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A REVIEW OF ECONOMIC AND TECHNOLOGICAL REQUIREMENTS OF SOLAR CELLS:

STATUS AND RESEARCH DIRECTIONS OF POLYCRYSTALLINE THIN FILM DEVICES*

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CONTENTS

Abstract

In this paper, the author discusses the arguments in favor of development of thin film solar cells, and the areas which pose problems to their development. Of the many materials combinations investigated, only CdS/Cu_2S, $CdS/CuInSe_2$ and $CdS/CdTe$ polycrystalline thin film polycrystalline cells have demonstrated efficiencies greater than 10%. Of these the first has effectively been abandoned, at least in the USA and discussion will be limited to these latter two.

The key factors governing the success of all solar cells are their cost, their efficiency and their stability. The cost of cells is governed by several factors, probably the most important of which is the capital equipment involved in their production. Examples are given of equipment in use at present and the potential for scale-up is discussed. The efficiency of cells can be described by fairly simple theory involving basic material and device parameters. Although the above materials largely meet the criteria, the devices themselves depend on other factors and it is pointed out that major improvement in the $CdS/CuInSe_2$ cells depend on reduction of the reverse saturation current. In the case of the $CdS/CdTe$ cells, prospective improvements depend on improved contacting to the CdTe. The long term electrical stability of cells is governed by the physical and chemical stability of the various components involved in the device construction. There is limited experience in this area; laboratory cells appear not to have a stability problem, whereas field tested cells have shown degradation of A.R. coatings and electrical contacts.

Finally, the problem areas relating to these cells, and promising future research directions are indicated. The latter include the problem of low open

circuit voltage in CdS/CuInSe$_2$, contacts to p-type CdTe, the development of p-type window layers, and research on cascaded thin film devices.

Introduction

For solar cells to make a large impact on the provision of electricity for terrestrial consumption, it seems inevitable that the thin film device will need to be successfully developed. The relatively high cost of single crystal silicon mitigates against its ever achieving cost competitiveness with conventionally generated electricity, except perhaps in remote areas where the comparison would be with diesel generators. In the medium term future, it is also possible that systems based on optical concentration of the solar flux onto highly efficient cascade cells utilizing sophisticated ternary and/or quaternary III-V alloy semiconductors, will have a substantial impact. Indeed, such systems may well prove to be the long term preferred option provided that satisfactory solutions can be found to the many fundamental and engineering problems. However, the possible success of the concentrator systems does not exclude other photovoltaic generators unless they prove to have a significant economic advantage. Since we are certainly not presently in a position to demonstrate with any degree of certainty whatsoever that this will prove to be the case, the sensible strategy, for the time being, is to pursue all practicable options. Thin film polycrystalline solar cells have made significant progress in recent years and three materials combinations have exceeded conversion efficiencies (whenever this term is used, it can be presumed that measurements have been made at 28°C, using the AM1.5 direct spectrum, normalized to 100.mWcm^{-2}; and under the atmospheric conditions defined in NASA TM 73702 (1) of 10%. The three devices are CdS/Cu$_{2-x}$S, CdS/CuInSe$_2$ and CdS/CdTe; and of these research on the first (at least in the USA) has largely been discontinued because of obdurate problems of stability. Of course, the efficiency of cells based on a-Si:H has also exceeded 10% (2) but these will not be discussed here since it is the intention to concentrate on polycrystalline devices and, in particular, on those based on CdS/CuInSe$_2$ and on CdS/CdTe. In fact, we shall be examining the various criteria for viability of thin film cells in general but will

attempt to illustrate the points by reference to these particular devices. Firstly, we shall examine the overall case for the expenditure of large sums of money on the development of thin film solar cells in terms of their economic prospects, next we shall discuss what properties are required of the materials and devices, thirdly we shall discuss the present status of $CdS/CuInSe_2$ and $CdS/CdTe$ cells, and finally, we shall point out those problems which presently appear to be the limiting factors and the research directions which are being followed in the hope of overcoming the problems and realizing the objective of technically and economically viable polycrystalline solar cells for large scale terrestrial utilization.

The Economics Thin Film Solar Cells

Thin film solar cells have several economic strengths and weaknesses which are generally balanced against each other in a costs/benefits analysis to show that the technology either is, or is not, likely to achieve cost-competitiveness with either methods of generating electricity. We shall briefly examine these arguments.

The arguments are usually based on a comparison with the costs associated with the production of single crystal cells. The actual cost of an individual cell depends on a number of factors, some of which can be estimated with reasonable accuracy. For example, having decided on the particular fabrication technique, one might then estimate the throughput of cells, (meters^2 per year), the capital cost and lifetime of the equipment, the efficiency of the cells, the labor cost, and whether single or double shift operation would be required. In addition to these more or less well known numbers, would be less tangible factors such as the prevailing discount rate (which is subject to large fluctuations), whether or not the capital was to be borrowed and the duration of the loan, maintenance costs, and the cost of the factory (and whether it would be rented or purchased). Furthermore, the total size of the market and the estimated share likely to be acquired by an individual company, plus their required return on investment, would affect the decision whether or not to compete in the field. Despite these many complicated factors, the claim is usually made that thin film production techniques are capable of yielding devices at a cost which will ultimately under-cut the

cost of electricity generated by silicon solar cells. More important is whether or not the thin film cells will under-cut the cost of conventionally or diesel generated electricity and, again, to predict the cost of energy from these sources at some date in the future is impossible. Previous calculations have often assumed a different rate of inflation of energy to that of money (3), usually the former being assumed greater than the latter. In recent years, the reverse has been the case, and this quirk of international economic forces alone would have been sufficient to spoil many a hitherto promising looking costs/benefits analysis. Possibly even more important than all the above agaries, is the influence of political policy; i.e., grants, tax-credits etc. These can change not only the cost projections but may have the effect of stimulating a market. Although it is perfectly reasonable for a utility company or a consumer to specify what the unit cost should be (because if that figure is not attained, the product i.e., the electricity, will remain non-competitive) it is much more difficult for a manufacturer, potential or otherwise, to predict with any certainty whether (or when) that target will be achieved. Despite these cautionary comments, there are many examples of low cost, large volume thin film production lines, and it seems more likely than not that the target figures based on the economic constraints, will be achieved. If there is a limitation, it is the obvious one of achieving a sufficiently high efficiency coincident with low production costs. Previous studies have shown that unless a particular minimum efficiency is exceeded, (the absolute value of which varies from time-to-time) the cells themselves could be zero cost but the system as a whole would remain non-viable because of excessive, area related, balance-of-system costs.

