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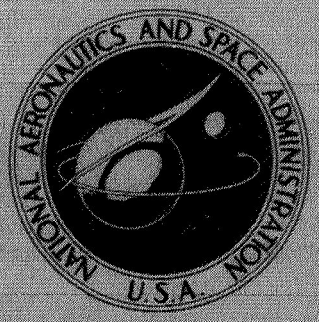

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OBSERVATIONS ON THE CUPROUS SULFIDE LAYER ON SINGLE CRYSTAL CADMIUM SULFIDE

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • SEPTEMBER 1970

1. Report No. NASA TM X-2073	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle OBSERVATIONS ON THE CUPROUS SULFIDE LAYER ON SINGLE CRYSTAL CADMIUM SULFIDE		5. Report Date September 1970 6. Performing Organization Code
7. Author(s) Joseph Singer		8. Performing Organization Report No. E-5727
9. Performing Organization Name and Address Lewis Research Center National Aeronautics and Space Administration Cleveland, Ohio 44135		10. Work Unit No. 120-33 11. Contract or Grant No.
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		13. Type of Report and Period Covered Technical Memorandum 14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

The topography of the copper (Cu) phase formed on single crystal cadmium sulfide (CdS) has been investigated by electron microscopy for reactions between CdS and both Cu^0 and Cu^+. With metal films, the reaction produced well-defined separated pits which were attributed to cuprous sulfide (Cu_2S) crystallites that had been removed prior to replication of the surface. Considerable variation in the topography of the reaction was found; this was attributed to differences in surface defect concentration in the CdS. The Cu_2S formed preferentially along prism plane traces. The reaction with Cu^+ was much more rapid and extensive.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
Cu_2S photovoltaic barrier in CdS Cu_2S, topotaxy on CdS CdS defects as reaction sites for Cu	Unclassified - unlimited

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*
Unclassified	Unclassified	13	$3.00

*For sale by the Clearinghouse for Federal Scientific and Technical Information
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SUMMARY

X-ray diffraction contrast (XRDC) and electron microscopy were used to study the reaction between cadmium sulfide (CdS) single crystals and an evaporated copper (Cu) layer of approximately 900 Å (900×10^{-10} m). In no case did XRDC show any indication of strain if the crystal was not heated, although evidence of reactions in such cases subsequently was plainly resolved by electron microscopy. Heating at 250° C did produce XRDC-resolvable strain which appeared as a uniformly contrasted area of diffracted intensity under the Cu stripe. Not all crystals showed this result to XRDC, but it was possible to activate crystals by a prior heat treatment at 500° C in helium. This suggested that heat-produced surface defects may act as nucleation sites for the 250° C reaction between Cu and CdS.

Electron microscopy was resorted to for further details of the reaction. The reacted surfaces were prepared for replication by dissolving the Cu phases on the surface of the CdS by potassium cyanide solution. The "room temperature control" (possibly as high as 40° C) surprisingly disclosed well-defined pits alined along, apparently, prism plane traces, where deformation defects are expected to be concentrated. This near-room temperature reaction was more intense on the Cd, or "plus," face of the (00.1) crystal; the pits were smaller, and less precisely alined, on the opposite face.

Reaction with Cu at 250° and 500° C for 15 minutes produced many more pits of more sharply defined hexagonal morphology than had the lower temperature reaction. These pits were up to 1.5 micrometer across and 0.1 to 0.2 micrometer deep.

Only the faintest indications of reaction were obtained with Cu films electroplated from a cyanide bath onto several CdS crystals, although a weak photovoltage, 170 millivolts, was obtained with such a film. This notable difference in reaction of CdS with electroplated Cu on one hand and evaporated Cu on the other remains unexplained.

Cu^+ solution reacted with CdS much more intensely than did Cu metal films, individual reaction sites being obscured in 30 seconds at 90° C. Nonetheless, greater intensity of reaction appeared to have occurred along prism plane traces.

