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**WASTE REDUCTION OPTIONS FOR MANUFACTURING
OF COPPER INDIUM DISELENIDE
PHOTOVOLTAIC CELLS**

M. P. DePhillips, V. M. Fthenakis and P. D. Moskowitz

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ABSTRACT

This paper identifies general waste reduction concepts and specific waste reduction options to be used in the production of copper indium diselenide (CIS) photovoltaic cells. A general discussion of manufacturing processes used for the production of photovoltaic cells is followed by a description of the U.S. Environmental Protection Agency (EPA) guidelines for waste reduction (i.e., waste minimization through pollution prevention). A more specific discussion of manufacturing CIS cells is accompanied by detailed suggestions regarding waste minimization options for both inputs and outputs for ten stages of this process. Waste reduction from inputs focuses on source reduction and process changes, and reduction from outputs focuses on material reuse and recycling.

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1. INTRODUCTION

The goal of this report is to assist in the development of a comprehensive waste management plan to ensure the economical and environmentally benign production of copper indium diselenide (CIS) photovoltaic cells. This study concentrates on the manufacturing phase of cell production. The suggestions put forth in this paper should be considered as part of a broader waste management plan that encompasses the entire life cycle (i.e., cradle to grave) of a photovoltaic system.

The basic unit for the current analysis is the process-level, which refers to a piece of equipment or a specific work station in a manufacturing plant. The various inputs and outputs at each process are then studied for waste reduction opportunities. Waste reduction from inputs focuses on source reduction and process changes, and reduction from outputs focuses on material reuse and recycling.

2. MANUFACTURING PHOTOVOLTAIC CELLS

This section briefly describes the major process steps used for manufacturing a photovoltaic cell. These steps will be broken down into inputs and outputs specific to CIS cell manufacturing in Section 5.

2.1 Substrate Selection and Preparation

The active layers of a photovoltaic cell are deposited on a substrate which can be plastic, glass or metal foil. The substrates are usually washed in a typical industrial detergent solution and rinsed with deionized water before further processing. In some cases, impurities, saw damage, or surface oxidation on the substrates must be removed by etching. The etching process is usually followed by rinses with deionized water and a final drying step using compressed air.

2.2 Metallization

Substrates or wafers are metallized to form a back-surface field and back contact and a front-surface current carrying grid. In general, the back and front metallization processes are accomplished separately with intermediate processes carried out in between. Evaporation and electroplating are the most frequently used process options in this step. Metal evaporation is conducted in a vacuum chamber at a pressure of 10^{-7} to 10^{-6} torr. In electroplating, wafers are first covered with a photoresist through mask that defines the metallization pattern. They are then exposed to a light source to polymerize the resist before they are dipped into a plating solution.

2.3 Transparent Contact Deposition

The purpose of this process is similar to metallization. When a glass substrate is used, a transparent conducting layer is required so that the sunlight can pass through to the active layers. Commonly used process options for transparent contact deposition are chemical vapor deposition (CVD) and sputtering. In the CVD process, gaseous feedstocks are brought into silica reactor by a carrier gas where they undergo a chemical reaction on decomposition at a high temperature (500° to 600° C) resulting in the deposition of a stable compound on the substrate surface. Indium oxide and tin oxide are frequently used feedstocks for the CVD process. Solid feedstocks are sputtered by either a high energy ion beam, a magnetron sputtering source, or a radio-frequency source in a vacuum chamber. The atoms released from the solids are subsequently deposited on a heated substrate. In some cases, the injection of a gaseous feedstock into the chamber is required to react with the solid particles and form the desired layer on the substrate.

2.4 Junction Formation

This process involves the formation of a p-n junction by either introducing dopants in the structure of intrinsic solid materials, or depositing layers of dopants on top of intrinsic layers (i.e., thin films). The active layers that form the p-n junction enable the cell to produce electricity. Therefore, the efficiency of the finished cell depends critically on the quality of the active layers formed in

this step. Several methods can be used for the deposition of CIS/CdS active layers, including co-evaporation, reactive sputtering, dip coating and spray pyrolysis.

