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Role of the dithiolate backbone on the passivation of p-GaAs(111)B surface

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ABSTRACT

Effects of the self-assembled layers of biphenyl 4,4′ –dithiol (BPDT) and 1,8 –octanedithiol (ODT) on the chemical and electronic properties of p-doped GaAs(111)-As terminated substrate, (p-GaAs(111)B), were investigated in order to evidence whether the hydrocarbon moiety plays a role in tailoring the semiconductor surface properties. The electrochemical properties of the BPDT and ODT coated p-GaAs(111)B substrates were studied by Electrochemical Impedance Spectroscopy (EIS). The structural and chemical changes caused by the dithiolate layers formed on p-GaAs(111)B substrates were monitored by Atomic Force Microscopy (AFM) and X-ray Photoelectron Spectroscopy (XPS) investigations, respectively. The XPS data showed that BPDT and ODT bind to p-GaAs(111)B via the thiol group. The ODT layer provides better protection against the further oxidation in air of p-GaAs(111)B substrate compared to the BPDT layer. The EIS investigations are in good agreement with XPS results, pointing to better insulating properties of the ODT layer compared to the BPDT layer in the electron transfer at the electrode/solution interface. The results evidenced that backbone plays an important role in tailoring the properties of p-GaAs(111)B substrate.

1. Introduction

Functionalization of semiconducting surfaces with organic molecules is of great interest due to the possibility of controlling the chemical and electronic properties of the surface. GaAs has remarkable optoelectrical and high electron mobility properties that may open various opportunities in designing electronic devices, chemical sensors [1] or biosensors [2,3]. However, the poor chemical stability and the presence of high density of surface/interface states represent an important impediment for using GaAs surfaces as platforms for new applications [4–6]. Functionalization of GaAs surfaces with self-assembled thiol monolayers may represent a good alternative for improving both their chemical stability [7,8] and their electronic properties [7,9]. We have recently reported that the 4,4′-thio-bis-benzenethiolate (TBBT) prevents the surface oxidation and reduces the deep and the shallow surface states of the p-GaAs(100) substrate [9].

Thiolates formed at GaAs surface may also alter the semiconductor work function as it was pointed out for the adsorption of 4,4′-tribenzenedithiol on GaAs(001) surface [10]. The electronic structure and the chain length of thiol monolayer formed on GaAs surfaces could also play a key role in controlling the conductivity of GaAs surfaces [11] and shaping the chemical properties of the substrate [12].

Therefore modifying the semiconductors surface properties by chemical self-assembling of thiols on GaAs surfaces could represent options for developing new electronic devices or biosensors. Particularly, the functionalization of GaAs surface with dithiols may open new perspectives in obtaining complex architectures because the dithiol may act as a linker between the substrate and the metal nanoparticles or molecules bounded to the top of free SH-end group [13,14]. However, the control of the semiconductor surface properties requires a good knowledge of the chemical thiol bonding, and its effect on the chemical and electronic properties of the semiconductor substrate.

In this work we investigated the influence of the hydrocarbon moiety on the electronic properties of p-GaAs(111)B by exploring the electrochemical behaviour of the p-GaAs(111)B surface functionalized with biphenyl 4,4′ –dithiol (BPDT) and 1,8 –octanedithiol (ODT) in H_2SO_4 solution. The electrochemical properties of the BPDT and ODT coated p-GaAs(111)B substrates and the influence of dithiolate films on the electronic properties of p-GaAs(111)B substrate were investigated by Electrochemical Impedance Spectroscopy (EIS). Changes in chemical composition and surface morphology of the semiconducting substrate brought by the dithiolate film were investigated by X-ray Photoelectron Spectroscopy (XPS) and Atomic Force Microscopy (AFM), respectively.

2. Experimental

Biphenyl 4,4′ –dithiol (BPDT) and 1,8 –octanedithiol (ODT) self-assembled layers were formed by immersing the freshly etched bare

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p-GaAs(111)B samples for 20 h in a well deaerated anhydrous butanol solution of 0.1 mM BPDT and 2 mM ODT, respectively. Prior to electrochemical investigations or thiolation step the p-GaAs(111)B electrodes were degreased in acetone, thoroughly rinsed with deionised water (Direct-Q 3UV System, Millipore) and etched in 1 N HCl solution. Yao at al. [15] showed that the preparation of the p-GaAs(111)B surface by etching it in 1 M HCl brings about a stable and (1 × 1) structure. The sample preparation was made in a Glove Box in order to avoid the contamination of the samples with O_2 atmosphere. BPDT (95% purity), ODT (99% purity), HCl (p.a.) and 2-butanol (p.a.) were purchased from Sigma-Aldrich and used without further purifications.

p-GaAs(111)B electrodes were prepared from highly Zn-doped wafers ($p = 1.40 \times 10^{19}$ cm^{-3}) supplied by GEO Semiconductor ((ULK) Ltd.) and mounted on Teflon holders having the rear part and the edges sealed by epoxy resin. Ohmic contacts to the sample were made by alloying with Ti-Pt-Au (18.5:7.5:74) using thermal evaporation technique.

Electrochemical Impedance Spectroscopy (EIS) measurements were carried out at room temperature in the dark, in well deaerated 0.1 N H_2SO_4 solution in a conventional three-compartment electrochemical cell, with an IM6 Zahner frequency analyzer. The Ag/AgCl electrode and a Pt wire were used as reference and counter electrodes, respectively. The impedance spectra were recorded within the frequency range of 0.3 and 5×10^5 Hz and fitted using Zview software (Scribner Associates Inc., Southern Pines, N·C).

