

# Precursors for enabling higher-efficiency silicon wafer solar cells

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## ABSTRACT

The manufacturers of silicon wafer solar cells are constantly looking into cost-effective ways to increase the efficiency of their solar cells. Most of these enhancements result from incremental improvements and can be achieved by optimizing existing processes. However, it is widely recognized that in order to further improve the silicon wafer solar cell efficiency, new solar cell architectures are required. This will in turn require new manufacturing processes, which will typically involve new production equipment and consumables. New consumables can play an important role in the applicability or success of a new process step; in this paper a specific focus will be on the precursors used for the deposition of surface passivation films, such as silicon nitride and aluminium oxide.

## Introduction

Table 1 gives a short, non-exhaustive summary of new (for silicon wafer PV) precursors that either have been recently introduced or are under serious consideration for inclusion in silicon wafer solar cell manufacturing processes. Most of these precursors are hazardous (e.g. toxic or pyrophoric) and thus require careful consideration before being allowed in pilot or high-volume manufacturing. These consumables, however, are not new to high-volume manufacturing in other sectors or even in PV. For example, trimethyl aluminium (TMA) is widely used in the chemical and semiconductor industries, such as for the synthesis of III–V compound semiconductors; phosphine (PH<sub>3</sub>) and diborane (B<sub>2</sub>H<sub>6</sub>) are extensively used for the manufacturing of thin-film transistor (TFT) displays as well as for thin-film silicon solar cells.

The requirements of silicon wafer solar cell manufacturing, however, are different from those of, for example, the semiconductor industry. The

profit margins in silicon wafer PV are currently (and are expected to remain) very low, and there is consequently a strong cost pressure on the entire supply chain.

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Precursors are generally available in various grades, where the lower-quality grades are typically significantly cheaper than their higher-quality-grade counterparts. The grade of the precursor is usually related to the purity level, with the lower grades having higher impurity levels. One development that is often seen is the introduction of ‘solar-grade’ precursors which have a significantly lower price than the ‘semiconductor-grade’

precursors. These precursor grades are developed by suppliers, such as Air Liquide, AkzoNobel and The Linde Group, in close collaboration with industry, research institutes or academic partners, as will also be seen later in this paper in the case of silane and TMA.

The kinds of impurity that can be tolerated are also highly dependent on the actual process or type of equipment that is used. For example, in the case of ion implantation it makes a big difference whether a mass-analysed or a non-mass-analysed system is used. Non-mass-analysed ion implanters (i.e. basically all currently available commercial ion implanters for silicon wafer solar cells) cannot discriminate between impurities on the basis of a difference in atomic mass and will consequently also introduce undesired impurities into the wafer. In the case of aluminium oxide deposition, the difference between using atomic layer deposition (ALD) or plasma-enhanced chemical vapour deposition (PECVD) is significant. ALD is in

Cell technology	Material	Most common precursors
Passivated emitter and rear contact (PERC), or Al local back-surface field (Al-LBSF) solar cells	AlO <sub>x</sub>	TMA
	SiO <sub>x</sub>	SiH <sub>4</sub> and N <sub>2</sub> O or OCTMS
	SiN <sub>x</sub>	SiH <sub>4</sub> and NH <sub>3</sub>
Ion-implanted solar cells	P dopant	PH <sub>3</sub>
	B dopant	BF <sub>3</sub> or B <sub>2</sub> H <sub>6</sub>
Heterojunction solar cells	a-Si:H	SiH <sub>4</sub> and H <sub>2</sub>
	B doping	TMB or B <sub>2</sub> H <sub>6</sub> (heavily diluted)
	P doping	PH <sub>3</sub>
	Transparent conductive oxide (TCO)	ITO target DEZ, TMA, TMGa, B <sub>2</sub> H <sub>6</sub>

Table 1. Precursors recently introduced or under consideration for use in solar cell manufacturing processes.

essence a low-temperature chemical vapour deposition (CVD) process and thus more strongly dependent on the reactivity of the molecules used, whereas PECVD employs highly reactive plasmas, which are considerably less selective.

The remainder of this paper will go into more detail on the precursor-related research that has been done for silicon nitride and aluminium oxide, with a focus on the application to silicon wafer solar cells.

