OXYGEN ELIMINATION AND NEW ELECTRONIC PROPERTIES OF SILICON DUE TO A TREATMENT BY A THERMAL PLASMA (Argon + 1% of H_2 or Argon + 10,6% of He).

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Abstract:

To have a better understanding about the role of chemical composition of thermal plasma interacting with a material, we have analysed particularly the influence of hydrogen in an argon plasma during the melting of silicon. Some impurities such as oxygen lead to defects which damage the crystal and the electronic properties of the material. The hydrogen introduced in the argon plasma modifies the electronic properties of the silicon. Of course the purification process by plasma depends on the thermal effect produced by the recombination of hydrogen atoms on the surface. Furthermore hydrogen participates to a decreasing of the residual content of oxygen by means of chemical reaction (oxides reduction). So the residual content of this element in the silicon (10^{16} at/cm^3) is lower than those obtained in CZ silicon (from 5.10^{17} up to $1,1.10^{18}$ at/cm^3).

I- Set up of the inductively coupled plasma treatment (5 MHz - 7 kW).

The RF plasma torch process is presented on fig. 1.

We increase the kinetic of silicon fusion when hydrogen is introduced in argon plasma [1, 2]. In order to separate the thermal and chemical effects of the hydrogen, we use helium which increases also the heat conductivity of the argon plasma but which is not able to produce Redox reactions.

The comparison of these two treatments Ar + H_2 and Ar + He in the same thermal conditions allows us to separate the physical and chemical roles on the silicon purification.

II- Influence of hydrogen in argon plasma on electronic properties of silicon.

Electrical properties of the final material are investigated by measurement of diffusion length by photoelectrochemistry [3].

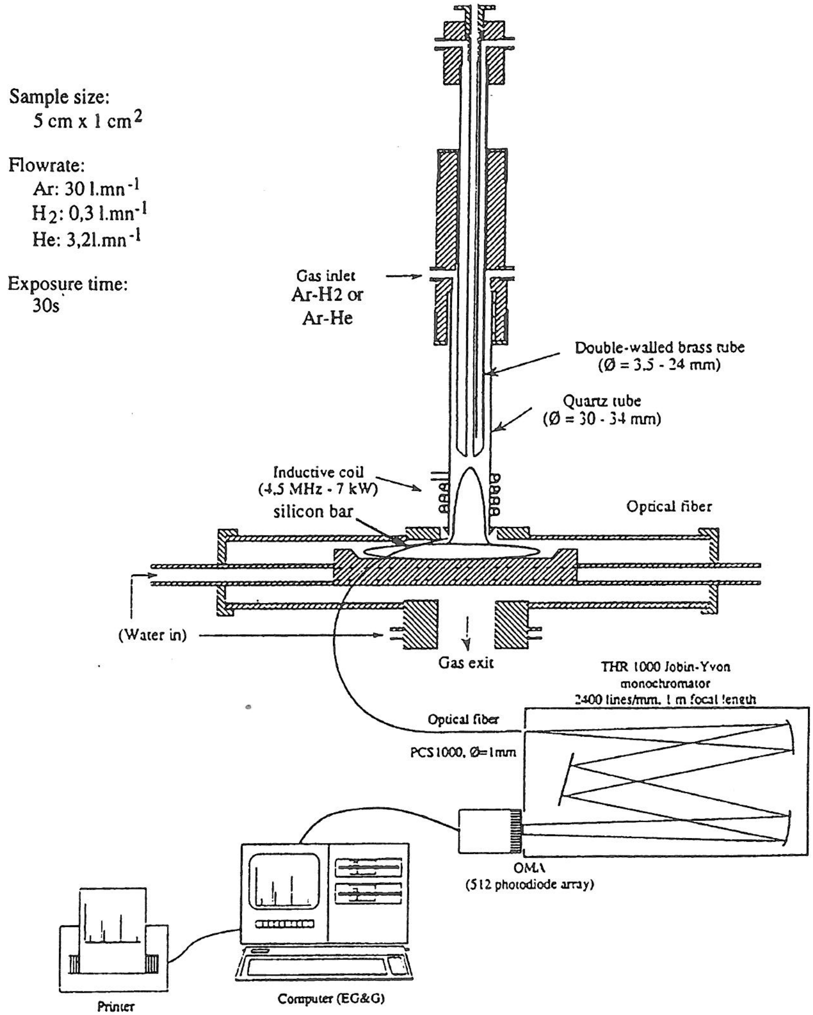
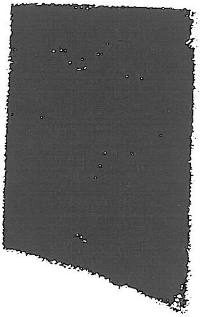


