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Exposure Assessment of Workers in Photovoltaic Panel Manufacturing

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UIC Illinois Injury Prevention Center

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Project Summary/Abstract

This report evaluates potential health hazards associated with employment in photovoltaic panel manufacturing plants. Because there are various manufacturing processes used to produce photovoltaic panels, this report discusses the most common manufacturing process currently in the United States. This process involves purification of the silicon, manufacturing of individual polycrystalline wafers, and the assembly of the final solar modules. The purification step creates ingots of highly pure metallurgical silicon. The ingots are then cut into thin sheets called wafers which are then cleaned and treated. In the final step, the module assembly puts all the pieces together for a complete solar panel.

The following video briefly describes these processes:
https://www.youtube.com/watch?v=5Sgmp1aUjnA

Other videos that may be helpful to understand the process:
https://www.youtube.com/watch?v=fZ1SC-vUe_I&app=desktop
https://www.youtube.com/watch?v=QZs5nxEvB9I&app=desktop
https://www.youtube.com/watch?v=9ozt7yfsRKU

It is strongly recommended that you view the videos above so that you can visualize the process and hazards discussed below.

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LIST OF ABBREVIATIONS

EIA	US Energy Information Administration
NIOSH	National Institute for Occupational Safety and Health
DSS	Directional solidification system
FVC	Forced vital capacity
FEV1	Forced expiratory volume in one second
EVA	Ethylene vinyl acetate

I. BACKGROUND/SCIENTIFIC RATIONALE

A. Background

Photovoltaic cells (solar cells) use a semi-conductive material that absorbs energy from sunlight to generate electricity or heat. China, Taiwan, Malaysia, Japan, Germany, and the United States (U.S.) are the primary manufacturers of solar cells[1]. There has been exponential growth in global production of solar cells since 2000. The production of solar cells quadrupled between 2009 and 2013, mostly due to a dramatic increase in production of solar cells in China and Taiwan[2]. The production of solar cells has the potential to produce over 20 gigawatt-peak/year in energy. In the U.S. in 2018, photovoltaic solar panels generated 0.49 quads (1 quad is 1 quadrillion BTUs) of energy out of 99 quads of energy consumed nationally. Solar power generation is expected to grow to 4 quads of energy by 2050[3]. In addition, the cost per megawatt generated by solar panels has been cut by more than half in the past 20 years; it is currently equivalently priced to natural gas and is half the price of the cost of energy generated by coal. With changes in technology, the U.S. Energy Information Administration (EIA) estimates that the cost per megawatt generated by solar panels could drop to $20/MWh compared to its current price which ranges between $50-80[4].

Europe, China, Japan, and the U.S. are the largest consumers of solar panels, accounting for over 94% of the solar systems installed in 2013[1]. The process of manufacturing photovoltaics uses materials that are highly toxic, but the complete product in proper working conditions have no emissions. Solar energy is estimated to prevent up to 89% of the greenhouse gas emissions globally[5].

B. A Description of Common Photovoltaic Panels

The three most basic types of photovoltaic panels are crystalline silicon, thin film, and multijunction. The most common material used as a semiconductor in solar panels is crystalline silicon; photovoltaics can be made from monocrystalline silicon or polycrystalline silicon. Polycrystalline silicon is the most commonly produced photovoltaic technology in the world, accounting for approximately half of the global market share[3]. Compared to 30 years ago, the use of thin film technologies has increased overall. The most common material in thin film photovoltaic cells is Cadmium telluride. Multijunction solar panels use multiple layers of thin film and have the highest efficiency but have not been as widely implemented because of the high cost. The most common materials used in multi-junction cells is gallium indium phosphide, gallium arsenide, and there are several additional emerging technologies in germanium photovoltaics[6]. This report will focus on the production of polycrystalline silicon solar panels which currently are the most commonly produced solar panels in the U.S.

