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**REGULAR ARTICLE**

# Controlling by Defects of Switching of ZnO Nanowire Array Surfaces from Hydrophobic to Hydrophilic: First-Principles Calculations

A.N. Stepanyuk* , R.M. Balabai

*Kryvyi Rih State Pedagogical University, 50086 Kryvyi Rih, Ukraine*

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One of the promising applications of nanowires is controlling their hydrophobicity. This can be achieved by modifying the structure and chemical composition of the nanowire surfaces. One-dimensional crystalline nanostructures, such as nanowires, are particularly interesting for wettability control, as superhydrophobic surfaces can be created by precisely adjusting the height and spacing between the nanowires. Zinc oxide (ZnO) nanowires attract significant attention due to their unique properties for superhydrophobic applications. Understanding the interaction between water molecules and ZnO nanowire surfaces is key to investigating their wetting properties and potential use in hydrophobic or hydrophilic coatings. In this study, first-principles calculations were employed to investigate the influence of crystallographic orientation and defects on the wettability of ZnO nanowires, as well as the energy landscapes for water molecule migration along ZnO nanowire surfaces. The results showed that the polar surfaces of ZnO nanowires exhibit hydrophobic properties, while the non-polar side surfaces are hydrophilic. The presence of surface defects in ZnO nanowires, such as oxygen or zinc vacancies, does not qualitatively change the wettability of the surfaces but increases the energy barriers of these processes. It is worth noting that the density of nanowires in the array, which was regulated by varying the distance between the wires, is not a critically important parameter, even when the ZnO nanowire surfaces are modified with defects. The qualitative nature of surface wettability remains unchanged when decreasing the distance between the wires, with only a slight increase in activation energies observed. The critical distances at which water molecules start interacting with the polar surfaces of ZnO nanowires were determined, providing insight into the spatial scale of surface-water interactions. The results of the study deepen the understanding of the mechanisms of reversible wettability of ZnO nanowires.

**Keywords**: ZnO nanowires, Surface wettability, Polar and nonpolar ZnO surfaces, Surface defects, First-principles calculations, Energy profiles of the water molecule motion, Electric charges.

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## 1. INTRODUCTION

One of the promising applications of nanostructures is the control of their surface hydrophobicity, which can be achieved by modifying the surface structure and chemical composition. One-dimensional crystals, or nanowires, are of particular interest for wettability control because manipulation of the height and step between nanowires can achieve a superhydrophobic structure. ZnO nanowires have unique structural and functional properties, making them advantageous for multifunctional superhydrophobic applications. ZnO nanowires have three different crystallographic directions of rapid growth, which allows the synthesis of various nanostructures with controlled growth [1-4]. Polar and nonpolar ZnO surfaces have different wettabilities. The relationship between ZnO surface wettability and different crystallographic orientations was studied by Wei and colleagues [5]. This team prepared ZnO thin films with crystallographic orientations ranging from purely polar surfaces to a completely nonpolar plane and observed a change in the water contact angle with the surface. However, other studies have reported different values of the water contact angle with the surface for ZnO nanowires [6]. Some of the hypotheses of these studies are: hydrophilic properties can be obtained by changing the height and density of nanowires; surface defects are responsible for the transition between hydrophilic and hydrophobic states of ZnO wires.

Therefore, understanding the mechanisms of reversible wettability at the atomic level is important for the development of practical applications of ZnO nanowires. In this study, the energy profiles of water molecule migration along different surfaces of ZnO nanowires without defects and with oxygen or zinc vacancies on the nanowire surfaces were obtained to do conclusions about the features of the physicochemical processes occurring in nanowires without water molecules and in the presence of water, and whether the nanowire surfaces are hydrophilic or hydrophobic [7].

## 2. METHODS AND OBJECTS OF RESEARCH

Zinc oxide (ZnO) in the wurtzite structure type has the following elementary cell parameters:

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[*] Correspondence e-mail: alexanderstepanyuk@gmail.com

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$a = b = 0.3249$ nm, $c = 0.5205$ nm. Oxygen atoms (O) form a double-layer close packing, in which zinc (Zn) atoms occupy half of the tetrahedral voids of same orientation. In the ZnO bulk, layers of both types of atoms alternate along the c-axis and cause crystal polarity: $Zn^{2+}$ ions form (0001) layers, $O^{2-}$ ions form (000$\bar{1}$) layers. Zn – O distances along the c-axis are 0.1992 nm, and in the other three directions, they are 0.1973 nm. In the hexagonal wurtzite structure, each anion is surrounded by 4 cations located at the vertices of a tetrahedron (the same for cations). This is a typical $sp^3$ coordination of covalent bonding, but ZnO crystal also has a significant ionic character (ionicity degree of 0.675). The electron configurations of O and Zn are, respectively: $1s^22s^22p^4$ and $1s^22s^22p^63s^23p^63d^{10}4s^2$.

