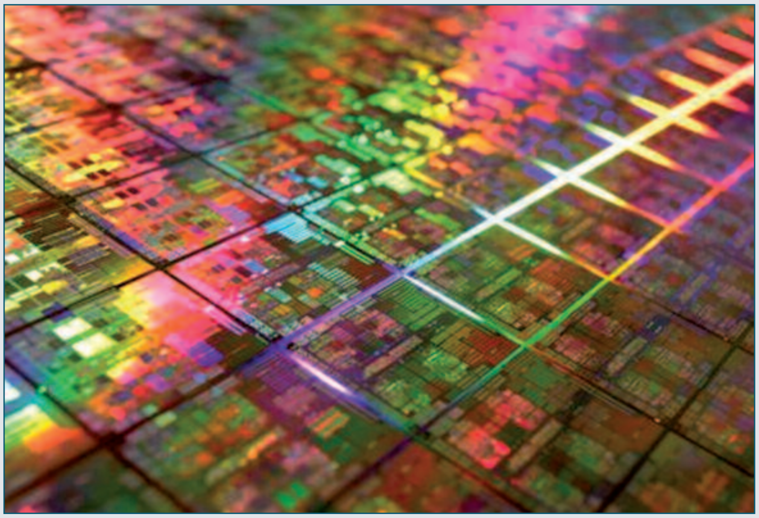

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HIGH YIELD RECYCLING PROCESS OF SILICON KERF FROM DIAMOND WIRE WAFERING

The possibility of recycling the silicon kerf produced during silicon wafering with diamond coated wire represents a major advantage of this wafering technology over the slurry based one. A silicon kerf reclaiming process aimed at the re-utilization of an internal silicon source meeting photovoltaic quality levels is presented.

It is well known that typically more than 40% of silicon is lost during wafering operations. The reclaiming of silicon from conventional wafering slurry made up of abrasive SiC grains and glycol has challenged several companies and research groups worldwide, but so far no industrial viable technology has been proven, due to the difficulty of completely removing very fine SiC particles. On the other hand, diamond wire wafering offers much more interesting perspectives for the recycling of silicon kerf for PV applications. The main results achieved by Garbo for the regeneration of silicon sawdust from diamond wire slicing mixture of coolant and kerf as well as its preparation for crystallization processes are presented and discussed.

Experimental

Single crystal silicon ingots have been sliced through a diamond coated wire immersed in a water-based coolant containing 3% of a surfactant with Meyer Burger DS264 wire saw [1].

The silicon kerf/coolant separation has been carried out through custom-made equipment installed on-site. The collected silicon kerf has been shipped to Garbo for processing. The purification of silicon consists of different chemical etching steps aimed at removing the contaminants introduced during cutting.

The as-received silicon kerf as well as the refined silicon have been characterized in terms of particle size distribution by means of static light scattering (Microtrac S3500), total metal contaminants via inductively coupled plasma optical spectroscopy (ICP-OES Perkin Elmer Optima 2100 DV) while total carbon and oxygen content have been measured via total combustion method (LECO CS-444) and inert gas fusion (LECO TC-436), respectively. After the chemical cleaning, the regenerated silicon is compacted into bricks of tunable shape through a proprietary process that optimizes the subsequent melting processes. The recycling process steps are schematized in the flow diagram depicted in Fig. 1.

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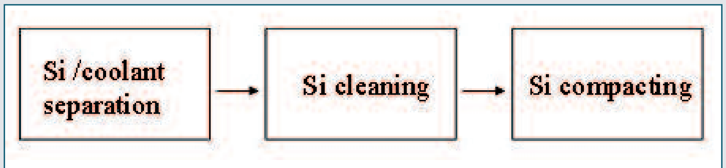