## Silicon nitride deposition

The main chemistry used for PECVD of silicon nitride in silicon wafer PV is based on silane ( $\text{SiH}_4$ ) and ammonia ( $\text{NH}_3$ ). Both these gases are hazardous: silane is a pyrophoric gas and ammonia is an irritating and flammable gas. Consequently, there have been extensive efforts to replace these gases by alternative precursors or deposition methods that are less hazardous. Physical vapour deposition (predominantly sputtering) is a commonly used method in other industries for the deposition of silicon nitride films. In the case of silicon wafer solar cells, however, silicon nitride not only serves as an anti-reflection coating but also has to provide bulk and surface passivation: hence the sputtering process cannot directly be transferred from other industries.

Fraunhofer ISE and Applied Materials have spent significant effort in optimizing the silicon nitride sputtering process for silicon wafer solar cells, as reported by Wolke et al. in 2004 [1]. The results obtained at that time were reasonably good and the process was consequently commercialized by Applied Materials on their ATON platform, with a number of systems being sold to the PV industry. The level of bulk and surface passivation, however, was typically found to be lower than that of its PECVD counterparts, and the sputtering process did not therefore gain significant traction in the PV industry. Oerlikon is currently the only company that offers a system for the sputter deposition of silicon nitride for silicon wafer solar cells [2], with the vast majority of the silicon wafer PV industry still using PECVD for the deposition of silicon nitride films.

Some work has been done on replacing silane by an alternative that is less hazardous but can still meet the performance and cost targets of the PV industry. In 2009 Khang et al. [3] published the results of a study in which a non-pyrophoric Si precursor

made by the company Sixtron was used for the deposition of a carbon-containing silicon nitride film. The solar cell efficiency results at that time were similar to those achieved by silicon nitride, and the process was tested on a pilot-scale level by various solar cell manufacturers. It is not clear, however, whether this precursor has actually been used in high-volume manufacturing. Hoex et al. [4], in 2006, also tested an alternative silane precursor for the deposition of PECVD silicon oxide films. Even though the performance was reasonable on dedicated test structures, the films did not perform as well in actual solar cell devices, and the process was consequently not transferred to the PV industry [5].

Various researchers have been looking at reducing the cost of ammonia, or at even using nitrogen gas as an alternative nitrogen source. ISC Konstanz in collaboration with Air Liquide investigated the impact of the ammonia precursor quality and the filling level of the cylinder on multicrystalline silicon wafer solar cell performance [6]. They found that the precursor grade could easily be reduced without impacting the solar cell efficiency. In the following year they reported some additional information regarding long-term stability, and it was determined that long-term stability was not affected, provided the grade of the ammonia was sufficiently high [7]. Typical industrial-grade ammonia was found to be insufficiently pure, while the intermediate grade demonstrated similar performance to that of semiconductor-grade ammonia and could therefore be used for solar cell manufacturing.

Hong et al. [8] from Eindhoven University of Technology investigated the deposition of silicon nitride using nitrogen gas instead of ammonia along with the expanding thermal plasma technology that was later commercialized by OTB Engineering (later OTB Solar and now part of the Meyer Burger Group). In that study it was found that the level of bulk passivation was lower when nitrogen was used instead of ammonia as a nitrogen precursor, and the ammonia process was eventually implemented in commercial systems.

## Aluminium oxide

Aluminium oxide was first investigated in the late 1980s by Hezel and Jaeger [9], who demonstrated reasonable levels of surface passivation on undiffused silicon surfaces. Interest

was rekindled in 2006 by the work done by Agostinelli et al. [10] and Hoex et al. [11]. Aluminium oxide is particularly interesting because of its intrinsic negative fixed charge, which makes it an ideal candidate for the passivation of p-type c-Si surfaces [12]. This was also quickly demonstrated at the solar cell device level on p-type passivated emitter and rear contact (PERC) and n-type passivated emitter and rear locally diffused (PERL) solar cells [13,14]. The original experiments were all performed using ALD to deposit the aluminium oxide film; however, very quickly it was shown that more conventional PECVD and sputtering could also yield aluminium oxide films with an adequate level of surface passivation [15,16]. ALD and PECVD used TMA as the aluminium precursor, while sputtering uses a solid aluminium target as the aluminium precursor.

The first technology that was transferred to the pilot level was PECVD by the company Roth & Rau (now part of the Meyer Burger Group) [17]. The biggest challenges of transferring the aluminium oxide process to the PV industry were the pyrophoric nature of TMA and the absence of a standard gas-delivery system. The PV industry was obviously used to handling pyrophoric gases, as almost all silicon wafer solar cell producers use silane as a silicon precursor for the deposition of their silicon nitride films. However, TMA is a liquid at room temperature: as a consequence, some sort of delivery system is required that converts the liquid TMA to its gaseous form for subsequent use in the PECVD or ALD process.