2.5 Passivation

This process is intended to grow an insulating barrier over the grain boundaries of the active layers. This will cut down carrier recombination and thus improve the open circuit voltage and the fill factor of the cell. Frequently applied passivation techniques in laboratory scale include anodic oxidation, heat treatment, and chemisorption.

2.6 Scribing

Scribing, which is sometimes required more than once during the manufacturing process, is mainly used to divide the large area thin-films deposited on substrates into narrow strips, forming the individual solar cells. The scribing can be performed mechanically or by lasers. The most commonly used lasers in photovoltaic industries are high-power units classified as class IV lasers by the American National Standards Institute and by the Bureau of Radiological Health of the U.S. Food and Drug Administration.

2.7 Anti-Reflective Coating

This process deposits an anti-reflective coating on wafers to decrease the loss of sunlight due to reflection. An anti-reflective coating (e.g., silicon monoxide and antimony trioxide) is typically applied through CVD or evaporation.

2.8 Cell Interconnection

The finished cells are assembled in this process to form operative modules. The cells are bonded together by interconnect buses and tabs soldered on the front and back of each cell. This is achieved in several operations including cell alignment, interconnect placement, string assembly,

solder re-flow, and final module interconnect. Thin-film cells are produced in sheets and, therefore, do not need mechanical interconnection.

2.9 Encapsulation

In a typical encapsulation process, the modules are placed on top of ethylene vinyl acetate (EVA) sheets backed by glass substrates. Another sheet of EVA is placed on top of the assembly, followed by a sheet of Tedlar. The sandwiched assembly is then baked in a vacuum laminator for sealing.

3. CIS CELLS

CIS is one of the highest optically absorbing semiconductor materials. It can also be deposited on large substrates using relatively inexpensive methods, making it a promising material for low-cost thin film photovoltaics. CIS cells have achieved a 14% efficiency for conversion and remains stable in direct sunlight. Figure 2 shows a process sequence for fabricating solar cells using CIS.

Figure 1

This process results in high disposal costs and requires cleaning every second day which made the procedure cost intensive. A second drawback is demonstrated in the case of CdS or CdS/ZnS deposition chambers. CdS is highly poisonous and a suspected carcinogen. Even short exposures to dust

Most of the feedstock material not deposited on the substrate is deposited on the deposition chamber walls and shielding. These deposits consisting of Cu, In, and Se compounds, are traditionally removed by mechanical or chemical means and disposed in secure landfills. Small amounts of metal particles may be drawn out of the chamber by vacuum pumps and collected on line filters from where it will also be removed and disposed.

Copper, indium and selenium sources are placed in vacuum system. The types of sources used are resistance-heated effusion cells, electron guns, and wire-rings. The sources are separated with shields to prevent contamination of one source from the vapor of another, without blocking passage to the substrate.

3.1 Coevaporation

Waste management for residuals from these processes have traditionally focused on end-of-the-line control options. In following paragraphs, we highlight such options for several junction formation alternatives, namely: coevaporation of Cu, In and Se, reactive cosputtering of Cu, spray pyrolysis of Cu, In and Se salts and dip coating of CdS.

may cause pulmonary edema and gastrointestinal poisoning. Chronic exposure may result in kidney dysfunction and prostate cancer. Consistent handling of large quantities of these substances may jeopardize health and safety of workers.

3.2 Reactive Co-sputtering of Copper and Indium

The deposition of CuInSe_2 takes place in a vacuum chamber with enclosed magnetron sputtering sources. Copper and indium are being sputtered from solid targets while selenium comes into the chamber in the form of selenium hydride gas (H_2Se). The vacuum deposition chamber will be in line with other vacuum chambers where metallization and CdS deposition take place. In this technique Cd target and H_2S reactive gas will be used, and the first active layer must be protected from etching by the sputtered particles. Gate valves and vacuum interlocks isolate the chambers and provide entrance and exit of the substrates with no vacuum disturbance.

Hydrogen selenide and hydrogen sulfide are both highly toxic and irritating gases. Hydrogen selenide can produce selenosis with symptoms such as nausea, vomiting, metallic taste, cough, sneeze, slight tightness of the chest and ultimately pulmonary edema. Equally hazardous, although in higher quantities, hydrogen sulfide attacks nerve centers. At lower concentration it acts as a respiratory irritant and a possible fire and explosion hazard.

