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Charge-controlled fixation of DNA molecules on silicon surface and electro-physical properties of Au–DNA–Si interface

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ABSTRACT

Light-induced fixation of DNA molecules on silicon surface was done and electro-physical properties of Schottky diodes with DNA on interfaces were investigated. Thymus DNA molecules were deposited on silicon from a water solution. Fixed molecular structures were observed with helium ionic microscopy and atomic force microscopy and then they were covered with thermal sputtered gold film. Obtained structures Au–DNA–(*n*-Si) were examined with current–voltage and frequency dependent admittance measurements. In darkness immobilizing of molecules leaded to form DNA ropes with thickness up to 10 nm and distances between them about 1 mkm. Fixation under illumination resulted in forming of single DNA mesh with thickness about 1 nm and cell size about 100 nm. Presence of molecular mesh on interface leaded to increasing of charge density controlled by metal Fermi level and improved diode quality. Presence of molecular ropes resulted in increasing of charge density controlled by semiconductor. From the estimation of interface state density values the origin of the states at the interface between DNA and silicon substrate is suggested to be DNA phosphate groups contacting or being close to the substrate surface.

1. Introduction

Unique physical–chemical properties of DNA and its ability to form self-organizing structures on substrates give perspective to develop new approaches for the future microelectronics technology. In particular, recently it was proposed to use DNA-molecules for the production of nanoscale electrical device components [1,2]. An important step of such kind of technology development is the fixation process control of DNA on the semiconducting substrate. Since the process is mainly defined by the charge transfer between the two species it was proposed recently [3] to control the conformation of macromolecules by using the substrates of different conductivity types as well as by the generation of minority carriers in semiconductors produced by the illumination with the light.

Electrical characteristics of DNA-based silicon diode structures are investigated in [4–6]. Results of these made it clear that the DNA diodes possessed high interface state densities up to 10^{12} cm^{-2} or more. However relatively thick interface films were created with drying of solution drops on silicon surfaces. That made difficulties for separation of direct DNA impact.

It was demonstrated [3] that on n-type silicon in the darkness or on the p-type under the illumination the molecules got together and formed ropes while on p-type silicon in the darkness or on the n-type under the illumination they formed the meshes of single DNA. Besides, the presence of self-assembly DNA at Au–Si interface was found to accompany with significant impact on the current–voltage (IV) characteristics of Au–DNA–Si Schottky-diodes [7] that was ascribed to the changes of the density of states (DOS) at the interface between silicon and the metal: DOS increased drastically in the presence of the ropes but practically vanished in the structures with single molecule meshes in comparison with the DOS of reference sample.

In this work in addition to dc IV measurements we applied frequency dependent admittance (AS) technique for more detailed study of the interface states of similar Au–DNA–Si structures with the multiple molecule ropes or single molecule meshes on n-type semiconductor. This allowed one to separate between the processes of the charged carrier exchange of DNA states with the semiconductor or with the metal. The values and energy distributions of the interface charge densities had been estimated and the possible origins of the states are discussed.

2. Samples

The solution of calf thymus DNA (Sigma) of 2.5×10^{-3}%, NaCl and $MgCl_2$ of 0.005 M was used for DNA deposition on the 5 mm × 5 mm substrates cut from n-type monocrystalline silicon wafers with mirror-like (0 0 1) surface and with a free electron concentration of

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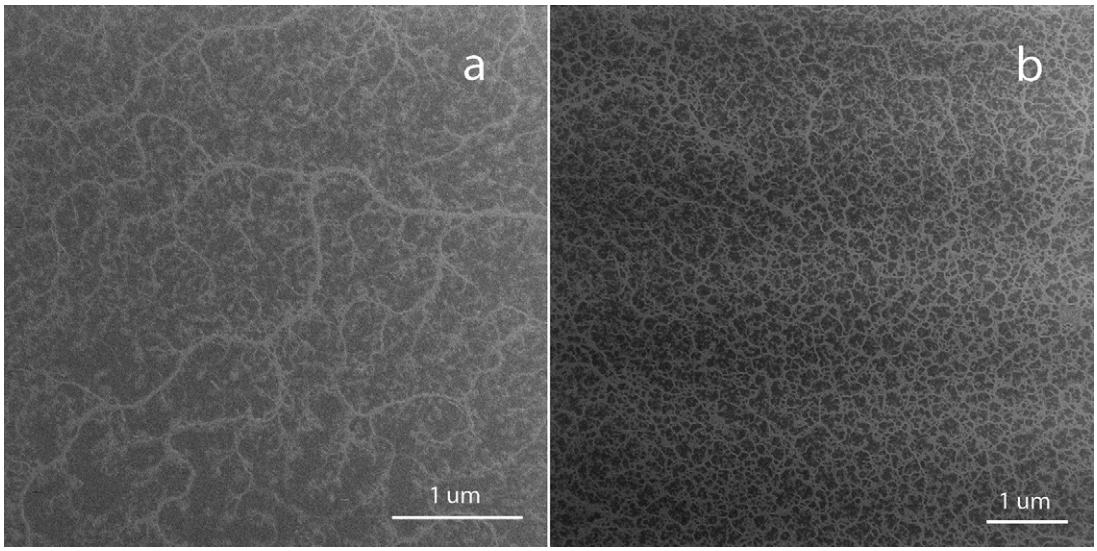

Fig. 1. HeIM images of silicon wafers with fixed DNA. Wide field of vision allows to realize express-analysis of surface after molecular fixation. (a) DNA ropes on silicon surface after fixation in darkness, image size of 4.0 μm × 4.0 μm and (b) DNA mesh on silicon surface after fixation under illumination, image size of 7.0 μm × 7.0 μm.

