Survey of Thin Film Photovoltaics in Germany

V. Sittinger, W. Diehl, and B. Szyszka,
Fraunhofer Institute for Surface Engineering and Thin Films IST, Braunschweig, Germany

ABSTRACT

Within the scope of limited non-renewable energy sources and the restricted capacity of the ecosystem for greenhouse gases and nuclear waste, sustainability is one important target for the future. Different energy scenarios show the huge potential of the photovoltaic at solving energy problems.

Accordingly, during the last decade PV had an average growth rate of over 45% per year. In 2008 the world-wide production of solar cells has grown to 7.9 GW [1]. And more than 12% of the recent production involves thin film technologies. These technologies have a high potential for cost reduction. The so called second generation of thin film solar cells based on a-Si:H/µc-Si:H, $Cu(In,Ga)(Se,S)_2$ or CdTe have material thicknesses of a few microns as a result of their direct band gap. The possibility of monolithic circuit integration offers an additional cost reduction potential as well as the use of large areas. Additional short energy pay back time is given. Above, new products e.g. flexible solar cells are possible. Nowadays roughly 150 companies are working in this field. Especially in Germany there are many companies focusing on thin film solar cells. Some of them have already started mass production. Schott Solar GmbH and Ersol Thin Film GmbH (takeover by Bosch GmbH) with the a-Si technology are collaborating in the development of a-Si/µ-Si tandem technology. The US company First Solar produces in Germany using the CdTe technology and the company, Roth & Rau will offer turn key lines for this technology in the near further. Würth Solar GmbH is using the $Cu(In,Ga)Se_2$ technology. There are further varying production lines under construction by companies for example at Avancis, Sulfurcell, Johanna Solar, and Solarion GmbH. Furthermore, the previously biggest company in the world wide solar market QCells started up different subsidiary companies for applying all these technologies (Sontor, Calyxo, Solibro). The company centrotherm build up the first 50 MW turnkey lines. And still, there are many companies even starting to ramp up production lines.

An overview of the research activity in different companies and with different thin film technologies will be given as well as different manufacturing and production processes.

INTRODUCTION

The energy supply today is based predominantly on limited non-renewable fossil energy carriers such as oil, gas, and coal or on nuclear energy carriers such as uranium. Among other things, problems with the continuity of supply are related to this, such as rising prices due to shortages and to instability in the countries where these resources are located. The risk of nuclear energy and atomic waste still remains unsolved. The occurring distinctive climatic change due to the rise in CO_2 [2] and the heating of the atmosphere is becoming increasingly serious as it causes problems such as floodings, heat waves and hurricane-like storms even in Germany. In the medium or long term future the range of problems can only be solved by switching to renewable energies from carriers such as wind, biomass, water power, geothermal power and solar energy. Currently, our global energy requirement is around $1.4 * 10^{14}$ kWh/a [3]. The IEA (International Energy Agency) forecasts that this will be doubled by the year 2050. This means that each day one power station with a capacity of 1 GW has to be built.

In comparison the potential offered by solar energy (amounting to $1.5 * 10^{18}$ kWh/a [4]) would cover our worldwide requirements many times. However, we need to ask for an intelligent and efficient utilization of this source. In recent years an enormous amount of development and expansion has occurred in the field of thin film photovoltaics, not only within industry but also in research institutes. An older survey of thin film solar cell technologies in Germany can be found in Diehl et al. [5].

MARKET SITUATION

In Germany the groundwork for the utilization of alternative energies was pushed forward in 2000 by the Renewable Energy Sources Act (EEG). This created a long-term security of investment for the manufacturers and operators of photovoltaic installations as well as an improved stimulus, implemented in the form of an annual decrease of about 10% of funding, depending on the installation and size, which compels the companies to offer cheaper and cheaper modules. Reductions in price are only possible when there is a relatively fast market

52nd Annual Technical Conference Proceedings, Santa Clara, CA, May 9–14, 2009 ISSN 0737-5921

growth. Above, further technical innovations are needed in order to get lower production costs and/or boost the module efficiency. Due to the EEG legislation, Germany has the largest PV market in the world. Accordingly, 1.5 GW_p (27% of the world market) was solely delivered in 2008 in Germany as well as 5.3 GW_p of total installed PV Power worldwide with 37% of global installations [invest in Germany]. Crystalline silicon-wafer technology was dominant with nearly 90% of the market and an annual growth above 30%.

