



In situ study of nitrobenzene grafting on Si(1 1 1)-H surfaces by infrared spectroscopic ellipsometry

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ABSTRACT

The binding of nitrobenzene (NB) molecules from a solution of 4-nitrobenzene-diazonium-tetrafluoroborate on a Si(1 1 1)-H surface was investigated during the electrochemical processing in diluted sulphuric acid by means of infrared spectroscopic ellipsometry (IR-SE). The grafting was monitored by an increase in specific IR absorption bands due to symmetric and anti-symmetric NO₂ stretching vibrations in the 1400–1700 cm⁻¹ regime. The p- and s-polarized reflectances were recorded within 20 s for each spectrum only. NB molecules were detected when bonded to the Si(1 1 1) surface but not in the 2 mM solution itself. Oxide formation on the NB grafted Si surface was observed after drying in inert atmosphere and not during the grafting process in the aqueous solution.

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1. Introduction

In situ investigations of Si surfaces during (electro)chemical modification are of high interest to understand reaction schemes and process steps. Beside the characterization of the grafted material such studies provide information about intermediate surface species during processing and species post-formed after the treatment in solution. Grafting of organic molecules is a widely used process to functionalize Si surfaces with respect to nanopatterning, passivation, changing electronic properties like work function and band bending [1–12] or to introduce the possibility of biochemical sensing by means of biocompatible Si substrates [13,14]. Functionalization of Si surfaces is performed by radical induced reactions. In this work, diazonium type molecules are used for which radicals can be produced via electron transfer from Si surface to the molecules. However, little is known about the processing itself which preferably can be investigated by means of in situ studies. So far, in situ investigations of such radical mediated reactions have been performed e.g. by in situ photoluminescence [3,5], photovoltage [3,5] and current-voltage techniques [2,15]. These experiments provide information on the charge transfer induced radical forma-

tion, and on electronic properties like interface recombination and charging of the organic/c-Si interface. No information about molecular orientation, the amount and type of surface species, and the role of side reactions, e.g. silicon oxide formation, can be extracted directly from these types of measurements. Therefore, cross-checking with a material specific method is desirable.

In this paper, we present in situ IR-SE experiments using a single reflection of a polarized IR beam [14,16] to investigate the grafting process of nitrobenzene (NB) from 4-nitrobenzene-diazoniumtetrafluoroborate (4-NBDT) in 0.01 M H₂SO₄ solution. Material specific absorption bands of the grafted 4-NB and the interface oxide species are discussed for different spectra recorded during and after the grafting process.

2. Experimentals

Fig. 1a shows the electrochemical cell used for the in situ IR-SE measurements. The working electrode (WE) was a float-zone Si wedge ((1 1 1) oriented side to the electrolyte, p-doped, 2–4 Ω cm) contacted and fixed by a steel frame on the backside (M). The electrolyte was pumped through or was exchanged by a sliding pump and silicone hoses via two in/out Teflon tubes (I/O) during the measurements. A Pt ring and Au wire served as counter (CE) and reference electrode (RE), respectively. The cell had a volume of about 5 ml and a quartz window (QW) permitted illumination with light. The electrode potential was controlled by a potentiostat (Bank PGS 88). The Si wedge was H-terminated prior

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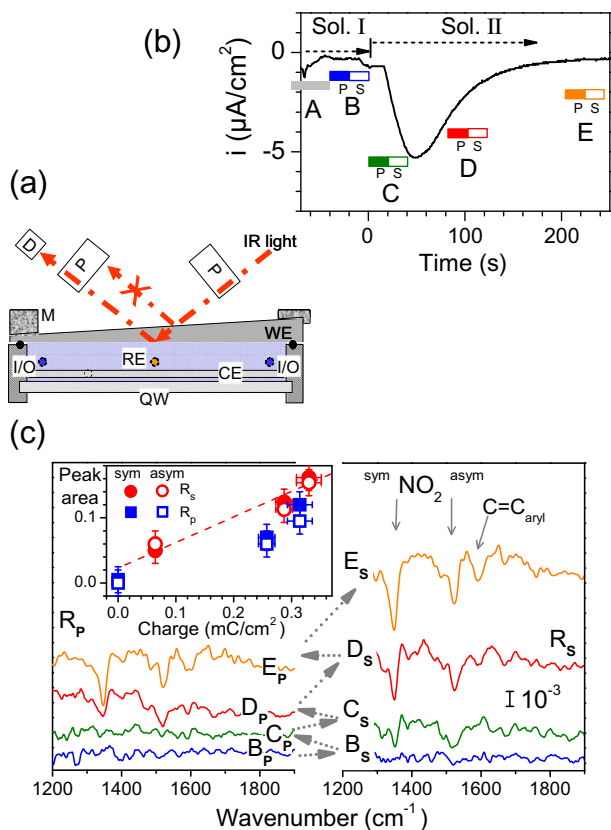
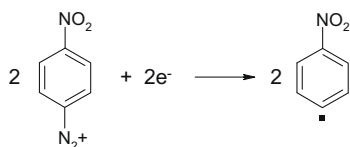


Fig. 1. (a) In situ electrochemical cell: top view with principle of IR light pathway, P: polarizer, D: detector (for details see text), (b) time behavior of the current flow through the Si wedge at -1.4 V in 0.01 M H_2SO_4 (solution I) and after exchange for the 4-NBDT containing solution (II), (sol. II = sol. I + 2 mM 4-NBDT). (c) Referenced in situ measured R_s (■) and R_p (□) spectra at time positions B, C, D and E; the horizontal bars reflect the time needed for recording s- and p-polarized reflectance spectra which is 20 s for each only. The spectrum of the Si wedge in 0.01 M H_2SO_4 served as reference (position A). The inset in (c) shows the integrated peak area of the symmetric and asymmetric vibrations of the NO_2 groups in the NB film for the s- and p-polarized reflectance as a function of the electric charge Q .

