HEALTH, SAFETY AND ENVIRONMENTAL ISSUES IN THIN FILM MANUFACTURING

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ABSTRACT: An investigation is made of Health, Safety and Environmental (HSE) aspects for the manufacturing, use and decommissioning of CdTe, CIS and a-Si modules. Issues regarding energy requirements, resource availability, emissions of toxic materials, occupational health and safety and module waste treatment are reviewed. Waste streams in thin film module manufacturing are analyzed in detail and treatment methods are discussed. Finally the technological options for thin film module recycling are investigated. It is concluded that there are no serious HSE bottlenecks for upscaling to production levels of 500 MWp/yr and that adequate methods are available for treatment of the manufacturing wastes. However, on the longer term issues regarding CdTe and CIS module waste treatment, In and Te resource availibility and module recycling need to adressed. Appropriate recycling methods for CdTe and CIS modules do not exist at present but the problem is being adressed by the PV industry.
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INTRODUCTION

In the MUSIC-FM project a study has been made on the upscaling of PV module manufacturing towards 500 MWp/yr both for crystalline silicon and thin film technologies. As a part of this project we investigated the Health, Safety and Environmental issues regarding manufacturing of thin film modules, i.e. modules based on amorphous silicon, cadmium telluride and copper indium selenide. While the results of the manufacturing and marketing studies are reported elsewhere at this conference [1], we will present in this paper the major findings of the Health, Safety and Environmental (HSE) study.

By adressing HSE issues in thin film manufacturing in an early stage of technology development we aim to adress potential bottlenecks in time and to stimulate the application of clean and safe technologies for the entire product life-cycle. In this way we expect that thin-film modules may continue to be positioned on the market as a sustainable technology. Also it will allow us to answer public concerns regarding the use of toxic substances and regarding energy pay-back times in a proper way.

In the next section we will start with a review of the existing knowledge with regard to HSE aspects of thin film modules in order to identify potential bottlenecks for large-scale introduction of these PV technologies. Among the issues addressed are: energy requirements during production, resource availability, emissions of dangerous materials, gas hazards, occupational health and safety and finally module waste considerations.

Subsequently we will present a thorough analysis of the wastes produced during the manufacturing of of 10MW p.a. of CdTe, CIS and a-Si modules and discuss the most effective ways for dealing with them. Thirdly we will discuss the technological options and possible strategies for recycling of thin film modules. We finish with the general conclusions and recommendations.

2. POTENTIAL BOTTLENECKS

Based on published study results from different authors [2-6] we have reviewed a number of Health, Safety and Environmental issues which might form a bottleneck if thin film modules are to be introduced on a large scale (500 MWp p.a. and beyond).

2.1 Energy requirements

The total amount of primary energy which is consumed in the production of frameless thin film modules, the Gross Energy Requirement (GER), has been estimated to be 1100 - 1900 MJ per m² of module area for present-day production technologies. This GER value includes the energy required for cell processing, for the production of input materials, for the production of capital equipment and the indirect process energy (heating, lighting, emission control). Not included is the (optional) module frame.

The higher GER value in the range represents amorphous silicon and CIS modules, while the lower value is found for CdTe modules manufactured by means of electrodeposition. Future improvements in production technology are expected to reduce the GER values to below 1100 MJ/m^2 [2].

Calculation of the energy pay-back time assuming a module efficiency of 5% respectively 10%, an irradiation of 1700 kWh/m²/yr, a system Performance Ratio of 0.80 (grid-connected system) and a thermal to electric conversion efficiency of 0.4 results in a value of 1.8-3 years for present-day technology, and below one year for future technology.

Note that these values are for a module only, without frame or support. The latter items may add considerably to the total energy pay-back time of a PV system, from 0.4 yr for a roof-integrated design and upto 1.2 yr for rack-mounted array with heavy steel supports (at 10% module efficiency).

2.2 Resource depletion.

At a module production level of 500 MWp/yr, the target within the MUSIC FM project, no problems with resource availabilty are expected. However, if we consider thin film PV as a technology for large-scale energy supply (e.g. 5% of world electricity supply, requiring a yearly module production > 10 GWp) then the availability of indium will become a bottleneck unless this metal is recovered from decomissioned modules or a substitute material is used. To a lesser extent the supply of tellurium may put a constraint on the large-scale deployment of CdTe modules.

