

Characterisation of the Doping of Porous Si with Er through Electrochemical Impedance Spectroscopy

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Rare earth doping of porous silicon is a very promising technique for the fabrication of all-Si light emitting devices at the 1.5 μ m wavelength. However, the lack of detailed knowledge of the mechanisms underlying the electrochemical Er doping (ECD) of the porous layers has, till now, been a major limitation for achieving the expected performances. As we will show, a key parameter of the Er ECD is the current density used during the process. We observed that using low current densities (LD), for equal amounts of transferred charge, leads to a significantly lower Er content in the porous layers with respect to using high current densities (HD). The threshold between "high" and "low" current densities depends on the sample characteristics, being related to the effective surface of the sample. The samples have been characterized by galvanostatic electrochemical impedance spectroscopy (GEIS) for various DC current densities. The GEIS results show a significant difference for LD and HD, and an additional semicircle in the Nyquist plot is visible for HD with respect to LD. This change in the ECD behavior is also observed when studying the applied voltage time evolution in constant-current ECD. With LD, a single transient is observed, while for HD a double transient ?? is observed, coherently with the appearance of an additional semicircle in the GEIS plots. Energy Dispersive Spectroscopy by Scanning Electron Microscopy (EDS-SEM) confirmed the significant difference in the Er content for LD and HD samples with equal total transferred charge, HD samples containing more than one order of magnitude additional Er atoms with respect to LD samples.

1. Introduction

The advance of microelectronics has significantly increased the demand for materials and devices to process more information at higher data rates. In this regard, the use of photons instead of electrons is a suitable solution, so that photonics, and particularly silicon photonics, has received great interest. Most of the required devices have been demonstrated in silicon, with one very significant exception: an efficient optical source. Actually, the lack of luminescence due to the indirect bandgap of silicon is a relevant drawback, so that despite its promising properties, no commercial silicon LED or laser is commercially available (Dragoman et al. 2000).

The search for cost-effective Si-based light emitting devices is of thus of particular concern. A possible solution is the doping of Si with rare earth metals to obtain light emission at 1.5 μ m (Reed and Kewell 1999). Doping with Erbium is one of the most promising techniques, since the trivalent erbium ion has an optical transition at 1535 nm, allowing access to telecommunications wavelengths (Kenyon, 2005).

Different forms of silicon have been investigated, including single crystal, polycrystalline, amorphous, nanocrystalline and porous Si: the last two may be considered as quantum-confined systems (Kenyon, 2005). Several techniques have been proposed to introduce optically active erbium into silicon, such as thermal diffusion, chemical vapor deposition and ion implantation.

In the case of Porous Silicon (PSi), Erbium may be introduced into the silicon matrix by electrically driven processes. The process starts from the electrochemically etching of the silicon substrate in HF electrolyte to make it porous, followed by the application of a cathodic potential in a solution containing erbium ions, promoting the diffusion of erbium into the porous silicon.

Although the large internal surface of porous materials makes the doping process quite complex, and thus worthy of investigation, most of the papers published in this field address the characterization of the doped layers more than the doping process itself, even though interesting luminescence properties have been shown (Bondarenko et al., 2005). A few papers have addressed the process, in particular the investigation by cyclic voltammetry of the Er diffusion process (Petrovich et al., 2000), on the effect of doping time (Najar et al., 2009), and on the evolution of the doping process as a function of several parameters (Mula et al., 2012a, 2012b).

Electrochemical techniques can also provide useful tools to understand the doping process through the use of appropriate surface-sensitive processes. Electrochemical Impedance Spectroscopy (EIS) is a very useful technique for porous materials (Carbó, 2009) and it has already been applied to study the oxidation of porous silicon in cyclic oxidation (Parkhutik and Matveeva, 2000).

The electrochemical doping of mesoporous silicon is a process where the role of kinetic effects in the electrochemical solution present within the PSi pores may be relevant and can be strongly influenced by the applied current and voltage. The effect of the operating parameters is important, in view of the optimization of the Er doping needed to obtain efficient light emitting devices.

In this study, the effect of the current intensity on the doping process has been investigated. In particular, the transient at the first stages of Er diffusion within the pores has been studied by GEIS.

