

Surface Engineering of Gallium Arsenide with 4-Mercaptobiphenyl Monolayers

Klaus Adlkofer,[†] Wolfgang Eck,[‡] Michael Grunze,[‡] and Motomu Tanaka^{*,†}

Lehrstuhl für Biophysik E22, Technische Universität München, James-Frank-Strasse, D-85748 Garching, Germany, and Lehrstuhl für Angewandte Physikalische Chemie, Universität Heidelberg, Im Neuenheimer Feld 253, D-69120 Heidelberg, Germany

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In this study, we propose a new method for engineering of stoichiometric GaAs [100] surfaces with self-assembled monolayers of 4-mercaptobiphenyl. In the first part, surface homogeneity and topography were studied by contact angle measurements and atomic force microscopy (AFM), where it was concluded that grafting of mercaptobiphenyl layers did not increase surface roughness. Thickness of the biphenyl layer was measured by ellipsometry, 10 ± 2 Å, suggesting that the surface was coated with a monolayer. After grafting, ellipsometric angles were stable for more than a week, which confirmed chemical stability of the coated surface in air. In the second part, electrochemical properties of GaAs with biphenyl monolayers were studied. Cyclic voltammograms revealed a significant suppression of electrochemistry by deposition of electrically insulating biphenyl monolayers. Indeed, impedance spectra measured at a cathodic potential (−350 mV) demonstrated that the interface resistance was remarkably increased by a factor of 50. Furthermore, both interface resistance ($3.2 \text{ M}\Omega \text{ cm}^2$) and capacitance ($0.45 \mu\text{F cm}^{-2}$) of the coated GaAs electrodes were stable for 22 h. Chemical modification of GaAs surfaces with mercaptobiphenyl monolayers as established here includes has a large potential toward for the flexible functionalization of GaAs-based semiconductor nanostructures with bio-organic molecular assemblies both in air and in aqueous electrolytes.

Introduction

Engineering of semiconductor surfaces with bio-functional molecules is of particular interest both scientifically and practically.^{1–4} Despite rapid developments in device technology, realistic applications of semiconductor surfaces in the field of life science have been impeded by some unfavorable properties of the materials. For example, although gallium arsenide (GaAs) can realize high electron mobility in nanostructures such as two-dimensional electron gas (2DEG)⁵ and quantum well (QW),⁶ the application of GaAs to living systems is difficult because of the complex electrochemistry at the GaAs/electrolyte interface. Although there have been several reports on the passivation of GaAs surfaces with various types of sulfides and mercaptos in contact with air or with metals,^{7–11} systematic studies on the passivation of GaAs surfaces under physiological conditions (in aqueous electrolytes, near neutral pH conditions) are still missing.

Deposition of organic self-assembled monolayers (SAMs) is a convenient method to prevent the decomposition of semiconductors in aqueous electrolytes as well as to provide various surface functions.¹² In the previous studies, we reported the electrochemical passivation of GaAs surfaces with octadecylthiol monolayers under physiological conditions, i.e., at neutral pH in aqueous electrolytes.^{13,14} Introduction of a “photochemical etching” procedure enables us to enrich elemental arsenides on the surface, which serve as binding sites for sulfide. The binding of sulfide to arsenide was verified by X-ray photoelectron spectroscopy (XPS), and the monolayer deposition resulted in a significant stabilization both in air and in aqueous electrolytes.

Nevertheless, this strategy includes two fundamental drawbacks: (1) the photochemical etching under UV irradiation might roughen or damage the surface, and (2) gauche defects of the alkyl chains results in disordered films. To avoid the first problem, we chose conventional HCl stripping that results in a stoichiometric GaAs [100] surface, when we investigated the photoluminescence from the near-surface indium arsenide (InAs) quantum dots in air before and after the monolayer coating.^{15,16} As previously reported,^{8,9} ODT monolayers on surfaces pretreated with HCl showed sufficient chemical stability in air, showing almost no changes in the surface state density. Concerning the second problem, however, ODT monolayers could not stabilize GaAs surfaces in aqueous electrolytes due to the presence of defects. In fact, IR spectroscopy had pointed out a highly canted structure with an average angle of 57° between the chain axis and the surface normal.^{8,9}

These disadvantages can be overcome if the thiol has a more rigid and bulkier hydrophobic backbone without conformational freedom. One of the promising candidates is a derivative of rigid 4'-substituted 4-mercaptobiphenyls, which provides various surface functions by flexible substitution. Bulkier biphenyl backbones (cross sectional area: 21 Å^2 ¹⁷) occupy larger area than alkyl chains (18 Å^2 ¹⁸), and therefore, they are expected to protect the surface against chemical degradation. Furthermore, in contrast to alkyl chains, “rigid” biphenyl backbones can also avoid the defect due to gauche defects. Many intensive studies have been conducted on the structure and electrochemical properties of self-assembled monolayers of 4-mercaptobiphenyls on metal surfaces.^{17,19–21} Furthermore, it has been demonstrated that this aromatic thiol monolayer could be cross-linked with low energy electrons, i.e., they can be applied as negative resists in nanolithography.^{22,23}

* Corresponding author. E-mail: mtanaka@ph.tum.de.

