Localization of reactive gases into inductive thermal plasma using solid target

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Abstract: In a process of silicon purification by an inductive plasma, the reaction rate between dissolved impurities (such as boron) and reactive gases (hydrogen and oxygen) depend on plasma parameters that have to be optimized. The present study uses an oxidation of solid targets (graphite or boron) to investigate those parameters, showing that the torch improves the reactivity, and that oxygen has to be injected into the outer flow of the plasma.

Keywords: Inductive plasma, thermal plasma process.

1. Purpose and motivation

A process using both inductive thermal plasma and electromagnetic stirring has been developed to purify silicon for photovoltaic application [1]. Reactive gases, oxygen and hydrogen, are added into argon plasma to volatilize impurities (mainly boron) contained in the liquid silicon impacted by the plasma jet. The reaction rate at the plasma-silicon interface depends on the reactive gas flow rates [2], but also on their distribution in the plasma jet, that can be modified by combining those gases with several argon flow provided to the torch at different inlets.

In this work, a solid target has been used in place of the molten silicon, in order to analyze the reaction rate distribution by looking at the carving depth after an hour of plasma treatment. The exhaust gas was also monitored on-line to determine the variation of the total reaction rate when a plasma parameter is changed.

The results are interpreted in terms of the quantity and distribution of the reactive species provided by the plasma. A graphite target has been used mainly to determine the distribution of reactivity for a simple oxidation mechanism, depending on the injection mode of oxygen. A boron target has been used to determine the sensitivity of the real purification reaction to the plasma parameters.

2. Experimental set-up and procedure

In a controlled atmosphere chamber, a double-flux inductive plasma torch with an injection probe is located above a solid target as shown in Fig.1. The target is heated by induction using a medium frequency coil (7kHz), across a cold crucible made of segmented copper.

The 40 kW torch at 3.4 MHz frequency is made of 8 sectors in copper with an inner diameter of 40 mm. The injector inner diameter is 6 mm.

The plasma torch is fed with three gas flows at flow rates given in Table 1. Each inlet can combine argon, oxygen or hydrogen, but the reactive gases (oxygen and hydrogen), cannot be introduced in the same flow for security reason.

Table 1: Global gas flow rates

<table>
<thead>
<tr>
<th></th>
<th>Outer</th>
<th>Intermediate</th>
<th>Inner</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow (l/min)</td>
<td>90</td>
<td>4</td>
<td>3</td>
</tr>
</tbody>
</table>

The solid target is either a graphite cylinder of diameter 200mm and height 20mm, or a boron plate of diameter 100mm and thickness 5mm placed upon a thick graphite cylinder to heat the boron by conduction. Two qualities of graphite have been used (ATJ and CS), the first have smaller particle size: 25 µm versus 750 µm. Both kind of graphite have low porosity around 15 % and their density is between 2370 and 2150 kg.m⁻³. The boron, pure at 99.9%, is made by sintering.

The surface temperature of the solid target is controlled with a pyrometer, and the pressure in the facility is regulated by the exhaust vane at 1.1bar. The exhaust gases are analyzed by ICP-OES in order to quantify oxygen (using its spectral line at 436.830 nm), carbon (247.857 nm) or boron (206.638 nm).

Before the beginning of the experiment, the entire chamber is flushed with argon to remove any trace of oxygen. The solid target is heated up to 1700 K for the graphite and 1400 K for the boron by induction. The argon plasma can be ignited either before or after the facility is back at
The atmospheric pressure (of argon). When the thermal equilibrium is reached, reactive gases can be added: oxygen for graphite studies and oxygen and hydrogen for boron.

From one experiment with graphite to another, the parameters that have been varied are the distance between the torch outlet and the graphite surface from 20 to 60 mm, the oxygen flow rate from 3.5 to 3.7 l.min⁻¹, the location of the oxygen injection: in the outer, intermediate or inner flow. For each experiment, the mass loss of graphite is quantified and the 3D attack profile is established with coordinate measuring machine. The continuous monitoring of the exhaust gases by ICP permits to control the stability of the condition and then that the progressive carving of the graphite surface doesn’t modify significantly the process.

For the experiment with the boron, the distance between the target and the plasma is 70 mm. Oxygen and hydrogen are introduced in the inner flow at a varying flow rate, in order to test the global reaction rate as a function of the gas injected.

3. Plasma reactivity

Graphite is easy to handle, to heat and provides only gaseous by-products, which eases the ICP-OES analysis in the exhaust line. To study the boron removal from molten silicon, a pure boron target is more relevant than graphite, and avoids the production of silica from the oxidation of silicon, that is a serious difficulty for quantitative analysis of the gas.

