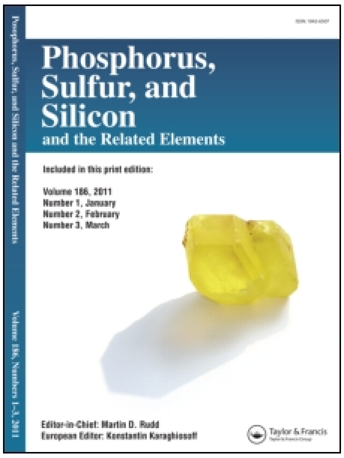

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

CHALLCOGENIDE PHOTOVOLTAIC SOLAR CELLS OF SPECIAL INTEREST

Clifford H. Champness[a]
[a] McGill University, Montreal, P.Q., Canada

To cite this Article Champness, Clifford H.(1988) 'CHALCOGENIDE PHOTOVOLTAIC SOLAR CELLS OF SPECIAL INTEREST', Phosphorus, Sulfur, and Silicon and the Related Elements, 38: 3, 385 — 397
To link to this Article: DOI: 10.1080/03086648808079733
URL: http://dx.doi.org/10.1080/03086648808079733

Phosphorus and Sulfur, 1988, Vol. 38, pp. 385–397
Reprints available directly from the publisher
Photocopying permitted by license only

CHALCOGENIDE PHOTOVOLTAIC SOLAR CELLS OF SPECIAL INTEREST

CLIFFORD H. CHAMPNESS
McGill University, 3480 University St., Montreal, P.Q.,
Canada, H3A 2A7

Abstract A brief review is given of those semiconducting selenides and tellurides that appear suitable for the absorber layer of a photovoltaic solar cell, with energy gaps in the range 1 to 2 eV. Furthermore, to obtain a lower cost cell, the semiconductor is also required to be used in the form of a thin polycrystalline film, necessitating a high optical absorption coefficient in the material. At the present time the two best chalcogenides meeting these requirements are the compounds $CuInSe_2$ and $CdTe$, both of which have been used in polycrystalline thin film structures with CdS, as the window layer, yielding conversion efficiencies of over 10%. They have also demonstrated very good chemical stability .

INTRODUCTION

The photovoltaic solar cell is a simple device, which converts radiant energy directly into electrical energy. Research on such cells has greatly increased in the past two decades because of the need for alternate non-fossil fuel energy sources for terrestial and space use. The most successful semiconductor for use in solar cells has been crystalline silicon, where devices with over 15% conversion efficiency are available commercially and over 20% has been obtained in the laboratory. However, a thickness of some 100 micrometers of silicon is required to obtain good performance and, since the material cost is an important part of the cost of a cell, this keeps the price above that of other competing energy source methods. Never-the-less, there are suitable substances which have much higher optical absorption coefficients, and in these, the photocurrent can be generated in a few micrometers of material, so that only a small amount of semiconductor is used. These substances can therefore be used for thin film solar cells, where the cost of the material is low. In some cases, these materials are selenides and tellurides and it is the object of this paper to review those of them that are likely to be the most useful. In this regard, it should be pointed out that although practically all semiconducting chalcogenides will show photovoltaic action in a junction arrangement, very few have the potential to be useful solar cells.

BASIC SOLAR CELL CONCEPTS

A photovoltaic cell is a semiconductor structure containing a built-in strong electric field region, which can be reached by mobile electrons or holes generated in the material by incident light. This region can be formed by a pn homojunction, a pn heterojunction or a Schottky junction. A conventional photovoltaic homojunction cell, such as that using crystalline silicon, consists (Fig.1) of a layer of n-type semiconductor, with a thickness of less than a micrometer, on a layer of p-type semiconductor with a thickness of more than 50 micrometers. Incident light, with a photon energy, $h\nu$, greater than the energy gap (E_G) of silicon (1.1 eV), creates electron-hole pairs in the material over a depth approximately equal to the reciprocal of the optical absorption coefficient. Here, h is Planck's constant and ν is the frequency of the light. The minority holes in the n-layer and the minority electrons in the p-layer diffuse to the junction region, where the built-in electric field sweeps them across, to create the photocurrent, which is observed from terminals attached to the two layers. On the illuminated side, the metal contact is usually in the form of a grid for collecting the current but allowing light to pass through it to the junction. If the n-layer and the p-layer are both of the same semiconductor, it is called a homojunction but if they consist of different semiconductors, it is called a heterojunction. Since most of the photons are absorbed in the base layer (the p-layer in Fig.1), this is often called the absorber, while the first layer through which the light passes is frequently called the window.