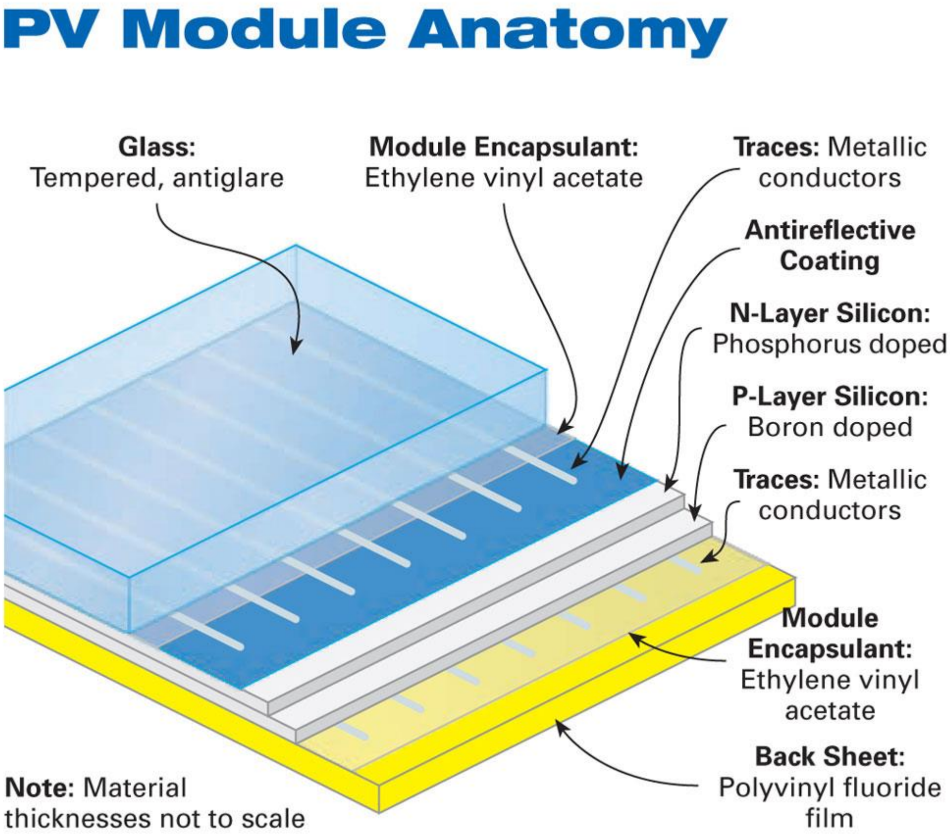
C. Importance

Identifying occupational hazards in the photovoltaic industry is complicated by several factors. Many processes are proprietary, there is little to no information on specific chemicals used in certain processes without cooperation from the manufacturing plant. Because of rapid changes to the technology, exposures are changing as well. Generally, most photovoltaic plants in the U.S. assemble the module but do not manufacture the individual solar wafers, which are most commonly manufactured in China. Furthermore, manufacturing plants have different degrees of robotic assembly lines; some lines may complete the entire process of module assembly while others may stop at soldering. Therefore, employees in this industry may have vastly different exposure profiles depending on the specific plant they work at, length of time on the job, and the area they work in. National Institute for Occupational Safety and Health (NIOSH) published an industrial hygiene characterization of the photovoltaic industry in 1980[7]. In this, they summarized that, in general, employee exposures to chemical hazards in this industry are likely low due to good controls. But they also noted a need for more detailed exposure assessments, especially for metallurgic and crystalline silicon and arsenic due to respiratory and carcinogenic effects[7]. They also noted a need for a deeper understanding of the toxicological effects of exposure to silane and chorosilanes[7].

It is important to first understand what the workers potential exposures are, determine which exposures are of highest concern, and then to estimate the level of exposure for the workers. To date, a comprehensive hazard and exposure assessment of photovoltaic manufacturers in the U.S. has not been conducted. NIOSH has also published a hazard assessment for the electronic component manufacturing industry; some employees in photovoltaic industry may share a few similar exposures to electronic component workers[8,9].

