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## X-ray and XPS studies of evaporated $\text{Cu}_x\text{S}$ thin films

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The structural changes in  $\text{Cu}_x\text{S}$  films have been monitored by x-ray diffraction and correlated to the chemical changes taking place on the  $\text{Cu}_x\text{S}$  surface, the latter monitored by XPS. The results show: evaporated  $\text{Cu}_x\text{S}$  films contained chalcocite, free copper phases, and probably a third phase (of sulfur); resistivity is related to the amounts of free Cu and S in the film; air heat treatments converted chalcocite to Cu deficient phases and resulted in the disappearance of the sulfide and predominance of  $\text{CuSO}_4 \cdot n\text{H}_2\text{O}$  and CuO; argon heat treatment tended to react Cu and S to form  $\text{Cu}_x\text{S}$ ; Cd is detected on the surface of  $\text{Cu}_x\text{S}$  deposited onto CdS and is significantly increased in amount by heat treatments. These results can be related to chemical processes occurring on  $\text{Cu}_x\text{S}/\text{CdS}$  and  $\text{Cu}_x\text{S}/(\text{Zn,Cd})\text{S}$  solar cells. For the CdS cell, oxides and sulfates of Cu and Cd are found on the  $\text{Cu}_x\text{S}$  surface and the sulfates are enhanced by the heat treatment in moist air. CuO and  $\text{CuSO}_4$  are formed in the absence of Cd, and dominate the  $\text{Cu}_x\text{S}$  surface.

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### I. INTRODUCTION

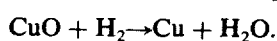
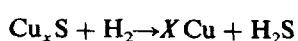
$\text{Cu}_x\text{S}/\text{CdS}$  and  $\text{Cu}_x\text{S}/(\text{Zn,Cd})\text{S}$  *p-n* heterojunctions have received considerable research attention because of their potential as efficient low cost thin film solar cells. But time dependent changes have been recognized as major problems for these junctions, and have been attributed largely to changes occurring in the  $\text{Cu}_x\text{S}$  layer. Hence, the importance of an improved understanding of chemical processes taking place in the  $\text{Cu}_x\text{S}$  after its formation.

Materials studies have been reported for  $\text{Cu}_x\text{S}$  formed on CdS and  $(\text{Zn,Cd})\text{S}$  by means of ion exchange.<sup>1-6</sup> In these studies, properties of the  $\text{Cu}_x\text{S}$  could be attributed in part to the presence of Cd and Zn in the substrate. In fact, for  $\text{Cu}_x\text{S}$  formed on these substrates, the surface chemistry is dominated by Cd (and Zn for  $\text{ZnCdS}$ ) which has diffused to the surface. It is the objective of this study to observe time dependent changes occurring on  $\text{Cu}_x\text{S}$  surfaces removed from the influence of the CdS or  $(\text{Zn,Cd})\text{S}$  substrates.

Previous studies of evaporated and sputtered  $\text{Cu}_x\text{S}$  films have been reported.<sup>7-11</sup> However, these studies have not included analyses of chemical species on the surface. This work attempts to correlate structural changes monitored by x-ray with chemical changes taking place on the  $\text{Cu}_x\text{S}$  surface, the latter monitored by means of XPS.

### II. EXPERIMENTAL

Polycrystalline films of cuprous sulfide ( $\text{Cu}_x\text{S}$ ) having chalcocite ( $x \approx 1.996$ ) as the major component were formed by vacuum evaporation of  $\text{Cu}_x\text{S}$  powder.<sup>16</sup> Initial x-ray diffraction of the powder showed that it consisted of copper deficient phases (anilite and diginite<sup>15</sup>). XPS indicated that in addition to  $\text{Cu}_x\text{S}$ , CuO and  $\text{CuSO}_4 \cdot n\text{H}_2\text{O}$  also existed on the surface of the powder granules. To reduce the surface oxide and expel the moisture from the powder, it was heated in  $\text{H}_2$  at 400 °C for 1 h. This produced a copper rich powder due to the reactions



This powder was evaporated from a tantalum boat onto Corning 7059 substrates held at temperatures in the 120–260 °C range. Film thicknesses depended strongly on sub-