INTRODUCTION

The photovoltaic cell, copper (Cu), or cuprous sulfide (Cu_2S), upon cadmium sulfide (CdS), has been studied from various aspects (refs. 1 to 3). However, the crystal chemistry of the copper-containing phase which is involved in the formation of the junction has not been reported. Some studies have been made of the copper phase within a CdS crystal utilizing copper incorporated during the growth of the CdS (refs. 4 and 5). The purpose of the present work has been to observe the copper phase which forms close to the surface of CdS by diffusion into a crystal that contained no copper initially. Observations were principally by electron microscopy; some X-ray diffraction contrast observations were also made.

EXPERIMENT

Cadmium Sulfide Crystals

These were basal plane sections, 1 by 1 centimeter by 2 millimeters thick, prepared by a commercial supplier from coarse-grained boules grown by a method similar to that described in reference 6. Crystals of this type are known to have bulk defects due to thermal stresses developed during cooling of the ingots; these occur especially along prism planes (ref. 7). The crystals were chemically polished by the potassium dichromate - sulfuric acid technique described in reference 8.

Reaction With Copper Metal and Copper Ions

Films of Cu, approximately 900 Å (900×10^{-10} m) thick, were evaporated at 10^{-5} torr as a 1 millimeter stripe through a mask onto chemically polished surfaces of CdS. The Cu thickness was monitored during evaporation by a quartz crystal oscillator which had been calibrated by an interferometric method. The temperature at the CdS surface was measured during one evaporation by a small (0.020 cm) thermocouple cemented to the CdS surface. Diffusion from the Cu film at either 250° or 500° C was done in a quartz furnace tube through which tank helium flowed continuously with an oil bubbler at the exit.

Some CdS crystals appeared to be less active than others in reacting with Cu films, as indicated by the presence or absence of the diffraction contrast effect described in the section X-ray Diffraction Contrast. Several of the less active crystals were chemically polished to a fresh surface and preheated at 500° C for 1/2 hour in flowing helium; the Cu was then evaporated and diffusion repeated. Etch-pitting was used to investigate the effect of the 500° preheat treatment; the sulfuric acid - potassium permanganate reagent,

reported to produce very small etch pits (ref. 9), was used on several crystals before and after 500° C preheat treatment and observed at magnifications up to 500.

CdS was reacted with Cu^+ ion only once; this experiment consisted of a 30-second dip at 90° C of the CdS crystal into a saturated aqueous solution of cuprous chloride (CuCl) (ref. 10).

Electroplated Copper Film

A single experiment was done with a barrier of Cu electroplated from a cyanide bath in essentially the procedure described in reference 11. The purpose was to apply the electron microscopy technique used here to test the assumption made in reference 11 that no reaction occurs at room temperature with an electroplated Cu layer. Prior to the preparation of the CdS surface for replication, the electroplated barrier was illuminated by a microscope lamp to test for a photovoltaic effect with a circuit containing a voltmeter of 1 megohm impedance.

X-Ray Diffraction Contrast

The X-ray diffraction contrast (XRDC) technique is based on the abrupt change in diffracted intensity in an X-ray reflection from a nearly perfect crystal which may occur at a zone of strain. The Lang technique (refs. 12 to 14) was used in this work in some early attempts to observe reaction between Cu and CdS through the strain that might be induced by such reaction. The (00.8) reflection of Cu radiation from the {00.1} face of CdS was employed. The resolution was about 8 micrometers.

A comparison "strain-image" by XRDC was produced by the epitaxy of zinc oxide (ZnO) upon CdS (ref. 15 and unpublished data obtained from G. A. Rozgonyi). The intimate adhesion of an epitaxial film was expected to produce XRDC at the edges of the ZnO area (ref. 13). For this purpose a 1200 Å (1200×10^{-10} m) film of ZnO was direct-current-sputtered as a stripe through a 1-millimeter mask onto a CdS crystal, and the (00.8) reflection was recorded on a plate with a 50-micrometer nuclear emulsion.

Electron Microscopy

CdS surfaces that had been exposed to copper in any form were cleared of Cu compounds by immersion in 1 molar potassium cyanide (KCN) (aqueous) and then replicated; two stage carbon replication with platinum shadowing was employed. This technique was

found to permit observation of the individual reaction sites where copper sulfide was presumed to have formed.

