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HIGH-PURITY WATER NEEDS FOR THE PV INDUSTRY — CHALLENGES AND OPPORTUNITIES

The solar photovoltaic (PV) market has demonstrated an aggregated global growth rate of more than 40% per annum over the last 10 years. Few industries can claim equivalent numbers, but solar PV has two big challenges ahead. Production costs need to go down in order for it to become more economically sustainable, while production capacity must continue to grow in order for PV to become a significant player in the global energy market (1). To achieve both goals, significant efficiency improvements are needed in the production process, as well as in balance-of-system costs.

Figure 1 illustrates the past history trend for the high-purity water (HPW) requirement within semiconductor manufacturing. As the need for higher quality ultrapure water (UPW*) was identified, the complexity and number of unit operations was increased in the treatment system to be capable of reliably producing the water to the specification that resulted in high yielding wafers. From the chart (see again Figure 1) there were several distinct periods of evolution of water treatment systems. Examples include deionized (DI), reverse osmosis (RO)/DI, UPW, and ultra UPW. And, if we consider history, there will more than likely be even more advanced treatment systems in the future. With more complexity, obviously the cost of capital and operations are increased. This always needs to be considered in the decision-making process before moving to the next level.

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ISSN:0747-8291.

Advancing the technology for the treatment system was always done after the improved quality requirements were identified. For example, semiconductor manufacturing engineers took note of a defect/fault that was concomitantly identified to be an excursion related to the water quality. Once this correlation was identified and verified, money was budgeted to advance the water treatment system to the next level of quality requirements. The bottom line is that manufacturing was never strategic about improving (spending money) the treatment system until a problem was identified. However once the problem was identified the solution had to be implemented ASAP. This led to some non-optimal solutions (cost/operational) due to time constraints during the development process.

For the PV manufacturing industry the HPW requirements are presently relatively low as compared to the semiconductor industry. There are no technical feasibility challenges to process the water to the required quality. The challenge in the PV industry is installing a treatment system that is economically designed for the PV manufacturing constraints.

In applications of HPW systems, the improvements would imply minimizing the cost of ownership without affecting the manufacturing yield. There are examples when attempts to reduce cost and seeking cheaper solutions have impacted manufacturing. One of the examples is the use of clean polyvinyl chloride (PVC) piping instead of commonly used polyvinylidene fluoride (PVDF). Clean PVC is a relatively new way of optimizing the cost; however, the quality of the material and method of installation require in-depth understanding of the risks.

It has been recently reported (2) that use of clean PVC resulted in substantial operation down time and cost impact in one of the semiconductor development

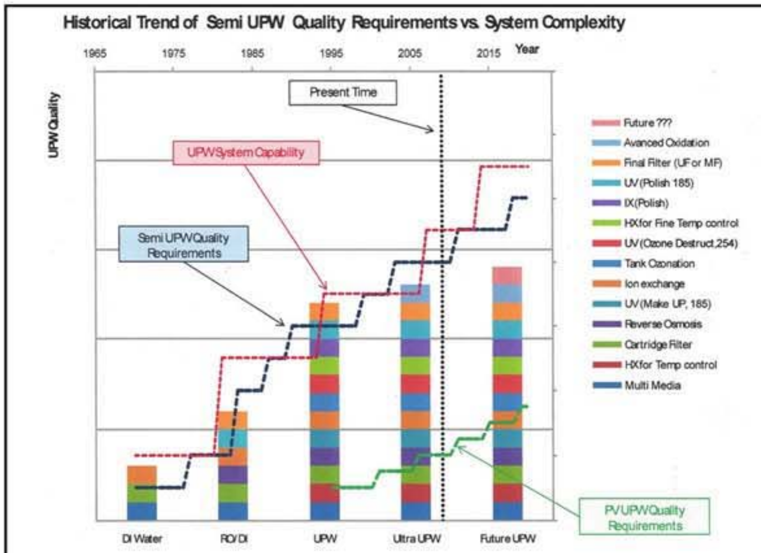

Figure 1. High-purity water technology evolution.

centers. The high level of particles dropped when PVC components were replaced with high-purity PVDF. Figure 2 demonstrates discoloration of the PVC in the areas where the material came in contact with UPW. Although there is no exact confirmation of the direct cause of the particle problem (material quality, installation method, or something else), it is apparent that reducing cost requires a data driven professional approach. In the end, excessive risk taking may cause much higher expenses than savings.

