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# Structural Dynamics Study of Hydration Shells on n-Ge(100) in Aqueous Solution with Electrochemical Control

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**Abstract:** Structural changes of the hydration shell of surfaces in aqueous solution are studied using attenuated total reflection infrared spectroscopy, under different electrode potentials and consequently different states of the solid/liquid interface.

## Introduction

Structural changes of the hydration shell of surfaces formed in aqueous solutions are essential to many chemical, physical and biological phenomena. Attenuated total reflection infrared (ATR-IR) spectroscopy is a powerful tool to investigate the hydration shells, via their vibrational modes. It allows for the detection of adsorbed water molecules without interference from gas phase vapor.

Ge exhibits a potential-dependent transition from a hydroxide covered to hydrogen terminated, hydrophobic surface when the applied potential is sufficiently negative. Here, we present a study using electrochemical combined ATR-IR, of the vibrational spectra of water under different electrode potentials and consequently different states of the solid/liquid interface.

## Experimental setup

Trapezoidal Sb-doped n-type Ge(100) crystals with an incidence angle of  $60^\circ$  is used in our electrochemical cell. IR spectra were recorded on a Vetex70 Fourier transform IR spectrometer in region of  $800\text{-}4000\text{ cm}^{-1}$  in p-polarization with 400 scans.

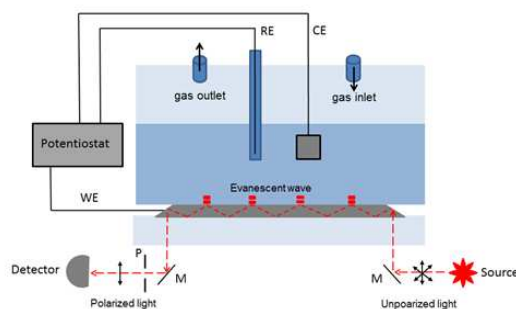


Fig. 1. Scheme of electrochemical and spectroscopic setup.

## Results

Under acidic condition, the germanium H-terminated surface is observed when polarization potential is below  $-0.45\text{VSCE}$  [1,2]. Figure 2 shows typical cyclic voltammograms (CVs) on Ge(100) in Ar saturated  $0.1\text{M HClO}_4$  solutions with pH value 1.4. At  $-0.3\text{ V}$ , a cathodic current peak is attributed to the change in surface termination from Ge-OH to Ge-H.

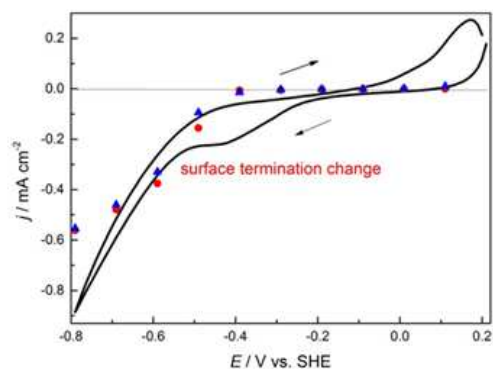


Fig. 2. Lines: CV of Ge (100) in Ar saturated 0.1 M HClO<sub>4</sub>. Arrows indicate the scan direction. The Horizontal dot line indicates zero current. Scan rate of CVs: 50 mV/s. Circles: Average currents during ATR-IR experiment in cathodic (red) and anodic (blue) direction.

The pH dependence of the occurrence of the Ge-H is further investigated by infrared spectroscopy. The potential window was set from 0.21 V to -0.79 V, before the hydrogen evolution takes place. Fig. 3 shows a series of ATR-IR spectra with potential control on Ge(100) in the range of 800-4000 cm<sup>-1</sup>. All spectra are collected in p-polarization with potential step pf 100 mV. The Ge-H termination gives a Ge-H stretching mode absorption at 1960cm<sup>-1</sup> in mid-IR region [2]. The absorbance signal at 1115 cm<sup>-1</sup> comes from the asymmetric Cl-O stretching mode of ClO<sub>4</sub><sup>-</sup> in solution [3,4]. There also shows the appearance and growth of OH bending (centered at 1640 cm<sup>-1</sup>) and stretching (centered at 3250 cm<sup>-1</sup>) modes [5,6] for Ge(100) surfaces under both decreasing and increasing electrode potentials, which can be interpreted as related to changes in the hydrogen-bonding pattern at the interface.