D. Summary of Polycrystalline Photovoltaic Panels Production

When high-purity polycrystalline silicon solar cells are first manufactured, several solar cells are connected in a layer, treated through several processes, and framed to create a complete solar panel. The panel edges are framed and topped with a top layer of glass and bottom layer of polyvinyl fluoride film for protection[9]. An encapsulating layer of ethylene vinyl acetate (EVA) covers the front and back of the panels to prevent the panel from shattering[9]. One layer of crystalline silicon cells is doped with electron acceptors, making up the n-type layer; phosphorous or arsenic are often used as the dopant in this layer[10]. A dopant is a substance used in manufacturing to achieve a desired electrical property in a semiconductor. Another layer of crystalline silicon is doped with a different electron donor, making up the p-type layer; boron, aluminum, or gallium are often used as the dopant in this layer[10]. This p-n junction improves conduction and allows the conversion of the intrinsic energy absorbed by the silicon to be converted into electrical energy[11]. Cells are treated with an anti-reflective coating for improved efficiency[10]. Individual cells in a panel are connected with metallic conductors, often made from silver. This allows the flow of electrons to be transferred to wires as a source of electricity[10].



Manufacturing Process for the Solar Cell and Solar Panel

There are three methods for manufacturing polycrystalline silicon wafers, with the most common being the direction solidification system (DSS). The three methods are heat exchange method (HEM), electro-magneto casting (EMC), and directional solidification system (DSS)[12].

During DSS silicon sand (SiO_2) is melted using an electric arc furnace to separate the silicon and oxygen, leaving metallurgic silicon. The metallurgic silicon is then further purified, bringing it to purity of at least 99.99999%. This consists of exposure to hydrochloric acid (HCl) and copper (Cu), producing trichlorosilane ($SiHCl_3$) gas. The trichlorosilane is exposed to hydrogen, producing silane gas (SiH_4), which is used to cast a highly pure polycrystalline silicon ingot. Before being cast the purified silicon is doped with an electron donor to create the p-type layer; boron, aluminum, or gallium are often used as the dopant in this process. A dopant is a substance used in manufacturing to achieve a desired electrical property in a semiconductor[11]. Ingots go through a series of cutting processes to create hundreds of thin polycrystalline silicon wafers.