In order to protect workers from these hazards the deposition line is surrounded with an airtight enclosure and vented into a scrubber using alkaline solution. The Cu , In , and Se by-products have been traditionally placed into a secure landfill. The total disposal costs would include actual disposal costs, drum handling, drum storage, drum transportation, and local fees and taxes.

4. WASTE REDUCTION STRATEGIES

The previous section demonstrated a waste management system that focuses primarily on treatment and disposal. It is stated, however, in the

guidelines of the EPA Strategy for Waste Reduction that treatment and disposal should be the last resort of a comprehensive waste management program. This strategy was initially put forth in the Pollution Prevention Act of 1990, which states:

"Source reduction is fundamentally different and more desirable than waste management and pollution control. Pollution should be prevented or reduced at its source wherever feasible. Pollution that can not be prevented should be recycled in an environmentally safe manner. In the absence of feasible prevention and recycling opportunities, pollution should be treated. Disposal of other releases should be used as a last resort."

Pollution prevention, an extension of EPA's existing programs encouraging waste minimization, is an effective way to reduce hazardous as well as non hazardous wastes. Waste minimization means the reduction, to the highest extent feasible, of any solid or hazardous waste that is generated or subsequently treated, stored, and later disposed. It focuses on source reduction and recycling activities that reduce either the volume or the toxicity of a waste stream. Pollution prevention broadens this concept to include minimizing the generation and therefore, release of all hazardous materials and waste to all environmental media. This strategy recognizes that many of the benefits of controlling pollution through proper treatment and disposal have already been achieved. Further environmental gains must now come from anticipating and preventing the generation of waste.

Pollution prevention is a process that requires continuous monitoring and improvement. A facility must make a long term commitment to this process and enact the program by conducting a thorough survey of all processes. This should determine the location of all generated waste and the contributing processes. Next a facility should identify prevention options, prioritize options/design projects, implement projects, and continuously monitor and evaluate projects. General alterations would include improved housekeeping, equipment change, process change, reformulated product, and chemical substitution. The optimum waste reduction program will reduce both waste quantity and toxicity.

4.1 Pollution Prevention Benefits

Pollution prevention yields both environmental and economical benefits. If all potential release points are identified unnecessary waste made be avoided instead of trying to controlled with pollution control equipment.

4.1.1 Environmental

Pollution prevention reduces risks inherent in managing waste streams and residues from traditional control methods. Since some control options (e.g., scrubbing) often change the form and concentrate a pollutant without, however, changing its toxic characteristics, pollution prevention at the source reduces the uncertainty with regard to the ultimate fate of a pollutant. Pollution prevention also reduces potential inter-media transfer of contaminants.

4.1.2 Economical

Prevention does not only reduce direct environmmnetal and health risks; it also gives financial benefits, including:

1. Savings in raw materials
2. Energy savings
3. Water conservation
4. Improved product quality due to close monitoring
5. Reduced down-time due to improved maintenance
6. Savings in waste disposal
7. Reduced future liability

Frequently the most significant financial benefits come from reduced liability by avoiding pollution. Pollution generators in the U.S. have been subject to potential unlimited liability for any harm caused by their wastes. The Resource Conservation and Recovery Act (RCRA) mandates that manufacturers have "cradle to grave" responsibility for the wastes that they generate. The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA, or Superfund Act) also enacts several liability provisions. This liability includes even future problems caused by wastes currently managed using the best known practices. Escalating costs of waste cleanups, and

potential for unlimited liability, make pollution prevention options even more compelling.

EPA suggests that companies evaluate the economic viability of a pollution prevention program by using a four tier approach. Table 1 displays these four tiers of economic viability.

Table 1 EPA's Four Tier Economic Review

Tier 0	Tier 1	Tier 2	Tier 3
Usual costs	Hidden Costs	Liability Costs	Less Tangible Costs
<ul style="list-style-type: none"> Processes Equipment 	<ul style="list-style-type: none"> Monitoring 	<ul style="list-style-type: none"> Penalties and Fines 	<ul style="list-style-type: none"> Consumer Responses
<ul style="list-style-type: none"> Process Materials 	<ul style="list-style-type: none"> Paperwork 	<ul style="list-style-type: none"> Future Liabilities 	<ul style="list-style-type: none"> Employee Relations
<ul style="list-style-type: none"> Direct Labor 	<ul style="list-style-type: none"> Permit Requirement 		<ul style="list-style-type: none"> Corporate Image

Tier 0 involves an analysis of usual costs including analysis of facility operations, developing options, and estimating the direct expenses of the options. An estimation of usual cost associated with both current and alternative practices should then be reported.

