SOLNOWAT Research for Atmospheric Dry Etching in Photovoltaic Cell Production

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Abstract*—SOLNOWAT develops a dry process alternative for the solar photovoltaic cell industry. The wet chemical steps are replaced by 0 Global Warming Potential (GWP) dry process steps, addressing the current unsustainable water usage in the photovoltaic solar cell manufacturing industry. It has been proven that atmospheric dry etching is superior to wet etching due to economic, environmental, and efficiency factors.

I. INTRODUCTION

The widely used wet etching technique in photovoltaic (PV) cells industry is to etch silicon dioxide over a silicon substrate by liquid-phase etchants [1]. The standard wet etching process flow comprises eight steps. After pre-check and pretreatment, the silicon wafers undergo texturing to reduce reflection losses of incident light, acid rinsing using HF and HCl, diffusion to add electrical conductivity, and then etching exposed edges using tetrafluoromethane (CF_4). After wet etching it goes through post-etching washing, anti-reflective coating deposition, contact printing and drying, ready to be tested as the finished PV modules [2]. However, wet etching is generally isotropic, so it is difficult to control and prone to high defect levels on Si wafers.

To create an integrated circuit on a 30cm wafer, it requires approximately 2,200 gallons of water; including 1,500 gallons of Ultra Pure Water (UPW), which consumes up to 3100 municipal water. So a large fabrication facility that processes say, 40,000 wafers a month, can use up 4.8 million gallons of water per day, this equates to the annual water consumption of a city of 60,000 people [3]. Clearly, the manufacture of semiconductors is highly water intensive.

Wet etching also requires large amounts of etchant chemicals which must be constantly replaced in order to keep the same initial etching rate. As a result, the chemical and disposal costs associated with wet etching are extremely high [4]. Therefore, the desire to produce Si-based photovoltaic materials at an acceptable cost with consistent performance as well as reproducibility has stimulated the ever-increasing industry of dry etching [5].

II. SOLNOWAT PROCESS

Anisotropic dry etching is generally considered to be superior to isotropic wet etching processes in the semiconductor industry. However, wet etching has remained an integral procedure in the manufacturing of photovoltaics used in solar panels primarily due to the fundamentally simple structure of photovoltaics that eliminated the need for precise nanoscale details [6]. Nines Photovoltaics' (Nines-PV) proprietary Atmospheric Dry Etching (ADE) process, developed as a result of the SOLNOWAT project, revolves around an etching process in a non-vacuum environment without the need for plasma and serves as a possible alternative to the wasteful wet etching process that is in use today [7]. Nines-PV submitted a patent application to the United States Patent and Trademark Office in early 2011, and the patent was officially granted in January 2017 [8].

The most promising photovoltaic production process that can be replaced with ADE technology are the various wafer surface etching procedures associated with the recovery from saw damage as well as texturization of the wafer surface. Saw damage encompasses surface damage on the silicon wafers stemming from the procedure that produces wafers from ingots and is a highly undesirable trait. Meanwhile, texturization involves the patterning of a photovoltaic cell surface in order to increase the light retention for improved efficiency of the solar cell [9]. Texturization of the wafer surface will enlarge the surface area and lower the reflectivity of the material, capturing more of the light that falls upon the surface. However, texuriation must be carefully controlled so that it integrates well with subsequent steps in the manufacturing process [8].

Unlike traditional dry etching procedures, the ADE process utilizes thermal energy instead of plasma to generate fluorine free radicals from F_2 gas that serves as the primary etchant of the silicon [10]. Instead of employing a vacuum environment, the reaction zone is kept free of foreign particles with a purge gas curtain as seen in Figure 1. F_2 gas is utilized as a 0-GWP chemical over traditional dry plasma etching chemicals such as SF_6 that are associated with high GWP [11]. By utilizing the surface features from the sawing process, a proper texture can be etched through the F_2-Si reaction mechanism.

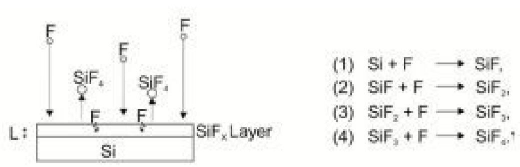

Fig. 1: Open ended continuous pass through of wafers allows a single side of the wafer to be processed via thermally activated etching gas [7].

Factors such as temperature of the etching gas, temperature of the wafer, total gas concentration and gas flux are the main controlled process parameters that determine the nanoscale surface morphologies. By etching an appropriate texture onto the surface of the wafer, very high levels of light absorption that are similar in performance to RIE photovoltaics called “black silicon” can be achieved. This texturization is superior to those produced by wet etching in that etching by traditional alkaline wet etching does not produce satisfactory antireflective properties in the surface due to the anisotropic nature of multicrystalline silicon [8].