2.3 Use and emissions of toxic materials

Although the use of cadmium or selenium compounds in solar cell modules may give rise to public concerns the risks of this should not be exaggerated. Considering CdTe and CIS layer thicknesses of a few µm the cadmium or selenium content of thin film modules is comparable or much lower than that of accepted products like NiCad penlight batteries, cathode ray tubes or plated metal sheets [6]. On the other hand one should note that CdTe modules with much thicker layers are also available on the market today and also that environmental regulations with regard to cadmium will be increasingly strict.

As regards module manufacturing it is clear that under normal operating conditions and if standard emission control measures are implemented no serious emissions to the environment are expected from the production of all three modules types.

However, for deposition processes with a low material efficiency and/or a high material consumption, like spraying or screen printing, it will be more difficult to achieve a low emission rate, than for a process like electrodeposition which has a high material efficiency and which takes place in an aqueous environment [3].

The occupational risks of thin film module manufacturing generally seem quite acceptable provided that normal industrial health and safety practices are implemented [5].

External safety risks from module manufacturing are mainly due to the storage and handling of explosive and/or toxic gases. The storage of large-quantities of silane for a-Si production and of hydrogen selenide for CIS production may pose serious safety risks for workers and public. For CIS the use of deposition methods which do not rely on the selenization process are therefore highly preferable [2,5].

Health risks resulting from the use of CdTe and CIS modules have been evaluated for a number of different exposure routes (e.g. emissions during a fire, emissions from broken modules). In all these cases the risks were found to be neglible or small [6].

Some uncertainty exists on the emissions to be expected from the waste of decommissioned CdTe and CIS modules. Leaching tests commissioned by BP Solar [3] have shown that their CdTe modules meet the proposed EC regulations for landfill of waste. On the other hand tests performed by Steinberger et al. [6] show that heavy metal leaching from CdTe and CIS modules from other manufacturers may exceed the limits set by German, Swiss and U.S. authorities.

A point to note here is that a glass/glass encapsulation will considerably reduce the leaching out of cell materials. Unfortunately many modules available on the market today are not provided with such a double glass encapsulation. A disadavantage of glass/glass encapsulation is that it will not facilitate module recycling.

As a-Si modules contain little or no toxic materials there are no problems concerning module waste. Given the large glass content of a-Si module waste they may even be recycled via standard glass recycling processes [2].

A life-cycle comparison of emissions on the basis of generated electricity shows that the estimated Cd or Se emissions from CdTe or CIS modules are comparable or lower than the cadmium or selenium emissions from coal-fired generation of electricity (0.6-10 g GWh for cadmium and 70 g/GWh for selenium). It should be noted, however, that a coal plant has several more, environmentally harmful emissions.

The emissions from CdTe and CIS module include the releases from Cd/Se winning, module manufacturing, fires in roof-top PV installations and from incineration of 10% of the module waste [2].

2.4 Conclusion

Our conclusion from this review is that there are no serious bottlenecks with respect to health, safety and environmental aspects which would be a limiting factor when scaling up thin film module production to 500 MWp/yr. However, if CdTe or CIS thin film technology is required to contribute significantly to the world energy supply (production levels > 10 GWp/yr) issues concerning resource availibilty, module waste handling and module recycling will need attention.

3. WASTE MANAGEMENT

An essential part of a production facility is the means by which wastes are managed and the environmental impact of the production process is kept to a minimum. In this section we look at the nature of wastes produced, and options for management of these wastes.

3.1 CdTe technology

The electrodeposition route to CdTe, used by BP Solar was evaluated. The wastes produced at each stage were identified and categorised into ten different types to which specific waste management processes could be applied. Many of the wastes are comparable to those produced by conventional silicon technologies for which suitable management practices exist. Others require a new approach and these are :

- Rinse waters containing Cd compounds. These solutions can be treated by a two stage precipitation/ion exchange system to remove Cd down to the 10ppb level. The solution can be disposed of by the trade effluent system, or re-cycled via the process DI water plant.
- Precipitated Cd solids and compounds can be recycled by conversion to Cd salts suitable for re-use in the CdS deposition process.
- CdS and CdTe coated plates which, for various reasons, have failed during production can be acid stripped of their Cd compounds and recycled using Cd extraction from the acids by ion exchange. Reclaimed Cd can be recycled to the start of the process.
- Failed laminates or modules can be disposed of via non ferrous smelters [7].
- Wastes generated by the interconnection process are

typically Cd compound dusts collected in a HEPA filter system. These loaded filters would be disposed of in controlled landfill sites.