In the case of a homojunction solar cell, it can be shown for ideal conditions that the optimum energy gap is around 1.5 eV, as indicated in Fig. 2. Physically, the reason for this is that if E_G is too large, then most of the solar spectrum is lost, since only photons with energy $h\nu$ larger than E_G can create electron-hole pairs. If, on the other hand, E_G is too small, the field in the junction depletion region is low, yielding a small open circuit voltage and a reduced conversion efficiency. For a thin film solar cell, another requirement is that the optical absorption coefficient must be high, so that the photocarriers are generated in a sufficiently short distance. This usually means that the energy gap must be direct, that is, the conduction band minimum must be at the same electronic wave vector k as the valence band maximum. The absorption coefficients for several semiconductors as a function of photon energy are compared in Fig. 3.

SELENIDES AND TELLURIDES FOR PHOTOVOLTAIC ABSORBERS

For the absorber layer of a thin film solar cell, the semiconductor should preferably have a direct energy gap in the range 1 to 2 eV. An exact E_G value at the maximum of the curve in Fig. 2 is not necessary because of the non-ideal features of actual cells, such as series and shunt resistance for example. The window material, on the other hand, should have a wide energy gap and should match the absorber in lattice parameter and electron affinity.

While there are a large number of semiconducting selenides and tellurides, many are not suitable for solar cell absorbers because their energy gaps lie outside the acceptable range or because rare metals are involved. Elemental tellurium, for example, does not qualify because its energy gap of 0.3 eV is too small. Table I is therefore a list of those materials with suitable E_G values on which some interesting photovoltaic results have already been obtained. The conversion efficiencies quoted are those obtained on small area devices (about 1 cm^2) under an illumination of 100 mW/cm^2.

Leaving out for the moment the first two materials in Table I ($CuInSe_2$ and $CdTe$), the next four compounds, when incorporated in cell structures, have yielded efficiencies in the range 5 to 8% in the last few years. Such values are promising, considering their early stage of development. Of these, the most work seems to have been done on $CdSe$ by researchers at Battelle, Frankfurt[4,5]. These workers have constructed a metal-insulator-semiconductor cell of the form $Au - ZnSe - CdSe$, as shown in Fig.

4, where the $ZnSe$ is a very thin, high resistance layer. Further development of cells with $CdSe$ and the other semiconductors in Table I is expected. However, the greatest amount of work has been done on structures using $CuInSe_2$ and $CdTe$, and these are now described separately.

CADMIUM TELLURIDE

Cadmium telluride is a II-VI semiconductor with a zinc blende crystal structure. It has an energy gap of nearly 1.5 eV, which is close to the ideal value for a homojunction solar cell. Since the energy gap is direct, it has a high absorption coefficient approaching 10^5 cm^{-1}, so that photocarriers are generated within a distance of less than a micrometer of the surface on which light is incident. It is thus very suitable for a thin film solar cell. Moreover, polycrystalline rather than single crystal films can be used, provided the minority diffusion length is greater than the grain size, which is easily achieved; the grain size itself must also be sufficiently large.

Despite the near-ideal energy gap, homojunctions of $CdTe$ have not yielded high conversion efficiencies. However, much greater success has been obtained using p-type $CdTe$ as the absorber in a heterojunction with window materials such as CdS, SnO_2 and indium-tin-oxide (ITO). Most work has been done on a $nCdS - pCdTe$ heterojunction, where there is a lattice mismatch of 11% but a relatively small difference in electron affinities, implying a small discontinuity in the conduction band edge at the junction. Not only has the $CdS - CdTe$ structure given higher efficiency than the earlier developed CdS-Cu_2S cell but it has also shown greater chemical stability.

Techniques for depositing thin films of $CdTe$ include hot wall vacuum evaporation[10], chemical vapour deposition[2], electrodeposition[11], spray pyrolysis[12], screen printing[13] and close space sublimation (CSS)[1,2] . With the CSS method, workers at Southern Methodist University[2] and at Kodak[1] have prepared cells with a conversion efficiency of more than 10%. Fig. 5 shows schematically the layer structure of a cell and Fig. 6 shows a schematic view of the system for the CSS method, in which the substrate and source of $CdTe$ are placed within a millimeter of one another. Both are heated externally by quartz lamps and, with the source at a higher temperature, atoms are deposited on to the substrate at a rate determined by the gas pressure in the reaction tube. To obtain the maximum efficiency of the cell, Kodak workers[1,14] found that it was necessary to have sufficient oxygen present; if the oxygen pressure was too low, the cell had a low efficiency with a buried homojunction in the $CdTe$, that is the p to n transition occurred inside the $CdTe$ and not at the interface with the CdS. With increase of oxygen pressure, the junction was moved nearer to the interface.

A technique which is more suitable for low cost mass production would appear to be screen printing. Using this method, Matsushita workers[13] have reported an efficiency of over 12% for small areas and some 5%[15] for areas of 30 x 30 cm^2. Other economic methods are electrochemical deposition[11] and spray pyrolysis[12], where efficiencies of 9 and 4% respectively have been reported.

