



# THE p-CuInSe<sub>2</sub>/n-CdS HETERODIODE: PHOTOVOLTAIC DETECTOR, SOLAR CELL AND LIGHT EMITTING DIODE

S. Wagner, J. Shay, H. Kasper

## ► To cite this version:

S. Wagner, J. Shay, H. Kasper. THE p-CuInSe<sub>2</sub>/n-CdS HETERODIODE: PHOTOVOLTAIC DETECTOR, SOLAR CELL AND LIGHT EMITTING DIODE. Journal de Physique Colloques, 1975, 36 (C3), pp.C3-101-C3-104. 10.1051/jphyscol:1975319 . jpa-00216289

HAL Id: jpa-00216289

<https://hal.science/jpa-00216289>

Submitted on 4 Feb 2008

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

## THE p-CuInSe<sub>2</sub>/n-CdS HETERO DIODE : PHOTOVOLTAIC DETECTOR, SOLAR CELL AND LIGHT EMITTING DIODE

S. WAGNER, J. L. SHAY and H. M. KASPER (\*)

Bell Laboratories Holmdel, New Jersey 07733, U. S. A.

**Résumé.** — Dans le cadre de notre programme exploratoire sur les possibilités d'applications des composés ternaires de type chalcopyrite, nous avons préparé des hétérodiodes CuInSe<sub>2</sub>/CdS. Ce sont des détecteurs photovoltaïques ayant un rendement quantique de 70 % dans la région spectrale de 550 à 1 250 nm. Dans une configuration de cellule solaire, une conversion de puissance a été obtenue avec un rendement d'environ 12 %. A température ambiante, ces hétérodiodes sont électroluminescentes sous polarisation continue directe avec un pic vers 1 400 nm.

**Abstract.** — In our exploratory program on the device potential of ternary chalcopyrite type compounds, we have prepared CuInSe<sub>2</sub>/CdS heterodiodes. These diodes are 70 % quantum efficient photovoltaic detectors in the wavelength range from 550 to 1 250 nm. In a solar cell configuration a power conversion efficiency of ~ 12 % has been reached. The heterodiodes electroluminesce under cw forward bias at room temperature with a peak near 1 400 nm.

**1. Introduction.** — At wavelengths higher than about 1.1 μm silicon photodetectors become very inefficient. Because of low pulse dispersion and low attenuation [1] (Fig. 1) light in that wavelength regime is attractive as a carrier in optical communications. Detailed feasibility studies at  $\lambda > 1.1 \mu\text{m}$  will require new sources and new detectors. Using CuInSe<sub>2</sub> as the active semiconductor we have made an efficient and fast photovoltaic detector which, by virtue of its broad band response, is also an efficient solar cell.

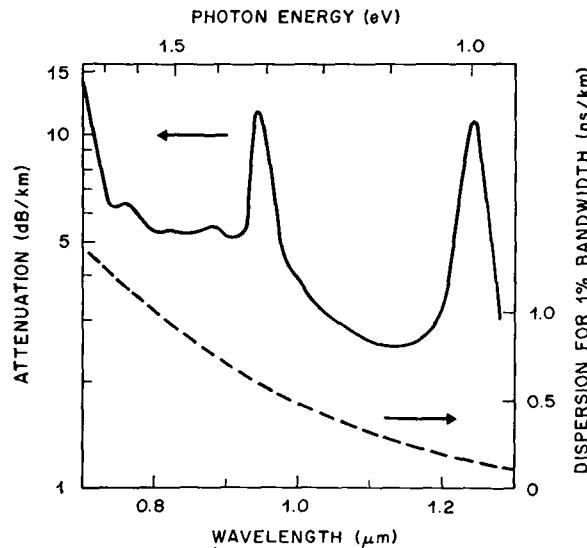


FIG. 1. — Lower part : pulse dispersion of an optical fiber.  
Upper part : attenuation in a low-loss, polymer-clad fused silica fiber [1].

In the p-CuInSe<sub>2</sub>/n-CdS heterodiode [2], the direct band gap of CuInSe<sub>2</sub> leads to a small ( $\sim 1 \mu\text{m}$ ) absorption length for shorter than band gap light. Minority carrier (electron) diffusion lengths, and lifetimes, may be comparatively short. Thus material with a relatively high density of defects, or with low crystalline perfection, can be used. In a heterodiode with a large gap top semiconductor the p-n junction can be located well below the device surface, thus removing the surface as a recombination site. An additional advantage is the low sheet resistivity of the top semiconductor, an important requirement for solar cells.