![Fig.2: Influence of plasma extinction on volatilization of (a) graphite and (b) boron targets.](image)

For both targets, the role of excited species was investigated by switching the plasma off during the experiment, while other parameters (gas fluxes, MF heating…) were kept constant. The plasma extinction leads to a decrease of 50% of the carbon signal upon the graphite target and a drastic reduction of 83% for the boron signal on the boron target (Fig.2). Thus the chemical reactivity is largely increased by providing excited species (atoms, radicals, ions) rather than a molecular mix of hot reactive gases. However, this evaluation of the reactivity of the plasma by ICP-OES is mainly qualitative with graphite, because the output gas contain some carbon monoxide and the bind energy of this molecule is very high 11.5 eV, so this gas is only partially dissociated in the ICP-OES.

The more drastic reduction of the volatilization rate with boron than with graphite can be explained by the injection geometry of reactive gases: for the graphite experiment of Fig.2, oxygen was injected in the outer flow whereas for boron experiments oxygen and hydrogen were introduced into the injector line. As explained in next section, the injection geometry plays an important role on the amount of excited species. An injection into the outer line leads to a lower degree of decomposition and excitation compared to the injector line, which explains the larger effect of the plasma extinction observed on the experiment carried out on the boron target compared to the graphite target.

The composition of injected gases plays also an important role on the volatilization of both graphite and boron. For graphite experiments, the reactivity of the plasma increases almost linearly with the total oxygen flow rate injected in the plasma. For boron experiments, the reactivity is low if only oxygen or only hydrogen is injected (Fig.3a), suggesting that the volatilized form is HBO, as for silicon purification [2]. With a sufficient amount of hydrogen, the volatilization is limited by oxygen: the boron signal is barely influenced while H₂O₂ varies from 1 to 6 (Fig.3b) whereas it was very low for H₂O₂—0 (see Fig.3a).

![Fig.3: Reactive gas fluxes influence on boron volatilization. Flows are given in l.min⁻¹.](image)

The mode of injection of the reactive gases has been studied with a carbon target, measuring the mass loss of the target during one hour. The results are given in the Table 2, where the efficiency is defined as the ratio of the moles of volatilized carbon (calculated from the mass loss) divided by the moles of atoms of oxygen injected during the whole experiment.

When oxygen is injected in the inner flow, the efficiency is higher because the reactive gas is present in the
hot zone of the plasma, and thus gives more reactive species such as atomic oxygen. The reduction of the distance plasma-target seems to increase the efficiency for the same reason (the reactive species have less time for the recombination). The graphite type (CS or ATJ) has no impact on the graphite reactivity with oxygen.

**Table 2**: Carbon volatilization efficiency at constant conditions

<table>
<thead>
<tr>
<th>O$_2$ injected in</th>
<th>Torch-graphite Distance (mm)</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outer flow</td>
<td>20</td>
<td>0.61</td>
</tr>
<tr>
<td>Outer flow</td>
<td>40</td>
<td>0.50</td>
</tr>
<tr>
<td>Outer flow</td>
<td>60</td>
<td>0.58</td>
</tr>
<tr>
<td>Auxiliary flow</td>
<td>40</td>
<td>0.47</td>
</tr>
<tr>
<td>Inner flow</td>
<td>40</td>
<td>0.89</td>
</tr>
</tbody>
</table>

4. Distribution of the reaction rate

The distribution of the reaction rate on the target surface is, after the mean reactivity, the second parameter to optimize for a boron removal process: as observed with liquid silicon [2] or with pure boron (see part 3.), the reaction can be stopped if there is too much oxygen, because of a slag formation. Therefore the torch conditions should be optimized to avoid high local concentrations of oxygen. Considering that the graphite reaction rate has been found proportional to the oxygen flow, this local limitation translates to a limit on the local volatilization rate of graphite. To maximize the total reaction rate without overwhelming that limit, one needs a reaction rate as homogeneous as possible on the whole target.

The distribution of reactivity has been analyzed using the carving depth of the graphite target, which should be directly proportional to the local concentration of “reactive” oxygen. **Fig.4** gives an attack profile obtained by a mechanical three-dimensional probing system.

The local maximum at the center of the disc is probably due to the stagnant point of the plasma flow gas. The attack profile is almost axisymmetric, except some regular “flower petals”, which corresponds to the sectors of the plasma torch.