RESULTS

X-ray diffraction contrast observations were made by viewing at magnifications of about 30 the diffraction images produced on fine-grained nuclear plates of 50-micrometer emulsion thickness. Figure 1 shows the strain image produced by the reference system ZnO on CdS. The ZnO stripe, about 1 millimeter wide, is between the double lines. As expected, the edges of the ZnO stripe mark the largest strain gradient caused by the misfit of the two lattices (refs. 12 to 14).

A film of Cu evaporated onto a CdS (00.1) surface produced no observable strain image, provided that the sample was not heated. Figure 2 shows a typical XRDC strain image, resulting from Cu diffusion, observed after a 250° C, 15-minute diffusion. Thickness of the copper layer was 900 Å (900×10^{-10} m). The photographic contrast due to the strain is less discernible in the figure than in the original plate. The contrast appears to be uniform throughout the band marking the copper stripe. This uniform contrast indicates that the strain is uniformly distributed throughout the stripe rather than

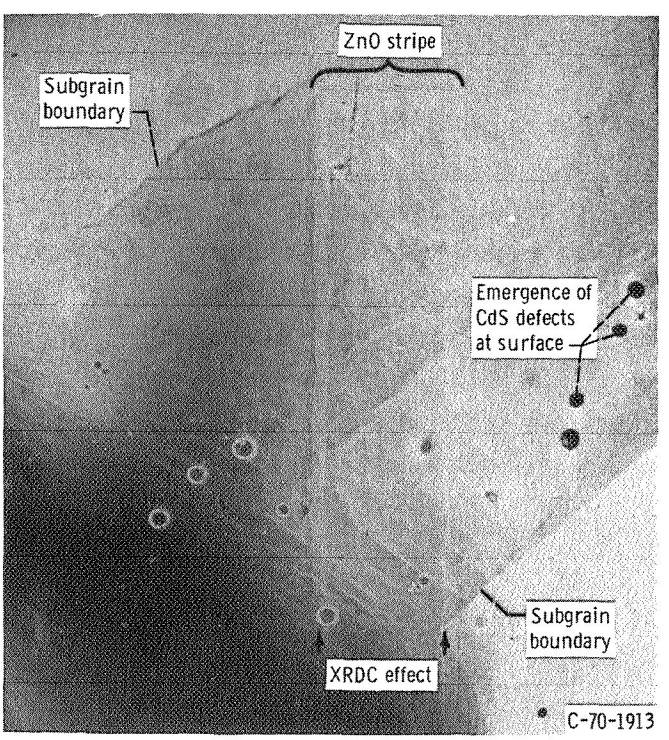

Figure 1. - Diffraction contrast on (00.8) surface of CdS from ZnO stripe on CdS. X15.

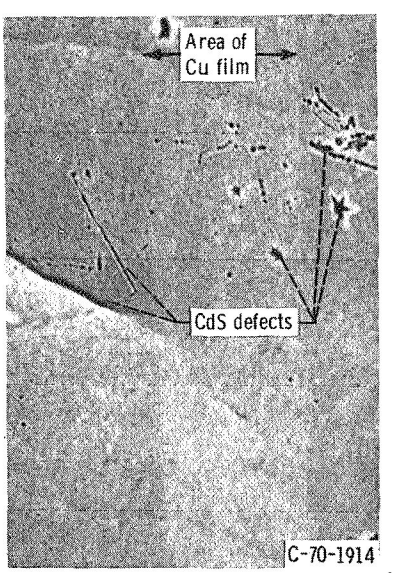

Figure 2. - Diffraction contrast on (00.8) surface of CdS from Cu film diffused at 250° C. X10.

concentrated at the edges as in the ZnO case. It is reasonable to expect that the type of strain would be different in the two cases, the ZnO case being epitaxial. In both figures 1 and 2, XRDC has also delineated surface defects and subgrain boundaries.