7×10^{14} cm^{-3}. Prior to the deposition the substrates were etched in buffered HF for 1 min to remove initial native oxide and to bring the surface of all substrates in an equal initial state. Though we believe that during the time of the next sample treatments and measurements the surface of the samples becomes recovered by the native oxide again. Then 10 mkl droplet of the solution was deposited on the substrate surface. After 10 min of exposure either in the darkness or under illumination the substrates were rinsed for 1 min with a jet of distilled water directed nearly parallel to the surface in order to remove unfixed macromolecules and then were dried in the air. The light-emitting diode TSHA5200 with wavelength of 890 nm and current of 40 mA was used as a light source. More detailed description of DNA fixation procedure can be found elsewhere [3,4].

Schottky gold contacts of a diameter of 1.5 mm and of a thickness of 30 nm were thermally evaporated in vacuum on the substrate surfaces with deposited DNA. Ohmic A1-Ga contacts were created on the backside of the samples by rubbing. Reference samples were prepared in the same way but using the solution without DNA.

IV and AS measurements were carried out at room temperature by using Keithley 6517B and Agilent 4294A, respectively. DNA conformation on a large scale was monitored with helium ionic microscopy (HeIM) Orion (Carl Zeiss) while quantitative topographic profiles were measured by atomic force microscopy (AFM) NanoScope IVa (Veeco). All measurements were carried out after week exposure of samples at room environment when electrical characteristics of diodes had stabilized.

HeIM and AFM images of the samples with DNA deposited in darkness and under the illumination are presented in Figs. 1a,b and 2a,c, respectively. Quantitative analysis of the images shows that when deposited in darkness DNA form ropes combining 10 molecules or more, with an average inter-rope distance of about 1 mkm (see Figs. 1a and 2a). Their thicknesses reached up to 10 nm (see vertical profiles in Fig. 2b). Illumination of sample during the deposition resulted in predominant formation of DNA meshes (see Figs. 1b and 2c) of a cell size of about 100 nm and of a thickness of about 1 nm (see vertical profiles in Fig. 2d). The latter value corresponds well to single DNA molecule thickness.

One should note that when the salt solution used for DNA deposition did not contain magnesium ions the density of DNA molecules fixed on the surface reduced drastically and only few molecules could be found on the entire area of the substrate.

3. Electro-physical properties of DNA on silicon

3.1. Theoretical background

The presence of interface layer between the metal and semiconductor gives rise to the formation of additional electronic states, which affect the electro-physical properties of Schottky diodes such as dc and ac current. The information about the density of interfacial state (DOIS) and its energy distribution (ED) can be obtained from the voltage-dependent measurements of dc-current (*I–V*), differential capacitance and ac-conductance. According to rectification theory [8] the current density of the Schotky diode is given by

$$J = A^{*}T^{2} \exp\left(-\frac{e\varphi_b}{kT}\right)\left[\exp\left(\frac{eU}{nkT}\right) - 1\right] \quad (1)$$

where φ_b is the barrier between semiconductor and metal, U is an external bias voltage, e is the electron charge, k is Boltzmann

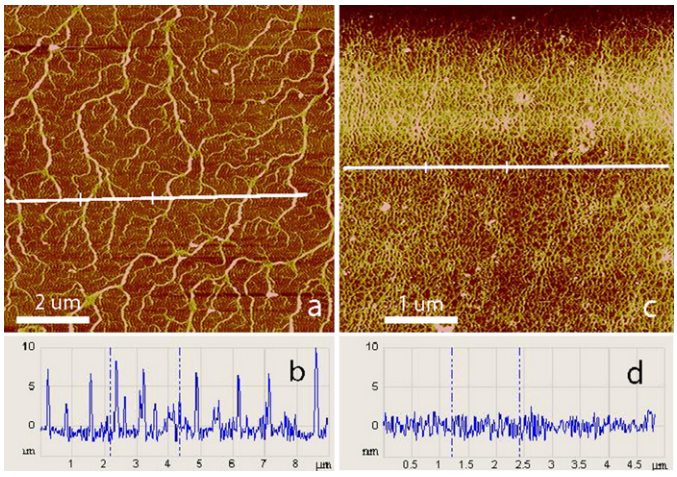

Fig. 2. AFM images of sample surfaces with fixed DNA and topographic profiles of surfaces. (a) DNA ropes on silicon surface after fixation in darkness, image size of 8.8 μm × 8.8 μm, (b) topographic profile of surface after fixation in darkness: ropes thickness run to 10 nm and inter-rope distances about 1 mkm, (c) DNA mesh on silicon surface after fixation under illumination with LED of wavelength 890 nm, image size of 4.4 μm × 4.4 μm, and (d) topographic profile of surface after fixation under illumination: mesh thickness about 1 nm, cell size about 100 nm.