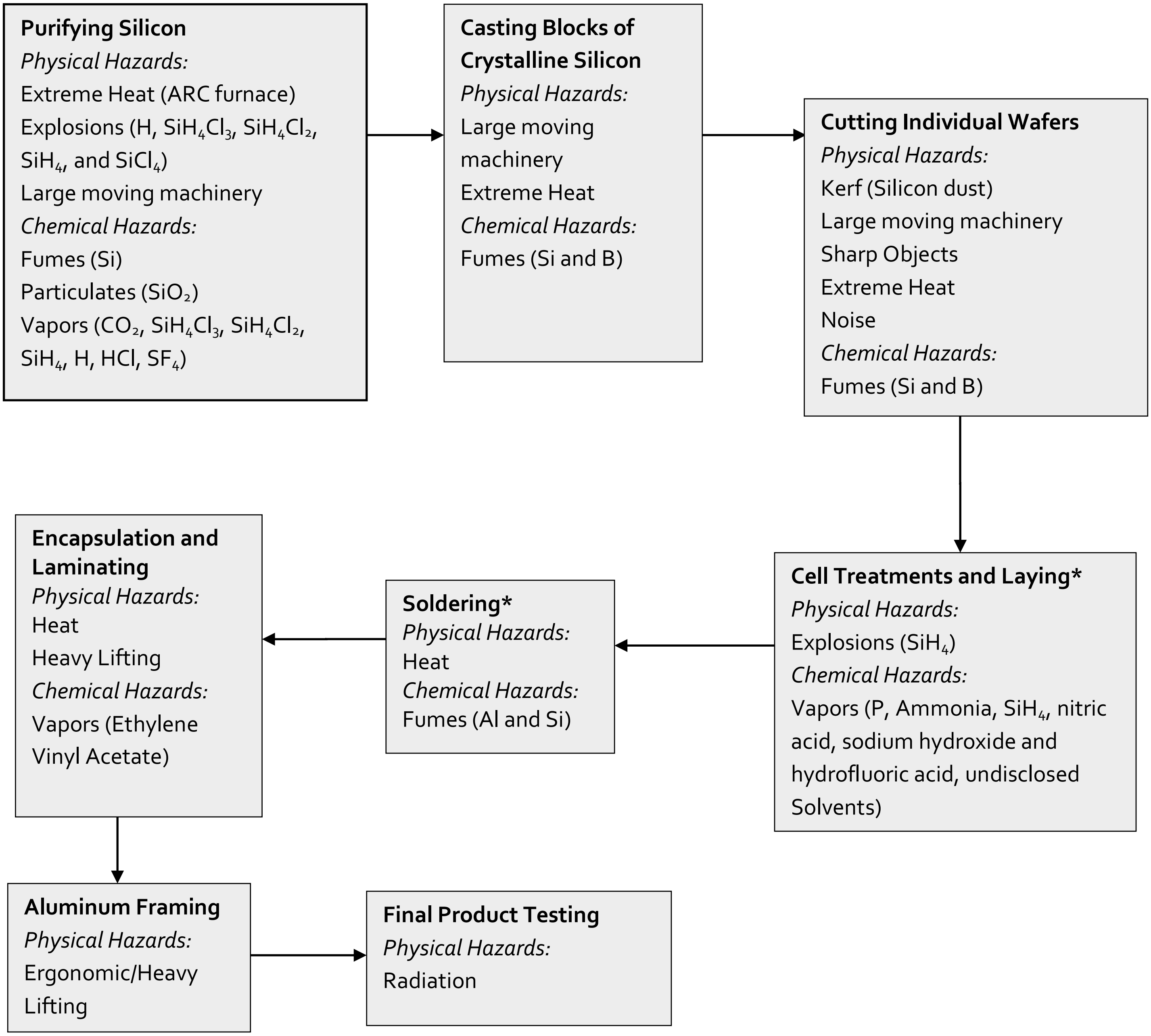
The surface of an individual wafer is textured to reduce reflection and increase absorption efficiency. Polycrystalline silicon wafers are often textured using photolithography or mechanical cutting with special saws or lasers. The wafers are then cleaned in acid using hydrogen fluoride vapor or hydrogen chloride. The wafers are doped with gaseous phosphorous, which involves a process of diffusion to create a thin film of phosphorous on top of the wafer. Phosphorous is an electron donor and make up the n-type layer. The p-n junction improves conduction and allows the conversion of the intrinsic energy absorbed by the silicon to be converted into electrical energy[11]. Edging and etching the surface of the wafers removes excess phosphorous. An anti-reflective treatment is applied to the wafer using plasma enhanced chemical vapor deposition. Silane (SiH_4) and ammonia vapors are used to produce this silicon nitride ($Si3N_4$) anti-reflective coating. Aluminum and silver pastes are applied to the wafers to act as the positive and negative conductive electrodes. Individual cells are finally examined and tested for quality.

Individual cells are soldered together in a single layer using either tin, silver, copper, or an alloy of the three. Two sheets of ethylene vinyl acetate (EVA) is placed over and under the layer of soldered cells. A piece of glass serves as the top most layer, protecting the cells from damage and bending. The back layer of a panel is most often made of a durable film that is protective but not as heavy as glass; the two materials used most often are tedlar polyestar tedlar (TPT) film or polyvinyl fluoride (PVF) film. The whole module is placed in a lamination machine which creates a vacuum and heats up the EVA to fully encapsulate the layer of individual cells. The panels are then tested for quality and then an aluminum frame is added to the module to reinforce and protect the edges of the solar panel. Finally, a silicone caulk is applied between the aluminum and glass panel to prevent materials from getting into the frame area.

E. Job Descriptions and Hazards

Many of the process in the manufacturing of solar panels are performed on a robotic assembly line and/or in a glovebox or cleanroom, mitigating many potential human health hazards. Robots are preferable to human labor because solar wafers are fragile, some treatment processes require a high degree of precision in a controlled environment, and many processes require high heat. Therefore, potential for exposure to chemical hazards via dermal or ingestion exposure is limited. Exposures via inhalation are the highest concern for those who work in the solar panel industry.

