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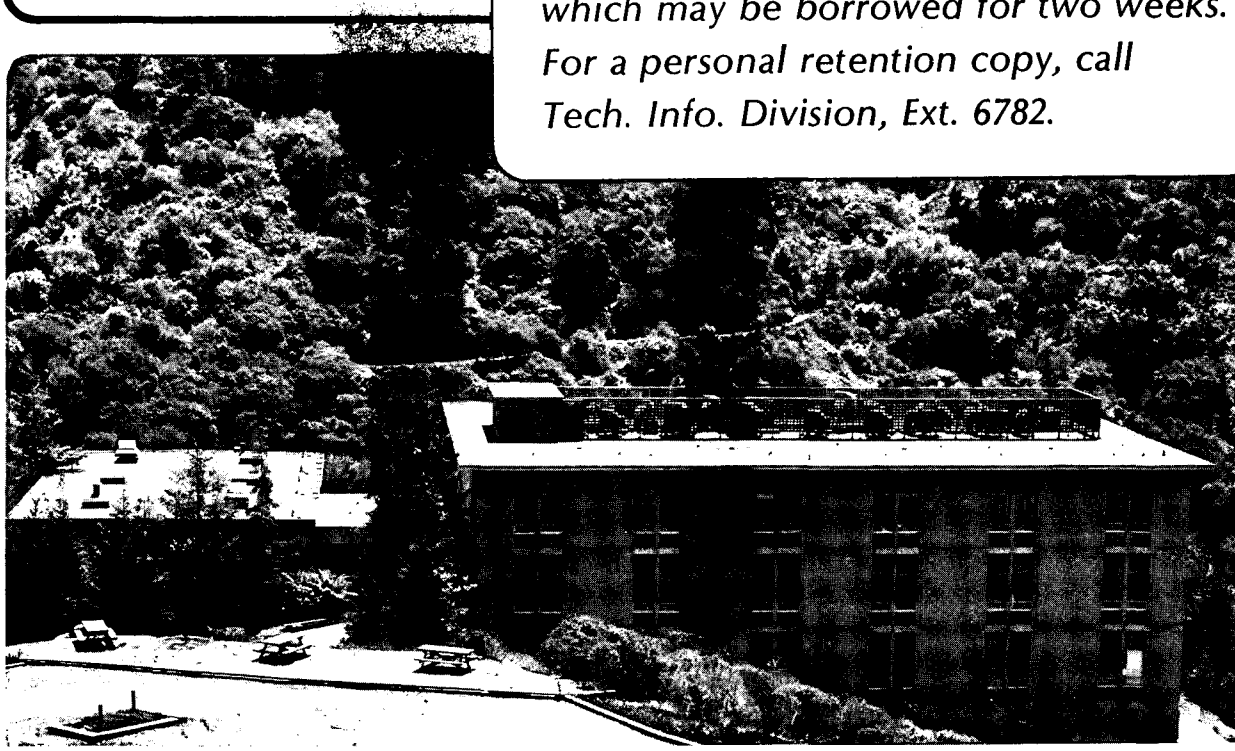

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Characterization of Single Crystal Cu_2S/CdS Heterojunctions by High Resolution Electron Microscopy

T. Sands, R. Gronsky and J. Washburn

Lawrence Berkeley Laboratory,
Materials Science and Mineral Engineering,
University of California,
Berkeley, California 94720

Abstract

The effect of CdS surface orientation on the phase distribution and morphology of the Cu_2S/CdS heterojunction has been investigated. The first high resolution transmission electron microscope (HRTEM) images of Cu_2S/CdS interfaces reveal the presence of the metastable tetragonal phase in heterojunctions formed in terraced CdS surfaces. This observation is rationalized by considering i) the effects of lattice misfit, and ii) the factors influencing the nucleation of h.c.p.-to-f.c.c. transformation dislocations. The implications of this result for the reproducible fabrication of high efficiency Cu_2S/CdS solar cells are discussed.

