SiliconPV 2024, 14th International Conference on Crystalline Silicon Photovoltaics
Silicon Material and Defect Engineering
https://doi.org/10.52825/siliconpv.v2i.1301

Published: 03 Feb. 2025

Recovery of Silicon Kerf by Oxidative Cleaning and Drying Process

Marion Chevallier[1,*], Jean-Baptiste Antoine[1], Francis Marchitto[1], Yoann Doré[1], Yun Luo[1], and Yohan Parsa[1]

[1]ROSI SAS, France

*Correspondence: Marion Chevallier, marion.chevallier@rosi-solar.com

Abstract. High quantity of slurries, kerf, are generated during ingot wafering and represent up to 40% of the silicon in weight. The highly pure silicon contained in kerf is contaminated with organics, metal impurities, water and an oxide layer. The recovery of the silicon could be an efficient way to reduce costs in the production of solar panels through material and energy savings. At high temperatures, organic contamination causes the formation of silicon carbide species that are difficult to segregate during kerf remelting into a pure silicon ingot. Also, during the fusion of silicon, temperatures up to 1500°C are reached and the mixture of silicon and water forms oxides and gases that reduce production yields and affect melting conditions. For these reason, purification and drying steps are required to ensure proper silicon raw material for remelting into ingots. So far, approaches using strong acidic or organic solvent are used to reduce contamination by organic compounds. In this study, more environmentally friendly processes were applied on authentic kerf waste to purify and dry silicon, to make it suitable as raw material for silicon ingot preparation. The amount of water and organic compounds were monitored along the process steps. Using aqueous oxidative processes in combination with filtration, kerf was cleaned and a total carbon reduction of at least 30% was observed. The control of humidity enables the convenient conditioning of purified kerf and effective drying reduced the moisture content to less than 5% wt.

Keywords: Kerf, Silicon, Recycling, Oxidative Process, Cleaning Process

1. Introduction

In recent years, silicon-based solar cells have become an important part of the renewable energy mix, not least because they generate no waste during energy production. Almost 94% of solar cells on the photovoltaic market are made from crystalline silicon [1,2]. In the production of crystalline solar cells, around 60% of total manufacturing costs are incurred in the production of silicon wafers [3]. The silicon ingots are cut into wafers using a multi-wire saw [4].

When cutting silicon ingots a large amount of slurry is formed which is named kerf. It contains highly pure silicon contaminated with organic molecules from the lubricants used for cutting, metal impurities from the wire, an oxide layer created in contact with oxygen and water [5] (Fig. 1).

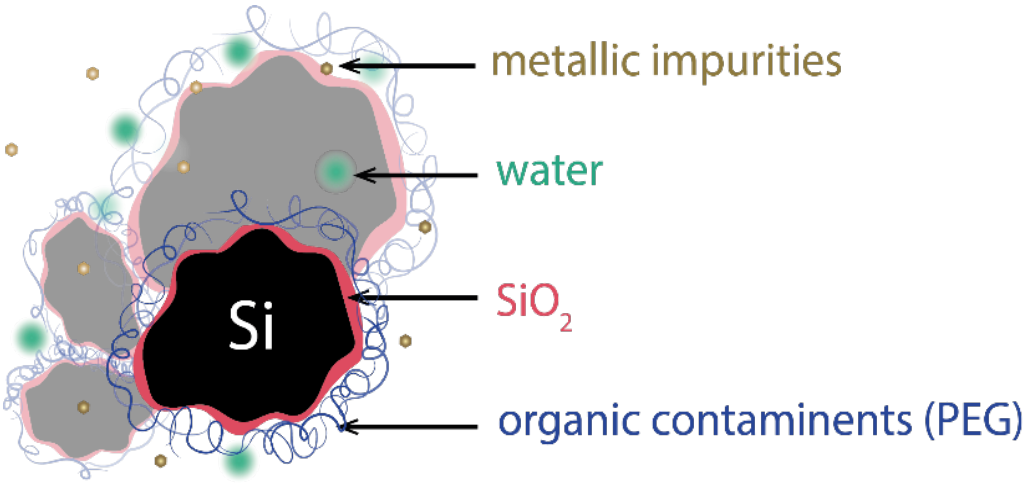

***Figure 1**. Schematic representation of kerf composition*

The creation of waste during cutting is not only an environmental disadvantage, but also an economic one, as it increases wafer manufacturing costs with slurry disposal costs. The silicon contained in this sludge is valuable and can be recycled. This aspect has been studied in recent years and depending on the intended use of the kerf (reusing the silicon in a metallurgical form, as a conductor in battery anodes [6] or reactive sintering composites ceramics [7] etc.) chemical [8,9], physical [10,11] or metallurgical [12,13] purification can be carried out.