Tier 1 estimates the hidden regulatory costs associated with current and alternative practices. First a facility should determine what is its regulatory status. Then estimate hidden capital expenditures (e.g., technology forcing regulations) and hidden expenses (e.g., hazardous waste storage tanks, disposal costs, etc.)

Tier 2 describes the cost protocol for estimating potential liability costs associated with hazardous waste and materials management. Two types of liabilities should be addressed; penalties and fines associated with non compliance and other future liabilities (e.g., personal injury, real property damage, etc.)

Tier 3 incorporates less tangible, subjective costs. A facility should determine whether a commitment to pollution prevention would strengthen consumer acceptance, employee/union relations and corporate image.

After completion of these steps a facility should be able to assess whether a pollution prevention program will be economically feasible.

4.2 Practical Aspects of Pollution Prevention

Pollution prevention options include use of materials, processes or practices that reduce or eliminate the creation of pollutants at the source. Implementation of pollution prevention requires attention to several aspects of a manufacturing operation (Berglund & Lawson, 1991), namely :

1) Product Design (e.g., choice of inherently safer or environmentally less benign materials); 2) Process Design 3) Plant Configuration; 4) Information & Control Systems; 5) Human Resources; 6) Research & Development; and 7) Organization.

4.2.1 Choice of Materials and Product Design

Choose less toxic or less flammable feedstock materials (e.g., CIS photovoltaic industry solid Se instead of H_2Se gas). Design products so that they are less toxic, less mobile, more suitable for recycling or easier to treat.

4.2.2 Process Design

A typical chemical process generates a number of solid, liquid, and gaseous waste streams. These can be categorized as inherent or intrinsic and extrinsic to the process materials. The inherent to the process materials include, unreacted raw materials, impurities in reactants, and undesirable by-products and spent auxiliary materials (e.g., oils or solvents).

The extrinsic wastes are related to operations rather than the process itself; These wastes include; maintenance waste and materials, waste generated during startup or shut down, fugitive emissions from pumps etc.

Getting rid of the intrinsic waste streams requires modification of the process. Such modification may require extensive R&D efforts, major equipment modifications. Sometimes, however, they are quite straightforward. An example is a change implemented recently by a project team at Dow's Pittsburgh plant. The team took a critical look at the use of nitrogen gas as a pressurizing agent to help transfer a raw material from a tank car to storage tank and then from the storage tank into reactor vessels. During this transfer, raw material would contaminate N₂ which would then need to be treated in a scrubber and disposed off. The team suggested a pumping system to replace the nitrogen eliminating, therefore, both the need for scrubbing and the losses of raw material.

Extrinsic waste streams can often be reduced and minimized through administrative controls, maintenance and operation procedures and minor material or equipment changes. In this respect a pollution prevention program should evolve from simple and obvious options to the more complex and demanding ones. For example a hierarchical approach could comprise the following 3 phases.

- First Phase
 - Good housekeeping, waste segregation, direct recycling
- Second Phase
 - Equipment modifications, process modifications, process control
- Third Phase
 - Complex recycling and reuse

Fundamental process changes

Changes in raw materials or catalysts

The first phase looks more at extrinsic streams whereas at Phase III, the emphasis is shifted to the process itself and the associated intrinsic wastes. Phase I is always cost effective; Phases II & III, if not driven by the need to comply to existing regulations, should be justified by cost-benefit analysis.

4.2.3 Plant Configuration

Two aspects of plant configuration are especially important in pollution prevention; these are i) process integration and ii) ease of maintenance and process change.

An integrated plant is one where most of by-products and coproducts are used within the plant itself, so that the transportation of raw materials, production by-products and waste is minimized. Some modern oil refineries, for example, are designed to minimize waste generation and conserve energy by feeding hot streams directly from one unit to the other. Another possibility of process integration is for a raw material supplier and an industry-customer to link their operations. This way the transportation hazard is eliminated and the storage hazard is reduced since only minimum quantities of a hazardous chemical are produced.