[†] Technische Universität München.

[‡] Universität Heidelberg.

In this paper, we report the highly stable surface coatings of a stoichiometric *n*-GaAs [100] surface with a mercaptobiphenyl monolayer. The coating procedure was optimized by variation in solvent and temperature. Homogeneity and hydrophobicity of the surfaces were characterized by atomic force microscopy (AFM) and water contact angle measurements. Thickness of the monolayer was determined by ellipsometry, assuming the refractive index of biphenyl, $n = 1.588$.²⁴ Electrochemical properties of the monolayer such as resistance and capacitance were quantitatively measured by cyclic voltammetry and impedance spectroscopy. The current–voltage scans exhibited that the monolayer deposition led to a remarkable suppression of electrochemistry at the GaAs/electrolyte interface. The electrochemical stability of the monolayer-coated GaAs substrate was carefully verified by impedance spectroscopy in the wide frequency region between 50 kHz and 1 mHz.

Experimental Section

Materials. Single crystalline Si-doped *n*-type GaAs [100] wafers with a doping ratio of $(2.2\text{--}3.4) \times 10^{18} \text{ cm}^{-3}$ were purchased from American Xtal Technology Inc. (Fremont, California). For electrochemical studies, an Ohmic contact was established from the backside of the wafer by electron beam vapor deposition of Ni (100 Å), Ge (200 Å), and Au (2500 Å). Synthesis of mercaptobiphenyl was reported elsewhere.¹⁹ All the other chemicals were purchased from Aldrich (Steinheim, Germany) and used without further purification. Freshly distilled ultrapure water (Millipore, Molsheim, France) was used throughout this study.

Sample Preparation. Prior to the surface modification, the samples were briefly sonicated in acetone (approximately 3 min) and rinsed with ethanol. The native oxide of GaAs was stripped by soaking the sample in concentrated HCl for 1 min, resulting in a stoichiometric GaAs [100] surface. Self-assembled monolayers were deposited by immersing freshly prepared substrates into 0.1 mM mercaptobiphenyl solution in dry ethanol at 50 °C for 20 h. The reactions were carried out under nitrogen (N_2) atmosphere to avoid surface oxidation. After deposition, the sample was taken out from the reactor, sonicated briefly (30 s) in ethanol, and dried by a N_2 flow.

Ellipsometry. Thickness of the mercaptobiphenyl monolayer was measured with a conventional point ellipsometer (Plasmos GmbH Prozesstechnik, München, Germany) at a constant wavelength ($\lambda = 632.8 \text{ nm}$) and a fixed angle of incidence (70°). To take statistical values for the background data and the layer thickness, 3 points were measured before and after monolayer deposition. Using the refractive index of biphenyl, $n = 1.588$,²⁴ the thickness of the monolayers were estimated.

Atomic Force Microscopy (AFM). Topography of the untreated, the freshly etched, and that of the monolayer-coated surfaces were characterized by atomic force microscopy (Nanoscope IIIa, Digital Instruments, Mannheim, Germany). A silicon cantilever with a spring constant of about 40 N/m was used to scan an area of $1 \mu\text{m}^2$ in tapping mode. Typical modulation amplitude and frequency were in the order of 10 nm and 300 kHz, respectively.

Contact Angle Measurements. Contact angles of water droplets were measured using a G10 contact angle meter (Krüss GmbH, Hamburg, Germany). Measurements were carried out in an ambient atmosphere at room temperature. For the static contact angle measurements, a sessile drop (volume $\sim 10 \mu\text{L}$) was formed at the end of a blunt-ended needle and placed on the substrates. The advancing contact angles were determined during the continuous growth of a droplet, while the receding

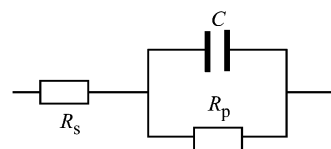


Figure 1. Simplified equivalent circuit model used for the impedance analysis. Details about simplification of the circuit model were described elsewhere.¹⁴ Serial resistance R_s corresponds to Ohmic contributions from the electrolyte and contacts. Parallel resistance R_p is attributed to Ohmic behavior of the interface, whereas C to the interface capacitance.

angles were measured during the volume reduction by suction. The overall accuracy throughout the contact angle measurements was within the range of $\pm 2^\circ$. Obtained images of the droplet were evaluated with an aid of DSA1 droplet shape analysis program.

