Advanced solar cell production requires a systems-level approach to achieve abatement goals

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Solar panel manufacturers strive to minimize cost and maximise efficiency of their modules. Their success is confirmed by the substantial decrease in $/Wp factor for the modules. In 2006, crystalline silicon based module prices were approximately 5.2$/Wp. By 2017, this had dropped to 0.42$/Wp, over an order of magnitude decrease in ten years.

There has also been a massive relocation of the cell and module manufacturing industry. In 2006, China and Taiwan produced ~7% of the world production of solar modules as expressed as MWp. At that time, over 40% of production was in Japan, and over 30% in Europe. By 2017, China and Taiwan dominated module manufacturing, with over 70% of the world production, ~60% of that being in China alone. Both Japan and Europe had dropped to less than 5%.

It is important to stress that $/Wp values are dominated by availability and cost of capital, land prices, environmental regulatory restrictions, and production scale – these parameters contribute to operating costs more than labor.

Module efficiency contributes to the $/Wp performance indicator. The table provides absolute and relative module efficiencies.

The best heterojunction modules are 50% more efficient than those modules based on thin films.

The Chinese government has been very actively promoting development of its manufacturing industries. Local manufacturing has been encouraged not only by the supply of cheap capital, but also by increased land availability. The installation of solar modules has been encouraged in China, like many other countries, by the implementation of feed in tariffs (FITs - long-term agreements and guaranteed pricing tied to costs of production). However, also like many countries, as the cost of the power generated by solar technology dropped, the Chinese government has reduced the FITs. In 2015, the average FIT was 0.95 RMB (0.95 Chinese yuan = $US 0.15)/kWh. In June 2018, this was dropped to between 0.65 to 0.75 RMB ($US 0.1-0.12)/kWh.

The Chinese government has also directed the market to encourage the manufacture of the modules using more efficient solar cells by adopting differential FITs. One such cell technology, passivated emitter and rear cell (PERC) has been encouraged by this differential tariff approach.

Technology	Module Efficiency	Relative Module Efficiency Increase vs 14% Absolute
Thin film	14-16%	0%-14%
Mono-crystalline and Czochralski silicon (mCz-Si) PERC	16-18%	14%-29%
Interdigitated Back Contact (IBC) Silicon Heterojunction	18.5%-21%	32%-50%
Relative efficiency = recorded module efficiency/14% -100%		
e.g. mCzSi at 18% module efficiency, relative efficiency = 18%/14%-100% = 29%		

Table 1. Typical Module Efficiencies

A conventional crystalline silicon solar cell comprises:

- Screen printed silver contacts
- Anti-Reflective Coating
- Phosphorus diffused, boron doped silicon wafers that form the P-N junction
- Aluminum Back Surface Field (Al-BSF)
- Aluminum contact layer.

In a PERC cell, two additional steps are employed. First, a rear surface passivation film is applied. The passivation of the rear surface is ensured by depositing a thin layer of aluminum oxide (Al_2O_3) using either fast atomic layer deposition (fast-ALD) or plasma enhanced chemical vapor deposition (PECVD) and gases such as trimethylaluminum $(CH_3)_3Al$ and nitrous oxide (N_2O). The SiNx capping layer, like the other silicon nitride layers, is created using PECVD deposition with silane (SiH_4) and ammonia (NH_3) as the primary process gases. Second, chemical or laser etching can be done to open the rear passivation film to absorb more light. The improvements achieved by employing the additional steps are:

- More light is absorbed.
- Less light is lost because of increased internal reflection.
- Electron recombination is reduced.

It is possible to achieve up to 1% absolute gain in efficiency by using this approach.

In the ALD process much of the trimethylaluminum is converted to alumina, but residual process gases can be found in the chamber exhaust gas – chamber process gas utilizations and conversion efficiencies vary depending on the tool manufacturer. The complete reaction does not occur.

