

Growth and characterization of thinfilm compound semiconductor photovoltaic heterojunctions

L. L. Kazmerski, F. R. White, M. S. Ayyagari, Y. J. Juang, and R. P. Patterson

Citation: *Journal of Vacuum Science & Technology* **14**, 65 (1977); doi: 10.1116/1.569173

View online: <http://dx.doi.org/10.1116/1.569173>

View Table of Contents: <http://scitation.aip.org/content/avs/journal/jvst/14/1?ver=pdfcov>

Published by the AVS: Science & Technology of Materials, Interfaces, and Processing

Articles you may be interested in

Origin of open circuit voltage in planar and bulk heterojunction organic thin-film photovoltaics depending on doped transport layers

J. Appl. Phys. **104**, 043107 (2008); 10.1063/1.2973199

Thin-film photovoltaics

J. Vac. Sci. Technol. A **23**, 1208 (2005); 10.1116/1.1897697

Effects of nonuniformity in thin-film photovoltaics

Appl. Phys. Lett. **80**, 4256 (2002); 10.1063/1.1483118

Growth and characterization of reactively sputtered thinfilm platinum oxides

J. Appl. Phys. **69**, 1596 (1991); 10.1063/1.347255

POLYMORPHISM IN SOME IVVI COMPOUNDS INDUCED BY HIGH PRESSURE AND THINFILM EPITAXIAL GROWTH

Appl. Phys. Lett. **10**, 282 (1967); 10.1063/1.1754812

ADVERTISEMENT



 Advance your technology or engineering career using the **AVS Career Center**, with **hundreds of exciting jobs** listed each month!

<http://careers.avs.org>



Growth and characterization of thin-film compound semiconductor photovoltaic heterojunctions*

L. L. Kazmerski, F. R. White,[†] M. S. Ayyagari, Y. J. Juang, and R. P. Patterson[†]

Department of Electrical Engineering, University of Maine at Orono, Orono, Maine 04473

(Received 21 September 1976)

The fabrication and characteristics of several vacuum-deposited photovoltaic heterojunctions involving ternary compounds (CuInSe₂, CuInS₂, and CuInTe₂) and a binary compound (InP) with CdS are described. The light and dark *IV* characteristics, spectral response data, and cell parameters (fill factors, open-circuit voltages, short-circuit currents, efficiencies) are reported for the thin-film solar cells.

PACS numbers: 84.60.Jt, 81.15.Ef, 72.40.+w

I. INTRODUCTION

The potential utilization of several materials as alternatives to present photovoltaic technologies (i.e., Si and Cu₂S/CdS) has received considerable attention recently.¹⁻⁴ For economical reasons, as well as for the possibilities of large-scale production, the thin-film approach is an effective method of device fabrication. However, if the thin-film device is to be cost-effective, device efficiencies in the range 10%–12% must be attained.⁵ To date, there have been only four materials utilized in devices (all in single-crystal form) with efficiencies exceeding this 10% figure: (1) silicon, (2) GaAs/Ga_xAl_{1-x}As, (3) CuInSe₂/CdS, and (4) InP/CdS. It is the latter two which form the basis for this paper.

The fabrication and characterization of several vacuum-deposited thin-film heterojunctions of ternary compounds (CuInSe₂, CuInS₂, and CuInTe₂) and of InP on CdS are reported here. These materials have some exceptional properties which present a potential for efficient photovoltaic conversion: (1) Their band gaps, summarized in Table I, are near the optimum for terrestrial solar conversion.⁶ All (2) are direct band-gap types,⁷ which minimizes the requirements for minority-carrier diffusion lengths. (3) In the cases of InP and CuInSe₂, the lattice matches with CdS (see Table I) are exceptionally good compared to the analogous Cu₂S/CdS cell,^{1,8} thus minimizing interfacial states. (4) The electron affinities of InP and of the ternary compounds are such as not to yield conduction band spikes with the *n*-type CdS.⁸⁻¹⁰ (5) Both *n*- and *p*-type thin films of CuInS₂, CuInSe₂, CuInTe₂, and InP have been grown so that homojunctions are possible. (6) The junction potential has been demonstrated for epitaxial CdS grown on single crystals of InP and CuInSe₂ with efficiencies exceeding 12%.^{1,8} A polycrystalline thin-film InP/CdS solar cell in which the InP layer is grown by chemical vapor deposition (CVD) has recently been reported.⁹ This 0.52 mm² device had a 2.8% conversion efficiency (AM1) and was extremely stable. The major limiting factor for that device was the rectifying contact between the InP and the carbon substrate. The properties of the materials under consideration are