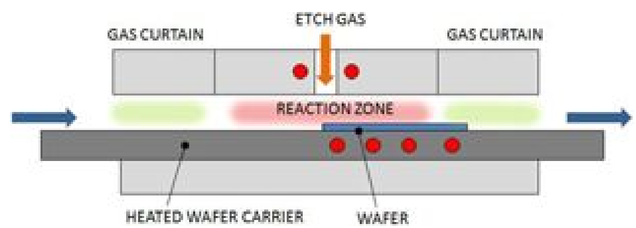

Fig. 2: Schematic of the atmospheric pressure dry etching (ADE) system [7].

The silicon wafers are processed in an in-line method and is fed through an ADE reactor that processes only one side of the wafer, ensuring that each side of the wafer can receive an independent treatment, a significant requirement in the production of high-quality solar cells. In this case, decoupling allows one side to be appropriately textured for light absorption while the other side is completely polished to obtain a high conversion efficiency. [12]

In addition, the ADE process boasts the ability to handle mono and multicrystalline silicon relatively equally. Although wet etching efficiency is highly dependent on the crystallographic structures of the swafer and requires different chemical recipes when handling mono or multi-crystalline silicon, the ADE F_2 process is utilizable for all types of wafers [8]. In many cases, the high rate of etching by the ADE technique in a continuous process extends to a higher throughput and yield for the whole photovoltaic production procedure [7].

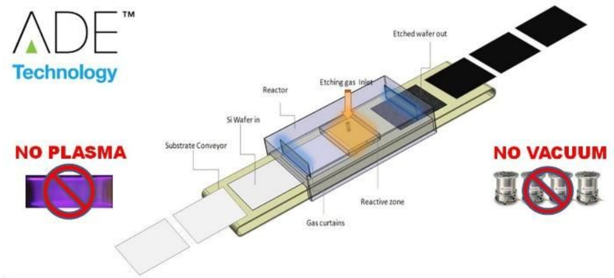

Fig. 3: Schematic of the ADE complete production line system [7].

Although the ADE process can only be applied to certain portions of the photovoltaic production process, integrating the new technique in place of the traditional wet etching process could possibly lead to great cost savings, which will be discussed in later sections. In addition, an increase in throughput for the manufacturer can be expected while complying with the ever-increasing number of environmental protection laws [13].

III. ADE BENEFITS

Dry etching is a process that has been tested and proven efficient in producing fibers, circuit boards, and other materials that require the removal of unprotected parts of a metal's surface. Even though dry etching is well-established and proven to have creditable results, it was never practical to change the wet etching process when producing solar cells to dry etching mainly because of its high costs and vacuum chamber requirements. However, the progress made in SOLNOWAT provides evidence that it may be practical to have dry etching using atmospheric pressure rather than vacuum while maintaining a lower cost. Reports made in February of 2017 estimate 25% cost savings for photovoltaic manufacturers which is approximately 20 million euros of annual savings [14]. Aside from being economically efficient, the SOLNOWAT project has viable experimental evidence to believe this process will have no global warming potential (GWP).

From a technical perspective, the F_2 gas implemented in the ADE process will reduce emissions and provide cost savings as well as energy savings in comparison to other industry standard compounds such as NF_3 and NF_6. While F_2 has been shown to have zero GWP, NF_3 produces 17,200 times more potent greenhouse gas than carbon dioxide (CO_2), while NF_6 is even higher [15]. Several companies, such as Solvay and The Linde Group provide low cost, modular, low energy consumption devices for onsite F_2 gas production. In addition, elemental fluorine has a significantly lower bonding energy than any other etchants, allowing substantially reduced power consumption compared to all other methods used to date [8]. While exact energy consumption figures have yet to be determined from the Nines-PV production machine (still in development), the promise of reduced overall energy consumption encouraging. The exact energy consumption will be calculated depending on the wafer size, energy conversion efficiency rate, and total energy consumed per Watt of energy produced by the resultant PV cells.

The shift from wet etching to dry atmospheric etching would reduce the water and chemical consumption immensely. Both the economic and environmental are directly correlated to the quantity of materials used in the manufacturing process of solar cells such as the large amount of distilled water and chemical baths.

