APPLICATION OF THE ENHANCED SELECTIVE IONIZATION METHOD TO SILICON PRODUCTION

Guido Parissenti*, Alfonso Niro**

*Politecnico di Milano, Dipartimento di Energia, E-mail: guido.parissenti@mail.polimi.it
**Politecnico di Milano, Dipartimento di Energia, E-mail: alfonso.niro@polimi.it

ABSTRACT

Present production methods of high graded pure silicon for electronics purposes involves usage of large quantities of energy, water and chemicals. The possibility to directly separate silica into its constituents with a single step would provide benefits in terms of energy consumption, logistics and environmental impact. This separation is feasible if performed by electromagnetic means on ionized silica and taking advantage of the ionization gap between oxygen and silicon, a process that can be called Enhanced Selective Ionization. In this paper the energetic feasibility of a direct separation of silica using the Enhanced Selective Ionization Method is evaluated in its energetic requirements and conversion yields. The preliminary power budget of a demonstrator devoted to verify the concept is presented. The energy cost per unit of silicon is compared with traditional production processes.

INTRODUCTION

The Enhanced Selective Ionization Method [1] is an improvement of the Selective Ionization process developed by NASA in the '80s [2][3] to extract oxygen from the soil of extraterrestrial planetary bodies. The process take advantage of the fact that at the same temperature the ionization level of oxygen is much lower than the ionization level of a number of common metals and metalloids. In this perspective the vaporization and heating of an oxide or a mixture of oxides up to a temperature at which this ionization gap is substantial allows to remove by electromagnetic means the metal ions, and to recover the neutral gaseous oxygen. This interesting concept can be applied to a number of devices developed in the past for isotope or mass separation such as the Calutron [4], the Archimedes mass filter [5] or the plasma separation process by ion cyclotron resonance [6].

In this paper the Enhanced Selective Ionization is applied to the silicon production from silica. Focusing on a single oxide allows to effectively trim the separation process improving the recovery yield and reducing the energy requirements.

THE Si-O IONIZATION GAP

Considering an operating pressure of 10^{-3} mbar compatible with the technologies mentioned above, which operate in vacuum conditions, we can calculate the Saha equations 1 for silicon and oxygen.

$$\frac{n_i n_e}{n_0} = 2\frac{Z_i}{Z_0}\frac{(2\pi m_e k_b)^{\frac{3}{2}}}{h^3}T^{\frac{3}{2}}\exp\left(\frac{-I}{k_b T}\right) \qquad (1)$$

The partition functions Z_i and Z_0 are taken from [7]. Fig.1 is obtained considering solely the ionization potential of the two elements, one independent from the other. These curves represent the equilibrium ratio of ionized to neutral atoms vs. temperature. As can be seen the ionization levels of the two elements are very different at about 7000 K. Oxygen is ionized below 1.4% while silicon above 74%. In a device in which the silica is vaporised and ionized, the silicon-oxygen ionization gap can be used to remove the neutral oxygen from the silicon anions: the first is insensitive to EM fields while the latests can be properly manipulated end extracted with a combination of electric or magnetic fields. It is for this reason that in Eq.1 only the first ionization level is assumed, in order to have the same mass-to-charge ratio for each atom of the same element: this strongly eases the plasma manipulation procedures, other than being reasonable from an energetic point of view due to the much higher second ionization energy that has to be provided to the ions to remove an additional electron. Being the Saha equation obtained for an element in equilibrium with itself it is not totally correct its application on a mixture: however in the real situation the presence of multiple species at the same time would produce an interaction between ions of the two elements, with the electrons lost by ionization being acquired by the most electronegative ions. In this way it is reasonable to state that the equilibrium situation, respect to the ionization values found with the Saha equation, would present lower percentage of ionized oxygen and an higher percentage of ionized silicon, making our estimation more conservative.

Summarizing, the ionization gap allows to consider in a separating device only the silicon ions behavior, because the neutrals are pumped away by the vacuum pump. Consequently the system can be greatly simplified respect to a device devoted to separate a range of elements, and can achieve higher efficiency and silicon yield.