Materials for efficient heterodiode detectors and solar cells must meet several requirements simultaneously. By selecting p-type CuInSe<sub>2</sub> as a partner of n-type CdS, we take advantage of the gamut of electronic and crystallographic properties offered by chalcopyrite type compounds. The pair p-CuInSe<sub>2</sub>/n-CdS satisfies all criteria for a heterodiode :

- large window by virtue of the wide band gap of CdS,  $E_g(\text{CdS}) = 2.42 \text{ eV}$  (300 K) [3] ;
- direct bandgap of the absorbing semiconductor, CuInSe<sub>2</sub>,  $E_g(\text{CuInSe}_2) = 1.01 \text{ eV}$  (300 K) [5] which is in the energy range for optimum solar power conversion  $E_g = 1$  to  $1.5 \text{ eV}$  [4] ;
- p-type CuInSe<sub>2</sub> to take advantage of the high mobility of minority carrier electrons,  $\mu_e = 300$  to  $700 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ,  $\mu_h = 10$  to  $30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  [6, 7] ;
- low resistivity of p-CuInSe<sub>2</sub>,  $\rho \cong 0.5 \Omega\text{cm}$  [6, 7], permitting a low  $I \times R$  drop in the bulk semiconductor, and a high fill factor in solar cell operation ;

(\*) Bell Laboratories, Murray Hill, New Jersey 07974, U. S. A.

— compatible lattice structures and good lattice match between CuInSe<sub>2</sub> and CdS. Thus, the density of interface states is minimized. Interface states may act as traps or as generation — recombination sites leading to unsatisfactory diode performance. CuInSe<sub>2</sub> has virtually no tetragonal distortion, i. e.,  $c/a \cong 2.00$ . Therefore the geometry of the (112) face of CuInSe<sub>2</sub> is identical to that of the basal plane of CdS. The linear lattice mismatch,  $\Delta a/a$ , is only 1.2 %, calculated from a (CuInSe<sub>2</sub>) = 5.782 Å [8] and  $\sqrt{2} \times a$  (CdS, wurtzite) = 5.850 Å [9];

— the electron affinity  $\chi$  of the small gap p-type material is lower than that of the large gap n-type partner, with  $\chi$  (CuInSe<sub>2</sub>)  $\cong$  4.3 eV and  $\chi$  (CdS)  $\cong$  4.6 eV. However, the work function of p-CuInSe<sub>2</sub>,  $\varphi(p\text{-CuInSe}_2) \cong 5.2$  eV, is higher than that of n-CdS,  $\varphi(n\text{-CdS}) \cong 4.8$  eV. Therefore, no interfacial spike is formed in the conduction band [10]. Electrons photoexcited in the CuInSe<sub>2</sub> encounter no potential barrier in transit to the CdS.

**2. Preparation.** — CuInSe<sub>2</sub> substrates are prepared from crystals grown by controlled solidification of near-stoichiometric melts. Usually the free surface of these crystals is the selenium, or B, (112) face. The metal, or A (112), face and the selenium face can be identified by their etching behavior which is assumed identical to that of ZnGeP<sub>2</sub> and of AgGaS<sub>2</sub> [11]. In aqua regia or 0.5 to 5 vol. percent Br<sub>2</sub> in methanol the A face etches shiny, the B face mat. After cutting, the platelets are annealed for 24 hours at 600 °C in saturated selenium vapor for maximum p-type conductivity ( $\rho = 0.5 \Omega\text{cm}$ ,  $N_A - N_D \cong 1 \times 10^{18} \text{ cm}^{-3}$ ). They are then etched for 10 to 30 s. in cold aqua regia, rinsed with distilled water and with methanol, mounted on a substrate holder, and transferred to the CdS growth apparatus.

The CdS is grown from a coaxial isothermal source [12]. Cadmium and sulfur are effusing from separate containers within the same heater which is held at  $\sim 350$  °C. The effusion orifices are adjusted so that highly conducting ( $\rho \leq 0.1 \Omega\text{cm}$ ) CdS films are grown on substrates held between 130 and 210 °C. The substrates are a distance of 10 cm from the source but can be separated by a shutter. The apparatus is placed within an oil-free (Vacsorb and Vacion pumps) vacuum station with a glass bell jar. The CdS layer is grown at a rate of  $\sim 0.15 \mu\text{m}/\text{min}$ . to a thickness of 5 to 10  $\mu\text{m}$ . Typical background pressure during growth is  $\sim 1 \times 10^{-5}$  torr.

