

Electrochemical passivation of gallium arsenide surface with organic self-assembled monolayers in aqueous electrolytes

Klaus Adlkofer, Motomu Tanaka,^{a)} Heiko Hillebrandt, Gerald Wiegand,
and Erich Sackmann

Lehrstuhl für Biophysik, Technische Universität München, D-85747, Garching, Germany

Tibor Bolom

Institut für Chemie Anorganischer Materialien, Technische Universität München, D-85747, Garching, Germany

Rainer Deutschmann and Gerhard Abstreiter

Walter Schottky Institut, Technische Universität München, D-85747, Garching, Germany

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Self-assembled monolayers of octadecylthiol (ODT) were reconstituted on freshly etched gallium arsenide (*n*-GaAs) for the electrochemical stabilization against decomposition of the surfaces (passivation) in aqueous buffers. The surface composition was evaluated by x-ray photoelectron spectroscopy to optimize the surface treatment before ODT deposition. Electrochemical properties of the monolayers were monitored by cyclic voltammetry and impedance spectroscopy. The impedance spectrum of the photoetched *n*-GaAs after the deposition of the ODT monolayer was stable in an aqueous electrolyte at *pH*=7.5 for more than 24 h within the sensitivity of our experimental technique. The effective passivation of GaAs surfaces is an essential step towards biosensor applications. © 2000 American Institute of Physics. [S0003-6951(00)01422-4]

Functionalization of semiconductor surfaces with bio-organic molecular assemblies are of great interest, especially for the design of biosensors based on electro-optical devices.^{1,2} Among various semiconductors, gallium arsenide (GaAs) is a promising material because of its large potential in the application for microstructured devices such as two-dimensional electron gas.³ As the application of this system has been impeded by the complex electrochemical processes at GaAs/electrolyte interfaces, most of the electrochemical studies have been performed in acidic or basic solutions.⁴⁻⁶ Organic self-assembled monolayers are suitable both to render the surface hydrophobic for further modification and to form thin insulating layers that prevent the electrochemical decomposition in aqueous electrolytes.⁷ There have been many studies on the passivation of GaAs surfaces with various sulfides and mercapto compounds in contact with air or with metals,⁸⁻¹¹ however, systematic studies on the passivation of GaAs surfaces under physiological conditions are still missing. In this letter, we demonstrate the successful passivation of *n*-GaAs in an aqueous buffer solution (*pH*=7.5) by self-assembled monolayers of octadecylthiol (ODT).

Single-crystalline *n*-doped GaAs [100] samples were purchased from Freiburger Compound Material GmbH (Freiberg, Germany) with a Te doping of $1-4 \times 10^{18} \text{ cm}^{-3}$. Prior to chemical etching of the native oxide, the samples were cleaned with acetone and ethanol and dried by a nitrogen flow. In order to fabricate dense and defectless thiol monolayers, complete removal of the native oxide and preparation of "arsenide-rich" surfaces are required, because arsenides on the surfaces serve as the binding sites for sulfide

atoms.^{8,9} To optimize the surface preparation before the functionalization, two chemical etching methods were attempted and the resulted surfaces were compared using x-ray photoelectron spectroscopy (XPS). Etch A is a conventional wet-chemical etching method, where the cleaned sample was dipped into concentrated HCl for 1 min.¹² Etch P is a so-called "photochemical etching" method, resulting in surfaces enriched with elemental arsenides.¹³ The cleaned sample was immersed into a mixture of HCl/H₂O (1/1 Vol), illuminated by a 500 W Xe-Hg arc lamp for 30 min. XPS measurements (LHS10, Leybold Heraeus) with an Al *K_α* source (1486.6 eV) were performed by hemispherical analyzer on the freshly etched samples. The peak area ratios of Ga to As were estimated with the self-developed peak-fitting routines.

Electrochemical properties of the surfaces were studied by cyclic voltammetry and impedance spectroscopy (VoltaLab 40, Radiometer Copenhagen). For these measurements, an Ohmic contact was established from the backside of the wafer by vapor deposition of Ni, Ge, and Au. The contact area of the surface to the electrolyte was about 0.28 cm². A Ag/AgCl electrode was used as the reference electrode, and a Au electrode as the counterelectrode, respectively. In all electrical studies, the potentials were applied versus the Ag/AgCl electrode. Instead of using rotating disk electrodes,⁴⁻⁶ we applied a constant flow of the electrolyte to our measuring chamber. As a standard electrolyte, degassed 10 mM phosphate buffered saline (PBS) of *pH*=7.5 containing 10 mM NaCl was used throughout the study.

