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ABSTRACT

The growth of Cu_{2-x}S in the (0001) basal face of single crystal cadmium sulfide has been studied with high resolution transmission electron microscopy (HRTEM) and diffraction. Cross-sectional $\text{Cu}_{2-x}\text{S}/\text{CdS}$ specimens and plan-view Cu_{2-x}S separated films were prepared from heterojunctions formed by the aqueous conversion of CdS to topotaxial Cu_{2-x}S . Low chalcocite films were found to form in two principal stages; 1) coalescence of low chalcocite islands and 2) an accelerated reaction localized at pores in the Cu_{2-x}S film. Several possible misfit accommodation mechanisms involving twinning, cracking, and a second copper sulfide phase were identified.

1. INTRODUCTION

Nearly thirty years of research and development of the photovoltaic copper sulfide-cadmium sulfide heterojunction have culminated in the present-day thin-film frontwall devices with efficiencies approaching ten percent [1]. However, viability as a terrestrial solar cell also requires reproducibility and stability, two areas in which the performance of the $\text{Cu}_{2-x}\text{S}/\text{CdS}$ solar cell is still questionable. Further breakthroughs in these two areas will require a detailed understanding of both the growth mechanisms of Cu_2S in CdS and the evolution of the interfacial region during heat treatment and long-term exposure at operating

temperatures. In this paper, the results of a TEM study of the as-prepared $\text{Cu}_{2-x}\text{S}/\text{CdS}$ heterojunction are presented. Within the framework of these results, an understanding of the relationship between misfit accommodation and growth of Cu_{2-x}S in the cadmium face of basal CdS is developed.

1.1 Structural Aspects of the $\text{Cu}_{2-x}\text{S}/\text{CdS}$ Thin Film Heterojunction

The polycrystalline n-CdS layer of the $\text{Cu}_{2-x}\text{S}/\text{CdS}$ solar cell is composed of columnar grains of the wurtzite structure with the c-axis preferentially oriented normal to the substrate (see the review of CdS layer fabrication procedures by R. Hill [2]). The wurtzite structure, being non-centrosymmetric, exhibits two basal faces, each with its own chemistry. Consequently, the HCl texture etch which precedes Cu_{2-x}S layer formation has radically different effects on the cadmium (0001) and sulfur (000 $\bar{1}$) faces. In this paper, only the flat basal portion of the etched cadmium face is considered. The growth of Cu_{2-x}S in the terraced and faceted faces of (0001) etch pits and (000 $\bar{1}$) hillocks is considered in a second paper [3].

After etching, the CdS film is dipped into an aqueous solution of CuCl at 95-98°C for several seconds. A large negative change in free energy [2] drives an exchange reaction between cations yielding a p-type copper sulfide absorber layer approximately 150 nm thick. The optimum phase and composition has been determined to be low chalcocite (a structure based upon the interstitial ordering of copper within a distorted h.c.p. sulfur network [4,5]) with $[\text{Cu}]/[\text{S}] \cong 1.997$ [2]. Unfortunately, several stable and metastable phases complicate the structure of the Cu_{2-x}S layer [6]. However, only one of these phases,

the f.c.c.-based tetragonal phase, is important to the following discussion. A summary of the relevant structural data is given in Table 1.

II. TEM SPECIMEN PREPARATION

In order to avoid the complicating effects of grain boundaries and high dopant levels, experiments were performed with undoped single crystal CdS (Eagle-Picher). Boules of CdS were cut into basal slices and mechanically polished. The final polish was accomplished with 1 μ m diamond paste. Work-damaged surface material was removed during a texture etch in fresh 37 % HCl at room temperature for 30-60 seconds. At this stage, CdS cross-section specimens were prepared by ion milling (as described below) and examined by electron diffraction to verify the presence of the wurtzite structure in the near-surface region. No sphalerite CdS was detected. The copper sulfide layer was formed in an aqueous solution of CuCl (6g/l) and NaCl (2g/l) (substrate preheated to conversion temperature) at 98°C for 8-12 seconds [8].

Plan-view separated Cu_{2-x}S films were formed by selectively etching away the CdS in HCl. Copper sulfide films were then floated onto grids and examined in the TEM within 24 hours of preparation. Cu_{2-x}S/CdS cross-sections were prepared by argon ion milling (4kV, 30 μ A specimen current, 14 tilt). Ion milling heating effects were kept to a minimum by utilizing an LN₂ cold stage. "Conventional" microscopy and diffraction and high resolution lattice imaging were performed with a Siemens 102 TEM ($C_s \approx 1.9$ mm) at 100 kV.

