

## Electrochemical study of ultra-thin silicon oxides

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This paper is devoted to the electrochemical investigation of ultra-thin wet silicon oxides growth. Chemical silicon oxides are generated during wet processes of the wafers in oxidizing media such as SC1 (NH<sub>4</sub>OH, H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O) and SC2 (HCl, H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O) solutions. The build up kinetics of SC1 and SC2 Si oxides was checked mainly by electrochemical impedance spectroscopy<sup>1</sup>.

On both p- and n-type silicon, the open circuit potential (OCP) showed a quite identical shift towards more positive values versus time, while the oxide was growing up in the oxidizing solution. The polarization resistance was observed to increase simultaneously. These results were assigned to a common property of n- and p-Si substrates regarding their chemical reactivity.

The oxide was modelled as a dielectric layer making a SIE capacitor (semiconductor/insulator/electrolyte). Electrochemical impedance spectroscopy showed different diagrams (figs 1 and 2), obtained respectively with p- and n-type Si in SC1 solution. Nyquist plots obtained at OCP, in the dark, at room temperature, indicated a gradual increase of the overall impedance, reaching a limiting value after about 3h30. The regeneration of the solution did not change significantly the impedance diagram, suggesting that an equilibrium regime, corresponding to equal rates of oxide growth and dissolution, was obtained. The different shape of Nyquist plots for n-Si is only due to the appearance of the depletion layer characterized by a second RC loop in the high frequency range as the substrate potential gets more positive. A symmetrical behaviour can be obtained with p-Si samples by applying a negative bias potential.

In alkaline SC1 solutions the oxide layer showed a non negligible permeability to ions, a property attributed to the acido-basic ionization of the Si-OH groups. The same oxide, in an acidic HCl solution resulted in a tenfold higher resistance. For this reason, the oxide growth rate in SC2 was extremely slow (fig. 3) leading to ten fold higher resistance values than in SC1. In fig. 3, one diagram concerns a bare H-Si surface in pure HCl solution. Upon addition of H<sub>2</sub>O<sub>2</sub> a sudden drop of polarization resistance appears followed by a gradual increase of the impedance representing the hindered access of reactants to the Si surface by the growing oxide layer.

Results lead to mechanisms which permitted to determine the etching rate of Si substrates under the SC1 oxide layer, and to deduce a growth of oxide islands in SC2 solutions. ATR spectroscopy confirmed the different oxide structure and growth mechanisms in acidic and alkaline oxidizing solutions.

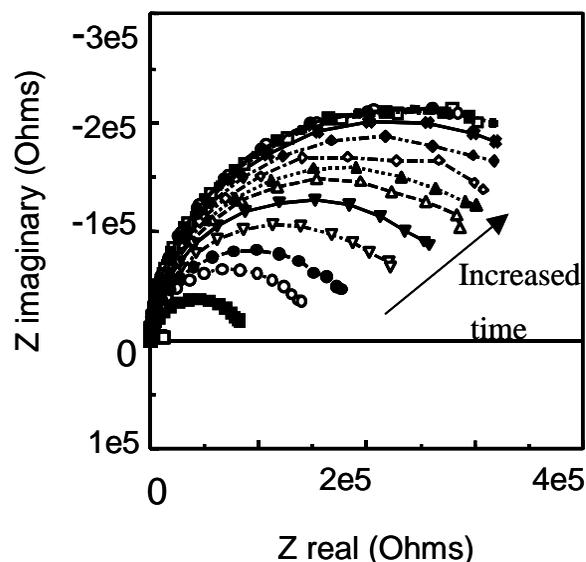


Figure1: Impedance plots of p-Si in SC1 solution

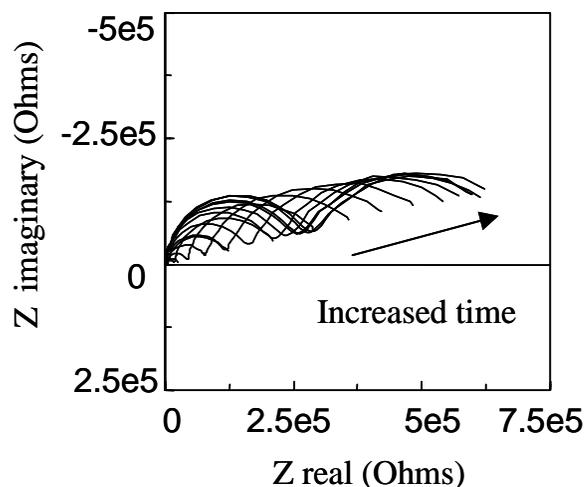


Figure 2 : Z plot evolution of n-type Si in SC1.

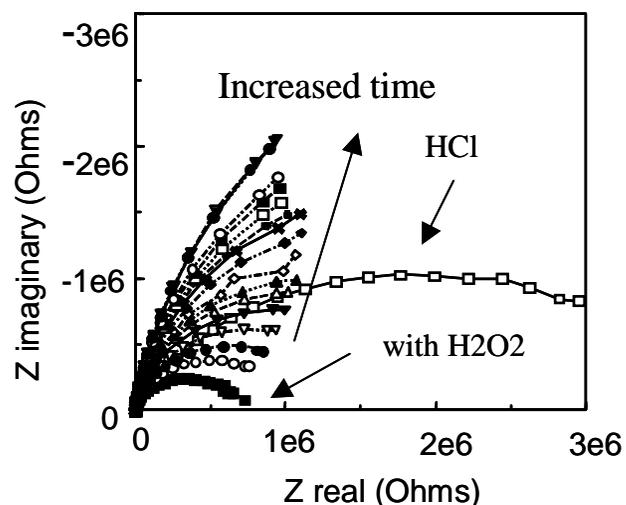


Figure 3 : Nyquist plots of p-Si in SC2 as a function of immersion time.

### References:

[1] V. Bertagna, R. Erre, F. Rouelle, D Levy, S. Petitdidier, J. Sol. State Electrochem. (in press) 2001.