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LETTERS

Real-Time Electronic Monitoring of Adsorption Kinetics: Evidence for Two-Site Adsorption Mechanism of Dicarboxylic Acids on GaAs(100)

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We show that the chemisorption of dicarboxylic acids on GaAs (100) is described well by a two-site mechanism, in contrast to benzoic acid adsorption which fits to a one-site mechanism. We do so by using a novel electrical method for direct measurement of adsorption kinetics. In the method we measure the current through a GaAs/(Al, Ga)As-based device, where the bare surface between two contacts is used as the adsorption domain. The results, which are in agreement with FTIR absorption equilibrium data, are obtained in ambient notwithstanding the notorious instability of GaAs surfaces under such conditions. We conclude that these acids chemisorb on the GaAs surface and that binding is significantly stronger for the di- than for the monocarboxylic acids.

The reaction of organic molecules with semiconductor surfaces to form chemisorbed layers of molecules is a basic step in the process of semiconductor surface modification and in building of supramolecular architectures on semiconductor surfaces. As such there is great interest in understanding the process and in monitoring it in real time. The latter can be accomplished with several techniques, such as IR absorption, using FT-IR, for monitoring submonolayer concentrations.[1] A more sensitive method is the microbalance in which the frequency change of an oscillating crystal indicates the amount of material adsorbed.[2−4]

In the present work, we use the effect that chemical surface modification has on semiconductor electronic properties to follow the kinetics of adsorption of dicarboxylic acids onto GaAs (100) surface. We do so by monitoring the current through a special multilayered GaAs-based device, composed of insulating

outer layers and a doped inner one (Figure 1, inset) with adsorption occurring on one of the insulating layers between two metal contacts, which serve to measure conductivity.

Contrary to Si, GaAs surfaces do not have a passivating native oxide layer. Hence, it is possible to chemically modify the surface states, their charge, and thus the *internal* field in the space charge layer. This is in contrast to common Si-based chemical sensors, which are sensitive to an *external* field between the gate and a reference electrode.[5] Measurements of the so-called surface conductance of semiconductors use the same geometry[6] and have been used for identifying the adsorption of simple organic molecules on Ge.[7] In the present configuration much higher sensitivity to surface processes is achieved by having a semi-insulating (Al, Ga)As layer between the semi-insulating GaAs substrate and the doped GaAs layer. Because of the space charge in the doped GaAs layer, such a structure leads to a concentration of maximum electron density at a depth of 30−50 nm from the exposed surface.[8] Therefore,
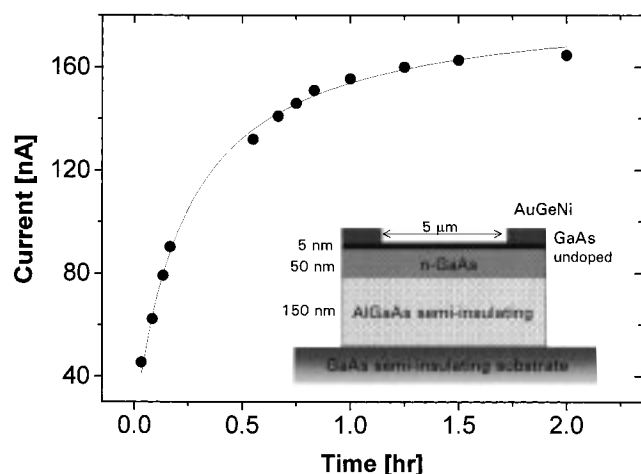
Figure 1. Current through the device shown in the inset, as function of time (circles). A potential of 200 mV was applied between the electrodes. The device was immersed in a 1 mM solution of DCDC in dry acetonitrile. The results from a calculation based on the TSLI model are shown as the solid line. (Inset) The GaAs-based device used in the present study. Adsorption occurs between the two Au−Ge−Ni electrodes, extending into the layers owing to alloying. The conducting path is in the n-GaAs next to its interface with the semi-insulating (Al, Ga)As layer.

small variations in surface charge lead to considerable changes in carrier concentration within the conductive layer.

The method's sensitivity, which depends also on the electronic carrier concentration in the semiconductor, is sufficient to determine the mechanism of the adsorption process. The results are compared to those obtained from direct IR absorption studies.

We and others have recently demonstrated that adsorption of a series of organic molecules on several semiconductors can affect their electronic properties in a controllable fashion, as it allows systematic change of their surface potential. We also reported IR evidence for the chemisorption of a series of simple benzoic acids on GaAs[9]. In this communication we use this sensitivity of GaAs to molecules absorbed on its *bare* surface, to control the resistivity of the above-described device.

We synthesized bifunctional organic molecules based on tartaric acid, disubstituted by *p*-cyanobenzoic acid, to provide the corresponding dicarboxylic acid (DCDC). This molecule has two sites that can bind to the surface.