Fig. 1: Experimental set up for silicon purification (5 MHz - 7 kW).

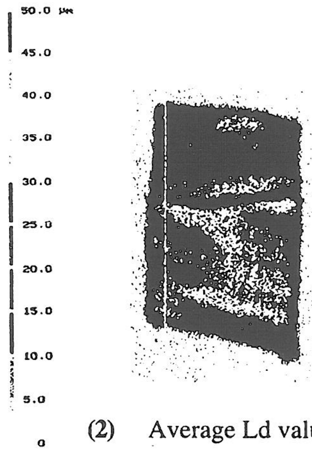
Silicon sample	Before plasma treatment Polix	After Ar plasma treatment with 1% of H_2	After Ar plasma treatment with 10,6% of He
Average diffusion length (µm)	50	70	75
Dislocations density (at/cm^3)	10^4	10^{6-7}	10^{6-7}

Table 1: Influence of the plasma treatment on the silicon diffusion length values and the dislocations density.

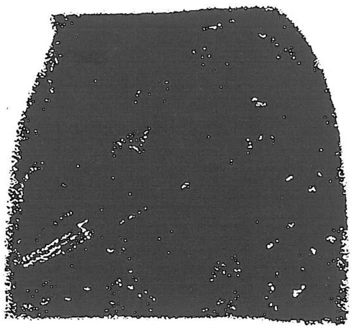
The results lead to increase diffusion length values of the sample treated by plasma (average Ld close to 70 µm) even if dislocation density of a such material is much higher (10^{6-7} at/cm^2) than for classical polycrystalline silicon (10^4 at/ cm^2) (Table 1). Nevertheless the crystallinity of this material is very heterogeneous and it produces large variations of diffusion length from 30 to 200 µm (Fig. 2).



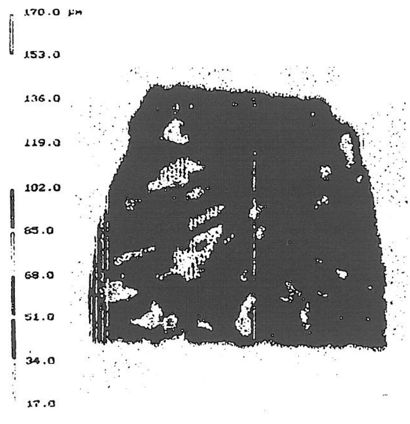
(1) untreated sample



(2) Average Ld value: 40 µm



(3) Plasma treated sample



(4) Average Ld value: 70 µm

Fig. 2: Macrography and 2D diffusion length mapping by photoelectrochemistry (c-Si Polix sample untreated: 1 and 2, and treated by ArH_2 plasma at 7 kW: 3 and 4).

The diffusion length measurement by photoelectrochemistry will give us the possibility to correlate both thermal and chemical effect of the plasma with the electronic properties of the material.

