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" Production and opportunities in thin films solar cells "

presented by:

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These are preliminary lecture notes, intended only for distribution to participants.



# CdTe Thin-Film Solar Cells

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## Introduction

Cadmium telluride is currently the most promising material for high efficiency, low-cost thin-film solar cells. Cadmium telluride is a compound semiconductor with an ideal 1.45 eV bandgap for direct light-to-electricity conversion. The light absorption coefficient of CdTe is high enough to make a one-micrometer-thick layer of material absorb over 99% of the visible light. Processing homogenous polycrystalline thin films seems to be less critical for CdTe than for many other compound semiconductors. The best small-area CdTe thin-film cells manufactured show more than 15% conversion efficiency. Large-area modules with aperture efficiencies in excess of 10% have also been demonstrated. The long-term stability of CdTe solar cell structures is not known in detail or in the necessary time span. Indication of good stability has been demonstrated. One of the concerns about CdTe solar cells is the presence of cadmium which is an environmentally hazardous material.

## The Main Raw Materials, Cadmium and Tellurium

Cadmium is mainly a byproduct of zinc production. The annual production of cadmium is about 20,000 tons. Its most important uses are in plating, batteries, pigments, and stabilizers of plastics. Tellurium is produced as a byproduct of copper purification. Its annual production is only 300 tons due to the low demand for tellurium.<sup>1</sup> Based on the typical amount of tellurium in copper ore, up to 5000 tons/year of tellurium could be produced with the present production of copper (and silver and the platinum group metals). The amount of both cadmium and tellurium needed in one square meter of CdTe thin-film PV panel is 5 to 10 grams, equal to a yield of 10–20 MWp (megawatt peak) per ton of each element in 10% efficient panels. Accordingly, the availability of the main raw materials is adequate for PV production up to 50–100 GWp/year, which is more than 1,000 times the total PV production in 1992. In order to make PV a visible contributor

to global electricity production, even more than this will be needed in the next 50 years. From the raw materials point of view, CdTe technology can be a significant contributor to PV production for several decades.

A commonly heard concern about CdTe technology is the toxicity of cadmium.<sup>2,3</sup> In CdTe PV panels, Cd is in the form of CdTe and CdS compounds, both chemically stable compounds. CdTe thin-film PV cells are encapsulated to protect the device against the environment—and the environment against the device. The environmental risks of the devices are therefore limited to hazards and to the disposal of the devices after their technical lifetime. There are studies on different hazards as well as on the handling of Cd in the cell manufacturing plant. In both cases the

situation is manageable. The end-of-life recycling of CdTe panels can be foreseen and should therefore be included as a cost factor of the technology.

## The CdTe Thin-Film Cell

A CdTe thin-film PV cell is generally based on a CdS/CdTe heterojunction. A multicrystalline form of undoped CdTe material is typically a high-resistivity p-type semiconductor. Doping CdTe, both p<sup>+</sup>- and n-type, is difficult. CdS shows n-type conductivity as a polycrystalline thin film. In spite of the 10% difference in the lattice constants of CdS and CdTe, they form an electrically excellent heterojunction, as shown by its high fill factors up to  $FF = 0.75$  in the devices made.

CdTe devices are generally made on a glass substrate (Figure 1). The first layer on the glass is a transparent electrode, often referred to as TCO (transparent conductive oxide, such as SnO<sub>2</sub>). The next thin-film layers are CdS, CdTe, and a back electrode which may be carbon paste or a metallic thin film. In an actual device, the thin-film structure is generally protected with another piece of glass laminated on top of the thin-film structure.

Manufacturing a CdTe thin-film PV cell is relatively straightforward. The transparent electrode (TCO) can be made with any known technique. Unlike the surface for amorphous silicon PV cells, a smooth TCO surface is preferable for CdTe cells. A smooth TCO surface minimizes the necessary thickness of the CdS layer and also serves as a good substrate for the crystallization of both CdS and CdTe layers. CdS makes a good heterojunction with CdTe. The bandgap of CdS is 2.42 eV, which results in a loss of the blue part of the solar spectrum (Figure 2).

It turns out that the spectral loss due to absorption in the CdS layer depends not only on the physical thickness of the CdS film, but also on the way it has been produced.<sup>4</sup> The latter may reflect variations in the density of the CdS film or its interaction with the TCO or the CdTe layer. The methods used in producing the CdS material are chemical bath deposition (CBD), MOCVD, sputtering, and atomic layer epitaxy (ALE).