The Nines Photovoltaics company claims the benefits for SOLNOWAT are dramatic reduction of water usage, very low-environmental-impact processing, advance process control, real time monitoring, high-throughput, high-yield, integrated industrial processing, and devices with increased efficiency. Other benefits include enabling thin wafer processing and surface decoupling (single sided), smaller footprint, low cost of ownership, faster production, and extensive review by a panel of cell manufacturers [1]. The environmental benefits are creditable by analyzing their process's significance compared to the wet etching process that is already in the market. Since the claims have yet to be applied in manufacturing, the advantages listed may not as plausible due to less controlled environment in an industrial setting and a larger scale process.

The main advantage to dry etching, in general, is its ability to produce defined details on the surface of a semiconductors. However, the production of solar cells does not need this precision in order to function properly. There are many drawbacks to dry etching as a manufacturing process such as high cost, implementation difficulties, low throughout, poor selectivity, and even potential radiation damage [13]. These disadvantages to any dry etching process is highly probable issues this type of dry etching faces as well. This is proven by the simple fact that currently, this technique has yet to be implemented in the industry for solar cells.

IV. ADE DISADVANTAGES

One major disadvantage to the ADE process is its heavy and almost exclusive reliance on fluorine gas. In a comprehensive study on the environmental impacts of the ADE process compared with incumbent techniques conducted by the Western Norway Research Institute and Huawei Technologies Sweden, the authors clearly noted that the high toxicity of fluorine requires heavy regulatory emission control requirements and exposure limits [16]. While the ADE process itself is a "dry" process, water is still required in the production and disposal of fluorine, as well as in electricity and compressed air production required for the process. The waste fluoride material must still be disposed of just as in the case of wet etching. In total, the research concluded that the total water consumption with acidic wet etching reached approximately 3.5 Liters per wafer, while the ADE process consumes approximately 0.5 Liters per wafer (Figures 4 and 5, respectively).

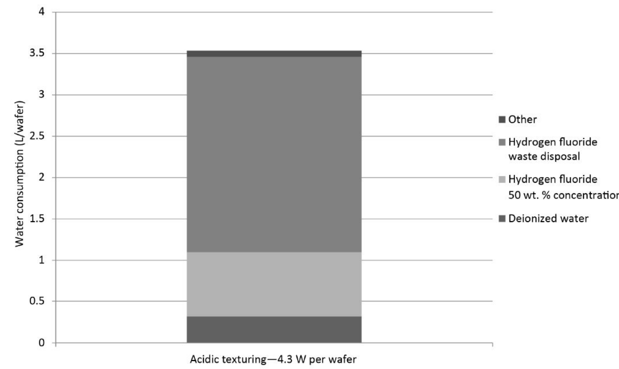

Fig. 4: Process contribution for total water consumption of the acidic texturing process of a 4.3 W wafer.

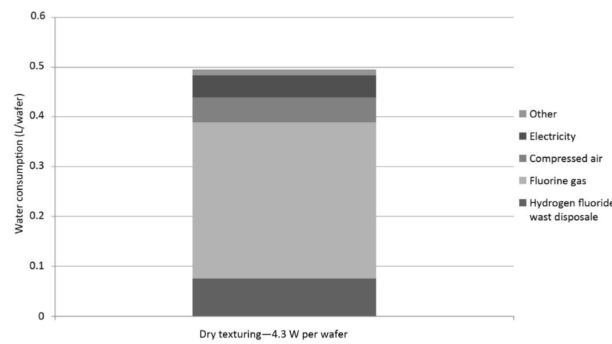

Fig. 5: Process contribution for total water consumption of the dry texturing process of a 4.3 W wafer.

While the report notes that the toxicity and environmental impacts of fluorine production are limiting, it also makes clear that the ADE process as a whole is more efficient and reduces the overall GWP of PV cell manufacturing by a minimum of 5-10%. The authors also recommend that further techniques to reduce energy consumption in the production of fluorine gas, as well as reduce the amount of fluorine gas used in the etching process would greatly improve the GWP value.

V. ECONOMIC OUTLOOK

After fully analyzing the SOLNOWAT technical aspects and procedures, the next step is to examine whether the proprietary technology is ready for industry-wide implementation. In other words, the dry etching technology must be proven to be economically viable if widespread adoption is to be expected. For current timeline considerations, the

SOLNOWAT research project lasted 24 months through funding from the European Union (EU) and was coordinated by Nines-PV, an Ireland based company focused on innovative process technology and equipment in the photovoltaic (PV) solar cell manufacturing industry [17] [18]. To clarify the outcome of the SOLNOWAT project, Nines-PV was contacted for comment and a response was received directly from the firm's C.T.O., Laurent Clochard, on February 12, 2018. After the conclusion of the SOLNOWAT project in 2013, the novel Atmospheric Dry Etching (ADE) process was patented and commercialized by Nines-PV [19]. According to Mr. Clochard, the ADE production process has already been sold to multiple research and development institutes in Germany. But more importantly, he claims that Nines-PV will have a multi-lane high-throughput production machine available by the end of the year. Although the response was relatively void of figures and statistics, the assurance of a market-ready ADE production machine by the C.T.O. is promising.