Electrochemical Measurements. Electrochemical properties of the freshly prepared surface and the surface coated with the monolayer were measured by cyclic voltammetry and impedance spectroscopy at room temperature (VoltaLab 40, Radiometer Analytical, Lyon, France). The contact area of the surface to the electrolyte was 0.28 cm^2 , and volume inside the chamber was about 1.5 mL. A Ag/AgCl electrode was used as the reference electrode, and a Au electrode as the counter electrode, respectively. Instead of using a rotating disk electrode, a constant flow of degassed 10 mM phosphate buffer with 10 mM NaCl (pH = 7.5) was applied. Five cycles of the voltammograms were measured within the potential range between -1000 mV and $+500 \text{ mV}$ with a constant rate of 25 mV s^{-1} . Impedance spectra were taken between 50 kHz and 1 mHz under sinusoidal potentials with an amplitude of $|U| = 10 \text{ mV}$. To estimate the electrochemical parameters quantitatively from the measured impedance data, the whole system was represented by simple ideal elements of a simplified equivalent circuit model composed of serial resistance R_s , interface capacitance C , and interface resistance R_p (Figure 1). The fitting errors through the data analysis were kept below $\pm 10\%$. Details of the fitting routine we used were described elsewhere.^{14,25}

Results and Discussion

Surface Homogeneity. Surface topography of a GaAs [100] substrate was characterized by AFM at several different locations within an area of $1 \mu\text{m}^2$. The untreated GaAs surface with native oxide showed a roughness rms of 2.8 Å (Figure 2a). The corresponding value after the HCl stripping was slightly increased to 3.3 Å , suggesting the surface roughening due to wet chemical etching. In fact, as seen in Figure 2b, there are several “peaks” with height of $5 \sim 10 \text{ nm}$, which could not be seen on the native oxide. This can be attributed to the surface roughening caused by wet chemical etching with HCl.²⁶ The grafting reaction resulted in the comparable roughness rms to that of a freshly etched surface, 3.5 Å , verifying that the grafted layer did not increase the surface roughness (Figure 2c). It should also be noted that the absolute peak height remained the same in the macroscopically large surface ($1\text{--}25 \mu\text{m}^2$).

The static water contact angle of freshly etched GaAs was $\theta_{\text{st(GaAs)}} = 41^\circ$. The advancing and receding contact angles were $\theta_{\text{adv(GaAs)}} = 46^\circ$ and $\theta_{\text{rec(GaAs)}} = 17^\circ$, respectively. Such a high hysteresis could be attributed to the surface heterogeneity (roughness) caused by etching as well as to the rapid oxidization of the native (i.e., freshly etched) GaAs surface. Deposition of biphenyls resulted in the static contact angle of $\theta_{\text{st(biphenyl)}} = 77^\circ$. The value obtained here is comparable to the corresponding values previously reported on Au [111] and Ag [111] grains,