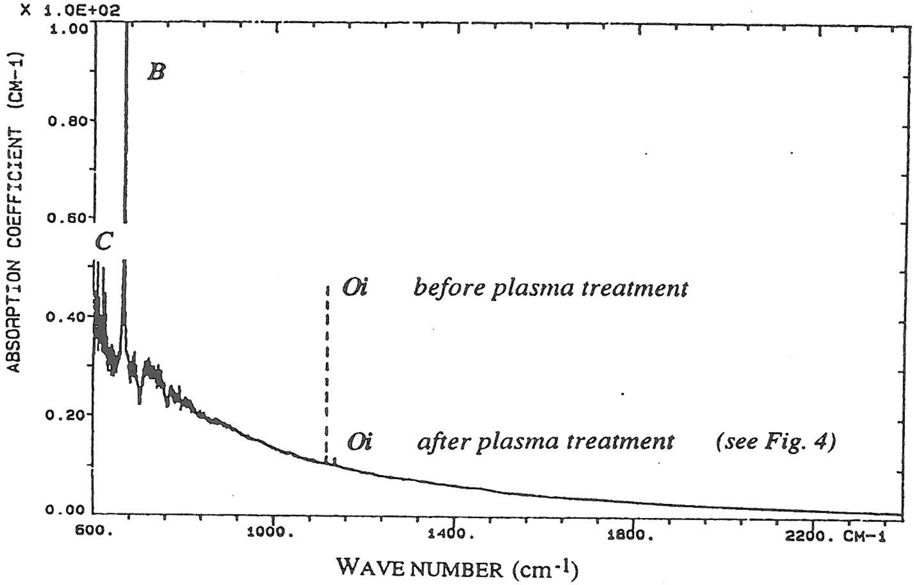


Fig. 3: FTIR (6K) spectra comparison between 2 Polix silicon samples untreated (dotted line) and treated by Ar + 1% H_2 plasma 6,44 kW (static fusion, gas flow 30 l/mn).

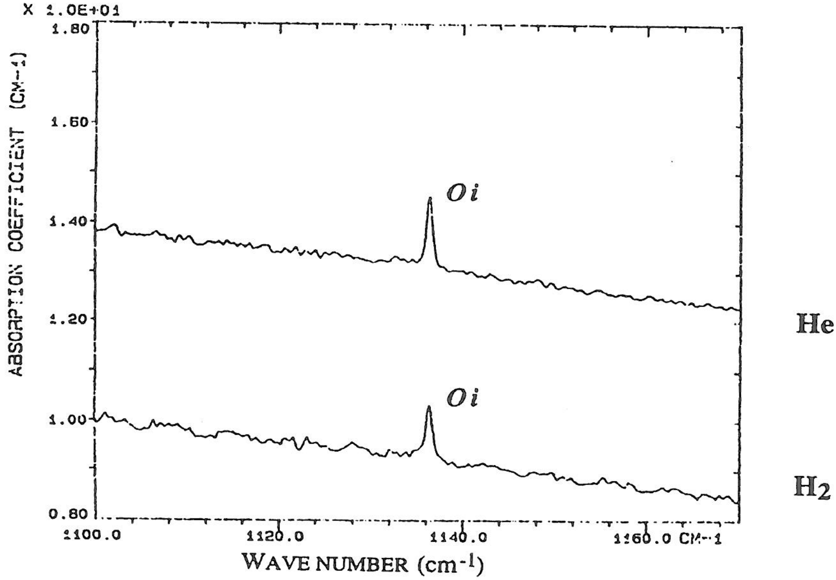


Fig. 4: FTIR (6K) spectra comparison between 2 Polix silicon samples treated by Ar + 1% He, and Ar + 1% H_2 plasma 6,44 kW (static fusion).

III- Ultimate elimination of oxygen in silicon by plasma technique.

a- Determination interstitial oxygen content in silicon.

After a plasma treatment Ar-H_2 the FTIR analyses at low temperature (6 K) show that the interstitial oxygen content is much more lower than in the starting silicon (from 3.10^{17} at/cm^3 down to 10^{16} at/cm^3) (Fig. 3).