One of the more important technical problems with $CdTe$ appears to be making low resistance ohmic contacts to the p-type material because of its high work function. However, special surface treatments and Sb-doping have permitted researchers to obtain satisfactory contacts. With further progress, it thus appears that $CdTe$-based structures are promising candidates for thin film polycrystalline solar cells.

COPPER INDIUM DISELENIDE

Copper indium diselenide is a semiconductor with a chalcopyrite crystal structure, which maintains the tetrahedral bonding of the related zinc blende structure. It has the highest optical absorption coefficient of any semiconductor (see Fig. 3) with a very steep absorption edge. This makes it ideally suited for a thin film polycrystalline photovoltaic absorber. While $CuInSe_2$ has a direct energy gap of just over 1 eV, which is somewhat small for a homojunction cell, it has yielded an efficiency of more than 12% as the p-type absorber in a heterojunction cell with n-type CdS as the window material. The lattice mismatch in this case is only about 1%, which means that a relatively low density of states arises at the interface with resultant small loss of photocurrent through interface recombination. Excess of selenium in $CuInSe_2$ makes it p-type and a deficiency n-type; a sufficient excess of indium also makes it n-type. With excess of copper, a second phase of Cu_2Se appears. However, as the phase diagram[16] shows (Fig.7), the single phase chalcopyrite is maintained with excess of several percent of indium. The elements Cu, Zn, Cd, Bi, Cl and Br have been reported as donors in the chalcopyrite and P as an acceptor.

Thin film polycrystalline $nCdS$-$pCuInSe_2$ cells have been fabricated by many methods, including triple evaporation[7,8], reactive[17] and nonreactive[18] sputtering and electrolytic deposition[19,20,21]. However, the most successful of these so far has been the co-evaporation method developed at the Boeing Aerospace Company[7,8]. In this method, the chalcopyrite is deposited as a double layer from separate sources of the three elements on to a molybdenum-coated alumina substrate. The layer structure is shown in Fig. 8. To obtain the best performance, the first deposited layer must be copper-rich with low resistivity, while the second layer should be more stoichiometric with higher resistivity. Similarly, the first layer of $CdZnS$ deposited on the chalcopyrite is undoped and of high resistivity and the second layer is indium-doped and of low resistivity. Thus, the low resistivity semiconductors adjacent to the metal films ensure low resistance contacts and the high resistivity "inner" layers ensure good junction integrity at the interface between the two semiconductors. It is also found necessary to heat-treat the cells to obtain the best performance. As in the $CdS - CdTe$ cell, oxygen plays an important role, and again a buried homojunction occurs if insufficient oxygen is present. With oxygen treatment, the junction, located by electron beam induced current (EBIC), is found to move towards the $CuInSe_2/CdS$ interface and higher efficiency is obtained. Fig. 9 shows a current-voltage characteristic of a Boeing $CdZnS - CuInSe_2$ cell[8] under illumination of 100 mW/cm^2 from a xenon lamp. With this form of cell, Boeing has obtained an illuminated short circuit current density of 41 mA/cm^2, which is the highest value obtained on any single junction photovoltaic cell. The $CuInSe_2$-based cell has also been shown to have excellent chemical stability and does not suffer from the performance degradation under continuous illumination found with amorphous silicon cells.

While the triple evaporation process has produced the best cells, it may not be the most economic method for large scale commercial production. Therefore, alternative methods of deposition are under active investigation. The most promising of these are: electrolytic deposition of copper and indium, followed by selenization in H_2Se (7% efficiency)[19], reactive sputtering of copper and indium in H_2Se (6%)[17] and single step electrolytic deposition (4%)[20].

While improvements in the processing and changes in the composition of the chalcopyrite could produce higher efficiencies, an increase in the energy gap of the window material should also benefit performance. To this end, efforts are being made to replace CdS (E_G = 2.4 eV) with $ZnSe$ (E_G = 2.8 eV)[22] or ZnO (E_G = 3.2 eV)[23]. Fig.10 shows the spectral response of a $ZnO - CdS - CuInSe_2$ cell[23], where the CdS is a very thin layer (50 nm) of high resistivity material. It is seen by comparison with a cell, made using the usual In-doped CdS, that the device with the ZnO window exhibits an extension of the response to shorter wavelengths. Thus, the attempt to use wider gap window materials may present opportunities to other selenides and tellurides with E_G-values larger than 2 eV.