Driven by International Technology Roadmap for Semiconductor (ITRS), HPW technology capabilities exceed by far the water technology needs of the PV industry. UPW OEM suppliers offer a variety of HPW components and applications, providing flexibility for optimization of PV plants. However, how can this optimization be conducted to ensure no impact to production? And, where is the thin line of lowest cost and impact to production?

The biggest challenge is to understand the sensitivity of the PV manufacturing processes. The dynamics of the fast growing and highly competitive industry does not allow clear definition of the water quality parameters that may impact the process. High diversity of the different manufacturing processes and confidentiality barriers do not allow obtaining representative data.

However, it is interesting to note that as far back as 2003 the National Renewable Research Laboratory, a government-run organization located in Golden, Colo., contracted Keshner and Arya (3) to investigate and report out the form and purity of materials needed for building solar cells. Water was not included within their list.

The topic of contamination from other sources was found in the literature, though. Volatile organic compounds migrating through service lines, such as oils used in compressors, have been identified as causing problems for the PV wafer substrate, resulting in metal grid lines that will move or peel (4, 5). But again, there is no mention of potential problems with unclean substrates and adhesion when the topic is water purity.

Lack of technical information and standards in the facility area requires ongoing risk management. Larger PV cell manufacturers have developed proprietary in-house standards. However, as new players enter the market they will look to third-party equipment suppliers in order to build a complete production line. This approach can only succeed if industry standards are agreed upon for the interfaces that are used by these systems. In contrast with numerous UPW standards for semiconductor industry, no HPW for PV water quality standard exists.

From Challenge to Opportunity

The Semiconductor Equipment and Materials International (SEMI) organization formed a task force (TF) to develop a standard that will support the required optimization including development of a HPW specification. The taskforce is comprised of members from PV manufacturing, suppliers, consulting, and

Figure 2. Discoloration of the PVC components.

engineering. The following methodology was applied:

1. HPW spec survey— the group developed a format of the survey that would allow gathering information on the current state-of-the-art of HPW specifications. In addition to water quality specifications, the survey contained specific questions addressing the system configuration.

2. Analysis of different HPW system configurations— this allowed better understanding of the effect of the UPW quality specification to the adequate system configuration, and potentially, the cost.

3. A literature survey and direct communication with PV industry experts.

The survey results. The survey conducted by SEMI provided the following information:

- Participants represented a wide spectrum of PV-related businesses: different PV cell manufacturing, universities, and equipment suppliers, among others.
- Some companies have internal HPW specs, some do not.
- Specific point-of-use requirements are uncommon, but exist in some places.
- As expected, participants were interested in standardization driven by both cost and quality concerns.

Reported HPW systems' configurations were characterized by the following:

- Most systems had a continuous recirculation distribution system (not a dead-end).
- Despite expected and reported low sensitivity to TOC, some systems employed ozonation.
- Although a relatively low resistivity requirement was expected, most of the systems had mixed beds (ion exchangers).
- Although dissolved oxygen control was not expected in a PV water system, use of membrane degasifiers was reported.
- Tight particle control was required, since most of the systems used either microfiltration or ultrafiltration as the last treatment process step.
- The whole spectrum of the piping materials is used (PVC, CPVC, PP, SS, PVDF, and PFA), probably indicating that some of the system might have had a history of semiconductor manufacturing in it.
- The participants reported a wide range of the capacity of the systems, from small <50 gpm to large >300 gpm.

Water quality specification in the survey can be summarized by the following:

- Relatively high (higher than expected) resistivity (>17.5 microsiemens per centimeter [μS/cm]).
- Low sensitivity to dissolved organics.
- Some required relatively tight specs for bacteria and particles.
- Requirements for total and reactive silica were much less stringent than the ITRS (6).
- Some indicated sensitivity to metals: iron (Fe), copper (Cu), and aluminum (Al) were reported more often. However, even for those, the spec was orders of magnitude higher than similar semiconductor specs (6).
- For the anions: sulfate, nitrite, and chloride were reported often.
- As expected, dissolved oxygen and temperature control were not required in most of the cases.

