Staying safe

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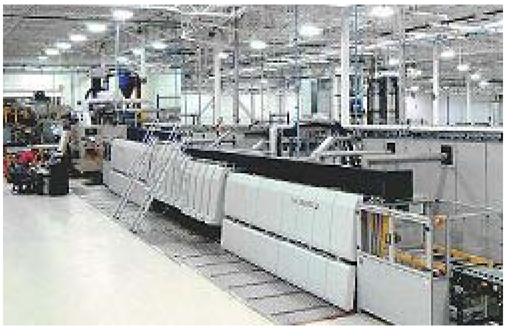
How the PV industry is to minimizing the hazards of solar cell manufacture



PV manufacturers are beginning to realise the need to implement recycling schemes and environmental standards to maintain their green credentials FIRST SOLAR

As PV manufacturing looks to make the step up from megawatt to gigawatt production, environmental issues arising from the manufacture and construction of solar cells need to be tackled head on in order to ensure that photovoltaic power can continue to represent itself as a green technology. Alasdair Cameron examines some of the issues.

So far, solar cell manufacturers have largely managed to escape public examination of the environmental side effects of PV production.There are two main reasons for this first: PV production is still a relatively small business and can function largely on the by-products of other industries, and secondly, to date, the companies involved have taken good care to reduce the harmful emissions of the PV manufacturing process. However if PV production were to increase by orders of magnitude and become a vast global industry, these standards could become much harder to maintain. But they must be maintained in order to protect the environment and ensure that PV continues to be a sustainable industry.

The environmental risks associated with PV manufacture depend on the specific type of cell being made

The issue is complicated by the fact that there is no one type of photovoltaic cell, but rather a range of different technologies using different raw materials and manufacturing processes.Thus the environmental impacts associated with PV manufacture depend on the specific type of cell being made (Table 1). These will be dealt with individually, followed by a look at some of the more general and legislative issues surrounding PV production.

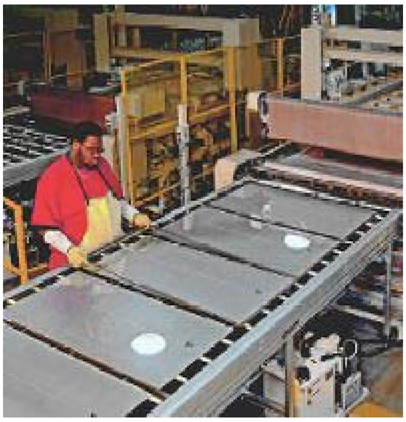
TABLE 1. Major hazards in PV manufacturing. (Source: Overview of potential hazards by Fthenakis.[1])

Cell type	Potential hazards
x-Si	HF acid burns
	SiH_4 fires/explosions
	Lead solder/ module disposal
a-Si	SiH_4 fires/explosions
CdTe	Cd toxicity, carcinogenicity, module disposal
CIS, CGS	H_2Se toxicity, module disposal

GaAs	AsH_3 toxicity, As carcinogenicity, H_2 flammability, module disposal

CRYSTALLINE SILICON

This type of cell is by far the most common available on the market (making up around 70% of all cells produced), and also the safest. Silicon itself is relatively harmless and poses little threat to the environment or health, unless turned into a fine dust and inhaled or eaten (incidentally this could only happen if the PV unit was actually ground up, and this is very unlikely). The other main material – glass – is also composed largely of silicon, meaning that the solar module itself contains no harmful substances. However several chemicals used in the manufacture of the cells, and also in their application – such as lead – could pose a potential problem to health and the environment, if not handled correctly.[1]



Staff working with cadmium telluride are monitored routinely to ensure that they experience no harmful side effects
FIRST SOLAR

Various dangerous caustic chemicals such as hydrofluoric acid (HF), nitric acid (HNO3) and sodium hydroxide as used to clean the silicon wafers and remove any oxidized residue. While such chemicals are extremely hazardous on contact or if released into the water system in large quantities, their use in industrial applications is routine and safety measures are well established.

Of more concern is the use of toxic gases as dopants in the production process. Hydrogen bromide, chlorine and phosphoric oxide trichloride are all used, and if uncontrolled could pose a major hazard to health within their immediate vicinity. However, proper use and maintenance of ventilation systems and fume cupboards should minimize any risk of exposure or environmental damage.[1]

In addition to the immediate hazards of using halogenated substances, some of these chemicals and their by-products are powerful greenhouse gases, many hundreds of times more potent than carbon dioxide. Clearly their release must be minimized to limit their impact on the environment and on the carbon pay-back time of the photovoltaic cells.