TANDEM CELLS

The energy in the solar spectrum, can in principle, be more fully exploited with a cascade of solar cells operating over successive wavelength ranges by using semiconductors with different energy gaps. For example, a two-terminal tandem cell is under development at the Institute of Energy Conversion, University of Delaware[24], consisting of a $CdS - CdTe$ cell and a $CuInSe_2$ cell sandwiched together, as indicated in Fig. 11. As light passes though them, higher energy photons are absorbed in the first cell and lower energy photons in the second. Another tandem cell (four-terminal) being developed at ARCO Solar Inc.[25] consists of a cell based on amorphous silicon, together with a $CuInSe_2$-based cell. For this structure an efficiency of 13.1% has already been reported.

REQUIREMENTS FOR PRACTICAL SOLAR CELLS

The requirements for a practical solar cell are high efficiency, long term stability under illumination and low cost of production. So far these requirements have not been met but important progress towards them has been made with the chalcogenides $CdTe$ and $CuInSe_2$. For these two materials, the long term cost targets established by the Solar Energy Research Institute, Colorado[26] are $30 per m^2 for modules and $50 per m^2 for cascade modules. To reach these targets, active area efficiencies of 17% are required at AM 1.5.

Se-CdO CELL

While the $Se - CdO$ cell, as indicated in Table I, has a solar conversion efficiency well below that required for a practical solar cell, it has despite this, been a successful commercial device for about half a century. This is because of its application in photometry for measuring illumination levels, arising principally from the fact that its spectral response is similar to that of the human eye. It is also quite sensitive at low light levels and is relatively cheap to manufacture. At AM1 illumination, the efficiency of commercial photometry cells is much less than 1% but through optimization of the fabrication processes, laboratory cells[9] have been made with nearly 2%, with the possibility of still higher performance.

SUMMARY

In summary, it would appear that $CuInSe_2$ and $CdTe$ are promising candidates for polycrystalline thin film solar cells for use in consumer electronics applications or solar cells. With further research, other selenides and tellurides may also prove to be useful for photovoltaic applications.

REFERENCES

1. Y. S. Tyan and E. A. Perez-Albuerne, Conf. Record 16th IEEE Photovoltaic Specialists Conf., San Diego, (1982), p.794.
2. T.L. Chu, S.S. Chu and S.T. Ang, Conf. Record 19th IEEE Photovoltaic Specialists Conf., New Orleans, (1987).
3. M. Ch. Lux-Steiner, R. Späh, M. Obergfell, E. Bucher, H. W. Schock and J. Kimmerle, Proc. of 2nd. Int. Photovoltaic Sci. and Eng. Conf., Beijing, (1986), p.600.
4. E. Rikus and D. Bonnet, Conf. Record 15th IEEE Photovoltaic Specialists Conf., Kissimmee, (1981), p. 1073.
5. E. Rikus and H. Richter, Proc. 6th E.C. Photovoltaic Solar Energy Conf., (D. Reidel Pub. Co., 1985), p. 856.
6. A. Segura, J.L. Valdes, A. Cantarero, F. Pomer, J.P. Martinez, B. Mari and A. Chevy, Proc. 6th E.C. Photovoltaic Solar Energy Conf., (Reidel Pub. Co., 1985), p. 773.
7. R.A. Mickelsen and W.S. Chen, Conf. Record 15th IEEE Photovoltaic Specialists Conf., Kissimmee (1981), p. 800.
8. W. E. Devaney, R. A. Mickelsen and W. S. Chen, Conf. Record 18th IEEE Photovoltaic Specialists Conf., Las Vegas, (1985), p. 1733.
9. C. H. Champness, J. K. Chen and K. Ghoneim, Conf. Record 17th IEEE Photovoltaic Specialists Conf., Kissimmee, (1984), p. 933.
10. T. Anthony, C. Fortmann, W. Huber, R. H. Bube and A. Fahrenbruch, Conf. Record 17th IEEE Photovoltaic Specialists Conf., Kissimmee, (1984), p. 827.
11. B.M. Basol, J. Appl. Phys., 55, 601 (1984).
12. H.B. Serreze, S. Lis, M.R. Squillante, R. Turcotte, M. Talbot and G. Entine, Conf. Record 15th IEEE Photovoltaic Specialists Conf., Kissimmee, (1981), p. 1068.
13. S. Ikegami, H. Matsumoto, H. Uda, Y. Komatsu, A. Nakano and K. Kuribayashi, Proc. 5th E.C. Photovoltaic Solar Energy Conf., Athens, (1983), p. 740.
14. Y.S. Tyan, F. Vazan and T.S. Barge, Conf. Record 17th IEEE Photovoltaic Specialists Conf., Kissimmee, (1984), p. 840.
15. H. Matsumoto, A. Nakano, Y. Komatzu, H. Uda and S. Ikegami, Tech. Digest 1st Int. Photovoltaic Sci. and Eng. Conf., Kobe, (1984), p. 393.
16. L.S. Palatnik and E. I. Rogacheva, Soviet Phys., Dokl. Akad Nauk., 12, 503 (1967).