Introduction

Although the Cu_2S/CdS photovoltaic cell has been studied for nearly thirty years, very little is known about the microstructure of the copper sulfide absorber and the morphology of the interface with CdS. Since those electrons which are photogenerated in the p-type copper sulfide layer must traverse both the copper sulfide absorber and the Cu_2S/CdS interface in order to contribute to the photo-current, any defects in these regions may have a deleterious effect on cell efficiency. Therefore, an understanding of fundamental structural characteristics such as absorber

phase, interface morphology, and misfit accommodation mechanisms is required for accurate device modeling. In addition, if efficient Cu_2S/CdS cells are to be fabricated with high yield, it will be necessary to determine the dependence of these fundamental structural characteristics on processing variables. This point is well illustrated by the recent work of Oktik, Russell and Woods.[1] These investigators found that cells formed on faceted hillocks of the etched $(000\bar{1})$ surface of CdS single crystals had high efficiencies in the as-prepared state, whereas cells formed on terraced off-basal surfaces had low efficiencies. An air-bake increased the efficiencies of the terraced cells. However, these efficiences remained below those of the as-prepared faceted cells. In this paper, the technique of cross-sectional high resolution transmission electron microscopy (XHRTEM) is applied to the characterization of single crystal Cu_2S/CdS heterojunctions. In particular, the XHRTEM results are shown to provide the structural information necessary to understand the relationship between surface orientation and Cu_2S/CdS cell efficiency.

Cadmium sulfide and copper sulfide phases

Cadmium sulfide has the wurtzite structure (interpenetrating h.c.p. networks of Cd and S separated by $\sim 0.375\vec{c}_o$). Since the wurtzite structure lacks a center of inversion symmetry, the (0001) and $(000\bar{1})$ faces are distinct. This distinction is apparent after etching in HCl (the texture-etch step of thin-film Cu_2S/CdS photovoltaic cell fabrication).[2] The morphology of the etched Cd(0001) and $S(000\bar{1})$ surfaces will be described in the Results section.

To form the Cu_2S/CdS heterojunction, the CdS is dipped into a CuCl solution at 99°C for several seconds. A topotaxial copper sulfide surface

layer approximately 150 nm thick results from the exchange of Cu^+ and Cd^{++} ions. The morphological evolution of this film is described in reference 3. The principal copper sulfide phase is low chalcocite, Cu_2S, a structure based upon the ordering of copper ions among the interstitial sites of a distorted h.c.p. sulfur network.[4] Recently, a second phase was detected for the first time in a Cu_2S/CdS heterojunction.[3] This "tetragonal phase"[5] is a metastable high-pressure polymorph of low chalcocite[6] and is based upon a distorted f.c.c. sulfur network. The following results show that the tetragonal phase can be a major component of the Cu_2S absorber, depending on the CdS surface orientation.

Lattice parameters. The lattice parameters of CdS, low chalcocite and the tetragonal phase are compared in Table 1.

Two important facts can be deduced from this table:

1) the tetragonal phase has a better with CdS in the basal plane and

2) planar low chalcocite-CdS interfaces inclined by $\sim 68^\circ$ to the basal plane contain a line or zero misfit (an invariant line).[7]

TEM specimen preparation

Undoped single crystal CdS (Eagle-Picher) was cut into basal slices and mechanically polished. The final polish was accomplished with 1 m diamond paste. Work-damaged surface material was removed during a texture-etch in fresh 37% HCl at room temperature for 30-60 seconds. The copper sulfide layer was formed in an aqueous solution of CuCl (6g/l) and NaCl (2g/l) at 99°C for 5-10 seconds[8] (substrate preheated to conversion temperature).

Plan-view separated Cu_2S films were prepared by selectively etching away the CdS in HCl. Copper sulfide films were then floated onto TEM

grids and examined in a Siemens 102 TEM at 100 kV. Cross-sectional specimens of Cu_2S/CdS interfaces were thinned by argon ion milling (4kV, 30μA specimen current, 14° tilt). Ion milling heating effects were kept to a minimum by utilizing an LN_2 cold stage. High resolution lattice imaging was performed with a JEOL - 200 CX HRTEM (C_s = 1.2 mm, top entry stage) at 200 kV.

Results

(0001) basal facet

The morphology of Cu_2S films grown into the basal facet of the Cd face was described in reference 3. These films were shown to be heavily textured with a high density of cracks on $\{\bar{2}110\}$. Low chalcocite was found to be the dominant copper sulfide phase, although plates of the tetragonal phase were detected in the deeper penetrations of copper sulfide adjacent to the $\{\bar{2}110\}$ cracks.