In the above list of parameters influencing cell costs, we have not included a contribution from the cost of the materials. Generally, we utilize films which are only of the order of one or two micrometers thick so that even very large areas, which would be required to generate significant amounts of electricity, do not represent a large part of the total cost. Possibly more important, however, is the actual availability of some of the materials used. In Table I, we show an assessment of several types of solar cell, including the two we have cited as being of special interest here, and have calculated the mass of the mineralogically scarce element required, per unit

generating capacity, per micrometer thickness. The calculation is based, very simply, on the approximate maximum efficiency of the particular device, observed to date at the laboratory level (4).

TABLE 1 - Principal Solar Cells Under Development

Semiconductor(s) Involved	Type of Cell	Rare Element	Density (Kgm^{-3})	Approximate Maximum Efficiency	Mass of Rare Element Required per GWp per μm Thickness (tonnes)	Mode of Operation
Si	single crystal		2200	20	20.7	Flat plate or low concentration
	amorphous thin film			11	12.0	
CdS/Cu$_2$S	thin film	Cd	8650	10	60.5	Flat plate
CdS/InP	single crystal InP	Cd and	8650	15	62.8	Only feasible with concentration
	all thin film	In	7310	5	57.6	
ITO[*]/InP	single crystal InP, thin film ITO	In	7310	16	50.4	Only feasible with concentration
CdS/CuInSe$_2$	thin film	Cd In Se	8650 7310	11	36.7 13.6 12.3	Flat plate
CdS/CdTe	thin film	Cd Te	8650 6240	11	58.8 18.1	Flat plate
GaAs/Ga$_x$Al$_{1-x}$As[+]	single crystal thin film	Ga	6095	23 5	37.1	Very high concentration flat plate

[*]ITO = Indium Tin Oxide (0.2 μm thickness film, 200 μm thickness crystal assumed)
[+]x taken as 0.2

TABLE 2 - World Mineral Statistics (5)

Material	Reserves (tonnes x 10^3)	Other Resources (tonnes x 10^3)	Annual Production Capacity (1980) (tonnes)
Si	unlimited	unlimited	2479[*]
Cd	754[**]	18,142	29510
Se	168	461	2547
Te	39	109	406
In	2	2	65
Ga	110	55	29

[*]This figure is the actual 1980 production level of polycrytalline silicon (source Monegon (6)). The remaining values in column 4 of the table are the predicted 1980 refinery capacities, the data being extracated from several articles in (5).

[**]As an indication of the uncertainties in mineral forecasting see (7).

In Table II we show a summary of mineral reserves, resources and refinery capacity for the various scarce elements itemized in Table I. Although the techniques of predicting the extent of reserves are notoriously prone to inaccuracies (much less those of predicting resources), these data at least give us an idea of potential problem areas. Clearly, the estimates of the total world reserves of indium and tellurium, suggest that the limited availability of these together, with a fairly restricted refinery capacity,

may well constitute a problem if the CdS/CuInSe$_2$ and CdS/CdTe cells are ever to be produced in large volume. With tellurium, the problem is less severe because much of the resources could be converted into reserves, given the necessary economic stimulus. With indium, however, we have a much more severe problem since both the resources and the annual world refinery capacity are extremely limited.

There is considerable contention in the photovoltaic community about the accuracy of these estimates and it is not our purpose here to comment on this. As with the financial arguments presented earlier, they are intended to be cautionary only. If indeed they were proved in time to be accurate, then undoubtedly they would constitute a most important economic argument for some and against other cells. Hence, the cost of the elements involved in the two most successful polycrystalline solar cells may well be limited to 1-2% of the total cell cost, but their availability may prove the dominant decisive factor in the long term.

In terms of materials costs, that of the substrates would be expected to dominate over that of the semiconductors.(6) If, for example, we consider an array generating 1 GWp with a conversion efficiency of 10%, then the required area would be 10^{7}m^2. Clearly, if the substrates for this were to be glass, the cost and production problems would be severe. Hence there is an active effort to develop low cost substrates. However, encapsulation will inevitably be required and since glass has been the most successful material used to date for this purpose, it may be difficult to find a replacement. Possibly, thin glass films could prove to be successful in this context, and these have been successfully deposited by RF sputtering in the past.

This concludes our discussion of the economic case for solar cells. It is apparent that the case is not as clear as some of the protagonists of this technology imply. Future fuel prices will determine what the proper targets should be for production costs, and production experience will determine whether they can be met. Since the long term solution to energy shortage problems is likely to involve a mix of technologies, it is only prudent to continue development even of those which, like photovoltaics are surrounded by economic uncertainties. To some extent, I believe, that the economics will take care of themselves; it is far more important, for the time, to

concentrate on improving device efficiencies. This will be the subject of the next section.

What Are the Qualities Required of Thin Film Solar Cells?

To make this technology a success, there must be several requirements fulfilled which, in the last analysis, all amount to reducing the cost of the energy generated over the lifetime of the cells. In one sense this is simply a detailed extension of the economic discussion of the previous section but here we identify three key topics which are presently being attacked. These are cell efficiency, the ability to produce large areas with a high throughput, and cell stability. All the economics of the cells are inherent in these three factors but rather than discussing these, which as has already been explained involves much gazing into crystal balls, we shall concentrate on what is needed to ensure high efficiency and what the limitations are, on what development of high throughput techniques is being undertaken and what special problems need to be addressed, and finally on what practical experience is available of the stability of the two devices of interest.