II. POLYSILICON PHOTOVOLTAIC PANEL PROCESS MAP



Purifying Silicon
Physical Hazards:
Extreme Heat (ARC furnace)
Explosions (H, SiH_4Cl_3, SiH_4Cl_2, SiH_4, and $SiCl_4$)
Large moving machinery
Chemical Hazards:
Fumes (Si)
Particulates (SiO_2)
Vapors (CO_2, SiH_4Cl_3, SiH_4Cl_2, SiH_4, H, HCl, SF_4)

Casting Blocks of Crystalline Silicon
Physical Hazards:
Large moving machinery
Extreme Heat
Chemical Hazards:
Fumes (Si and B)

Cutting Individual Wafers
Physical Hazards:
Kerf (Silicon dust)
Large moving machinery
Sharp Objects
Extreme Heat
Noise
Chemical Hazards:
Fumes (Si and B)

Cell Treatments and Laying*
Physical Hazards:
Explosions (SiH_4)
Chemical Hazards:
Vapors (P, Ammonia, SiH_4, nitric acid, sodium hydroxide and hydrofluoric acid, undisclosed Solvents)

Soldering*
Physical Hazards:
Heat
Chemical Hazards:
Fumes (Al and Si)

Encapsulation and Laminating
Physical Hazards:
Heat
Heavy Lifting
Chemical Hazards:
Vapors (Ethylene Vinyl Acetate)

Aluminum Framing
Physical Hazards:
Ergonomic/Heavy Lifting

Final Product Testing
Physical Hazards:
Radiation

*Human exposure to hazards in these processes may be minimal. Process is often done on a robotic assembly done and/or done in a glovebox or cleanroom.

III. SUMMARY OF CHEMICAL HAZARDS FOR EACH STEP OF THE PROCESS

Step 1 – Purifying Silicon

Employees involved in the manufacturing process of purifying silicone may potentially be exposed to several chemicals, primarily through the route of inhalation.

Chlorosilanes ($SiHCl_3$ and SiH_2Cl_2), silane (SiH_4) and hydrogen chloride are toxic and highly volatile, they react explosively when exposed to water[13]. Chlorosilanes and silane can also spontaneously ignite and under some conditions explode[13]. Silane and chlorosilanes can enter the body through inhalation and can irritate the skin, eyes, and respiratory tract[14]. Exposure to sulfur dioxide occurs most commonly through inhalation, exposure can cause irritation to skin, eyes, and respiratory tract[15]. Silicon tetrachloride can cause skin burns and is also an eye and respiratory irritant[16]. Gaseous hydrogen chloride can cause respiratory irritation or burning when inhaled. Hydrogen chloride when cooled to room temperature forms hydrochloric acid crystals and can cause skin burns[17]. Carbon Dioxide can have effects on the respiratory and cardiovascular system. Symptoms that can occur from exposure includes headache, dizziness, restlessness, malaise, and increased heart rate[18].

Step 2 – Casting Blocks of Crystalline Silicon

Purified metallurgical silicon and is doped with boron (creating the p-layer) and cast into blocks called ingots. Workers may be exposed to boron and silicon fumes. Acute exposures to both boron and silicon can cause respiratory irritation[19,20].

Step 3 – Cutting Individual Wafers

The primary health and safety concerns in this process are from exposure to and inhalation of kerf dust. Kerf dust is generally defined as the dust that forms when using a saw to cut through material[21]. The size of the dust is dependent on the width of a saw blade[21]. Acute inhalation of kerf dust can cause respiratory irritation. Long term inhalation can cause silicosis, and pneumoconiosis[22].

Step 4 - Cell Treatments and Laying*

Many different potentially hazardous chemicals are used during the treatment of the individual wafers (see diagram above). However, wafers are treated and processed on a robotic assembly line, therefore human exposure potential is low. The primary health and safety concern is inhalation exposures to chemicals used in reactor cleaning. Cleaning and maintenance of these wafers involves solvents such as nitric acid, sodium hydroxide, and hydrofluoric acid. Workers are most commonly exposed to ammonia via inhalation, which can cause respiratory irritation, wheezing, chest pain, and pulmonary edema. Exposure to airborne nitric acid can cause respiratory irritation, bronchitis, and/or pulmonary edema[23].

Step 5 – Soldering*

Liquified aluminum and silver are added to the silicon wafers. This process is again completed on a robotic assembly line, therefore a low a potential for these fumes to be inhaled by workers. If inhaled, these may cause respiratory irritation[24].

Step 6 - Encapsulation and Laminating

This process involves vacuum sealing and heating the photovoltaic module. At room temperature ethylene vinyl acetate (EVA) is stable and, but when heated it becomes gaseous and the inhaled EVA can cause respiratory irritation[25].