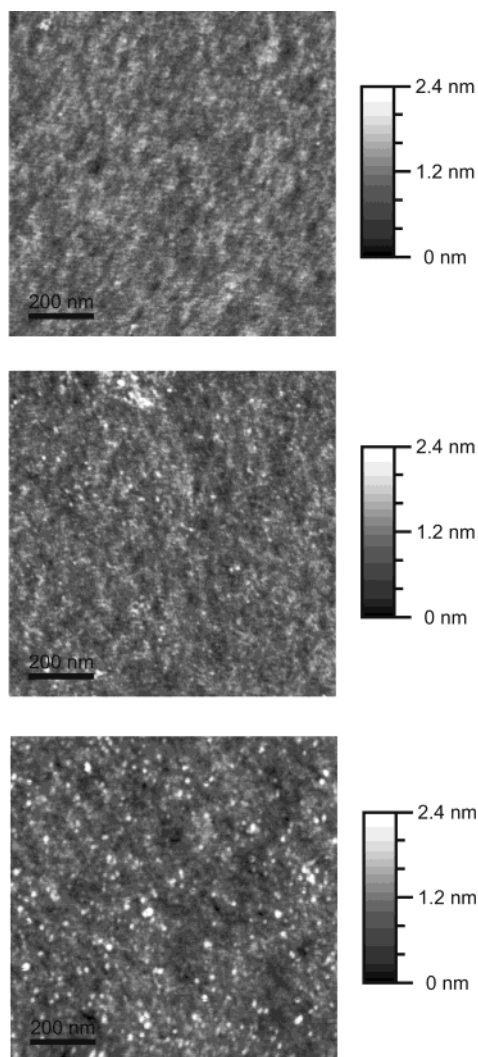


Figure 2. Tapping mode AFM images of (a) untreated GaAs with native oxide, (b) GaAs shortly after wet chemical etching, and (c) GaAs coated with a mercaptobiphenyl monolayer. Roughness rms values calculated within $1 \mu\text{m}^2$ are (a) 2.8 \AA , (b) 3.3 \AA , and (c) 3.5 \AA , respectively. Though wet chemical etching slightly increased the roughness, deposition of biphenyl layers did not cause roughening of GaAs surface.

$70 \sim 85^\circ$.^{20,27} Hysteresis between the advancing and receding angles was comparable to that of freshly prepared GaAs surfaces, $\theta_{\text{adv}}(\text{biphenyl}) - \theta_{\text{rec}}(\text{biphenyl}) = 85^\circ - 62^\circ = 23^\circ$. As observed by AFM, roughness rms values of the freshly etched and coated GaAs surfaces were comparable. Thus, it is plausible that the observed hystereses arise from the roughness of the substrate. In fact, similar hysteresis ($\sim 20^\circ$) was also found for the same monolayers on Au surfaces prepared by evaporation at room temperature.²⁷

Layer Thickness. The thickness of the mercaptobiphenyl layer was determined by ellipsometry. A reproducible value, $10 \pm 2 \text{ \AA}$ was determined, suggesting the grafting of a monolayer. Experimental errors in the obtained thickness are mostly due to the chemical instability of the freshly etched GaAs, which makes the background measurements rather difficult. Nevertheless, it should be pointed out that the obtained ellipsometric parameters (Ψ and Δ) were reproducible after more than one week, confirming the chemical stability of the coated surface. There have been several reports on the thickness of mercaptobiphenyl monolayer on gold measured by ellipsometry. For example, Tao et al. estimated the thickness of 9.4 \AA ,²⁰

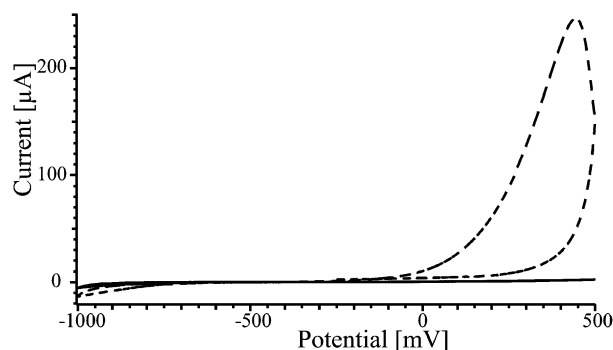


Figure 3. The first scan of cyclic voltammograms of freshly etched GaAs (broken line) and biphenyl-coated GaAs (solid line). Each voltammogram was measured in 10 mM phosphate buffer with 10 mM NaCl (pH = 7.5) within the potential range between -1000 mV and $+500 \text{ mV}$ at a constant rate of 25 mV s^{-1} . Current across the interface was suppressed by deposition of biphenyl monolayers.

while the one reported by Kang et al. is 14 \AA .²⁷ It should be noted that both of these studies assumed the smaller refractive index of 1.462 for the monolayer, which is a typical value for alkyl chains.²⁴ We chose the refractive index of bulk biphenyl for the analysis ($n = 1.588$), which might result in a slightly different monolayer thickness. Previously, Geyer et al. determined an average tilt angle between the phenyl ring and the surface normal by near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, $15 \pm 5^\circ$.²² Thus, the apparent deviation between the obtained thickness and the corresponding values on Au can be related either to (a) different refractive indices chosen for the data analysis, or to (b) different orientation of biphenyl backbones on GaAs and on Au. Although further conformational characterization is required, the ellipsometric thickness we obtained here also suggests that the grafted biphenyls take a small tilt angle from the surface normal. Furthermore, recent XPS results confirmed sulfide–arsenide coupling (unpublished data), which showed qualitative similarity to those observed for ODT monolayers.¹⁴

