ECONOMICAL AND TECHNICAL STUDIES FOR THE PRODUCTION OF SOLAR GRADE SILICON BY PLASMA ZONE MELTING TECHNIQUE

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ABSTRACT

The aim of our project is to propose a process which is able to produce photovoltaic silicon with an industrial price which is around 50 F/kg. We have chosen to purify metallurgical grade silicon by reactive plasma zone melting. The characteristics of the product indicate a ultra high purity (lower than 0,1 ppm) with a resistivity of "p" type (near 0,2 Ω.cm), and the efficacity of the cell could be 10 %. From fundamental point of view the reactive plasma permits the silicon to be melted and to react with impurities in order to keep them in the slag on the surface. The transfer of matter seems to be controlled by a high degree of convection in the liquid.

I. INTRODUCTION

The aim of this project is to produce solar grade silicon in conditions which are economically advantageous. The plasma technique relies on melting a partial zone of a bar of silicon in a reactive atmosphere. The problem is that of eliminating the principal impurities in the metallurgical grade silicon in order to achieve a resistivity in the region of 1 Ω.cm. The work parameters of the process are the nature of the plasma, the mechanical variables (temperature, speed, distance between plasma and the bar), and the quality of the metallurgical grade silicon (M.G.Si). The physico-chemical properties of the silicon produced allow a link to be made between the conditions in which treatment occurs, the chemical purity of the product and its photovoltaic yield. A consideration of economic factors concludes the presentation.

II. CHARACTERISTICS OF THE TECHNIQUE AND THE EXPERIMENTAL APPARATUS

The method of extraction by the liquid-solid plasma technique relies on the principle of the melting by zone of a bar placed horizontally in a cooled copper crucible. The particularities of the process are :

1 - A partial melting of the bar so that the silicon act as a crucible.

2 - A concentration of impurities towards the liquid phase thanks to the very high temperature of the plasma.

3 - Process out of equilibrium, Benard's convection structures control the mechanism of the transfer of matter towards the surface of the bar.

4 - The three interfaces at which purification occurs are :

- The liquid-solid interface is responsable for the rejection of impurities in the liquid phase (role of the distribution coefficients.

. The liquid-slag interface ; the slag traps the highly soluble impurities in the liquid phase by forming complex silicates.

. The slag-reactive plasma interface allows to evaporate off the metals and metalloïdes impurities which have high vapour pressure.

The plasma used is a high frequency Torch (12 kW) employing a mixture of Argon-Hydrogen-Oxygen (8). The speed at which the crucible is displaced is between 20 and 120 cm/h.

Silicon used and results obtained

Metallurgical grade silicon contain between 30000 and 1000 ppm of impurities, the content of highly undesirable impurities (Ti, V, W, Mo, Cr..., B, Al, Fe) varying from one manufacture to another.

The results in tables 1 and 2 show the characteristics of the material at the out set and the results obtained after it has undergone for treatments in reactive plasma and a process of acid etching, designed to eliminate the surface slag.

The degree of resistivity of the end product is in region of 0,2 Ω.cm, the chief remaining impurity being of the "p" type (mesuring by spreading resistance).

III. ELIMINATION OF THE BORON

The elimination of the boron seems to occur through a chemical reaction taking place between boron and the oxygen which accounts for the appearance, on the one hand, of volatile oxides, and the other hand of a slag which is rich in boron (SiO_2 + y B_2O_3). Elimination tests have been carried out, using electronic grade silicon doped with boron having a resistivity of 0,011 Ω.cm and a resistivity of 3 Ω.cm or respectively 74 ppm and 34 ppb of boron. The choice of reactive atmosphere : argon, oxygen, hydrogen achieved the elimination of 40 ppm of boron for the sample at 74 ppm and 20 ppb for the sample at 34 ppb. Figure 2 shows that the amount of boron eliminated depends on :

1 - The oxygen content of the plasma

2 - Then the surface evaporation.

