



Electrochemical impedance spectroscopy of carboxylic-acid terminal alkanethiol self assembled monolayers on GaAs substrates

Lingling Wu^a, Fernanda Camacho-Alanis^a, Homero Castaneda^{b,1}, Giovanni Zangari^{c,1}, Nathan Swami^{a,*}

^a Department of Electrical Engineering, 351 McCormick Road, PO Box 400743, University of Virginia, Charlottesville, VA 22904, United States

^b Battelle Memorial Institute, Energy Systems, 505 King Avenue, Columbus, OH 43201, United States

^c Department of Materials Science, 395 McCormick Road, PO Box 400745, University of Virginia, Charlottesville, VA 22904, United States

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ABSTRACT

Adsorbate-induced charge depolarization can influence the organization of self assembled monolayers (SAMs) on semiconductor surfaces, especially as a function of the SAM functional group, SAM length and substrate dopant level and type. Based on systematic differences in the frequency response of the electrochemical impedance and phase data for carboxylic acid (COOH) terminal alkanethiol monolayers of varying alkane chain length assembled on GaAs substrates of different dopant level and type, we assessed the relative monolayer quality through fits to an appropriate equivalent circuit analog to compare the proportion of defects and SAM-induced semiconductor depolarization. At the open circuit potential in the NaCl–phosphate buffer, while SAMs on p+ GaAs were of marginally better quality than those on p GaAs, SAMs on n+ GaAs exhibited a far superior quality than those formed on n GaAs. COOH-terminal SAMs of longer chain lengths formed higher quality monolayers at all the substrate doping levels. COOH-terminal SAM modified n and n+ GaAs surfaces were passivated and stable over a wider voltage range than SAM modified p and p+ GaAs surfaces, from cyclic voltammetry. The poorer quality of COOH-terminal SAMs formed on GaAs substrates at the lower doping levels is attributed to the disorder as a result of the enhanced degree of charge depolarization at these surfaces, as substantiated by systematic variations in the space charge capacitance upon SAM modification that suggest a negative surface dipole.

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1. Introduction

The quality of alkanethiol self assembled monolayers (SAMs) as judged by their coverage and organization is highly dependent on charge depolarization at the surface [1], which can be varied through SAM alkane chain-length [2–4], and the functional groups in the monolayer [5–7]. Additionally, on semiconductor surfaces, monolayer quality can also depend on the substrate doping level and type [8]. Terminal functional groups on SAMs are routinely applied to systematically control wetting [9], electrical [10] and chemical [11,12] properties of metal and semiconductor surfaces. Specifically, SAMs with the carboxylic acid terminal group are widely applied to engineer interfaces for electrical, electrochemical and biosensor applications since: (i) the surface charges resulting from their adsorption can modify electron transport mechanisms [13,14]; (ii) they provide suitable seeds for chemical reactions, such as the formation of metallic layers due to de-protonation of the terminal group [12,15–17]; and (iii) they can be applied to modulate

inter-molecular forces within the species of a pure or mixed monolayer through hydrogen-bonding interactions [18]. Recent studies have observed variations in monolayer organization due to charge depolarization induced by the SAM electrical dipole at the substrate [19], as well as due to the alkane chain length of the SAM [20,21]; and these two properties are in turn interrelated due to the effect of molecular-length on the resulting dipoles [22,23]. Hence, the study of monolayer quality as a function of varying charge depolarization due to varying alkane chain length, as well as semiconductor doping level and type is essential for the development of interfaces with modulated semiconductor band-bending for applications within molecular device junctions as well as chemical and biological sensors [24,25].

Surface charge modulation on semiconductor surfaces for purposes of surface state passivation within photovoltaics [26,27], as well as for surface modulated field-effect transistor (FET) type sensor devices [28], is a topic of great emerging interest. While semiconductor dopant level and type have been used traditionally to modulate band-bending, recent studies have explored the use of functional groups within SAMs for molecular tuning of semiconductor band-bending and electronic structure, to enable the modulation of the Schottky barrier [29], conductivity [14,30], and reactivity [11,31,32]. Hence, there is a need to understand the effect

* Corresponding author. Tel.: +1 434 924 1390; fax: +1 434 924 8818.

E-mail address: nswami@virginia.edu (N. Swami).

¹ ISE member.

of semiconductor dopant level and type on the quality of SAMs, especially for SAMs with functional groups that result in charge depolarization at the semiconductor surface [33].

In prior work the effect of semiconductor dopant level and type on SAM quality has been studied on silicon substrates by FTIR and contact angle techniques [8]. It was reported that dense monolayers of 1-octadecene were formed on n, p and p+ silicon, but not on n+ silicon. Similar systematic studies on the quality of relevant SAMs on GaAs, as a function of substrate doping have not been reported. Electrochemical impedance spectroscopy (EIS) is a powerful technique to characterize SAMs [34,35]. Defects within the monolayer can be evaluated through the determination of pinhole density, as has been applied towards the characterization of coatings [36,37]. The phase information of the impedance spectra can be used to probe the degree of ideality of the capacitor formed as a result of monolayer chemisorption [36–38]. Additionally, the effect of induced dipoles upon bonding of the molecular monolayer to the semiconductor can be characterized by probing modifications to the space charge capacitance (C_{SC}). In this study we apply EIS in complement with cyclic voltammetry to probe the variations in quality of carboxylic-acid terminated monolayers for varying charge depolarization at the GaAs surface, which is accomplished through varying alkane chain length of SAMs formed on GaAs and varying the substrate dopant level and type (p+, p, n, and n+). SAM quality as inferred by EIS is found to depend on GaAs substrate dopant level and type, which we attribute to varying degrees of charge depolarization and varying susceptibility of the GaAs surface to oxidation.