In addition to the PV survey, analyses of typical HPW/UPW system configurations were conducted by consulting UPW vendors. The summary is presented by Table A.

The needs of PV endusers' requirements differ from those in semiconductor when it comes to high-purity water used during production. This is driven by different (lower) sensitivity to water quality parameters, and higher sensitivity to facility system cost.

The HPW specification being developed by SEMI PV TF takes into account the following ideas:

1. The specification refers to a point-of-use (POU) water quality.

2. It is a guide, and therefore complete analytical methods are not contained within. A selected list of optional analytical methods is found in the related sections.

3. The taskforce evaluated different qualities of water. A matrix of that evaluation is shown in Table A. This evaluation provides cost consideration, based on the idea that higher quality requirements require additional investment in the treatment process. The four qualities, A, B, C, and D, presented refer to 4 typical configurations of HPW treatment systems. The cost impact for reaching the water quality characteristics inside the range (i.e., A-B, C-D, etc.) is considered to be insignificant when compared to the cost of reaching the highest quality related to that range.

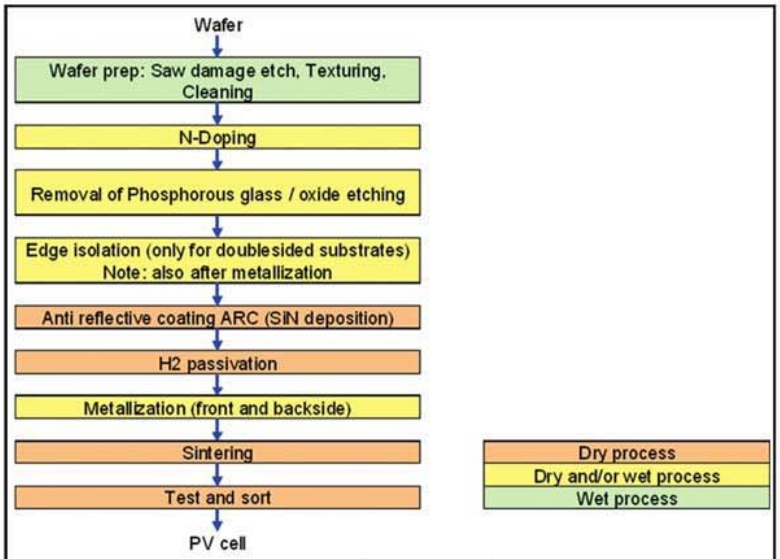

Figure 3. Typical screen-printed crystalline silicon cell.

	Buried contact cell (BC)	Boron back-surface-field cell (BSF)	Heterojunction with intrinsic thin layer cell (HIT)	Interdigitated back contact cell (IBC)	Emitter wrap through cell (EWT)
Inventor	University NSW	Solarworld	Sanyo	Lammert & Schwartz	
Man	BP Solar	Solarworld	Sanyo	SunPower	Advent Solar
Step 1	Sawdamage etch, texturing and cleaning	Sawdamage etch, texturing and cleaning	Sawdamage etch, texturing and cleaning	Sawdamage etch, texturing and cleaning	Laser hole drilling into p-type silicon wafer
Step 2	P2O5 deposition on front side	Boron coating	Deposition of i-type and of p-type a-Si:H to the front side	Boron diffusion	Sawdamage etch, texturing and cleaning
Step 3	CVD SiN dep on front side	Boron drive-in	Deposition of i-type and of n-type a-Si:H to the rear side	Boron glass removal	Screen printing of diffusion barrier containing an open channel
Step 4	Laser groove	Boron glass removal	Deposition of TCO to the front side	Rear-side SiNx	Phosphorous diffusion
Step 5	Groove damage etch and cleaning	Phosphorous diffusion	Deposition of TCO to the rear side	Front side Boron etching	Phosphorous glass etching
Step 6	Heavy POCl3 P diffusion and shallow P2O5 co-diffusion	Phosphorous glass removal	Ag silk screen contact print to the front side	Oxidation	SiN deposition on front and rear side
Step 7	Al evaporation to the rear	Edge isolation	Ag silk screen contact print to the rear side	Pattern of rear side for P diffusion	Al printing to p-type region in channels
Step 8	Rear contact diffusion	SiN deposition	Contact sintering	Rear side P diffusion	Ag printing to n-type region and connecting holes
Step 9	Electroless plating of Ni	Screen printing front side	Contact solder coating	Front-side oxide etching and texture	Firing
Step 10	Sintering	Screen printing rear side	IV measurement and sorting	Front-side P diffusion	IV measurement and sorting
Step 11	Etching	Firing		Diffusion glass removal	
Step 12	Electroless plating of Cu and Ag	IV measurement and sorting		SiN deposition on front and rear side	
Step 13	Laser edge isolation			SiNx patterning for contact points	
Step 14	IV measurement and sorting			Al sputtering	
Step 15				Al patterning	
Step 16		Dry process		Plating Ni, Cu, Ag	
Step 17		Dry and/or wet process		Annealing	
Step 18		Wet process		IV measurement and sorting	