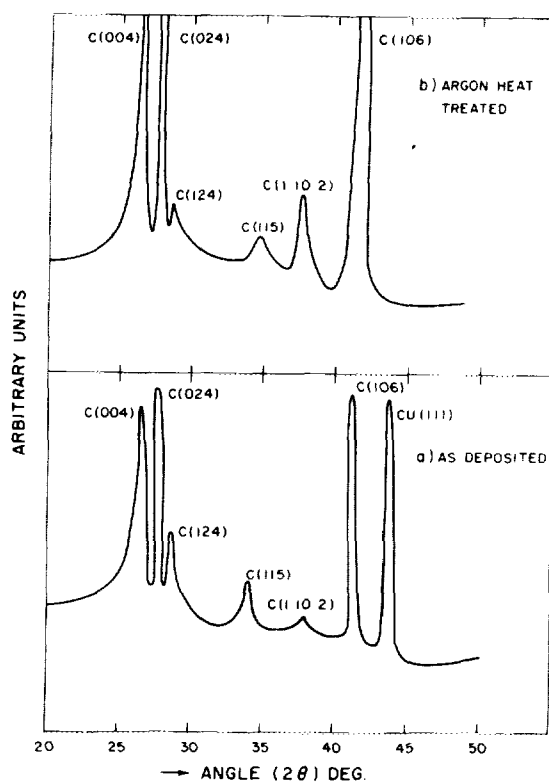


FIG. 1. X-ray diffraction patterns of evaporated  $\text{Cu}_x\text{S}$  film (a) as-deposited, (b) following argon heat treatment (24 h, 250 °C).

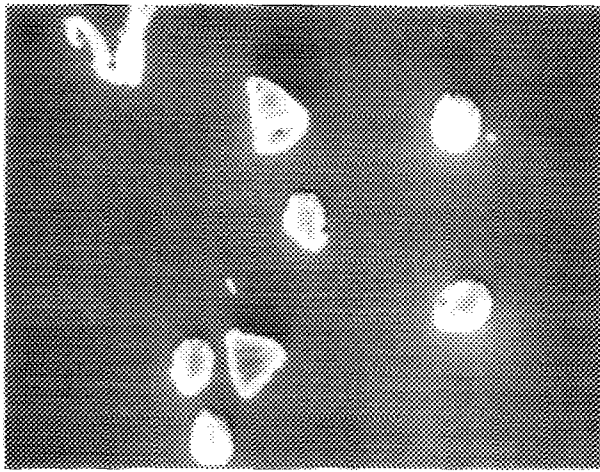


FIG. 2. SEM picture of an evaporated Cu, S film on glass (2000 ×).

strate temperature, being 4–5 times larger at 120 °C than at 260 °, other things being equal. Film thickness at a substrate temperature of 150 °C was typically 0.2 μm.

X-ray measurements were made on a Siemens diffractometer using CuK $\alpha$  radiation. XPS measurements were done on a Dupont 650 ESCA machine. Sheet resistance and SEM/EDAX measurements were also made. These measurements were made prior and subsequent to heat treatments, as discussed below.

### III. RESULTS AND DISCUSSION

Figure 1(a) shows an XRD pattern for an as-deposited film (substrate temperature = 150 °C). Elemental copper is indi-

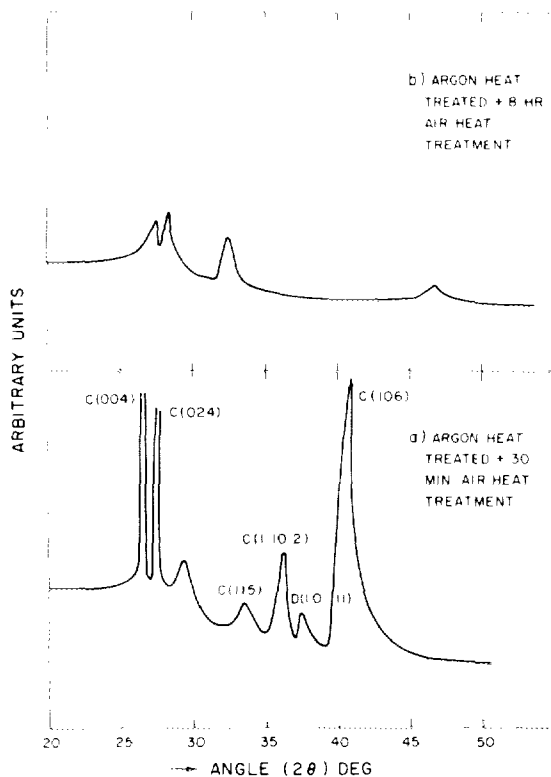


FIG. 3. X-ray diffraction patterns of evaporated Cu<sub>2</sub>S film (a) after argon heat treatment (24 h, 250 °C) plus air heat treatment (30 min, 150 °C), (b) after argon heat treatment (24 h, 250 °C) plus air heat treatment (8 h, 150 °C).