2. Materials and methods

Porous Si layers were prepared by electrochemical etching in the dark of n^+ -doped (100) oriented crystalline Si wafers, with a resistivity in the 3-7 mOhm/cm range (Siltroni)x. The etching solution was HF/H₂O/Ethanol in a 15/15/70 proportion, following the procedure described elsewhere (Mula et al., 2012a, 2012b). Hydrofluoric acid solution (48 wt % in H₂O) and Ethanol (99.8%) were purchased from Sigma Aldric. The external area of the porous layers, that is the area of the Si wafer that has been etched for the formation of the porous layer, was 0.9 cm². A schematic of the cell used is shown in figure 1.

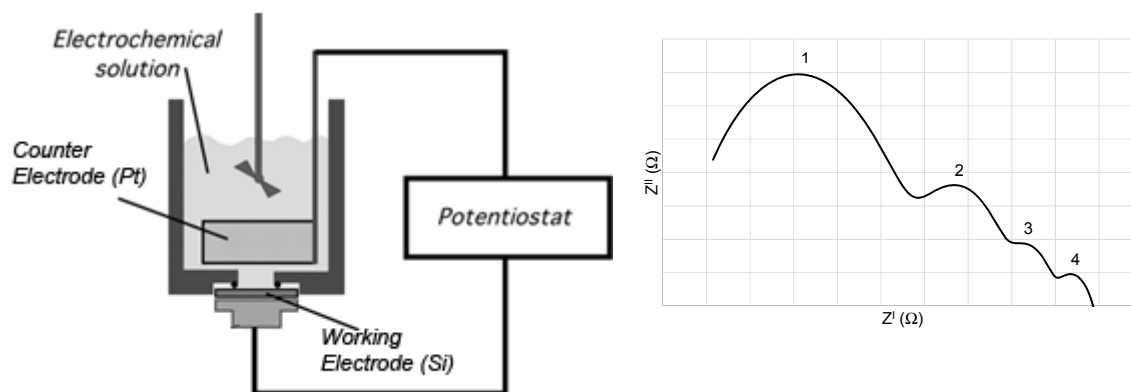


Figure 1: Sketch of the Electrochemical cell and example of a Nyquist plot

All electrochemical processes were performed using a PARSTAT 2273 potentiostat (Princeton Applied Research).

The Er doping of the Porous Si layers was carried out electrochemically using a 0.11 M solution of $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in Ethanol (EtOH) in a constant current process. The Er doping currents used were in the range 5×10^{-2} to 1 mA.

The EIS measurements and the Er doping process were always performed using the same electrochemical cell used for the Porous Si and the same Er solution. The measurements were made using a constant bias current of 0.1 mA, a frequency range from 100 kHz to 100 mHz and an AC amplitude of 10 μA . The results are reported as Nyquist plots, and the right hand side of Figure 1 shows an example, similar to those obtained in this work: the labeling of the circles will be used in the discussion of the experimental data.

3. Results and discussion

The general behavior of electrochemical Er doping performed at constant current, show a transient of potential at the beginning of the process, followed by a pseudo-steady state value. The final value of the potential depends, on the applied current. The study of the transient may be quite complicated in the case of porous Si, because of the large internal surface, but it can give crucial information, since it is related to the formation of the interfaces. Electrochemical Impedance Spectroscopy may give a good understanding of the initial stages of the doping process, in particular on the state of the interfaces. In this work, the impedance measurements were carried out under galvanostatic conditions.