POWER REQUIREMENT ESTIMATION

To provide an estimation of separation yields and required power an approach similar to those used by [3] is considered. The separation process can be subdivide into three phases:

1. vaporization of the input material and atomization at 298 K

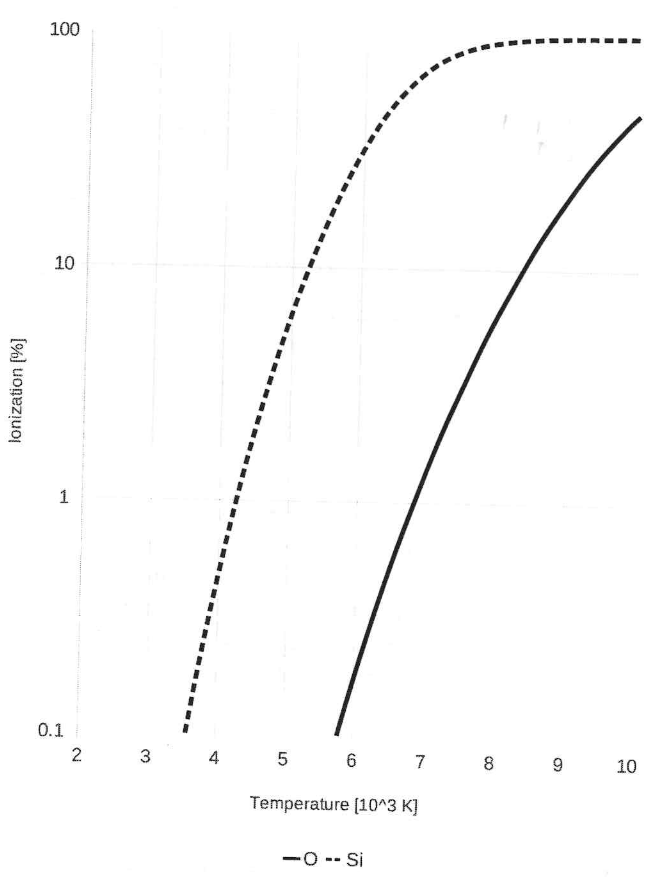

Figure 1. Ionization Vs Temperature of SIlicon and Oxygen at P=10^{-3} mbar

according to [8]

$$E_{at}(SiO_2) = -\Delta_f H^0(SiO_2, 298K) + \\ + \Delta_f H^0(Si(g), 298K) + 2\Delta_f H^0(O(g), 298K)$$

2. ionization and temperature rise to equilibrium condition at the temperature T_s required for the separation. It is assumed that ΔH^{T_s-298K} of ions is the same of neutral atoms.

$$E_{\Delta T}(Si(g) + 2O(g), T_s) = i_{Si}E_i^1(Si) + 2i_O E_i^1(O) + \\ + \Delta H^{T_s-298K}(Si(g)) + 2\Delta H^{T_s-298K}(O(g))$$

3. separation of the ions by EM means.

where i_{Si} and i_O are ionization level of silicon and oxygen at the temperature T_s, which in this case is 7000 K. Calculations results in a required power to vaporize and ionize silica reported in Tab.1.

Table 1. Sum of the silica vaporization energy, ionization energy and heating up to 7000 K

SiO_2	kWh/mol	kWh/kg	kWh/ton
$E_{at}+E_{\Delta T}$	0.81	13.5	13459

Following the approach of [9], to estimate the power requirement of a demonstrator capable of performing such separation we need to take into account an heating system, a pumping device, a ionization equipment and a separation section in which a **B** field is created. The demonstrator working model is depicted in Fig.2 and is a modification of the Calutron concept in which the vaporization and ionization stage by electron beam are substituted by a plasma torch and an RF plasma ionization stage.