17. T.C. Lommasson, H. Talieh, J.D. Meakin and J.A. Thorton, Conf. Record 19th IEEE Photovoltaic Specialists Conf., New Orleans, (1987).

18. J.H. Erner, R.B. Love, A.K. Khanna, S.C. Lewis and F. Cohen, Conf. Record 18th IEEE Photovoltaic Specialists Conf., Las Vegas, (1985), p. 1655.

19. V.K. Kapur, B.M. Basol and E.S. Tsang, Conf. Record 18th IEEE Photovoltaic Specialists, Conf., Las Vegas, (1985), p. 1429.

20. I. Shih and C.X. Qiu, Conf. Record 19th IEEE Photovoltaic Specialists Conf., New Orleans, (1987).

21. F.J. Pern and R. Noufi, Conf. Record 19th IEEE Photolvoltaic Specialists Conf., New Orleans, (1987).

22. A. Nouhi, R.J. Stirn and A. Hermann, Conf. Record. 19th IEEE Photovoltaic Specialists Conf., New Orleans, (1987).

23. R. R. Potter, C. Eberspacher and L. B. Fabick, Conf. Record. 18th IEEE Photovoltaic Specialists Conf., Las Vegas, (1985), p. 1659.

24. J.D. Meakin, R.W. Birkmire, L.C. DiNetta, P.G. Lasswell and J.E. Phillips, Solar Cells, **16**, 447 (1986).

25. D.L. Morel, K. Mitchell, R. Wieting, R. Potter, C. Eberspacher, D. Tanner and C. Fairchild, Conf. Record 18th IEEE Photovoltaic Specialists Conf., Las Vegas, (1985), p. 876.

26. K. Zweibel, H. Ullal and R. Mitchell, Conf. Record 19th IEEE Photovoltaic Specialists Conf., New Orleans, (1987).

TABLE I

Selenides and Tellurides suitable for Photovoltaic Absorbers

Semiconductor	Energy Gap (eV)	Conductivity Type	Cell Structure (and AM1 Efficiency*)	Ref.
$CuInSe_2$	1.04 (direct)	p,n	$nCdZnS - pCuInSe_2$ (12%)	7,8
$CdTe$	1.5 (direct)	p,n	$nCdS - pCdTe$ (10.5%)	1,2
$CdSe$	1.7 (direct)	n	$Au - ZnSe - nCdS$ (7.2%) (M.I.S. cell)	4,5
$InSe$	1.3	p,n	I.T.O.–$pInSe - Au$ (8%)	6
WSe_2	1.2/1.3	p,n	I.T.O.–$pWSe_2$ (6.8%)	3
Cu_2Se	1.3	p	$CdS - Cu_{2-x}Se$ (5.4%)	
Se	1.85 (indirect)	p	$CdO - Se$ (1.5%)	9

* Small area efficiency (~ 1 cm^2)

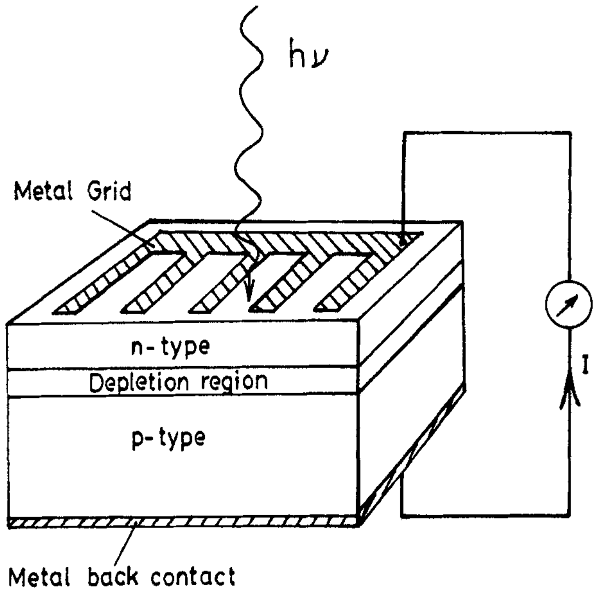

Fig.1 Schematic view of a pn-junction solar cell.