Terraced off-basal surfaces

Both the etched Cd and S faces were found to contain terraced off-basal surfaces. Figure 1 is a scanning electron microscope (SEM) image of a hexagonal etch pit in the (0001) CdS surface. Note that the etch pit walls are terraced, as are portions of the surface adjacent to the etch pit. Similar terraced surfaces were observed on the hexagonal hillocks of the etched sulfur face. After conversion to copper sulfide, the Cu_2S films formed in terraced surfaces remained thin (Figure 2), whereas the films formed in basal facets were heavily textured (as described above). Electron diffraction showed that the films formed in the terraced surfaces were composed primarily of the f.c.c. based tetragonal phase. It is also interesting that these f.c.c. films were uncracked and contained {111}

stacking faults (visible in Figure 2).

The cross-sectional image of Figure 3 reveals the basal habit of the tetragonal phase ($\{111\}_{f.c.c.} \parallel (0001)$ CdS). The interface contains a high density of ledges. An inclusion of low chalcocite is also visible in this image. Note that the low chalcocite-CdS interface nearly contains the invariant line (indicated). In fact, a low chalcocite-CdS interface which deviates substantially from the invariant line has not been observed.

Pyramidal facet

Figure 4 is an SEM image of an etched CdS $(000\bar{1})$ surface containing faceted hillocks. Conversion of pyramidal facets to copper sulfide resulted in low chalcocite films. Figure 5 is a XHRTEM image of a pyramidal hillock. Again, the low chalcocite-CdS interface is at a steep angle to the basal plane (as indicated by the low chalcocite-CdS moire fringes). No tetragonal phase was detected in these films.

Discussion

These observations can be rationalized on the basis of two factors which depend on local surface orientation:

1) lattice misfit and

2) nucleation and propagation of 1/3 $\langle 10\bar{1}0 \rangle$ h.c.p.-to-f.c.c. transformation dislocations (on every other close packed plane).

(0001) basal facet

The nucleation of transformation dislocations is difficult because the surface is parallel to the dislocation glide plane. Thus, low chalcocite (h.c.p.) will form in the early stages of the reaction, even though the tetragonal phase has a better lattice match with the CdS basal plane. However, as the reaction continues, the stress due to the 4.4% misfit

with CdS in the basal plane eventually results in $\{\bar{2}110\}$ cracks in the film. These cracks provide nucleation sites for transformation dislocations, thereby fascilitating the formation of the tetragonal phase. The resulting film is a mixture of low chalcocite and the tetragonal phase.

Terraced off-basal surfaces

The lattice misfit results directly in resolved shear stresses on the basal plane when the surface orientation is off-basal, thereby facilitating the nucleation of transformation dislocations. Stress due to misfit between the tetragonal phase and CdS in the c direction can be partially relieved by the surface. Residual misfit in the plane can be accommodated by slip on inclined {111} planes. Consequently, the resulting tetragonal phase films remain thin and uncracked.

Pyramidal facet

A pyramidal facet at 63° from the basal plane nearly contains a low chalcocite-CdS invariant line. In addition, the c-misfit of the tetragonal phase can not be efficiently relieved by the surface. These factors combine to encourage the continued growth of low chalcocite.

Conclusion

The results of Oktik, Russell, and Woods[1] can be explained as follows; high efficiency cells formed on pyramidal facets contain only the low chalcocite phase. Thus, the Cu_2S-CdS interface is h.c.p.-h.c.p. and nearly contains the invariant line so that a minimum density of misfit dislocations is required.

The absorber layers of the low efficiency cells formed in the terraced surfaces are composed primarily of the tetragonal phase. The terraced nature of the tetragonal phase (f.c.c.)-CdS (h.c.p.) interface results

in a high density of bonding errors in the sulfur network (at the cores of interfacial transformations dislocations, for example). The beneficial effects of the air-heat treatment may be explained by the bond-saturating effects of one or more components of the air atmosphere (e.g. hydrogen). Furthermore, it is likely, pending determination of the optical properties of the tetragonal phase, that the tetragonal phase films are too thin ($<$500Å) to allow optimum absorption of the incident photons.