After CdS growth the back side of the CuInSe<sub>2</sub> substrate is polished with fine sandpaper, rinsed with methanol, and provided with a gold contact by application of AuCl<sub>3</sub> solution at 50 to 70 °C. Then a wire is attached to the Au with silver paste, or the entire back is silverpasted to a piece of copper sheet. For contact to the CdS a eutectic Ga-In alloy is wiped on, or In is soldered to the CdS. Either is connected to Au

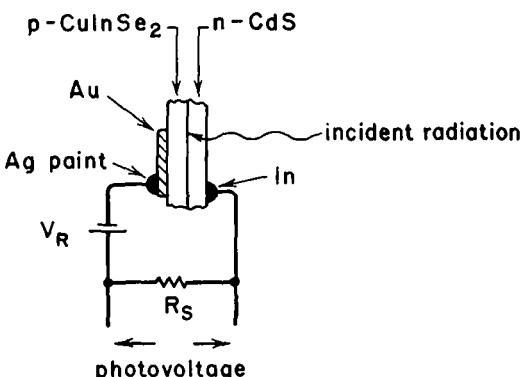


FIG. 2. — Sketch of a CuInSe<sub>2</sub>/CdS diode in a photodetector configuration. In a solar cell no external bias is applied.

wire. A schematic diagram of the diode in photodetector configuration is given in figure 2.

On solar cells antireflection coatings are prepared by evaporation of silicon monoxide from a baffled source boat held at 1100 °C. The SiO film growth is monitored *in situ*: the heterodiode is illuminated with a chopped He-Ne laser beam ( $\lambda = 0.633 \mu\text{m}$ ), and the voltage developed across an external resistor is lock-in amplified and recorded as a function of time. The SiO deposition rate is constant because the temperature of the SiO source is closely controlled. The photoresponse then varies sinusoidally as a function of time. In order to optimize the antireflection coating for  $\sim 0.8 \mu\text{m}$  light, the SiO layer is grown about 25 % longer than necessary for maximum photoresponse to 0.633  $\mu\text{m}$  light. The wavelength of 0.8  $\mu\text{m}$  corresponds more closely to the mean of the solar photon density distribution passing through the window of the CuInSe<sub>2</sub>/CdS cell (Fig. 3a and 3b).

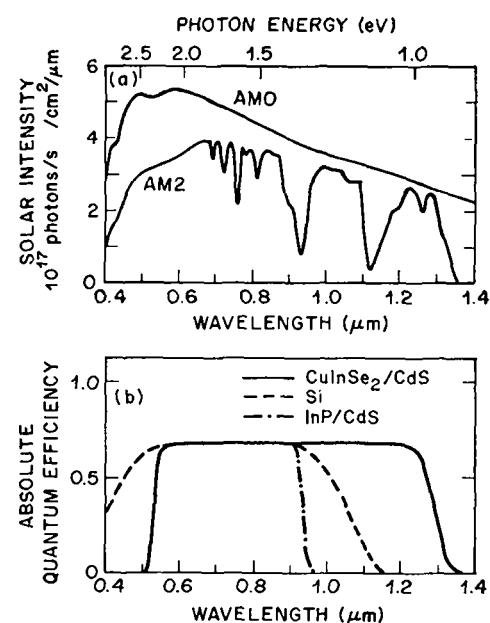


FIG. 3. — (a) Solar photon flux at air mass 0 and at air mass 2; (b) Spectral response of silicon, InP/CdS and CuInSe<sub>2</sub>/CdS detectors.

**3. Results and discussion.** — The absolute quantum efficiency as a function of wavelength of the CuInSe<sub>2</sub>/CdS diode without antireflection coating is displayed in figure 3b. Shown for comparison are the efficiency curves of a typical silicon photodiode and of the InP/CdS heterodiode [12]. The quantum efficiency is uniformly 70 % over the entire window, from 0.55  $\mu\text{m}$  (absorption in CdS) to 1.25  $\mu\text{m}$  (transmission through CuInSe<sub>2</sub>). Neither Au/n-CuInSe<sub>2</sub> Schottky barrier [7] nor n-p CuInSe<sub>2</sub> homojunction [13] detectors exhibit a uniformly high response over this broad a spectral range.

