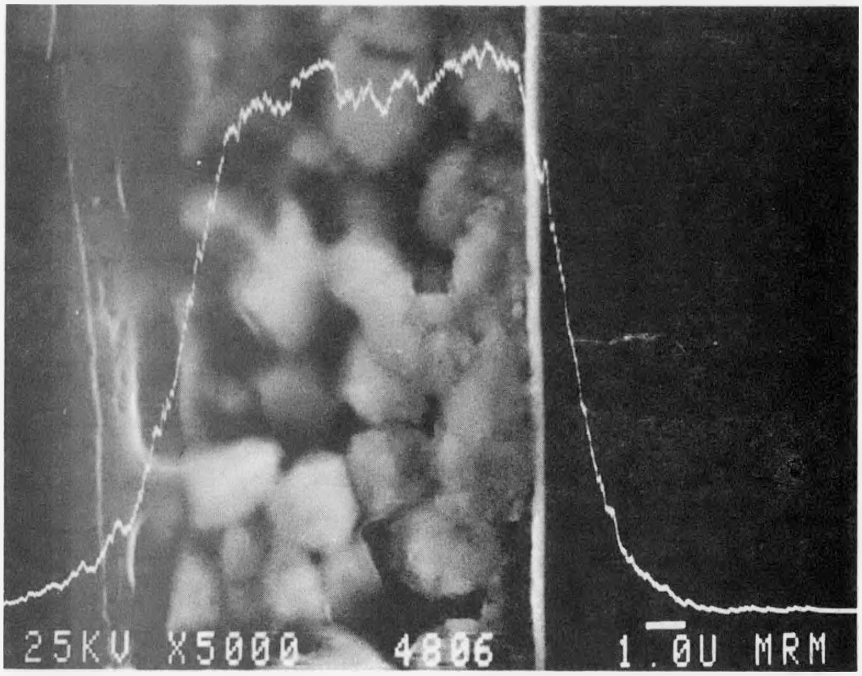

Figure 35. Cadmium line scan of CdS film on indium oxide coated glass.

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