Efficiency

The efficiency of a solar cell(9) is dependent on the properties of the absorber, of the window layer, of the junction between them, on losses at the external electrical contacts and on optical losses. Assuming that with careful design the latter two losses can be made very small, we shall concentrate on the properties required of the two semiconductors and on their interface.

In brief, the properties required of the absorber are that it should (10):

i) have a bandgap somewhere around 1.5 eV since this is near the optimum for photovoltaic conversion.

ii) have a large optical absorption coefficient for all wavelengths less than that corresponding to that of the band-gap; this ensures that minimal thicknesses are required which minimizes the materials requirement.

iii) have as long a minority carrier diffusion length as possible; this ensures that the photogenerated carriers diffuse to the junction and are swept across it by the internal field before recombination can occur.

Similarly, the properties of the window layer (assuming that we are dealing with heterojunctions) are that it should:

i) have as large a band-gap as possible so that it transmits freely across the solar spectrum. Typical window layers are indium tin oxide (with a band-gap of about 3.7 eV) and CdS (with a band-gap of about 2.42 eV). Clearly, the latter cuts off at a longer wavelength than desirable.

ii) have as low a resistivity as possible. This enables the thickness to be reduced without the film presenting a large resistance to the lateral flow of current to the grid lines. Also, the spacing of the grid lines can be increased for low resistivity window layers, which reduces the shading losses.

iii) be straightforward to form ohmic contacts.

iv) have large diameter, vertical, grains, or have passive grain boundaries. In this way, it is possible that the performance of poly-crystalline devices can approach that of single crystal cells.

Figures 1 and 2 show the absorption spectra of several semiconductors including those under special consideration here. As regards the interface, there are again several criteria which should be used to guide the choice of the two materials.(11) These are as follows:

i) there should not be a severe mismatch of the electron affinities of the window and absorber layers. Such a mismatch can lead to a discontinuity in the edges of the conduction and/or valence bands and this can impede the movement of photogenerated carriers across the junction.

ii) there should not be a large crystallographic mismatch between the two
films. The presence of mismatch causes recombination centers which lead
to increased reverse saturation current, and a reduced fill-factor and
open circuit voltage.

iii) the coefficients of thermal expansion of the two materials should be as
nearly equal as possible. Since deposition of one semiconductor onto the
other is at elevated temperature (e.g. a substrate temperature of about
220°C is used for the deposition of CdS onto $CuInSe_2$) strain can be
caused upon cooling, and this again causes interface states which
increase the reverse saturation current.

iv) the two materials should ideally be non-reactive. This means that they
should not react chemically, and should not interdiffuse. Although such
effects are nearly impossible to avoid on an atomic scale, they are
actually undesirable because they negate, or at least reduce, the value
of design criteria.

In principle, there are many materials combinations which meet these
criteria both individually and as a combination but in practice, very few
yield efficient devices. Other guidelines can be used to define the necessary
optical and electrical properties of the components of a window layer
heterojunction solar cell. The monochromatic photocurrent of such a device
can readily be shown to be (to a good first approximation)

$$J_L = K \left[1 - \frac{\exp{(-\alpha W)}}{1 + \alpha L} \right] \qquad (1)$$

where K is a constant dependent on the photon flux at the junction, α is the
optical absorption coefficient for the particular wavelength radiation, W is
the width of the depletion region between the two semiconductors, and L is the
minority carrier diffusion length (in general, for electrons, since we
virtually always consider p-type absorbers and n-type window layers). To
ensure $n \approx 1$, we simply require that the products αW and/or αL are large for
the absorber. Since the flux generates excess electron/hole pairs in the

absorber, it follows that we wish as much of the depletion field to be located therein as possible. Hence, a further design requirement is that the absorber be much less heavily doped than the window layer. The actual width of the de.letion layer (and hence the required doping of the absorber) should be of the order of $1/\alpha$. For typical absorbers and useful wavelengths this quantity is ~ 0.3 μm; and to obtain values of W of this magnitude or greater requires the doping density of the absorber to be 10^{16}-10^{17}cm^{-3}. Although values less than this range lead to larger values of W and, theoretically, higher collection efficiency, in practice they can also lead to the problem of excessive series resistance losses. Since we wish most of the depletion field to appear across the absorber, to increase the drift component of the collected photocurrent, we can also specify the impurity concentration of the window layer. It is also possible to improve the design by creating graded impurity profiles which have the effect of extending the depletion region.(11)

Assuming that the simple photo-diode equation can be applied, the open-circuit voltage of a solar cell can be written, to a good approximation, as

$$V_{oc} = \frac{AkT}{e} \ln\left(\frac{J_L}{J_o}\right) \tag{2}$$

where A is the diode ideality factor, k, T and e are respectively Boltzmann's constant, absolute temperature and electronic charge, and J_o is the reverse saturation current. It follows from this equation that the ratio (J_L/J_o) should be as large as possible. The efficiency of a cell is given by

$$\eta = J_L \cdot V_{oc} \cdot F \tag{3}$$

where F is the fill-factor of the cell. F also depends on maximizing (J_L/J_o), in the absence of losses due to series and shunt resistance, and hence on minimizing J_o. Thus, the latter quantity closely influences two of the three parameters governing device efficiency. Since for many devices, J_L approaches the theoretical limit for the particular absorber/window layer combination, much of the remaining potential for efficiency improvement lies in reducing J_o. There are nine possible contributions to J_o (11) but, for heterojunctions, the most significant is often found to be due to

recombination via interface states. In fact, the reverse saturation current (or rather its reduction) is probably the single most important target for device improvement. To minimize J_0 requires that the volume of the films is free of an excessive density of recombination centres, that the interface is as free of defect states as possible, and that the contacts are not problematic. Also, it is necessary to ensure that interdiffusion and chemical reactions at the interface are minimal. A large variety of analytical techniques is used to investigate these problems and these will be discussed in the next paper.