Of equal concern from an ecological point of view is the use of lead-based solders in the points of the solar cells, as well as the use of large quantities of cleaning agents and solvents in the cutting, etching and polishing of cells. However, to help eliminate these problems,the silicon-PV industry has embarked on a programme of waste minimization, in which several simple steps have been taken to greatly reduce the amount of damage which could be caused to the environment. Key measures include recycling stainless steel cutting saws, recovering silicon carbide from waste slurry, and in-house neutralization of acid and alkali solutions.[1]

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The issue of waste lead is also being tackled. Early PV modules did not comply with international leaching standards and so could not have been land-filled. One company has recently developed a leadfree solder material for use in its solar cells, and is offering it to other interested parties. This should greatly reduce any problems associated with decommissioning. However so far this is not widely commercially available.

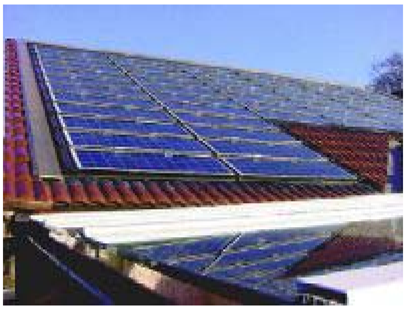
THIN FILM CELLS

Amorphous silicon

As with crystalline photovoltaic modules, the principle dangers surrounding amorphous silicon (a-Si) involve the hazardous substances used in its manufacture. In particular, the production of a-Si cells requires the use of large amounts of silane gas (SiH_4).This is an extremely flammable and explosive gas which spontaneously ignites in concentrations over 4.5%. Depending on the amount of silane being stored, minimum perimeters must be established around the manufacturing site, in the range of 15–100 metres.[1]

While handling this gas in small quantities can be done reasonably safely assuming proper measures are put in place, the dangers would be greatly increased if a-Si production were to be increased to the 100 MW or GW scale.The sheer amounts of silane gas that would need to be moved around could present difficulties for local communities.

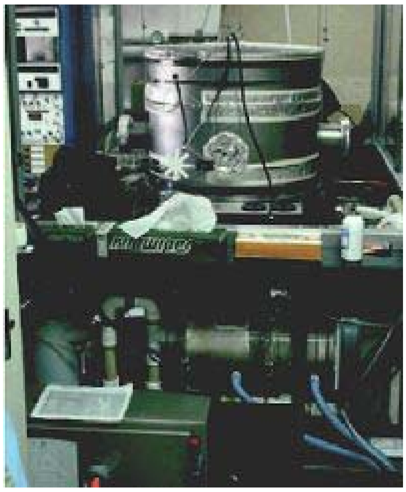
Cadmium-Telluride cells



All crystalline silicon modules may contain hazardous substances such as lead solder and brominated flame retardants RWE SCHOTT SOLAR

Although safe to use, photovoltaic cells made using cadmium could potentially pose a number of significant problems regarding their safe disposal and manufacture.Pure cadmium is a highly poisonous element produced as a by-product of zinc extraction, where it is frequently disposed of in unenvironmentally friendly ways by the mining industry. Even at low levels it can prove toxic, leading to symptoms such as fragile bones, hypertension, and eventually death. It is also assumed to be carcinogenic in chronic cases. Presently 98% of cadmium is used in paints, pesticides, stabilizers and batteries. In the US for example,only about 1.5%–3% of total cadmium is used in the solar industry. Due to its toxicity, regular monitoring of staff at CdTe plants is needed to help ensure that chronic poisoning does not occur.[1]

While the use of cadmium is banned or limited in many instances, particularly where it is hard to recycle or take care of, European Union regulations do not currently prohibit its use in photovoltaic cells, since it is in a stable non-metallic form (typically CdTe), and is not soluble in water.