CdTe has been deposited by many different methods such as electrodeposition, close-spaced sublimation (CSS), close-spaced vapor transport (CSVT), spraying, screen printing, MOCVD, and ALE. Each deposition method is completed with a heat treatment with cadmium chloride. CdCl<sub>2</sub> is used as a solvent in the production of single-crystal II-VI compounds.<sup>5</sup> CdTe forms a solid solution with CdCl<sub>2</sub>, with a melting point of only about 500°C

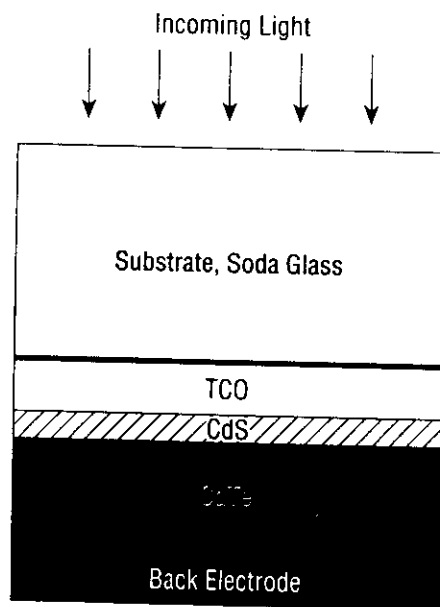


Figure 1. CdTe thin-film PV cell structure.

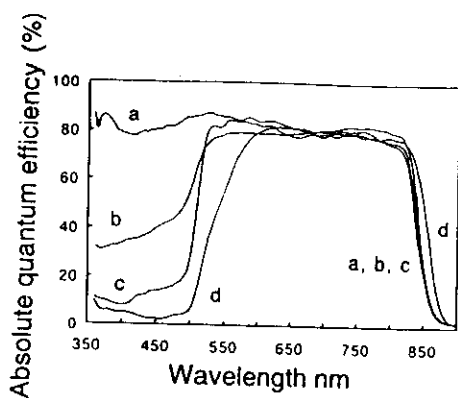


Figure 2. Spectral response of some experimental thin-film CdTe solar cell structures. (a) Thin CdS (~10 nm), abrupt CdS/CdTe junction, (b) mixed CdS<sub>x</sub>Te<sub>1-x</sub> layer at the window/n-type side of the junction, (c) thick CdS (~200 nm), abrupt CdS/CdTe junction, (d) thick CdS (~200 nm) and a mixed CdS<sub>x</sub>Te<sub>1-x</sub> interface layer in the junction (samples by Microchemistry Ltd).

at the eutectic point. The cadmium chloride treatment recrystallizes the CdTe thin film and enhances its electrical characteristics. This can be observed even in CdTe films made by ALE. The films show good crystallinity just after the deposition as seen by x-ray diffraction (Figure 3a). The substrate surface and the CdS layer play important roles in the crystalline orientation of CdTe. The CdTe layer of Figure 3a is made on a smooth indium tin oxide surface in the same ALE process as the CdS. Individual crystallites with visible hexagonal shapes can be detected after a heat treatment with CdCl<sub>2</sub> (Figure 3b and 3c).

The thickness of the CdTe layer is typically 1.5–3 μm. For light absorption, 1.5 μm is sufficient, and a thicker layer may be advantageous for large crystallites. Also, a thick CdTe layer reduces the formation of pinholes. After the deposition and cadmium chloride treatment, CdTe is typically a high-resistivity p-type semiconductor. The difficulty of doping is typical for all ionic II-VI semiconductors.<sup>6-8</sup> The conductivity type is mainly determined by native defects or nonstoichiometry. A positive consequence of the doping difficulty is that the purity of the raw materials is less critical; a negative consequence is the difficulty of making a good p<sup>+</sup> layer necessary for a good ohmic contact.

In many of the demonstrated high V<sub>oc</sub> devices, a phosphoric acid etch has been applied on the CdTe surface prior to the deposition of the contact material. Acid treatment results in a Te-rich surface and phosphoric acid may also result in a p-

type doping effect by phosphorous atoms diffusing into the CdTe lattice near the surface. It may also enhance the contact formation by roughening the surface. One approach to an effective p<sup>+</sup> layer and a good ohmic contact is the use of a contact paste that has a narrow bandgap, or a higher work function tellurium compound such as mercury telluride or zinc telluride together with conducting particles such as carbon. Copper and gold in the contact material are also observed to improve the V<sub>oc</sub> and the ohmic contact. Copper may form a Cu<sub>2</sub>Te phase in an acid-treated CdTe surface layer. Gold maintains a substantial mobility in the CdTe material, resulting in a stability problem in the CdTe device. This reflects a general concern about CdTe devices. While doping is very much based on native defects and nonstoichiometry, a high performance level and good stability may compete with each other.