Production of Large Area Thin Film Solar Cells

So far we have discussed considerations relating to the possible competitiveness of solar cells, the availability of materials, and the fundamental physical design criteria. In this section we shall return partly to the economic aspects in the sense that we shall consider what means are being examined for large scale production of devices. However, the need to deposit large areas of film with very specific properties, very quickly, raises a number of separate problems which are not of an economic nature. CdS/CuInSe$_2$ cells are usually fabricated entirely by vacuum deposition the most well tried having been developed by the Boeing Corporation (12). This technique consists of three-source deposition of the CuInSe$_2$ and a single source for the CdS, as seen in Fig. 3. The substrates are usually of very limited area and deposition is usually quite slow. The construction of a typical cell is shown in Fig. 4. Although efficiencies have reached 11% for these small area cells, to commercialize them will require rapid throughput of large areas, whilst still maintaining high efficiencies. Exactly the same comments can be made of the CdS/CdTe cells; these have also exceeded 10% conversion efficiency and show great potential.

We shall now consider what the requirements are of the large area processes and shall then mention a few of the techniques being examined.

Production Rates

For photovoltaics to make a significant impact on electricity supply in the USA it would appear that they eventually need to be introduced at a rate

of around, 10 GW of generating capacity per year. This means that there should probably be around twenty such machines each with a capacity of about 50 MW.(13) For a device efficiency of 15% and an area utilization of 80%, this would require on output of 4.2×10^5 m^2 per year. As:uming 5000 hours of operation per year, this corresponds to 80 meter^2 per hour, or 2.2cm/sec for a width of 1 m. If the length of the deposition region is 100 cm (assuming a batch coater), then the coating duration will be about 50 seconds, so that if the required thickness of the absorber is 5000 Å, the deposition rate will be about 5500 Å/min. Although this is readily attainable, it must be remembered that all the required film properties must be maintained throughout the production schedule.

Potential Problems

i) Pinholes

The films must be pinhole free otherwise shorts will be formed which can severely degrade device performance. The origin of pinholes is usually particulate matter and this can be due to inadequate substrate cleaning or to falling debris from within the deposition system. Hence, great care will need to be paid to the cleanliness of the substrates and the interior of the deposition systems and this will need to be incorporated on a routine basis to avoid loss of yield.

ii) Thickness Non-Uniformities

Whatever the method of deposition used, there is inevitably a distribution of the material emitted from the source(s) and hence of film thickness. For the absorber layer this could be an important consideration since it is not only necessary to ensure the thickness is greater than some minimum value, but also that it is not excessively thick which would result in materials wastage and loss of time.

iii) Compositional Non-Uniformities

For compound semiconductors it is necessary to maintain the required composition across the entire substrate area to ensure consistency of

electrical and optical properties. When two or more elements are being evaporated, it may be possible to reduce departures from stoichiometry by using several carefully distributed sources of each material. In the case of sputter deposition, the problem may be lessened by using large area targets.

iv) Angle of Incidence Effects

It is known for evaporation that the grains of a polycrystalline film tend to align themselves towards the vapor stream. In the case of evaporation from several spatially distributed sources, the problem can be expected to be more complicated. It is not difficult to see that the properties of films of varying grain alignment and surface texture would be very unpredictable. In all the above cases, the effects would be to lead to a distribution of film and, hence, of cell properties. It is not difficult to show that the effect of this is to degrade the overall performance to that of the poorest areas. Virtually nothing is known about these effects in large scale production. Although the above comments have been aimed specifically at vacuum deposition, it is certain that the same problems will arise in all methods.

Methods Presently Under Investigation

The problem of large area rapid deposition, is already being investigated and several methods are being considered. For evaporation of $CuInSe_2$, (using open boats and Knudsen effusion cells) thorough studies have been made of the problems arising in scaling up from laboratory scale. The problems are not simply ones of scale but involve non-linear differential equations.[14] The difficulties of scale-up have been usefully illustrated by analogy with laboratory and production scale genetic engineering. Reactive magnetron sputtering is also under consideration.[13] This method involves sputtering from two metal targets (copper and indium) in a partial pressure of H_2Se. Other methods with the potential for large area coating of $CuInSe_2$ include alloy plating, close spaced vapour transport, and electrodeposition. In the case of CdTe deposition the methods being investigated include chemical vapour transport, electrodeposition, and hot-wall evaporation. Although substantial

progress has been made, research has been too limited to exploit the potential fully. In terms of area the largest successful CdS/CuInSe$_2$ cells fabricated so far are approximately 100 cm^2 with an efficiency of 6.2%; for CdS/CdTe, devices of up to 4000 cm^2 have been produced with an efficiency of 5%. A summary of these is shown in Fig. 5. Although these results are extremely promising, much more effort needs to be made. Careful studies of the physics of growth of the films have in general not been made and certainly the relationship of the growth parameters to the device physics, is an unexplored area.

Device Stability

It is of great importance that solar cells maintain their electrical output, without degrading, for about twenty years, if the system economics are to stay competitive. Many mechanisms of degradation can occur. Since several interfaces are involved in the device structure, chemical reactions o. interdiffusion can take place and these will certainly affect device performance. However, degradation of the external contacts appears to be the cause of such instabilities as have been observed. CuInSe$_2$ devices has shown excellent stability after exposure to simulated sunlight for over 9000 hours in a controlled environment. However, degradation of the front contacts of unencapsulated cells has been observed during outdoor testing, and this appears to be due to attack of the aluminum grids by water vapor and chlorine. The solution to this problem probably lies in the development of adequate encapsulation, or of more sophisticated grid structures. As yet, no studies on the stability of CdTe based cells have been sponsored by DOE/SERI. However, two of the companies involved in manufacturing devices (Kodak, Matsushita) have performed preliminary studies. The former has obtained some evidence of contact degradation whilst the latter has not observed any degradation of performance on their screen printed cells. We may conclude from this that problems of stability appear to be minimal compared with other cells, for example CdS/Cu$_2$S, and that such instability as is evident is due to degradation of aspects of the cell other than the two semiconductors. This is most encouraging, since the latter problems tend to be inherent, whilst the former are technological and do not present a

fundamental limitation.