Some crystals produced XRDC after Cu diffusion at 250° C, others did not. Also, some crystals which produced XRDC failed to do so upon repeating the experiment with a freshly exposed surface prepared by chemical polishing well below the first reaction layer. In several cases, the "inactive" surfaces were induced to produce XRDC by heating the fresh chemically polished surface at 500° C in helium for 1/2 hour. Etch-pitting before and after the 500° C preheat treatment was employed to investigate this "activation"; the reagent produced no etch pits before the preheating and irregularly spaced groupings of small etch pits (~10 μm) after the preheating.

These observations apply to the positive, or Cd, face of the (00.1) plane; the opposite face yielded a uniform matte finish to the reagent both before and after heating. This identification of the (00.1) faces was based on several reports with different etches (refs. 16 and 17) having in common the formation of matte surfaces on the negative, or sulfur, face and well-defined etch pits on the shinier-etched face, ultimately related back to the X-ray diffraction identification of the polarity (ref. 16). (It should be pointed out that a serious confusion in ref. 16 was corrected later, ref. 17.)

It was apparent that the XRDC technique would be unable to resolve sufficient detail; therefore an electron microscope technique was applied to the problem.

Electron microscope observations were based on the technique of dissolving away the residues on the Cu-reacted CdS surface by immersion in a KCN solution so that replicas could disclose surface sites eroded by reaction with Cu. With the intention of establishing a "blank," or a control without Cu diffusion, a Cu film was removed by KCN 15 minutes after it had been vapor deposited on a clean CdS (+00.1) surface. Observation of unexpected reaction (fig. 3) led to repeating the experiment on the (-00.1) surface, and again reaction was observed (fig. 4). Pits, depicted in the figures as elevations, mark the sites where, despite the absence of deliberate diffusion treatment, copper sulfide is presumed to have been formed, and then removed by KCN. The tendency of the pits to lie along lines 60° and 120° apart plainly assigns the reactive sites to traces of the prism planes, {10.0} and {11.0}, where deformation defects are expected (ref. 7). This alinement is more pronounced on the (+) face, where the pits are also larger. Measurement of the CdS surface temperature during a typical Cu evaporation yielded a reading of 40° C; presumably, therefore, the reaction had occurred at a temperature not appreciably higher. Figure 5 is typical of the surface obtained after reaction of CdS crystals with Cu at 250° C for 15 minutes, followed by slow cooling and finally replication after KCN leaching. This replica was taken at an edge of the Cu band marked in the figure. The pits do not differ appreciably in size (0.5 μm to 50 Å (50×10^{-10} m)) or depth (~0.2 μm) between the near-room temperature and the 250° C

