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Single-thermal-source formation of $Zn_xCd_{1-x}S$ thin films

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Thermal sublimation of atomically homogeneous $Zn_xCd_{1-x}S$ powders from a single source results in films that are nonuniform in a direction normal to the substrate. This is attributed to initial preferential sublimation of Cd from the charge and is verified by energy dispersive x-ray analyses of film cross sections and of the charge residue. These results are related to the utility of this technique for forming $Zn_xCd_{1-x}S$ films for photovoltaic applications.

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Thin films of zinc cadmium sulfide ($Zn_xCd_{1-x}S$, $0 \leqslant x \leqslant 1$) have been formed by a variety of techniques [1-5] and studied for application to photovoltaic devices. [4,5] The film formation methods include rf sputtering,[1] multisource evaporation, [2-4] and spray pyrolysis.[5] Near-stoichiometric $Zn_xCd_{1-x}S$ films with properties dependent on zinc content and deposition conditions were reported for all of the above cases.

Reports have recently been made of zinc cadmium sulfide films formed by single-source evaporation of solid solutions of CdS and ZnS in the desired proportions. [6,7] Even though these films were intended for photovoltaic applications, independent verification of the film composition (compared to that of the starting material) and uniformity was not reported in either case.

Evaporated $Zn_xCd_{1-x}S$ film studies using double[4] and concentric[8] source arrangements have been reported by us previously. In addition, we have formed films of this type by evaporating atomically mixed powders from a single source. These films were found to have compositions differing substantially from the starting material, with a large composition gradient existing in a direction normal to the substrate.

Atomically homogeneous powders of $Zn_xCd_{1-x}S$ [9] were evaporated onto zinc-plated copper-foil substrates from a graphite source. The substrate temperature was maintained at 300 °C, with source temperatures in the 1100–1150 °C range. The average deposition rate was about 1 μm/min, with final thicknesses being in the 15–20-μm range.

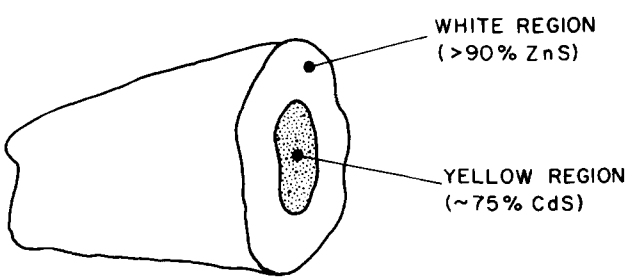

FIG. 1. Cross-sectional view of a mixed-sulfide charge residue remaining in the source following a run. The initial charge was ~20 at.% zinc (80% cadmium).

The three films reported here were formed from powders with initial compositions of $x = 0.068$, 0.138, and 0.202. (These atomic compositions correspond roughly to 5, 10, and 15% zinc weight compositions, which cover a range appropriate for $Cu_2S/Zn_xCd_{1-x}S$ solar-cell studies. [4-8]

Cu_2S layers were formed by means of the wet ion-exchange process, which has been reviewed in detail elsewhere.[10]

Typical cell data for the three compositions are seen in Table I. The listed zinc-content values represent the starting material (not the films). V_{oc} is the open-circuit voltage and J_{sc} is the short-circuit current density. The cell areas were ≈ 4 cm^2, and the measurements were performed under calibrated tungsten illumintation.

The open-circuit voltages, especially for the higher zinc-content samples, are substantially higher than for Cu_2S/CdS cells. However, these results were not reproducible with the precision desired. In addition, cross sections of postdeposition mixed-sulfide charges remaining in the graphite source appeared highly nonuniform and indicated initial preferential sublimation of cadmium. Thus, more detailed composition analyses of the films were performed.

Energy-dispersive x-ray analyses (EDAX) were made on an evaporation charge residue and on three mixed-sulfide film cross sections. A typical mixed-sulfide residue cross section is shown in Fig. 1. EDAX spot scans were made in the yellow central region and near the edge (white region). The white region is almost entirely ZnS, with the yellow region being mostly CdS. Thus, the conclusion is that cadmium sublimes preferentially (with an equal amount of sulfur), leaving behind a ZnS-rich charge. From examination of charges remaining from runs of varying times, it was found that the yellow region decreases in size with deposition time and eventually disappears. Thus, if an entire charge is evapo-

TABLE I. Typical cell data for the three compositions.