Problem Areas and Major Research Directions

1) Low V_{oc} in CdS/CuInSe$_2$ Cells

Empirically, it has usually been found that the open circuit voltage of cells is approximately 2/3 the energy gap of the absorber. This is the case for many absorbers, but the rule certainly does not apply to CuInSe$_2$ for which typically V_{oc} = 400-450 mV, i.e., less than 1/2 Eg. The reason for this is uncertain other than that it is due to excessively large values of J_o. However, as we have already pointed out, there are many possible causes of this and the particular contribution has never been isolated. Since it also limits the fill-factor to less than 70%, it is vitally important that this problem be addressed. Recently, there has been considerable discussion about the nature and location of the active electrical interface in these cells. EBIC data imply that the devices are actually buried homojunctions (although the mechanism(s) by which type conversion occurs is (are) still very much under discussion. Spectral response data however, tend to contradict this theory. If indeed the buried homojunction model is correct, then we would expect V_{oc} to be substantially lower than if the heterojunction model applies. Since improvement of the device efficiency largely depends on improving V_{oc}, it is critical that this issue be resolved. If V_{oc} could be improved to nearer 600 mV, then an efficiency approaching 15% could be achieved.

To resolve this problem will necessitate improving our knowledge of the defect chemistry and the role of extrinsic doping of CuInSe$_2$. These are fundamental issues which are arising at a time when the device is already being commercialized. That they have not been resolved already is probably due to two reasons. Firstly, straightforward technology enabled relatively high efficiencies to be achieved without there appearing to be a need to study the materials at the fundamental level. Secondly, CuInSe$_2$ is unusual as an electronic material, in that its only evident application is in solar cells. Hence the wealth of background information available for many materials does not exist for CuInSe$_2$. The future of this material probably depends on this situation being remedied.

ii) Controlled Contacting to and Extrinsic Doping of p-CdTe

Single crystals of CdTe can be doped n-type or p-type with an excess of Cd or Te respectively. Extrinsic n-type doping with indium of both single crystals and films is also possible. It is also possible to produce low resistivity p-type crystals, but extremely difficult to produce highly conductive p-type polycrystalline thin films. In general, the impurities tend to segregate at the grain boundaries. It appears that oxygen incorporation during processing or after deposition, improve the conductivity. This observation is rather similar to that of the effects of junction movement in CdS/CuInSe$_2$ cells. To produce p-type films reliably and reproducibly requires much more effort in this area.

The contacting problems to p-type CdTe can be summarized as follows:

- Low resistivity (< 10 Ω cm) n-type films of CdTe can be produced and these permit very thin tunnel junctions of low contact resistance to be made with certain metals. Such low resistivities cannot be achieved for p-type films.

- The electron affinity of n-type CdTe is about 4.3 - 4.5 eV which is almost equal to its work function for degenerate, low resistivity material. For p-type material, the work function is approximately 6.0 eV. Ohmic contact to n-type material requires metals with a work-function around 4.4 eV, for p-type material a metal with work function greater than atoub 5.8 eV is required. Many of the former are available, whilst there are none of the latter.

The contact resistance between a metal and a semiconductor is governed by the height and the width of the potential barrier between the two. As explained, it is difficult to make either small for p-type CdTe. Since there are quite severe losses associated with poor quality contacts, again this is an area which will certainly receive considerable attention.

iii) Development of p-type Window Layers

All window-layers presently available are n-type and certainly there

is no p-type semiconductor with a band-gap approaching that of materials like ITO and ZnO. This is a somewhat limiting situation since it removes the possibility of exploring the potential of window layer heterojunctions using n-type absorbers. Both CdTe and $CuInSe_2$ are available in n-type form and may have advantages over the p-type absorbers. However, the materials which can be made p-type, highly conductive and transmissive, have a band-gap less than even that of CdS (~ 2.5 eV) so that absorption losses near the maximum of the solar spectrum would be prohibitive. It is possible that materials such as $CuGaS_2$ with its band-gap of 2.8 eV may be suitable or, indeed, other alloy systems could be developed. However, to date little effort has been devoted to this topic.

iv) Research Into Cascade Cells

Thin film cells have just the same possibility of being grown in tandem or cascade form as do the ternary III-V alloy devices. Optimum devices, theoretically, would utilize a top-cell with an absorber band-gap of about 1.6-1.8 eV and a bottom cell with an absorber band-gap of 0.9 - 1.1 eV. This is shown diagrammatically in Fig. 6. Several materials possibilities exist including $CuInSe_2$, a-Si:H, HgCdTe, for the lower absorber, and a-Si:C:H, CdTe for the upper absorber. Also, the material $CuGaSe_2$ should be nearly ideal particularly from the point-of-view of compatibility in $CuInSe_2$. There are also other alloys based on CdTe which have great potential. With any of these systems the production problems are severe since it is necessary to maintain high quality materials properties throughout the deposition of many layers and over fairly wide temperature ranges. However, the very high potential efficiencies are attractive and cascaded thin film systems have much to offer. Research in this area is comparatively limited at present and efficiencies appear to be limited by poor quality contacts to CdTe (in a CdS/$CuInSe_2$: CdS/CdTe cell). A typical device construction is shown in Fig. 7 and, in this configuration, efficiencies of several percent have been recorded (15).

v) Advanced Deposition Research

The major obstacle to investigating large scale production technologies

is their cost.   Hence, far more effort has been devoted to improving the efficiency of small area devices than to studying the host of problems associated with large area deposition.   Presumably as the small area efficiencies and the prospects for commercialization improve, more attention will be given to scale-up problems.   Perhaps the main point to be remembered is that the efficiency of large areas will always be less than that of small areas and so the materials quality must be superior for the former, if efficiencies are to be maintained.   Virtually no research has been done on the nucleation and growth of the absorber films $CuInSe_2$ and $CdTe$ and, not surprisingly, the films and cells tend to be somewhat ill-defined.   This situation must change before large area deposition can be made practicable.

