Does the Solar Industry Need High Purity Performance Chemicals?

High purity chemicals are vital to the industry’s drive toward grid parity

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High purity chemicals will become increasingly important as PV manufacturers drive toward grid parity.

The financial crisis of 2009 saw Module ASP’s collapse by up to 40% compared to pre-crisis prices seen in 2008. These lower prices have driven module, cell, and wafer manufacturers to require lower prices from their upstream suppliers as well as from their process chemical vendors. Throughout the solar cell manufacturing process, a variety of chemicals, including HF, HNO_3, NaOH, KOH, $POCl_3$, H_3PO_4, SiH_4, and NH_3 are utilized. Figure 1 illustrates some of these chemicals and where they are used in the cell making process.

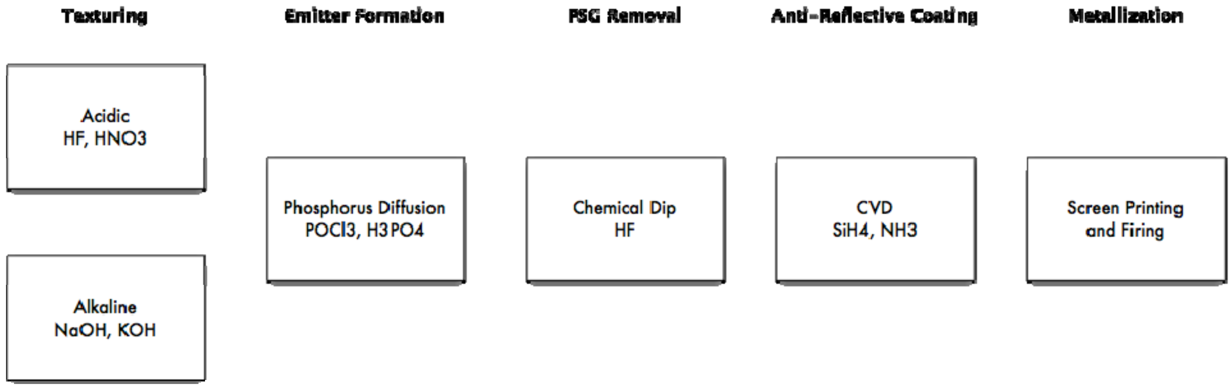

Figure 1. Process flow digram for standard solar cell manufacturing.

It was only a few years ago that solar cells were made using recycled or rejected silicon from the semiconductor industry. These cells were usually made in warehouses and treated with commodity chemicals. Flash forward to 2010 and the industry now consumes more polysilicon than semiconductor - no more hand-me-downs for us. Furthermore, the cells are processed in clean rooms that rival some of the most sophisticated semiconductor fabs. Why then is the solar industry satisfied with chemicals that are of lower purity than the silicon wafers now in use?

To achieve the increases in solar cell efficiency and production yield required to achieve grid parity, the industry must continue to turn to high purity performance chemicals used in texturing, emitter formation, phosphosilicate glass (PSG) removal, ARC deposition and metallization.

The remainder of this article will focus on the phosphorus diffusion step and the advantages of using a performance chemical for the solar cell manufacturer.

Phosphorus Diffusion

The traditional P-N Junction is formed by diffusing phosphorus (an N-Type dopant) onto a Boron doped (P-Type) silicon wafer. This diffusion can occur in a batch diffusion furnace using phosphorus oxychloride ($POCl_3$) or in an inline furnace using a spray-on phosphoric acid (H_3PO_4). It is the formation of the P-N Junction that enables the generation of electricity through the photovoltaic effect.

Once a photon hits the top of the solar cell, an amazing series of events must take place for electricity to be created. First, the photon must be absorbed by the semiconductor material. This will only happen if the photon is not either reflected off the surface of the cell, or passed through the cell entirely. Next, the absorbed photons must be converted to charge carriers.Third, charge separation of the carriers must take place within the cell (at the P-N Junction). Finally, the carriers must be extracted as electricity through an external circuit before they are lost through carrier recombination.

A significant amount of research has been conducted that has established the correlation between minority carrier recombination lifetime and the ultimate efficiency of the solar cell. This correlation has been demonstrated regardless of the type of wafer whether it be monocrystalline, or multicrystalline. There are currently several test available that can be conducted inline on a production solar cell line, or offline using a stand-alone testing unit to test for minority carrier lifetime at each step in the cell manufacturing process. For example, the Quasi-Steady-State area-averaged lifetime measurement method has been proven to effectively predict the ultimate cell efficiency in multicrystalline cells. For more details on this see Sinton, R.A., “Predicting multi-crystalline solar cell efficiency from life-time measured during cell fabrication”, Proceedings of 3rd World Conference on Photovoltaic Energy Conversion, 2003. p. 1028-1031, Volume 2.