TABLE I. Copper to sulfur EDAX signal ratios for copper nodule and Cu, S film regions before and after argon heat treatment.

	Nodule	Cu, S film
As-deposited	2.58	1.19
After heat treatment	1.56	1.35

cated by the strong Cu(111) reflection. [A Cu (200) peak, which is not shown, was also observed.] There is considerable overlap between the orthorhombic djurleite and chalcocite peaks, particularly between  $d$  values of about 3.1 and 3.4 Å. We have attributed the major peaks to chalcocite for the following reasons: (1) Resistivity values are about 100 Ω-cm, not characteristic of djurleite; (2) Films are copper rich and djurleite is a copper deficient phase; (3) The best diagnostic peak for chalcocite is (106) at 40.8 °, and this is the strongest peak seen.

XRD showed that between 120–260 °C all as-deposited films are composed of chalcocite and free copper. Copper nodules were evident under SEM examination, as shown in Fig. 2. The amount of free copper increased with substrate temperature, which is consistent with other reports.<sup>7,8</sup>

After deposition, a film was heat treated in argon at 250 °C for 24 h. The resulting x-ray pattern is shown in Fig. 1(b), which indicates the complete disappearance of elemental copper (within the sensitivity of XRD) and an increase in the intensity of the main chalcocite peaks.

Subsequent heat treatment of the same film in air resulted in a reduction in chalcocite peak intensity and the appearance of djurleite peaks, as anticipated [Fig. 3(a)]. When the

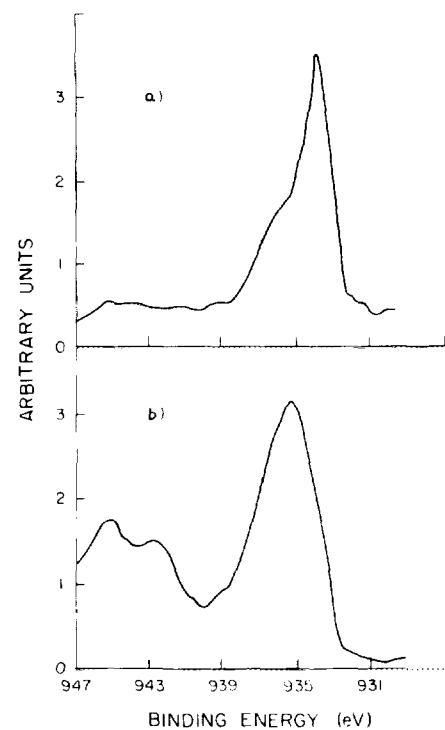


FIG. 4. Copper  $2p_{3/2}$  photoelectron spectra for (a) as-deposited Cu<sub>2</sub>S film, (b) following argon heat treatment (24 h, 250 °C) plus air heat treatment (8 h, 150 °C). Mg K $\alpha$  radiation ( $E = 1253.6$  eV).

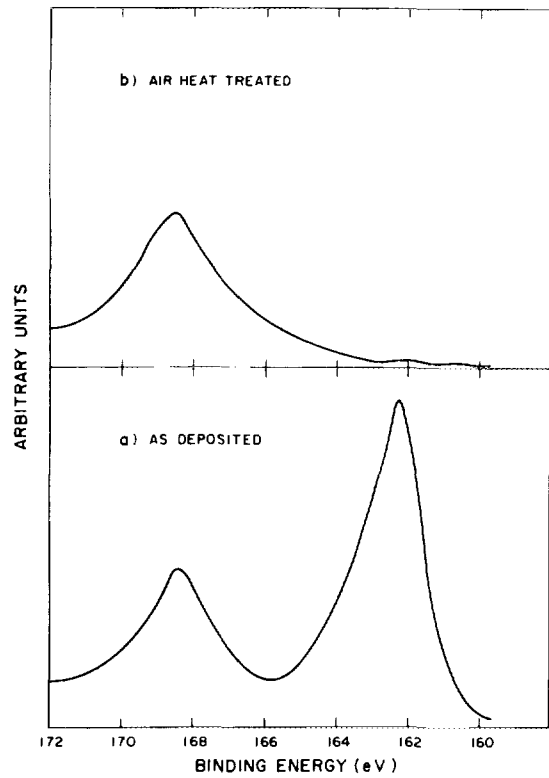


FIG. 5. Sulfur  $2p$  spectra for  $\text{Cu}_x\text{S}$  film (a) following argon heat treatment, (b) following argon treatment plus 8 h air heat treatment.