outlined in Table I and comparative data are included for Cu₂S.

This paper discusses these heterojunctions. The vacuum deposition of the materials is examined. Light and dark *IV* characteristics, spectral response, and device parameters (efficiencies, fill factors, open-circuit voltages, and short-circuit currents) are reported for these thin-film solar cells.

II. DEVICE FABRICATION

The CuInS₂ and CuInSe₂ films were grown by a dual-source deposition technique employing a resistive heat alumina crucible for the single-phase ternary compound and a Ta boat for either S or Se.^{10,11} The second source alters the S or Se content which, in turn, controls carrier type. For the *p*-type films used in this investigation, the carrier concentrations were of the order 3–4 × 10¹⁶/cm³ for CuInSe₂ and

TABLE I. Summary of properties of materials used in this investigation. Cu₂S is included for comparison.

	Crystal ^a structure	Lattice parameters (Å)	% Mis- match ^b with CdS	<i>E_g</i> ^a (eV)	<i>μ</i> _{crystal} ^a (cm ² /V s)	
					<i>n</i>	<i>p</i>
CdS	Wurtzite	<i>a</i> = 4.136 <i>c</i> = 6.716		2.42	250	
InP	Sphalerite	<i>a</i> = 6.869	0.32%	1.34	4600	150
CuInSe ₂	Chalcopyrite	<i>a</i> = 5.782 <i>c</i> = 11.62	1.16%	1.01–1.04	320	10
CuInS ₂	Chalcopyrite	<i>a</i> = 5.523 <i>c</i> = 11.12	5.59%	1.55	200	15
CuInTe ₂	Chalcopyrite	<i>a</i> = 6.179 <i>c</i> = 12.36	5.62%	0.96	200	^c
Cu ₂ S	Orthorhombic	<i>a</i> = 11.88 <i>b</i> = 27.33 <i>c</i> = 13.49	3.6%	1.2 ^d		25

^aAt room temperature.

^bUsual growth for the two materials.

^cNot reported. Thin-film values ~12.

^dIndirect gap transition; all others, direct.

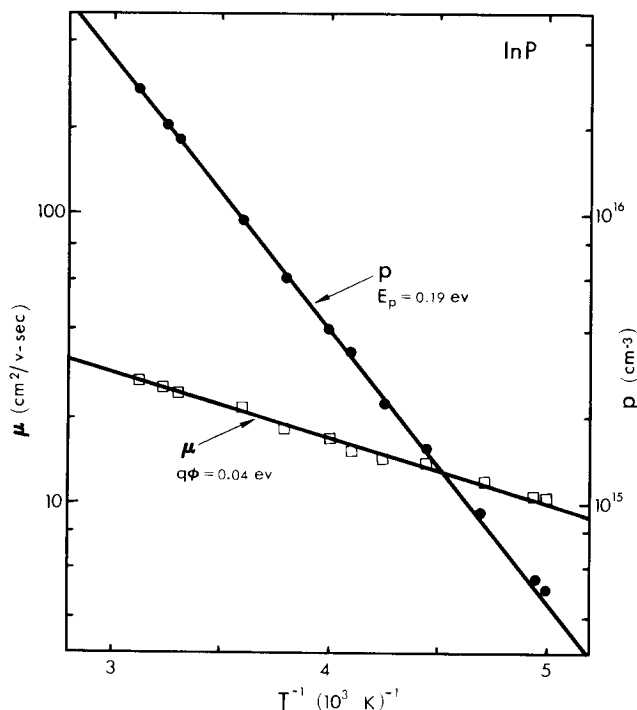


FIG. 1. Dependence of hall mobility μ and carrier concentration P for p -type vacuum-deposited InP thin film. Film thickness is 1.4 μm ; substrate temperature is 500 K. (Elemental two-source deposition technique.)