Schematics of the various delivery systems are shown in Figs. 1–3. In all cases, the gas line between the gas-delivery system and the reactor is heated to prevent condensation of the TMA in the gas line. All gas flows are controlled by a mass flow controller (MFC), and the liquid TMA flow in the direct injection system is controlled by a liquid flow controller (LFC).

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*Bubbler systems* (Fig. 1) are typically used to evaporate TMA in a research environment or even in semiconductor manufacturing, but the gas-flow requirements for PV are unfortunately not compatible with bubbler systems. In addition, bubbler systems experience significant downtime during canister changes.

The next possible solution is the *vaporizer system*, which basically consists of a liquid-delivery system and a vaporizer, as shown schematically in Fig. 2. The vaporizer contains a controlled volume of TMA kept at an elevated temperature and thus supplies a pure precursor gas that can be controlled by an MFC. Subsequently this pure precursor gas is mixed with a desirable flow of carrier gas and transported to the process chamber through a heat-traced line (to prevent condensation). The advantage of this system is that the precursor flow can be independently controlled from the carrier flow, unlike in the case of the bubbler system; moreover, higher precursor flows can be obtained. One of the main downsides of the vaporizer system is that there is a significant amount of liquid TMA in the liquid-delivery system as well as the vaporizer, which obviously poses more of a challenge from a risk-management point of view.

The more recent systems use the *direct injection method* (Fig. 3), whereby the liquid TMA flow is controlled by an LFC and subsequently evaporated and mixed in a controlled evaporator mixer (CEM) unit. In this way, a large amount of liquid TMA is present in only one location, which is easier to manage from a safety point of view.

A schematic of what a factory-wide TMA-delivery system could look like is shown in Fig. 4. The two TMA vessels (one in service and one in standby) are kept in a dedicated liquid-delivery room. The liquid TMA is then transported via small-diameter (double-contained) pipes to the various production tools.

The discussion above illustrates an important ‘challenge’ that is often neglected when introducing new technologies to the PV industry: even though the precursor is intensively used in other industries, the actual implementation in high-volume PV manufacturing is not just a simple copy-and-paste, especially when the precursor introduces a new hazard category (e.g. a liquid pyrophoric) to the factory. In the case of aluminium oxide, most equipment companies developed their own ‘unique’

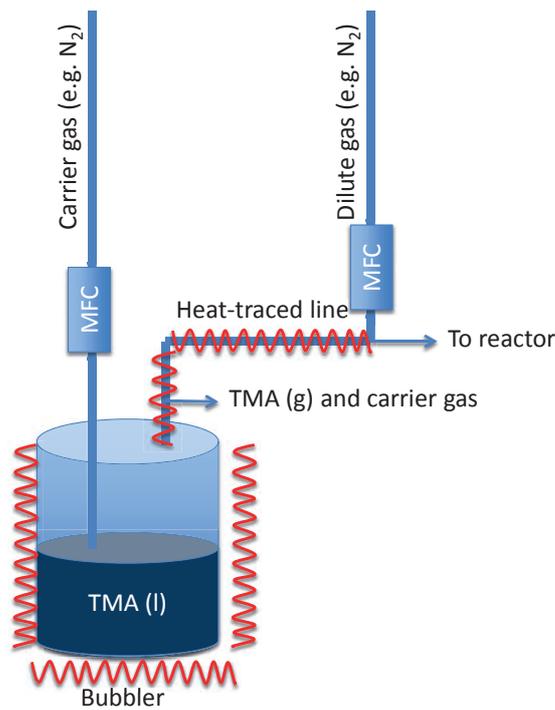


Figure 1. The easiest solution for converting liquid TMA (l) to gaseous TMA (g) is a bubbler system, whereby the liquid TMA canister is heated and a carrier gas is ‘bubbled’ through the TMA liquid. A mixture of carrier gas and TMA exits from the top of the bubbler system; this mixture is then mixed with another inert gas to dilute the precursor to the desired concentration.

