CABRISS
RECYCLING OF SI-KERF FROM PV

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ABSTRACT: The European Horizon 2020 project CABRISS [1] aim to implement a circular economy for solar cells based on recycled, reused and recovered materials. One important pillar in this project is the recycling of silicon kerf from diamond wire cutting of wafers and blocks. The first objective is to optimize Si-kerf environment in order to facilitate silicon recycling. The second is to demonstrate the full purification of Si-kerf at industrial scale. A recycling process has to be flexible since the silicon kerf will vary in shape, size, contamination level and concentration from source to source. CEA, FerroPem and Resitec have achieved interesting results on this topic within the CABRISS project. Important topics for investigation have been the influence of additives and sawing conditions [2], wet and dry mechanical separation methods and further purification by pyro metallurgical processes. Si-kerf has been recycled into 2-4N silicon powder in pilot scale and industrial scale with an acceptable oxygen content. This material has been successfully melted, purified and used for ingot production. There are also several safety topics that need to be investigated for scale up of the recycling process. Recycling of Si-kerf has been demonstrated at an industrial scale.

Keywords: Silicon, Recycling, Sustainable, PV Materials

1 INTRODUCTION

The European Horizon 2020 project CABRISS [1] aim to implement a circular economy for solar cells based on recycled, reused and recovered materials. This paper is related to the activity of recycling the Si-kerf from diamond wire cutting of wafers and blocks. Traditional slurry with silicon carbide and glycol has not been a topic of this project. The CABRISS project concerns also other parts of the value chain for PV production such as recycling of broken cells or end of life panels, recycling of indium and silver, and other topics [1].

The process of cutting silicon ingots into wafers suitable for solar cells has a kerf loss of approximately 40% by weight silicon. There is progress to reduce thickness of diamond wire, which will reduce the kerf loss. The kerf loss from block cutting is in the range of 5%. Diamond wire is today more commonly used for mono silicon, but in the CABRISS project, both mono, mono like and multi silicon have been considered.

Several R&D project have aimed to recycle Si-kerf from PV. Several processes have also been established and some patented. To our knowledge no process have been successfully industrialized so far. This has mainly been a result of recycling cost and investment cost in combination with low prices for PV silicon in the last years. Resitec has focused on a cost efficient process for recycling the Si-kerf into 2-4N silicon for use in novel solar cell concepts or alternative markets. FerroPem and Silicio FerroSolar have focused on further melting and purification of the recycled kerf to produce ingots. CEA has focused on Si-kerf recycling and mechanisms to passivate the Si-kerf. Recycled silicon kerf has been used in conventional and novel solar cell concepts within the CABRISS project.

Recycling of Si-kerf is energy efficient. Considerable amounts of energy have been consumed to produce PV quality silicon. Resitec estimates its process to give an energy saving of >15MWh pr 1000kg Si-kerf compared to conventional production of similar Si-powder. Through the CABRISS project, we have also seen that recycled Si-kerf have applications outside of the PV industry.

2 EXTRACTION OF SI-KERF

Si-kerf from diamond wire cutting exists in highly diluted coolant (water + additives) from the cutting process. There are variations in particle size of the silicon particles depending on the method for cutting, wire thickness, wire speed etc. A typical particle size distribution of Si-kerf from diamond wire wafering is shown in figure 1. The average particle size is 1.7 µm and a 90% point at 4.3 µm. These are small particles that are challenging to process.

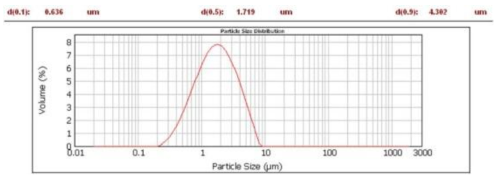

Figure 1: Particle size distribution of Si-kerf from diamond wire wafering measured by Malvern Mastersizer at Resitec.