$7\text{--}9 \times 10^{15}/\text{cm}^3$ for CuInS_2 films. Grain sizes were in the range 1–2 μm and the films indicated a preferential (112) growth (i.e., the [221] axis perpendicular to the substrate). The CuInTe_2 films were flash evaporated from a Ta source to provide p -type characteristics.¹⁴ The hole concentrations therein were $1 \times 10^{16}/\text{cm}^3$, and grain sizes were approximately 0.4 μm .

Initially, a single source deposition method was attempted to grow the desired InP films. However, single-phase films could not be produced using this method, even after examining a large range of deposition rates (1–500 $\text{\AA}/\text{s}$) and substrate temperatures (300–600 K). Elemental In and P (both crystalline and amorphous) were detected by electron diffraction for all these films. InP films deposited at low T_{sub} or high rates contain significant elemental phosphorous. At high T_{sub} or low rates, large elemental indium excesses resulted. Therefore, a two-source method involving elemental deposition of In and P from separate Ta boats was developed. The mobility and carrier concentration dependence upon film temperature are shown in Fig. 1 for a film grown at a substrate temperature of 500 K. Grain sizes exceeding 1 μm were observed. Single phase quality in the films (i.e., no free In or P) could be controlled over a 0.8- cm^2 substrate area for this particular deposition configuration which had a 16-cm source-to-substrate separation. The temperature dependence of the parameters of the InP films correspond to that predicted for films dominated by the grain boundary scattering mechanism¹⁵:

$$\mu = \mu_b \exp(-q\phi/kT) \quad (1)$$

and

$$p \propto \exp(-E_p/kT), \quad (2)$$

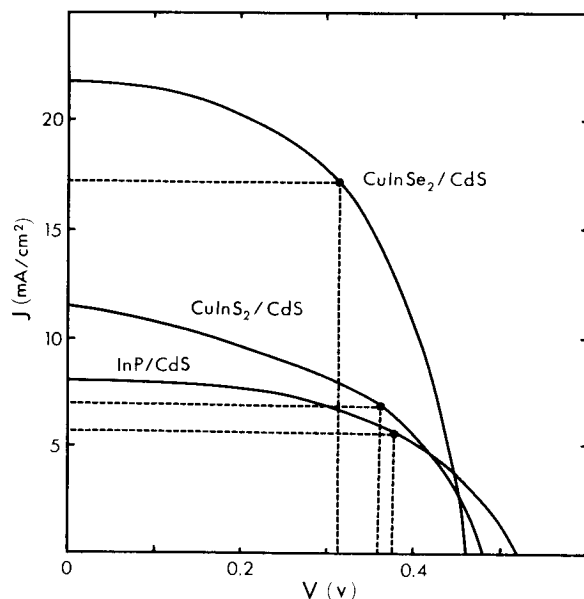


FIG. 2. Light IV characteristics for thin-film $\text{CuInSe}_2/\text{CdS}$ (area = 1.2 cm^2) $\text{CuInS}_2/\text{CdS}$ (area = 0.124 cm^2), and InP/CdS (area = 0.124 cm^2) heterostructures. Fill factors are 0.54, 0.45, and 0.51, respectively.

where $q\phi$ and E_p are the grain-boundary scattering potential and carrier-concentration activation energy, respectively, and μ_b the effective mobility which depends on the boundary density and nature as well as on the bulk crystalline mobility.

The CdS was evaporated from a Ta-baffled source. The CdS films had a c -axis orientation on all the films in this study. Carrier concentrations were of the order $n = 2 \times 10^{17}/\text{cm}^3$ with $>1 \mu\text{m}$ grain sizes.