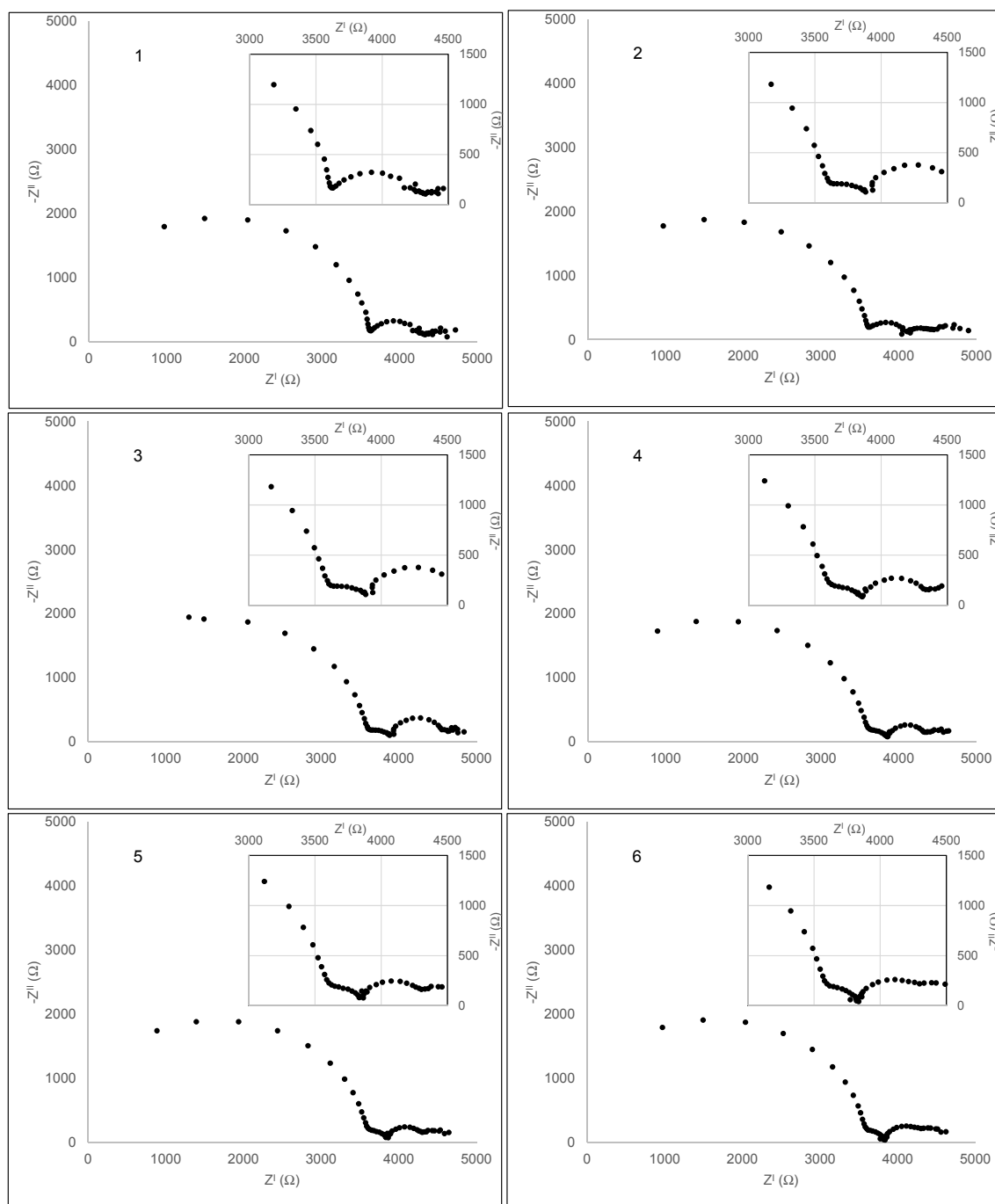


Figure 2. Evolution of Nyquist plots on a 5 μm -thick Porous Si sample during the doping process

The process was carried out at a variable number of time intervals, and the samples were characterised after each interval. In Figure 2 the evolution of the GEIS response is reported as Nyquist plot for a series of 6 cycles made in fast sequence with an interval between each measurement of about 10 seconds. A 5 μm -thick Porous Si sample was submitted to a constant current of 0,1 mA. The cycles reported in the figure are in sequence, from 1 to 6.

The main feature of this spectrum is the presence of four distinct semicircles which may indicate different contributions to the whole behaviour of the sample. The semicircles were numbered as shown in figure 1, for a clearer discussion.