Due to the fine particles and large volumes of cutting fluid with a low content of silicon particles (typically 0.5-2%), it is important to have an efficient method for dewatering the particles. Suitable equipment for efficient dewatering in two steps have been identified and tested in pilot and industrial scale.

Diamond wire cutting is used normally with water as fluid with the addition of a coolant additive. Several types of additives are available commercially and there are recommendations from the producers of the cutting equipment. Alternative additive systems have also been developed. In CABRISS, CEA has investigated different types of additives and their effect on oxidation of the kerf [2]. It is important to avoid oxidation of the kerf as much as possible during recycling to keep its quality high. Figure 2 shows results on oxidation for different types of coolant used by CEA.

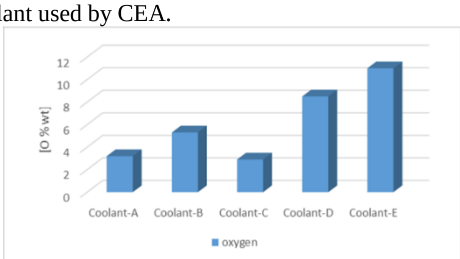

Figure 2: Oxygen in recycled Si-kerf with different coolant additives from investigations done by CEA.

It is essential that the Si-kerf is passivated before recycling. Unless passivated, the kerf will start oxidizing due to the oxygen available in water. This reaction is exothermic, and in a storage tank of Si-kerf /water slurry, there will be a temperature increase depending on the solids concentration in the water. The oxidation reaction develops large amounts of hydrogen. The oxidation which develops hydrogen results in a deterioration of the silicon quality and creates a serious safety problem. Reaction rate will depend on particle size (available surface area), temperature and other parameters. This is a safety risk during scale-up from lab to industrialization. Reliable passivation methods have been developed and tested in pilot and industrial scale. Hydrogen concentrations need to be monitored at all times.

3 RECYCLING OF SI-KERF

Si-kerf has been recycled from diamond wire wafering and block cutting. The particle size may vary and the wafer kerf is normally finer particles compared to the kerf from block cutting. Material from mono- and multi silicon has been recycled.

CEA has studied recycling of Si-kerf from a conventional process and from an optimized process. The recycling was done in connection with a diamond wire wafering saw using a water based coolant and achieved a high purity Si powder with the chemical analysis shown in figure 3. This is material recycled in pilot scale from a standard industrial type diamond wire wafering saw.

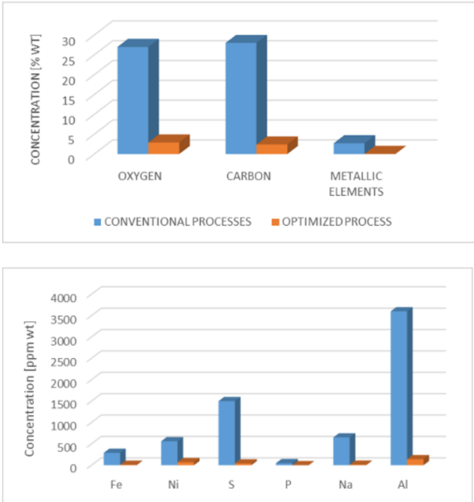

Figure 3: Results from recycling of Si-kerf at CEA from a conventional process and an optimized process.

The results from figure 3 show a significant reduction in carbon, oxygen and metallic elements, particularly aluminum. These are important parameters for using the material to produce ingots or other use in PV.

Resitec have recycled Si-kerf from block cutting and wafering of both mono and multi silicon. The sources for Si-kerf have been Fraunhofer THM and other sources outside the CABRISS consortium. The recycling is done in pilot scale of 10-100kg and also demonstrated in industrial scale > 1000kg batches. Resitec has aimed to have a cost efficient process to produce a cheap substrate which is used further in the CABRISS project or to produce silicon powder with purity suitable as feedstock for further purification steps for PV use. Purity of 99,5-99,9% have been achieved in industrial scale and 4N purity in pilot scale. Figure 4 shows results for 99,5% silicon powder recycled from a block cutting process. This material may need further purification steps prior to PV ingot production or it can be in alternative PV applications.