Step 7 - Aluminum Framing/Module Assembly

Module assembly is not a likely pathway for chemical exposure to these metals. There may be some ergonomic hazards when this process is not automated.

Step 8 - Final Product Testing

The main health and safety concern in this process is exposure to radiation. The photovoltaic module is tested by emitting a light onto the module and measuring the output of electricity that was converted.

IV. RECOMMENDED SURVEILLANCE PROGRAM TO BETTER CHARACTERIZE OCCUPATIONAL EXPOSURES

Table 1: A timeline of steps

Time Frame	Process	Who/Where
Baseline Week 0	General medical examination Pulmonary function test	All employees
First Month	Observe processes, interview employees, gather information on processes, review administrative records	All areas of manufacturing plant. 2-3 employees in each manufacturing area. Administrators.
Year 1- One week per season	Air samples for ambient air quality	General work areas for each manufacturing process
Year 1 – One week per season	Air samples for estimating personal exposures	Breathing zones
Year 1 - One randomly assigned week per season	Daily log of health effects recorded by employee	All employees
Year 2-3	Air samples for ambient air quality, one week per season.	General work areas for each manufacturing process
Year 2-3	Air samples for ambient air quality, one week per season.	General work areas for each manufacturing process
Year 2-3	Daily log of health effects recorded by employee	Only employees that reported moderate to severe symptoms in year 1
Year 3 – End of study	General medical examination Pulmonary function test	All employees

Phase 1: Observation and Interview Workers

Researchers will begin the exposure assessment by talking to employees in all areas of the manufacturing plant. We will characterize what each work day looks like for them and what activities they preform throughout each day of the work. We will also ask employees to describe other recurrent tasks that may not be conducted daily. In addition, it is important to get a detailed description of the maintenance and cleaning process for the manufacturing equipment, and the materials used for maintenance and cleaning. We will also review the OSHA 300 log and employment records. We will specifically attempt to capture data regarding turnover rates (where an employee leaves the company) and requests for change in position for each job, which may indicate which jobs are the most problematic.

The goal of this phase is to provide a detailed description of each job at the manufacturing site, look for potential points of exposure in the processes, and understand the cleaning and maintenance processes for the machinery in the plant. The information we gain in this phase will be used to inform decisions or modifications to phase 2 and 3, to conduct this study as efficiently as possible.

Phase 2: Measuring General Workplace (Ambient) Exposure Levels

There are three main buildings in this manufacturing plant: (1) the ARC furnace and wafer cutting area, (2) an area with an assembly line for processing the polycrystalline silicon wafer, and (3) an area where the whole photovoltaic module is assembled. The goal for this phase is to measure ambient air quality in each main manufacturing building for the hazards relevant to the area.

ARC Furnace/Wafer Cutting Area:

For carbon dioxide, OSHA has a permissible exposure limit of 5000 ppm (9000 mg/m^3) in an 8-hour time weighted average (TWA)[27]. Carbon dioxide will be measured with TCD Gas Bag sampler following the OSHA ID172 methods for measuring carbon dioxide[27].

Silane will be measured using an electrochemical cell, and silicon dioxide will be measured by a dual ionization chamber. Riken offers a commercially available monitor that can measure both simultaneously. There is no commercial monitoring system specific for chlorosilanes, but if silane is present it is assumed chlorosilanes are present too. It is assumed that the proportion of silane to chlorosilane will be consistent because these are produced as byproducts of the purification process. Further analysis may need to be conducted to verify this assumption[28]. There is no OSHA PEL for silane, the NIOSH REL and ACGIH TLV is 5 ppm (6.6 mg/m^3) based on an 8-hour TWA[29].

Sulfur Dioxide will be measured using IC sampling with bubbler and hydrogen peroxide, following OSHA guidelines for validated method #7446-09-5[29]. The OSHA PEL for sulfur dioxide is a TWA of 5 ppm (13 mg/m^3), but the NIOSH REL is TWA 2 ppm (5 mg/m^3)[27].