ODT was purchased from Aldrich GmbH (Steinheim, Germany), and recrystallized in acetone. The other chemicals were also purchased from Aldrich GmbH, and used without further purification. The self-assembled ODT monolayers were deposited under a nitrogen atmosphere by immersing

^{a)}Author to whom correspondence should be addressed; electronic mail: mtanaka@ph.tum.de

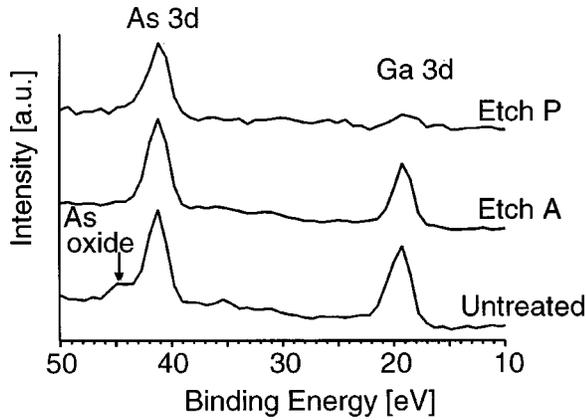


FIG. 1. Ga 3d and As 3d core-level spectra by XPS; untreated *n*-GaAs surface, *n*-GaAs surface freshly prepared by etch A (conventional etching), and *n*-GaAs surface freshly prepared by etch P (photochemical etching). The peak area ratio of Ga to As: 0.7 (untreated, after etch A); 0.16 (after etch P).

freshly prepared substrates into 1 mM ODT solution in dry ethanol (water content <0.005%, packaged with a crown cap) for 20 h.

The chemical compositions of the freshly etched surfaces were studied by XPS in terms of As 3d and Ga 3d core levels (Fig. 1). For comparison, the spectrum of the untreated surface is also shown. Concerning the native oxide, a distinct As-oxide peak (at a binding energy of ~45 eV, indicated by an arrow) had disappeared after both etching procedures by XPS standard. The surface prepared by etch A showed a peak area ratio of Ga to As of 0.7, which is the same as the value for the untreated surface. On the other hand, the corresponding ratio for the surface prepared by etch P was drastically reduced to a value of 0.16.

The cyclic voltammogram of the photoetched (etch P) *n*-GaAs is shown in Fig. 2 (dotted line). Independent of the etching methods, the current was minimal at around $U = -360$ mV. After deposition of the ODT monolayer, both oxidation and reduction at the interface were drastically suppressed (Fig. 2, solid line). It is still noticeable that the global shapes of the curves were changed after several potential cycles, when a positive potential was applied. To avoid the electrochemical decomposition of the surface, this zero-

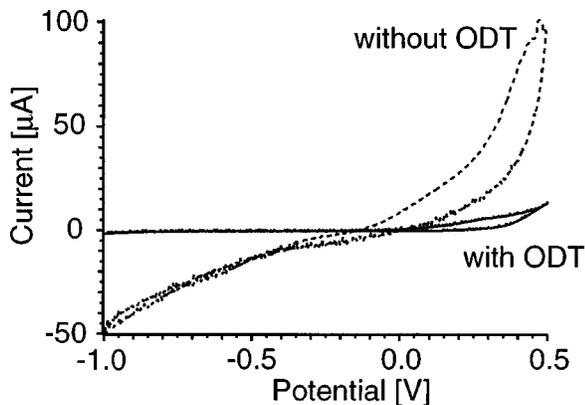


FIG. 2. Cyclic voltammograms of *n*-GaAs before (dotted line) and after (solid line) the deposition of the ODT monolayer in a PBS buffer ($pH = 7.5$). For both cases, the surfaces were prepared by etch P.

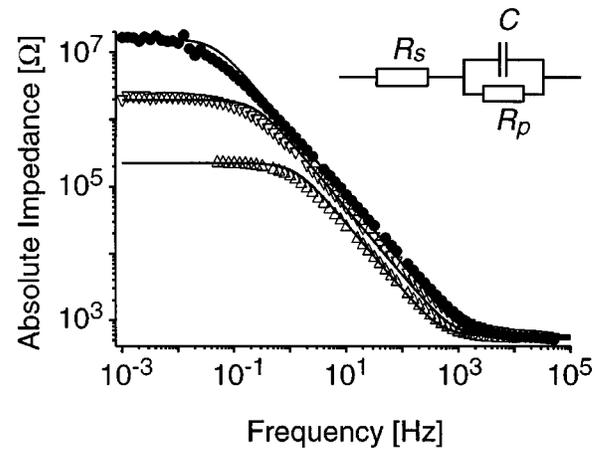


FIG. 3. Impedance spectra of *n*-GaAs directly after etch P (Δ), the same sample after 22 h (∇), and *n*-GaAs functionalized with ODT (\bullet) are exhibited. The symbols represent the measured data, while the solid lines correspond to the fits according to the equivalent circuit model composed of the serial resistance R_s , the capacitance C , and the parallel resistance R_p . As the surface of the freshly etched GaAs was not stable, the data of this surface were measured in a smaller frequency range from 50 mHz to 10 kHz. After the functionalization, the spectrum was totally stable for more than 24 h in the frequency range from 1 mHz to 100 kHz.

current potential of $U_{j=0} = -360$ mV was applied in all electrical measurements.