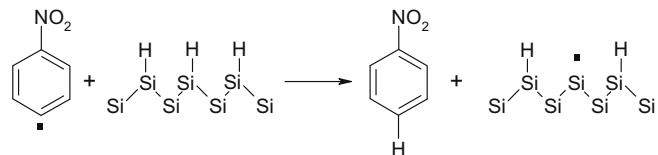
to the experiments by use of standard Piranha oxide/ NH_4F (40%) treatment [17]. The 4-NBDT salt was cleaned by several re-crystallization procedures. The IR-SE measurements have been performed with an ellipsometer externally attached to a Bruker Vertex 70 Fourier Transform spectrometer [18,19]. The ellipsometric parameters $\tan\Psi$, Δ and the p- and s-polarized reflectance spectra (R_p and R_s) were determined from intensity measurements at four polarizer azimuths, while the analyzer was fixed at 45° or $90^\circ/0^\circ$ with respect to the plane of incidence. The time to record R_p or R_s was slightly below 20 s at 64 scans, using a mercury-cadmium-telluride (MCT) detector. No Δ spectra have been recorded for this limited numbers of scans because of the not sufficient signal to noise ratio.

The reaction scheme for grafting of NB from the 4-NBDT onto $\text{Si}(1\ 1\ 1)$ is as follows [2]:

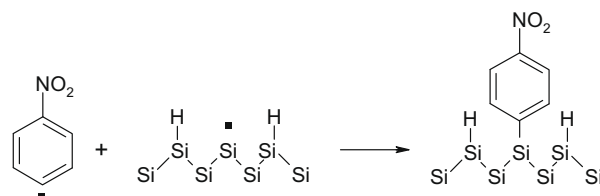
Start reaction (radical formation):



Si surface activation (formation of intermediate Si dangling bonds by abstracting H-atom):



Si surface reaction (bonding of a radical to the Si dangling bond):



3. Results and discussion

Fig. 1b shows the time behavior of the current flowing through the Si wedge at a constant potential of -1.4 V in the 4-NBDT free 0.01 M H_2SO_4 solution (I) and after exchange for the 4-NBDT containing solution (II, sol. I + 2 mM 4-NBDT). The negative current peak after exchange of the solution (I) by (II) indicates the grafting process [4,20]. The referenced R_p and R_s spectra recorded at times B, C, D, and E are plotted in Fig. 1c, where the horizontal bars reflect the time for the p- and s-polarized state of the IR-SE measurements, respectively. There are no bands observed in the spectrum just before the exchange for solution (II). When the current starts to increase, new absorption bands at 1349 cm^{-1} and 1520 cm^{-1} arise due to symmetric and anti-symmetric NO_2 stretching modes from the grafted NB molecules [21]. These bands increase in intensity with ongoing time of grafting (R_s is measured after R_p as indicated by the arrows in Fig. 1c), indicating the formation of a NB film on the surface. Spectra recorded at longer times of processing show no distinct change in the IR peak intensities, i.e. the grafting process is completed when the current has decayed (position E).

To ensure that the IR-peaks between 1340 and 1600 cm^{-1} are due to grafted NB on the Si surface, we used another Si wedge covered by a very thin oxide layer (prepared in piranha solution) and measured the spectra in solutions (I) and (II) (see Fig. 2a), respectively. The referenced spectrum ($\tan\Psi_{\text{sol. (II)}}/\tan\Psi_{\text{sol. (I)}}$) shows no absorption peaks in the NO_2 stretching mode region. Obviously, the concentration of 2 mM 4-NBDT in the solution is too low to show an IR response. Therefore, the observed IR peaks in the 1340 – 1600 cm^{-1} region are due to the grafted NB molecules only (see Fig. 2b, $\tan\Psi_{\text{Si-NB/sol. II}}/\tan\Psi_{\text{Si-H/sol. I}} (= \tan\Psi_{\text{Pos. D}}/\tan\Psi_{\text{Pos. A}})$). The dashed and grey line in Fig. 2 represents the calculated spectrum using the following procedure. The transport of infrared radiation in the silicon wedge of the in situ cell is described by formulae (1). The incidence angles at the different interfaces were used as given in Refs. [14,16].

$$\rho_{\text{eff}} = \rho'_{\text{air/silicon}-59.2^\circ} * \rho_{\text{silicon/NB-layer}-13.8^\circ} * \rho'_{\text{silicon/air}-12.3^\circ} \quad (1)$$

with $\rho = \frac{r_p}{t_s} e^{i\Delta r}$ and $\rho' = \frac{t_p}{t_s} e^{i\Delta r}$, where t_p and t_s are the p- and s-polarized transmission coefficients, respectively. The measured spectra were simulated in an isotropic three layer model: silicon/NB-layer/water. A thickness of 2.5 nm, $n_\infty = 1.31$ and two resonances in the Lorentz oscillator model were used in the calculation of ellipsometric $\tan\Psi$ spectra for the NB-layer. In this model the dielectric function $\hat{\epsilon} = \epsilon' + i \cdot \epsilon''$ is calculated from the sum of harmonic

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