Semiconductors, 2024, Vol. 58, No. 10

Interaction between a silicon nanowires surface and molecules of NH_3 and HCl: DFT model and experiment

© *N.A. Svinkin*[1], *V.M. Kondratev*[1,2], *R.G. Polozkov*[1,3], *A.D. Bolshakov*[1,2,4]

[1] Alferov University,
194021 St. Petersburg, Russia
[2] Moscow Institute of Physics and Technology (State University),
141701 Moscow, Russia
[3] Peter the Great Saint-Petersburg Polytechnic University,
195251 St. Petersburg, Russia
[4] St. Petersburg State University,
199034 St. Petersburg, Russia
E-mail: nik-svinkin@mail.ru

Received May 3, 2024
Revised July 24, 2024
Accepted October 30, 2024

Theoretical and experimental studies of the interaction processes of the surface of silicon nanowires with NH_3 and HCl molecules have been carried out in connection with the possibility of creating gas sensors that have potential for use in healthcare. The DFT approach has been conducted to show that the experimental results can be explained by the redistribution of the electron density between adsorbed molecules and the silicon surface. It is possible due to the resistive response of Si nanowires to changes in the concentration of NH_3 and HCl vapors experimentally established.

Keywords: Silicon nanowires, gas sensing, ammonia, hydrochloric acid, DFT.

DOI: 10.61011/SC.2024.10.59938.6461A

Silicon is a classic material of modern micro- and nanoelectronics [1]. It is widely used to fabricate sensoric devices applied in medical care, in industry and in natural science [2,3]. Nanostructures with large ratio of surface area to volume, such as silicon nanowires (Si NWs) are of special interest. Large adsorption capacity in combination with processability make these materials one of the most prospective to create sensing elements of gas sensors [4–6]. Besides, currently other applications of NWs are widely studied [10–12].

This paper relates to theoretical and experimental study of adsorption properties of Si NWs in view of possibility to create based on them of the effective adsorption sensors of ammonia and hydrochloric acid. Detection of NH_3 and HCl is interesting in view of medicine, as these substances are products of various biologic processes in the human body. Their concentration in biologic fluids of the human can be used to evaluate the human health [2].

To study processes of interaction of ammonia and hydrogen chloride with surface of Si NW the modeling of adsorption of molecules NH_3 and HCl on surface Si(100) was performed using software ORCA 4.2.1 [13,14] by method wB97X-D3/6-31G. For correct simulation a silicon cluster was prepared with Si(100) orientation, the size of 4×4 bulk silicon lattice cells, and thickness of 4 atomic layers. Dangling bonds in all directions, except studied, were passivated by hydrogen atoms (H). Analyte molecule was drawn to rest free surface Si(100). The geometry was optimized only for atoms of two „top“ layers, and for atoms of adsorbate molecule, rest atoms play role of skeleton and were fixed by program (it is expected that atoms in three and further layers from surface have same configuration as atoms in bulk of crystal). Figure 1 shows results of calculation for complexes Si(100), Si(100)+NH_3 and Si(100)+HCl, for easy perception part of complex is hidden. Images are made using Chemcraft [15].

Distribution of charge density in clusters is presented in maps of electrostatic potential (ESP-maps) plotted and visualized using packages MultiWFN [16,17] and VMD [18], respectively. Color indication shows energy of interaction of test positive charge with complex in kcal/mol. Negative values indicate attraction, positive - repulsion. So, white color indicates excess of positive charge, and black color — excess of negative charge. Figure 2 shows ESP-maps for studied complexes.

Quantitative results of modeling are summarized in Table, where Si$-$X means distance between atoms N or Cl and neighboring Si after optimization; Δ(Si$-$Si) — change of bond length of dimer on surface of crystal upon interaction with adsorbate molecule (NH_3 or HCl); ΔQ_{MPA} — charge on adsorbate molecule, calculated via Mulliken Population Analysis [19]; ΔE — bond energy of adsorbate molecule on silicon surface, which was determined as change of full energy of complex after adsorption of analyte molecule. Note that one molecule of hydrochloric acid takes more electron density from Si NW, then ammonia molecule gives away. From this more significant change of Si NW resistance is observed in the first case as compared to the second case. Besides, Table shows that adsorption of HCl molecule is more energy beneficial then of NH_3 molecule,

