Electrical characterization of organic monolayers/silicon hybrid structures

I V Malyar¹, V O Lukyanova¹, E G Glukhovskoy¹, S B Venig¹ and D A Gorin¹
¹ Department of Nano- and Biomedical Technologies, Saratov State University, Astrakhanskaya, 83, Saratov, 410012, Russia

E-mail: imalyar@yandex.ru

Abstract. Hybrid structures consisting of an n-Si substrate covered with a cationic polyelectrolyte layer and an anionic dye layer were fabricated. Their electrical properties were characterized using tunnel current measurements by a tungsten probe. The obtained I-V curves were analyzed using a modified diode equation. We found out that adsorption of the cationic polyelectrolyte decreases the barrier height of n-Si/organic monolayer/W structure, while adsorption of the low molecular weight anionic dye increases it. The results demonstrate that along with thermionic mechanism other ones are present which prevail at low voltage. In particular, electron tunneling dominates for a single monolayer on the silicon substrate, while, apparently, the Pool–Frenkel mechanism is typical for two monolayers.

1. Introduction
Hybrid structures consisting of organic and inorganic components are a subject of interest in various research fields [1] as they combine well-known and developed inorganic materials with a huge amount of organic ones properties of which can be varied in wide ranges. In particular, such structures based on inorganic semiconductors can be used in microelectronics [2], sensors [3] and photovoltaic applications [4].

There are several models describing electron transfer in hybrid structures [2] which defines their electrical properties. Moreover, models of charge transport through organic molecules were also elaborated [5] to estimate electrical properties of hybrid structures with thick organic layers. Therefore, the conduction mechanism for a certain hybrid structure should be considered separately.

In the present work we examine the electrical properties of hybrid structures consisting of a silicon substrate covered with a cationic polyelectrolyte monolayer and an anionic dye layer using tunnel current measurements.

2. Experimental details
Wafers of n-Si (100) with native oxide and specific resistivity of $\rho = 3-6 \ \Omega \cdot \text{cm}$ were used as substrates. They were cut into 13 mm × 13 mm squares and treated in a peroxide-ammonia solution to remove organic contaminations and to activate negative OH-groups on the surface [6]. Then a cationic polyelectrolyte polyethylenimine (PEI) was adsorbed under different conditions as it was described in [7], i.e. some silicon substrates were illuminated during PEI adsorption. However, a halogen lamp (Philips 13186 EPX/EPV) was used as a light source to maximize effect of illumination instead of a He-Cd laser. According to [7], illumination increases the negative surface charge of silicon substrates due to tunneling of photogenerated electrons into the native oxide. Thus, it enhances interaction
between the negatively-charged substrate and cationic polyelectrolyte molecules decreasing both thickness and roughness of the adsorbed monolayer.

Similarly, an anionic dye Photosens consisting of sulfonated hydroxialuminum phthalocyanines AlPcS\(_x\) with \(x = 2, 3\) or 4 (the mean \(x = 3.1\)) \[8\] was adsorbed. The deposition time and AlPcS\(_x\) concentration were 10 min and 0.2 mg/mL, respectively.

Thus, 7 different types of samples were prepared: \(n\)-Si, \(n\)-Si / PEI, \(n\)-Si / PEI\(^{ill}\), \(n\)-Si / PEI / AlPcS\(_x\); \(n\)-Si / PEI / AlPcS\(_x\)^{ill}; \(n\)-Si / PEI\(^{ill}\) / AlPcS\(_x\); \(n\)-Si / PEI\(^{ill}\) / AlPcS\(_x\)^{ill}, where superscript “ill” indicates illumination during adsorption.

Electrical properties of the samples were characterized using tunnel current-voltage (I-V) curves measured with a tungsten probe by means of NTEGRA Spectra (NT-MDT, Russia) under ambient conditions. A conducting carbon tape was used as a bottom contact. Initially, the sample surface was scanned in the constant current regime. Then ten I-V curves were measured in each of six selected points on the scan by applying a linear bias from -5 to +5 V to sample, while probe was grounded.