The impedance spectra of the photoetched (prepared by etch P) *n*-GaAs surface in a PBS buffer before and after the monolayer deposition are presented in Fig. 3. The impedance data of the system were analyzed in terms of the absolute values of the complex impedance $|Z|$ and the phase shift ϕ . The impedance spectra of the photoetched *n*-GaAs can be interpreted by the equivalent circuit given in Fig. 3.¹⁴ The serial resistance R_s corresponds to the Ohmic behavior of the electrolyte and the contacts in the high-frequency regime. The capacitance C represents the capacitive contribution from the GaAs/electrolyte interface. The parallel resistance R_p is attributed to an Ohmic behavior of the GaAs/electrolyte interface.

The electrical parameters were first calculated for the freshly photoetched *n*-GaAs. The serial resistance yielded the value of $R_s = 0.57$ k Ω cm². The interface capacitance and resistance yielded $C_0 = 2.0$ μ F cm⁻², and $R_{p0} = 63$ k Ω cm², respectively. The interface capacitance C_0 is represented by

$$\frac{1}{C_0} = \frac{1}{C_{SC}} + \frac{1}{C_{GCS}}, \quad (1)$$

where C_{SC} is the capacitance of the space-charge region of the semiconductor, and C_{GCS} is the capacitance of Gouy–Chapmann–Stern (GCS) layer formed in the electrolyte.¹⁴ C_{CGS} is the series connection of the capacitance of the Helmholtz layer C_H and the capacitance of the diffuse layer C_{diff} ,

$$\frac{1}{C_{GCS}} = \frac{1}{C_H} + \frac{1}{C_{diff}}. \quad (2)$$

As $C_H \geq 140$ μ F cm⁻² and $C_{diff} \geq 0.9$ F cm⁻² in this experimental system, the C_0 is dominated by the capacitance of the space-charge region C_{SC} .

The impedance of the freshly photoetched surface increased in contact with an aqueous buffer. R_p and C versus time are plotted in Fig. 4. R_p was increased to R_{p1}

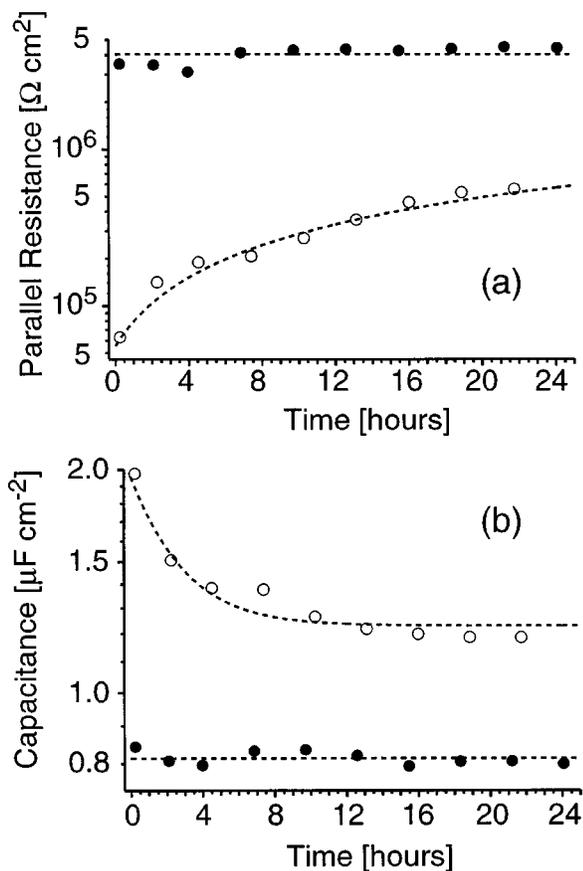


FIG. 4. Changes in (a) parallel resistance R_p and (b) interface capacitance C versus time before (○) and after (●) the monolayer deposition. Before the functionalization, $R_{p0} = 63 \text{ k}\Omega \text{ cm}^2$ was continuously increased to $R_{p1} = 0.56 \text{ M}\Omega \text{ cm}^2$ after 24 h, while C was decreased from $C_0 = 2.0 \mu\text{F cm}^{-2}$ to $C_1 = 1.2 \mu\text{F cm}^{-2}$. After the monolayer deposition, both R_p and C kept constant; $R_{p2} = 4.0 \text{ M}\Omega \text{ cm}^2$ and $C_2 = 0.81 \mu\text{F cm}^{-2}$, respectively.