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Figure Captions

Fig. 1. SEM image of etched Cd face of CdS single crystal. "A" is basal facet, "B" is terraced etch pit wall, "C" is terraced off-basal surface. Arrow indicates $\langle\bar{2}110\rangle$ direction.

Fig. 2. TEM image of separated Cu_2S film. Thin portion of film is terraced etch pit wall containing the tetragonal phase. Arrow denotes $\langle\bar{2}110\rangle$ direction.

Fig. 3. XHRTEM image of tetragonal phase (tet)-CdS interface. CdS basal planes are edge-on and horizontal. Low chalcocite (lch)-CdS interface is visible at left (invariant line is indicated). CdS is in $[\bar{2}110]$ zone-axis orientation, Tet. and lch. in [010] zone-axis orientation.

Fig. 4. SEM image of etched S face of CdS single crystal.

Fig. 5. XHRTEM image of low chalcocite (lch.)-CdS interface is S-face hillock. Interface is inclined to the beam direction resulting in moire fringes. CdS basal planes are edge-on and horizontal. CdS is in $[\bar{2}110]$ zone-axis orientation. Lch is in [010] zone-axis orientation.

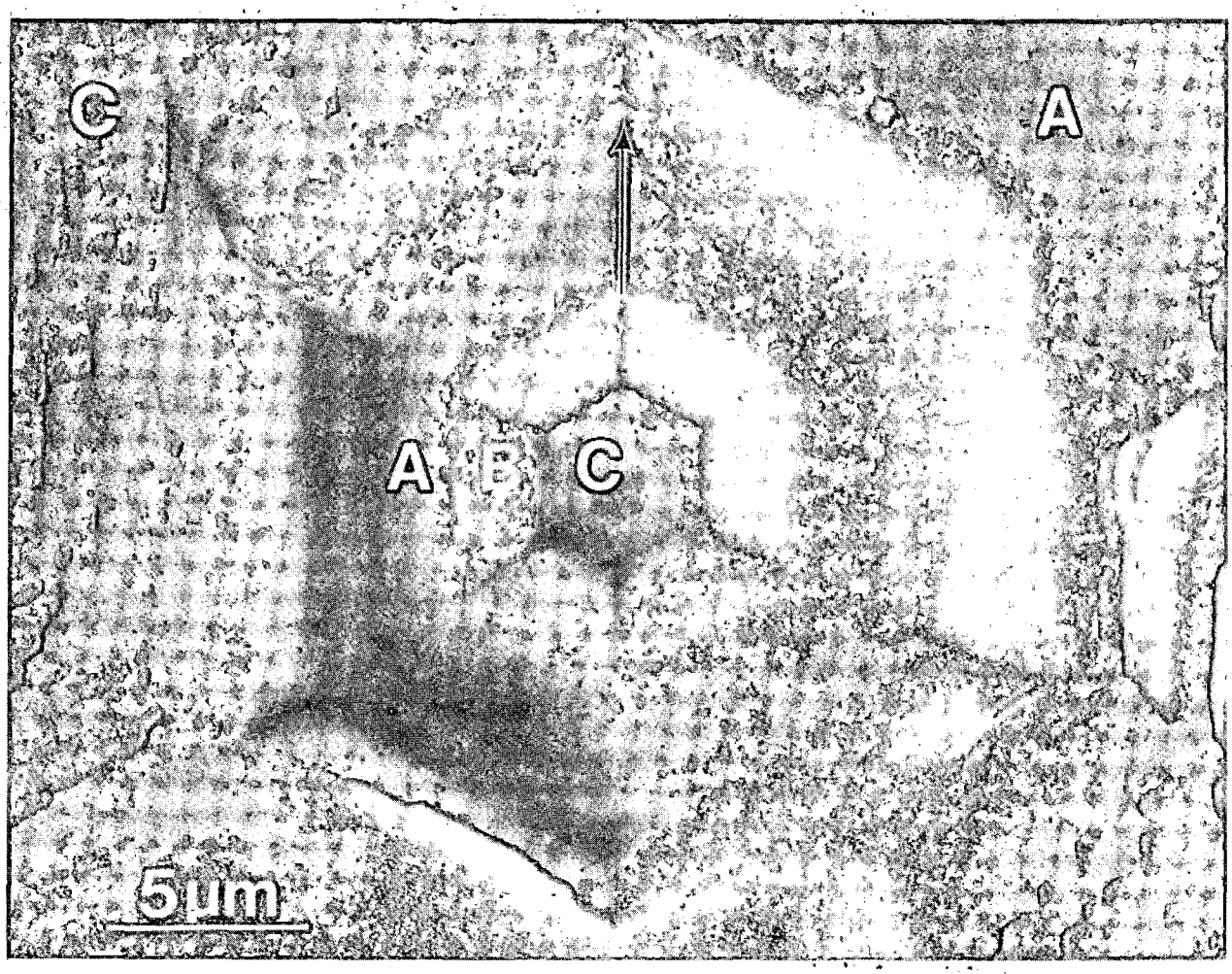

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Fig. 1