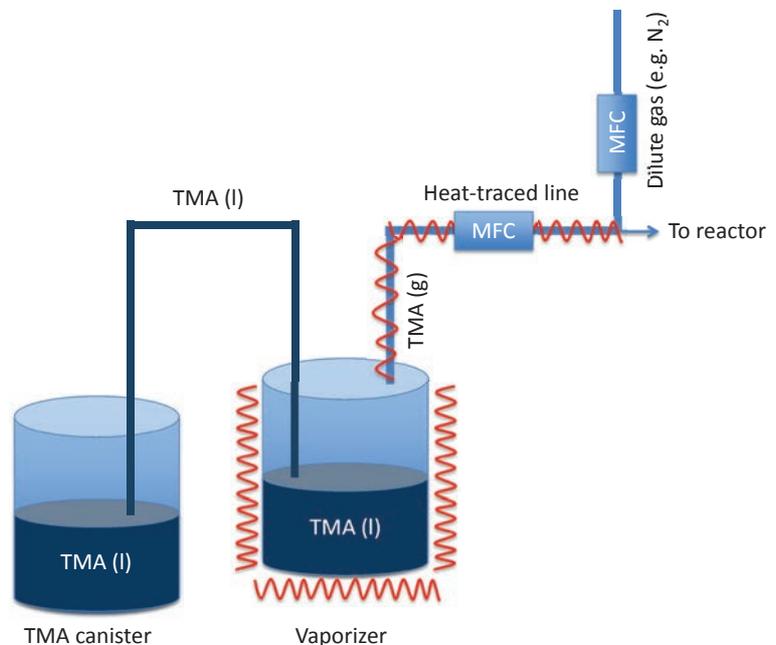
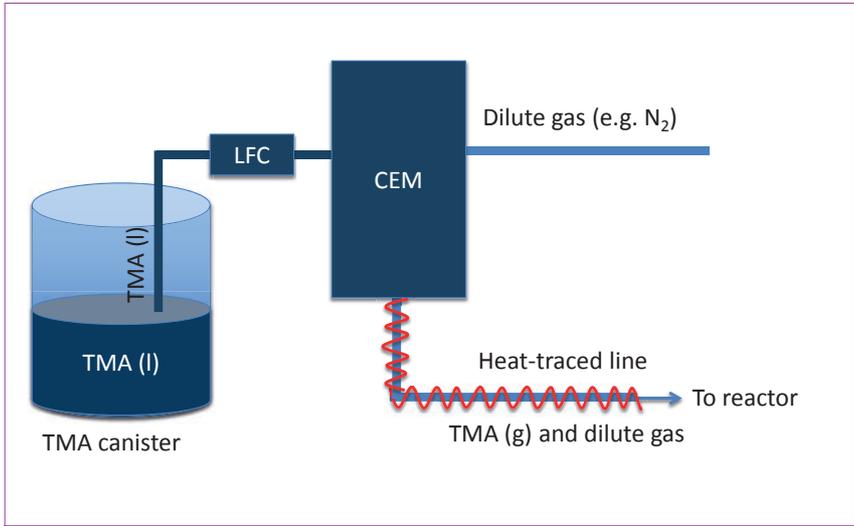
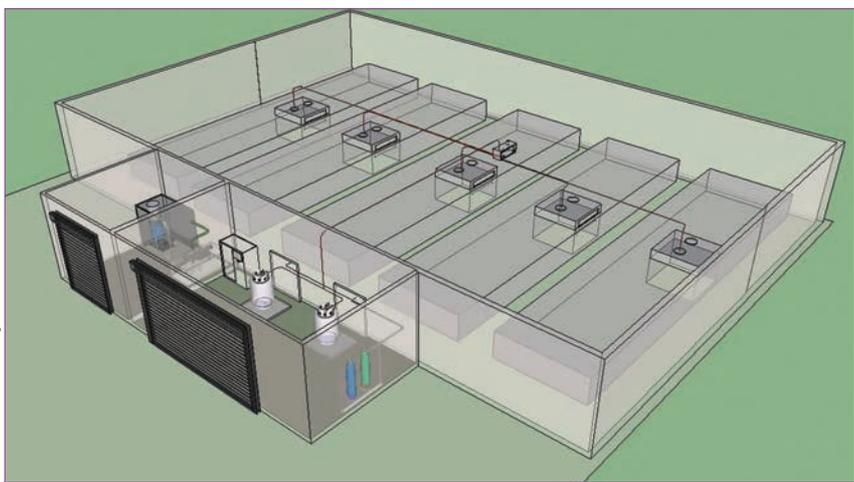


Figure 2. The vaporizer system for converting liquid TMA to gas is more advanced than the bubbler system. Here, a so-called ‘vaporizer’ is kept at an elevated temperature and allows the extraction of a pure TMA gas, which is then mixed with a carrier gas.