Atomic Force Microscopy (AFM) measurements were carried out at the scale of 2×2 μm^2 in true™ non-contact mode recommended for non-destructive sample scan with a XE-100 apparatus from Park Systems equipped with flexure-guided, cross-talked eliminated scanners. We used ultra-sharp tips (NCHR type from Nanosensors^{TM}), with typically 8 nm tip radius, 125 μm length, 30 μm width and 42 N/m spring constant/~330 kHz resonance frequency. Each sample was investigated on several regions of the surface, usually in the center and other 4 marginal points, to check the reproducibility of the AFM investigations. The AFM images were processed with XEI (v 1.8.0) program from Park Systems for displaying purpose and root mean square roughness (S_q) evaluation.

AFM micrographs were analyzed by using the fractal theory which allows obtaining information about the self-similarity of surfaces or structures at molecular scales. The fractal analysis of AFM micrographs consists in computing these images by using different methods in order to obtain a number known as the fractal dimension, D. This parameter describes how much corrugated/porous/agglomerated are the analyzed objects or surfaces and gives information about their self-similarity. A fractal dimension, D, close to 2 means a smooth surface, almost a plane one whereas a fractal dimension close to 3 describes a very rough surface.

In the present paper, we used two methods to compute the fractal dimension: the correlation function method more appropriate for short range correlations [16] and the variable length scale method more appropriate for long range correlations [17].

XPS investigations were carried out with a SPECS spectrometer equipped with a monochromatized Al Kα-anode radiation source operated at 300 W. Both wide survey and high resolution spectra were obtained for all samples at pressures lower than 2×10^{-9} mbar and at pass energy at 100 eV and 20 eV, respectively. The spectra were fitted by using the SDP v7.0 software (XPS International).

3. Results and discussion

3.1. AFM

The surface morphology of the bare, BPDT and ODT coated p-GaAs(111)B substrates was analyzed by AFM investigations. The AFM images shown in Fig. 1 reveal significant changes in the surface morphology after the chemical modification of the p-GaAs(111)B surface that could be attributed to dithiolate layer formed on p-GaAs(111)B surface.

The bare p-GaAs(111)B sample shows a very smooth surface with a S_q of <3 Å (Fig. 1a). The surface roughness parameter S_q was calculated as:

$$S_q = \sqrt{\frac{1}{MN}\sum_{k=0}^{M-1}\sum_{l=0}^{N-1}\left(z(x_k, y_l)\right)^2}.$$

The surface profile (line scan along the horizontal scanning direction, i.e. z-corrugation profile) of the bare p-GaAs(111)B substrate points to variations of ±0.5 nm (Fig. 1a). The AFM images of the p-GaAs(111)B samples immersed in anhydrous butanol solution of dithiols for 20 h and afterwards dried in air are shown in Fig. 1b and c. The corrugation changes in the z-profile are of ±1 nm after chemical modification of the p-GaAs(111)B surface with dithiols (Fig. 1b and c), higher than at the bare substrate. These results are in good agreement with the increase in surface roughness from 0.29 nm observed at bare

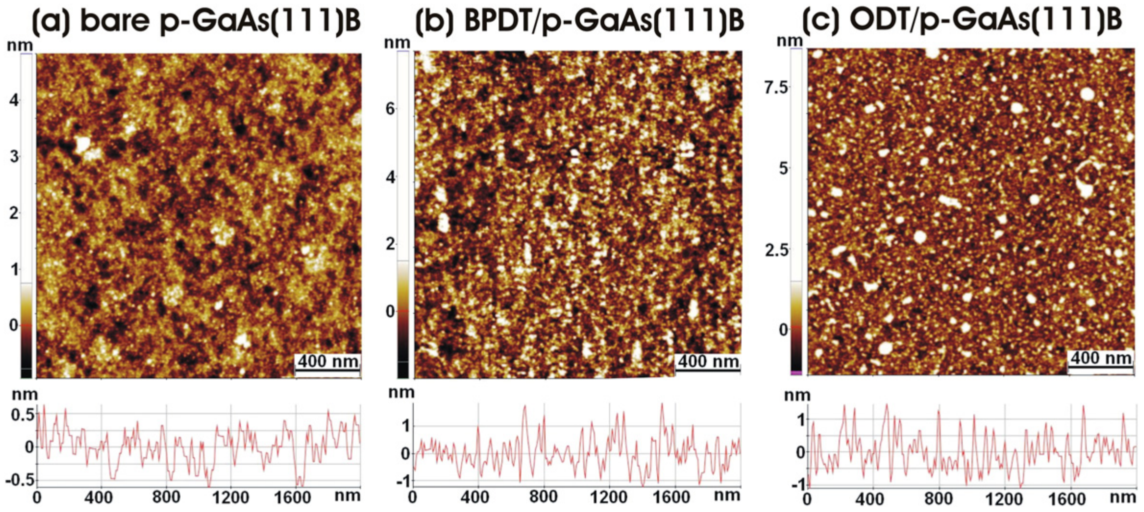

Fig. 1. 2D AFM images at the scale of (2×2) μm^2, for the bare p-GaAs(111)B surface (a), BPDT covered p-GaAs(111)B (b) and ODT covered p-Gas(111)B (c) samples. Below each AFM image, characteristic surface profiles (line scans) are shown.