The second aspect of plant integration is the ease of maintenance. Maintenance is important in prevention; in the chemical process industry, for example, more than 1/4 of the emissions are attributed to fugitive emissions. An effective program to minimize such emissions involve not only selecting equipment (e.g. pumps) with low leak potential but also placing the equipment in such a way so that is easy to reach and conduct testing and maintenance.

4.2.4 Information and Control

An effective pollution prevention program requires an information and control system (usually computer based) to 1) track the wastes in the facility and 2) monitor process conditions in order to minimize upsets. Such a system can help minimize waste and byproduct formation.

4.2.5 Human Resources

Employees are often the best source of waste reduction ideas. It is important, therefore, that the employees are well trained on prevention, and given incentives to suggest improvements.

4.2.6 Research and Development

R&D is required to support a continuous improvement in environmental issues. There are at least three areas where R&D is the key for preventing pollution: 1) New process, increased process efficiency, new catalysts with better selectivity, activity and life span; 2) separation technology to purify, segregate and treat waste streams; and 3) monitoring and detection (qualitative and quantitative) of potential pollutants.

4.2.7 Organization

Effective pollution prevention plans require a strong commitment from the management and continuous vigilance from both administrators and technical personnel. Furthermore, the company must be organized and run so that it allows staff interaction and team work.

4.3 Recycling

Recycling plays an important role in any pollution prevention program. Recycling is the reformation or reprocessing of a recovered material. In a broad sense, it also includes re-use of process materials and re-manufacturing of process tools. Incentives to recycle include: 1) Reduction of disposal costs, especially for hazardous waste as defined by the RCRA; 2) reclamation of valuable materials; and, 3) re-use of process materials (e.g., glass, plastics, solvents, etc.) Facilities which include recycling as part of a comprehensive program should be aware of two major approaches; closed loop and open loop systems.

In closed loop systems, recovered materials and products are suitable substitutes for virgin material. They are thus returned to the manufacturing process to be used in production of the same part or product again. Open loop recycling occurs when recovered material is recycled one or more times before disposal. This pathway usually involves more than one additional facilities to collect, store, and manufacture the waste into a new product. For materials as complex as photovoltaic cells, both approaches could be used simultaneously to maximize recycling opportunities.

When a suitable strategy and infrastructure appears to be in place, recycling is enhanced by: Ease of disassembly, material identification, simplification and parts consolidation, material selection and compatibility. These processes, collectively known as source separation are possibly the most cost intensive part of the recycling process. When recycling, however, is incorporated into a pollution prevention program, a facility can anticipate and optimize the recycling stage by presorting material, design products with recyclable material and separate waste streams.

5. WASTE REDUCTION OPTIONS

There are some basic waste reduction strategies that a manufacturing plant should practice regardless of a specific material. They range from better housekeeping to installation of new equipment to implementation of novel recovery technologies. Some examples of waste reduction options available to

wet dipping deposition processes are listed in Table 2. These practices are categorized in: Easiest, More Difficult, and Most Difficult.

Table 2 Waste Reduction Strategies

EASIEST	MORE DIFFICULT	MOST DIFFICULT
Train employees on proper hazardous materials and waste reduction	Apply flow restriction devices such as pH-controlled and pressure-controlled shutoffs	Use water treatment methods to eliminate the natural contaminants of water
Keep process station clean and orderly to eliminate spills and leaks	Install multi-stage rinses with a countercurrent system	Select chemicals which generate less sludge (ask your supplier for recommendations).
Operate chemical bath process initially at a lower than normal concentration to reduce film build-up and drag-out. Then, over time, gradually add reagents until full strength is achieved	Install devices and implementation procedures to conserve water such as installing turbulence devices and increasing the contact between the water	Use techniques to recover metals from the wastewater or use techniques to regenerate process baths such as evaporation, reverse osmosis, ion exchange, electrolysis, and /or high surface electro-refining
Increase the operating temperature to lower the viscosity and reduce film build-up and drag-out	Apply techniques to recover etchant through filtration and regeneration	Segregate waste streams to avoid the unnecessary generation of sludge
Apply wetting agents to reduce the surface tension of the solutions and lower the viscosity and reduce film build-up and drag-out	Use methods to extend the life of the photoresist stripper	Dewater sludges
Maintain the best rack orientation to achieve maximum drag-out	Change from chelating to non-chelating agents	Treat waste stream to recover metals
Withdraw racks at a slower rate		
Install drainboard between process and rinse tanks		
Recapture processed chemicals from drag out tank		