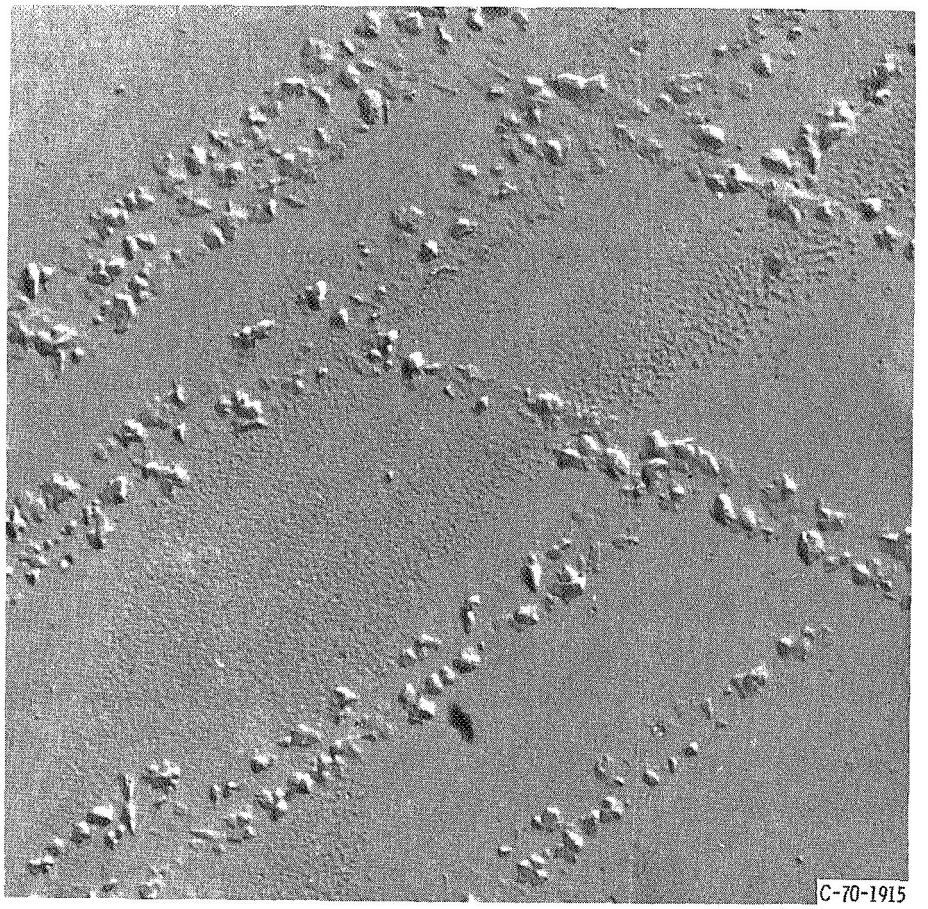

Figure 3. - Pits from near room temperature reaction of Cu film on + (00.1) surface of CdS. X11 000.

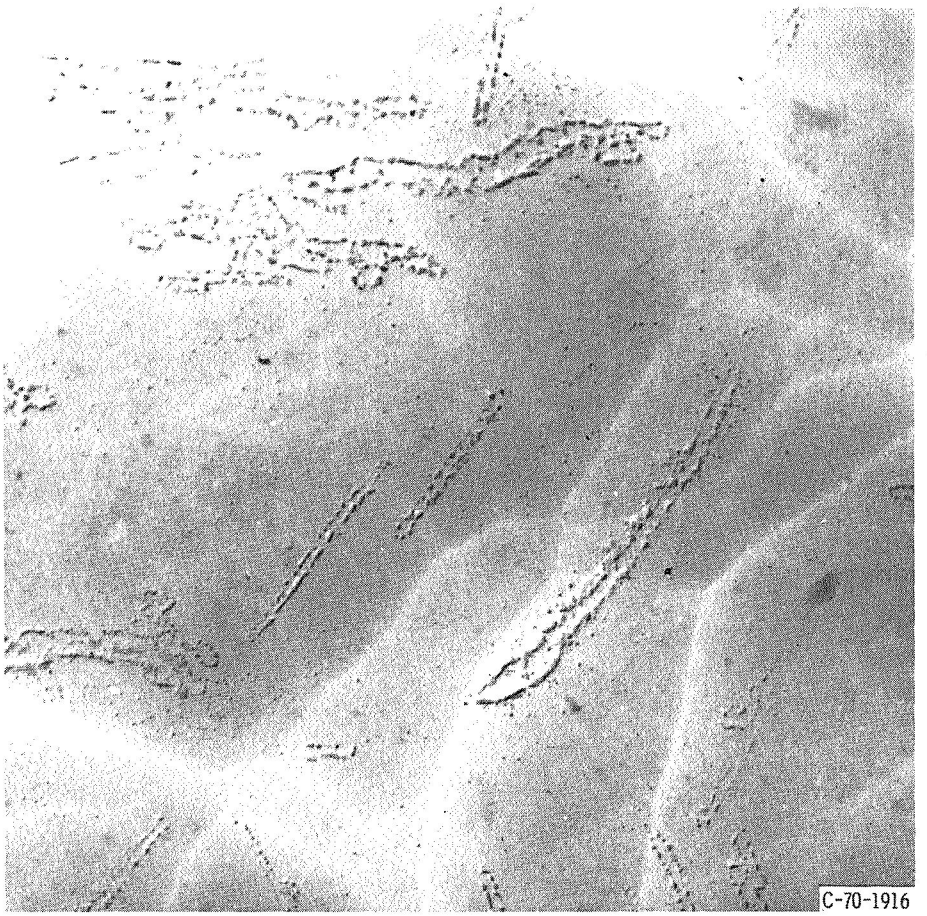

Figure 4. - Pits from near room temperature reaction of Cu film on - (00.1) surface of CdS. X11 000.