## Device Performance

Table I summarizes some of the recent achievements in CdTe solar cells. The best conversion efficiency (15.8%) has been reported by the University of South Florida. The deposition techniques used in this device are CBD for the CdS n-layer and close-spaced sublimation for the CdTe layer. The high short-circuit current reflects either a very thin CdS layer or chemically modified CdS with an increase in the bandgap and a more effective utilization of the blue part of the solar spectrum. Increasing the bandgap generally makes the doping even more difficult. In this case, the high open-circuit voltage of the device indicates successful doping both in the n-side and the p-side of the junction.

The CdTe deposition has been made at about a 600°C substrate temperature. The high temperature may have an important effect on the crystallization of the CdTe material; it may, on the other hand, become

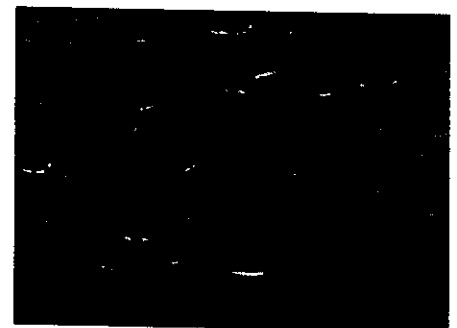
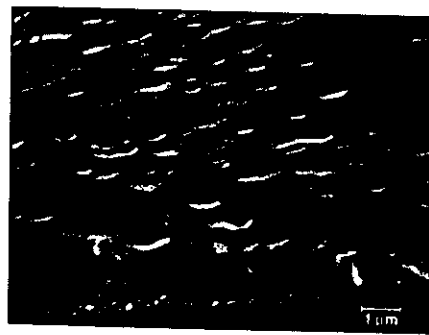
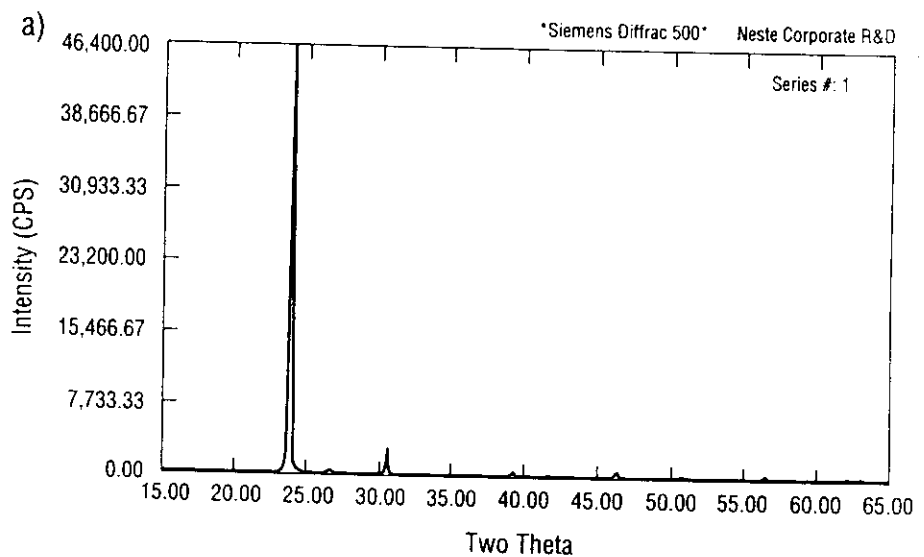


Figure 3. (a) X-ray diffraction spectrum of a CdTe thin film made by ALE. (b) SEM picture of typical ALE CdTe after deposition. (c) SEM picture of an ALE CdTe thin film after cadmium chloride treatment. For (b) and (c), the surface is treated with 1% Br/MeOH etch to enhance the visibility of the grain boundaries (samples and analysis by Microchemistry Ltd).