Sections 5.1 to 5.10 displays and describes the inputs and outputs involved with each step of the manufacturing process. The suggested waste reduction options are based solely on these inputs and outputs. They demonstrate examples of what a pollution prevention program might encompass when enacted by CIS cell manufacturers. As mentioned, the first step in implementing a program of this type would be a full scale detailed survey of every step within the following processes.

The following sections are discussed in accordance with the EPA's hierarchy of pollution prevention. Source reduction being the primary form of waste reduction, followed by recycling, and treatment and disposal being a last resort. Some basic housekeeping tips that can be applied for each process step

include segregating raw and waste material containers, segregating different waste materials in separate containers, purchasing materials in bulk or large containers, controlling inventory to reduce waste and properly labeling all containers and process tanks.

5.1 Substrate Preparation

5.1.1 Inputs

All work done with glass should be done in an area where any broken glass can be easily collected without the threat of commingling with other debris. Masks and gloves should be made of material that can easily be washed and reused.

5.1.2 Outputs

Wood crates should be reused repeatedly. Broken glass should be collected and recycled. There many available recycling venues and technologies for recycling all types of glass. Cutting wheels should be resharpened when needed and subsequently reused. Gloves and masks should be washed and reused. Glass grindings can be collected and stored with the broken glass if it is the same type of glass. The contents of the filters should be analyzed if there are any valuable metals in the filter they should be collected and possibly sold to a recycler/smelter. The amount of detergent solution leaving the process can be controlled by placing flow control valves on the system.

5.2 Wash/Deposit Electrode

5.2.1 Inputs

The use of deionized water is a good way to enable the system to operate efficiently. Plumbing modifications, including the installation of flow control valves to reduce water usage, can decrease water requirements, volume and assist in metal reclamation.

5.2.2 Outputs

For all outgoing waste streams, modify plumbing to separate the ones containing metal contaminants. This change facilitates the recovery of metals and segregates part of the wastewater from heavy metals contamination. If economically viable, install metal recovery units (e.g., ion exchange, electrolytic metal recovery, etc.). The coated aluminum shields should be washed using a benign solution (e.g., alkaline cleaners).

5.3 Cut Isolation Scribe

5.3.1 Inputs

Gloves and masks should be made of materials that are easily washed, reused and recycled. Automatic flow controls should be installed to reduce the amount of rinsing water used. Other possible ways of reducing rinsing water is to install multiple rinse tanks in a counter-current series system,

agitate the bath to increase efficiency, and use sprays or mist for rinsing.

3.2 Outputs

Wash reuse and recycle gloves and masks. Metals and glass which can be reused or sold could be recovered from recycling defective modules.

5.4 Metallization

5.4.1 Inputs

Gloves and masks should be made of materials that are easily washed, reused and recycled. Automatic flow controls should be installed to help reduce water usage. Lower the concentration of plating bath constituents; while increasing plating solution temperature to compensate plating

efficiency. Using non-ionic wetting agents (e.g., DI water) will reduce solution surface tension. Cover baths with lids when not in use to reduce evaporation.

5.4.2 Outputs

Install dragout collection tanks. Send spent acid/alkaline solutions back to the manufacturer for recovery. Recycle and re-use spent rinse water using metal recovery techniques such as ion exchange, reverse osmosis, and electrochemical recovery. Separate used oil from other wastes and segregate all other waste streams. Withdraw panels at a slower rate to allow maximum drainage. Extend drip time and install drip racks. Use in-line recovery techniques by installing drainage boards, with splash guards between tanks, to route dragout into the correct process tank. Install wringer rolls or air wipes at the exit from strip or wire plating tanks. Regenerate plating solutions through filtration.