Fig. 1 - Process steps for Si kerf recycling

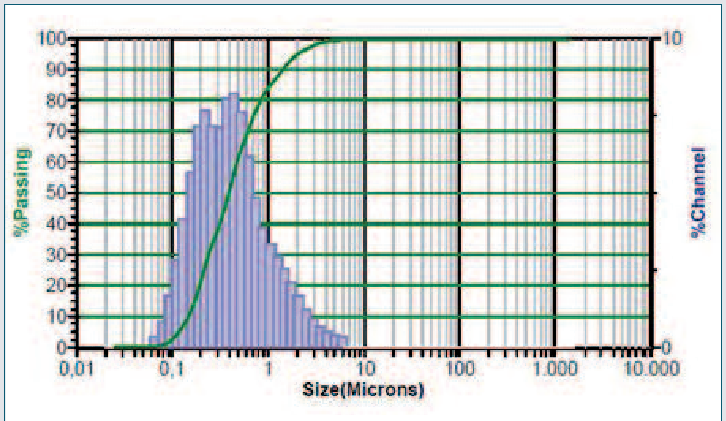

Fig. 2 - Particle size distribution of the Si kerf

Tab. 1 - Oxygen content comparisons

	O wt %	wt % loss for oxide removal
Garbo system	3	~6
Traditional system	10-15	~20-30

Results and discussion

Si kerf/coolant separation

A critical step for the reclaiming of silicon kerf and coolant from diamond wire sawing mixtures is the identification of a proper technology for the silicon /coolant separation. Fig. 2 reports the typical grain size distribution of the silicon particles which shows that more than 80% of silicon is in the submicron range.

The segregation of the ultrafine silicon particles from the coolant enables the on-site reclaiming of more than 95% of solid-free coolant potentially to be reused in cutting as well as a silicon kerf material with the highest silicon content. Tab. 1 compares the typical oxygen percentages from oxidation of the kerf collected with Garbo proprietary system and that of a kerf collected with a traditional decanter + drying step system. It can be observed that the amount of oxygen in the first case is significantly lower than in the second, thus entailing a much lower amount of oxidized silicon to be removed in the cleaning step and a substantially higher silicon recycling yield. Additionally, such a Si kerf collection implies an easier and more cost effective silicon recycling due to lower consumption of chemicals and a lower amount of waste streams.

Si kerf cleaning

The as-received kerf is contaminated with metals due to the contact of the kerf with the metal wire and the metal components of the saw. These metals are concentrated on the surface of the silicon particles and can therefore be removed by etching some monolayers of the particle surface via acid washing. Tab. 2 reports the measured surface metal impurities before cleaning and after the cleaning carried out by Garbo.

It can be seen that the most important metal contaminant is the nickel deriving from the abrasion of the outer nickel layer of the wire where the diamond particles are embedded. After the cleaning, the total metal impurities are drastically reduced to a few residual ppm.

The final level of purity is close to 6N for metals, thus meeting solar grade requirements [2]. Higher purity in terms of total metals can be achieved by performing a deeper chemical etching which removes a thicker layer of silicon surface at the expense of the silicon recycling yield. Besides metals, the carbon content in the silicon material has been measured. In the incoming kerf, a value of up to 2.2% of carbon has been measured.

Such a high carbon contamination derives mainly from organics contained in the sawing process, as revealed from a multiphase carbon analysis in which the various forms of carbon are distinguished as a function of their combustion temperature (Fig. 3). The organic matter in the kerf originates from the coolant, the mounting beam and the glue used to fix the ingot onto the beam. Inorganic carbon represents less than 1% of the total carbon, and it is ascribed to diamond particles pulled out from the wire.

The removal of organic carbon from the kerf has been accomplished via chemical and thermal treatments, while separation of diamond particles is currently under study. It is worth mentioning, however, that it is not straightforward to predict the effect of a carbon content of ca. 200 ppm wt in form of diamond particles in the final silicon ingot obtained after directional solidification.

Theoretically, this carbon level exceeds the solubility of carbon in silicon and SiC precipitates might be expected in the ingot [3]. However, factors like kinetics, oxygen content in the charge etc may influ-

Tab. 2 - Metal impurities measured by ICP-OES

Element	Before cleaning ppm wt	After cleaning ppm wt
Al	3.05	0.08
Ca	5.6	0
Cr	3.2	0.29
Co	0.3	0.06
Cu	2.4	0.6
Fe	20.7	1.24
Mn	0.2	0.05
Na	2.55	0.2
Ni	155.8	0.19
Zn	0.38	0.13
Total	194.24	2.84