Figure 4. Variations in crystalline manufacturing schemes.

4. The combination of the survey responses as well as the taskforce member assessment regarding the effect of water quality on the manufacturing process and cost impacts (see again Table A) resulted in the definition of two water qualities as shown in this document.

It should be noted that two typical configurations of the highest target quality water are not typical for PV, and are provided for reference only, or as potentially required if the sensitivity of PV manufacturing approaches that of semiconductor. The above systems' configurations and materials of construction can be differentiated by significant difference in cost and water quality performance. This analysis helped to define the recommended HPW specification.

Literature survey and direct communication with the PV industry experts. The literature survey did not unveil much information, as it is either confidential or limited in the HPW area. The personal communication (7) yielded the following information:

- Particles and resulting pinholes are considered critical only when visible from about 0.5 m (any material).
- Metal particles and ions are the only contamination sources that had an observed impact on efficiency and yield.
- Not all metals are critical (high diffusion rate of some of them may cause crystal defects). Mainly three metals are considered critical: iron (Fe), copper (Cu), and gold (Au). Specs in the material are in the parts per million (ppm) range.
- In the future, UPW quality will become more important for high-efficiency processes on one hand because the raw material becomes cleaner, and on the other hand processes are introduced such as plating instead of screen printing, which are more contamination sensitive.

Relevance to PV Processes

There are two different types of the PV cells:

1. Crystalline (silicon or compound semiconductor based): manufacturing processes are relatively similar to conventional integrated circuit (IC) processing without the challenge of the technology scaling.

2. Thin-film process is a silicon (Si)-based, or compound semiconductor based: especially the Si-based processes are similar to traditional non-wet coating processes, as known from the thin-film transistor (TFT) display industry. Compound semiconductor bases are using liquid steps, as well as future organic, or nanomaterial-based processes.

Crystalline silicon companies are currently dominating the market for PV cells with thin-film companies growing faster. The crystalline Si manufacturing from solar-grade Si to ready-to-sell modules is split into three major process steps, which all have different requirements to HPW. Here is a rundown of those process steps:

1. Wafer manufacturing— similar to chemical mechanical planarization (CMP) and grinding processes in integrated circuit (IC) manufacturing with less focus on micro-scratches.

2. Cell manufacturing— with typical etching and cleaning processes, similar to IC manufacturing (this is the area on which this article is focused).

3. Module manufacturing with little or no water used.

TABLE A
Typical Configuration of HPW systems

UPW Quality	*Level A* *Ultra-high purity*	*Level B* *High Purity*	*Level C* *High Quality*	*Level D* *Standard*
Re (MΩ·cm)	>18.2	>18.2	>17	>10
TOC (ppb)	< 1	< 5	<20	< 100
Critical metals (ppb)	<0.01	< 0.05	< 0.1	< 0.5
Particles (#/L)	<500	< 3,000	< 10,000	< 10,000
Size of the critical particle (μm)	0.05	0.05	0.2	0.3
Bacteria (#/L)	0 (excl. sample contamination)	0 (excl. sample contamination)	10	100
Total Si (ppb)	0.3	3	20	50
B (ppb)	NA	NA	NA	NA
DO (ppb)	NA	NA	NA	NA
Typical UPW System Configuration				
Pretreatment (~1 MΩ·cm)	RO, RO-RO; IX-RO;	RO, IX; RO-RO; IX-RO	RO; RO-RO; IX-RO	IX; RO, RO-RO; IX-RO
Make-up	UV- MB; or UV-CE-DI-MB, UV-EDI-	UV- MB; or UV-CEDI-MB		
Polish	(O_3)-UV-MB-UF	UV-MB- MF (0.05 μm)	MB-MF(0.1 or 0.2 μm) , or CEDI-MB-MF (0.1 or 0.2 μm)	AB-CB-MF (0.2 μm); or CEDI MF(0.2 μm)
Distribution material				
Supply	PVDF	PVDF, PP	PP, PVC	PP, PVC
Return	PP	PP, PVC	PP, PVC	PP, PVC

Thin film processes are integrated into one production.