Table I: Characteristics of Thin-Film CdS/CdTe Solar Cells

CdTe Deposition Process	Area (cm <sup>2</sup> )	Efficiency (%)	J <sub>sc</sub> (mA cm <sup>-2</sup> )	V <sub>oc</sub> (mV)	FF	Organization	Ref.
CSS	1.05	15.8*	25.09	843	0.745	USF	10
Electrodeposition	0.02	14.2	23.5	819	0.74	BP Solar	13
ALE	0.12	14.0	23.8	804	0.73	Microchemistry	11
Spray	0.30	12.7*	26.21	799	0.605	Photon Energy	12
Screen Printing	0.3	12.5	23.6	870	0.61	KAIST	14
CSS	0.388	11.6*	22.16	797	0.654	Battelle Europe	15
CSS	1.08	11.3*	22.57	833	0.60	NREL	16
Screen Printing	1.02	11.3	21.1	797	0.67	Matsushita	17
Electrodeposition	1.068	11.2*	22.36	767	0.696	AMETEK	18
PVD	0.191	11.0*	20.09	789	0.692	IEC	19

J<sub>sc</sub> = short-circuit current, V<sub>oc</sub> = open-circuit voltage, \*measured by NREL.

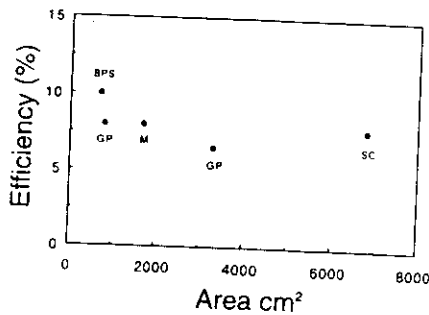


Figure 4. Aperture conversion efficiencies of thin-film CdTe solar modules. BPS = BP Solar, GP = Golden Photon, M = Matsushita, and SC = Solar Cells.

a limiting factor in scaling up the process on a large-area low-cost soda glass substrate necessary in manufacturing.

Figure 4 summarizes some published efficiencies of CdTe modules of different aperture area. In spite of a clear difference between the performances of large-area modules and the small-area laboratory samples, it seems that the CdTe technology is more easily scalable into large areas than the other known thin-film solar cell technologies. The largest CdTe module, 2 × 4 square feet, recently has been introduced by Solar Cells Inc., Toledo, Ohio. The total output power of the best-measured module was 53 Wp, which corresponds to an aperture efficiency of 7.8%.<sup>20</sup>

The information available on the long-term stability of the CdTe devices is quite limited. Results from the longest test runs,

two years for 1' × 1' modules, have been published by BP Solar.<sup>13</sup> According to their observations, no continuously ongoing degradation occurred.

### Summary

Thin CdTe technology is a potential technology for cost effective PV modules in the near future. Key questions will be the long-term stability combined with high conversion efficiency. There are indications of both of those necessary features. Also, the scalability of the technology looks promising. The availability of the raw materials will not be a limitation for large-scale production of CdTe solar cell devices.

### Acknowledgments

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MRS 1994 Spring Meeting Abstract Deadline: November 1, 1993

Keynote Address

## Solar Energy - a Dream or a Necessity ?

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*There is an urgent need for new sources of energy. Presently the use of fossil fuels covers about 80% of the primary energy production [1]. With present usage the proven oil and natural gas reserves last for about 50 years [2]. On the same time there is an increasing concern of the climatic and other environmental consequences of burning the fossil fuels. Solar energy represents a huge resource of energy that could technically cover the whole global need of electricity. About 0,1% of the solar insolation onto the earth is stored into the annual growth of biomass [3,4]. Utilization of the biomass in energy production is an indirect way of utilizing solar energy. In biomass growth the light energy conversion factor is a little bit below 1%. When further converted into electricity in a combustion process the final sunlight - biomass - electricity conversion efficiency is about 0,3%. Direct conversion of sunlight into electricity can be made with photovoltaic cells with 10-15% conversion efficiency. With today's technology the whole present production of electricity would need a light collection area of 5 million hectares. This is less than 1 % of the deserts on the earth.*

*Penetration of solar electricity has been mainly restricted by the low prices of fossil fuels. On the same time the competitiveness of solar cells suffers from low production volumes. For a wide utilization of the technology the production volumes of photovoltaic panels shall be increased by a factor of 1000, which technically could be made in 25 to 30 years. As long as solar electricity is used as an additional energy source in connection with the existing power grid no storage of electricity will be needed. In stand alone systems and in large scale production of solar electricity an energy storage system will be needed. The strongest candidate for large scale energy storage is hydrogen technology based on electrolysis by solar electricity for hydrogen generation and fuel cell technology for converting the hydrogen back to electricity. Efficiency of such sunlight - electricity - hydrogen - electricity conversion chain with today's technology is 4 - 5%.*