The devices were fabricated completely *in situ*, and illumination was only through the CdS layer. Substrate temperatures were controlled (± 2 K) using conduction heaters and were monitored using foil thermocouples mounted on the substrate surface facing the evaporation source. The substrates

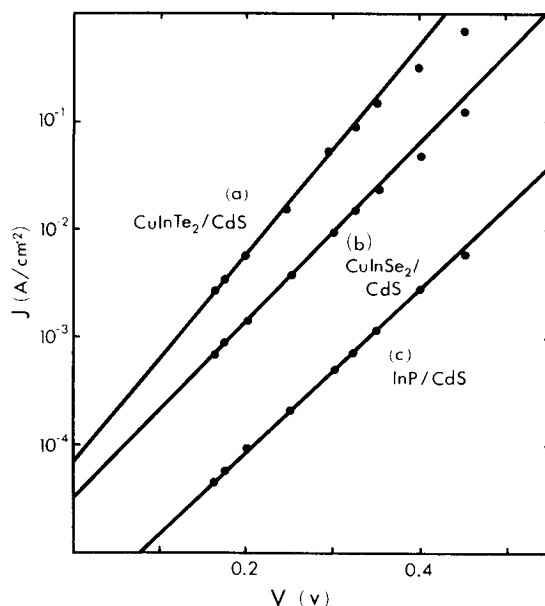


FIG. 3. Forward JV characteristics for (a) $\text{CuInTe}_2/\text{CdS}$, (b) $\text{CuInSe}_2/\text{CdS}$, and (c) InP/CdS heterostructures.

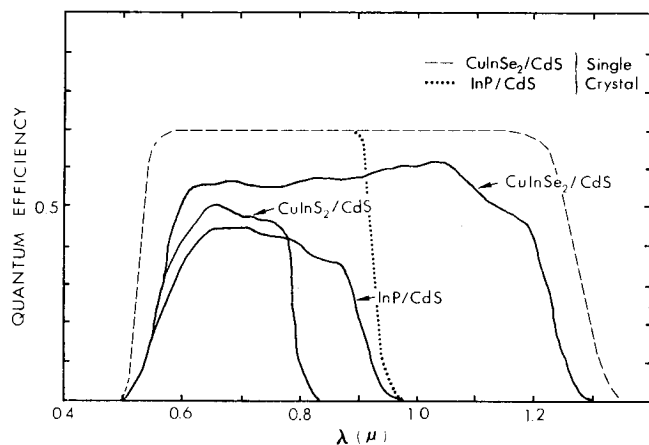


FIG. 4. Spectral-response characteristics for $\text{CuInSe}_2/\text{CdS}$, $\text{CuInS}_2/\text{CdS}$, and InP/CdS thin-film devices. Curves for single-crystal cases have been included (See Ref. 1.).

were polished alumina with a Zn–Au metallization for back contact. A 2–4- μm ternary film was deposited, with $T_{\text{sub}} = 475\text{ K}$ for CuInSe_2 , 450 K for CuInS_2 , and 520 K for CuInTe_2 . The InP layer was 1–2 μm , using a 600 K substrate temperature. In each case, the CdS film was grown on the particular underlayer at $T_{\text{sub}} = 475\text{ K}$. This film, which is essentially a window for solar radiation, was 4–6 μm in thickness. Thinner films tended to have pinholes, causing shorts. Finally, an In fingered contact was used as a top electrode and allowed passage of 75% of the incident radiation. The In was vacuum deposited. Four parallel $0.7 \times 0.8\text{-cm}$ fingers were utilized for the 1.2- cm^2 devices and two $0.05 \times 0.25\text{-cm}$ fingers for the others. The ternary devices were annealed in a 10^{-1} Pa vacuum at 353 K for 10 min before taking measurements.³

A tungsten-halogen (type ELH lamp) source with $100\text{-mW}/\text{cm}^2$ incident radiation was used for light IV measurements, with the devices held at 301 K. The lamp was calibrated with a $\text{Cu}_2\text{S}/\text{CdS}$ standard cell (ERDA/NASA Z66). Spectral response measurements could be taken over the range 0.3–1.6 μm .