Although PV companies use different proprietary processes, there is a clear commonality in most of the Si-based processes (see Figure 3).

Although the PV manufacturing is not as complex and diverse as IC manufacturing, there is an obvious diversification from the standard process (see Figure 4), offering more sophisticated process sequences.

Table B summarizes the relevance of the HPW parameters to the specific manufacturing steps.

PV HPW Specification

The TF consolidated the inputs and released an industry technical ballot (Yellow) to SEMI's PV list of interested endusers and suppliers alike. Results of the balloting were to be reviewed in November 2009. Table C presents the recommended specification that was submitted for the Yellow Ballot.

Note: Table C was presented as a draft at the 2009 ULTRAPURE WATER Micro conference in Portland, Ore. To obtain the full version of the specification, please refer to http://www.semi.org.

Table C indicates that significant portion of the spec parameters are not driven by the process needs. However, the need for controlling other parameters results in the side effect of having the rest of the constituents removed. On the other hand, maintaining non-critical parameters within specification will ensure proper control of the facility system operation, and as a result, reliable control of the critical parameters.

The specifications used by many manufacturers are driven by semiconductor manufacturing experiences. Since the plant design typically includes polishing resins, the quality is typically not a problem.

In PV cells metals like iron have shown detrimental effects, though not many studies have been conducted yet. Other specifications such as for organics and anions have not been covered by published scientific work. Some of the specifications above have to be seen as facility monitoring specs (e.g., if no silica is detected, the ion-exchange resin is not saturated and would not released any metals). Or, if the particle concentration is low in the HPW, metal particles would probably be low as well. Organics have not been reported as a risk factor to the process, but it may enhance an adherence of particles.

On the other hand, cell efficiency is a key driver for the industry, and metals play an important role both as particles causing shorts, and as ions causing direct chemical contamination. Further examination, testing, and standardization are required to determine future direction.

Given that not much is known about the effect of HPW quality to PV manufacturing, it is important to establish rigorous process control for tracking the performance of the water system versus manufacturing performance. This would require the following actions:

- Establish a baseline to determine levels that give current yields.
- Compile meaningful data by estab-

TABLE B
Effect of HPW Parameters on Crystalline PV Manufacturing

Wet Process Step	*Competing with Other Dry Processes*	*Relevance to HPW Quality*	*Future Trends*
Saw damage etch and texturing	Dry SF_6 texturing	Temperature and chemical concentration control [10]	Ionic contamination and particles may become important
Phosphoric acid deposition by brushing	POCl3 deposition	Concentration control	Risk of dopant variation and metal contamination
Etching of boron or phosphorus glass	Dry etching processes	Concentration control	Risk of dopant variation and metal contamination
Etch isolation and cleaning before SiN deposition	Laser cleaning	Metal particle deposition and metal ions contamination (Cu, Fe, Au) – most critical step for metal and particle contamination	Will continue to be the main efficiency driver for wet processes
Electroless plating of Ni, Cu, and Ag	Screen printing	Relatively sensitive to particles and metals	Organic contamination should be expected
Special parterning processes (non-standard)	Dry etching	Relatively sensitive to particles and metals	Growing sensitivity to particles and metals

lishing a sampling schedule, documenting normal levels and variation, and monitoring trends over time.

- Monitor causes of fluctuations such as feedwater quality (especially seasonal changes), internal operational activities, component change outs, regenerations, RO cleanings, and system modifications such as distribution piping additions/reductions, valves, and pumps.
- Communicate baseline data and changes in water quality back to the process engineers. This will aid in tying water quality to changes in yield (or in vindicating the water system during a yield loss).