- Emissions to air, such as ammonia gas, can be treated by scrubbing and solvent emissions can be treated by incineration.
- The capital cost for Cd waste treatment has been estimated as 600k ECU for a 10MW plant.

3.2 CIS technology

The study focused on the copper indium diselenide technology used by ZSW, i.e. co-deposition of materials by sputtering. Like CdTe many wastes are such that existing management practices will be suitable. Several types of waste arise which will require specific treatment. These are :

- Rinse waters containing Cd salts and CdS solid, from the deposition of the CdS buffer layer, can be treated as above for CdTe.
- Coated glass which already has one or more layers deposited. Economic processes to remove the layers of Mo, CIS, CdS. ZnO from these glasses are important and need to be developed.
- Molybdenum which accumulates in the vacuum plants. If cleaning is done by sandblasting, molybdenum will be strongly diluted with the blasting material. Since molybdenum is non hazardous, the used sand can be disposed of with low costs provided they are not contaminated with other harmful substances. Sputter targets can be recycled.
- CIS deposition wastes accumulated in the equipment, and dust generated by the patterning processes, are an ill defined mixture of the elements Cu, In, Ga and Se and of various compounds thereof and represent a high value for recycling. Currently no suitable procedures for recovery of the elements from the wastes exist. Until they do disposal in controlled landfill sites will be necessary.
- Emissions to air, such as ammonia gas, can be treated by scrubbing and solvent emissions can be treated by incineration
- For failed modules non ferrous smelters provide a suitable route to disposal [7].

3.3 Amorphous silicon

This evaluation is based on data supplied from the PST pilot line, in Putzbrunn, Germany. There are three process steps which produce emissions and waste materials that may be subject to environmental requirements. These are :

- Emissions from the plasma enhanced chemical vapour deposition (PECVD) reactor resulting from a-Si deposition. The waste streams are treated by use of a burn chamber operated with methane and air. The conversion products are retained by filters for subsequent disposal in a controlled landfill site.
- Emissions from the PECVD reactor resulting from plasma etching of the deposition chamber (cleaning). SF_6 is used in the plasma etching of the deposition chambers. Some of it goes through the reaction in an unconverted form and the rest is either oxidised to a mixture of SiF_4 and SF_2 or reduced to a mixture of SiF_4 and SO_2 which are released to atmosphere, in compliance with the local air emission limitations. SF_6 is a gas with a very large “greenhouse effect” (1 kg of SF_6 is equivalent to 25,000 kg of CO_2). Emissions of this gas are therefore undesirable from an environmental point of view and alternatives to SF_6 should be evaluated.

In addition there will be non toxic waste streams resulting from glass handling and cleaning, frame offcuts, etc.

3.4 Conclusions

The nature and quantities of wastes generated by a 10MWp CdTe plant, CIS plant and a-Si plant have been established. Present waste management procedures will enable the satisfactory treatment of the wastes from the CdTe (electrodeposited) plant. Further work is needed to improve the raw material utilisation for the CdS deposition process.

For CIS many of the current waste management technologies will be effective, however further work will be needed to improve the CIS deposition process to increase utilisation of raw materials, particularly In and Se, to develop processes to recover In and Se from coated glass waste, packaged glass waste, wastes from the CIS deposition system and dusts generated by the patterning processes.

For a-Si most of the necessary waste management procedures are already well established. One area that should be further evaluated is to reduce or replace the SF_6 gas used to clean deposition chambers.

4. MODULE RECYCLING OPTIONS

At present there are no plants which specialise in the recycling of spent thin film PV modules and to date it was acceptable to dispose of off-specification and end-of-life thin film PV modules in landfill sites. Large scale production of thin film PV modules as examined in the MUSIC-FM project, however, will demand an appropriate recycling technology to address issues such as resource preservation, minimisation of environmental liability, energy conservation and reduction of landfill disposal costs.