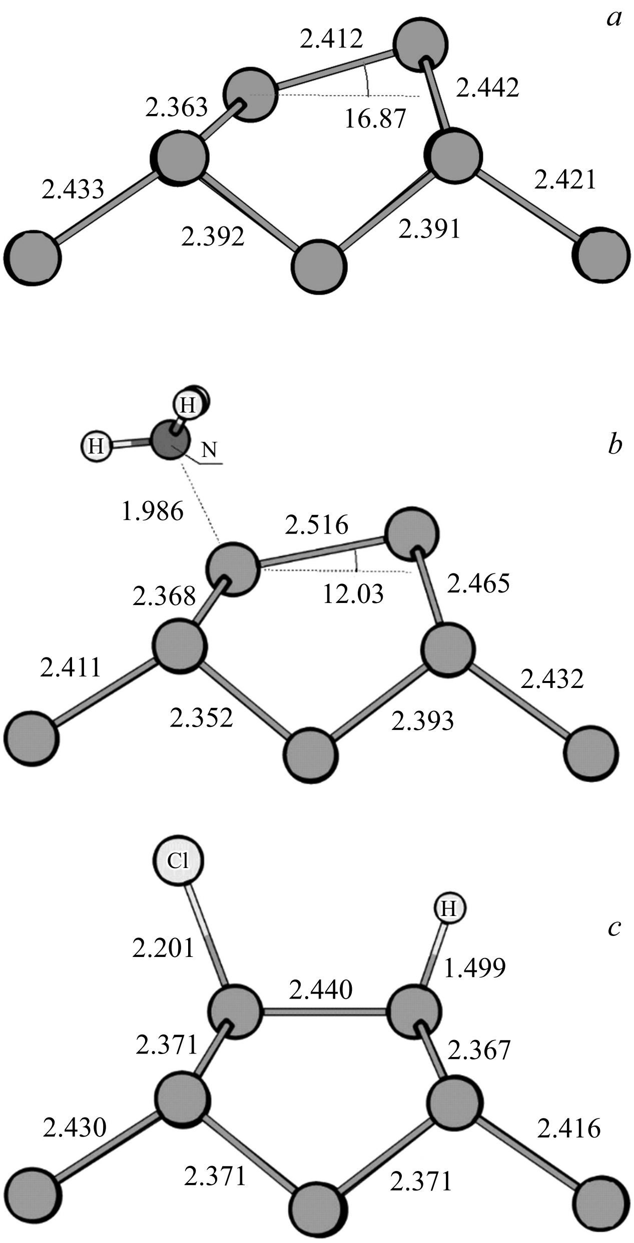

Figure 1. Optimized geometry of studied complexes: *a* — Si(100), *b* — Si(100)+NH_3, *c* — Si(100)+HCl. Designations: atoms of adsorbate molecules are named, unnamed atoms — Si. Lengths are given in Å, angles — in degrees.

hence, probability of adsorption of individual molecule of hydrochloric acid is higher. These circumstances lead to the fact that the resistive response in the case of hydrochloric acid adsorption will be more noticeable than in the case of ammonia adsorption, which is observed in the experiment.

Based on the modeling results, an experimental study was performed of the adsorption properties of 10 μm long Si NWs, which were obtained by the method of plasma-chemical cryogenic etching of the boron-doped silicon crystal in the direction (100) [20]. Further Si NWs were separated from the substrate using ultrasound and relocated on the substrate with deposited drop casting rod gold contacts (spacing 10 μm) by drop-by-drop method [20]. As a result over 26 000 Si NWs were electrically connected parallel to each other. As sensing response we estimated

Characteristics of interaction of molecules NH_3 and HCl with surface Si(100) as per results of DFT-modeling

	Si(100)+NH_3	Si(100)+HCl
Si−X, Å	1.986	2.201
Δ(Si−Si), Å	0.104	0.028
ΔQ_{MPA}, e	0.275	−0.386
ΔE, eV	2.8	3.5