### **Direct conversion of light into electricity**

The possibility of direct conversion of light into electricity with solar cells has been known for several decades. Most of today's solar cells are made of silicon material, the material widely used in electronic components. A solar cell is typically a thin slice of crystalline silicon material treated in such a way that an internal electric field is built up across the slice. Light absorbed by the cell generates positive and negative electrical charges which are collected to opposite sides of the cell by the inbuilt electric field. Electrical current can be

driven out of the cell from electrodes at the opposite faces of the cell.

Typical unit cell has about one square decimeter surface area and is able to produce about 1,5 watts of electrical power in direct sunlight. In industrialized countries an average family uses about 5000 kWh of electricity per year. In most populated areas this amount of electricity can be produced with a solar cell array of 20 to 40 m<sup>2</sup> in surface area.

Solar cell systems have no mechanically moving parts. They are pollution free and noiseless and they possess a very long operational lifetime. A

solar cell system produces electricity when sun is shining onto the cells. For dark times a storage of electricity is needed. In small systems chargeable batteries can be used. In large scale solar electricity production new storage concepts will be needed. The strongest candidate for solving the problem of storage is the use of electricity-hydrogen-electricity conversion.

### Cost of solar electricity

When making a solar cell installation the investor in practice pays his 30-50 years' electricity bill in advance. Accordingly, the price of the produced electricity is determined by the price of the installation and the interest to be counted to the money paid. Table 1. summarizes the resulting price of electricity starting from today's system price and some assumed interest levels counted to the money invested.

Interest rate (%)	PV system cost \$/Wp			
	10	5	2	
15	0.76	0.38	0.15	\$/kWh
10	0.52	0.26	0.10	
5	0.32	0.16	0.07	
0	0.15	0.08	0.03	

Table 1. Price of solar electricity at different system prices and interest rates. The calculation assumes a depreciation period of 30 years and solar insolation of 2000 kWh/m<sup>2</sup>/year.

According to Table 1. solar electricity reaches the price level of 3 ... 7 US cents per kilowatt hour provided that the interest rate used in the calculation is below 5% and that the system price reaches the level of 2 \$/Wp. The 2 \$/Wp system price is technically achievable by evolution of production technology as a consequence of increased production volumes.

### History and future of the production of electricity

Ninety percent of today's global production of electricity has been started since 1950 [5], Figure 1a,b.

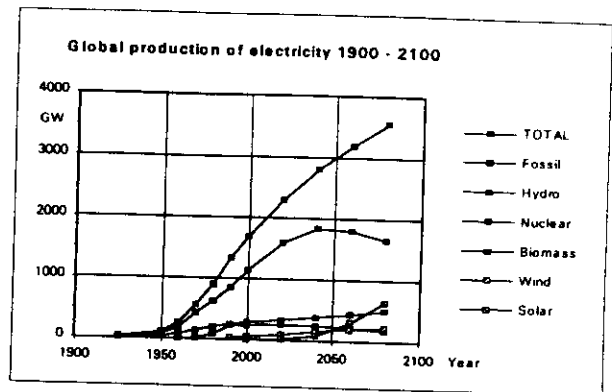


Figure 1.a. Global production of electricity. The history is based on UN statistics. The future shows a "slow development scenario".

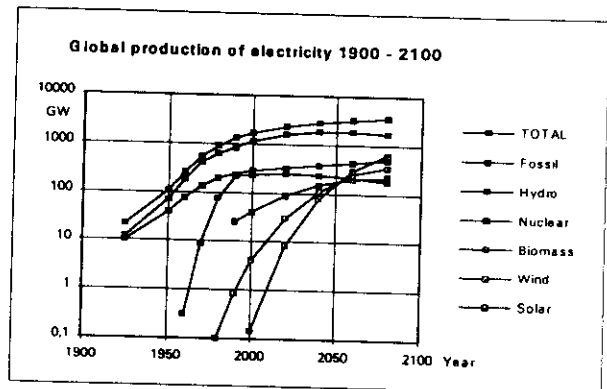


Figure 1.b. Data of figure 1.a. presented on a logarithmic scale.