3. Results and discussion

Figure 1 demonstrates typical I-V curves for different samples. All dependences reveal rectification, which is typical for the Schottky barrier. Therefore, these curves were analyzed using a diode equation with ideality factor \(n\) indicating different conductance mechanisms:

\[
I = I_s \exp \left\{ \frac{qV}{nk_B T} \left[ 1 - \exp \left( \frac{-qV}{k_B T} \right) \right] \right\}
\]

where \(I_s = \sigma A^* T^2 \exp \left( \frac{-q\phi_{Bn}}{k_B T} \right)\) is the saturation current, \(q\) is the elementary charge, \(A^*\) – the effective Richardson constant, \(\sigma\) – contact area, \(q\phi_{Bn}\) – the Schottky barrier height for electrons, \(T\) – temperature, \(k_B\) is the Boltzmann constant.

In report \[9, 10\] the equation (1) was used to analyze I-V curves for semiconductor/organic monolayer/metal hybrid structures, where along with thermionic current mechanism other ones occur. Therefore, the ideality factor exceeds 1. The direct branches of experimental I-V curves were plotted in \(\ln I\) vs. \(V\) scale (figure 2) using the following equation:

\[
\ln \left[ \frac{I}{1 - \exp \left( -\frac{qV}{k_B T} \right)} \right] = \ln \left( \sigma A^* T^2 \right) + \frac{q}{k_B T} \left( -\phi_{Bn} + \frac{V}{n} \right).
\]
Figure 2. Typical I-V characteristics of an n-Si substrate and ones covered with polyethylenimine (PEI) and sulphonated hydroxyaluminum phthalocyanine (AlPcSx) monolayers. Superscript “ill” indicates illumination during adsorption of organic monolayer.

The curves presented in figure 2 reveal a linear dependence at high voltage and nonlinear one at low voltage. The linear region corresponds to thermionic (Schottky) emission and, thereby, the ideality factor can be extracted from its slope, while the Schottky barrier height can be estimated from its interception of ln I axe. However, the contact area is necessary to define. According to [11] a radius of freshly etched tungsten probes is about 40 nm, then, suggesting that electron tunneling occurs only from a surface layer of δ = 1 nm, the effective contact area, σ, for electrons can be calculated as [12]:

\[ \sigma = \frac{\pi d^2}{4}, \]

where \( d = 2\sqrt{R^2 - (R - \delta)^2} \) — is an effective diameter. Thus, the effective contact area is \( \sigma = 248.7 \text{ nm}^2 \) and term \( \ln(\alpha t^2 T^2) \) for n-Si (100) is equal to -9.82. Table 1 presents calculated averaged parameters.

The results in table 1 demonstrate that deposition of the organic monolayer changes both the barrier height and the ideality factor. The barrier height drastically depends on the surface state charge which is negative for n-Si substrates [13]. Therefore, deposition of positively-charged PEI decreases the barrier height and, on the contrary, negatively-charged dye increases it. Both organic layers significantly increase the ideality factor. Its high values for all samples indicate non-thermionic current mechanisms which, apparently, prevail at low voltage and correspond to nonlinear regions in figure 2. Moreover, deposition conditions, i.e., photoassistance during adsorption, also influence the barrier height and the ideality factor. Since illumination increases electrostatic interaction between a silicon substrate and adsorbed molecules, then it enhances the effect of organic layer on hybrid structure parameters. In particular, photoassisted adsorption of a polyelectrolyte enhances electrical passivation of silicon surface [14].

There are several current mechanisms in dielectrics as tunneling, thermionic emission, Frenkel-Poole emission, etc. [2, 13]. Therefore, we plotted I-V curves in a double logarithmic scale (figure 3) to find out the current mechanisms at low voltage from the power law relation \( I \propto V^\alpha \).

All curves in figure 3 were approximated by linear dependences, and an exponent \( \alpha \) was calculated from their slopes (Table 1). We observe a reciprocal proportion between the ideality factor \( n \) and the exponent \( \alpha \) for hybrid samples, i.e., \( \alpha \cdot n = \text{const} \). Constant is equal to 3.55±0.15 for Si/PEI samples and 2.35±0.13 for Si/PEI/AlPcSx samples. Thus, these parameters are complementary.