Electrochemical Characteristics. The first scan of cyclic voltammograms of freshly etched GaAs is presented as a broken line in Figure 3, exhibiting a large oxidation at anodic potentials. In comparison to our previous results from the “photoetched” surface coated with amorphous arsenide layer,¹³ the maximum oxidation current of the bare GaAs was about 2–3 times larger. On the other hand, the reduction at the GaAs/electrolyte interface is smaller. As the current across the interface was almost zero between -550 mV and -250 mV , we chose a bias potential of -350 mV for the following impedance spectroscopy experiments, which is not only close to the middle of this potential range but also almost at the same condition as in the previous studies (-360 mV). Global shapes of the current–voltage scans were also different after each bias sweep, corresponding to the electrochemical instability of bare GaAs surfaces. In contrast, current across the interface was dramatically suppressed by deposition of biphenyl monolayers (Figure 3, solid line). Here, the biphenyl monolayer blocks the access of aqueous electrolytes to the GaAs electrode. Furthermore, it should be noted that the current signals after biphenyl coating was significantly smaller than those measured after ODT coatings, suggesting better insulating properties of biphenyl monolayers.

Figure 4 shows the impedance spectra, i.e., plots of absolute impedance and phase shift versus applied frequency, of bare GaAs shortly after etching (\blacktriangle , \triangle) and after 22 h (\blacktriangledown , \triangledown). As the freshly etched GaAs were highly unstable, the first several spectra were measured in a smaller frequency range from 50

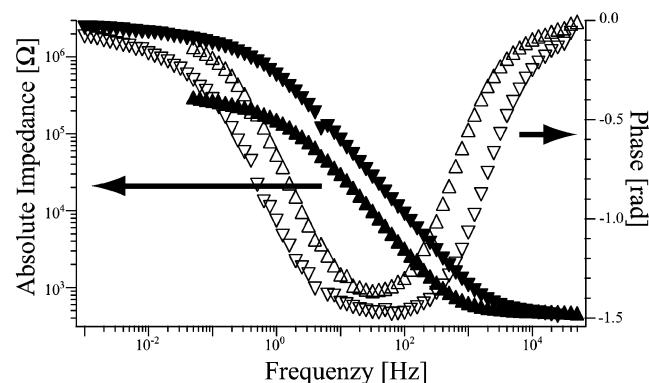


Figure 4. Absolute impedance and phase shift of bare GaAs shortly after etching (Δ , ∇) and after 22 h (\blacktriangledown , \blacktriangledown), plotted as a function of applied frequency. Due to the rapid surface decomposition, the first several spectra were measured from 50 mHz to 50 kHz. Spectra revealed continuous drift in 22 h.

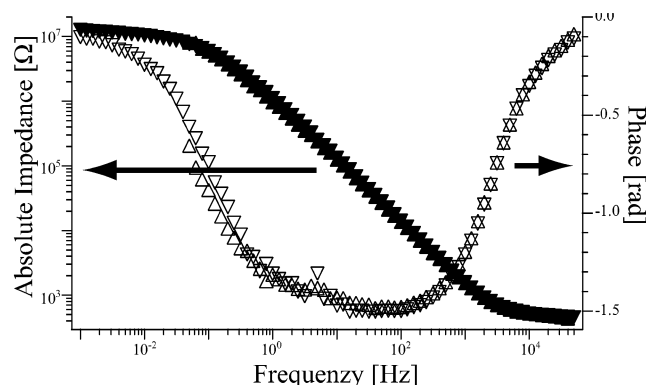


Figure 5. Impedance spectra of GaAs coated with a mercaptobiphenyl monolayer. Spectra were reproducible within a wide frequency range between 1 mHz and 50 kHz for more than 22 h.

mHz to 50 kHz. Impedance spectra revealed continuous and irreversible drift in 22 h. On the other hand, impedance spectra of biphenyl-coated GaAs were stable within the frequency range between 1 mHz and 50 kHz for more than 22 h (Figure 5). The measured spectra were analyzed with the equivalent circuit model in Figure 1. Quantitative changes in the electrochemical properties of GaAs electrodes with and without biphenyl coating are given in Figure 6a and Figure 6b, by plotting interface resistance R_p and capacitance C as a function of time, respectively. Interface resistance of the bare GaAs electrode shortly after the etching ($t = 0$ h) was $R_{p0} = 64 \text{ k}\Omega \text{ cm}^{-2}$, shifting to $R_{p1} = 0.46 \text{ M}\Omega \text{ cm}^{-2}$ after 22 h. Interface capacitance C also drifted from $C_0 = 1.9 \mu\text{F cm}^{-2}$ to $C_1 = 0.69 \mu\text{F cm}^{-2}$, too. Deposition of mercaptobiphenyl monolayer caused a remarkable increase in interface resistance by a factor of about 50, $R_{p2} = 3.2 \text{ M}\Omega \text{ cm}^{-2}$, while the interface capacitance was reduced to $C_2 = 0.45 \mu\text{F cm}^{-2}$. This coincides with the results from cyclic voltammetry experiments, showing that the biphenyl monolayer blocks electrochemistry at the interface effectively. In contrast to the results from the bare GaAs surface, both R_p and C of the coated GaAs kept constant for 22 h within the accuracy of our experiments. Thus, it has been concluded that electrochemical passivation of GaAs surfaces in aqueous buffer (pH = 7.4) could successfully be achieved by deposition of mercaptobiphenyl monolayers.