There are striking messages in Figures 1. While the need for new sources of energy is urgent, the delay in achieving a visible change in the production structures will take several years. Also, there are very few technologies able to respond to the need of increased electricity production and the replacement of the role of the fossil fuels. There are some remarkable resources available in hydropower. Wind potential is smaller than hydropower, nuclear power is limited by the acceptability of the technology as well as the resources of uranium. Biomass has potential in limited areas and in small local units but it can not be considered as a covering general solution for electricity production. Figure 2 summarizes the availability of known primary energy sources for the next two centuries.

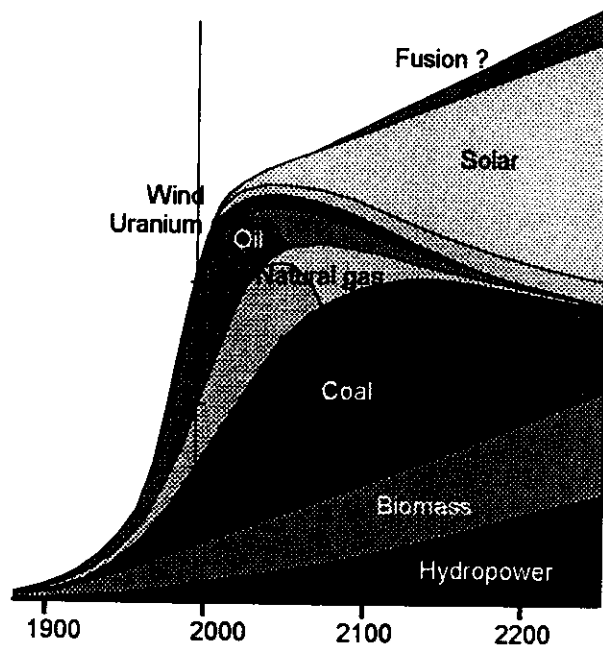


Figure 2. Availability of known primary energy sources. Proven reserves of oil and natural gas are for less than 50 years at present consumption level. Coal reserves are somewhat larger. One can expect certain extension for all fossil fuel reserves at higher production cost.

In Figure 2 the darker area in the fossil fuels, oil, natural gas and coal refers to proven recoverable resources. The lighter parts are extensions expected. One can also see the modest role of uranium nuclear power. For the 5% share in primary energy for about 100 years we have to accept active nuclear wastes for millions of years ahead. Fusion is still a big questionmark. Fuel reserves for fusion plants were practically unlimited but the technology for maintaining the necessary reaction temperature as well as problems with construction materials are unsolved. The complexity and the material demands of the system do not give promise to low cost electricity.

Solar energy is the only known technology having potential to widely solve the energy problem in long term both cost effectively and in an environmentally agreeable way. In fact, solar electricity is an elegant way of utilizing nature's big fusion reactor, the sun. Three days solar insolation onto the earth corresponds to the energy content of all proven resources of fossil fuels. Technically, implementation of solar energy could be accelerated significantly. The development, however, is dominantly determined by economical factors which does not allow the merging energy technologies to take over as long as there are low

cost fossil fuels available. For solar electricity the key factor in competition with conventional energy production is the production volume of the solar cells and modules rather than new technological breakthroughs.

The future availability of fossil and nuclear fuels is not the only driving force towards new sources of energy. In fact, the main motivation in restricting the usage of fossil fuels is the concern of climatic changes due to an increase of carbon dioxide in the atmosphere. The curves of Figure 2 suggest, however, that the available reserves of fossil fuels will be burned out anyway, restrictions will only have a modest influence on the time span for that. While the focus of the discussion is in carbon dioxide and the greenhouse effect there is less attraction in other problems of burning such as oxides of nitrogen and sulfur. For responsibility in climatic concerns the cleanness of burning and the efficiency of burning are of high importance and those are the factors we can effectively influence by using advanced combustion technologies. Also, responsibility and advanced skills in using energy become more and more important.

#### Need of land area for solar electricity

Technically large usage of solar energy for electricity production as well as for the production of heat and hot water for households could be realized using present technologies. As stated in the introduction a household can be electrified with about 20 m<sup>2</sup> of solar panels without compromising the standards of living. For hot water a few squaremeters of solar heat panels is enough.