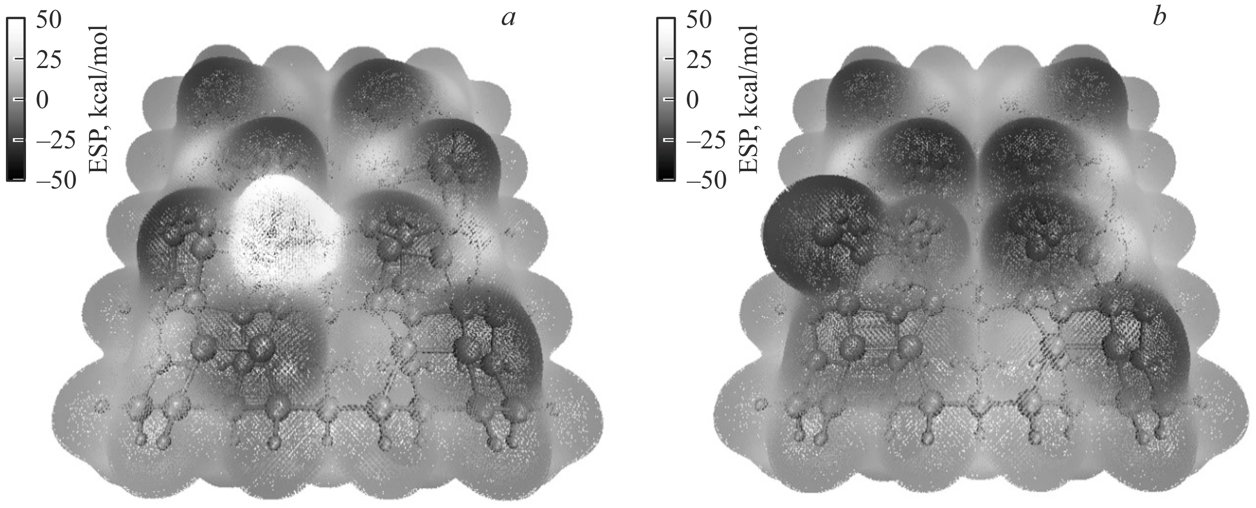

Figure 2. ESP-maps of studied complexes: *a* — Si(100)+NH_3, *b* — Si(100)+HCl.

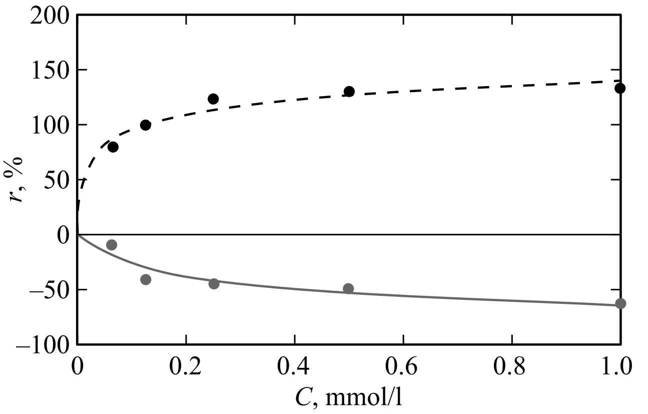

Figure 3. Relative resistance of samples in presence of NH_3 (solid gray curve) and HCl (dashed black curve) vapors.

change of active resistance of sensor based on NW in the presence of ammonia vapors, obtained from aqueous solution NH_3 with concentrations in range of 0 to 1 mmol/l, as compared to reference medium — water vapors. Measurements were performed using impedance meter Z500P. The measurement results are shown in Figure 3. Relative resistance of sensor r was determined as follows:

$$r = \frac{R_{\text{media}} - R_{H_2O}}{R_{H_2O}} \cdot 100\%, \qquad (1)$$

where R_{media} — sample resistance in the presence of analyte, R_{H_2O} — sample resistance in water vapors.

Under this study we show the possibility of qualitative and quantitative detection of ammonia and hydrochloric acid using sensors based on Si NWs. It was determined that during adsorption a redistribution of electron density occurs between the crystal surface and the adsorbate molecule, which can explain the change in resistance observed in the experiment.

Acknowledgments

V. Kondrat'ev and R. Polozkov thanks the Ministry of Science and Higher Education of the Russian Federation (Grant FSRM-2023-0009) A. Bol'shakov thanks the Ministry of Science and Higher Education of the Russian Federation (agreement 075-03-2023-106, project FSMG-2021-0005)

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] S. Oda, D. Ferry (ed.). *Silicon nanoelectronics* (Boca Raton, CRC Press, 2017).