Effects of Grafting Conditions. Prior to the detailed surface characterization, effects of the grafting conditions (solvents, concentration, reaction time, and temperature) on the monolayer properties were systematically studied. Impacts of solvents were first examined by carrying out the grafting reaction in three

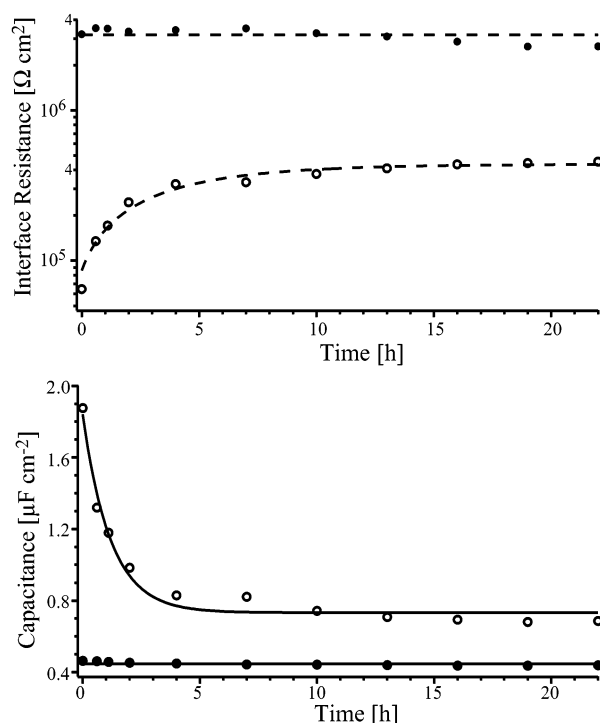


Figure 6. Changes in (a) interface resistance R_p and (b) interface capacitance C versus time before (\circ) and after (\bullet) the monolayer deposition. R_p of bare GaAs was increased from $R_{p0} = 64 \text{ k}\Omega \text{ cm}^{-2}$ to $R_{p1} = 0.46 \text{ M}\Omega \text{ cm}^{-2}$, while C was decreased from $C_0 = 1.9 \mu\text{F cm}^{-2}$ to $C_1 = 0.69 \mu\text{F cm}^{-2}$. Deposition of highly insulating monolayers stabilized the interface, where both R_p and C kept constant; $R_{p2} = 3.2 \text{ M}\Omega \text{ cm}^{-2}$ and $C_2 = 0.45 \mu\text{F cm}^{-2}$, respectively. The lines are given to guide the eye.

TABLE 1: Effects of Solvents on Monolayer Properties^a

solvent	d [Å]	R_p at $t = 0$ h [$\text{M}\Omega \text{ cm}^{-2}$]	R_p at $t = 2$ h [$\text{M}\Omega \text{ cm}^{-2}$]
DMF	2	0.61	1.3
toluene	6	1.3	1.9
ethanol	6	1.6	2.1

^a Mercaptobiphenyl layers were grafted in dimethylformamid, toluene, and ethanol at r.t. for 20 h. Ellipsometric thickness d , interface resistance R_p shortly after grafting ($t = 0$ h), and R_p after 2 h ($t = 2$ h) are compared. The sample prepared in ethanol resulted in the highest electrochemical resistance, and was chosen as the solvent for the following experiments. Note that all the layers showed electrochemical instability monitored by impedance spectroscopy.