Non-centralized production of electricity is a special opportunity offered by solar technologies. Installations can be made close to users minimizing the transfer distances. Rooftop and facade panels may serve as integrated construction parts of houses. Centralized electricity production can be solved with same basic components. Figure 3 shows the distribution of earth surface area and the area of solar cell arrays needed to supply the whole present production of electricity using today's solar cell technology.



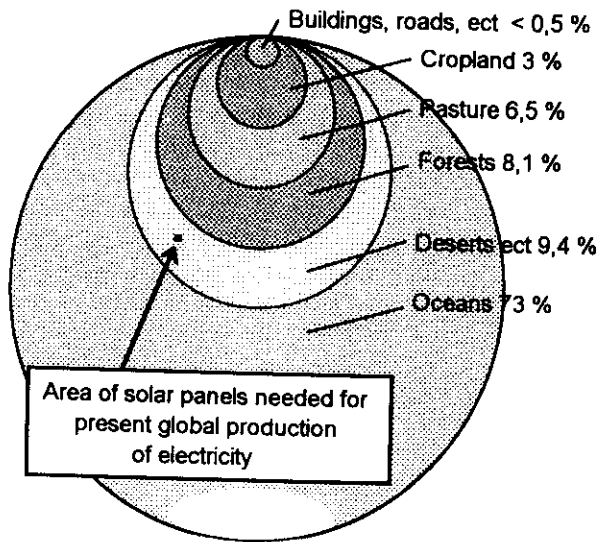


Figure 3. Distribution of the earth area in different categories. Solar panel area needed to supply all presently used electricity is about 0,1 % of the desert areas on the earth.

### Promoting of solar electricity

As stated before the key factors in guiding the development are the economical considerations. For merging technologies it is always difficult to replace existing technologies without an advantage either in price or in the performance of the product.

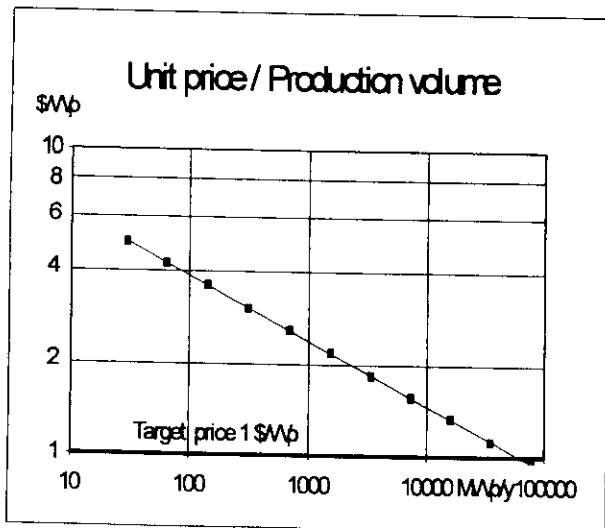


Figure 4. Learning curve of solar module production. Increase of the production volume by a factor of 1000 will decrease the price to about 1/5 of present prices.

As long as the product is electricity, the user cannot see difference between the production means. In any business area the economical structure built up has an important influence and role in accepting changes. In the case of electricity, power utilities produce electricity in centralized power plants. The electricity produced is then distributed to customers through power grid.

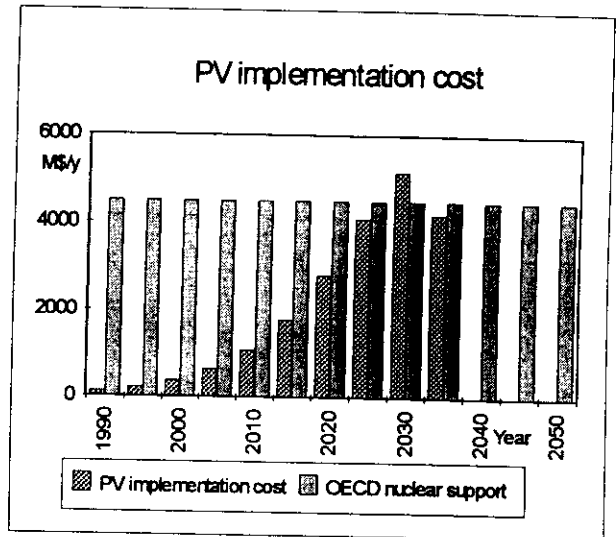


Figure 5. Implementation cost of solar electricity technology as compared to public R&D support into nuclear energy in the OECD countries.

For power utilities change toward non centralized electricity production would mean a remarkable change in operation and the income structure. Serving local small scale solar power generation would mean sales or leasing of solar modules to customer.