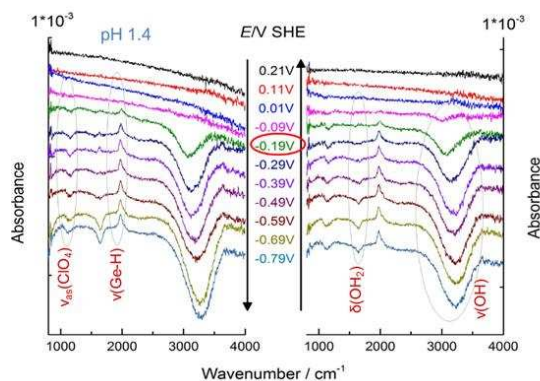


Fig. 3. ATR-IR spectra on Ge(100) in Ar atmosphere (electrolyte: HClO<sub>4</sub> pH 1.4) for p-polarization in direction of (left) decreasing potentials and (right) increasing potentials.

The bulk water effect is subtracted from real experimental data with reflcalc simulation, as shown in Fig. 4, to leave out only the interfacial water influenced spectra. The shoulder peak in region 3200-3700cm<sup>-1</sup> splits into two smaller distinct bands. The one centering at 3440 cm<sup>-1</sup> corresponding to the stretching modes of bulk intermolecular water absorbance. The peak centered at 3060 cm<sup>-1</sup> should be assigned to the highly structured ice-like water mentioned before, which is formed because of interfacial water molecules interacting with both Ge-H surface and other neighboring water in aqueous solution.

The new band appearing at 3640 cm<sup>-1</sup> under lower potentials (-0.59~-0.79V) is ascribed to free water molecules (molecules not associated in hydrogen bonding) directing OH bond to the Ge-H surface. OH stretching spectra qualitatively shows the presence of a dangling OH peak and a broad band with seemingly two components often labeled as the “liquid-like” and the “ice-like” bands. The existence of free OH groups helps to investigate the real time potential dependent movement through different phases occurring at the Ge/water interface.

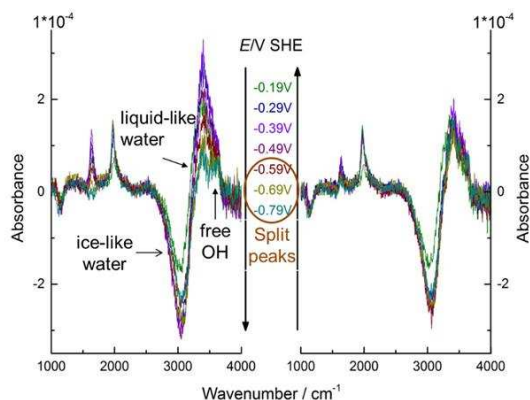


Fig. 4. Subtracted IR spectra for 0.1M HClO<sub>4</sub>(pH 1.4) electrolyte (subtract standard bulk water spectra from experimental water spectra).

There is a depleted water layer exists between water and the hydrophobic substrate, which produces a hydrophobic gap with potential dependent width. Negative applied potential leads to reduce water density and increase the gap width.

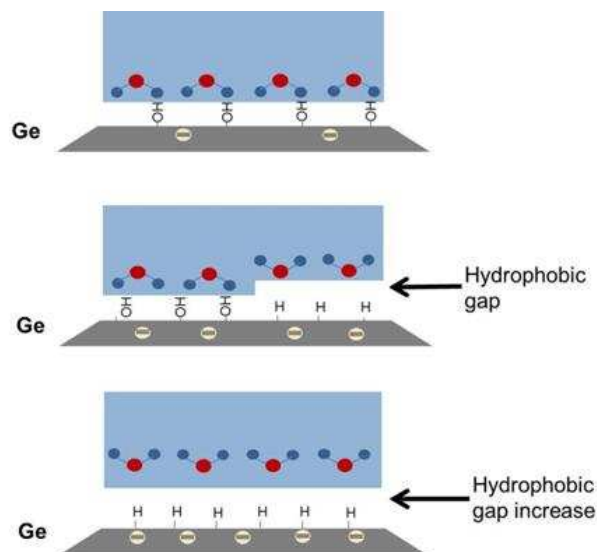


Fig. 5. Hydrophobic gap increase on Ge(100) in acidic electrolyte under Ar atmosphere in direction of decreasing potentials.

## Acknowledgement

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