The FTIR spectrum band of Si-O-Si at 1136 cm^{-1} is registrated at a temperature of 6 K. Starting from standard curve on which absorption coefficient of 1 cm^{-1} corresponds to $0{,}84.10^{16}$ at/cm^3 of interstitial oxygen atoms, we can conclude that the oxygen content of the raw material (3.10^{17} at.cm^{-1}) decreases up to $1{,}3.10^{16}$ at.cm^{-1} with helium and 10^{16} at.cm^{-1} with hydrogen (fig. 4). The FTIR spectra confirm also a decrease of boron and carbon content in the silicon after plasma treatment.

b- Determination of the total residual oxygen content in plasma treated silicon.

In order to determine if interstitial oxygen is precipitated or really eliminated from silicon bar during hydrogenated plasma treatment, some measurements of total residual oxygen content in silicon before and after plasma treatment are investigated.

Table 2 shows results obtained by FTIR at 298K before and after RTA (Rapid Thermal Annealing) treatment of our silicon samples. This treatment consists on a RTA which allows to turn precipitated oxygen form into interstitial one. The rapid cooling down induces the quench of total residual oxygen into interstitial sites in silicon sample.

	FTIR 298K before RTA	**FTIR 298K after RTA**		**FTIR 6K**
	[O interstitial] at/cm³	*[O interstitial] at/cm³*	*% O precipitated*	*[O interstitial] at/cm³*
Before plasma treatment c-Si Polix	$3{,}15.10^{17}$	$3{,}4.10^{17}$	7,35 %	3.10^{17}
After plasma treatment Ar + 1% H_2	$< 5.10^{16}$	$< 5.10^{16}$	/	$1{,}3.10^{16}$
After plasma treatment Ar + 10,6% He	$< 5.10^{16}$	$< 5.10^{16}$	/	10^{16}

Table 2: Total residual oxygen content of silicon samples treated by hydrogenated thermal plasma.

These results confirm those obtained by FTIR. The elimination of residual oxygen in silicon bar during Ar/H_2 plasma treatment is obtained with a purification coefficient of 23 for the helium treatment and 35 for hydrogen treatment. Then the thermal effect of hydrogen on the elimination of the oxygen is predominant, nevertheless the chemical effect allows us to enhance the kinetic of purification: the evaporation of impurities oxides under the thermal effect of the plasma and the chemical reactivity of hydrogen by the formation of volatile impurities hydroxides see the main mechanism of oxygen residual elimination by ArH_2 plasma (fig. 5).

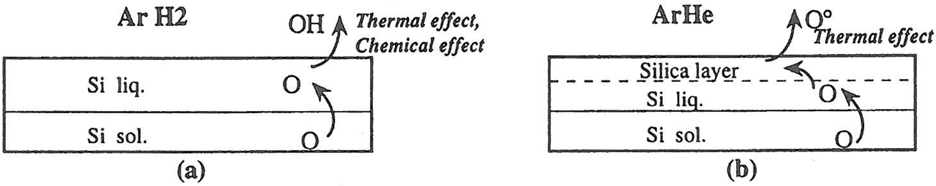


Fig. 5: Proposition of an oxygen elimination mechanism under ArH_2 and ArHe thermal plasma.

Furthermore measurements by SIMS and ERDA confirm that hydrogen content in the plasma treated silicon is lower than the detection limit (5.10^{15} at/cm^3). Nevertheless some residual hydrogen might passivate the crystalline defects (grain boundaries, dislocations, twins ...) and specially vacancies obtained after oxygen elimination. That can explain in our case the improvement of electronic properties by ArH_2 plasma. We can underline the silicon bars embrittlement and its hardness increase after hydrogenated plasma treatment.

IV. Conclusion and future.

In conclusion the experimental conditions of plasma technique (Thermal and solubility gradients) lead to shift the limit of purification of silicon bar. The elimination of silicon residual oxygen by hydrogenated thermal plasma explains the increase of the average diffusion length of minority carrier from the homogeneous value of 50 µm up to the heterogeneous one of 70 µm which the maximum is about 200 µm.

This result underlines the specificity of the plasma techniques for silicon refining while the monocrystal of silicon produced by CZ process contents residual oxygen of two orders of magnitude more.

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