A linear dependence (\( \alpha \approx 1 \)) between tunnel current and voltage for Si/PEI samples indicates electron tunneling through a rectangular barrier [15]. According to [16] the slope value of about 0.5 indicates the Pool–Frenkel mechanism in Si/PEI/AlPcSx samples. However, we suppose a combination of mechanisms mentioned above for these samples. In addition, we suppose a complex conductivity mechanism consisting of thermionic (Schottky) emission and electron tunneling for a silicon substrate without any organic coating.
Table 1. The calculated parameters of an n-Si substrate and ones with poly(ethylenimine) (PEI) and sulphonated hydroxyaluminum phthalocyanine (AlPcSx) monolayers. \( n \) is the ideality factor, \( \varphi_b \) is the Schottky barrier height, \( \alpha \) is an exponent in the power law connecting tunnel current and applied voltage. Superscript “ill” indicates illumination during polyelectrolyte adsorption.

| Parameters | Si | Si/PEI | Si/PEI\textsuperscript{ill} | n-Si / PEI / AlPcS\textsubscript{x} | n-Si / PEI\textsuperscript{ill} / AlPcS\textsubscript{x} | n-Si / PEI / AlPcS\textsubscript{x}\textsuperscript{ill} | n-Si / PEI\textsuperscript{ill} / AlPcS\textsubscript{x}\textsuperscript{ill} |
|------------|----|--------|-----------------------------|-----------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| \( n \)    | 1.81 | 3.65   | 3.16                        | 7.37                        | 6.57                                          | 5.93                                          | 4.88                                          |
| \( \varphi_b \), mV | 373±5 | 336±5  | 331±5                       | 360±6                       | 371±7                                        | 401±5                                        | 428±5                                        |
| \( \alpha \) | 1.58 | 1.01   | 1.07                        | 0.31                        | 0.35                                          | 0.43                                          | 0.45                                          |

4. Conclusions
We fabricated hybrid structures based on the n-Si substrates with organic monolayers of the cationic polyelectrolyte (PEI) and the low molecular weight anionic dye (Photosens). Electrical properties of the samples were characterized using tunnel current measurements. We observed rectification in I-V curves; therefore, the modified diode equation was used to calculate the barrier height and to monitor the current mechanism. We found out that adsorption of PEI decreases the barrier height for n-Si, while adsorption of Photosens increases it. The results demonstrate that along with thermionic mechanism other ones occur which prevail at low voltage. In particular, electron tunneling dominates for a single monolayer on a silicon substrate, while, apparently, the Pool–Frenkel mechanism is typical for two monolayers.

Acknowledgements
This work was supported by the Russian Science Foundation (grant 14-12-00275) and Russian Federation President Grant for young scientists.

References
[1] Sanchez C, Belleville P, Popalld M and Nicole L 2011 *Chem. Soc. Rev.* **40** 696
[2] Ortiz R P, Facchetti A and Marks T J 2010 *Chem. Rev.* **110** 205
[3] Wang S, Kang Y, Wang L, Zhang H, Wang Y, Wang Y 2013 *Sensors and Actuators B: Chemical* **182** 467
[4] Wright M and Uddin A 2012 Solar Energy Materials & Solar Cells 107 87
[5] Ulgut B and Abruna H D 2008 Chem. ReV. 108 2721
[6] Aswal D K, Lenfant S; Guerin D; Yakhmi J V, Vuillaume D 2006 Anal. Chem. Acta 568 84
[7] Malyar I V, Gorin D A, Stetsyura S V, Santer S 2013 Langmuir. 29 16058
[8] Svenskaya Y, Parakhonskiy B, Haase A, Atkin V, Lukyanets E, Gorin D, Antolini R 2013 Biophysical Chemistry 182 11
[9] Vilan A, Shanzer A and Cahen D 2000 Nature 404 166
[10] Hiremath R K, Rabinal M K, Mulimani B G and Khazi I M 2008 Langmuir 24 11300
[11] Malyar I V, Gorin D A, Stetsyura S V 2012 Proc. SPIE 8700 870009
[12] Feenstra R M, Stroscio J A and Fein A P 1987 Surface science 181 295
[13] Sze S 1985 Semiconductor Devices: Physics and Technology, 2nd ed (Wiley: New York)
[14] Stetsyura S V, Kozlowski A V, Malyar I V 2015 Technical Physics Letters 4 168
[15] Simmons J G 1963 Journal of Applied Physics 34 1793
[16] Nabok A V, Hassan A K, Ray A K and Toldi G N 2002 Materials Science and Engineering 22 387