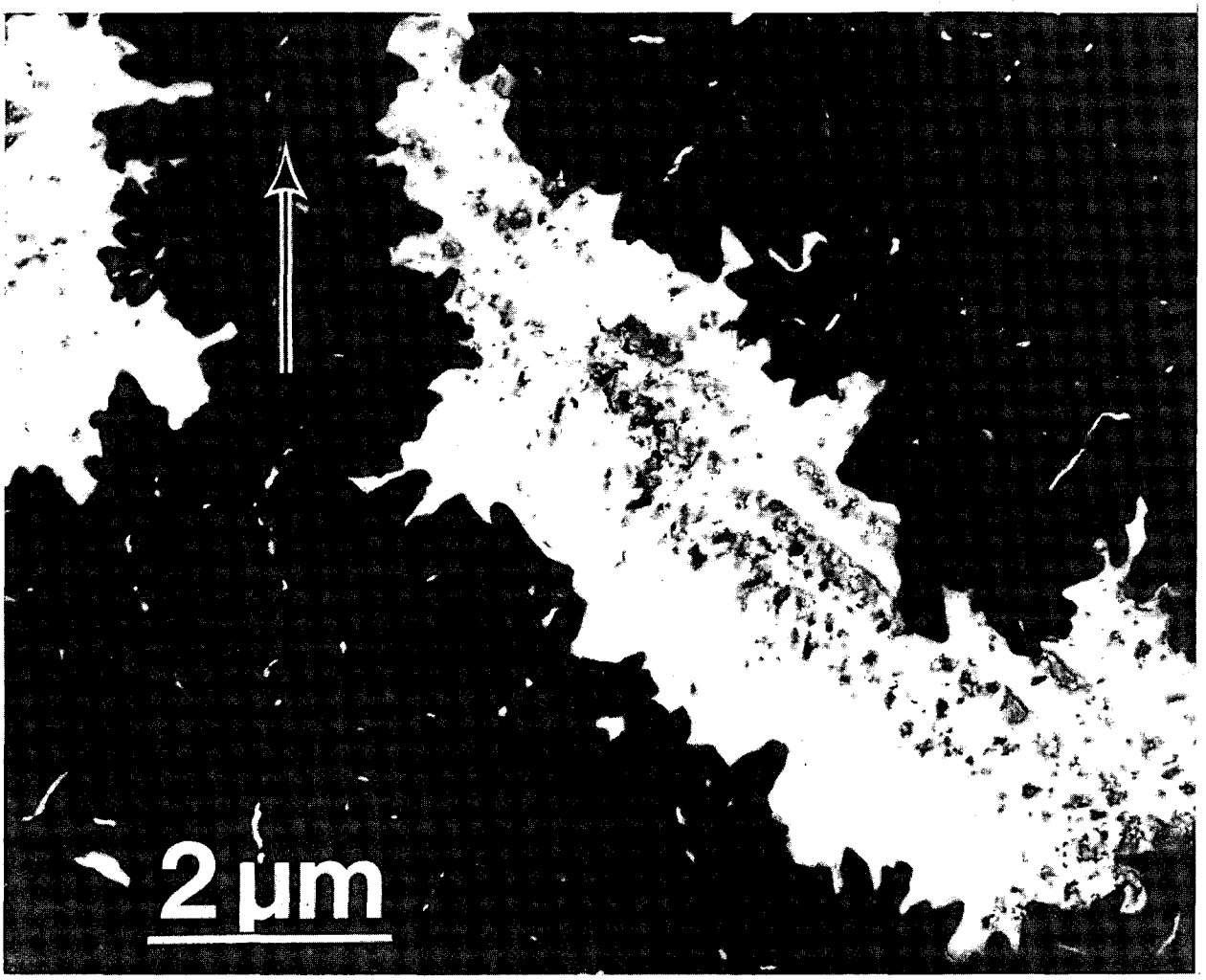

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Fig. 2

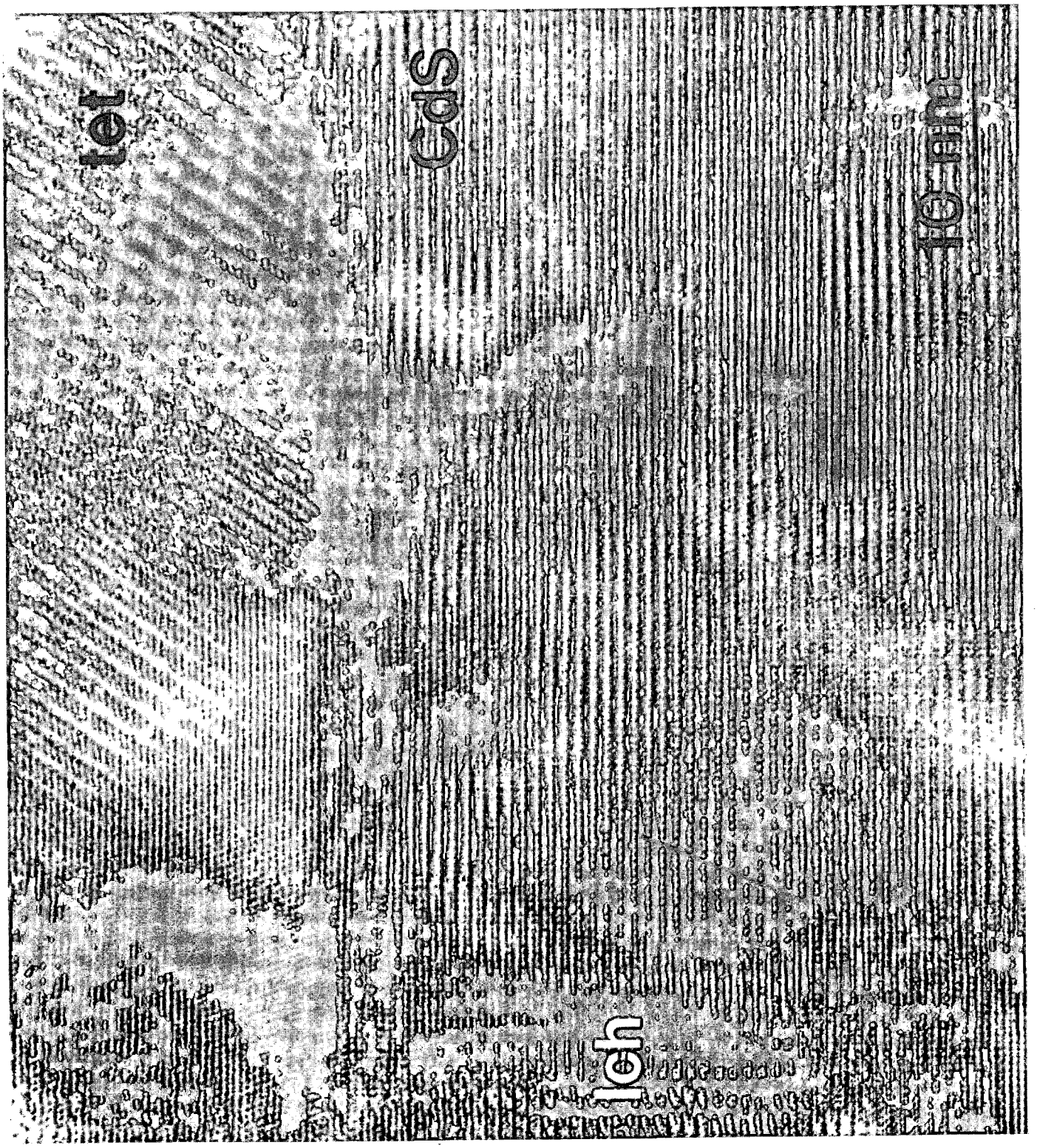

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Fig. 3

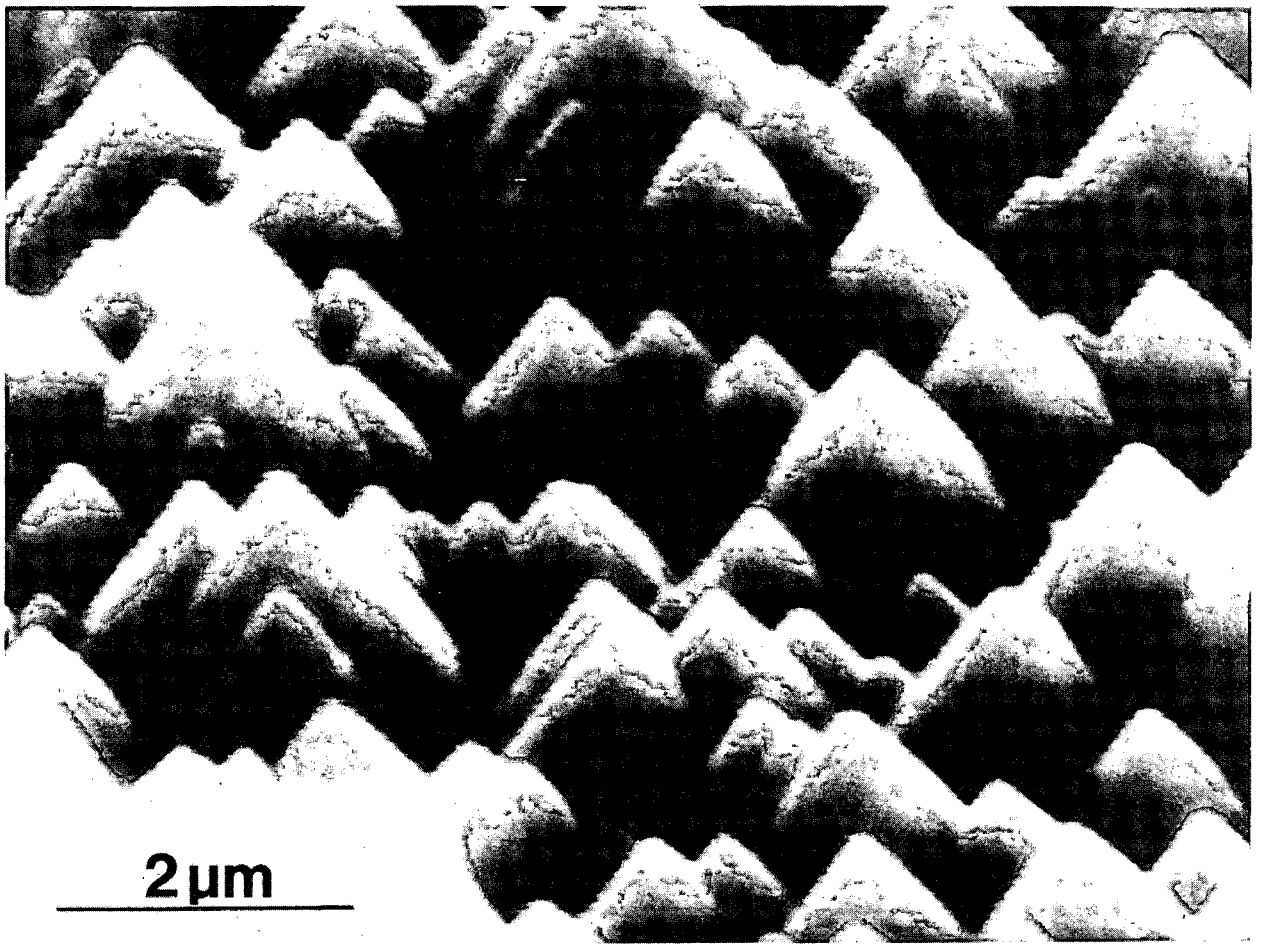

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Fig. 4

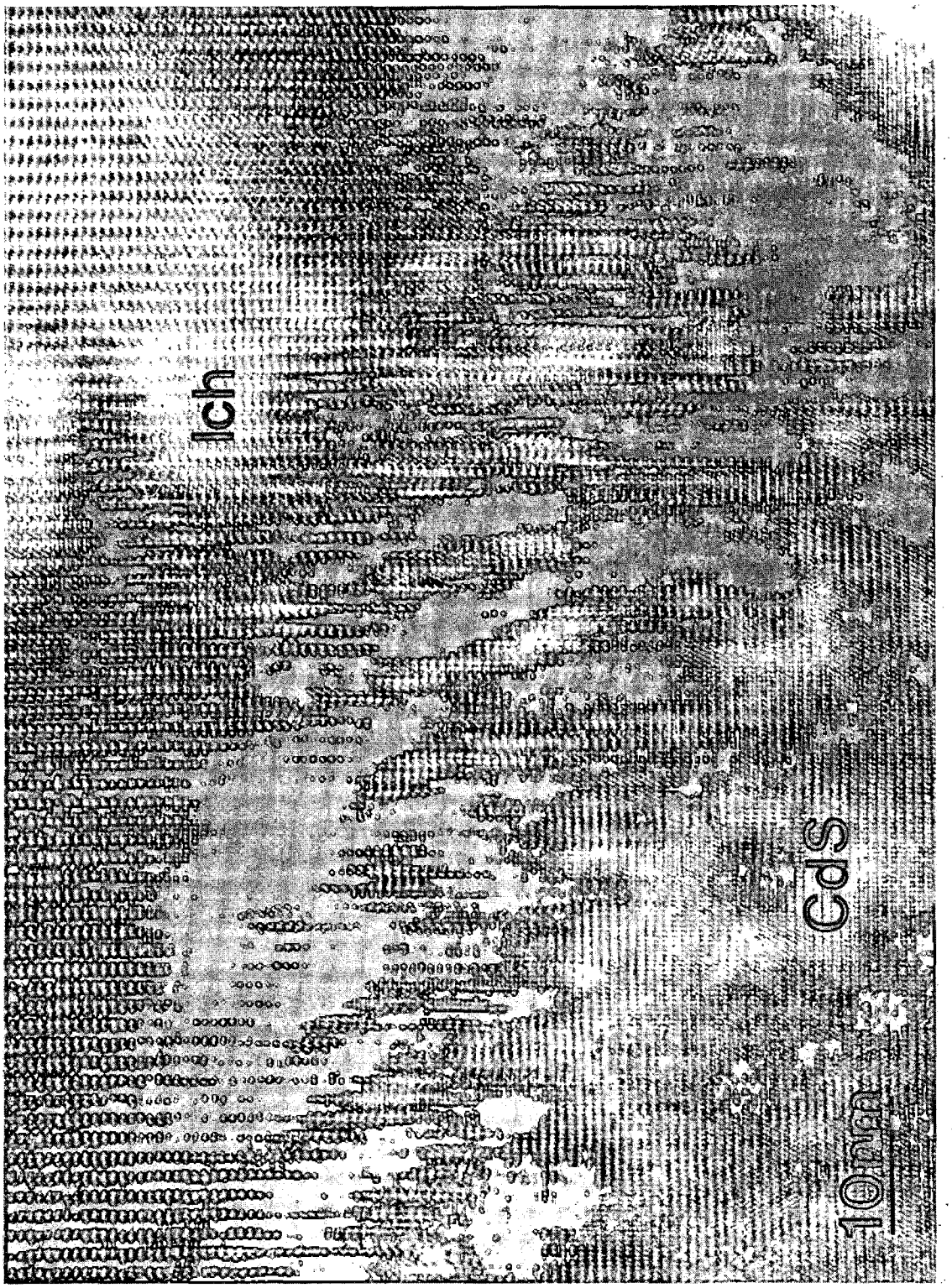

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Fig. 5

Table 1: Comparison of Lattice Parameters

phase (S network)	a_{eff}[nm] (%misfit)	c_{eff}[nm] (%misfit)
CdS (h.c.p.)	a_o = 0.4137	c_o = 0.3358
low chalcocite[4] (h.c.p.)	d_{030} = 0.3961 (-4.38)	d_{004} = 0.3374 (+050)
tetragonal phase[5] (f.c.c.)	d_{100} = 0.4008 (-3.20)	d_{102} = 0.3268 (-2.77)

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