Conclusions

Although many economic studies have been made of the probable cost-competitiveness of solar cells, it is our belief that there are too many variables for these calculations to be reliable.   If indeed there is an economic restriction, for the thin film devices based on $CuInSe_2$ and $CdTe$, it would be the availability of In and Te.

Simple theoretical considerations indicate that the major improvements to be made with $CuInSe_2$ cells are with V_{oc} and the fill-factor, both of which depend on reducing J_o.   With the CdTe cell much of the potential improvement in performance will rely on improving the contact to the p-type material.

For the cascade cells, operational devices have already been demonstrated but there are considerable problems.   Contacting the CdTe is again problematic, but there is the additional difficulty of avoiding interdiffusion of the various films and of providing transparent tunnel junctions. Optimization of either the two or four contact technique must be achieved. Finally, much more detailed studies of film and device properties need to be made, even at the laboratory scale, if the large area high throughput production techniques are ever to be successful.

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Figure 1. Thin-Film Heterojunction Solar Cells: Optimal Use of the Solar Spectrum.
Shown are the absorption coefficients of CdTe and CuInSe₂; transmission curves for various heterojunction partners (window materials) under study; and photon flux density (linear in energy, eV) for the AM 1.5 Global Spectrum.
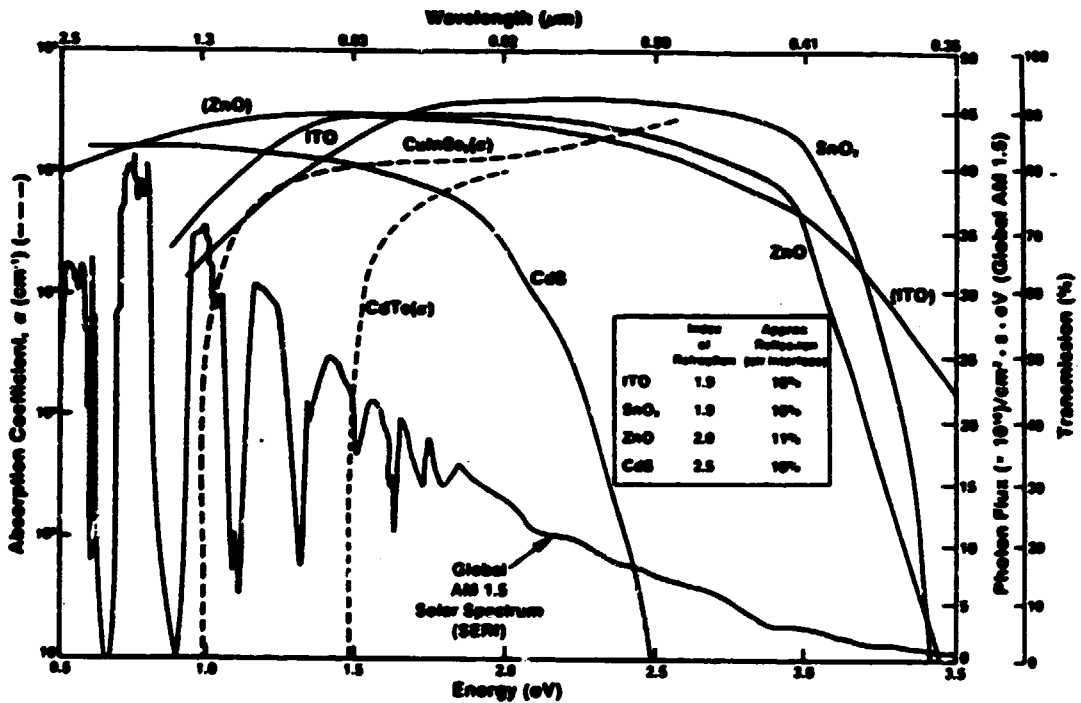
Figure 2. Absorption Coefficients of Various Thin-Film Semi-conductors.
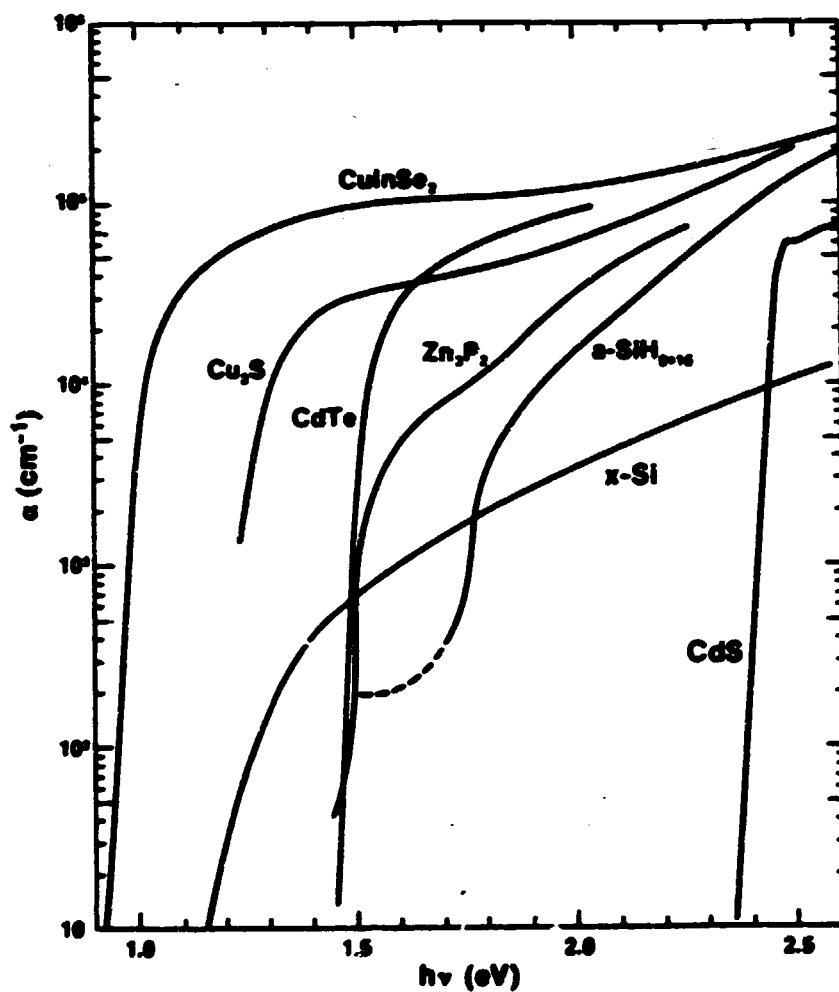
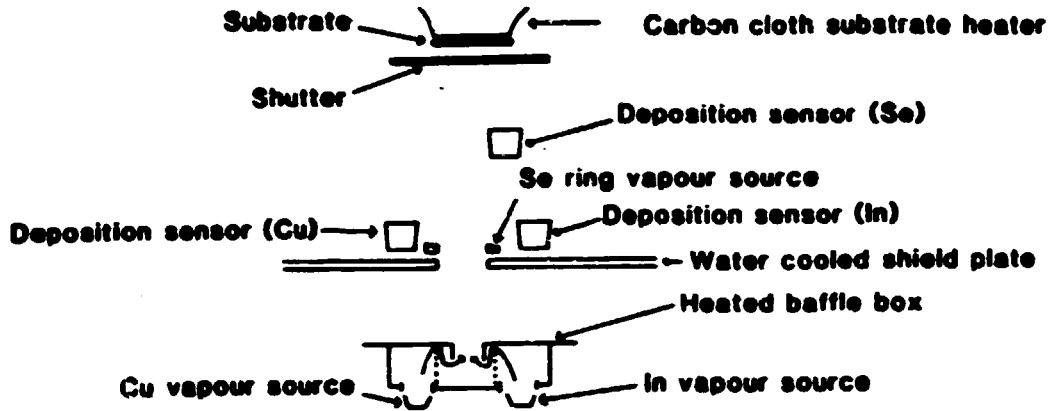## Figure 3. Three Source Deposition of CuInSe₂.