III. RESULTS AND DISCUSSION

The light IV characteristics for thin-film $\text{CuInSe}_2/\text{CdS}$, $\text{CuInS}_2/\text{CdS}$, and InP/CdS heterostructures are presented in Fig. 2. The highest efficiency for this group has been measured for the $\text{CuInS}_2/\text{CdS}$ cell (5.42%). This device has received the most attention in this laboratory, and a “best” efficiency of 5.7% has been reported.³ Its area (1.2 cm^2) is larger than for the other devices discussed in this paper: the InP/CdS and $\text{CuInSe}_2/\text{CdS}$ were 0.124 cm^2 in area and the limitations in performance for both was that of reduced short-circuit currents. Current densities in excess of $15\text{ mA}/\text{cm}^2$ were reported for the single-crystal analogue of InP device.¹ The limitation here is probably due to grain-boundary recombination, and no attempt has been made to alter grain size and thus control this mechanism. This is, however, the first report of an *in situ* vacuum-deposited thin-film InP/CdS cell. The open-circuit voltage ($V_{\text{oc}} = 0.51\text{ V}$) is encouraging, but high series resistance can be noted in this and the $\text{CuInS}_2/\text{CdS}$ characteristics. The back contact provides the greatest con-

tribution to this problem as it was for the CVD-grown polycrystalline cell.¹⁰

The $\text{CuInS}_2/\text{CdS}$ device (see Fig. 2) had a measured efficiency of 2.55%. It is by far the best produced to date and the junction characteristics are very sensitive to even small stoichiometry differences in the CuInS_2 . Little photovoltaic effect was recorded for the $\text{CuInTe}_2/\text{CdS}$ device, although fair diodes could be fabricated. Figure 3 presents the dark forward characteristics for (a) $\text{CuInTe}_2/\text{CdS}$, (b) $\text{CuInSe}_2/\text{CdS}$, and (c) InP/CdS heterojunctions, respectively. J varies as $\exp(qV/nkT)$ in each case where $n = 2.08$ for the $\text{CuInSe}_2/\text{CdS}$ and $n = 2.34$ for the InP/CdS devices. These values indicate that the generation–recombination process dominates, as expected.^{16,17}

The spectral responses for three heterostructures are shown in Fig. 4. In each case, the low wavelength cutoff is due to absorption by the CdS . The high wavelength cutoff is due to the absorption limit of each of the other films. These limits correspond well to the calculated values (i.e., $\lambda = 1.22\text{ }\mu\text{m}$, CuInSe_2 ; $\lambda = 0.80\text{ }\mu\text{m}$, CuInS_2 ; and $\lambda = 0.92\text{ }\mu\text{m}$, InP) and those for the single-crystal cases.⁸ However, the magnitude of the quantum efficiency for the InP/CdS device is about half that published by Shay *et al.*⁸ This is indicative of the considerable recombination encountered by the photo-induced carriers in these relatively high-defect density films. However, the somewhat better fill factor (0.51) than that reported by Bachmann *et al.*⁹ indicates that the back contact is less of a problem in this case than for CVD.

The stability of these solar cells has not been investigated in detail. The InP and CuInSe_2 have shown no degradation over a period of weeks in normal ambients. Some problems have been observed using Auger spectroscopy on these devices.¹⁸ The most critical is the diffusion of Cd into the ternary film at temperatures exceeding 700 K. This problem was reported for single-crystal Cd -diffused CuInSe_2 diodes¹⁹ and is undergoing further investigation for these heterostructures.

This study has demonstrated the fabrication of several heterojunction solar cells using vacuum-deposition techniques. A summary of this work with comparisons to single-crystal devices and theoretical calculations is presented in Table II. Each device obviously needs further examination in order to determine its viability. The $\text{CuInSe}_2/\text{CdS}$ cell presently seems the best suited for vacuum deposition since the control of the

TABLE II. Device summary—Efficiencies.