Notwithstanding this, higher growth rates are expected for thin film photovoltaics than for the wafer-based technology [6]. Among other things, this is also to be attributed to limitations in the supply of the silicon raw material. Regardless of the expansion in production capacities, the quantity of raw silicon available has not been able to keep up with existing growth. In addition, the price for the feedstock doubled within a three year period [7]. The European Photovoltaic Industry Association (EPIA) is expecting thin film technology to grow to 20% by 2010. Studies conducted by the Q-Cells company show that wafer-based technology still possesses a high potential for reducing costs. At the same time, thin film technologies can achieve comparable or even lower manufacturing costs per W_p despite their lower efficiency [8].

In the meantime, the sales volume due to photovoltaic technology has reached 7 billion € 2008 in Germany German manufacturers of photovoltaic equipment have sold machines up to the value of 875 million € [9]. A large number of companies in Germany is active in the field of thin film photovoltaics, both as installation manufacturers and as makers of photovoltaic modules.

POTENTIAL OF THIN FILM PHOTOVOLTAICS

The potential of crystalline silicon wafer technology for reducing costs is limited by the high costs of materials due to the indirect band gap of the semiconductor and the resultant high thickness of the absorber. In contrast, thin film solar cells based on a-Si, $Cu(In,Ga)(Se,S)_2$ or CdTe have absorber thicknesses of just a few microns on account of their direct band gap. Another potential for savings is offered by the possibility of circuit integration since this means the modules can be applied to large surface areas. Basically the solar cells can be deposited on a substrate in two different configurations (see Figure 1). In the superstrate configuration a transparent conductor is applied to a glass plate, followed by the absorber system. Finally the metal back contact is deposited. In the substrate configuration it is the metal back contact which is deposited first, followed by the absorber system and front contact.

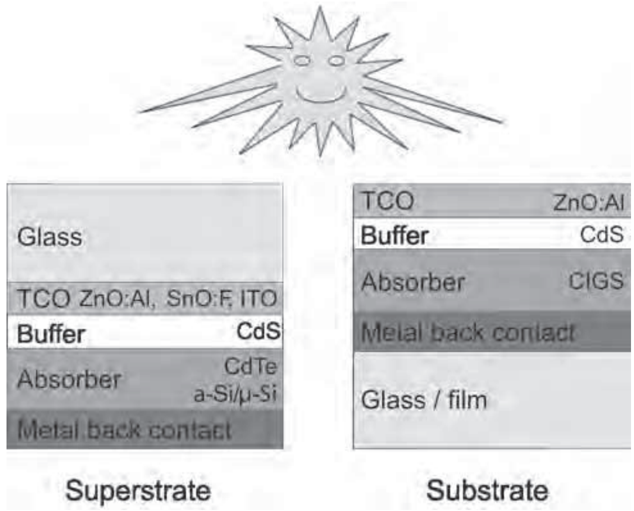

Figure 1: Superstrate and substrate configurations of a solar cell.

Depending on the material, the maximum theoretical efficiency is set by the energy band-gap via the so-called Shockley-Queisser limit [10]. The cell and module efficiencies achieved so far are considerably lower, as shown in Figure 2 [11].

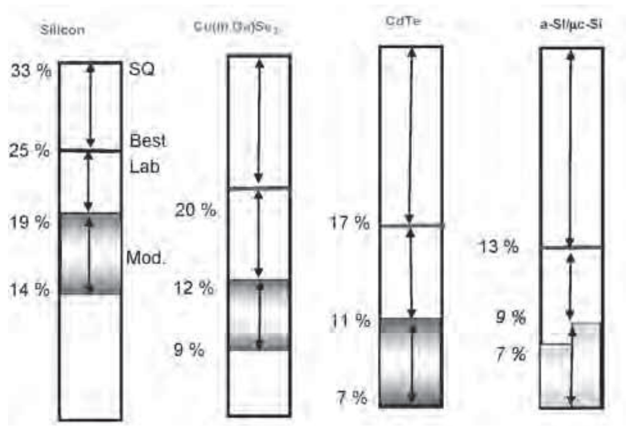

Figure 2: Efficiencies of different materials according to U. Rau [11].