An increasing number of thin film PV manufacturers are researching into possible in-house recycling strategies to reduce costs and environmental impacts. In the near-term thin film PV manufacturers will rely on the utilisation of existing recycling technologies in related industries. Existing recycling processes for non-ferrous metal smelters, NiCd and lead/acid batteries, glass, fluorescent lighting and television tubes were thus scrutinised with respect to their economic and environmental costs and benefits for the thin film PV industry.

4.1 Technology options

In some recycling industries, the off-specification or end-of-life PV modules would have a certain reclaim value. Unframed PV modules could be recycled as sheet or container glass. But while chemically cleaned sheet glass would have an estimated value of about 0.01-0.02$/W [8], container glass recycling is generally not economic due to its lower standard of cleanliness. The total reclaim value for recycling thin film PV modules using NiCd and lead /acid recycling facilities would be less than the processing costs and PV manufacturers/users would actually be charged for the recycling of the PV module.

The electronics industry are at present recycling fluorescent lighting and television tubes but have not considered the recycling of thin film PV modules. However, given the techniques used for stripping the deposited material from the glass it should be possible to adapt the techniques used in this industry to recycle thin film PV modules [9].

Other recycling industries such as primary non-ferrous metal smelters can use PV modules due to the high content of glass as feedstock with no financial remuneration to the PV industry. However the recovery of the metals on a cost only basis is not viable due to the very small amounts present. Secondary smelters and cement kilns, developed for use in treating hazardous materials could be used to process PV modules for their metal content [7].

4.2 Possible strategies for PV module recycling

Attempts have been made by several PV manufacturers to develop processes using established technologies for in-house recycling off-specification and end-of-life thin film PV modules. The recycling technologies were selected based upon the potential low cost of implementation and the minimisation of environmental side effects from processing.

Hydrometallurgical based separation procedures were investigated for the recycling of CdTe PV modules. Costs for the treatment processes for CdTe based PV modules vary from 3.6 ECU/m^2 for chemical treatment to 5.4 ECU/m^2 for mechanical removal of the semiconductors by impingement of the substrate with water pressurised to 40,000psi. The latter treatment is more desirable from an environmental aspect as it does not use any harsh chemicals but its disadvantage is that it can only be used on large pieces of glass. ($\sim$1ft^2). Both costs include capital, maintenance and labour costs and are based on 1 MW/year throughput [8].

Two options for the recycling of a-Si PV modules were identified. The first option involves the recycling of a complete encapsulated module as feedstock for secondary glass production. The second option entails substrate re-use, by etching away the active layers and re-using the substrate with the TCO layer. As the performance of modules with a re-used substrate is similar or sometimes even better than the performance of a virgin substrate this recycling technique would give benefits in terms of cost reduction, as glass and TCO make up 30-40% of the costs of the module.

4.3 Conclusion

In the near term, PV manufacturers can only utilise existing recycling technologies as detailed above. None of the mentioned technologies are ideal for PV module recycling. This is due to the fact that the small quantities of the materials within the PV module make the recycling of these materials unattractive to the various industries.

It is probable that recycling will impose a financial cost which the manufacturers will have to bear. It is therefore important for the PV industry to develop thin film modules that are more easily recycled, but not to compromise environmental, health and safety considerations.

5. FINAL CONCLUSIONS AND RECOMMENDATIONS

Our conclusions are that for the considered thin film modules (CdTe, CIS, a-Si) and process technologies:

- there are no serious health, safety and environmental bottlenecks for upscaling to production levels of 500 MWp/yr;
- adequate methods are available for treatment of the manufacturing wastes;
- on the longer term, however, issues regarding CdTe and CIS module waste treatment, In and Te resource availibility and module recycling need to adressed;
- appropriate recycling methods for CdTe and CIS modules do not exist at present but the problem is being adressed by the PV industry.

Finally we recommend:

- to improve the material utilization in the deposition of CdS, CIS and metal contact layers;
- to discourage the use of SF_6 (and other fully fluorinated compounds) for plasma etching in view of their very high contribution to the greenhouse effect;
- to investigate module encapsulation methods which facilitate module recycling;
- that the PV industry continues and expands its efforts with regard to the development of recycling strategies for PV modules.

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