It has also been established that impurities found in the silicon wafer or introduced by the phosphorus diffusion process will contribute to recombination and a lower minority carrier lifetime test result after the diffusion process. Specifically, the existence of 3d transition metals have been found to dramatically reduce lifetime. For example, McHugo, Thomson, Perichaud and Martinnuzi found a direct correlation between regions of high concentrations of Iron, Chromium, and Nickel and areas of high minority carrier recombination in multicrystalline cells. “Direct Correlation of Transition Metal Impurities and Minority Carrier Recombination in Multicrystalline Silicon” http://www.als.lbl.gov/als/compendium/AbstractManager/uploads/Madalsd.pdf. A study by Westinghouse Research Laboratories found that the worst lifetime killers are, in order of decreasing severity, **molybdenum, titanium, vanadium, chromium, manganese, iron, aluminum, nickel, copper, magnesium, zinc, and calcium**. Davis, J.R., Rohatgi, A., Rai-Choudhury, P. Blais, P., and Hopkins, R.H., 13th IEEE Photovoltaic Specialty Conference, Washington DC. June 1978, p. 490.

Which brings us back to the benefit of high purity performance chemicals. Take for example the guideline specification for POCl3 intended to be used by the solar industry currently promulgated at International Standards Committees by commodity chemical manufacturers:

Assay	>99.9%

Typical Metals Analysis (ppb)

Aluminum	<10
Arsenic	<10
Barium	<10
Boron	<10
Cadmium	<10
Calcium	<10
Chromium	<10
Copper	<10
Iron	<10
Lead	<10
Lithium	<10
Magnesium	<10
Manganese	<10
Nickel	<10
Potassium	<10
Sodium	<10
Tin	<10
Titanium	<10
Vanadium	<10
Zinc	<10

Now look at the data sheet for a high purity performance POCl3 currently being sold by Peak Sun Silicon:

Specifications

Assay	>99.9%
Purity	
(Metals Basis)	>99.99999%
Color (APHA)	<5

Typical Metals Analysis (ppb)

Aluminum	<1
Arsenic	<3
Barium	<1
Bismuth	<1
Cadmium	<1
Calcium	<3
Chromium	<1
Cobalt	<1
Copper	<1
Gallium	<1
Gold	<1
Iron	<3
Lead	<1
Lithium	<1
Magnesium	<2
Manganese	<1
Mercury	<5
Molybdenum	<1
Nickel	<1
Niobium	<1
Potassium	<2
Silver	<1
Sodium	<5
Strontium	<1
Tin	<1
Titanium	<1
Vanadium	<1
Zinc	<3

Real World Results

While performance chemicals introduce significantly fewer impurities into the silicon wafer, during the diffusion process, the real proof is in the results experienced by customers using high purity chemicals in their production lines. Review for example, the results from the customer below:

Carrier Lifetime

156mm multicrystalline cells
Lifetime measurement ~24 microseconds after standard diffusion
Using Performance Chemicals vs. Commodity Chemicals

Test results:
200 reference wafers from Tier I Vendor
Lifetime using commodity POCl3 = 20.47 ms
Lifetime using performance POCl3 = 28.27 ms
Increase of 17.8% over 6 mo. average existing process
Increase of 38.1% in test conditions

Cell Efficiency

156mm multicrystalline cells
Using Performance Chemicals vs. Commodity Chemicals

Test results:
FF[%] Increase of 0.28%
Pmpp[Wp] Average Increase of 0.75%
Pmpp[Wp] Best Cell Increase of 1.26%

Through switching from commodity process chemicals to performance chemicals this customer was able to achieve better carrier lifetime after the diffusion process which led directly to an increase in overall cell efficiency. The customer also achieved improved bin distribution and yield. This was all accomplished without modifying and / or improving the diffusion recipe to take advantage of the performance chemical. Experience in working with customers has also demonstrated that a customer willing to perform R&D to maximize the benefit of the performance chemical should be able to achieve even better results as reflected by the large increase in carrier lifetime after the diffusion step.

Translating Real World Results Into Increased Profit

While an average conversion efficiency increase of 0.75% (as seen in the example above) may seem insignificant, when introduced across the line in a 100 MW cell fab, the results are significant:

	Facility (in MW)	Wafers / Yr	Average Efficiency	Watts / Yr	Cell ASP $/W	Revenue
Commodity Chemical	100	28,571,429	3.500	100,000,000	$1.25	$125,000,000
Performance Chemical	100	28,571,429	3.526	100,750,000	$1.25	$125,937,500
					Increase	$937,500

At $1.25 per watt ASP, the increase in profit for this 100 MW cell fab approaches $1,000,000 USD. The increase in profit pays for the POCl3 and still results in a significant decrease in cost per watt for the cell manufacturer.

Conclusion

Performance chemicals such as high purity $POCl_3$ can increase carrier lifetime, cell efficiency, and cell fab yield. All of these results can be easily achieved through substituting performance chemicals with low rates of impurities for the commodity chemicals currently used on solar cell lines today. For Cell Process Engineers willing and able to conduct research and development throughout the cell line, even greater results can be achieved. In the drive toward grid parity, performance chemicals will become a critical component utilized by solar cell fabs - and, yes - the solar industry does need high purity performance chemicals!

Where to purchase $POCl_3$

For more information on high purity $POCl_3$ or to request a quote, please contact Targray Technology International, at http://www.targray.com/solar/.