RESEARCH ACTIVITIES, PRODUCTION AND PROCESS TECHNOLOGIES

Thin film technology based on amorphous and microcrystalline silicon

The earliest concept for thin film solar cells is based on amorphous silicon. Thin film micromorph solar cells made of amorphous (a-Si:H) and microcrystalline silicon (µc-Si:H) can be produced by plasma-enhanced chemical vapor deposition (PECVD) or deposited by hot-wire CVD processes at temperatures of 100 – 300°C. This is permitted by the use of cheap substrates such as glass, steel foils or plastic. Since 1980 the Phototronics (PST) division of Schott Solar GmbH is working in this field. Today it offers a broad range of products to supply electrical power to watches, pocket calculators, lamps and so on as well as large-format power-supply modules in open-air installations, on rooftops and for photovoltaic systems integrated into buildings. A semitransparent version of standard modules can be created by laser structuring. A further advantage is the very low dependence of efficiency on temperature, which means that good module outputs can be achieved even at high temperatures. The temperature coefficient which describes the fall in efficiency with temperature is only about -0.1 percent per degree centigrade for a-Si:H solar modules. For crystalline silicon the temperature coefficient is mostly around -0.4 percent per degree centigrade which means that the fall in efficiency with rising operating temperature is higher than with a-Si:H solar cells [12].

In the meantime manufacturers are offering even larger installations for producing amorphous silicon. A great advantage has been installations developed for the display industry. The first vendor in the solar field was Oerlikon AG with its KAI 1200 system. Figure 3 shows on the left a KAI 1200 PECVD reactor, which applies the so-called plasma box concept and can coat 20 modules simultaneously with a-Si:H or µc-Si:H. On the right a system is shown which uses LPCVD processes in the low-pressure range to manufacture front contacts made of zinc oxide doped with boron (ZnO:B).

Figure 3: On the left, a PECVD KAI 1200 system, on the right a TCO 1200 system for fabricating a-Si modules on 1.4 m^2 [13].

Following acquisition of a laser manufacturer, Oerlikon AG now offers complete turnkey installations for producing the a-Si:H modules. As customers, Schott Solar GmbH, ErSol Thin Film GmbH and Inventux AG in Germany have been equipped with these installations (approximately 30 - 40 MW). Another manufacturer is Applied Materials AG, who offers PECVD installations for substrates measuring 5.7 m^2. As customers, Sunfilm AG, Malibu GmbH, Signet Solar GmbH and Masdar PV have been equipped with 20 - 60 MW fabrication lines in Germany. Another 25 MW PECVD in-line installation using 1.4 m^2 substrates from Applied Materials is being operated by Sontor GmbH, a wholly-owned subsidiary of Q-Cells AG. This system type will not be further developed. An additional vendor on the market is Leybold Optics GmbH, who offers systems for module sizes 1.4 x 1.1 m^2. Since April 2009 Sunfilm AG and Sontor GmbH merge to become one of the leading manufacturers of silicon-based thin film modules in the world [13].

Additionally, all installation manufacturers offer the option of fabricating not only modules from amorphous silicon but also tandem modules consisting of one layer of amorphous and one layer of microcrystalline silicon. The advantage of the tandem cell is its higher efficiency. This happens due to the different band gaps of the materials and the different utilization of the solar spectrum resulting from this which can be seen in Figure 4.

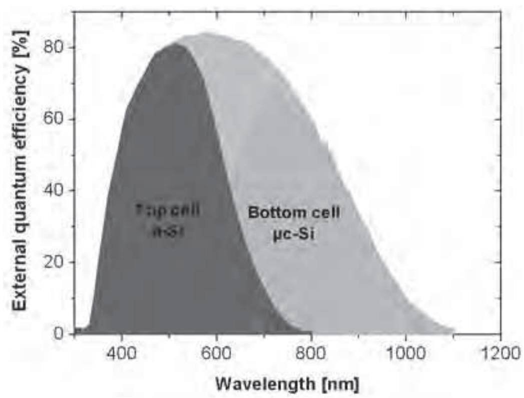

Figure 4: Quantum yield spectrum of an amorphous silicon cell (a-Si) and a micromorphous tandem cell (a-Si/µc-Si).