$2Al(CH_3)_3 + 24N_2O(g) = Al_2O_3 + 6CO_2(g) + 9H_2O(g) + 24N_2(g)$

This means that trimethylaluminum, nitrous oxide, carbon dioxide, methane, and water all pass to the abatement system along with any process nitrogen and nitrogen that is also used as the vacuum pump purge.

In the silicon nitride process, the full reaction does not occur.

$3SiH_4(g) + 4NH_3(g) = Si_3N_4 + 12H_2(g)$

This means that silane, ammonia, and hydrogen all pass to the abatement system along with any process nitrogen and pump purge nitrogen.

What are the hazards associated with the gases mentioned above, and how are these hazards managed?

Silane, hydrogen, ammonia, methane, and trimethylaluminum are highly flammable gases.

Ammonia and nitrous oxide are both toxic with IDLH (immediately dangerous to life or health) levels of 300ppm and 100ppm respectively.

Ammonia is ecotoxic and releases to air and water are regulated in all jurisdictions.

Carbon dioxide, nitrous oxide, and methane are global warming gases and, from 2019, nitrous oxide will be included in the IPCC guidelines. Releases of this gas will need to

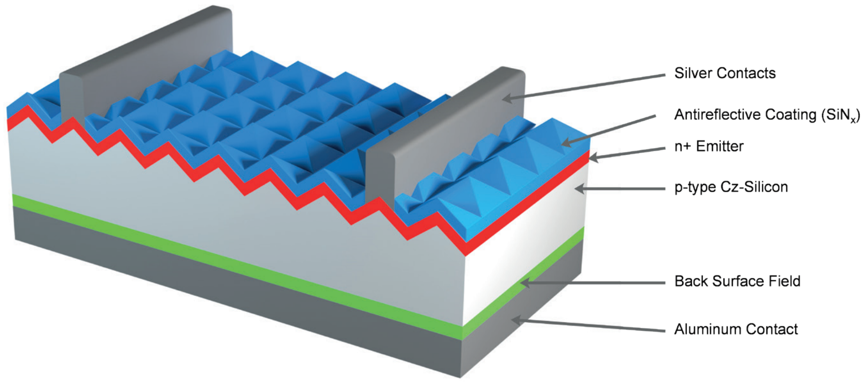

Figure 1 – Conventional Crystalline Silicon Solar Cell

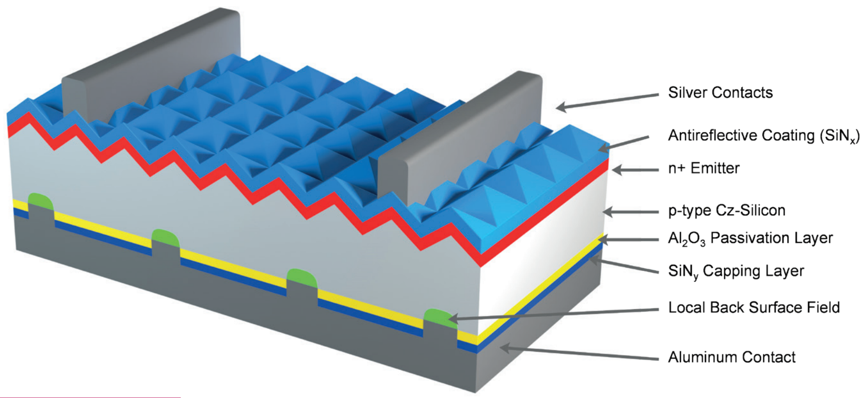

Figure 2 – PERC Technology Crystalline Silicon Solar Cell

Gas	Property	Symbol
Ammonia	Toxic, Flammable, Ecotoxic	
Silane	Toxic, Flammable	
Trimethylaluminum	Toxic, Flammable	
Hydrogen	Flammable	
Methane	Flammable, Global Warming	
Nitrous Oxide	Toxic, Oxidising, Global Warming	
Carbon Dioxide	Global Warming	

Table 2. Some of the process gases used in PERC technology solar cell manufacture and the hazards associated with use.