In the present case, we aim to recycle kerf into metallurgical silicon. An issue with organic contamination is the formation of silicon carbide species at high temperatures, that are very stable and difficult to seggregate during the remelting into pure silicon ingot. Also, when temperatures reach up to 1500°C for the fusion of silicon, the mixture with water can form oxides and gases that reduce production yields and affect melting conditions. Moreover, the decomposition of water into dioxygen and dihydrogen causes risks of explosion. For this reason, a drying step is required to ensure a water content in purified kerf.

Organic impurities are generally polymers derived from ethylene glycol. Efficient ways to reduce the contamination in such organics have been described using notably advanced oxidation processes to reduce the size of the polymer chains by oxidative cleavage [14].

In this study, a diversity of environmentally friendly oxidative processes, including chemical and physical processes, were applied to silicon kerf to assess the processes efficiency. In addition, steps of conditioning and drying are developed to enable the use of dried, purified silicon in a suitable form for subsequent purification process.

2. Materials and Methods

2.1 Materials

The kerf used in this study comes from COMTEC SOLAR.

The treatments assessed in this study imply the use of hydrogen peroxide (H_2O_2, 30% wt.) up to a final concentration of 240 mM for oxidative treatment, sodium and potassium persulfates and a Fenton's reagent prepared with $FeSO_4$ and H_2O_2. Ultrasonic treatments were conducted in water with various ultrasound frequencies including low (20, 37 and 80 kHz) and high (547 and 680 kHz).

2.2 Process and Analytical Methods

2.2.1 Kerf Cleaning

The removal of impurities was performed in a stirring tank with a string blade at room temperature. The kerf was diluted to represent 30% of the total weight. Once the mixture looks homogeneous and after a minimum of 30 minutes, the mixture is filtered using vacuum filter at laboratory scale (less than 5 kg) or press filter at semi-industrial scale (up to 15 kg). An excess of oxidant was used for each test to achieve the following molar ratio: 4:1 oxidant/silicon atom.

2.2.2 Kerf Conditioning and Drying

For kerf conditioning, the control of humidity was managed by manual addition of electro-deionized water. For the drying step, we used a tank that can be heated up to 130°C with a heating envelope. For usual drying, the temperature was set between 80 and 130°C.

2.2.3 Analytical Methods

To assess the percentage of water contained in kerf, a complete drying in a ventilated oven at 110°C was performed. Water mass percentage H was calculated by comparing water mass contained in kerf (difference between the mass before and after ventilated oven drying) and the initial kerf sample mass as presented by the following equation:

$$H\ (\%) = \frac{m_{kerf\ before\ drying} - m_{kerf\ after\ drying}}{m_{kerf\ before\ drying}} \quad (1)$$

The amount of organic compounds in the kerf was assessed by elemental carbon analysis. Kerf samples were manually crushed with a mortar and dried in a ventilated oven at 110°C. The analysis was performed by Eurofins® using inductive gas analysis.

MALDI-TOF MS (matrix-assisted laser desorption ionization time-of-flight mass spectrometry) was conducted in positive linear mode on solid and liquid samples using linear positive mode at Université Grenoble Alpes.

3. Results and Discussion

3.1 Kerf Cleaning

In this work, the kerf cleaning focused on the reduction of carbon impurities. The tests were carried out on a laboratory scale and then scaled up to a semi-industrial one.

The first results we obtained concern the treatment of kerf in four stages. The first step is manual crushing that increased the carbon contamination in the kerf. Manual crushing was performed by crushing the kerf with a stainless steel mallet. The kerf crumbles under the stress applied by human action, without any jolting. Other mechanical crushing techniques are currently developed to avoid additional carbon contamination. The following steps deal with a first water rinsing and filtration that reduce carbon contamination by 18%, and secondly an oxidative treatment which involves washing with hydrogen peroxide (240 mM) and filtration that reduced carbon contamination by 17% (Fig. 2). These simple processes prove the possibility to reduce the carbon contamination by a third.