5.5 Absorber Formation

5.5.1 Inputs

Source reduction techniques for water reduction and reusing gloves and masks discussed in previous section are applicable here. All gases should be handled carefully, and the system should be checked periodically for leaks. All work with a solid mixture of Se and

KOH should be done in a confined area to ease collection and segregation of the Se debris.

5.5.2 Outputs

All defective coated glass should be separated from other collected material and either recycled on site or sold to a participating recycler to reclaim the metals in the coating. Coated wipes should be separated and recycling and metal recovery options should be explored. All contaminated filters should be separated and recycled for reuse and metal reclamation. Either in-house or off site recycling options should be explored for metal recovery from oil containing Se, and S. All solid Se debris should be collected and reused.

5.6 Junction Formation

5.6.1 Inputs

Gloves and masks should be dealt with in the same manner as previous sections. Cadmium produces hazardous waste so great care should be taken in its use. Only personnel trained in handling the substance should do so in and areas where any debris and Cd

contaminated material can be segregated, consolidated and safely stored. All equipment coming into contact with this material should be designated for this sole purpose, cleaned and labeled accordingly. In-line recovery systems should be installed to minimize the contamination of parts that come into contact with the Cd.

5.6.2 Outputs

Any Cd debris and contaminated material should be collected and separated from other waste materials. They can either be reclaimed on site by implementing a metal recovery process (e.g., ion exchange, electrolytic metal recovery, etc.) or sold to an outside recycler. Both filters and the metals they contain should be recycled and reused.

5.7 Cut / Interconnect

5.7.1 Inputs

Reduce of inputs as stated in previous sections. Purchase and use an optimum amount of nitrogen and metal to avoid excess. Keep metal work area clean so metal tips do not need to be washed prior to recycling. Keep glass work separate from other waste materials.

5.7.2 Outputs

CIS contaminated exhaust should be filtered, and the filters subsequently cleaned and reused. All metals should be collected, separated, reused or recycled. Defective module should be collect^{ed}, disassembled and its various components recycled. Products with similar composition (e.g., cathode ray tubes, electronic circuit boards, and automobile glass) can be examined for recycling prospects. Minimize air flow around the operations to minimize the flow of exhaust.

5.8 Deposit Transparent Conductor (TC)

5.8.1 Inputs

Gloves and masks are addressed in prior sections. Minimum amounts of argon and nitrogen should be used. All piping and transport equipment should be tested for leaks and kept clean. Plumbing should be modified with flow control valves,

clear identification of water inflow and outflow valves, and by the use of timers or foot pedals to control water usage.

5.8.2 Outputs

Gloves and masks are discussed in previous sections. All waste oil should be separated from other waste material and recycled either on or off site. The effluent mix should be a separate waste stream and with the reduced water usage recovery of contaminants should be easier. Defective coated models are discussed in the previous section. Manufacturers of cathode ray tubes are successfully removing lead from the tube's front screen, a similar technology can be employed for the zinc coated glass.

5.9 Transparent Contact, Cut, Isolation & Scribe

5.9.1 Inputs

All inputs should be handled in a similar manner as in section 5.7.1.

5.9.2 Outputs

All outputs should be handled in a similar manner as section 5.7.2.

5.10 Finishing & Lamination

5.10.1 Inputs

Solder ribbon and solder should be made from the most benign materials possible. Subsequently, the toxicity of waste stream would also be reduced. Primer should be applied using equipment with high transfer efficiency such as electrostatic

applicators and use a charged screen with electrostatic system to reduce edge buildup and to capture and reuse over-spray.

5.10.2 Outputs

CIS dust exhaust should be captured with a filter and recycled. The automobile glass industry is developing ways to remove lamination from windshields, and similar techniques can be employed for removing the lamination off the defective modules. All razors should be collected and reused. All framing material, primarily polyurethane, can be collected and reused. The broken glass should be collected and recycled either on site or by a outside operation.