A test lab for PV production showing protection measures for handling small amounts of silane gas. Note the perspex scrubber below the tank NREL

One of the principle concerns regarding this type of solar cell has been the potential effects of very high temperature on the cells – such as would occur in an accidental fire. The melting point of CdTe is 1050ºC, meaning that the usual temperatures of residential fires would not be hot enough to cause the release of the chemicals. However in industrial fires where other fuels are present, temperatures could potentially be high enough to melt the cadmium, causing it to run to the edge of the units. Tests conducted in the laboratory have shown that this can indeed happen, raising the concern that significant amounts of CdTe (as opposed to pure cadmium) could be released into the environment.However, in additional tests where whole CdTe modules were exposed to temperatures of 1100ºC, it was found that the liquid cadmiumtelluride was captured in the molten glass of the module, rendering it effectively harmless.This means that while there is some potential for the release of CdTe, the vast majority should be captured in inert glass droplets. In any case, the presence of any cadmium is likely to be far less of a danger than the fire itself.[2] Furthermore,the amounts of cadmium involved are very small.(As a comparison, a small nickel–cadmium battery which can be found in almost every household, contains about 2500 times more cadmium than an average PV module, and would be far less resistant to fire.)

The best way to prevent contamination of the environment is to ensure that there is correct and responsible disposal of CdTe solar cells once they reach the end of their useful lives. Landfilling may be inappropriate as there is potential for leaching to occur.Therefore current industry practice involves the take-back and recycling of modules to recover cadmium and other valuable components.

It is important to remember, when discussing cadmiumcontaining cells, that the cadmium used is not produced specifically for PV cells, but is already present as a waste product of the mining industry (typically zinc manufacture). This means that if it is not being used in PV, it will still be produced and disposed of in the same quantities, often through other methods which disseminate it into the environment much more quickly, such as in pesticides. In any case, the amounts of cadmium which could be released into the environment by solar cells in a worst case scenario are actually very low, with current estimates at around 0.02g/GWh.[2,3] In any case the cadmium used in PV cells is in a very stable form as it is bound up with tellurium.Comparisons with coal power which have been made in the past are false, as they compared day-to-day, unavoidable cadmium emissions from coal power stations, with exceptional, worst-casescenario emissions from solar units.[2] Under normal circumstances coal power stations emit 360 times more cadmium into the air per kWh than is needed in a solar cell per kWh generated.

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Copper-Indium-Selenium (CIS) cells

Since the toxicities of copper, indium and selenium are relatively low, the main problems associated with this type of cell involve the use of hydrogen selenide (H_2Se), a poisonous chemical which resembles arsine (AsH_3). It is classed as ‘Immediately Dangerous to Life and Health’ (IDLH) at 1 ppm. Chronic poisoning may also occur. To protect staff from exposure, the deposition system that uses the H_2Se should be enclosed under negative pressure and all exhaust gases passed through an emergency control scrubber. As with cadmium, employees should be monitored to ensure they are not being exposed to low level poisoning.[1]

Recycling of wire saws and the sludge they produce can help to minimize the waste from silicon PV plants PHOTOWATT INTERNATIONAL;

High efficiency Gallium-Arsenide cells

Originally designed for space applications, these cells are coming to the fore again thanks to their use in concentrating PV systems. This is because they can achieve far higher conversion efficiencies than crystalline silicon or amorphous silicon cells, and so make the best use of concentrated sunlight.

GaAs cell production uses a variety of toxic hydride gases, such as arsine (AsH_3) and phosphine (PH_3), which must be handled with care so as to prevent their release into the general environment. Indeed such are the relative quantities of these gases needed that a 10 MW per year plant would require 23 tonnes of AsH_3, 0.7 tonnes of PH_3, 1500 tonnes of hydrogen and 7 tonnes of metal organics. Since such quantities of gas could only be delivered by tube trailers, the consequences of a serious accident in one of them would be catastrophic. Fortunately, as mentioned above, most GaAs units will be used in concentrating PV modules, and not in flat-plate modules, meaning the quantities of solar material needed will be much smaller than with other types of system.[1] Thus the number of really large plants required would be relatively low, and production facilities in the 1 MW range could be distributed over a wider area.

PROBLEMS OF LEACHING

Due to the use of some of the chemicals mentioned above, there are problems with the landfilling of certain PV modules as leaching may occur. The standard test for leaching is the Toxicity Characterization Leachate Profile (TCLP), set up by the US Environmental Protection Agency. These are done by taking a small piece of the substance and soaking it in a set amount of water for 24 hours, before measuring the amount of leachate in the water.To date most amorphous-Si cells that have not had their lead removed have not passed TCLP leaching tests. Of the cadmium-telluride cells, only the Apollo cells produced by BP Solar and those produced by First Solar have passed, while many of the crystalline silicon cells failed lead leachate tests by around 30% (i.e. there was 30% more leached material in the leachate than allowed by law).