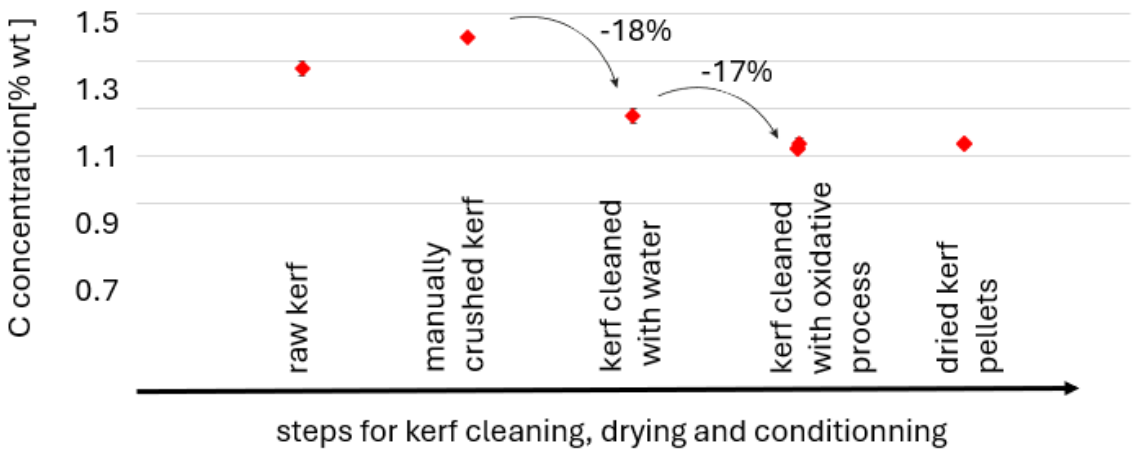

***Figure 2**. Carbon concentration in kerf sample after each process step*

The reduction of organic contamination reduces the probability of silicon carbide formation during the melting of purified kerf to form silicon ingots. Complementary advanced oxidizing treatments have been tested to remove organic contaminants and involve water, acetone, hydrogen peroxide, sodium persulphates and the Fenton mixture of iron (II) sulphate and hydrogen peroxide. Ultrasound was also used to test its physical and chemical effects on the carbon content of kerf.

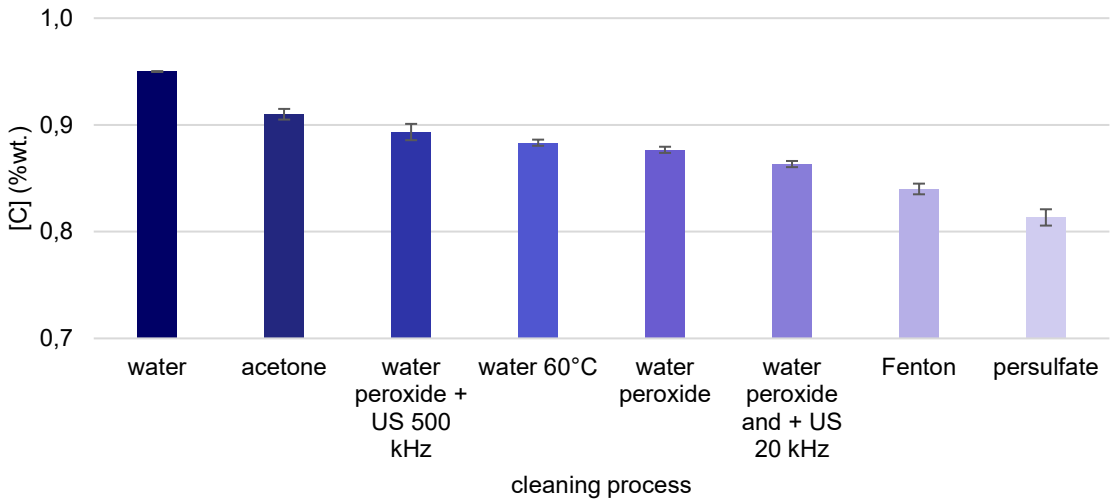

***Figure 3**. Carbon concentration in kerf samples after various oxidizing processes*

A reduction of more than 40% compared to the initial value is observed in the case of washing with aqueous mixtures containing hydroxyl ions (notably Fenton process) or sulphates (process involving persulphates) as shown on Figure 3. The reduction in carbon content should be taken into account when improving processes, but the risks associated with the use of substances such as hydrogen peroxide and persulphates could be a deterrent when choosing an industrial scale-up.

A comparison of the organic compounds removed and degraded from the surface of the kerf (upper diagram) with the organic compounds still present in the kerf (lower diagram) was carried out using MALDI-TOF mass spectrometry and is shown in Figure 4. The cleaning and oxidative processes enabled the polymer chain size to be reduced from 35 to less than 5 units.