The OSHA PEL for silica dust is based on the percent of silicon dioxide in the material, the OSHA PEL is a TWA of 80 mg/m^3/%SiO$_2$[27]. The NIOSH REL is a TWA of 6 mg/m^3. Kerf (silica dust) will be measured using x-ray diffraction using a low ash PVC with cyclone sampler, following OSHA guidelines for validated method # 14808-60-7[29].

Wafer Processing Area:

The OSHA PEL for ammonia is a TWA of 50 ppm (35 mg/m^3)[27]. The NIOSH REL is a TWA of 25 ppm (18 mg/m^3)[28]. Ammonia will be monitored using HPLC/UV sampling with an Anasorb 747 coated with Sulfuric Acid, following OSHA validated method # 7664-41-7[29]. Silane will be measured using an instrument from Riken previously mentioned.

The OSHA PEL and NIOSH REL for nitric acid are the same, 8-hour TWA of 2 ppm (5 mg/m^3)[27]. Nitric acid will be measured using IC sampling with silica gel, following OSHA partially validated method # 7697-37-2[29].

Other solvents used for cleaning the machinery may also need to be monitored. This is dependent on the information acquired in phase 1, and if there is a commercially available instrument to measure these.

Module Assembly Area:

There is no OSHA PEL for EVA, but there are NIOSH recommendations for its monomer vinyl acetate. The NIOSH REL for vinyl acetate is a 15-minute ceiling limit of 4 ppm (15 mg/m3)[28]. EVA will be monitored using TG-MS following guidelines set by PerkinElmer[30].

Phase 3: Estimating Personal Exposures

The goal for this phase is to monitor air in personal work zones (specifically breathing zones) to estimate individual exposures by specific jobs. This will include sampling in areas where workers spend time and estimating the amount of time in each area. Sampling will be conducted in breathing zones of the workers. For the chemical hazards where on-body technology exists, we will use sampling tools that affix to the workers body, otherwise fixed monitors will be set up at the typical height of the workers' breathing zones and located in the area where the worker spends the most time (based on the data collected in step 1). We will also place monitors in areas near entry or exit of materials, especially for the glovebox and heated processes. This phase will allow us to build a job-exposure matrix and estimate daily exposure to workers in each area.

Health Outcomes Assessment

General Medical Examination - There will be an annual medical assessment for all current employees (beginning and end of the calendar year), and for all new employees prior to the initiation of work. All workers will be consented prior to using their medical information for the analysis. All workers will have the option to refuse to have their medical information used in the analysis. No biomarkers will be collected for this study.

Pulmonary function – Spirometry will be performed for measures of pulmonary function. Workers will have their lung function tested at the beginning and end of the study period. New hires will have their lung function tested before they start and at the end of the study period. Measurements of interest are expiratory forced vital capacity (FVC) and forced expiratory volume in one second (FEV1). The ratio of FEV1/FVC will also be calculated.

Workers will be asked to maintain a daily log of symptoms experienced for a total of four separate weeks throughout the study period, one week per season. Weekly assignments for participant logs will be selected at random. The year will be divided up into spring, summer, fall, and winters seasons. Each participant will complete 7 days of logs for symptoms, including days off work. People who report experiencing symptoms will be asked to complete an additional week of daily logs per season. This will allow us to better assess the time of day and activities occurring when these symptoms arise. The survey will be modified based on feedback from employees collected in phase 1 of this study to account for any complaints not identified on the log below.

The following table is an example of an entry for one day.

Name/Worker ID:___________________________________ Date: ___________________________

Was today a work day? (please circle) YES NO

Did you experience any of these symptoms while working today? Please check box for Yes or No.			**Approximately what time did these symptoms begin?**	**AM or PM? (Please circle)**	**Please describe the activity you were doing when symptoms began and approximate location in facility.**
	No	**Yes**	*If you answered "Yes", please answer all line questions*		
Difficulty breathing				A.M. / P.M.	
Respiratory irritation (sinus, nose, lungs, respiratory tract)				A.M. / P.M.	
Excessive coughing and/or sneezing				A.M. / P.M.	
Headache				A.M. / P.M.	
Dizziness				A.M. / P.M.	
Weakness				A.M. / P.M.	
Numbness				A.M. / P.M.	
Confused state				A.M. / P.M.	
Any other symptoms? (List them here)					

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