Of the cadmium-telluride cells, only the Apollo cells produced by BP Solar and those produced by First Solar have passed standard leaching tests

Even if the cells are incinerated they must still be treated with care as the remaining ash will contain a high proportion of heavy metals,meaning that the potential for leaching is there if the residue is landfilled.[1,4]

DISPOSAL OF PV MODULES IN RELATION TO WEEE LEGISLATION AND ROHS

In the European Union at least, the two main laws which could impact on the production and disposal of photovoltaic materials would be the Waste Electrical and Electronic Equipment (WEEE) legislation and the rules regarding the Regulation of Hazardous Substances (RoHS). These laws control which substances can be used in manufacturing, in what quantities, and how they should be disposed of.However PV is not covered in either the WEEE legislation or the ROHS directive so the restrictions imposed by these laws do not apply. Furthermore the use of lead in solder has been exempted from legislation, as, at present, there are no fully tested and reliable alternatives.

As well as PV modules, inverters needed in PV systems are also exempt from the WEEE laws, although there was initially some confusion on this matter.The inverters themselves must still be dealt with carefully as they can contain harmful compounds such as PVC.

Other substances which are banned under the RoHS law (which will come into force on 1 July 2006) include mercury, chromium and brominated flame retardants such as polybrominated biphenyls (PBB) and polybrominated diphenyl ether (PBDE).These are used in electrical equipment to prevent any flames from spreading and have been used in inverters. Alternatives to their use should be found.[4,5] (See Table 2)

TABLE 2. Inclusion of PV products in EU legislation. (Source: Proceedings of the 20th EPSEC in Barcelona, 2005. Provided by ECN.[5])

	WEEE	RoHS
PV modules	not included	not included
PV in consumer products (watches etc.)	Yes	Yes
Inverters, charge controllers	Initially unclear	not included
Lead in solder, or glass		exempt

RECYCLING AND TAKE-BACK SCHEMES

While PV modules for electric power applications are not covered by either WEEE or RoHS laws, PV manufacturing companies should be expected to take a lifetime approach to their products and must make provisions for the proper collection and recycling of potentially hazardous components. In fact, several PV manufacturing companies have already taken steps in this direction. Deutsche Solar is currently running a pilot programme for the recycling of its polycrystalline silicon cells and modules.After the removal of polymers and laminates the cells can be de-metallized and re-pressed into usable silicon wafers.Japanese company Sharp uses a system where it re-melts the silicon, for recasting into ingots.While this is quick and easy, it uses considerably more energy than reprocessing the wafers directly, therefore increasing the energy pay-back time of the solar modules produced. First Solar is running a take-back and recycling programme of its own CdTe modules. It has a programme in place which tracks all the modules that are sold, which will make them easier to collect at the end of their lifetimes.First Solar has also launched a 'pay as you go'insurance scheme, whereby money is set aside at the time of purchase to cover the costs of safe disposal in the event of the company going out of business. Similarly Solar World AG has set up a take back programme for its own modules.[4,5]

Companies are investing in mechanical innovations to make the dismantling process simpler

In order to make such recycling projects easier, companies are investing in mechanical innovations to make the dismantling process simpler. Screws joining the frame to the laminate can be made of shape-memory-alloys, compounds which 'remember' a given shape. These will act as normal screws until they are heated, at which point they will lose their thread and be far easier to remove.Other such measures include reducing the adherence of the primary polymer layer in crystalline silicon cells, possibly by adding another polymer layer with a higher affinity to the primary layer. This should make both layers easier to remove.Work is also underway to develop alternatives to the ethylene vinyl acetate (EVA) laminate layer used in such cells.[5]

CONCLUSIONS

The most important thing for the solar manufacturing industry is to address the issue head on, and not to wait until they are forced to act. In order for the industry to survive and continue to prosper it must continue to be an environmentally responsible industry.This after all is the reason for its existence.

To achieve this several things can be done. Recycling and take back schemes should be expanded to salvage potentially dangerous and valuable products. If these take-back schemes were voluntary and adopted by the whole industry this could have the added benefit of lowering the risk to the industry from regulatory uncertainty. Products should be designed to make recycling as easy as possible, and more efficient methods of recycling should be researched and developed. Substances which are hazardous should be phased out were possible or handled in a responsible, less harmful way. Above all, a lifecycle approach must be developed. If these steps are taken, it seems reasonable that the PV industry will continue to expect the high level of public support it currently enjoys.[5]

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