Figure 4. CdS/CuInSe₂ Cell Structure Showing Deposition Temperatures and the Relative Composition of Elements During Deposition (Boeing).

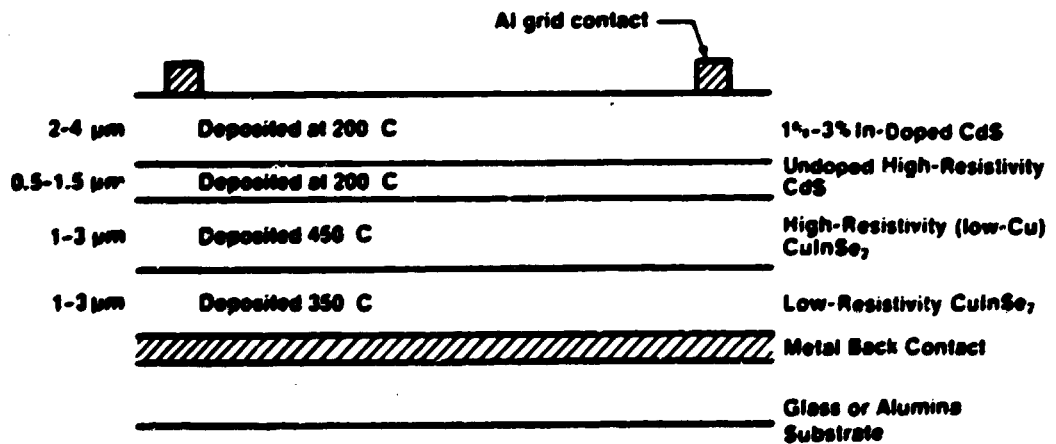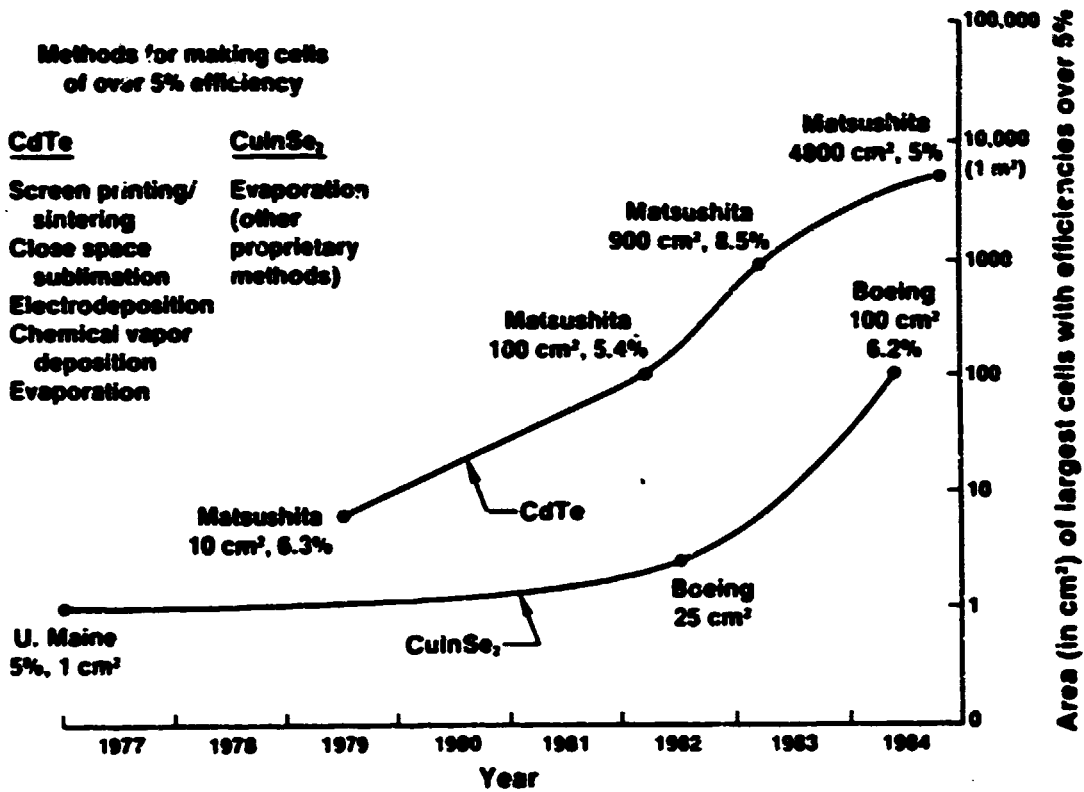## Figure 5. Large-Area Polycrystalline Thin-Film CdTe and CuInSe₂ Cells.