IV. PHOTOVOLTAIC PROPERTIES OF THE END PRODUCT

Starting with metallurgical grade silicon 99,5 % (5000 ppm of impurities) we obtained a silicon of very high purity (lower than one ppm of impurities in all) having a resistivity of 0,2 Ω.cm. It is a material of "p" type not compansated of which the short circuit current is 400 mV. The measurement of the yield of the photopile obtained from small samples (1,6 cm^2) was compared with that obtained electronic grade silicon treated in the same conditions.

	Surface	VCO (mV)	Yield	Yiedl obtained with a large surface and an antireflective coating
Polycristalline electronic grade silicon (wacker) treated with plasma	1,6 cm^2		4,7 à 5,2 %	9 %
Metallurgical grade silicon treated with plasma (polycristalline)	1,6 cm^2	400 mV	4,5 %	8 %
Electronic grade silicon (monocristalline)	78 cm^2	600 mV		12 %

Hence the polycristalline silicon appear to be very promising as much for its high level of purity as for its photovoltaïc yield which will probably be able to reach 10 %.

V. CONCLUSION AND ECONOMIC STUDY

The economic analysis of the process has been carried out by comparison with the American work published at the San Diego Congress. It underlines the interest of the process which seems very likely to be worth exploiting industrially exploitation. Our technique shows very clearly that it is the mechanism of convection which controls the purification of silicon. The nature of the plasma, its thermic action, its reactivity and the surface temperature in the region of 2300 K prove the fact that diffusional mechanisms are henceforth to be discounted and that the speed at which the bar can be purified can reach 120 cm/h. The theoretical model of the transfer of matter is at present fully developed in the laboratory.

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The characteristics of the photopiles were produced by
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et M. SIFFERT, C.R.N. Strasbourg FRANCE.

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Fig. 2 : Elimination of the boron by evaporation and drainage in function of the purcent of oxygen in the plasma

Raw material : Electronic silicon 0,011 Ωcm that is 74 ppm weight of boron

Results obtained after four pass at 40 cm/h.

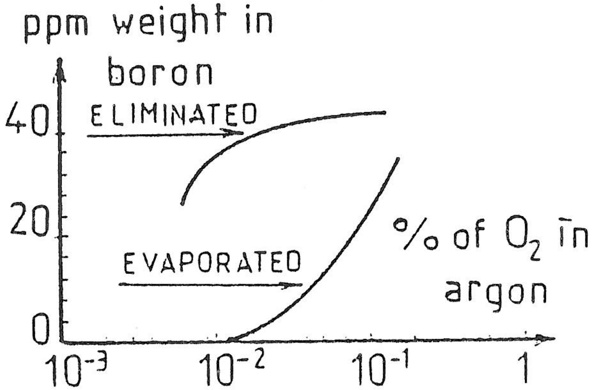


Tableau I : Analyse du silicium métallurgique en ppm poids. Analyse par radioactivation spectro de masse à étincelle.

Impuretés	MG.Si 1	MG.Si 2	MG.Si 3
Al	3000	290	≈ 200
As	< 0,08	0,84	1,40
Au		0,00028	0,026
Ag	0,2	0,10	0,043
Ba	20	< 4	< 5
C	1900		
Ca	2000		
Ce		0,002	0,007
Co	5	3,6	0,66
Cr	40	87	9,70
Cs		< 0,01	< 0,008
Cu	40	2	23
Eu		0,007	0,0006
Fe	1800	742	60
Ga	1,5	< 0,64	< 0,3
HF		< 0,2	0,006
La	10	1,4	0,008
Mn	43	250	< 2,2
Mo	10	13,7	1,8
Na	7,8	1,15	302
Ni	80	< 25	33
O	4000		
Sb	0,07	0,045	0,11
Sc	0,62	0,064	0,0037
Sm		0,006	0,0005
Ta	0,002	0,007	0,0008
Th		< 2	< 0,78
Ti	160	141	53,1
Zn	40	< 1,9	< 1,7
Zr	0,3	2,75	< 2,77