A large manufacturer of process control valves has implemented such waste reduction techniques to cut its disposal costs for waste from its plating lines, waste oil and coolant from machining operations, and 1,1,1-trichloroethane from vapor degreasers (Spearot, 1993). Before starting the waste reduction program, facility personnel identified waste streams and developed mass balances of input materials and wastes. The company invested \$500,000 in necessary equipment and operations and they saved, in 1992 alone approximately \$2 million in waste disposal and raw materials cost alone; these savings do not include the costs associated with reduced future liability from disposal and reduced regulatory paperwork. Specifically, the following waste reduction techniques were employed:

- Closed-loop ion exchange for electroless nickel, chrome and zinc, to recover the metal content of the rinse waters and feed this back into the process bath;
- Plate out of electroless nickel onto steel wool for sale as scrap metal;
- Oil separation from the recycled machining coolant and reduction in the number of cutting oils used;
- Use aqueous degreasers from parts cleaning; and
- Installed powder coating systems for painting and reformulating chrome and lead based paints to eliminate the metal content.

6. ECONOMIC CONSIDERATIONS

Properly implemented pollution prevention programs should reduce manufacturing cost in addition to reducing waste. As discussed in Section 3, these cost reductions are not always obvious. This section summarizes the various types of economic benefits that pollution prevention provides.

A pollution prevention project by definition reduces or eliminates potential liability costs by reducing or eliminating the source of the hazard from the production process. Liability costs include; penalties and fines, personal injury and property damage.

Two types of costs are to be considered in assessing environmental liability; direct and contingent costs. Direct costs include; monitoring, training and preparing manifest forms. Contingent costs are costs that may materialize if a certain event occurs. Examples of these costs are less than obvious, however, some identifiable ones that a pollution prevention program might help avoid are; penalties resulting from exceeding a permitted emission limit; an off-site spill during transport of waste; a leak of a lined and permitted hazardous waste landfill; disposal of waste at a non-permitted site and an acute event leading to environmental consequences.

In order to weigh these costs when determining whether implementing a pollution prevention program is economically feasible, EPA suggests and offers guidelines for a Total Cost Assessment (TCA) of facility operations. A TCA is

the comprehensive, long term financial analysis of pollution prevention projects. It provides a structures analysis of all operating costs over an extended period of time with the intent of improving the financial picture of a pollution prevention investment. For example, a product may be less expensive than its less toxic alternative to initially purchase, however, a TCA might determine that the long term costs (e.g., handling and disposal) might make the product more expensive than a more benign alternative. Thus TCA enhances the competitiveness pollution prevention projects with regard to traditional capital budgeting. Encompassing the four tier method discussed in Section 3, a TCA can assist in the decision-making process associated with pollution prevention.

CONCLUSION

A thorough analysis of the manufacturing process of CIS photovoltaic cells prevents several ways to reduce the waste stream. Pollution prevention and its related issues can permit system designers to minimize photovoltaic product costs, wastes, and potential risk to public health through a comprehensive waste reduction program.

REFERENCES

Keoleian, Gregory A., Menerey, Dan. Life Cycle Design Guidance Manual. EPA600/R-92/226, January 1993

Moskowitz, P.D., Kalb, P.D., Lee, J.C., and Fthenakis, V.M. An Environmental Source Book on the Photovoltaics Industry. BNL 52052, Upton, NY, 1986.

Moskowitz, P.D., Fthenakis, V.M., and Lee, J.C. Potential Health and Safety Hazards Associated with the Production of Cadmium Telluride, Copper Indium Diselenide, and Zinc Phosphide Photovoltaic Cells. BNL 51832, Upton, NY, 1985.

Pollution Prevention 1991, Progress on Reducing Industrial Pollutants, EPA, 21P-3003, United States Environmental Protection Agency, Office of Pollution Prevention, Washington DC October 1991

Pollution Prevention Benefits Manual Volume 1: The Manual. United States Environmental Protection Agency, Office of Policy, Planning and Evaluation and Office of Solid Waste, Washington DC October 1989.

Total Cost Assessment: Acceleration Industrial Pollution Prevention through Innovative Project Financial Analysis, EPA/741/r-92/002 EPA, 21P-3003, United States Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington DC May 1992.

Spearot, R. M., Pollution Prevention Makes Good Sense,

Vigon, B.W., Tolle, D.A., Cornaby, B.W., and Latham H.C.; Life Cycle Assessment Guidelines and Principles. EPA-600 R 92-245 Feb. 1993.