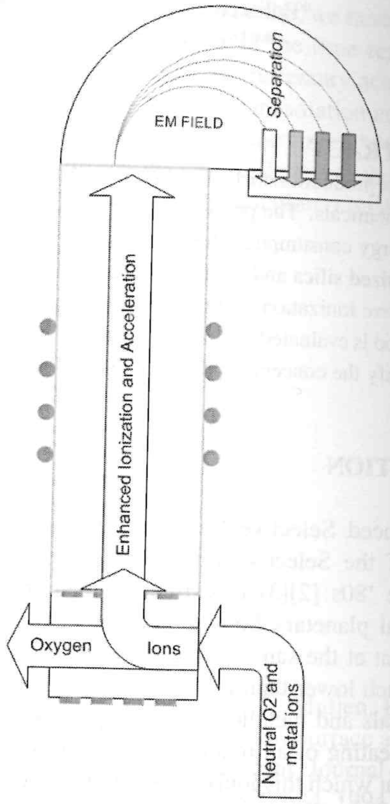

Figure 2. Enhanced Selective Ionization Concept for oxide separation applied to Calutron technology

Refractory material such as SiO_2 requires an heat flux up to 100 MW/m^2 to be vaporized [10]. For a demonstrator as a first estimation an evaporator area of 10 cm^2 can be considered acceptable, requiring about 100 kW of vaporization and ionization power. To heat the plasma we can assume to use as an intermediate stage an antenna as used in the VASIMR Thruster VX-100 experiment [11], in which a 75 kW RF source is used to heat the plasma up to 500 eV thanks to the ion cyclotron resonance mechanism. The required pumping power can be estimated in 25 kW (Varian NHS-35 pump) while the separation stage was already estimated in [9] in about 25 kW, for a total of 225 kW for about 7.43 kg/h of processed silica. Yields are reported in Tab.2.

Table 2. Separation yields for silica

SiO_2 $\dot{m}$ (kg/h)	Si yield (kg/h)	O_2 yield (kg/h)	Waste (kg/h)
7.43	2.56	3.91	0.96

As can be seen the waste product, which is simply calculated as the silicon which is not ionized plus the oxygen which is ionized, account for about 13%. It is not a small value but as said it has to be considered that in a mixture of gases the ionization rates are reasonably shifted towards an higher Si ionization and a lower O ionization, making this loss an upper limit value. Consideration are also to be made in comparison with present silicon production processes. The total energy required to produce 1 kg of silicon with the Enhanced Selective Ionization can be quantified in:

$$\frac{225\,\mathrm{kW}}{2.56\,\mathrm{kg/h}} = 87.8\,\mathrm{kWh/kg} = 316\,\mathrm{MJ/kg}$$

COMPARISON WITH PRESENT PRODUCTION PROCESS

The above calculated power can be compared with the energy breakdown to produce 1 kg of pure silicon with the conventional process. According to [12] the lower bound of the required energy to obtain 1 kg of electronic grade silicon wafer is 2127 kWh, which can be reduced to 1056 kWh if the process stops to the production of the electronic grade single crystal silicon ingot or even to 403 kWh if the process is stopped at the creation of the polysilicon. No estimations can be made, at this stage, about the purity of the Silicon collected at the end of the Enhanced Selective Ionization device, but a consideration is possible about impurities: oxygen is removed in two steps, neutral atoms are pumped away while the 1.4% of oxygen that ionizes is directed outside the silicon collector due to the different mass to charge ratio and cyclotron radius. The same happens to other impurities present in the silica, which follows different trajectories than silicon ions and are collected elsewhere. In order have a comparison, Tab.3 shows the aforementioned energies and the yields at the different steps of the conventional process along with the 87.8 kWh/kg of the Enhanced Selective Ionization Process (ESI).