The CuInSe<sub>2</sub>/CdS detector is especially useful at  $\lambda > 1.1 \mu\text{m}$  where silicon detectors are not sufficiently sensitive. Beyond 1.1  $\mu\text{m}$  the attenuation curve of figure 1 was measured with CuInSe<sub>2</sub>/CdS.

Devices with small area and low space charge capacitance prove to be fast detectors. Figure 4 shows the pulse response of a device with 0.25 mm diameter excited with Ne laser ( $\lambda = 0.54 \mu\text{m}$ ) pulses. Taking account of an instrumental response time of  $\sim 5 \text{ ns}$ , the observed fall time is about 5 ns.

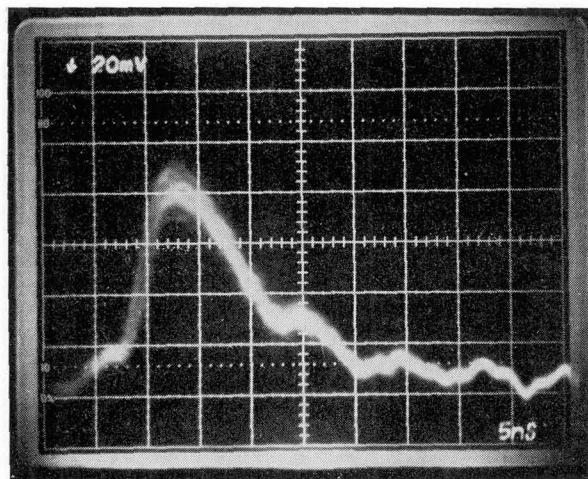


FIG. 4. — Response of a 0.25 mm diameter CuInSe<sub>2</sub>/CdS heterodiode excited with 0.54  $\mu\text{m}$  pulses.

Their broad-band spectral response (Fig. 3b) makes these diodes efficient solar cells. In early cells the power conversion efficiency was limited to  $\sim 5 \%$  [2]. These devices exhibited poor reverse resistance. During studies on small-area detectors microcracks were noticed in the CuInSe<sub>2</sub> substrates. When diodes are delineated by etching or by scribing so that these cracks are excluded from the active area, high reverse resistances ( $\sim 10 \text{ M}\Omega/\text{mm}^2$  at 1 V bias) and high solar efficiencies are observed. With antireflection coatings these devices with areas of about 1  $\text{mm}^2$  exhibit an open circuit voltage of 0.49 V, a curve fill factor of 0.60, and 12 % solar power efficiency on a clear day with  $\sim 92 \text{ mW/cm}^2$  insolation. Thus CuInSe<sub>2</sub>/CdS is one of the four existing solar cells with efficiencies over 10 %. The others are Si homo-

diodes, and GaAs/Ga<sub>x</sub>Al<sub>1-x</sub>As and InP/CdS heterodiodes. About 1 cm<sup>3</sup> large efficient solar cells should be feasible since it is known that large crack-free CuInSe<sub>2</sub> crystals can be grown by zone melting (Parkes and coworkers, ref. [7], and Bridenbaugh, unpublished).

The question of crystal growth leads to a closely related area where more work needs to be done. What is the nature of the native defects which are responsible for p- or n-type conductivity? Are they identical with, or tied to, the fast diffusing species which leads to a change in conductivity even at the low temperatures of CdS growth? This change is demonstrated by the capacitance-voltage characteristic of a heterodiode (Fig. 5). Close to the interface, the net acceptor concentration in CuInSe<sub>2</sub> has dropped from an initial value

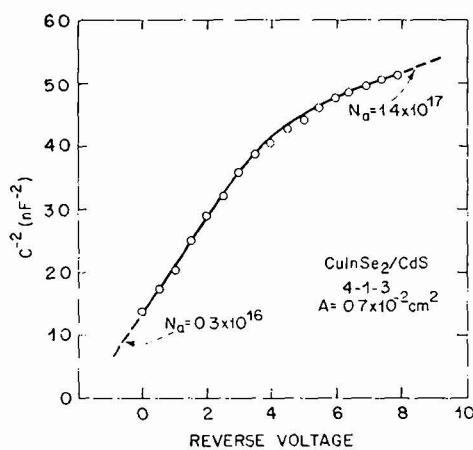


FIG. 5. — Capacitance (1/C<sup>2</sup>) — voltage characteristic of a CuInSe<sub>2</sub>/CdS diode showing depletion of acceptors near the interface.