[2] Y. Xu, X. Hu, S. Kundu, A. Nag, N. Afsarimanesh, S. Sapra, S.C. Mukhopadhyay, T. Han. Sensors, **19** (13), 2908 (2019).

[3] S. Joo, R.B. Brown. Chem. Rev., **108** (2), 638 (2008).

[4] M. Akbari-Saatlu, M. Procek, C. Mattsson, G. Thungström, H.-E. Nilsson, W. Xiong, B. Xu, Y. Li, H.H. Radamson. Nanomaterials, **10** (11), 2215 (2020).

[5] V.M. Kondratev, I.A. Morozov, E.A. Vyacheslavova, D.A. Kirilenko, A. Kuznetsov, S.A. Kadinskaya, S.S. Nalimova, V.A. Moshnikov, A.S. Gudovskikh, A.D. Bolshakov. ACS Appl. Nano Mater., **5** (7), 9940 (2022).

[6] V.M. Kondratev, E.A. Vyacheslavova, T. Shugabaev, D.A. Kirilenko, A. Kuznetsov, S.A. Kadinskaya, Z.V. Shomakhov, A.I. Baranov, S.S. Nalimova, V.A. Moshnikov, A.S. Gudovskikh, A.D. Bolshakov. ACS Appl. Nano Mater., **6** (13), 11513 (2023).

[7] S.S. Nalimova, V.M. Kondrat'ev. 2020 IEEE Conference of Russian Young Researchers in Electrical and Electronic Engineering (EIConRus), 987-990 (2020).

[8] E.A. Levkevich, A.I. Maksimov, S.A. Kirillova, S.S. Nalimova, V.M. Kondrat'ev, A.A. Semenova. 2020 IEEE Conference of Russian Young Researchers in Electrical and Electronic Engineering (EIConRus), 984-986 (2020).

[9] S.A. Kadinskaya, V.M. Kondratev, I.K. Kindyushov, A. Kuznetsov, K.N. Punegova. 2022 Conference of Russian Young Researchers in Electrical and Electronic Engineering (ElConRus), 958-961 (2022).
[10] M.A. Anikina, P. Roy, S.A. Kadinskaya, A. Kuznetsov, V.M. Kondratev, A.D. Bolshakov. Nanomaterials, **13** (1), 56 (2022).
[11] A. Kuznetsov, P. Roy, D.V. Grudinin, V.M. Kondratev, S.A. Kadinskaya, A.A. Vorobyev, K.P. Kotlyar, E.V. Ubyivovk, V.V. Fedorov, G.E. Cirlin, I.S. Mukhin, A.V. Arsenin, V.S. Volkov, A.D. Bolshakov. Nanoscale, **15** (5), 2332 (2023).
[12] A. Kuznetsov, E. Moiseev, A.N. Abramov, N. Fominykh, V.A. Sharov, V.M. Kondratev, I.I. Shishkin, K.P. Kotlyar, D.A. Kirilenko, V.V. Fedorov, S.A. Kadinskaya, A.A. Vorobyev, I.S. Mukhin, A.V. Arsenin, V.S. Volkov, V. Kravtsov, A.D. Bolshakov. Small, **19** (28), 2301660 (2023).
[13] F. Neese. WIREs Comput. Mol. Sci., **2** (1), 73 (2012).
[14] F. Neese. WIREs Comput. Mol. Sci., **8** (1), e1327 (2017).
[15] G.A. Zhurko. *Chemcraft — graphical program for visualization of quantum chemistry computations* (Ivanovo, Russia, 2005). https://chemcraftprog.com
[16] T. Lu, F. Chen. J. Mol. Graphics Model., **38**, 314 (2012).
[17] T. Lu, F. Chen. J. Comput. Chem., **33** (5), 580 (2012).
[18] W. Humphrey, A. Dalke, K. Schulten. J. Mol. Graphics, **14** (1), 33 (1996).
[19] R.S. Mulliken. J. Chem. Phys., **23** (10), 1833 (1955).
[20] V.M. Kondratev, I.A. Morozov, E.A. Vyacheslavova, A.S. Gudovskikh, S.S. Nalimova, V.A. Moshnikov, A.D. Bolshakov. J. Phys.: Conf. Ser., **2015** (1), 012068 (2021).

Translated by I.Mazurov