Electrodissolution of p-Ge in Aqueous NaOH.
Steady-state and Impedance Investigations.

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The research on anodic dissolution of Ge has been very active in the period in which technology was interested in this material as the core of semiconductor-based devices[1-3]. Since the decline of interest for Ge preceded the advent of modern frequency response analysis techniques, no thorough impedance investigation is available in the literature. Besides having fundamental interest, this investigation may be a useful basis to study the electrochemical behavior of $Si_{1-x}Ge_x$ alloys which are important in many current technological applications.

We have considered Ge electrodissolution in alkali (pH 12-13). The j-E curve of Fig. 1 shows, on sweeping the potential from the negative limit in a positive direction, the onset of anodic current with a Tafel region, then a current plateau and finally a steep increase of current with potential. The plateau current is proportional to the OH^- concentration in solution and to the square root of the rotation rate, a typical Levich behavior. Considering that the oxidation reaction involves 4 electrons per Ge atom[2,3] (in this case mostly holes h^+ from the valence band), the observed current plateau corresponds to consumption of about 5 OH^- per Ge atom, according to the reaction scheme

$$Ge + 5\,OH^- + (4-\lambda)\,h^+ \rightarrow HGeO_3^- + 2\,H_2O + \lambda\,e^-$$

which is consistent with the fact that $HGeO_3^-$ is the predominant Ge species in solution at the given pH.

Figure 2 shows two typical impedance spectra recorded at potentials well negative to the diffusion plateau region. They consist of a high frequency capacitive loop, associated with the space charge, merged with a loop due to charge transfer resistance and double layer capacitance; at lower frequencies, besides a diffusion loop visible at –0.4 V but not at –0.5 V, two additional loops are detected, whose nature changes from inductive to capacitive upon increasing the potential.

A simplified version of the classical literature model proposed by Beck and Gerischer[2] has been used to calculate both the steady state and impedance behavior.
The proposed mechanism consists of three electrochemical steps: (i)oxidation, involving water molecules, of Ge(0) to dihydroxilated Ge(II) by two holes; (ii) oxidation by one hole of Ge(II) to Ge(III) in a step requiring OH^-; (iii) oxidative dissolution of Ge(III) proceeding either by hole capture or electron injection, leaving behind again a Ge(0) species. Calculations have been performed for the limiting cases of pure Depletion Layer Control and pure Helmholtz Layer Control[4]. Calculated impedance diagrams reproduce the essential features of the experimental ones.

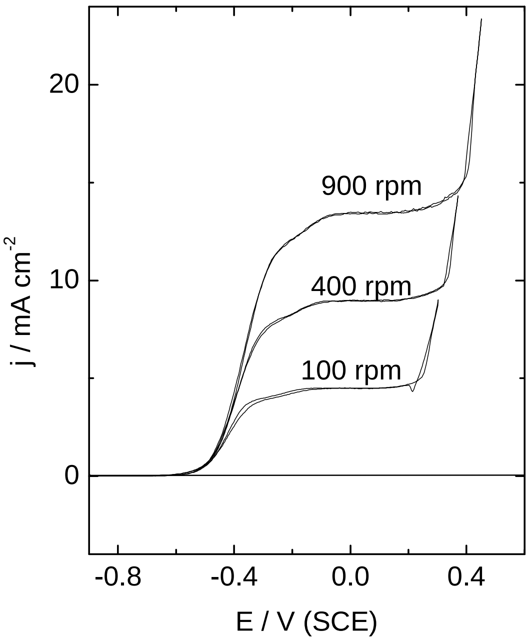

Figure 1. Cyclic voltammetry (20 mV s^{-1}) recorded at a RDE p-Ge electrode in 0.01 M NaOH, support electrolyte $NaNO_3$ (1 M total concentration).

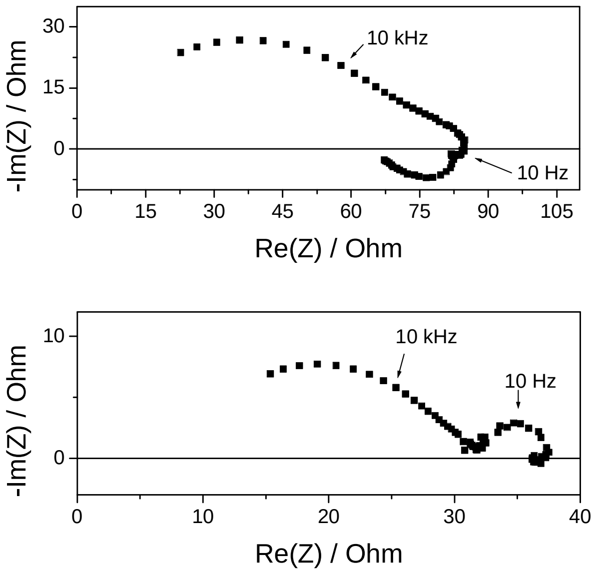

Figure 2. Impedance spectra recorded at a RDE p-Ge electrode (900 rpm) in 0.1 M NaOH, supporting electrolyte $NaNO_3$ (1 M total concentration). Surface area 0.28 cm^2. Applied potential: –0.5 V_{SCE} (top) and –0.4 V_{SCE} (bottom).

References

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3. P.J. Boddy, *J. Electrochem. Soc.* **111**, 1136 (1964).
4. D. Vanmaekelbergh and P.C. Searson, *J. Electrochem. Soc.* **141**, 697 (1994).