The system cost of a solar electricity installation is strongly dependent on production volumes. Figure 4 shows an estimated dependence of solar module price on the unit cost.

For wide use of solar electricity the production of the solar panels must be increased by a factor of 1000. This will take the cost down to about 1/5 of the present prices which can be considered as a target price for solar electricity competitive with conventional electricity production. If we decided to accelerate the implementation of solar electricity by subsidizing the installation cost to 1/5 of today's prices, we would end up with a subsidy need less than the public support on nuclear energy research during the same time, Figure 5.

The learning curve estimate of Figure 4 is based on a technology analysis of present solar cell



material	production 1992 (kton)	recoverable reserves (kton)	PV peak power equivalence of the reserves (MWp)
Copper	8 000	600 000	20 000
Indium	0,14	2,3	
Selenium	1,8	75	
Cadmium	20	1000	200 000
Tellurium	0,078	20	

Table 2. Availability of raw materials for CIS and CdTe thin film solar cells. Present global production of electricity corresponds to a PV peak power requirement of about 5 000 000 MWp.

### Large scale energy production with photovoltaics

A natural concept for implementing photovoltaic electricity is the use of grid connected panel arrays on roofs. The big advantage of grid connected systems is that it is immediately applicable. An educative value in locally generated solar electricity is that it reminds individuals of their chance and the responsibility in taking care of clean environment. Grid connected systems also eliminate the need of electricity storage as long as the share of photovoltaic electricity production relatively small. With 20% annual growth in photovoltaic installations it will take more than 40 years before the share of solar energy exceeds 10% of global electricity production. Locally the situation might be different and storage of electricity becomes important.

In very large scale solar electrification storage shall be an integral part of the system. A straightforward solution to this would be electricity - hydrogen - electricity conversion.

Hydrogen can be generated by decomposing water into hydrogen and oxygen by electrolysis. With present devices this can be done with about 85% conversion efficiency. In an integrated energy concept hydrogen would be generated at solar cell fields and transported to users via gas pipe lines similar to present natural gas lines.

Conversion from hydrogen back to electricity can be made either by using turbine techniques as used with the natural gas or by utilizing fuel cell technology which is capable to higher conversion efficiency than gas turbines. The volume of hydrogen pipelines would be enough to serve as the storage for daily variations. Most probably, an optimum solution would be a combination of centralized and local energy production.

In large scale solar electrification global decision making will be needed in order to effectively utilize sunny waste land for electricity production.

Figure 7 shows a global energy concept based on solar electricity and hydrogen. The land area needed for solar electricity/hydrogen generation for all present energy production (not only electricity) is indicated with small squares in the sun belt area. For primary energy transportation hydrogen pipelines are used. At certain points hydrogen is then converted back into electricity or possibly refined to liquid fuels for traffics needs.

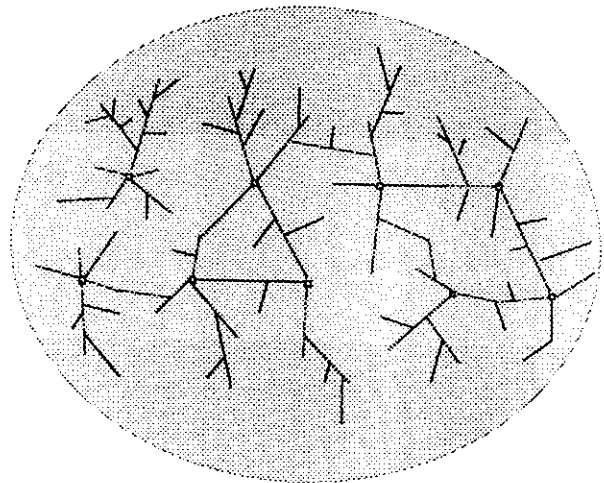


Figure 7. An energy concept based on solar electricity - hydrogen - electricity conversion. For solar cell array plants supplying all present energy needs a total earth area of about 50 million hectares (=0,1% of the earth area) would be needed.

## **Conclusions**

Solar energy can be considered as a workable total concept for energy production. Implementation can be made stepwise starting from small scale non-centralized electrification either grid connected or equipped with chargeable batteries. For very large scale energy production global hydrogen based concept will be needed. The development of the energy production is mainly driven by today's economical criterias. For a steady development towards a sustainable solution firm political decisions and international understanding will be needed.

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