One condition for using nanocrystalline silicon is the presence of a rough, transparent, conductive oxide (TCO) which elongate the path taken by light within the µc-Si. This is necessary because, due to its indirect band gap, this material has a low absorptivity. The advantage of roughened TCO can be seen in Figure 5. Here the ZnO:Al which was roughened by means of etching with hydro chloride acid [14] is compared with the SnO_2:F from Asahi which is already grown with a rough structure.

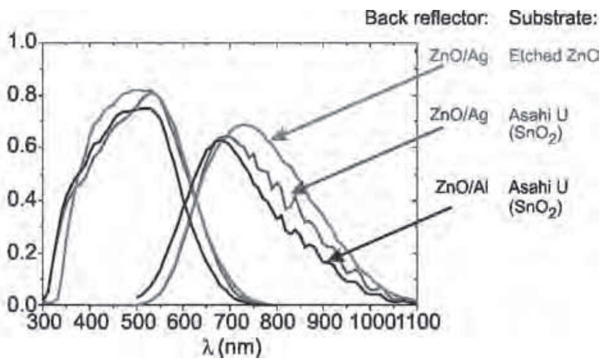

Figure 5: Quantum yield spectra of a-Si/µc-Si solar cells with different TCOs [15].

The roughness of the surface causes the light path to be lengthened, and this, particularly in the infrared wavelength region, results in an increase in the quantum yield. Further research is in progress in particular in department IEF5 of the Forschungszentrum Jülich. Researchers are currently working on increasing deposition rates on the one hand, and on an optimized light trapping structure on the other.

In this connection, they are striving to obtain optical and electrical improvements in not only the TCO but particularly in the intermediate layers as well as optimization of the back reflector. As with all types of solar cell, investigation of the interfaces is of critical importance to increasing cell efficiencies.

CIGS-based thin film technology

The chalcopyrites group is characterized by a crystalline structure made up of three different types of atoms (A, B and C). The corresponding notation is $A_I B_{III} C_{VI2}$. Here the superscripts denote the classification of the atoms into different groups of the periodic table. Known examples include $CuInS_2$, $CuInSe_2$ and $CuGaSe_2$. The highest efficiencies are achieved with $Cu(In,Ga)Se_2$ solar cells with a band gap of 1.15 eV. The complete solar cell consists of a 4 µm thick layered structure, which is applied by different coating processes to the substrate at a temperature of around 400 - 550°C. The record efficiency achieved so far is 19.9% [16]. There is a wide variety in the methods used to manufacture the $Cu(In,Ga)(Se,S)_2$ (CIGS) absorber. Würth Solar, together with the Center for Solar and Hydrogen Research (ZSW), has developed a linear evaporation process. A similar method is used at Solibro (a subsidiary of Q-Cells) in collaboration with the University of Uppsala. Solarion uses plasma-enhanced evaporation to enable deposition at low temperatures (400°C) onto a polymide foil. Another technique is sputtering Cu/In and Ga, which is then, depending on the company, converted into CIGS in a rapid thermal processing (RTP) oven in a selenium and/or sulfur atmosphere. This principle is used by Avancis, Sulfurcell Solartechnik and Johanna Solar Technology while CIS Solartechnik GmbH and Odersun AG apply an electrochemical process to deposit Cu, In and Ga with an RTP process following. Nanosolar takes a different way to produce the absorber: printing with CIGS pastes, followed by an RTP process.

Figure 6 shows the typical procedure employed in CIGS module production. Once the metallic back contact has been fixed to the substrate, the absorber can be applied by a variety of different methods. The illustration shows co-evaporation at approximately 500°C and sputtering and subsequent selenisation or sulfurisation at approximately 550°C. After the absorber a buffer layer is applied wet-chemically, followed by an intrinsic ZnO layer and the conductive ZnO front contact.