2. Experimental methods

2.1. Materials

The n, n+, p, p+ type (001) GaAs surfaces (respectively: Si doped at $2.2\text{--}2.4 \times 10^{16} \text{ cm}^{-3}$, Si doped at $2.2\text{--}2.4 \times 10^{18} \text{ cm}^{-3}$, Zn doped at $4.2\text{--}6.0 \times 10^{17} \text{ cm}^{-3}$, Zn doped at $1.1\text{--}1.3 \times 10^{19} \text{ cm}^{-3}$) were used for deposition of the investigated molecules. Alkane chain length was varied using 16-mercapto-hexa-decanoic acid (16-MHDA) 90%, 11-mercaptoundecanoic acid (11-MUDA) 95%, 8-mercaptooctanoic acid (8-MOA) 96% (Aldrich, used as received).

2.2. Sample preparation

The deposition procedure for SAMs on GaAs was based on prior work [12,39–41]. Prior to deposition, wafers were cleaned with acetone for 10 min, followed by etching with 30% NH_4OH for 1 min to remove the oxide. The GaAs substrate was then rinsed with anhydrous ethanol and dried with N_2 , and then immediately placed into the de-aerated SAM deposition solution containing 5 mM of the respective mercapto-carboxylic-acid solution in ethanol and in 5% aqueous ammonia, as optimized within prior work [39,42]. The solution was continuously purged with N_2 and heated to 50°C for 8 h in an enclosed flask to reduce evaporative loss (<10%), and achieve SAM deposition on a GaAs surface free of oxide. Since carboxylic acid terminated surfaces form bilayers due to hydrogen bonding [16], the SAMs were washed in a 10% acetic acid (CH_3COOH) solution in ethanol to ensure monolayer formation. An alternate set of samples was also prepared by SAM deposition in similar solutions, but at room temperature for 24 h under N_2 environment, as performed within prior work [20], to enable a comparison of the SAMs deposited by these two different methods.

2.3. Electrochemical measurements

The freshly prepared SAM modified GaAs surfaces were used as working electrodes to measure the impedance at room tempera-

ture. The contact area was 0.09 cm^2 . A calomel electrode (SCE) was used as the reference electrode, and platinum gauze as the counter electrode. A solution of 10 mM phosphate buffer and 10 mM NaCl (pH = 7.5) was used as the electrolyte. Impedance spectra were collected with a Solartron 1260 instrument, covering the frequency range between 0.1 Hz and 1 MHz with 6 points per decade and using a sinusoidal potential with amplitude of $\pm 10 \text{ mV}$. All the impedance experiments were carried out at open circuit potential (variable for the different samples) and in the dark to eliminate variations arising from generation of charge carriers through illumination. To fit the impedance spectra we used the program Z-view (Scribner Associates, Inc.). Current-voltage characteristics using cyclic voltammetry were performed at a scan rate of 10 mV/s , starting from the open circuit potential (OCP) value to -1.5 V to 0.5 V and back to OCP (all values versus the SCE), for each of the bare and SAM modified GaAs surfaces studied herein.

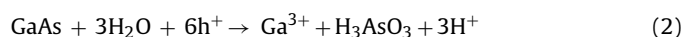
3. Results and discussion

3.1. Stability of COOH-terminal SAM modified GaAs of varying substrate doping

Cyclic voltammetry (CV) was used to characterize the stability of carboxylic acid terminal SAM modified GaAs surfaces in a phosphate buffered salt solution, for surfaces of varying substrate dopant values (n+, n, p+, and p). From prior work, it is known that a sufficient concentration of holes (h^+) can break the GaAs bonds as per the following reaction [43–45]:



The oxidized species in the reaction can either dissolve or form an oxide film, depending on the dopant level and type [46,47]. SAM-induced passivation of GaAs at each of the respective substrate doping levels can arrest this oxidation reaction [48,49]. The CV data of Fig. 1(a) and (b) (half-cycle of CV shown for clarity, with full-cycle in (c)) show that upon modification of the n+ and n GaAs surfaces with 16-MHDA SAMs, the background current arising from capacitance was decreased by an order of magnitude in comparison to that of the respective bare GaAs surface, since the monolayer behaves as a barrier by blocking the electron transfer. This reduction in current was observed over the complete range of voltage studied herein, suggesting that COOH-terminal SAM modified n and n+ GaAs surfaces were well-passivated. This is also apparent in the full-cycle CVs of Fig. 1(c), based on observation of stable CV data for subsequent scans on the SAM modified surface, while the bare n+ GaAs surface exhibits instability due to corrosion in this particular electrolyte. In comparison, this capacitive current in Fig. 1(d) and (e) for 16-MHDA SAM modified p+ and p GaAs surfaces with respect to bare GaAs was decreased only at negative bias voltages by approximately one order of magnitude upon SAM modification, while the current at positive bias was comparable to bare GaAs, with a shifting of redox peaks to higher voltages on the SAM modified surfaces. This is apparent in CVs of SAM-modified p+ GaAs in Fig. 1(f), based on the increase in current values within the second CV scan versus the first, to equal to that on the bare p+ GaAs surface, suggesting desorption of the monolayer. These observations suggest that unlike the SAMs on n and n+ GaAs, the SAM-modified p and p+ GaAs surfaces were not stable enough to enable passivation of the surface at anodic voltages (positive bias region) in the NaCl/phosphate buffer electrolyte. We hypothesize that while carboxylic acid terminal SAMs were able to passivate p and p+ GaAs surfaces at negative bias values, surface dissolution induced by holes (h^+) occurs at positive bias values, through the reaction in Eq. (2) [50]:



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