Prix des différents matériaux de départ

MG.Si 1 98% de silicium → 3 F/kg

MG.Si 2 99,7% de silicium → 7 F/kg

MG.Si 3 99,95% de silicium → 25 F/kg

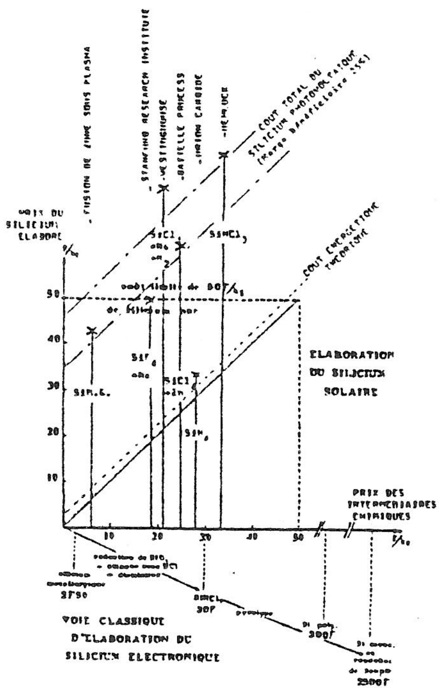
Impuretés	Purification obtenue à partir du silicium métallurgique 1	Purification obtenue à partir du silicium métallurgique 2	Pureté du silicium Wacker polycristallin
Ag		< 0,008	< 0,001
Al	< 1		< 0,5
As		0,014 ± 0,001	< 0,0005
Au	0,00002	< 0,00003	< 0,00003
Ba	0,9	< 0,4	< 0,15
Br		< 0,02	
C			
Cd		< 0,10	
Ce		< 0,010	< 0,001
Co	0,008	< 0,0003	0,0007
Cl	0,02		0,002
Cr	0,01	< 0,00027	0,003
Cs		< 0,003	< 0,001
Eu		< 0,0001	
Fe	1	< 0,02	< 0,4
Ga		< 0,002	
HF	0,015	< 0,001	< 0,002
K		< 0,01	
La		< 0,0001	
Mn	0,003	< 0,0001	< 0,005
Mo		< 0,003	< 0,002
Na		< 0,002	
Ni		< 0,10	
P			
Sb		< 0,0002	< 0,00005
Sc	0,0001	< 0,00001	< 0,00001
Ta		< 0,003	
Th		< 0,003	
Ti		< 0,06	
Pb			
V	0,0004		0,002
W		< 0,03	< 0,0004
Zn	0,001	< 0,00024	< 0,26
Zr	0,07	< 0,019	< 0,24

< Ces résultats indiquent que la teneur est inférieure à la limite de détection de la méthode employée.

Tableau II : Résultats obtenus par fusion de zone sous plasma. Comparaison avec le silicium polycristallin Wacker.

Tableau III— *Comparaison économique des techniques d'élaboration du silicium solaire.*

[Economic comparison of technics for the treatement of solar grade silicon.]



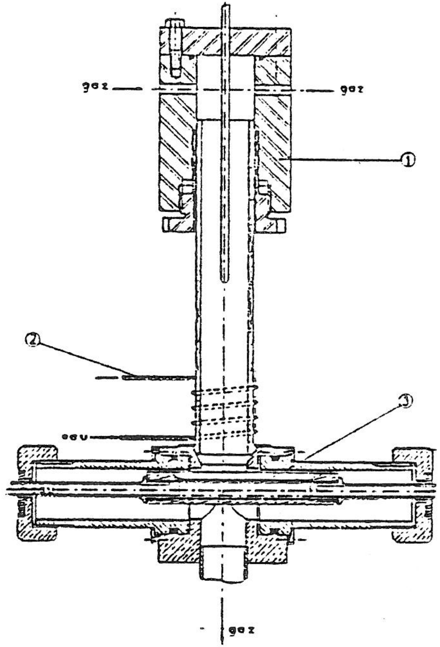


Fig. 1. — Installation de fusion de zone sous plasma : 1. Tête d'amenée du fluide plasmagène (Ar + H_2). 2. Inducteur d'alimentation électrique (40 MHz–4 kV). 3. Nacelle refroidie.