different solvents (DMF, toluene, ethanol) at room temperature for 20 h. The surface characteristics of the resulting surfaces, e.g., ellipsometric thickness d , interface resistance R_p immediately after the grafting ($t = 0$ h), and R_p after 2 h ($t = 2$ h), are summarized in Table 1. As presented in the Table, the reaction in DMF resulted in a very poor coating, where the ellipsometric thickness was merely 2 Å. The interface resistance was increased by a factor of 10 from that of freshly etched GaAs, however, the impedance spectra were not stable. Using toluene and ethanol as solvents, the surface coverage was remarkably improved. Ellipsometric thickness amounted to 6 Å, and the interface resistance increased up to more than 1 $\text{M}\Omega \text{ cm}^{-2}$. The instability in impedance spectra could still be observed, but the drift was much smaller in comparison to the one prepared in DMF. Based on the highest interface resistance obtained, we chose ethanol as the solvent. Nevertheless, the impedance spectra of the sample prepared in ethanol showed a clear instability. We also increased the concentration of mercaptobiphenyl (e.g. 1 mM) as well as the reaction time (e.g. 40 h),

TABLE 2: Effects of Reaction Temperature on Ellipsometric Thickness d , and Interface Resistance R_p at $t = 0$ h and $t = 2$ h^a

T [°C]	d [Å]	R_p at $t = 0$ h [MΩ cm ²]	R_p at $t = 2$ h [MΩ cm ²]
r.t.	6	1.6	2.1
35	5	1.8	2.0
50	10	3.2	3.2

^a Here, the reactions were carried out in dry ethanol for 20 h. Although there were almost no differences between the samples prepared at r.t. and at 35 °C, the grafting at 50 °C resulted in an improved surface coating.

but these often resulted in heterogeneous and obviously too thick layers ($d > 16$ Å), suggesting the formation of multilayers. At the next step, the monolayers prepared at different reaction temperatures, i.e., r. t., 35 °C, and 50 °C were compared (Table 2). The samples prepared at r.t. and at 35 °C did not exhibit any clear differences in ellipsometric thickness (5, 6 Å), and showed similar shifts in interface resistance R_p from approximately 1.7 to 2.1 MΩ cm² in 2 h. On the other hand, the sample prepared at 50 °C showed clear increase in thickness (10 Å) and in the interface resistance, 3.2 MΩ cm². In fact, this resistance remained stable for more than 22 h, as presented in Figure 6.

Conclusions

We proposed a new method of engineering GaAs [100] surfaces by deposition of 4-mercaptobiphenyl monolayers. Contact angle measurements and AFM measurements demonstrated that the grafted monolayer did not cause roughening of the surface. Thickness of biphenyl layer was measured by ellipsometry, 10 ± 2 Å, by assuming the refractive index of biphenyl, $n = 1.588$. The obtained thickness showed reasonable agreement with those reported for the mercaptobiphenyl monolayers on metal surfaces, suggesting the deposition of monolayers with a small tilt angle to the surface normal. To confirm the covalent coupling of mercaptobiphenyl and surface arsenide, changes in chemical composition of GaAs surfaces before and after the grafting can be studied by high-resolution X-ray photoelectron spectroscopy (HRXPS). In As 3d core level spectra, peaks from elemental As and As bonded to the sulfur headgroup could be observed. The attachment of mercaptobiphenyl to GaAs was also supported by the appearance S 2p spectra, too (Shaporenko et al., unpublished results).

Cyclic voltammetry exhibited that deposition of biphenyl monolayers resulted in a clear suppression of electrochemistry at pH = 7.5. Indeed, impedance spectra measured at a cathodic potential (−350 mV) demonstrated that the interface resistance was significantly increased by a factor of 50. Furthermore, both interface resistance (3.2 MΩ cm²) and capacitance (0.45 μF cm^{−2}) of the coated GaAs electrodes were stable for 22 h within a wide frequency range between 1 mHz and 50 kHz. Further experiments such as Mott–Schottky analysis and photoluminescence measurements will provide deeper insight of the influence of mercaptobiphenyl monolayers on electronic structures.

On metal surfaces, it has been demonstrated that biphenyl monolayers have large potentials toward versatile modifications of surface functions. For example, aromatic backbones can be cross-linked with low energy electrons, which even allows for chemical nano-lithography.^{22,23} The first approach is promising to realize even more stable surface coating in aqueous electrolytes, while the second allows for “local” conversion of surface functions so that surface density of the functional groups can

be quantitatively defined. As demonstrated in our previous studies,^{1,2,4,28} chemically robust, hydrophobic surfaces of organic monolayers can further be modified by deposition of ultrathin ($d < 10$ nm) polymer films and model biomembranes. Moreover, the same surface chemistry can directly be transferred onto various semiconductor heterostructures in the proximity of GaAs surfaces,^{15,16} which might realize sensitive detection of specific recognition and selective transport in biological membranes.