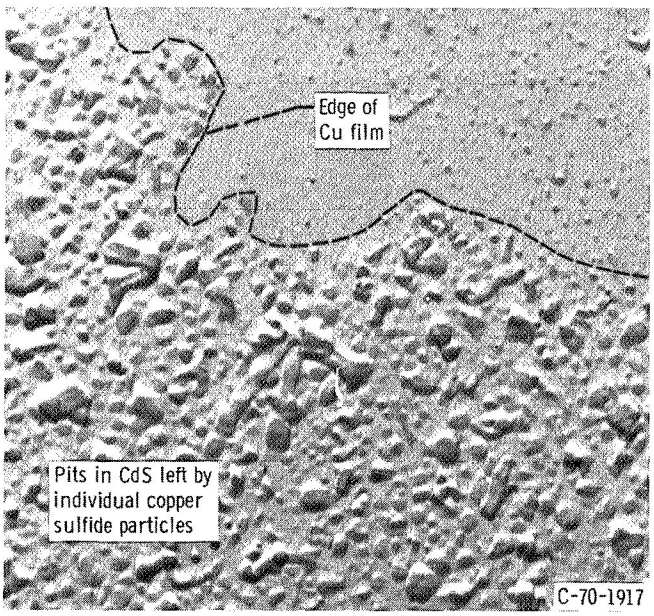

Figure 5. - Electromicrograph of CdS surface after KCN removal of reaction products resulting from 15-minute, 250° C diffusion from evaporated Cu film. X18 200.

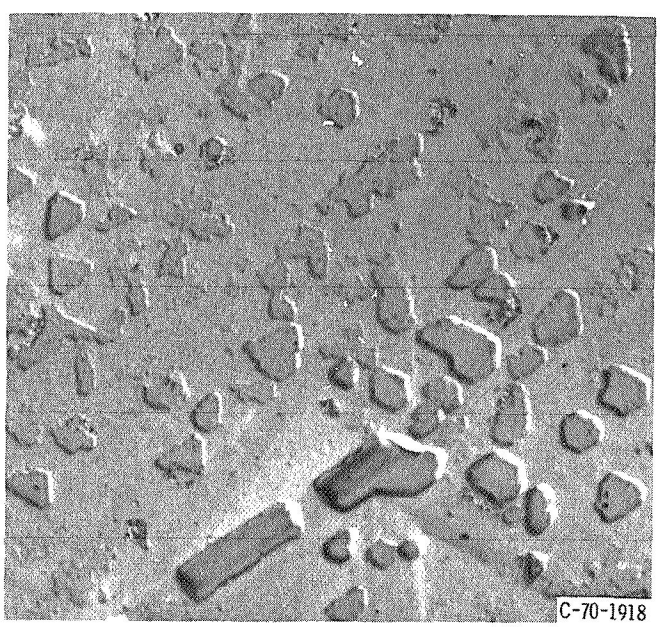

Figure 6. - EM replica of CdS surface after KCN removal of reaction products resulting from 30-minute, 500° C diffusion from evaporated film. Note approach to hexagonal morphology. X11 000.

diffusions, although many more reaction sites are evident in the latter. The 250° C result shows at least obscuration of the preference for the prism plane traces.

Figure 6 depicts a reaction at 500° C for 1/2 hour. Here the reaction product reached grain sizes of 1 to 1.5 micrometer, although the depth of reaction seems to be no greater. The morphology of the product is more plainly hexagonal for many grains than is apparent for the lower reaction temperatures.

As discussed in the section EXPERIMENT, the possibility of reaction between an electroplated Cu layer and a CdS surface was of interest. An adherent Cu film was electroplated as in reference 11; the photovoltage obtained as described above was 170 millivolts. For comparison, Bube and Williams (ref. 11) obtained approximately 250 millivolts in a similar experiment. Finally the surface was leached by KCN and replicated. Only vague indications of possible reaction in a few places were obtained; at least, no approach to the reaction intensity of figures 3 and 4 was observed.