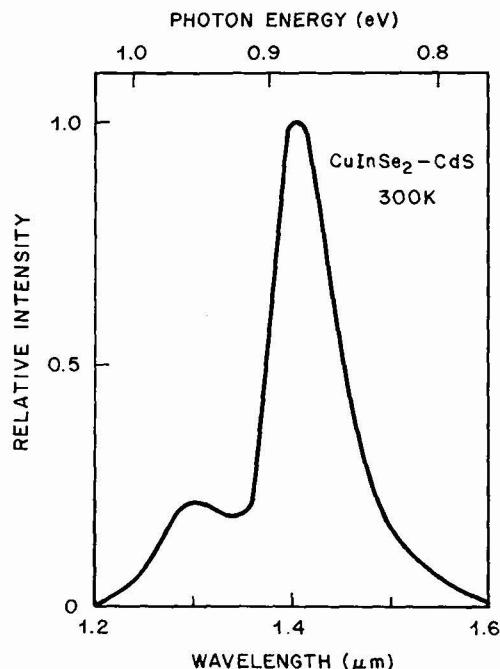


FIG. 6. — d. c. electroluminescence of a CuInSe<sub>2</sub>/CdS diode.

of  $\sim 1 \times 10^{18} \text{ cm}^{-3}$  to  $\sim 3 \times 10^{15} \text{ cm}^{-3}$ . There are indications that the rate of diffusion responsible for this drop depends strongly on the stoichiometry of the crystal.

The CuInSe<sub>2</sub>/CdS heterodiodes also electroluminesce at room temperature with an external quantum efficiency of about 10<sup>-4</sup>. Figure 6 shows the direct current luminescence spectrum. To date, we have not studied the electroluminescence in detail nor have we attempted to improve on the efficiency.

**4. Summary.** — The p-CuInSe<sub>2</sub>/n-Cds heterodiode has been proven to be an efficient and fast photodetector. It is one of the four solar cells with power efficiencies higher than 10 %. Its potential as a light emitting diode requires further study.

**Acknowledgments.** — We would like to acknowledge the competent assistance by Mrs. A. A. Pritchard and Messrs. L. M. Schiavone, F. A. Thiel and A. L. Albert.

### References

- [1] BLYLER, L. L. Jr, HART, A. C. Jr, JAEGER, R. E., KAISER, P. and MILLER, T. J., Technical Digest of the Topical Meeting on Optical Fiber Transmission, TuA5-1, Williamsburg, Va., Jan. 7-9 (1975).
- [2] WAGNER, S., SHAY, J. L., MIGLIORATO, P. and KASPER, H. M., *Appl. Phys. Lett.* **25** (1974) 434-5.
- [3] CARDONA, M., SHAKLEE, K. L. and POLLAK, F. H., *Phys. Rev.* **154** (1967) 696-720.
- [4] LOFERSKI, J. J., *J. Appl. Phys.* **27** (1956) 777-784.
- [5] SHAY, J. L., TELL, B., KASPER, H. M. and SCHIAVONE, L. M., *Phys. Rev. B* **7** (1973) 4485-90, Fig. 6 and 8.
- [6] TELL, B., SHAY, J. L. and KASPER, H. M., *J. Appl. Phys.* **43** (1972) 2469-70.
- [7] PARKES, J., TOMLINSON, R. D. and HAMPSHIRE, M. J., *Solid State Electron.* **16** (1973) 773-7.
- [8] PARKES, J., TOMLINSON, R. D. and HAMPSHIRE, M. J., *J. Appl. Cryst.* **6** (1973) 414-6.
- [9] REEBER, R. R. and KULP, B. A., *Trans. Met. Soc. AIME* **233**, (1965) 698-702.
- [10] MILNES, A. G. and FEUCHT, D. L., *Heterojunctions and Metal-Semiconductor Junctions* (Academic Press, New York) 1972.
- [11] ABRAHAMS, S. C., BARNS, R. L., BERNSTEIN, J. L. and TURNER, E. H., *Solid State Commun.* **15** (1974) 737-9.
- [12] WAGNER, S., SHAY, J. L., BACHMANN, K. J. and BUEHLER, E., *Appl. Phys. Lett.* **26** (1975) 229-30.
- [13] YU, PH. W., FAILE, S. P. and PARK, Y. S., *Appl. Phys. Lett.* **26** (1975) 384-5.