Zinc content x	V_{oc} (V)	J_{sc} (mA/cm^2)
0.068	0.494	11.7
0.138	0.524	9.4
0.202	0.576	1.1

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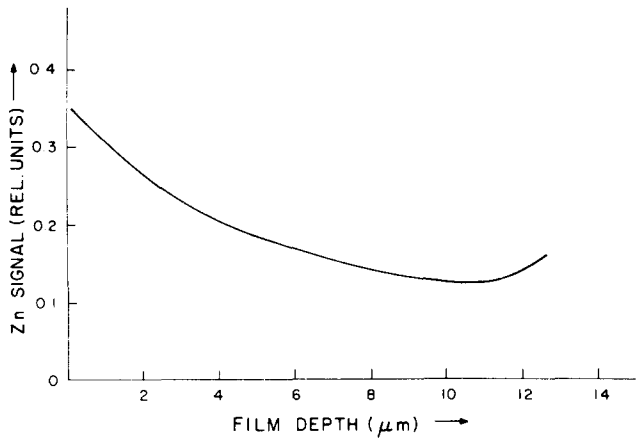

FIG. 2. EDAX line scan across a polished-film cross section. Initial charge was ~20 at.% zinc.

rated, the latter part of the deposition should be rich in zinc compared to cadmium. EDAX analyses of film cross sections verify this conclusion. An EDAX line scan made across a polished cross section is shown in Fig. 2. (The initial charge composition was $x = 0.202$.) The film is cadmium rich near the substrate and zinc rich near the film surface. (The slight increase of the Zn signal near the substrate is attributed to Zn originating from the Zn-plated Cu substrate.) The Zn signal decreases by nearly a factor of 3 from the top surface toward the film interior. This corroborates the initial preferential sublimation of Cd as discussed above.

Table II shows EDAX spot scan data taken at three locations across each of the film cross sections. (The "near-surface" and "near-substrate" scans were made about 2 μm from the respective interfaces.)

These data are consistent with those of Figs. 1 and 2. It is seen by comparing the first two columns of Table II that there is only a weak correlation between the initial charge and the film surface compositions. The final zinc content near the film surface will depend on the thermal history of the charge (heat-up, preheat, etc.) and on the deposition time. However, with correct instrumentation, these variables could probably be controlled, and even though the films would not be uniform, a reproducible gradient could perhaps be established. With such films, however, a more serious problem exists with respect to their application to $Cu_2S/Zn_xCd_{1-x}S$ solar cells. The Cu_2S layer will extend down grain boundaries, into the lower-zinc-composition region of the $Zn_xCd_{1-x}S$. Thus, the junction will be comprised of a distributed parallel combination of zinc regions of varying composition. Due to lower barrier height,[4] the lower-zinc-composition region (i.e., lower edge of the grain

TABLE II. Variation of zinc content in a direction normal to the substrate for three cross-sectioned films.

Initial charge (%)	Near surface (%)	Center (%)	Near substrate (%)
6.8	11.2	3.4	2.3
13.8	12.7	4.6	4.3
20.2	14.6	7.4	4.9

boundary) will dominate the voltage characteristic of the cell. The nonuniformity of the $Zn_xCd_{1-x}S$ layer and grain-boundary penetration of the Cu_2S result in junctions whose properties are difficult to control in a reproducible fashion. Even a rapid blow-out of the charge from a thermal source will still not preclude preferential sublimation of the components. This is not to say that a true flash evaporation could not result in a uniform film. However, a better alternative is probably to employ one of already proven methods referred to earlier.

We have verified that thermal sublimation of atomically homogeneous $Zn_xCd_{1-x}S$ powders from a single source results in films highly nonuniform in a direction normal to the substrate. This is due to initial preferential sublimation of Cd from the charge and is verified by energy-dispersive x-ray analyses of film cross sections, and of the charge residue. Even though $Cu_2S/Zn_xCd_{1-x}S$ heterojunctions made from these films exhibit increased open-circuit voltages, the film nonuniformity is a detrimental factor. Other film formation techniques such as sputtering, multisource evaporation, or spray pyrolysis result in films more suitable for photovoltaic applications. The single-source method, however, could potentially find application in an area where a graded composition (resulting in a graded band gap, for example) is desirable.

[1]D.B. Fraser and H.D. Cook, J. Vac. Sci. Technol. **11**, 56 (1974).
[2]W. M. Kane, J.P. Spratt, L.W. Hershinger, and I.H. Khan, J. Electrochem. Soc. **113**, 136 (1966).
[3]D. Bonnet, Phys. Status Solidi A **11**, K135 (1972).
[4]L.C. Burton and T.L. Hench, Appl. Phys. Lett. **29**, 612 (1976).
[5]R.S. Feigelson, A. N'Diaye, S. Yin, and R.H. Bube, J. Appl. Phys. **48**, 3162 (1977).
[6]V.D. Vankar, S.R. Kas, P. Nath, and K.L. Chopra, Phys. Status Solidi A **45**, 665 (1978).
[7]S. Martinuzzi, J. Oualid, D. Sarti, and J. Gervais, Thin Solid Films **51**, 211 (1978).
[8]L.C. Burton, B. Baron, T.L. Hench, and J.D. Meakin, J. Electron. Mater. **7**, 159 (1978).
[9]Compositions with $x = 0.068$, 0.138, and 0.202 were obtained from the General Electric Co., Lamp Division, Cincinnati, Ohio.
[10]L.R. Shiozawa, R. Augustine, G.A. Sullivan, J.M. Smith III, and W.R. Cook, Jr., Aerospace Research Laboratories Report ARL 69-0155, 1969.

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