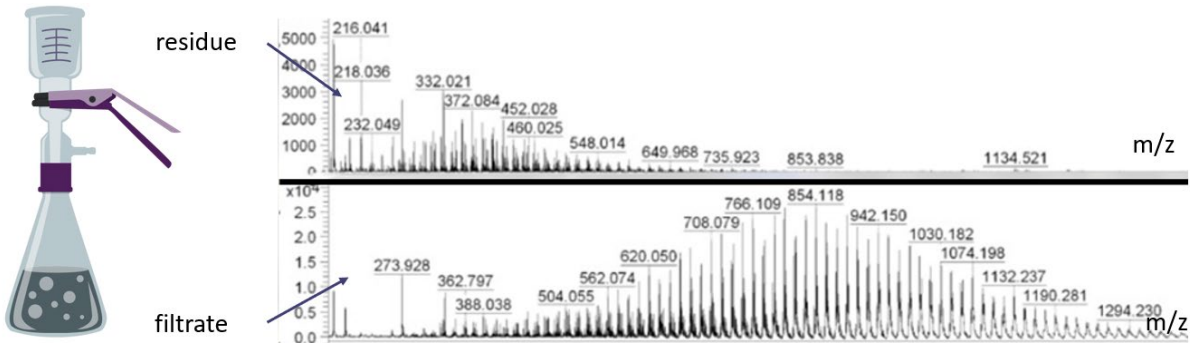

***Figure 4**. MALDI-TOF mass spectra of residue after filtration (top) and filtrate (bottom), respectively.*

3.2 Kerf Conditioning and Drying

After filtration, kerf contains between 42 and 50% wt. of water which is too high to be processed into a silicon ingot. It is also important to obtain regular molds of a certain size to ensure a continuous, reliable supply to the melting process.

For these reasons, kerf conditioning was developed that was able to prevent the aggregation of small particles thanks to humidity control. No numerical data can be shown here because of the lack of monitoring possibilities during the run. A drying step follows and consists of heating the purified material up to 130°C to reduce water content to an average of 5%.

A global scheme of the process is shown in Figure 5. It appears that a total carbon reduction of at least 30% was observed (Fig. 4), reaching a final value of 0.95% wt. and average content in water of 5% wt.

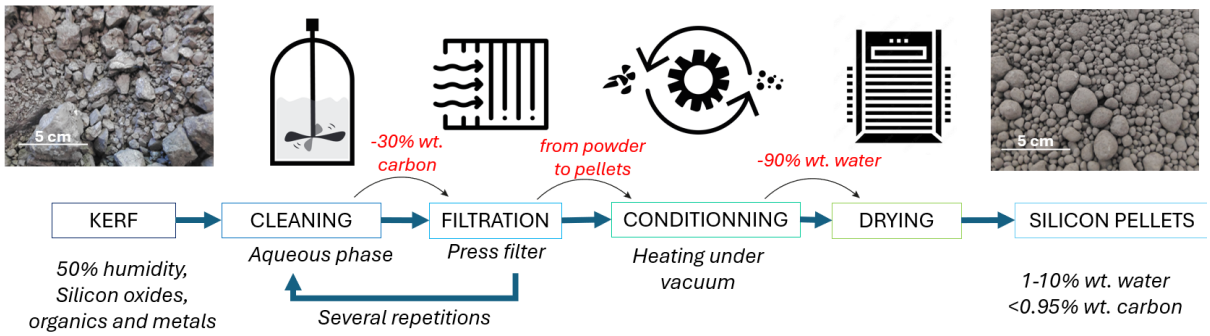

***Figure 5**. Global scheme of kerf cleaning, drying and conditioning processes*

4. Conclusion

The production of spherical silicon pellets containing less than 10% water and 0.95% carbon in weight was demonstrated through the cleaning and drying of authentic raw kerf. The pellets will further be used to demonstrate the feasibility of kerf remelting into silicon ingot as part of a European project. Studies already underway will provide us with more data on the possible reduction in organic contaminants. Further studies will be developed to consider the reduction of metallic and oxide layer contamination to improve the yield and purity of silicon ingots.

Data availability statement

The data supporting the results of your article/contribution can be accessed by sending an email to author Marion Chevallier at the corresponding email address marion.chevallier@rosi-solar.com

Author contributions

In this work Marion Chevallier and Jean-Baptiste Antoine carried out the experiments. Marion Chevallier led the investigation of the data collection and results, did the visualization and writing of the published work. Francis Marchitto and Yoann Doré developed the instruments that enabled the experiments to be carried out. Yohan Parsa conceptualized and supervised the work and participated to funding acquisition for the project leading to this publication.