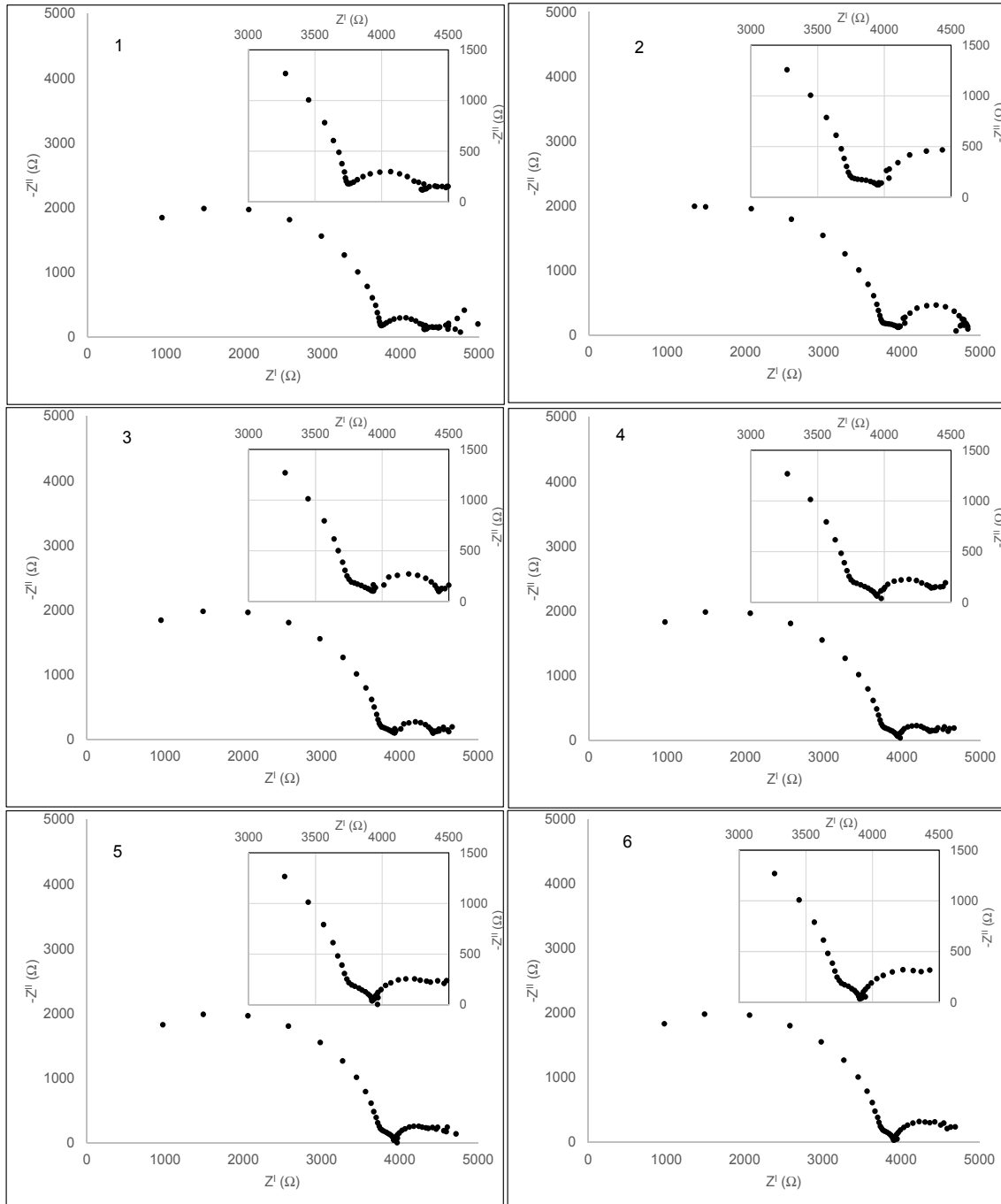


Figure 3. Evolution of Nyquist plots on a 2.5 μm -thick Porous Si sample during the doping process

As a first approximation, under the conditions of constant current adopted in this work, charge transfer mainly controls the rate of the doping process (Mula et al., 2012a).

Under this assumption and considering that each GEIS cycle corresponds to the same amount of charge passed through the electrochemical cell, during each cycle a constant amount of Erbium is transferred to the Si sample. We can then assume that the sequence of GEIS cycles may be read as a kind of step by step doping-process.

The high frequency semicircle (denoted as 1 in figure 1) remains unmodified throughout the process, while the second progressively moves towards higher frequencies until it is half covered by the first semicircle.