III. RESULTS

Micrographs of separated films at the earliest observable stage indicated that the initial reaction produced small islands of low

chalcocite. As the reaction proceeded the islands grew laterally and coalesced. The pores remaining between the islands were, in many cases, bounded by inclusions of the tetragonal phase (Fig. 1). In addition, six variants of microtwins were found in both the interior and at the edges of the low chalcocite islands. Dark-field micrographs (not shown) using the $1\bar{1}02$ -type twin reflections showed that the twins were thin plates inclined to $[0001]$ and elongated along $\langle 2\bar{1}10 \rangle$. The best fit with the diffraction and microscopy data is provided by the $\{0\bar{1}13\}$ reflection twin which effectively expands the copper sulfide lattice by 10% in a $\langle 01\bar{1}0 \rangle$ direction [3].

The next stage of the reaction began at the pores. These pores acted as short-circuit diffusion paths for the reacting species resulting in a locally accelerated reaction. As the penetrations deepened, the pores developed into cracks on $\{\bar{2}110\}$, thereby facilitating further reaction with the solution (Fig. 2(a)). A film in the final heavily textured form is imaged in Fig. 2(b). Cross-section micrographs revealed that the deeper penetrations consisted of a mixture of low chalcocite and the tetragonal phase (Fig. 3).

IV. DISCUSSION

The observed reaction sequence can be rationalized as follows: The initial exchange reaction forms small coherent islands of low chalcocite. At this stage, the nucleation of the tetragonal phase (in the absence of large stresses) is inhibited by the fact that the surface is parallel to the glide plane of the required transformation dislocations ($1/3 \langle 10\bar{1}0 \rangle$ on every other close-packed sulfur plane). As the islands grow laterally and vertically, the 4.4 % misfit between low chalcocite and CdS can no

longer be accommodated by elastic deformation alone. The stress is partially relieved by the introduction of microtwins and martensite-like tetragonal phase inclusions at the island edges where the stress build-up is high.

The pores remaining in the film now act as conduits for diffusion of the reacting species. Consequently, the CdS adjacent to the pores is rapidly converted to copper sulfide. These deeper penetrations cause further stress build-up due to the mismatch in the basal plane. To accommodate this stress the pores become elongated and form microcracks on $\{2110\}$. The thicker penetrations then merge to form the heavily textured film described in the results. It should also be noted that as the microcracks develop they expose $\{2110\}$ planes which can serve as the nucleation sites for transformation dislocations and misfit dislocations with Burgers vectors in the basal plane. A combination of 15 % tetragonal phase and the remainder, low chalcocite, results in a perfect match with unstrained CdS in the $\bar{c}$ direction. This fact, combined with the favorable value of a_{eff} for the tetragonal phase (Table 1), may explain the presence of the tetragonal phase in the deeper penetrations of the copper sulfide adjacent to the cracks [9].

V. ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

- Fig. 1. Tetragonal phase inclusion at island edge in low chalcocite separated film. Arrow indicates a $\langle 2110 \rangle$ sublattice direction. Note antiphase boundaries on (200) low chalcocite (upper right). These boundaries are commonly found in low chalcocite films grown in basal CdS substrates [5]. Low chalcocite and the tetragonal phase in $[001]$ and $[40\bar{1}]$ zone-axis orientations, respectively. The 060 lch. and 020 tet. spots are located at arrow in inset diffraction pattern.
- Fig. 2. a) Separated film showing film morphology during early stages of reaction b) Film in final highly textured state. Arrow indicates a $\langle \bar{2}110 \rangle$ sublattice direction.
- Fig. 3. Cross-section image of deep penetration near crack. Slight misorientation of specimen accounts for black/white contrast of twinned tetragonal phase. CdS is in $[\bar{2}110]$ zone-axis orientation. L.ch. and tet. are in $[010]$ zone axis orientation. Arrowed spot in diffraction pattern is 0002 CdS, 204 l.ch. and 110 tet.

XBB 839-8241

Fig. 1

XBB 839-8242

Fig. 2

XBB 839-8243

Fig. 3

TABLE 1. Comparison of Lattice Parameters

phase	$a_{\text{eff}}(\text{nm})$ (%misfit)	$c_{\text{eff}}[\text{nm}]$ (%misfit)
CdS	$a_0 = 0.4137$	$c_0 = 0.3358$
low chalcocite [4]	$d_{030} = 0.3961$ (-4.38)	$d_{004} = 0.3374$ (+0.50)
tetragonal phase [7]	$d_{100} = 0.4008$ (-3.20)	$d_{102} = 0.3268$ (-2.77)

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