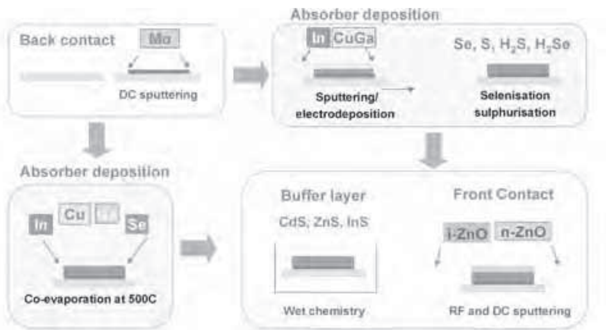

Figure 6: Typical deposition methods used in the production of CIGS solar cells [17].

The company which has made the most progress is Würth Solar, which has set up the first CIGS production line. This has a capacity of 30 MW and an average module efficiency of 12% [18]. The module measures 1.2*0.6 m^2. A further expansion of production is in the planning stage. Sulfurcell Solartechnik GmbH has a pilot line with a capacity of 5 MW in operation. Sulfurcell attains an efficiency of 8.6% on a module area of 1.25*0.65 m^2 [19], and this year they will establishment a 75 MW production line [20]. Avancis GmbH, a joint venture of Shell and Saint-Gobain, is setting up a 20 MW production line in 2008. Here the module size is 1.6*0.6 m^2 and expansion to 120 MW is already in preparation. The best efficiencies achieved so far with 0.3*0.3 m^2 modules are around 13% [17]. Other activities in Germany include the establishment of a 30 MW production line by Johanna Solar, a 35 MW production line (on flexible metal foil) by Global Solar Energy and a 30 MW fabrication plant by Odersun AG which coats the CIGS onto copper tape. Both CIS Solartechnik and PVFlex Solar GmbH are in the pilot stage. Centrotherm AG is the first manufacturer of turnkey systems for CIGS. The ramp-up phase for a 50 MW plant, at a module size of 1.5 m², is about 15 months after order [21].

Figure 7 shows the typical band diagram for a CIGS solar cell with the research areas which will be necessary in the future.

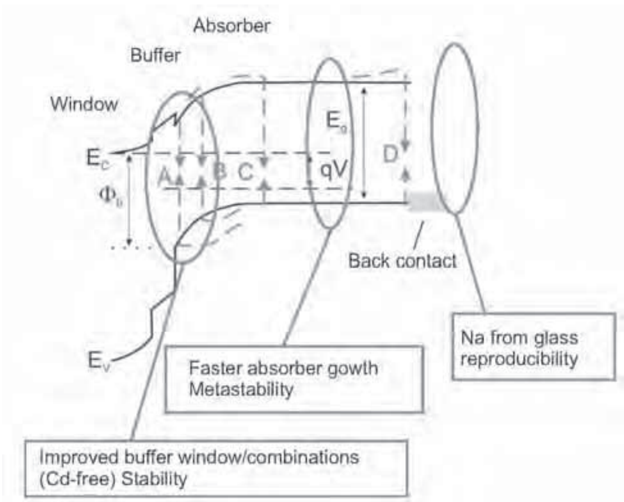

Figure 7: Band diagram of a CIGS solar cell showing the necessary main research areas for the future [10].

To achieve high efficiencies a CIGS solar cell needs a sodium source. Here the sodium serves not only as a 'fluxing agent' in CIGS absorber production but also as a 'passivating agent' for grain boundaries. Precise monitoring of the sodium proportion would be desirable. Faster growth of the absorber is also an important cost factor during production. Above of decisive importance to a high efficiency is the CIGS/buffer interface. An improved boundary would reduce the recombination of charge carriers and make a contribution to a higher efficiency. Furthermore, with a view to better product acceptance, efforts are being made to produce a cadmium-free buffer. Further strategies for improving the CIGS absorber are outlined in a paper by Professor Schock [22].