The simplest descriptions of the adsorption kinetics of DCDC can be presented either by a one- or a two- site Langmuir isotherm.[10] The one-site Langmuir isotherm (OSLI) was reported for self-assembled silane on silicon[1] and thiols on gold.

For OSLI, the dependence of coverage on adsorption time is given by [11]

$$\theta = \frac{1 - e^{-\alpha\beta t}}{\alpha}, \quad \text{with} \quad \alpha = 1 + \frac{1}{KC}, \quad \beta = \frac{k_a C}{N_0}, \quad \text{and}$$

$$K = \frac{k_a}{k_d} \quad (1)$$

where k_a and k_d are the rate of adsorption and desorption, respectively, C is the concentration of the adsorbate in the solution, and N_0 is the surface adsorbate concentration at full coverage.

In the case of a two-site Langmuir isotherm (TSLI), the coverage dependence on the time is

$$\theta = \frac{1 - e^{\delta t}}{\alpha - \frac{e^{\delta t}}{\alpha}} \quad \text{where} \quad \delta = \beta\left(\alpha - \frac{1}{\alpha}\right) = \frac{k_d}{N_0}\left(1 + \frac{K_a C}{K_a C + 1}\right)$$

$$(2)$$

In the case of steady state

$$KC = \frac{\theta}{(1 - \theta)^2} \quad (3)$$

Figure 1 presents the drain-source current measured through the GaAs device for a constant bias voltage, as a function of time, after inserting it into a 1 mM DCDC solution in acetonitrile. The change in the current could be fitted only to the TSLI model (eq 2). From the fit, the equilibrium constant, $K = K_a/K_d$, for the adsorption−desorption process was found to be $(3.3 \pm 1.5) \times 10^6$ M^{-1}.

To verify these measurements, the adsorption was also monitored via attenuated total reflectance (ATR) FTIR. Owing to experimental difficulties in performing "real-time" *kinetic* measurements, the GaAs ATR crystal was inserted into solutions of different concentrations of DCDC for 1 h, until *equilibrium* was reached. The crystal was then removed from the solution and rinsed, and the amount of adsorbed molecules was measured with a Bruker IFS 66 FTIR spectrometer. The relative coverage, θ, was deduced from the absorption peaks corresponding to the presence of the C=O, C−O, and CO$_2^-$ functional groups.[9] The equilibrium constant extracted from this study, based on eq 3, is $(3 \pm 1) \times 10^6$ M^{-1}, in excellent agreement with the value derived from our kinetic measurements. This is significantly larger than the 2×10^4 M^{-1} value, found for the one-site/molecule adsorption (OSLI) of simple benzoic acids on GaAs (100).[9]

Surprisingly, the results given here show a linear relation between the number of adsorbed molecules and the device response. This can be understood by realizing that

(1) Conductivity is via free electrons in the "channel" between the doped GaAs and semi-insulating (Al, Ga)As layers.

(2) The bare surface is negatively charged; i.e., the channel is depleted.

We then assume that

(3) Each adsorbed molecule decreases the negative surface charge by the same amount.

(4) In contrast to, for example the work of ref 7, equilibrium in the semiconductor is reached much faster than the time required to establish the chemisorption equilibrium situation.

Reduction of surface charge opens the channel, via the resulting change in surface potential. Simulations, using straightforward application of Poisson's relation, show that this process is linear under the conditions of our experiments.[12]

Preliminary results show that the device can be used for monitoring adsorption processes on GaAs surfaces both in liquid and in gas[13] and can serve to measure processes occurring on the surfaces of a variety of dielectric materials (e.g., SiO$_2$). This is possible because the current flow through the device is sensitive to any change in the surface charge. Hence, if the GaAs is coated with a thin layer of dielectric, then adsorption on the surface of the dielectric will result in a change in the charge at the interface between the dielectric and the GaAs and therefore can be monitored.

The device complements, in several aspects, other existing methods for monitoring chemistry on surfaces, especially adsorption. Its characteristics are very sensitive to the nature of the adsorbate−substrate interaction, since they actually amplify changes in charge distribution between the adsorbate

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and the substrate. Therefore, it may evolve in a general purpose sensor for surface processes, even if no mass change is involved. Being based on GaAs, it has short response time; i.e., it can monitor fast processes.

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(12) In the simulations the free carrier concentration was increased up to a factor of 4 (in accordance with the experimentally measured change in current). The mobility was assumed to be constant. This gave a built-in voltage of 0.2 V at full coverage (saturation current). This voltage was converted to surface charge, using a flat plat capacitor analogy (cf. refs 6). For this specific structure ($\epsilon = 13.1$ and $d = 55$ nm), 0.2 V corresponds to a change of only 10^{-3} electron/adsorbed molecule, or 100 C/mol. For this calculation we used 40 Å^2 as footprint of the DCDC molecule, a value measured using a Langmuir−Blodgett trough.

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