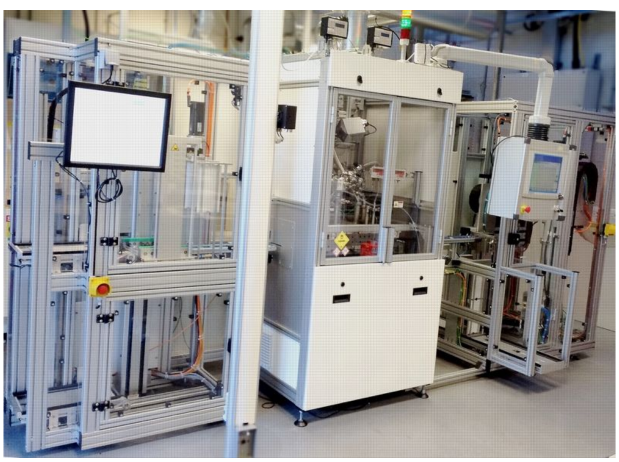

Fig. 6: Fully automated 1000 W/h ADE texturing pilot line machine produced by Nines-PV [16].

Another vital consideration for any firm in the business of manufacturing and marketing solar cell production machinery is the health of the global solar market. When the solar market is in an economic downturn, solar production companies are reluctant to risk investment into new and relatively untested manufacturing technology. As a result, they usually tend to fall back on the well-tested wet etching industry standard methods. For example, the Solar Energy Industries Association reported in December 2017 that the current solar marking in the United States alone has declined nearly 51% over the previous 2016 numbers [20]. However, the solar market in general is highly susceptible to a range of factors including government subsidies which help to greatly reduce consumer installation costs and drive up manufacturing profits. In his response, Mr. Clochard directly referenced a major PV market downturn in recent years but noted that the market has now recovered, and Nines-PV is seeking additional funds to fast-track the ADE process for entry into the industrial market [19].

In addition, the poised success of the ADE process has been confirmed by sources outside of Nines-PV itself. According to a February 2, 2017, report by The Irish Times, major PV cell producers could see their manufacturing costs drop by up to 25%, or roughly 20 million Euros per year thanks to ADE technology [14]. Considered a milestone for the firm, Nines-PV shipped its first ADE production system in 2013, capable of producing 50 to 60 wafers at a time, although it was used mainly for further research and development than for mass production [4]. The Irish Times report also makes mention of the challenges facing the adoption of ADE technology, including the necessity of high-throughput machines. However, Nines-PV claims to have their first complete high-volume production machine ready by the end of this year.

Lastly, the report references the sharp market downturn caused in part by an oversupply of Chinese-produced solar panels flooding the global market and in turn forcing many EU manufacturers into bankruptcy and further increasing investment hesitancy [14]. But Nines-PV founder and chief executive Edward Duffy remained optimistic, explaining that the "capacity put in by Chinese firms has now been eaten up," and "there's a shift now to retrofit the current capacity with new, low-cost solutions" [14]. Mr. Duffy boldly predicts the global market opportunity for dry etching production machines will exceed $1 billion, and the company already has a Chinese agent acting as a liaison with major Chinese solar firms.

VI. CONCLUSION

The success of the ADE process in the global solar cell manufacturing process will be largely dependent on the ability of Nines-PV to successfully produce and market their first mass-production machine on the scheduled timeline. With the solar market fully recovered and expanding at an ever-increasing rate, demand is high for a PV cell manufacturing process that can reduce costs, increase efficiency, and eliminate the massive global warming potential (GWP) of current wet etching technology.

REFERENCES

[1] "Wet and Dry Etching Theory," Wet and Dry Etching Theory - UF Chemical Engineering. [Online]. Available: http://ww2.che.ufl.edu/unit-ops-lab/experiments/semiconductors/etching/ Etching-theory.pdf. [Accessed: Feb. 13, 2018].

[2] Niclas, D. W, "Solar Cell Production: from silicon wafer to cell," Sinovoltaics - Your Solar Supply Network, 11-Oct-2015. [Online]. Available: http://sinovoltaics.com/solar-basics/solar-cell-production-from-silicon-wafer-to-cell/. [Accessed: Feb. 12, 2018].