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References and Notes

- (1) Sackmann, E.; Tanaka, M. *Trends Biotechnol.* **2000**, *18*, 58.
- (2) Hillebrandt, H.; Wiegand, G.; Tanaka, M.; Sackmann, E. *Langmuir* **1999**, *15*, 8451.
- (3) Purucker, O.; Hillebrandt, H.; Adlkofer, K.; Tanaka, M. *Electrochim. Acta* **2001**, *47*, 791.
- (4) Hillebrandt, H.; Tanaka, M.; Sackmann, E. *J. Phys. Chem. B* **2002**, *106*, 477.
- (5) Baumgartner, P.; Engel, C.; Abstreiter, G.; Böhm, G.; Weimann, G. *Appl. Phys. Lett.* **1995**, *66*, 751.
- (6) Baumgartner, P.; Engel, C.; Abstreiter, G.; Böhm, G.; Weimann, G. *Appl. Phys. Lett.* **1994**, *64*, 592.
- (7) Lunt, S. R.; Ryba, G. N.; Santangelo, P. G.; Lewis, N. S. *J. Appl. Phys.* **1991**, *70*, 7449.
- (8) Nakagawa, O. S.; Ashok, S.; Sheen, C. W.; Mårtensson, J.; Allara, D. L. *Jpn. J. Appl. Phys.* **1991**, *30*, 3759.
- (9) Sheen, C. W.; Shi, J. X.; Mårtensson, J.; Allara, D. L. *J. Am. Chem. Soc.* **1992**, *114*, 1514.
- (10) Asai, K.; Miyashita, T.; Ishigure, K.; Fukatsu, S. *Surf. Sci.* **1993**, *306*, 37.
- (11) Seker, F.; Meeker, K.; Kuech, T. F.; Ellis, A. B. *Chem. Rev.* **2000**, *100*, 2505.
- (12) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533.
- (13) Adlkofer, K.; Tanaka, M.; Hillebrandt, H.; Wiegand, G.; Sackmann, E.; Bolom, T.; Deutschmann, R.; Abstreiter, G. *Appl. Phys. Lett.* **2000**, *76*, 3313.
- (14) Adlkofer, K.; Tanaka, M. *Langmuir* **2001**, *17*, 4267.
- (15) Adlkofer, K.; Duijs, E. F.; Findeis, F.; Bichler, M.; Zrenner, A.; Sackmann, E.; Abstreiter, G.; Tanaka, M. *Phys. Chem. Chem. Phys.* **2002**, *4*, 785.
- (16) Duijs, E. F.; Findeis, F.; Deutschmann, R. A.; Bichler, M.; Zrenner, A.; Abstreiter, G.; Adlkofer, A.; Tanaka, M.; Sackmann, E. *Phys. Status Solidi B* **2001**, *224*, 871.
- (17) Ulman, A. *Acc. Chem. Res.* **2001**, *35*, 855.
- (18) Nyburg, S. C.; Lüth, H. *Acta Crystallogr.* **1972**, *B28*, 2992.
- (19) Sabatani, E.; Cohen-Boulakia, J.; Bruening, M.; Rubinstein, I. *Langmuir* **1993**, *9*, 2974.
- (20) Tao, Y.-T.; Wu, C.-C.; Eu, J.-Y.; Lin, W.-L. *Langmuir* **1997**, *13*, 4018.
- (21) Frey, S.; Stadler, V.; Heister, K.; Eck, W.; Zharnikov, M.; Grunze, M.; Zeysing, B.; Terfort, A. *Langmuir* **2001**, *17*, 2408.
- (22) Geyer, W.; Stadler, V.; Eck, W.; Zharnikov, M.; Götzhäuser, A.; Grunze, M. *Appl. Phys. Lett.* **1999**, *75*, 2401.
- (23) Götzhäuser, A.; Eck, W.; Geyer, W.; Stadler, V.; Weimann, T.; Hinze, P.; Grunze, M. *Adv. Mater.* **2001**, *13*, 806.
- (24) *Handbook of Chemistry and Physics*; Lide, D. R., Ed.; CRC Press Inc.: New York, 1997.
- (25) Hillebrandt, H.; Tanaka, M. *J. Phys. Chem. B* **2001**, *105*, 4270.
- (26) Osakabe, S.; Adachi, S. *Jpn. J. Appl. Phys.* **1997**, *36*, 7119.
- (27) Kang, J. F.; Ulman, A.; Liao, S.; Jordan, R.; Yang, G.; Liu, G.-Y. *Langmuir* **2001**, *17*, 95.
- (28) Tanaka, M.; Kaufmann, S.; Nissen, J.; Hochrein, M. *Phys. Chem. Chem. Phys.* **2001**, *3*, 4091.