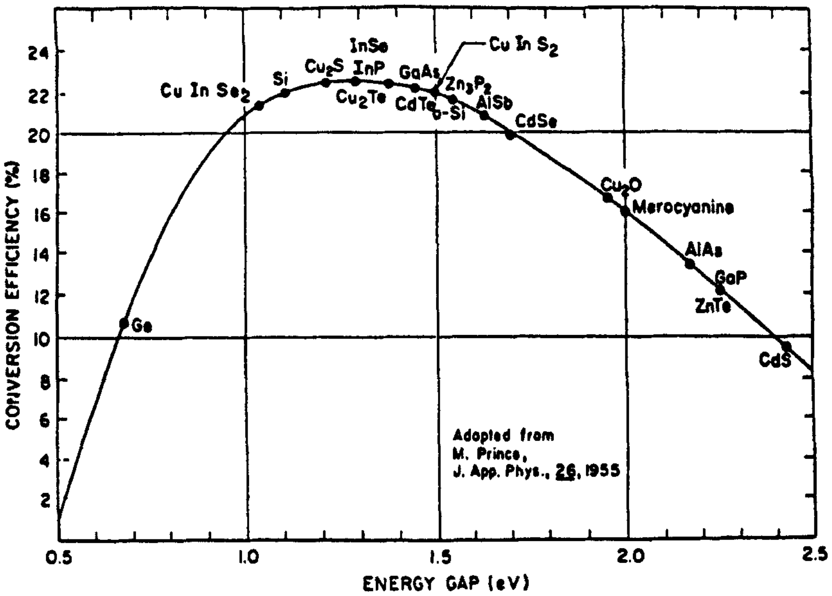

Fig.2 Theoretical variation of solar conversion efficiency with energy gap for ideal homojunction cells.

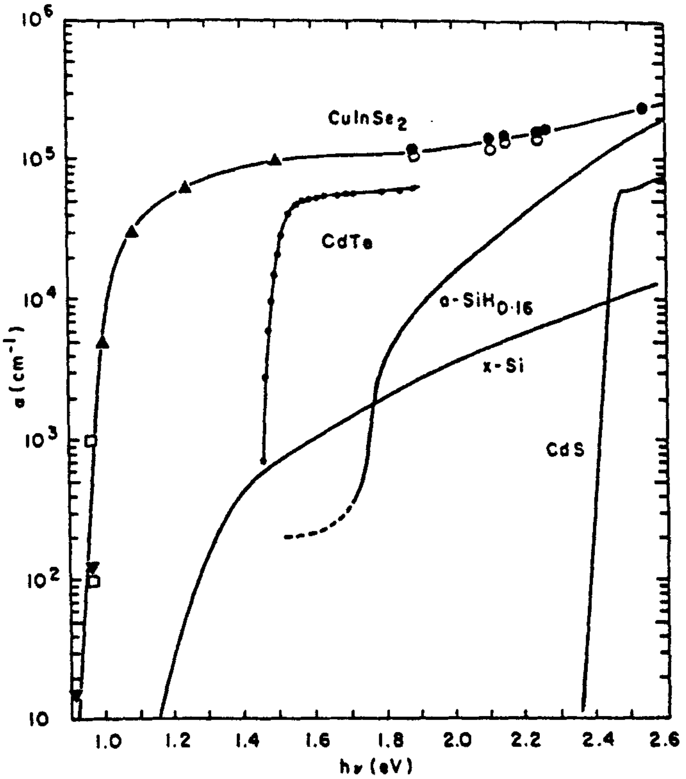

Fig.3 Variation of optical absorption coefficient with photon energy for several semiconductors.

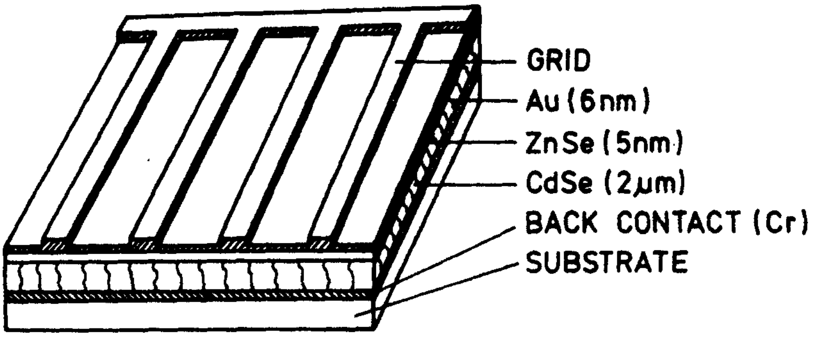

Fig.4 Schematic view of a CdSe metal-insulator-semiconductor cell fabricated by Battelle Institute, Frankfurt (refs. 4,5).

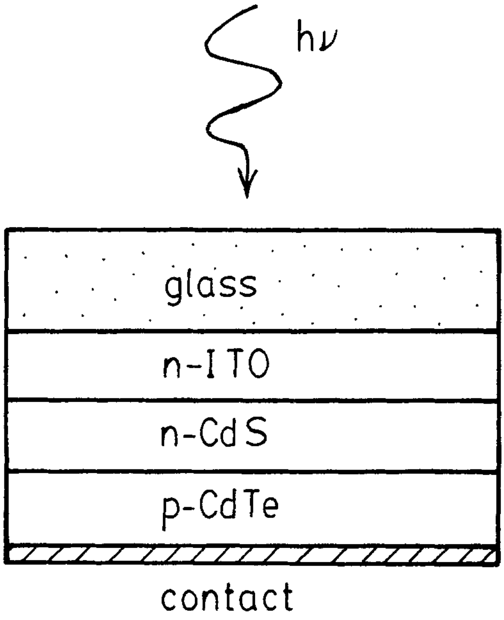

Fig.5 Schematic view of the layer structure of a thin film CdS-CdTe cell.