Table 3. Enhanced Selective Ionization and conventional process comparison

	Energy [kWh/kg]	Energy ratio	Si yield [%]
ESI	88	1	34.5
Polysilicon	403	4.6	34.0
Single crystal ingot	1057	12	17.0
Silicon wafer	2127	24.2	9.5

CONCLUSIONS

It is evident from Tab.3 that the Enhanced Selective Ionization obtains the same yield of the Polysilicon stage with about one fifth of the required energy. It must also to be remarked that the energy estimation for the Enhanced Selective Ionization is an upper limit, while as declared in [12] the calculation for the conventional process is a lower limit. In addition here is not considered the consumption of chemicals and waters that is required for the silicon production with the conventional process, and the unavoidable related pollution. The energy saving can be theoretically raised by 24 times if an electronic grade final product is obtained with the implementation of a procedure for the direct uniform deposition of silicon in wafer shape. In conclusion we can state that Enhanced Selective Ionization is a possible efficient alternative to the present silicon production process.

NOMENCLATURE

H	Enthalpy (kJ/mol)
$\Delta_f H^0$	Enthalpy of formation (kJ/mol)
E_i^1	First ionization energy (kJ/mol)
$E_{\Delta T}$	Ionization and heating energy (kJ/mol)
E_{at}	Atomization energy (kJ/mol)
h	Plank constant (J/s)
I	Ionization energy(J)
k_b	Boltzmann constant (J/K)
m_e	Electron mass (kg)
n_0	Neutral density (m^{-3})
n_e	Electron density (m^{-3})
n_i	Ion density (m^{-3})
T	Temperature (K)
Z_i	Ion partition function $(-)$
Z_i	Neutral partition function $(-)$

REFERENCES

[1] G. Parissenti and A. Niro. Improvements in plasma raw material recovery by application of the selective ionization concept. *XXIX Congresso UIT sulla Trasmissione del Calore*, Torino, 20-22 Giugno 2011.

[2] W. H. Steurer. Extraterrestrial material processing. *Jet Propulsion Laboratory*, Doc. JPL-82-41, 1982.

[3] W. F. Carroll. Research on the use of space resources. *Jet Propulsion Laboratory*, Doc. JPL-83-36, 1983.

[4] E. O. Lawrence. Methods of and apparatus for separating materials. *US Patent 2709222*, May 24, 1955.

[5] J. Gilleland, S. Agnew, B. Cluggish, R. Freeman, R. Miller, S. Putvinski, L. Sevier, and K. Umstadter. Application of archimedes filter for reduction of hanford hlw. *WM02 Conference*, Tucson, AZ, February 24-28, 2002.

[6] D. A. Dmitrii A Dolgolenko and Y. A. Muromkin. Plasma isotope separation based on ion cyclotron resonance. *Phys.-Usp.*, 52(4):345, 2009.

[7] A. W. Irwin. Polynomial partition function approximations of 344 atomic and molecular species. *The Astrophysical Journal Supplement Series*, 45:621–633, April 1981.

[8] E. V. Bogatyreva and A. G. Ermilov. Energy stored in mineral raw materials during mechanical activation. *Inorganic Materials*, 44(2):197–202, Feb 2008.

[9] G. Parissenti and A. Niro. Power dissipation in heavy metals recovery from incinerator ashes. *XXVIII Congresso UIT sulla Trasmissione del Calore*, Brescia, 21-23 Giugno 2010.

[10] A. Putvinsky, S. F. Agnew, T. Ohkawa, and L. Sevier. Induction plasma torch liquid waste injector. *US Patent 6410880B1*, Jun 25, 2002.

[11] J. P. Squire, F. R. Chang-Diaz, T. W. Glover, M. D. Carter, L. D. Cassady, W. J. Chancery, V. T. Jacobson, G. E. McCaskill, C. S. Olsen, E. A. Bering, M.S. Brukardt,

and B. W. Longmier. Vasimr performance measurements at powers exceeding 50 kw and lunar robotic mission applications. *International Interdisciplinary Symposium on Gaseous and Liquid Plasmas, Akiu/Sendai, Japan*, September 5-6, 2008.

[12] E. D. Williams, R. U. Ayres, and M. Heller. The 1.7 kilogram microchip: Energy and material use in the production of semiconductor devices. *Environ. Sci. Technol.*, 36:5504–5510, 2002.