[3] "8 Things You Should Know About Water &Semiconductors." July 11, 2013. [Online]. Available: http://chinawaterrisk.org/resources/analysis-reviews/8-things-you-should-know-about-water-and-semiconductors/. [Accessed: March 01, 2018.]

[4] Thierry Corporation, "Plasma Knowledge: Dry Etching (Plasma Etching) and Wet Etching," Feb 12, 2016. [Online]. Available: http://www.thierry-corp.com/plasma/knowledge/dry-etching-and-wet-etching. [Accessed: Feb 13, 2018].

[5] D. S. Ruby, P. Yang, S. Zaidi, S. Brueck, M. Roy, and S. Narayanan, "Plasma etching, texturing, and passivation of silicon solar cells," *AIP Conference Proceedings*, 1999.

[6] Moreno, M. et al., "A comparative study of wet and dry texturing processes of c-Si wafers for the fabrication of solar cells," Solar Energy, vol. 101, pp. 182-191, Mar. 2014. [Online]. Available: Science direct, https://www.sciencedirect.com. [Accessed: Feb. 15, 2018].

[7] Nines Photovoltaics, "Technology", 2018. [Online]. Available: http://www.nines-pv.com/ade-technology/. [Accessed: Feb. 15, 2018].

[8] Duffy, E, et al. "Method and apparatus to control surface texture modification of silicon wafers for photovoltaic cell devices," U.S. Patent 0 069 204, March 21, 2013. [Accessed: Mar. 1, 2018].

[9] Dani, I. et al., "Atmospheric-Pressure Plasmas for Solar Cell Manufacturing," Contributions to Plasma Physics, vol. 49, num. 9, pp. 662-670, Nov. 2009. [Online]. Available: Wiley Online Library, http://onlinelibrary.wiley.com. [Accessed: Feb. 15, 2018].

[10] Kafle, B. et al., "Plasma-free dry-chemical texturing process for high-efficiency multicrystalline silicon solar cells," Energy Procedia, vol. 92, pp. 359-368, 2016. [Online]. Available: Science Direct, https://www.sciencedirect.com/science/ article/pii/S1876610216305409 [Accessed: Feb. 15, 2018].

[11] Dresler, D. et al., "Novel industrial atmospheric pressure dry texturing process for silicon solar cell improvement," 27th EU PVSEC 2012 [Online]. Available: Researchgate, https://www.researchgate.net/publication/234057899_Novel_Industrial_Atmospheric_Pressure_Dry_Texturing_Procress_for_Silicon_Solar_Cell_Improvement. [Accessed: Feb. 15, 2018].

[12] Zhe Liu, et al.,"Optical Modeling of Alkaline Saw-Damage-Etched Rear Surfaces of Monocrystalline Silicon Solar Cells", Photovoltaics IEAvailable: IEEE Xplore [Accessed: Mar 1, 2018] EE Journal of, vol. 4, pp. 1436-1444, 2014. [Online].

[13] E.Chen, Harvard, "Wet and Dry etching" Applied Physics 298. [Online]. Available:

http://www.mrsec.harvard.edu/education/ap298r2004/Erli%20chen%20Fabrication%20III%20-%20Etching.pdf. [Accessed: Feb 15, 2018].

[14] C. O'Brien, "Irish Firm's Invention Puts Cheap Solar Power on the Horizon," The Irish Times, 2017. [Online]. Available: https://www.irishtimes.com/business/technology/irish-firm-s-invention-puts-cheap-solar-power-on-the-horizon-1.2959245. [Accessed: Feb. 10, 2018].

[15] Solvay "Solvay develops on-site fluorine gas production units to dramatically decrease greenhouse gas emissions in the photovoltaic and semiconductor industry" [2018]. Available: https://www.solvay.com/en/media/press_releases/20110823-onsan.html

[16] Andersen, AIMS Energy, Volume 2, Issue 4, "Cradle-to-gate life cycle assessment of the dry etching step in the manufacturing of photovoltaics cells" [2014]. Available: http://www.aimspress.com/fileOther/PDF/20140406.pdf

[17] EU Commission, CORDIS, "SOLNOWAT Report Summary," 2014. [Online]. Available: https://cordis.europa.eu/result/rcn/141315_en.html. [Accessed: Feb. 15, 2018].

[18] Nines Photovoltaics, "About Us," 2018. [Online]. Available: http://www.nines-pv.com/about-us/. [Accessed: Feb. 14, 2018].

[19] L. Clochard, private communication (email), February 12, 2018.

[20] Solar Energy Industries Association, "U.S. Solar Market Insight," 2017. [Online]. Available: https://www.seia.org/us-solar-market-insight. [Accessed: 14-Feb-2018].