Gas	Process	Typical Flow
Input Gas SiN		
Ammonia	Silicon Nitride Steps	5-10slm
Silane		2-3slm
Output gas – flows are process and tool dependent but will include silane, ammonia, and hydrogen		
Input gas ALD		
Trimethylaluminum	ALD step	0.1g-0.2 g/m
Nitrous Oxide		4-6slm
Output gas – flows are process and tool dependent but will include trimethylaluminum, nitrous oxide, methane, carbon dioxide, and water.		

Table 3. Examples of flows of gases used in PERC technology solar cell manufacture.

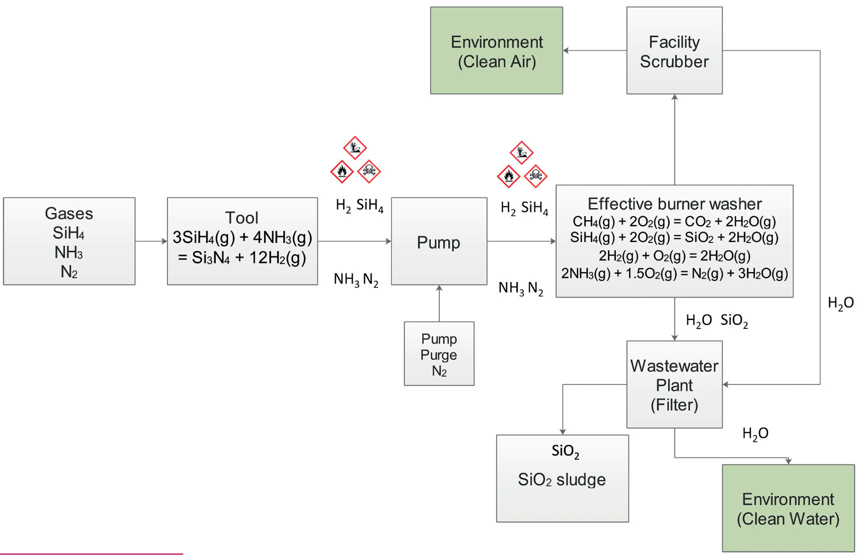

Figure 3 – Flow sheet for thorough SiN abatement

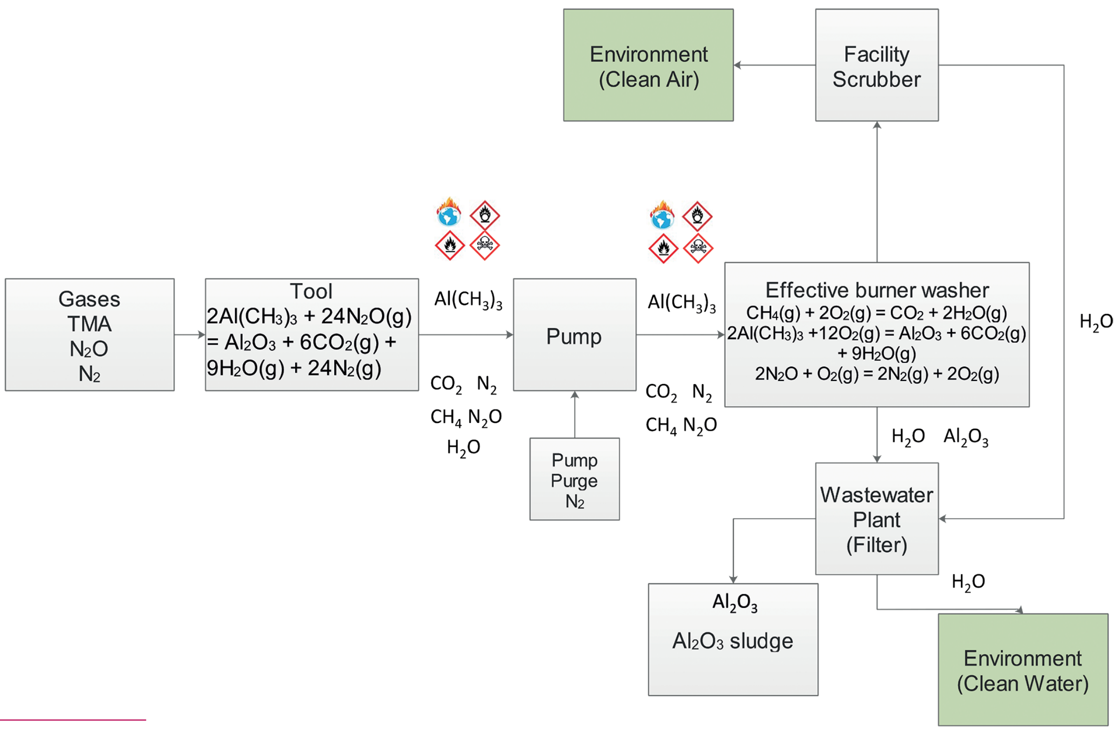

Figure 4. Flow sheet for thorough ALD abatement

be managed/reported as part of the 2015 Paris Climate Agreement.

Typical process gas flows (excluding nitrogen) are shown in table 3.

We have already stressed that these gases can be pyrophoric and toxic. The most effective route for the management of these flammable gases is to burn them in a fuel (usually methane) and air mixture and then water scrub the resulting products. The burning of the methane provides both an ignition source and a high temperature to ensure effective destruction of the compounds.

$CH_4(g) + 2O_2(g) = CO_2 + 2H_2O(g)$

$SiH_4(g) + 2O_2(g) = SiO_2 + 2H_2O(g)$

$2H_2(g) + O_2(g) = 2H_2O(g)$

$2NH_3(g) + 1.5O_2(g) = N_2(g) + 3H_2O(g)$ (appropriate conditions are required to ensure NO_x formation is minimised).

$2Al(CH_3)_3 + 12O_2(g) = 6CO_2(g) + Al_2O_3 + 9H_2O(g)$

If controlled carefully, abatement of nitrous oxide can also be achieved.

$4N_2O + CH_4(g) = CO_2(g) + 4N_2(g) + 2H_2O(g)$.

The resulting very fine oxide powders from the silicon and aluminum compounds (d < 1μm) are often filtered by reverse pulsed HEPA filters to remove particulate from the abatement exhaust gases. Other technologies, such as wet electrostatic precipitators, can also be employed for the same fine solids collection duty. Any solids

