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Field - dipole interactions in L-cysteine-thiolate self assembled at p- and n-GaAs(100) electrodes

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ABSTRACT

L-cysteine-thiolate monolayers spontaneously self-assembled on p- and n-GaAs(100) electrodes have been investigated by electrochemical impedance spectroscopy in H_2SO_4 solutions. On p-doped samples a potential-induced reversible proton transfer occurs within the L-cysteine-thiolate layer during both forward and backward potential scans; in contrast, on n-doped samples it is observed only in the reverse scan. The XPS data and the fractal analysis of the AFM images point to the field - dipole interactions operating distinctively in the L-cysteine-thiolate layer formed at p- and n-doped semiconducting substrates as the origin of the observed difference. The interaction of this small but highly polar molecule with the electrostatic field driven by the diffuse distribution of the excess charge in the semiconductor subsurface region both in equilibrium and under polarization conditions turned out to play a key role in determining the optimal orientation of the two polar groups. The latter one seems to be a prerequisite for the potential-induced internal proton transfer.

1. Introduction

L-cysteine, one of the two natural thiol-containing amino acids, has both the ability to build self-assembled layers on solid surfaces and the possibility to exchange protons with the environment. These properties recommend it not only as an excellent bio-linker for various bio-applications (such as preparing new biocompatible materials or exploring biomolecular recognition processes) but also as a very attractive molecule for fundamental studies on the electronic and electrostatic interactions at electrified interfaces (such as the influence of the multifunctionality and field-effects on the molecular self-assembling process). As for any amino acid, the amino and the carboxylic functional groups of the L-cysteine-thiolate layer formed at electrode surfaces readily ionize and, depending on pH, neutral, cation, anion and zwitterion species may coexist partially or all together. Filimon et al. [1] reported that the protonation/deprotonation of the amino and carboxyl groups is reversible and entirely controlled by the pH of the contact solution.

This small but complex organic molecule has also a large dipole moment regardless of its pH-depending electrical state (neutral, cation, anion or zwitterion) [2]. The electrode charge should have, therefore, a major impact on the configuration of the adsorbed species and thus, on the interactions developed within the adsorbate layer. Damaskin and Frumkin [3] pointed out a long time ago that due to their large dipole moment, zwitterions formed by ϖ-amino acids are oriented with the carboxyl-head toward the positively charged electrode surface and with the amino- head toward the negatively charged ones. Moreover, Brolo et al. [4] reported that L-cysteine adsorbed on Ag with the protonated amino group facing the surface undergoes a potential-induced reorientation at more negative potentials.

We have recently reported that monolayers of L-cysteine-thiolate self-assembled on p-GaAs(100) electrodes exert a complex molecular control over their electrochemical behavior in solutions with different pH [5]. The combined XPS and AFM investigations performed before the EIS measurements revealed that pH values lower than 5.5 influence mainly the zwitterion self-organization as a compact layer resulting in lower surface passivation against the further oxidation, whereas pH values higher than 5.5 bring conformational changes due to the proton exchange with the electrolyte solution. A reversible potential-induced proton transfer occurring inside the L-cysteine layer accompanied by concurrent charge minimization both in the organic overlayer and the semiconductor depletion region was observed regardless of pH. Still, the XPS and AFM data obtained after the EIS investigations

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pointed out chemical and structural changes depending on the pH conditions.

L-cysteine has three potential binding centers represented by the amino, carboxylate and sulfhydryl functional groups, which may be equally involved in a chemisorption bond with a metal or semiconductor substrate. Our XPS results showed that only the thiol head is involved in the chemisorption bond of the self-assembled monolayers of L-cysteine-thiolate spontaneously formed at p-GaAs(100) in aqueous solutions (pH 4.25). However, since the doping type is decisive for the sign of the semiconductor space charge region, this might influence the nature of the chemical bonding as well. At open circuit, the Fermi level is usually higher than the redox potential of the electrolyte for an n-doped semiconductor electrode, whereas that of the p-doped semiconductor it is lower. Electronic equilibrium is thus reached by an electron transfer from the electrode into the solution resulting in a positively charged space charge region of the n-doped semiconductor and from the solution to the electrode creating a negative charge in the space charge region of the p-doped semiconductor. Therefore, the highly polar cysteine species are expected to be oriented with the group $-COO^-$ towards a positively charged surface as it is the case of n-doped semiconducting substrates, whereas at the negatively charged surfaces of the p-doped ones, the $-NH_3^+$ moiety should be titled to the substrate surface. Besides, as the applied potential shifts not only the semiconductor Fermi level but also the bending of the band edges and hence the charge of the depletion region, this is expected to be accompanied by changes in the orientation of the adsorbed dipole.

In this paper we report a combination of in-situ (Electrochemical Impedance Spectroscopy, EIS) and ex-situ (Atomic Force Microscopy, AFM, and X-ray Photoelectron Spectroscopy, XPS) data concerning the electrochemical behavior of the L-cysteine covered p- and n-doped GaAs(100) electrodes at low pH (0.45). Density Functional Theory, DFT, calculations have also been performed in order to get a deeper insight into the chemical interaction between this organic molecule and the semiconductor substrate.