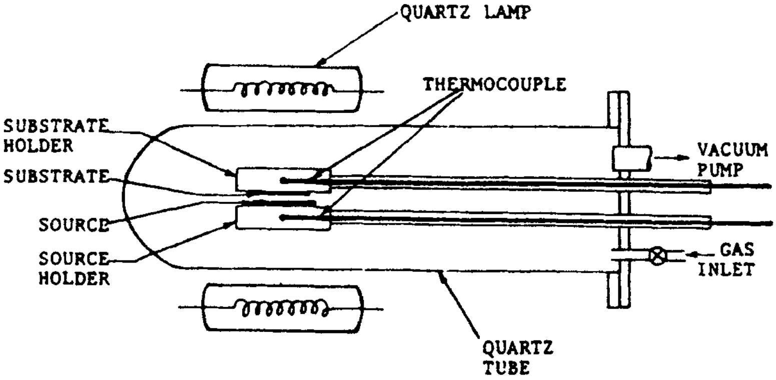

Fig.6 Schematic diagram of the close-spaced sublimation apparatus used for deposition of CdTe films (ref.2).

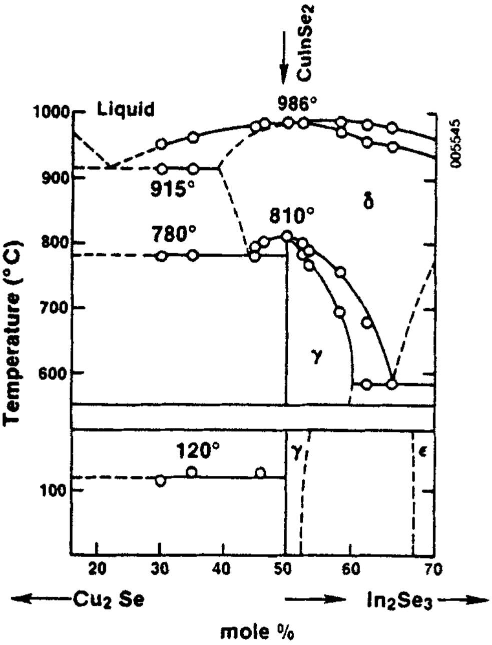

Fig.7 Pseudobinary phase diagram for the Cu_2Se-In_2Se_3 system according to ref.16.

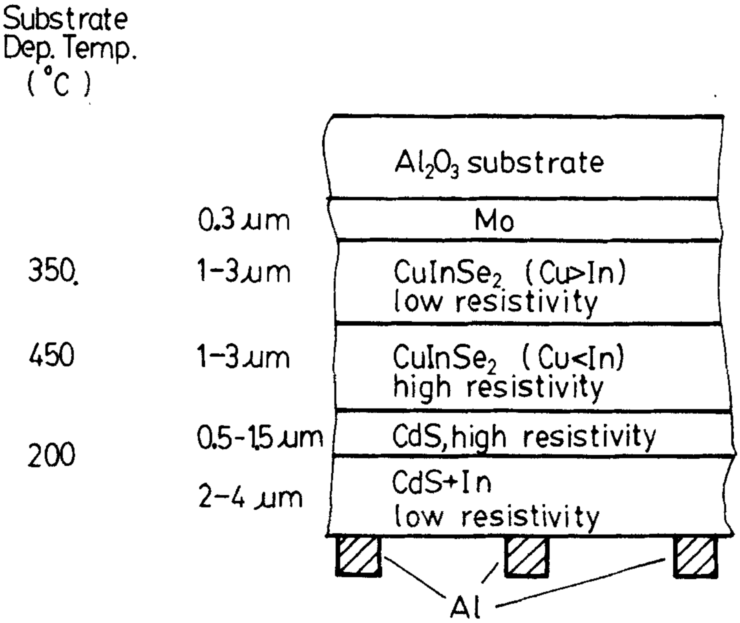

Fig.8 Layer structure of the CdZnS-$CuInSe_2$ cell developed by Boeing (refs. 7,8).