From semiconductor UPW experience it is important to establish proactive maintenance methodology that would allow: effective response to preventing HPW excursions from impacting the process yield.

Summary

One of the biggest challenges facing the PV industry is achieving production cost targets for equivalent competitive manufacturing wattage output. Lower cost can be reached in a number of ways, such as via manufacturing cost improvements of the PV wafer, cell, and module production. Similarly to the semiconductor industry, this is expected to occur via more energy efficient PV cells coupled with lower cost PV manufacturing.

Both factors are expected to require a higher manufacturing complexity of the PV products in the future and, as a result, cleaner manufacturing environments and potentially improved UPW quality. Current state-of-the-art UPW technology provides solutions for any UPW quality anticipated in the future. However, the challenge is related to cost versus quality optimization of the UPW design. Incremental UPW investments may not translate proportionally to improved water quality. Given the relatively short history of the PV industry, the PV UPW design and water quality requirements are yet to be standardized. This can create a risk of both insufficient quality and excessively high cost of the facility systems.

Diversity of the PV processes makes the task even more complicated. SEMI, under the direction of their PV Group, formed a task force that has taken on the challenge to provide the industry with the UPW quality standards that could be used for new system designs as well as a guide for existing systems. The large number of different PV technologies increases the complexity to the task of standardizing the water quality requirements, thus resulting in the need to introduce a tiered approach. Since the time that the original work began on this article, the proposed HPW specification mentioned within was balloted to the PV industry and published by SEMI. Uncertainty of the effect of water quality to PV production will require proper ongoing process control.❑

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Additional Resource

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Endnote

*In the text, the term UPW refers to semiconductor-grade water produced in microelectronics facilities. Its quality parameters are defined under the International Technology Roadmap for Semiconductors (ITRS).

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TABLE C
Recommended HPW Specifications

Parameter	*Range of Performance*		*Justification*
	High Purity	*Standard Purity*	
Resistivity on-line @ 25°C (Mohm–cm)	>17.5	>10	Plant operation
TOC on-line (ppb)	<20	<200	None for PV / Experience from semiconductor
Dissolved oxygen on-line (ppb)	NA	NA	
On-line particles/L (micron range)			
0.1–0.2	<1,000	NA	Real problem are metal particles
0.2–0.3	<100	<10,000	
0.3–0.5	<10	<1,000	
>0.5	<1	<100	Pinholes
Bacteria (cfu/L)	<10	<100	Equipment operation
Silica			
Silica — total (ppb as SiO_2)	<20	<50	Plant operation
Silica — dissolved (ppb as SiO_2)[Note 1]	<20	<50	Plant operation
Ions & metals (ppb)			
Ammonium, bromide, chloride, fluoride, nitrate, nitrite, phosphate, sulfate	<1	<10	None reported
Antimony, arsenic	<1	<10	Not clear, to be studied, experience from semiconductor.
Copper	<1	<10	Relevant for performance
Gold	<1	<10	Relevant for performance (NEW)
Iron	<1	<10	Relevant for performance
Lead, aluminum, cadmium, manganese, nickel, chromium, tin, titanium, vanadium, zinc	<1	<10	Not clear, to be studied, experience from semiconductor.
lithium, sodium, potassium	<1	<10	Not clear, to be studied, experience from semiconductor.
Magnesium, calcium, barium	<1	<10	Not clear, to be studied, experience from semiconductor.

Note 1: Total Si is defined as the leading specification parameter. Typically dissolved Si presents the majority of the total Si in the defined spec range. Measuring dissolved Si may be chosen for convenience or for cost optimization reasons.

Coauthor Slava Libman, Ph.D., has been a senior process engineer with the U.S. operations of M+W Group since 2008. He previously worked 10 years with Intel Corp. Dr. Libman holds a doctorate in environmental engineering from the Technion, Israel Institute of Technology and is a licensed professional engineer from the state of Iowa. He works on the ITRS and SEMI committees for UPW spec development, and is a member of the Water Reuse and Membrane Process Committes of the American Water Works Association and Water Environment Federation.

This paper was given at ULTRAPURE WATER Micro 2009, which was conducted in Portland, Ore., Nov. 4-5, 2009.

Key words: DI WATER, MONITORING, SEMICONDUCTORS, SOLAR, STANDARDS