CdTe-based thin film technology

CdTe is a direct band-gap II–VI compound semiconductor with a band gap in the 1.44 eV range. Using CdTe as an absorber in a solar cell means a good exploitation of the solar spectrum due to the size of the band gap. Together with the readiness which is needed for the solar cell structure this is one of the positive properties of the CdTe solar cell. The CdTe layer is deposited by sublimating CdTe granules at 700°C onto the glass/front contact/n-CdS system at 500°C. Following activation with chlorine gas, the CdTe layer is polycrystalline with crystallites in a columnar arrangement and lateral grain sizes in the 1 - 2 µm range. The complete solar cell consists of a layered structure with a thickness of about 8 µm.

Currently CdTe-based thin film technology has the lowest production costs. The largest producer in thin film and second largest overall technologies is the US company, First Solar [1]. In Germany First Solar is operating a 175 MW production line with an average module efficiency of 9 - 11%. The module size is 1.2*0.6 m². First Solar is planning to expand its international production capacity to 1.1 GW by 2009 [7].

Figure 8 shows the cost savings achieved by mass production.

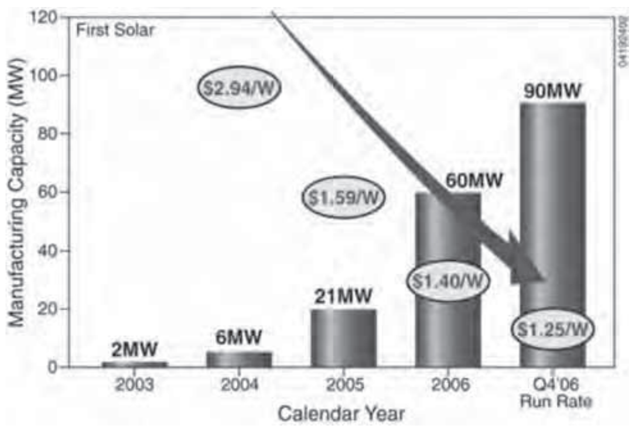

Figure 8: Thin film CdTe manufacturing capacity and cost reductions per calendar year at First Solar [23].

In 2004 First Solar had decreasing manufacturing costs. As shown in the diagram the costs fell from $2.94/W (6 MW) to $1.25/W (90 MW). Meanwhile the costs are about $0.98/W [7]. For the year 2012 costs of $0.65 to $0.70 per W are expected due firstly to increased productivity and secondly to an improved efficiency and higher yield [7,23]. Another manufacturer of CdTe modules is the Q-Cells subsidiary, Calyxo GmbH, which is setting up a 60 MW production line. Antec Solar GmbH was the first thin film company to start on the production of CdTe modules in 2001. This company, which since that time declared insolvency twice, has a 10 MW plant for producing CdTe modules with a module size of 1.2*0.6 m^2. Figure 9 shows how this plant is organized.

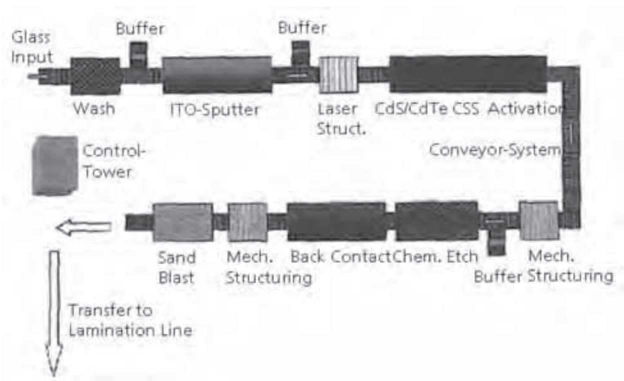

Figure 9: Arrangement of the Antec Solar's CdTe line [24].

Figure 10 shows the band diagram for an activated and a non-activated CdTe solar cell. In the case of the non-activated cells, at the interface between absorber and buffer there are very many interface states across which the electron-hole pairs recombine and thus no longer contribute to the solar cell current.