Competing interests

The authors declare that they have no competing interests.

Funding

This work is part of European Project ICARUS. This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 958365.

Acknowledgement

The authors would like to thank EIC, EIT InnoEnergy, Itochu, French Tech, SIMAP et Grenoble INP.

References

[1] D.Ginley, M.A. Green, R. Collins, "Solar energy conversion towards 1 Terawatt" MRS Bull, 33 (4) 355-364 (2011) https://doi.org/10.1557/mrs2008.71

[2] B. Parida, S. Iniyan, R. Goic, "A review of solar photovoltaic technologies", Renw. Sust. Energ., 15 (3) 1625-1636 (2011) https://doi.org/10.1016/j.rser.2010.11.032

[3] G. Mesaritis, E. Symeou, A. Delimitis, S. Oikonomidis, M. Jaegle, K. Tarantik, C. Nicolaou, T. Kyratsi, "Recycling Si-kerf from photovoltaics : A very promising route to thermoelectrics", J. Alloy Compd, 775, 1036-1043 (2019) https://doi.org/10.1016/j.rser.2010.11.032

[4] N. boutoutchent-Guerfi, N. Drouiche, S. Medjahed, M. Ould-Hamou, F. Sahraoui, "Disposal of metal fragments released during polycrystalline slicing by multi-wire saw", J. Cryst. Growth, 447, 27-30 (2016) https://doi.org/10.1016/j.jcrysgro.2016.04.017

[5] H.S. Gopala Krisma Murthy, "Evolution and present status of silicon carbide slurry recovery in silicon wire sawing", Resour. Conserv. Recy., 104, 194-205 (2015) https://doi.org/10.1016/j.resconrec.2015.08.009

[6] N.P. Wagner, A. Tron, J.R. Tolchard, G. Noia, M. Pawel Bellmann, "Silicon anodes for lithium-ion batteries produced from recovered kerf powders", Journal of Power Sources, (414), 486-494, (2019) doi.org/10.1016/j.jpowsour.2019.01.035.

[7] X. Jin, Y. Zhuang, P. Xing, J. Kong, X. Zhou, [ceramics] X. Han,"Preparation of reactive sintering Si3N4-Si2N2O composites ceramics with diamond-wire saw powder waste as raw material", Journal of Hazardous Materials, 400, 123145 (2020) doi.org/10.1016/j.jhazmat.2020.123145

[8] K.Tomono, S. Miyamoto, T. Ogawa, H. Furuya, Y. Okamura, M. Yoshimot, R.Komatsu and M. Nakayama, “Recycling of kerf loss silicon derived from diamond-wire saw cutting process by chemical approach”, Separation and Purification Technology 120, 304-309 (2013). doi.org/10.1016/j.seppur.2013.10.014

[9] Y. Zhang, W. Sheng, L. Huang, C. Zhang, X. Tang, X. Luo, “Recovery of silicon kerf waste from diamond wire sawing by two-step sintering and acid leaching method”, Journal of Cleaner Production (265) 121911 (2020), doi.org/10.1016/j.jclepro.2020.121911.

[10] L. Zhang, A. Ciftja, “Recycling of solar cell silicon scraps through filtration, Part I: Experimental investigation, Solar Energy Materials and Solar Cells”, (92) 11, 1450-1461 (2008) doi.org/10.1016/j.solmat.2008.06.006.

[11] S.A. Sergiienko, B.V. Pogorelov, V.B. Daniliuk, “Silicon and silicon carbide powders recycling technology from wire-saw cutting waste in slicing process of silicon ingots”, Separation and Purification Technology, (133), 16-21 (2014) doi.org/10.1016/j.seppur.2014.06.036.

[12] L. Huang, A. Danaei, M. Fang, S. Thomas, X. Luo, M. Barati , “A metallurgical route to upgrade silicon kerf derived from diamond-wire slicing Process “, (18) 32619-8 (2019) doi.org/10.1016/j.vacuum.2019.02.019

[13] G. Chen, Y. Li, L. Huang, J. Peng, L. Tang, X.Luo, “Recycling silicon kerf waste: Use cryolite to digest the surface oxide layer and intensify the removal of impurity boron”, Journal of Hazardous Materials, (423) 126979, (2022), doi.org/10.1016/j.jhazmat.2021.126979

[14] L. Pietrelli, S. Ferro, A. P. Reverberi and M. Vocciante, "Removal of polyethylene glycols from wastewater: A comparison of different approaches", Chemosphere (273), 129725 (2021). doi.org/10.1016/j.chemosphere.2021.129725