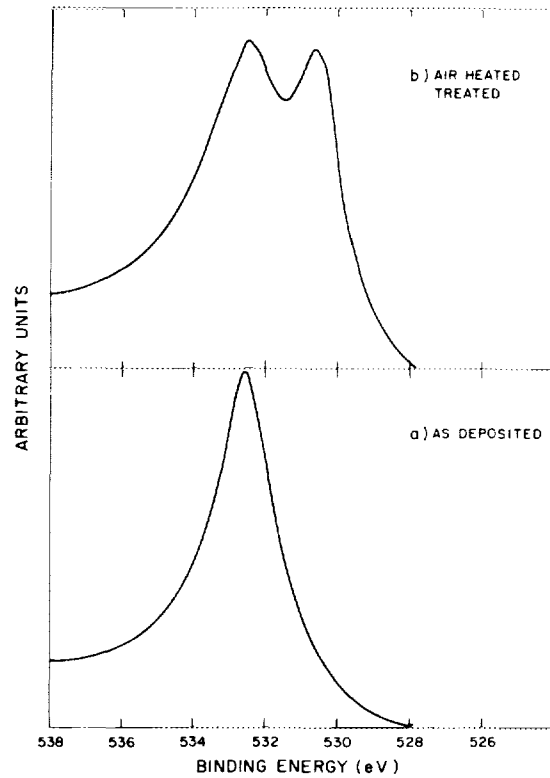


FIG. 6. Oxygen  $1s$  spectra for  $\text{Cu}_x\text{S}$  film (a) following argon heat treatment, (b) following argon treatment plus 8 h air heat treatment.

same sample was air heat-treated for 8 h, the crystallinity was reduced and the x-ray peaks became nonidentifiable [Fig. 3(b)]. This phenomenon is at present not understood.

EDAX of copper nodules and intermediate film regions was done for as-deposited and argon heat-treated samples. Table I shows Cu/S peak-height ratios for these locations before and after heat treatment. Even though the Table I data should be viewed somewhat qualitatively, the changes in Cu/S caused by heat treatment are consistent with the x-ray patterns of Fig. 1. The copper nodules are apparently being transformed into copper sulfide. It is expected that more extensive heat treatment would bring the Cu/S ratios for the nodules and film regions even closer to equality.

Film sheet resistance was measured just after deposition, after argon heat treatment, and after air heat treatment. The resistivity values were about 100, 10–20, and  $0.02 \Omega \text{ cm}$ , respectively. The resistivity is apparently linked to the amount of free copper present. These results are consistent with reports on sputtered and evaporated films.<sup>7,10</sup>

XPS measurements were made on  $\text{Cu}_x\text{S}$  samples evaporated onto glass, and onto CdS films. The as-deposited samples on glass show  $\text{Cu}_x\text{S}$  to be dominant on the surface, with small amounts of  $\text{CuSO}_4 \cdot n\text{H}_2\text{O}$  and possibly CuO also present.

Figures 4–6 show photoelectron spectra for copper ( $2p_{3/2}$ ), sulfur ( $2p$ ), and oxygen ( $1s$ ) for  $\text{Cu}_x\text{S}$  deposited onto glass, before and after heat treatment. Prior to heat treatment, the Cu  $2p_{3/2}$  peak energy corresponds to the sulfide, but the peak breadth indicates multiple peaks [Fig. 4(a)]. After heat treatment in air, the spectrum shows a shake-up satellite structure indicative of  $\text{Cu}^{+2}$  compounds [Fig. 4(b)]. The sulfur  $2p$

