

ANALYSIS OF THE PEAK CURRENT OBSERVED DURING ANODIC DISSOLUTION OF Si IN HF SOLUTIONS

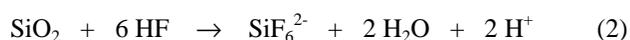
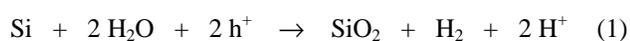
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The voltammogram for the anodic dissolution of n-Si under strong illumination in water/ethanol/HF solutions shows a characteristic peak current (i_{ps}). In fact, it is observed for p-type Si in the dark and for n-type Si under strong illumination.¹⁻⁷ At potentials lower than the potential of i_{ps} , porous Si is formed, while at higher potentials electropolishing is observed. The height of the peak is the same in both cases, and depends only on the temperature, the concentration of fluoride species in solution and the hydrodynamics. However, the relation between i_{ps} and these parameters is the subject to some discussion.

In this study⁸, the influence of temperature, HF concentration and rotation rate on the photo-anodic dissolution of a n-type Si rotating disk electrode in water/ethanol/HF solutions has been investigated. It has been found that the peak current was under mixed kinetic/diffusion control. A first analysis of this current using a simple Koutecky-Levich equation resulted in kinetic and diffusional currents comparable to values found by other authors. The reaction order for the kinetic current was a non-integer, again in agreement with what was found by others. However, for kinetically determined results, a non-integer reaction order is physically not very meaningful. Furthermore, it precludes the Koutecky-Levich equation, which is only valid for first order reactions.

To shed some light on this discrepancy, the overall reaction taking place at the current peak was split up into two reactions: the anodic oxidation of Si to an oxide and the chemical dissolution of this oxide by HF:



The dissolution reaction was found to be second order in HF concentration (see Fig. 1). A Koutecky-Levich-like equation for a second order reaction was derived. Combining this with the reaction for the anodic oxidation resulted in an equation that described the peak current as a function of the rotation rate of the electrode and the bulk HF concentration at different temperatures:

$$X^2 + \frac{D}{6k_2^{1/2}\delta} X - \frac{D}{6\delta} [\text{HF}]_b = 0$$

in which
$$X = \left(\frac{2F}{i_{ps}} - \frac{1}{k_1 p_s} \right)^{-1/2}$$

The peak current was analysed according to this equation. A good fit over almost three orders of magnitude was

obtained between the calculated and the experimental currents (see Fig. 2).

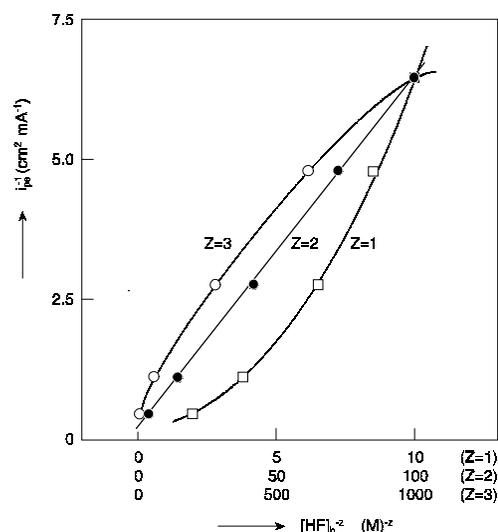


Fig. 1. i_{ps}^{-1} as a function of $[\text{HF}]_b^{-2}$ for three different values of z (1, 2 and 3) in the kinetically determined regime.

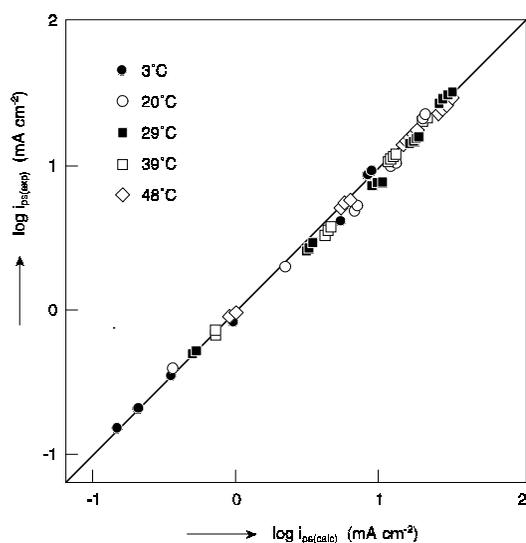


Fig. 2. Comparison of the experimental values of the peak current, $i_{ps(\text{exp})}$, with the calculated values, $i_{ps(\text{calc})}$, for every HF concentration, rotation rate and temperature examined.

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