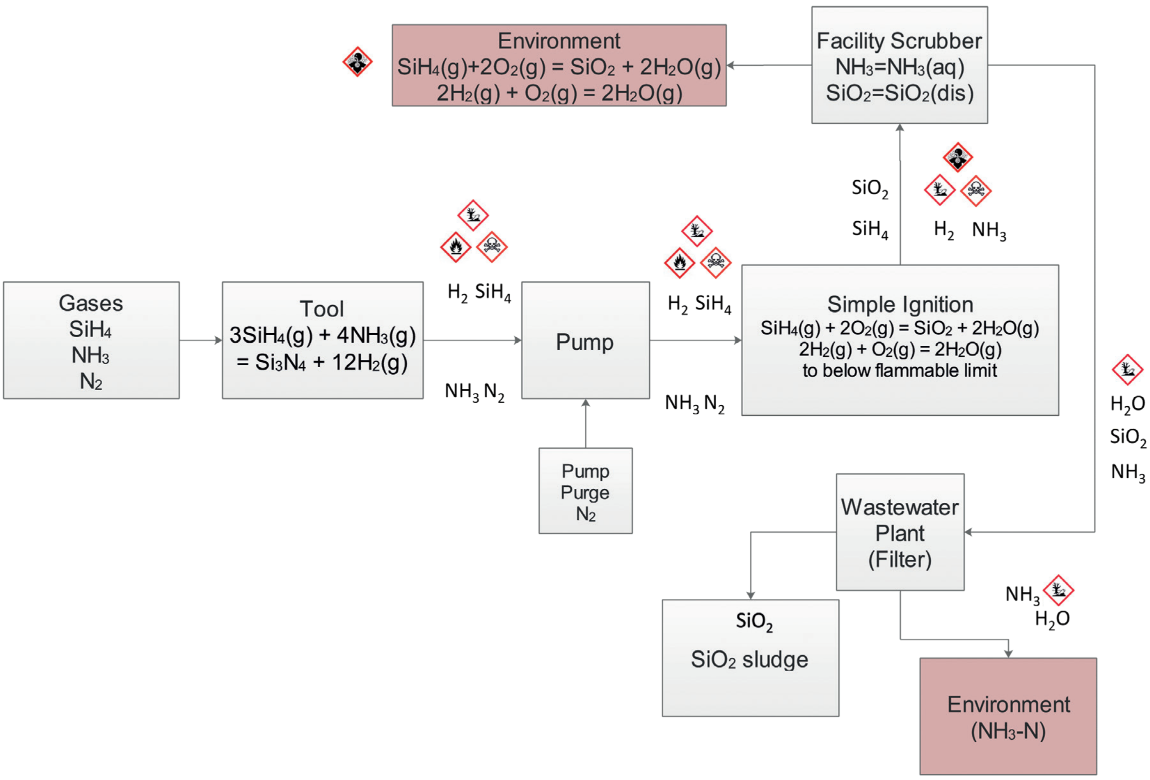

Figure 5 – Flow diagram for simple ignition and scrubbing only SiN.

collected in the waste water from the abatement unit can be removed by flocculation and filtration in a waste water treatment plant.

This thorough abatement approach ensures:

- That the flammable gases are rendered inert.
- That any solids are collected and not discharged to atmosphere or water.
- Ammonia is destroyed and not discharged to the environment (air or water).
- Nitrous oxide and methane are destroyed and prevent contributing to global warming.

This thoroughness does entail cost. Many manufacturers will take one of two less expensive, and less effective, approaches.

1. Dilution of the gases and wet-scrubbing
   - Ammonia will be wet-scrubbed.

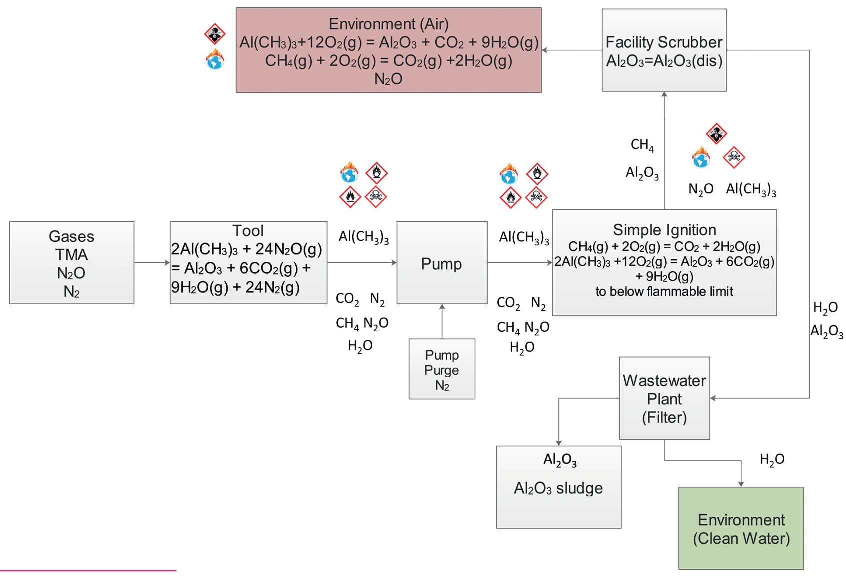

Figure 6 – Flow diagram for simple ignition and scrubbing only ALD.