	Theory ^a	Experimental	
		Single crystal ^a	Thin film
InP/CdS	17%	12.5%	2.1% ^b 2.8%
$\text{CuInSe}_2/\text{CdS}$	15%	12%	5.7% ^c 5.4% ^b
$\text{CuInS}_2/\text{CdS}$	—	—	2.55% ^b

^a See Ref. 8.

^b This study.

^c See Ref. 3.

^d CVD grown, see Ref. 9.

ternary evaporation process over larger areas has been demonstrated. In addition, the efficiency of this solar cell is already in the range of other thin-film photovoltaic devices. More work on InP deposition remains to be done. Several other growth techniques incorporating CVD of InP are probably better candidates for large scale production of this particular device if the back contact problem can be overcome.^{9,20,21}

* Supported by NSF-RANN.

† NSF Undergraduate Research Participant

¹ S. Wagner, J. L. Shay, K. J. Bachmann, and E. Buehler, *Appl. Phys. Lett.* **26**, 229 (1975).

² J. J. Woodall and H. J. Hovel, *J. Vac. Sci. Technol.* **12**, 1000 (1975).

³ L. L. Kazmerski, F. R. White, and G. K. Morgan, *Appl. Phys. Lett.* **29**, 268 (1976).

⁴ L. C. Olsen and R. C. Bohara, *Proceedings of the 11th Photovoltaics Specialists Conference, Phoenix* (IEEE, New York, 1975), p. 381.

⁵ E. A. DeMeo, "Assessment of CdS Photovoltaic Arrays for Large Scale Electric Utility Applications", Report WS75-21, prepared for EPRI, Dec. 1976 (unpublished).

⁶ J. J. Loferski, *J. Appl. Phys.* **27**, 777 (1956).

⁷ H. M. Kasper, *Proceedings of the 5th Material Research Symposium* (U.S.

Natl. Bur. Stand. Spec. Pub. 364, Solid State Chem.) July, 1972.

⁸ J. L. Shay, S. Wagner, K. Bachmann, E. Buehler and H. M. Kasper, *Ret.* **4**, pp. 503-507.

⁹ K. J. Bachmann, E. Buehler, J. L. Shay, and S. Wagner, *Appl. Phys. Lett.* **29**, 121 (1976).

¹⁰ J. L. Shay, S. Wagner, and J. C. Phillips, *Appl. Phys. Lett.* **28**, 31 (1976).

¹¹ L. L. Kazmerski, M. S. Ayyagari, G. A. Sanborn, and F. R. White, *J. Vac. Sci. Technol.* **13**, 139 (1976).

¹² L. L. Kazmerski, M. S. Ayyagari, and G. A. Sanborn, *J. Appl. Phys.* **46**, 4865 (1975).

¹³ R. F. C. Farrow, *J. Phys. D: Appl. Phys.* **7**, 2436 (1974). Also, M. B. Panish and J. R. Arthur, *J. Chem. Thermodyn.* **2**, 229 (1970).

¹⁴ For Analogous System, see B. Elliott, R. D. Tomlinson, J. Parkes, and H. M. Hampshire, *Thin Solid Films* **20**, 525 (1974).

¹⁵ R. L. Petritz, *Phys. Rev.* **104**, 1508 (1956).

¹⁶ C. T. Sah, R. N. Noyce, and W. Shockley, *Proc. IRE* **45**, 1228 (1957).

¹⁷ C. T. Sah, *IEEE Trans. Electron Devices*, **ED-9**, 94 (1962).

¹⁸ R. Cooper and A. J. Merrill (unpublished).

¹⁹ B. Tell, S. Wagner, and P. M. Bridenbaugh, *Appl. Phys. Lett.* **28**, 454 (1976).

²⁰ K. S. Dzampaer, *Inorg. Mater.* **9**, 34 (1973).

²¹ R. C. Clarke, B. D. Joyce, and W. H. E. Wilgoss, *Solid State Commun.* **8**, 1125 (1970).