Figure 7 represents the KCN-leached surface following a 30-second reaction at 90° C between a CdS crystal and CuCl solution (ref. 10). The reaction plainly was much more extensive than those produced with metal films (ref. 18). No well-defined crystal forms were discerned, but distinct indications of preferential reaction along prism plane traces can be observed.

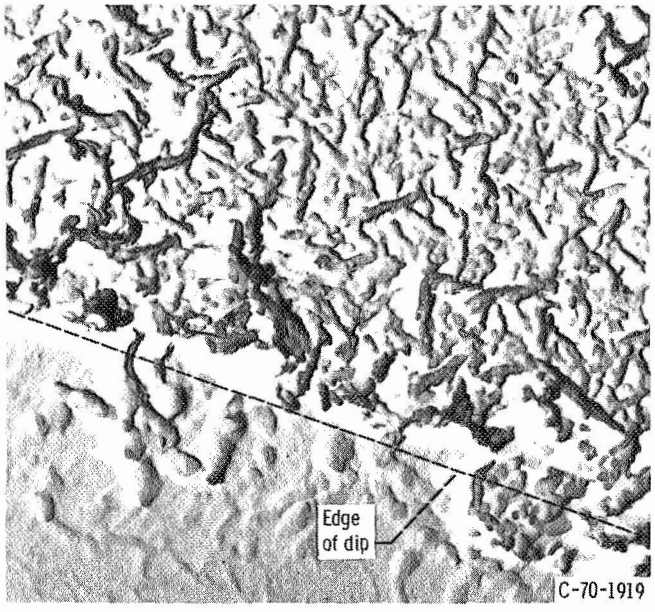

Figure 7. - Surface resulting from 30-second dip of CdS in CuCl solution. X11 000.

DISCUSSION

The superior resolution of the electron microscopy technique over that of the XRDC was required for significant detail to be seen in the reaction between Cu and CdS.

Much variability was observed from crystal to crystal and even between successive, freshly prepared, surfaces in the same crystal as regards reactivity with metallic Cu in the temperature range from near room to 500° C. Although no study was attempted to explain this variability, a clue resides in the observed selection of reaction sites for the room temperature reaction along prism plane traces in the basal plane. Since these traces very likely mark the emergence of dislocations associated with growth strains in the synthesis of the crystals (ref. 7), it seems reasonable to explain variability of reactivity by variability in the defects occurring on different CdS surfaces. This hypothesis could be tested by doing similar experiments with crystals grown by other methods (refs. 7 and 11). Some effect of surface defects was illustrated by the revival of the ability of a crystal to react at 250° C with a reapplied Cu film. The correlated appearance of etch-pit sites following a 500° C preheating is strongly suggestive of heat-created defects as the cause of the enhanced susceptibility to reaction with Cu. No attempt was made to determine the nature of the postulated thermally produced defects.

The ability to obtain a photovoltage from the electroplated Cu layer without significant observable reaction having occurred tends to support the thesis in reference 11 of photoemission into the CdS. This cannot be taken as conclusive evidence, however, because of the variability in the reaction of CdS noted in this study. In contrast, the appreciable reaction reported here near room temperature for evaporated Cu is surprising; unknown aspects of the CdS surface in the two experiments being compared may be involved in the difference.

SUMMARY OF RESULTS

Electron microscopy has been employed to observe the reaction between copper (Cu) metal and Cu^+ ion at the surface of cadmium sulfide (CdS) crystals; X-ray diffraction contrast did not have sufficient resolving power to observe the details but did show strain produced by Cu diffusion. Reaction was studied between Cu metal and CdS near room temperature as well as at 250° and 500° C and between Cu^+ ion and CdS at 90° C. For each of these reaction conditions, characteristic reaction effects were noted. The marked tendency for reactions to develop along traces of prism planes on the (00.1) CdS

faces was particularly prominent. One observation made with an electroplated Cu film was inconclusive, in that only vague indications of reaction were obtained.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, June 17, 1970,
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