**Figure 3. The most commonly used way of converting liquid TMA to gas is the direct injection method, whereby the TMA liquid flow is controlled and then converted to TMA gas in a controlled evaporator mixer (CEM) unit.**



Source: The Linde Group

**Figure 4. Schematic illustration of a factory-scale TMA-delivery system.**

[18]. The Solar Energy Research Institute of Singapore (SERIS), in collaboration with AkzoNobel and SoLayTec, reported similar results on an industrial-scale ALD reactor [19,20]; the deposited layers were investigated in great detail and no significant difference in performance or composition could be detected.

It is expected that the precursor suppliers can reduce costs even further by selective purification of TMA, thereby focusing on, for example, the most detrimental impurities (e.g. metals), while disregarding inert or non-reactive impurities, which are not harmful to the process and thus do not need to be removed. Similar work has been carried out by The Linde Group in the case of thin-film silicon solar cells [21].

Research groups are currently also working on alternatives to TMA for the deposition of aluminium oxide. Eindhoven University of Technology, in collaboration with Air Liquide, have shown that dimethylaluminium isopropoxide (DMAI) can be used instead of TMA as a precursor for the deposition of Al<sub>2</sub>O<sub>3</sub> [22]. DMAI has a low pyrophoricity compared with TMA; the properties of the aluminium oxide films grown using DMAI were comparable to those of the aluminium oxide films grown using TMA for higher deposition temperatures. The paper by Pots et al. [22] also presents a good overview of the various aluminium precursors that could be used for ALD of aluminium oxide.

In contrast to silicon nitride, which is the standard front-side anti-reflection coating, there are alternatives to aluminium oxide for use in, for example, PERC or local back-surface field solar cells. And some companies decide, on the basis of the standard industrial practice of hierarchy of hazard control, that the risk level associated with TMA is too high; consequently, a substitute solution is implemented, even when the technical performance is slightly lower and the cost are potentially higher.

**“It is very important to consider precursors in the early stages of technology development in order to avoid delays in the later stages of technology deployment.”**

solutions, which often underwent modifications when transitioning from pilot-scale to high-volume manufacturing. In the author’s view, it would have been better if the equipment companies had quickly agreed on a ‘standard’ and had only differentiated on the production equipment side. This would have also allowed further cost reductions, as a significant portion of the cost of TMA is associated with the canister and the transport. Fortunately, the PV sector can benefit from existing safety training that is available from the precursor suppliers, as liquid pyrophorics are widely used in other industries; for example AkzoNobel has a dedicated ‘Metal Alkyls Safety Lab’ in Deventer (The Netherlands), where personnel from equipment suppliers or solar cell manufacturers can receive (partly hands-on) training.

Another significant concern in the initial stages was the fact that TMA is a fairly expensive precursor. The price

level of the TMA that is conventionally used in the semiconductor industry is prohibitively high for PV, even when only very thin aluminium oxide layers of thicknesses in the range 10–30nm are required. In order to produce semiconductor-grade TMA, various purification steps have to be executed to bring the contamination level down to an acceptable level. It was quickly established that the requirements for solar are not that stringent, since the TMA is not used for the fabrication of an active material. Hence, various companies have been releasing so-called ‘solar-grade TMA’ that meets the performance and cost targets of the PV industry.

Eindhoven University of Technology, in collaboration with Air Liquide, showed that aluminium oxide films grown using solar-grade TMA demonstrate a similar level of surface passivation performance to that of layers grown using semiconductor-grade TMA on a lab-scale ALD reactor

## Conclusion

Universities, institutes and companies are making very good progress in the development of new high-efficiency silicon wafer solar cells. The success of these developments depends not only on the performance of these new solar cell designs but also on the availability of the whole supply chain required to mass produce these new solar cells. This paper has specifically looked at the precursor part of the supply chain for silicon nitride and aluminium oxide. Especially in the case of aluminium oxide, it is clear that this part of the supply chain is essential for the success of the technology, and it might still take a while before the ideal solution is found. This paper has also highlighted that it is very important to consider precursors in the early stages of technology development in order to avoid delays in the later stages of technology deployment.

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