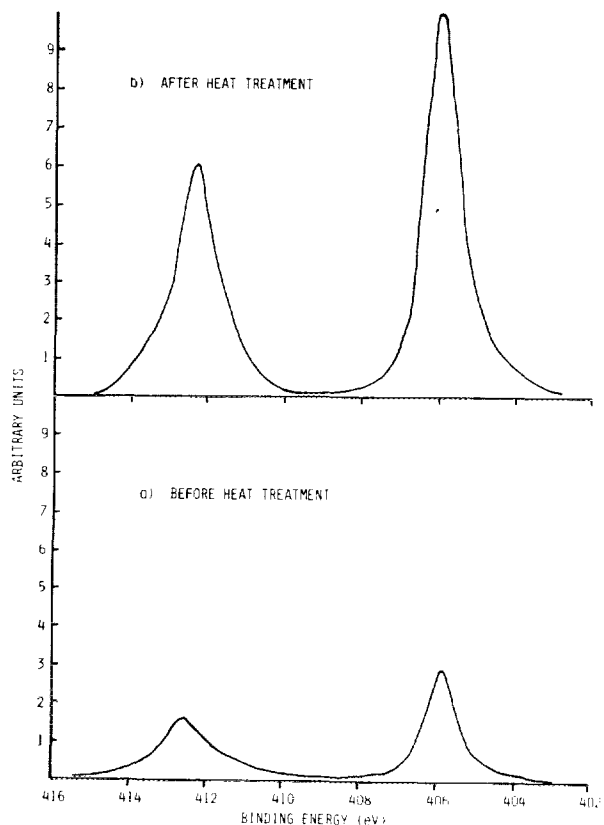


FIG. 7. Cadmium  $3d_{5/2}$  (406 eV) and  $3d_{3/2}$  (412.5 eV) spectra for  $\text{Cu}_x\text{S}$  film deposited onto CdS film (on glass) (a) as-deposited, (b) after heat treatment ( $\text{H}_2$ , 24 h,  $150^\circ\text{C}$ ).

spectrum before heat treatment [Fig. 5(a)] shows two peaks at about 162 and 169 eV, corresponding to the sulfide and sulfate, respectively.<sup>12</sup> Following heat treatment, no sulfide peak (only the sulfate) is evident [Fig. 5(b)]. In Fig. 6, the oxygen 1s peak energy [Fig. 6(a), as-deposited] corresponds to either absorbed oxygen or oxygen bound in the sulfate. Following heat treatment [Fig. 6(b)], the spectrum indicates the presence of CuO (at 530 eV) and  $\text{CuSO}_4 \cdot n\text{H}_2\text{O}$  (532 eV).

$\text{Cu}_x\text{S}$  evaporated onto a CdS film (on glass) showed a much higher degree of orientation, with x-ray patterns resembling those for  $\text{Cu}_x\text{S}$  formed topotaxially on CdS. In addition, XPS measurements indicate the presence of cadmium on the  $\text{Cu}_x\text{S}$  surface immediately following deposition of the  $\text{Cu}_x\text{S}$  film, with a large increase in the Cd signal following heat treatment (see Fig. 7). This verifies that the substrate (i.e., CdS) represents a source of cadmium which diffuses into the  $\text{Cu}_x\text{S}$  during and subsequent to its deposition. For topotaxially formed  $\text{Cu}_x\text{S}$ , this cadmium is in addition to any that remains frozen in the  $\text{Cu}_x\text{S}$  at the termination of ion exchange.

These results can be related to chemical processes occurring on  $\text{Cu}_x\text{S}/\text{CdS}$  and  $\text{Cu}_x\text{S}/(\text{Zn,Cd})\text{S}$  solar cells. For the CdS cell, oxides and sulfates of copper and cadmium are found on the  $\text{Cu}_x\text{S}$  surface, the sulfates enhanced by heat treatment in moist air. These results indicate that cupric oxide and sulfate form in the absence of cadmium, and dominate the  $\text{Cu}_x\text{S}$  surface in that case.

In conclusion: (1) Evaporated  $\text{Cu}_x\text{S}$  films contained the chalcocite and free copper phases, and probably a third phase (of sulfur); (2) Argon heat treatment tended to react the copper and sulfur to form  $\text{Cu}_x\text{S}$ ; (3) Film resistivity was apparently linked to the amounts of free copper and sulfur in the film; (4) As-deposited films exhibit sulfide ( $\text{Cu}_x\text{S}$ ) on the surface. Air heat treatments resulted in disappearance of the sulfide and predominance of  $\text{CuSO}_4 \cdot n\text{H}_2\text{O}$  and CuO; (5) Air

heat treatment converts chalcocite to copper deficient phases; (6) Cd is detected on the surface of  $\text{Cu}_x\text{S}$  deposited onto CdS, and is significantly increased in amount by heat treatment.

## ACKNOWLEDGMENTS

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<sup>16</sup>Cerac Pure, 200 mesh, nominal purity 99.999%.