**Fig.5** compares the etching profile (averaged on the whole surface to get a reactivity function of the radius) for the three different oxygen injection modes. The addition of oxygen through the injector (inner) results in a profile deeper and narrower. The oxygen has a high reactivity but it confined close to the axis of the discharge. At the contrary, when oxygen is mixed with the outer flow, the carbon volatilization is more regular but is less efficient. In this case oxygen is distributed in the whole plasma (giving a more homogeneous reaction rate) but some oxygen does not participate in the reaction (because it has not enough residence time to diffuse up to the target). For the auxiliary oxygen injection, the attack profiles are highly dependent on thetorch geometry.

5. Analysis and discussion

The total reactivity on a graphite target, which varies linearly with the amount of injected oxygen, can be explained by a diffusion-controlled reaction mechanism, which is commonly admitted as the predominant mechanism for graphite oxidation at 1500K<T<3500K [3]. Therefore the observed increase of reactivity when the plasma in switched on has to be linked to an increase of the diffusion rate in the boundary layer along the target. This could be explained by a higher diffusion coefficient of atomic oxygen compared to molecular hydrogen, to modifications in the fluid flow or in the gas properties in the outer part of the boundary layer. A numerical study is scheduled to get more insight into those phenomena along graphite and silicon targets. The increased efficiency when the oxygen is injected in the inner flow or when the target is closer to the torch (**Table 2** and **Fig.5**) are further indicators of this increased diffusion rate when the reactive gases are provided at a higher enthalpy.

For the boron target, in the temperature range 1300-1500°C, one can deduce the most probable products of reaction by looking at thermodynamic calculations (**Fig.6**): the main products of boron oxidation are a liquid slag (B$_2$O$_3$), and gaseous [HBO] and [BO]. Due to the low...
probability of reaction mechanisms involving several atoms at very low concentrations, complex gaseous species such as \((\text{BO})_2\) and \((\text{B}_2\text{O}_3)\) are excluded from the analysis (their formation kinetic rate would be very low, and incompatible with the high gas velocity). Consequently a simultaneous injection of oxygen and hydrogen is needed in order to form \([\text{HBO}]\), which is the most volatile boron containing species formed at temperature around 1500°C.

At a given temperature boron volatilization is maximized when both \([\text{HBO}]\) and \([\text{BO}]\) concentrations are high. That supposes an oxygen concentration high enough to maximize the two volatile species concentrations, but not too high in order to avoid the formation of the liquid oxide \((\text{B}_2\text{O}_3)\) that stops the reaction because this slag insulates the solid boron from the gaseous reactants. In our experiment the volatilization rate, as seen from the ICP-OES analysis of gaseous products, is almost linear with oxygen flow. For a high oxygen flow rate (~0.2 l.mn⁻¹) the experimental boron signal given by the ICP-OES monitoring of gases becomes unstable, which corresponds to the \((\text{B}_2\text{O}_3)\) droplets formation. Working at a temperature above 1450°C and with limited oxygen flow prevents the formation of liquid \((\text{B}_2\text{O}_3)\).

Considering the above limitation due to oxide layers, it is very important to control the reactivity distribution on the target, and therefore to control the distribution of reactive species impacting the boundary layer, and diffused up to the target. The reaction steps in silicon are certainly not the same as for graphite, but we observed that the purification rate in silicon, at constant gas flow rate and plasma conditions, seems not to increase with temperature [4]. It even decreases because of a reduction of the activity of dissolved boron when the temperature increases. Therefore, the purification reaction is probably not controlled by chemical kinetics, but rather by diffusion as for graphite, and the carving profiles presented in part 4 are good indicators of the reactivity provided by the torch.

Comparing the maximal depth of the carving profile obtained on graphite (Fig.5) to the efficiency indicating the total rate (Table 2) is thus a key point to choose plasma conditions to optimize the purification rate in silicon, avoiding the formation of a silica layer. Referring the ratio of the maximal depth for the profiles “inner” and “outer” of Fig.5, we could inject about 3 times more oxygen into the outer gas than into the injector, before arriving at the same maximum local rate (or local amount of reactive species). Even with a lower efficiency of oxygen injected in the outer flow (0.5 versus 0.9, see table 2), the injection of a triple flow of oxygen in the outer flow seems more interesting.

It has been verified on the silicon purification facility in our laboratory, that the maximum possible oxygen flow in the outer gas before the apparition of a silica layer, is about 3 times the maximum oxygen flow in the inner gas. The reactivity seems also better, and oxygen injection in the outer flow, as a result of this study, has been chosen for the industrialization of the process.

Acknowledgments

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References


![Fig.6: Total amount of boron in the gas phase (B-gas) and repartition between oxides.](image)