$= 0.56 \text{ M}\Omega \text{ cm}^2$, and C was reduced to $C_1 = 1.2 \mu\text{F cm}^{-2}$ after 22 h. The changes in the electrical parameters of the GaAs/electrolyte interface observed might be attributed to a layer formation process at the interface, which had been reported for other systems at intermediate pH.⁴

The electrical parameters after the monolayer deposition were fitted very well by the same equivalent circuit model, corresponding to the formation of a homogeneous dielectric layer at the interface. The fitting yielded the electrical parameters of $R_{p2} = 4.0 \text{ M}\Omega \text{ cm}^2$ and $C_2 = 0.81 \mu\text{F cm}^{-2}$. The impedance spectrum appeared stable in the accuracy of our experiments for more than 24 h in the frequency range between 1 mHz and 100 kHz. The interface capacitance after the monolayer deposition C_2 can be described by the additional capacitive contribution of the monolayer according to

$$\frac{1}{C_2} = \frac{1}{C_0} + \frac{1}{C_m}, \quad (3)$$

by assuming that C_0 is not affected by the ODT monolayer. From the capacitance of the ODT monolayer C_m , one can estimate the monolayer thickness d :

$$d = \frac{\epsilon_0 \epsilon}{C_m}, \quad (4)$$

where ϵ_0 is the permittivity of free space and ϵ is the dielectric constant of alkyl chain, $\epsilon = 2.1$.^{15,16} From the obtained value of $C_m = 1.4 \mu\text{F cm}^{-2}$, the thickness of the ODT monolayer was estimated, $d = 14 \text{ \AA}$, which is in a good agreement with the thickness of the ODT monolayer on GaAs reported in the literature.^{10,11} However, it should be noted that it is very difficult to determine the thickness of ODT monolayers quantitatively only by electrical measurements, because the capacitance for the freshly etched surface (C_0) is intrinsically unstable.

n -GaAs prepared by etch A was also functionalized with ODT, but R_p still showed instability after several measurements (data not shown). This result suggests that the arsenide-rich surfaces generated by the etch P procedure allowed the formation of more dense ODT monolayers.

Recently, we reported the fabrication of high-resistance polymer/lipid composite films on indium-tin-oxide electrodes.¹⁷ This functionalization method enables us to control the thickness of the insulating polymer layers within the nm scale. Furthermore, these composites can provide biocompatible interfaces that are suited for the reconstitution of lipid membranes and for the incorporation of ion channels. As the hydrophobicity and stability achieved in this study are sufficient to deposit polymer films, this will be the next step to functionalize semiconductor devices based on GaAs.

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¹E. Sackmann, *Science* **271**, 43 (1996).

²E. Sackmann and M. Tanaka, *Trends Biotechnol.* **18**, 58 (2000).

³P. Baumgartner, C. Engel, G. Abstreiter, G. Böhm, and G. Weimann, *Appl. Phys. Lett.* **66**, 751 (1995).

⁴S. Menezes and B. Miller, *J. Electrochem. Soc.* **130**, 517 (1983).

⁵I. Uhlendorf, R. Reineke-Koch, and R. Memming, *J. Phys. Chem.* **100**, 4930 (1995).

⁶Z. Hens and W. P. Gomes, *J. Phys. Chem. B* **103**, 130 (1999).

⁷A. Ulman, *An Introduction to Ultrathin Organic Films: From Langmuir-Blodgett to Self-Assembly* (Academic, Boston, MA, 1991).

⁸S. R. Lunt, G. N. Ryba, P. G. Santangelo, and N. S. Lewis, *J. Appl. Phys.* **70**, 7449 (1991).

⁹E. A. Miller and G. L. Richmond, *J. Phys. Chem. B* **101**, 2669 (1997).

¹⁰O. S. Nakagawa, S. Ashok, C. W. Sheen, J. Martenson, and D. L. Allara, *Jpn. J. Appl. Phys., Part 1* **30**, 3759 (1991).

¹¹C. W. Sheen, J. X. Shi, J. Martenson, A. N. Prikh, and D. L. Allara, *J. Am. Chem. Soc.* **114**, 1514 (1992).

¹²S. M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1985).

¹³J. M. Woodall, P. Oelhafen, T. N. Jackson, J. L. Freeouf, and G. D. Pettit, *J. Vac. Sci. Technol. B* **1**, 795 (1983).

¹⁴A. Bard, *Electrochemical Methods* (Wiley, New York, 1980).

¹⁵R. Benz, O. Fröhlich, P. Läger, and M. Montal, *Biochim. Biophys. Acta* **394**, 323 (1975).

¹⁶J. P. Dilger, L. R. Fisher, and D. A. Haydon, *Chem. Phys. Lipids* **30**, 159 (1982).

¹⁷H. Hillebrandt, G. Wiegand, M. Tanaka, and E. Sackmann, *Langmuir* **15**, 8451 (1999).