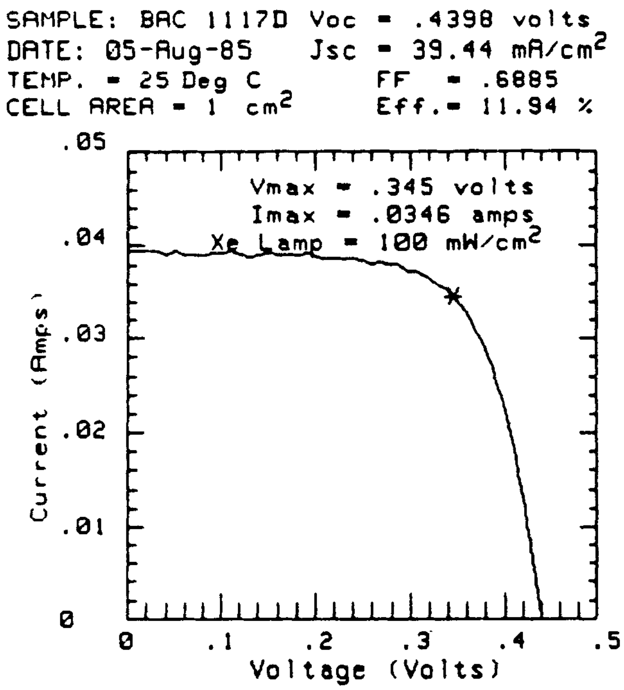

Fig.9 Illuminated current-voltage characteristic of a CdZnS-CuInSe$_2$ cell fabricated by Boeing (ref. 8).

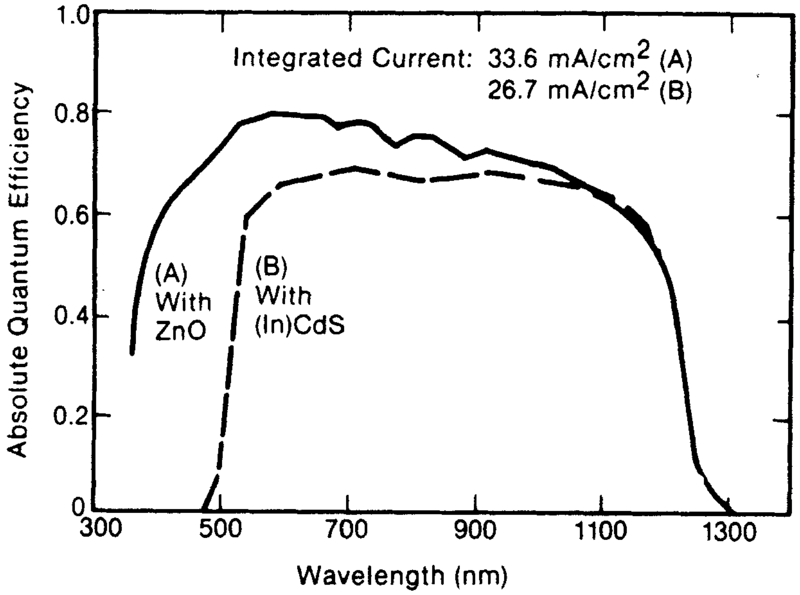

Fig.10 Spectral response of two CuInSe$_2$ cells, one with a ZnO window and the other with an In-doped CdS window, fabricated by ARCO Solar (ref. 23).

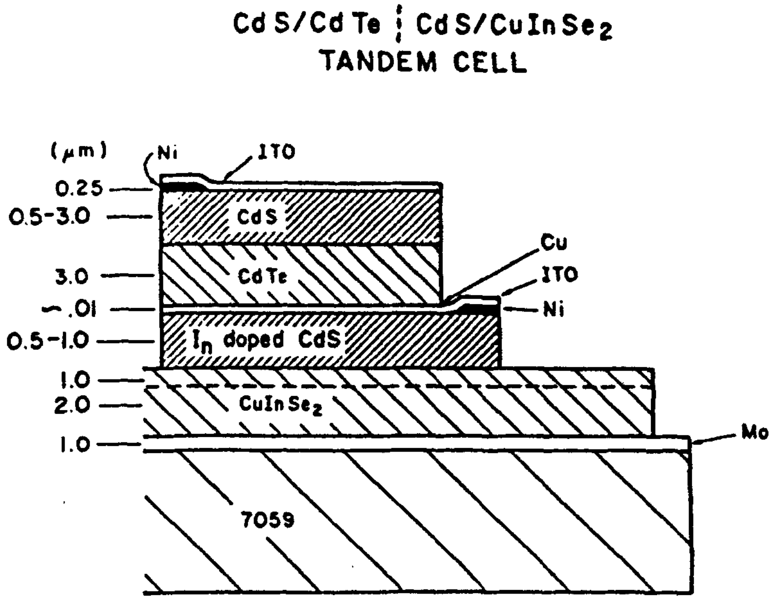

Fig.11 Schematic diagram showing the structure of a tandem cell under study at the University of Delaware (ref. 24) using CdTe and CuInSe$_2$.