Methods for making cells
of over 5% efficiency

CdTe

Screen printing/
sintering
Close space
sublimation
Electrodeposition
Chemical vapor
deposition
Evaporation

CuInSe₂

Evaporation
(other
proprietary
methods)

Matsushita
4900 cm², 5%
(1 m²)

Matsushita
900 cm², 8.5%

Boeing
100 cm²
6.2%

Matsushita
100 cm², 5.4%

Matsushita
10 cm², 6.3%

CdTe

Boeing
25 cm²

U. Maine
5%, 1 cm²

CuInSe₂

Year axis: 1977 1978 1979 1980 1981 1982 1983 1984

Area (in cm²) of largest cells with efficiencies over 5%:
100,000 — 100.000
10,000 — 10.000
1000
100
10
1
0

Figure 6. Iso-Efficiency Curves for Two-Cell, Four Terminal Cell.

AM1 Four Terminals
27° C

Bottom-Cell Bandgap (eV)
1.50
34.0
34.9
35.7
36.6
1.25
1.00
0.75

Top-Cell Bandgap (eV)
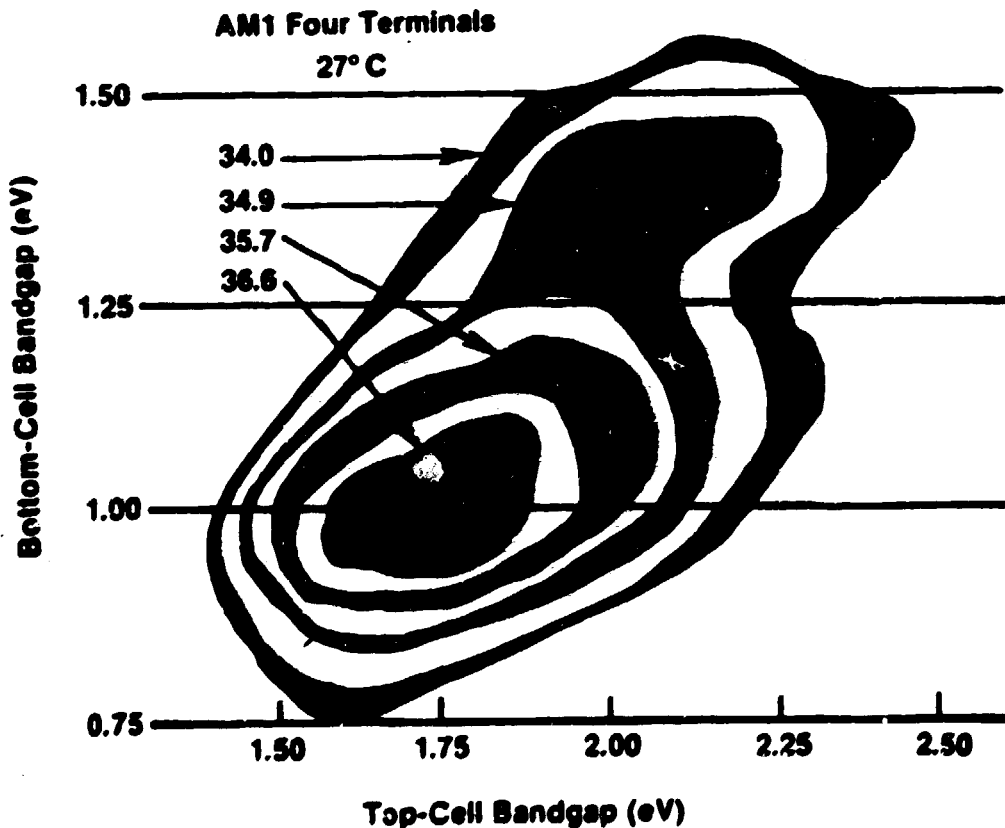1.50   1.75   2.00   2.25   2.50

Figure 7. Two-Junction, Four-Terminal Optically Stacked Poly–crystalline CdTe/CuInSe₂ Solar Cell.

Conceptual Design

100 mW (1 cm²)

Glass
TCO
CdS
CdTe
TCO

R_1 11 mW (for η_1 = 11%)

dielectric

TCO (or grid)
CdS
CuInSe₂
Mo

R_2 3.85 mW (for η_2 ~ 11%)

Metal or Glass Substrate

Total: 14.85 mW

Total Cell Efficiency of ~ 15%

No. of Photons with 1.0 eV < E < 1.5 eV ≅ 35% of Photons with 1.0 eV < E < 2.4 eV (CdS cutoff)