Si-type	Purity [wt%]	Particle size distribution [µm]			Fe [%]	Al [%]	Ca [%]	Other elements [%]
		D10	D50	D90				
Fine, poly	>99,5	1	5	15	<0,02	<0,2	<0,02	<0,01
Coarse, poly	>99,3	10	25	110	<0,06	<0,7	<0,02	<0,01

Figure 4: Results of recycled Si-kerf from a block cutting process and a picture of the dry silicon powder.

Several tests were performed at different scale to optimize the process. A recycling process for Si-kerf at industrial scale has to be flexible to fit into the existing production system of an industrial source for Si-kerf. Figure 5 shows the particle size distribution for recycled

Si-kerf from wafering of silicon by diamond wire. This test was done in pilot scale. Scale up of this process is currently on going at Resitec.

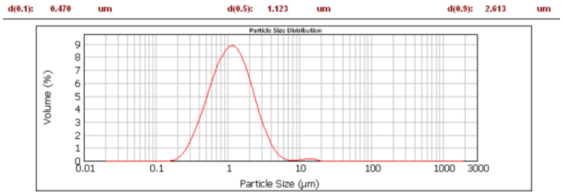

Figure 5: Particle size distribution measured by Malvern Mastersizer at Resitec.

Figure 6 shows an analysis of elements in the recycled Si-kerf from wafering with diamond wire saw. This is the same material as shown in figure 5. The analysis are done with GDMS by EAG Laboratories in France. Materials from the different recycling tests have been further used in the CABRISS project as feedstock for conventional routes for ingots or in novel routes as a silicon powder.

Element	Concentration [ppm wt]	Element	Concentration [ppm wt]
Li	< 0.005	Pd	< 0.005
Be	< 0.005	Ag	< 0.01
B	0.09	Cd	< 0.01
C	-	In	Binder
N	-	Sn	< 0.1
O	-	Sb	< 0.05
F	1.1	Te	< 0.01
Na	6.7	I	< 0.001
Mg	8.0	Cs	< 1
Al	3.4	Ba	0.25
Si	Matrix	La	0.17
P	5.7	Ce	0.24
S	13	Pr	0.08
Cl	2.1	Nd	0.10
K	2.9	Sm	< 0.005
Ca	62	Eu	< 0.005
Sc	0.04	Gd	< 0.005
Ti	0.31	Tb	< 0.005
V	0.01	Dy	< 0.005
Cr	0.35	Ho	< 0.005
Mn	0.19	Er	< 0.005
Fe	7.4	Tm	< 0.005
Co	0.05	Yb	< 0.005
Ni	62	Lu	< 0.005
Cu	2.7	Hf	< 0.05
Zn	2.7	Ta	< 1
Ga	0.10	W	0.25
Ge	1.1	Re	< 0.01
As	0.17	Os	< 0.005
Se	< 0.05	Ir	< 0.005
Br	< 0.01	Pt	< 0.01
Rb	< 0.01	Au	< 0.01
Sr	0.24	Hg	< 0.05
Y	0.01	Tl	< 0.005
Zr	0.06	Pb	0.71
Nb	0.02	Bi	< 0.005
Mo	0.09	Th	0.01
Ru	< 0.001	U	0.007
Rh	< 0.001		

Figure 6: Analytical results of elements in recycled Si-kerf from wafering of silicon at an industrial site. The oxygen content was 4,3% and the carbon content was 0,56%. The elements are measured by GDMS and the O and C level are measured by IGA, both analysis are performed by EAG Laboratories in France.

4 MELTING AND PURIFICATION

The recycled Si-kerf was supplied within the CABRISS project for multiple different PV applications. These are melting, hot pressing, plasma spray and further purification steps.