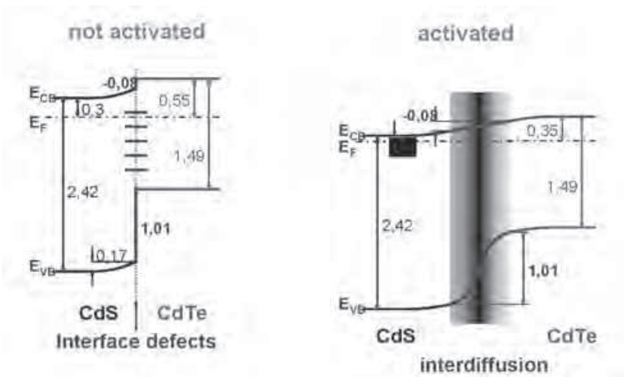

Figure 10: Band diagram of an activated and a non-activated CdTe solar cell [25].

In order to create a good CdTe solar cell the chlorine-gas activation is of decisive importance as it passivates the interface.

Similar to other cell types it is of enormous importance to understand the situation at boundaries because this leads the way up to high efficiencies and improved stability.

OUTLOOK

Due to the German Energy Supply Act the local photovoltaics market will continue growing. The predicted cost reduces will require companies to implement a continuous improvement in efficiency and simultaneously low cost processes. This must be achieved by a constant increase in research performance. It is the aim to reduce power generation costs as fast as possible, down to or below the range of costs which can be reached with conventional energy carriers. In this respect the German industrial and research landscape is very well seted up. Industry aspires to cover 12% of power requirements throughout Europe by 2020 by means of photovoltaics (EPIA). Currently, in Germany approximately 1% of power requirements are covered.

Germany is very well prepared for taking over a globally leading role in thin film photovoltaics alongside the established crystalline silicon technology.

REFERENCES

1. W. P. Hirshman, Little smiles on long faces 2008, *Photon International*, March 2009.

2. Intergovernmental Panel on Climate Change (IPPC) Report 2007, http://www.ipcc.ch/ipccreports/ar4-syr.htm.

3. US Department of Energy 2006.

4. Eurec Agency/Eurosolar WIP: Power for the World - A Common Concept.

5. W. Diehl, V. Sittinger, B. Szyszka, S*urface and Coatings Technology* 193, 2005.

6. A. J. Waldau, JRC, PV Status Report 2007.

7. J. Herron, For less then one dollar 2008, *Photon International*, March (2009) p. 64.

8. F. Holtzapfel, PV Industry Forum, Munich, 2008.

9. Invest in Germany GmbH, January 2009, www.invest-in-germany.com.

10. W. Shockley and H. J. Queisser, *J. Appl. Phys.* 32, (1961), p. 510.

11. U. Rau, 7th ICCG Conference, Eindhoven, 2008.

12. B. Rech, Photovoltaik – Neue Horizonte, FSV Conference 2003.

13. Press release, Sunfilm dated 28. 04. 2009 www.sunfilm.com/en/communication.

14. O. Kluth, B. Rech, L. Houben, S. Wieder, G. Schöpe, C. Beneking, H. Wagner, A. Löffl, H.W. Schock, *Thin Solid Films* 351 (1999).

15. J. Müller, B. Rech, J. Springer, M. Vanecek, TCO and light trapping in silicon thin film solar cells, *Solar Energy* 77 (2004) 917–930.

16. press release, NREL, www.nrel.gov/news/press, 2008.

17. P. Mogensen, PV Industry Forum, Munich, 2008.

18. press release, Würth Solar dated 04.08.2008.

19. A. Meeder, A. Neisser, U. Rühle, N. Meyer, 22nd European Photovoltaic Solar Energy Conference, 2007, Milan, Italy.

20. Press release, Sulfurcell GmbH 2008.

21. D. Schmid, PV Industry Forum, Munich, 2008.

22. H.W. Schock, 22nd European Photovoltaic Solar Energy Conference, September 2007, Milan, Italy.

23. H.S. Ullal, B. Roedern, 22nd EPSEC, Milan, 2007.

24. M. Harr, D. Bonnet, 17th European Photovoltaic Solar Energy Conference, Munich, 2001.

25. J. Fritsche, A. Klein W. Jaegermann, *Adv. Eng. Mater.* 7 (2005), 914.