2. Experimental

The working electrodes were prepared from Zn doped ($p = 1 \div 1.1 \times 10^{19}\ cm^{-3}$) and Si doped ($n = 3 \div 3.8 \times 10^{18}\ cm^{-3}$) GaAs(100) wafers from the AXT Company (GEO Semiconductor (UK) Ltd.) mounted on Teflon holders with the rear part and the edges sealed by epoxy resin. Back ohmic contacts to the sample were provided by alloying with Au–Zn alloy (p-doped) and Au–Ge–Ni alloy (n-doped) using the thermal evaporation technique. The L-cysteine-thiolate film was formed by immersing the semiconductor substrates in 2.5 mM aqueous solution (pH 4.25) for 20 h. The GaAs samples were previously degreased in acetone, washed with deionised water (Direct-Q 3UV System, Millipore) and properly etched (p-GaAs(100) in H_2SO_4:H_2O:H_2O_2 (5:1:1) and n-GaAs(100) in H_2SO_4:H_2O_2:H_2O (3:1:1) and 6 N HCl). L-Cysteine (99 % purity) was purchased from Sigma-Aldrich and used without further purification.

EIS investigations were performed with an IM6 Zahner frequency analyzer. Impedance spectra recorded between 0.3 and 3×10^5 Hz were fitted using the ZView software (Scribner Associates Inc., Southern Pines, N.C.) and a conventional equivalent circuit (consisting in a serial connection of the electrical contributions of the semiconducting electrode and the organic overlayer) that was previously described [5]. Measurements took place in well deaerated 0.1 N H_2SO_4 solutions (pH 0.45) in the dark and at room temperature.

AFM measurements were carried out in non-contact mode with an XE-100 from Park Systems using sharp tips (<8 nm tip radius) of PPP-NCHR type from Nanosensors™ of 125 μm length, 30 μm width and 42 N/m spring constant/~330 kHz resonance frequency. The AFM instrument is equipped with flexure-guided, cross-talked eliminated scanners which have an "out of plane motion" of less than 2 nm over a 50 μm scan distance. In order to increase the measurement resolution, we have used the so-called "low voltage mode" for the voltage which controls scanners. This improves the lateral resolution of the X-Y scanner up to 0.076 nm and allows a vertical resolution of the Z scanner of 0.025 nm. At least 2-3 samples were prepared and tested for each condition provided that no discrepancy was detected. All samples have been scanned at two different imaging scales: $8 \times 8\ \mu m^2$ and $2 \times 2\ \mu m^2$.The Image Processing Program (XEI – v.1.8.0) developed by Park Systems was used to represent the AFM micrographs in the enhanced color view mode.

The fractal analysis of the AFM images was carried out with the height correlation function and the variable length scale methods, which were previously described [6].

The fractal dimension is computed in the height correlation function method [7] from a log-log curve of the height correlation function, G (r), versus the square correlation distance, r.

$$G(r) \equiv < [h(x) - h(\vec{x} + r)]^2 >, G(r) \sim r^{2(3-D)}, r << L, \quad (1)$$

where h is the height of each surface point of coordinate, x, and L is the size of the analyzed area. If self-similarity is obeyed, the log-log curve is a straight line with the slope 3-D, where D is the fractal dimension. The domain, where the log-log curve is a straight line defines the self-similarity range.

With the same end in view, the variable length scale method [8] uses the log-log curve of the root mean square deviation of the surface, $R_{q\varepsilon}$, versus the interval size (ε):

$$R_{q\varepsilon} = \frac{1}{n_\varepsilon} \sum_{i=1}^{n_\varepsilon} \sqrt{\frac{1}{P_\varepsilon} \sum_{j=1}^{P_\varepsilon} Z_j^2} \quad (2)$$

where z_j is the jth height variation from the best fit line within the interval i, and p_ε is the number of points in the interval ε. The domain where the curve is a straight line is the self-similarity range and the slope of the straight line gives the roughening exponent H. The fractal dimension D can be calculated as $D = D_T - H$, where D_T is the topological dimension of the embedding Euclidean space ($D_T = 3$ for surfaces).

A SPECS spectrometer equipped with a monochromatized Al Kα-anode radiation source operated at 400 W was used for the XPS investigations. The wide survey and detail spectra were taken for all the samples examined in the AFM measurements, at pressures lower than 2×10^{-9} mbar and at a pass energy of 100 eV and 20 eV, respectively. The binding energy scale was referenced to the C1s peak at 285.00 eV. Peaks were resolved with the SDP v7.0 software (XPS International) and assigned by considering reliable literature reports. The spectra were fitted using Voigt peak profiles and either a linear or a Shirley background depending on the background shape.

DFT calculations were performed with the Gaussian 03 package [9], using the B3LYP functional set [10] and the 6-31G** basis set [11]. Simulation of the aqueous solution took into account the Polarizable Continuum Model (PCM) [12] within the Self-Consistent Reactions Field method (SCRF) [13]. The Gabedit (V2.4.8) graphical interface [14] was used to represent the optimized geometries.