FerroPem in France did several small scale tests for melting the material and these tests resulted in a scale-up for > 300 kg tests at Silico FerroSolar in Spain. Both companies are a part of Ferro Atlantica. Analysis of melting tests by FerroPem is shown in figure 7.

Sample	Analysis	Al	Ca	Fe	Ti	Cu	Mn	Ni	P	B	Cr	V	W
359	before melting (ppmw)	213,8	77,2	94,1	5,6	9,5	<2	<2	2,5	<2	2,6	<2	<5
359	after melting (ppmw)	207,0	12,6	77,0	3,5	5,8	<2	2,1	2,7	<2	2,3	<2	<5
327	before melting (ppmw)	821,1	197,1	370,5	3,8	63,8	<2	3,1	4,6	2,8	4,9	<2	<5
327	after melting (ppmw)	626,0	13,5	224,0	2,0	42,8	<2	3,1	2,4	2,9	3,8	<2	<5

Sample	Analysis	C (%)	O (%)	S (%)
359	before melting (ppmw)	0,045	1,855	< 0,05
359	after melting (ppmw)	0,015	0,17	<0,05
327	before melting (ppmw)	0,0525	2,265	< 0,05
327	after melting (ppmw)	0,028	0,19	< 0,05

Figure 7: Analysis of Si-kerf after melting tests at FerroPem.

Figure 7 shows a reduction in several of the metallic elements and oxygen and carbon. Figure 8 shows similar results from trials in larger scale at Silicio FerroSolar.

Sample	Kg in	Al	Ca	Fe	Ti	P	B	Cu	Cr	K	V	Ni	Na	Kg out
Resitec initial kerf	**1000**	173,0	66,3	108,2	3,8	1,1	<1	15,1	4,0	7,1	0,0	2,6	14,0	**827**
TES 1-2	230	433,1	1,4	139,1	3,6	1,1	<1	14,1	5,9	2,4	<1	2,7	0,7	129
TES 3-4	150	833,8	40,7	296,6	11,6	2,3	<1	10,1	6,7	4,8	0,6	2,8	2,3	138
TES 5-9	365	1355,9	79,0	359,6	19,7	2,3	<1	16,6	10,2	3,0	0,4	4,1	2,7	320
TES 10-13	255	773,7	60,7	852,9	8,6	2,7	<1	12,3	8,4	6,5	0,5	3,4	2,0	240

Figure 8: Results of metallic elements (ppmw) after large scale melting tests. ICP-OES measurements are done by Silicio FerroSolar.

The results show that the material did not reach PV purity, but needs further purification to reach the traditional PV specifications. The further purification step to reach the solar grade quality can be done through the confidential Silicio FerroSolar process. This is currently being tested. Figure 9 shows the purification route suggested.

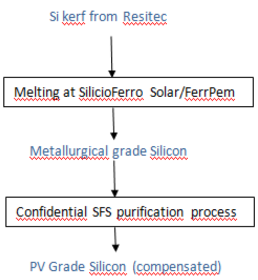

Figure 9: Suggested route for purification of Si-kerf to PV grade.

In figure 10, we can see a picture of the melted material with its origin in recycled Si-kerf. This material is from the tests by Silicio FerroSolar in Spain in larger scale as shown with chemical analysis from figure 8.

Figure 10: Picture of silicon chunks from melted and solidified material with its origin in Si-kerf.

Sintef worked on the further purification of Si-kerf by melting and these results are presented separately [3].

5 CONCLUSIONS

Through the CABRISS project a method for recycling of Si-kerf has been developed. Work by CEA has shown in pilot scale how an optimized process for Si-kerf recovery can give a high purity (4N) with low oxygen content. Resitec has developed a process for recycling of Si-kerf which has been demonstrated in pilot and industrial scale for producing 2-4N Si-powder. FerroPem and Silicio FerroSolar have used the recycled material for melting and solidification with good yield and have shown further purification in melted stage. Further up-scaling tests are in progress.

6 REFERENCES

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