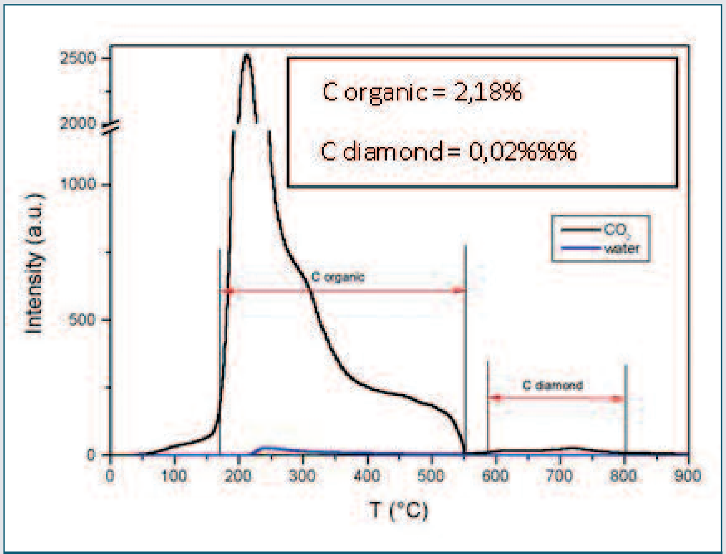

Fig. 3 - Carbon contamination in the incoming kerf

ence the amount of carbon that really dissolves in the silicon as well as the formation and location of inclusions.

Therefore, the carbon refining possibilities during crystallization need to be investigated in order to understand up to what extent diamond contamination is acceptable in the recycled kerf. On the other hand, the reclaiming of silicon from conventional slurry containing polyethylene-glycol and SiC particles has shown that the SiC content cannot be reduced below 7 wt% in the recycled silicon before melting processes [4]. Hence, the contamination of SiC abrasive particles renders the silicon kerf recycling from slurry much more challenging compared to the case of diamond wire wafering.

Si kerf compacting

Besides correct Si kerf collection and deep cleaning, another fundamental step for the complete silicon recovery is the densification of the regenerated silicon powder into compacted material ready to be charged in the crystallization process.

The compaction of the silicon kerf is needed for three main reasons, namely: i) avoid the transport and handling of ultrafine and potentially explosive powder, ii) assure the complete meltability of the silicon preventing the formation of un-melted powder platelets in the crystal, iii) increase the density of the powder to maximize crucible loading factor. Although the compaction of powders is a well known process in metallurgical and ceramic processes, the densification of silicon powders with no addition of cross-contaminations is not trivial. Garbo has patented and implemented a contamination-free compacting process

Fig. 4 - Example of Garbo Si compact

which enables to obtain tunable silicon compacts with a density of up to 1.6 g/cm^3. Fig. 4 shows an example of Si compact that can be achieved in our process.

Conclusions

In conclusion, the recycling of Si kerf from diamond wire sawing as presented in this paper shows very promising results. The main achievements so far obtained are the following:

- a silicon kerf/coolant separation system and kerf collection system that allow on-site reclaiming of coolant and a minimized oxygen content in the kerf have been implemented;
- a chemical cleaning process capable of removing metal impurities up to a 6 N purity has been demonstrated;
- a silicon densification process yielding contamination-free silicon compacts with adjustable shape and with a density of up to 1.6 g/cm^3 has been achieved.

On-going investigations are dedicated to decreasing the carbon contamination deriving from diamond particles.

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References

[1] J.-I. Bye *et al*., Proc. of the 24th European Photovoltaic Solar Energy Conference, 2009.
[2] L.J. Geerligs *et al*., Proc. 20th European Photovoltaic Solar Energy Conference, 2005, Vol. I, 619.
[3] T. Nozaki *et al*., *J. Electrochem. Soc.,* 1970, **117**, 1566.
[4] T.Y. Wang *et al*., *J. Crystal Growth,* 2008, **310**, 3403.

RIASSUNTO

Processo di recupero ad alta resa di sfridi di silicio dal taglio dei wafers con filo diamantato

La possibilità di riciclare gli sfridi di silicio derivanti dalle operazione di taglio dei wafers con filo diamantato rappresenta un grande vantaggio di questa tecnologia di taglio rispetto a quella tradizionale a base di sospensioni abrasive. Il processo di rigenerazione degli sfridi di taglio dei wafers mira a riutilizzare una sorgente interna di silicio che soddisfa i requisiti di qualità per l'applicazione fotovoltaica.