ELECTROCHEMICAL ENGINEERING OF SI SURFACES BY ORGANIC LAYERS

P. Hartig[1], J. Rappich[1] and Th. Dittrich[2]

[1] Hahn-Meitner-Institut, Abt. Si-Photovoltaik, Kekuléstr. 5, D-12489 Berlin, Germany;
[2] TU-München, Physikdepartment E16, James-Franck-Str. 1, D-85748 Garching, Germany

Electrochemical deposition of organic molecules can be performed via radical formation from diazonium salt solutions at cathodic potentials [1]. The electron transfer from silicon (Si) to the diazonium ion, i.e. the radical formation, is monitored by current-time measurements at fixed potential. Fig. 1 shows the current transients for atomically flat (a) and rough (b) hydrogenated, and rough oxidized (c) p-Si(111) at -1.2 V vs. Au in 0.01 M H_2SO_4 during deposition of 4-nitrobenzene. The current increases strongly when the diazonium salt solution is added to the supporting electrolyte and decreases exponentially during the first 30 s of deposition on atomically flat hydrogenated p-Si(111), see fig. 1(a). The exponentially decay of the current density can be explained by a decrease of the amount of Si-H adsorption sites during the deposition of the first 4-nitrobenzene monolayer. At longer times, the current decreases with $t^{-1/2}$, indicating a diffusion limited current flow. Diffusion coefficients for different deposited benzene molecules on atomically flat Si(111) surfaces are shown in tab. 1 as calculated from the current decay. The values of the diffusion coefficients are in the order of 10^{-8} cm^2s^{-1}. These values are in between the diffusion coefficient of organic molecules in organic solids (10^{-10} cm^2s^{-1}) [2] and organic liquids (10^{-5} cm^2s^{-1}), respectively [3].

In contrast to atomically flat Si surfaces, rough hydrogenated Si(111) surfaces show only an exponential decay of the current. The current decreases not below the initial value of current density in 0.01 M H_2SO_4. The current density during deposition of 4-nitrobenzene on p-Si(111) covered with a native oxide does not decay substantially and thick organic layers are formed.

Deposition of an organic monolayer is only possible on atomically flat hydrogenated Si(111) surfaces due to the inhibition of current transfer across a closed benzene monolayer with well ordered organic molecules. The perpendicular orientation of organic molecules to the p-Si(111) surface results in a change of the band bending (ΔU_{PV}) with respect to the hydrogenated surface. ΔU_{PV} depends on the strength of the dipole moment of the organic molecule and is measured in-situ by the photovoltage technique. Fig. 2 shows ΔU_{PV} as a function of the calculated effective dipole moment perpendicular to the Si(111) surface for various benzene compounds. There is a linear dependence between ΔU_{PV} and the effective dipole moment of the benzene molecule. That means that the band banding of the p-Si(111) surface is tunable by the choice of the appropriate organic molecule deposited on the surface [4]. Photoluminescence measurements show no correlation between the amount of nonradiative recombination centers on the H-terminated Si(111) surface and the deposited first monolayer. Si-C bonds are no nonradiative recombination active centers as measured under UHV conditions [5].

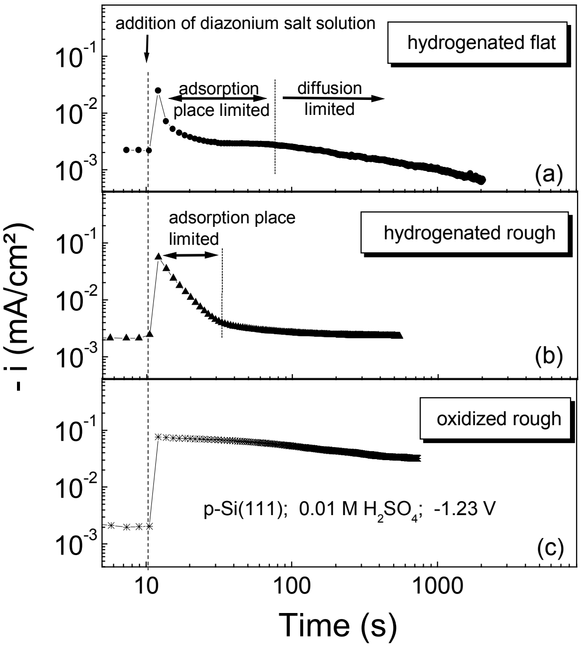

Fig. 1: Current transients for atomically flat (a) and rough (b) hydrogenated, and rough oxidized (c) p-Si(111) at -1.2 V vs. Au in 0.01 M H_2SO_4 during deposition of 4-nitrobenzene (addition of 5 mM diazonium salt solution at 10 s).

compound	D (10^{-8} cm^2s^{-1})
bromobenzene	20
nitrobenzene	5
methoxybenzene	5
dichlorobenzene	0.5

Tab. 1: Diffusion coefficients obtained during electrochemical deposition of different benzene compounds on p-Si(111).

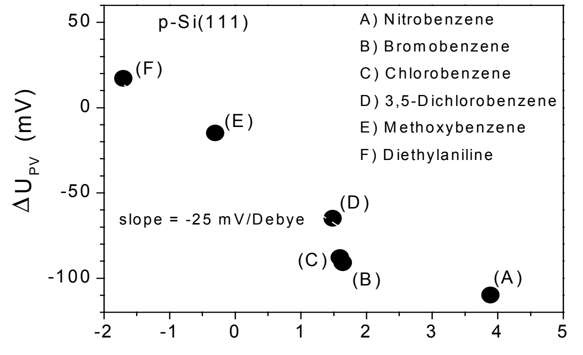

Fig. 2: Change of the photovoltage (ΔU_{PV}) as a function of the calculated effective dipole moment perpendicular to the Si(111) surface for various benzene compounds.

[1] C.H. Villeneuve, J. Pinson, F. Ozanam, J. N. Chazalviel, and P. Allongue, Mat. Res. Soc. Symp. **451**, (1997) 185

[2] R.P. Podgorsek and H. Franke, Appl. Phys. Lett. **73** (1998) 2887

[3] Grimsehl- Lehrbuch der Physik (Teubner Verlagges. 1990), Vol. **4**, 371

[4] P.Hartig, T. Dittrich, and J. Rappich, J. Electroanal. Chem. **524-525** (2002) 120

[5] T. Dittrich, T. Bitzer, T. Rada, V. Yu. Timoshenko and J. Rappich, Solid-State Electronics **46** (11) (2002) 1863-1872