Compound	Nat. Limit 15m stack Grade II			Beijing Limit 15m stack Grade II		
	Conc. mg/Nm³	Mass kg/h	Per. mg/Nm³	Conc. mg/Nm³	Mass kg/h	Per. mg/Nm³
Silica Dust	60mg	1.9	1	10	0.78	0.5
Alumina Dust	Not included			20		0.08
Nat – National limit GB16297 Per - Facility boundary limit concentrations						

Table 4. Stack emission limits GB16297 and DB11-501-2017 for selected solids.

'Manufacturers will need to choose and implement an effective abatement strategy, not only to manage hazardous gases safely, but also to prevent breach of both national and local regulations relating to the release of particulates...'

Parameter	Surface water grade					Integrated waste water grade		
	I	II	III	IV	V	I	II	III
pH	pH 6-9							
Solids (SiO_2) mg/l	No limit declared					20-70	30-150	400
NH_3-N mg/l	0.15	0.5	1	1.5	2	10-15	15-25	No limit declared

Table 5. Waste water emission limits GB8978 for solids and ammonia.

- Nitrous oxide will be released to the environment and contribute to global warming.
- Methane and hydrogen released to the environment will gradually oxidize in the air by photolytically generated hydroxyl radicals. This mechanism can also oxidize silane and trimethylaluminum to fine oxide particulates.

2. Provision of a simple ignition source to encourage incineration of flammable gases if above their lower flammable limit to be followed by wet-scrubbing.

- Ammonia will be wet-scrubbed.
- If above the flammable limits, then the flammable gases will undergo partial oxidation to an extent that is controlled by the operating conditions. Solid oxides of silicon and aluminium compounds ranging from 0.5µm to 10µm can be generated. These cannot be effectively wet-scrubbed without a specialised scrubber and hence released to the environment.
- Residual flammable gases will experience the same fate as described above – with further potential for fine dust releases.
- Nitrous oxide cannot be destroyed by this route and will be released to the environment contributing to global warming.

What regulations and guidelines are in place to limit releases of such gases to the environment?

In China, controls of stack and facility boundary emission releases of chemicals to the atmosphere should ensure compliance with both National Regulations (GB16297) and local regulations, such as DB11-501-2017 in Beijing.

Type	Annual Average µg/m³	24-h average µg/m³
PM2.5	Class I 15 Class II 35	Class I 35 Class II 75
PM10	Class I 40 Class II 70	Class I 50 Class II 150

Table 6. Chinese Regulations Ambient PM 2.5 and PM 10

Dispersion ensures that members of the public near to the facility boundary are not exposed to any significant hazard.

It should also be stressed that dilution is not permitted as a pollution mitigation mechanism under Chinese law.

Wastewater discharge limits are also controlled depending on the point of release. Discharges to natural water sources are heavily restricted.

We have already commented that the dust particle size can be very small. Most of the dust created by these mechanisms will fall into the category of PM2.5 (signifying particles size of less than 2.5µm). In 2012, China revised the limits for ambient average PM2.5 and PM10.

PM10 particles are trapped within the upper respiratory tract when inhaled. The smaller PM2.5 particles can interfere with lung function and lead to premature deaths amongst the elderly, the young, and those with impaired pulmonary function.

Summary and conclusion

We have described how the manufacture of solar cells and modules has:

3. Become more efficient as measured by $/Wp.
4. Been encouraged by the Chinese government to transition from Japan and Europe to China.
5. Recently concentrated on the more efficient solar cells, such as those manufactured using the PERC technology.

We have also described the potential pollution risks associated with the production process and several alternative strategies to abate these risks. There is clear difference in the thoroughness of abatement achieved than by the alternatives. Manufacturers will need to choose and implement an effective abatement strategy, not only to manage hazardous gases safely, but also to prevent breach of both national and local regulations relating to the release of particulates (including PM2.5 and PM10 particles), as well as both the current and impending IPCC guidelines.

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