Kinetics of Surface Reactions on n-Ge(111) studied by Different Transient Techniques
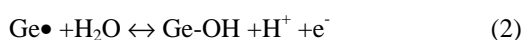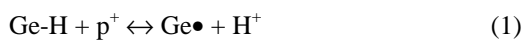
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In electrochemical systems the surfaces of covalent semiconductors such as Si and Ge are usually modified by adsorbed H or OH species with covalent bonding. These different surface states can strongly influence kinetics and mechanism of surface sensitive electrochemical reactions. In the case of Si the hydrogen terminated Si-H surface formed in HF/NH_4F solutions is stable in solutions with pH up to about 8 and above 14 at potentials more negative with respect to the open circuit potential. Under anodic polarization conditions, however, Si-H surfaces are irreversibly oxidized and passivated by SiO_2. On the other hand Ge surfaces can be reversibly modified to Ge-H or Ge-OH by cathodic or anodic polarization, respectively. In this work the dynamics of surface states of Ge are investigated.

Advanced pulse techniques allow the determination of i(t), q(t) and C(t) in a time range 1 µs < t < 1 ks [1]. In contrast to common impedance measurements, multi pulse techniques allow the determination of capacity in dependence on potential and time C(U, t) [2]. Obtained data can be analysed by the Mott-Schottky-model [3]. In this paper we present results on the kinetics of surface reaction on n-Ge studied by different pulse techniques.

Different surface states (Ge-OH and Ge-H) were found on n-Germanium [4]. These two surface termination can be controlled by potential (Ge-H at U < -0.2 V, Ge-OH at U > 0.1 V in 0.5 M H_2SO_4) (Fig. 1). The surface reaction $H_{ad} \leftrightarrow OH_{ad}$ is reversible and can be described by:

$$Ge\text{-}H + p^+ \leftrightarrow Ge\bullet + H^+ \qquad (1)$$

$$Ge\bullet + H_2O \leftrightarrow Ge\text{-}OH + H^+ + e^- \qquad (2)$$

Starting from Ge-H, the reversible reactions (1) and (2) were investigated by anodic pulse experiments. Fast surface states e.g. radicals were formed at relatively short times (t < 10 ms) due to the breaking of Ge-H-bonds (1). Then, OH-groups were generated and a Ge-OH monolayer was formed at polarization potentials U_P > 0.1 V and longer times (t > 10 ms) (2).

The formation of surface states and information about the potential distribution at the n-Ge/electrolyte interface were obtained by fast C(U)-measurements [2] and verified by simulations. The Mott-Schottky-analysis of fast C(U)-data yielded flatband potentials U_{fb} between -0.39 V (GeH) < $U_{fb}(\theta_{OH})$ < 0.045 V (GeOH). The potential drop is defined by (3) with $\Delta\phi_H$' = const and $\Delta\phi_{Dip}$ = f(q).

$$\Delta\phi = \Delta\phi_{SC} + \Delta\phi_H{}' + \Delta\phi_{Dip} \qquad (3)$$

The shift of flatband potentials yields a contribution $\Delta\phi_{Dip}$ of OH dipoles to the total potential drop $\Delta\phi$ at the interface. The reaction (1) and (2) was also studied by cathodic pulse experiments starting from Ge-OH.

In a comparison between simulations and fast C(U)-measurements we obtained an additional potential drop in Ge due to existing surface states $\Delta\phi_{SS}$. The potential drop in the semiconductor depends on the number of surface states N_{SS}. The total potential drop is defined by (4) with two time dependend terms.

$$\Delta\phi = \Delta\phi_{SC}{}' + \Delta\phi_H{}' + \Delta\phi_{Dip}(t) + \Delta\phi_{SS}(t) \qquad (4)$$

We studied the kinetics of the surface reaction as a function of U and θ. For $\theta_H = \theta_{OH} = 0.5$, i.e. $\Delta\phi_{Dip}$ = const., the equilibrium potential $U_0 = 0.01$ V, the exchange current density $i_0 = 0.1$ µAcm^{-2} and the transfer coefficient $\alpha = 0.7$ were determined from Tafel-plots.
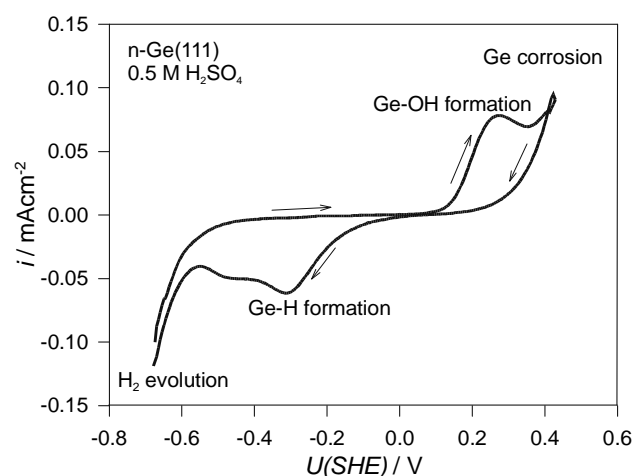

Fig. 1: Cyclic voltammogram of n-Ge(111) in 0.5 M H_2SO_4

[1] M.M. Lohrengel in Electrochemical and Optical Techniques for the Study and Monitoring of Metal Corrosion, Kluwer Academic Publishers, 1991, p 69
[2] U. König, M.M. Lohrengel, J.W. Schultze Ber. Bunsenges. Phys. Chem. 91 (1987) 426
[3] U. König, J.W. Schultze in Interfacial Electrochemistry, Marcell Dekker, New York, 1999, pp 649 -672
[4] H. Gerischer, A. Mauerer, W. Mindt Surf. Sci. 4 (1966) 440