The third semicircle (see Figure 1 again for the numbering) shows an interesting behaviour. This feature is almost absent in the first measurement and rapidly develops becoming quite significant on the GEIS spectra, reaching its maximum visibility around the fourth cycle. For later cycles a fourth, low frequency, semicircle becomes progressively significant and tends to merge with the third one. This behaviour is fully reproducible, qualitatively and quantitatively.

In order to understand how this behaviour depends on the particular experimental configuration, on the total transferred charge or on the transferred charge per unit developed surface, we performed the same kind of measurement under the same conditions, but using samples with half the thickness. If the observed behaviour would depend on the transferred charge the GEIS will follow the same behaviour as that depicted in Figure 2. In contrast, if the behaviour depended mainly on the transferred charge per unit internal surface, the signal should scale according to the sample thickness, which should be directly proportional to the internal surface.

Figure 3 reports the results obtained for a series of GEIS measurements performed under the same operating conditions adopted for the results in Figure 2 but on a Porous Si sample half the thickness. The first result to be noticed is that the behaviour of the spectra in Figure 3 is analogous to that of Figure 2, with four separated semicircles evolving as the GEIS cycles proceed. However, if we compare each cycle with the cycle with a double ordinal in Figure 2 they are strikingly similar: cycle 2 of Figure 2 and cycle 1 of Figure 3 show identical behaviour with a quite small third semicircle. The maximum amplitude of the third semicircle is observed in the cycle 4 for Figure 2 and in cycle 2 for Figure 3. This comparison can be made for each spectrum with the same result. This may indicate that from its very beginning the Er doping process is essentially dependent on the transferred charge per unit internal surface.

Given the presence of the four semicircles and the fact that their presence appears to be a constituting feature of the Er doping process of Porous Si, each semicircle can be tentatively assigned to a distinct process occurring at the Si surface.

The first semicircle, at the high-frequency side, stays unmodified in all cases and can be attributed to the response of the bulk Si, which is not affected by the doping process. The second semicircle may be interpreted as the response of the porous layer.

In the Er-doped samples, the second semicircle progressively merges with the first semicircle; this may be explained by the fact that the doping process will progressively hinder the response of the Porous Si inner surface due to the changes induced in its electronic and chemical properties by the accumulation of Er atoms. The doping process may also increase the electrical conductivity of the Porous Si layer: if this is the case this, in turn, will lower the time constants of the charge transfer process, that will then become closer to those of the bulk Si, so merging the two responses.

The third semicircle in the spectra of Figure 2 and Figure 3, almost not present in the first GEIS cycle, expands rapidly in later cycles and then decreases again. The fourth semicircle is at the lower frequencies and increases continually with the GEIS cycles.

We attribute the third semicircle to the effects of phenomena in the liquid phase near the Porous Si surface, mainly to the formation of Er^{3+} concentration gradients, which may be relevant in the first cycles. The response of these gradients can be masked by other phenomena, evidenced by the fourth circle, as the number of cycles increases.

To interpret the last semicircles, it is worth noting that, during the electrochemical Er doping of Porous Si using an ethanolic solution of Er salts, the formation of a jelly-like deposit within the pores and on the surface of Porous Silicon has been observed, which showed the characteristic of lanthanide hydroxides (Petrovich et al, 2000). This deposit, much denser than the original solution, may dramatically reduce the diffusion rate of Er^{3+} . Similar results were obtained also in a previous work, in which Porous Si samples with different thickness were utilised, and characterized through GEIS within a frequency range from 100 kHz to 100 mHz and AC amplitude of 10 μA (Mula et al, 2014).

4. Conclusions

The early stages of constant current Er doping of n⁺-type Porous Si layers were characterized by Electrochemical Impedance Spectroscopy under galvanostatic conditions. Results show an in series process, mainly controlled by the resistance to the Er transfer. In particular, a new resistance appears after some cycle: we suggest that this can be attributed to a jelly-like deposit, containing Er, which interferes with the electrochemical doping process. Moreover, the formation of the jelly-like deposit seems unaffected by changes in the sample thickness.

This dependence found on samples of different thicknesses shows that higher current intensities lead to higher amount of Er within the porous structure, the charge transferred during the process being the same.

Further work is in progress to correlate the response of GEIS analyses with the photoluminescence emission of erbium doped porous silicon.

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