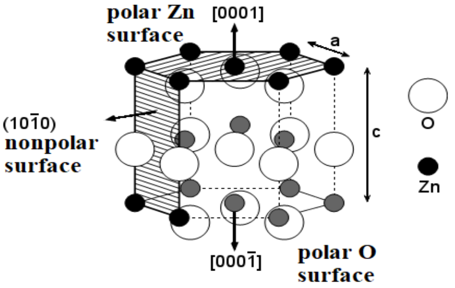

**Fig. 1** – Atomic structure of the ZnO crystal

The wurtzite crystal is bounded by the following surfaces: non-polar (10$\bar{1}$0) surface and (1120) surface, polar (0001) surface terminated by Zn ions and polar (000$\bar{1}$) surface terminated by O ions (Fig. 1). All four types of surfaces with atomic arrangements as in the bulk can be obtained by ion beam deposition followed by annealing at not very high temperatures.

The algorithm of the code used to obtain all the results of this numerical study is based on the following: the local density approximation of the electronic density functional theory, the Bachelet-Hamann-Schlüter pseudopotential from first principles and the supercell method [6-16]. The calculations were performed under the following conditions: the summation over the Brillouin zone of the artificial supercell was replaced by a calculation at one Γ-point. The self-consistent iterations of the Kohn-Sham equations were stopped if the results of the current iteration calculation coincided with the previous one with a predetermined error. The atomic basis was not optimized.

The laboratory coordinate system used in the author's software package is rectangular, and the calculation algorithm assumes translational symmetry in the atomic system under study. Therefore, an artificial orthorhombic supercell was initially developed, the unit cell of which is a rectangular parallelepiped. The parameters of the unit cell of this supercell and the atomic basis were determined as the objects of the study (Fig. 2).

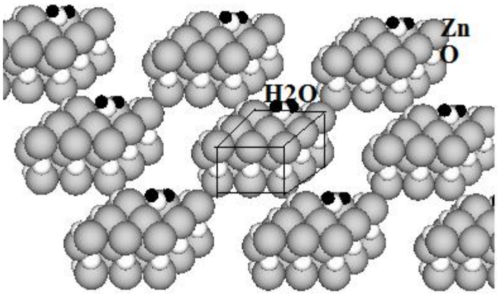

**Fig. 2** – Fragment of a ZnO nanowire array with a wurtzite crystal structure grown along the c-axis: layers of Zn/O/Zn/O ions create a sequence in the [0001] direction

Four groups of atomic objects were created: I – two nanowires per unit cell of the artificial superlattice, II – two nanowires and two water molecules, III – two nanowires with one vacancy ($V_O$ or $V_{Zn}$) on the surface of each, IV – two nanowires with one vacancy ($V_O$ or $V_{Zn}$) on the surface of each and two water molecules. Water molecules were placed in different positions relative to the nanowires. The distance between the water molecules and the nanowire surfaces was not less than the sum of the radii of the surface atoms of the wires and the nearest atoms of the water molecules. Translation of the unit cell with the atomic basis described above along the directions of the crystallographic axes **a**, **b**, **c** of the artificial superlattice, which are conjugated for these objects with the axes X, Y, Z of the Cartesian coordinate system, leads to the creation of an infinite array of wires (see Fig. 2).

In this case, the translation parameters were chosen in such a way as to avoid interaction between the wires in the **c** direction, and this parameter did not change during the numerical experiment, while the translation parameters in the **a**, **b** directions, on the contrary, changed to reveal the effect of the size of the space between the side surfaces of the wires in the array on their hydrophobicity.

For each atomic configuration, which corresponded to different fixed positions of water molecules, the total energy (formula 1) and electric charge (formula 2) in the vicinity of the atom α of the wire closest to the water molecule were calculated:

$$\begin{aligned}\frac{E_{total}}{\Omega} = {} & \sum_{\vec{k},\vec{G},i} |b_i(\vec{k}+\vec{G})|^2 \frac{\hbar^2}{2m}(\vec{k}+\vec{G})^2 + \frac{1}{2}4\pi e^2 \sum_{\vec{G}}{}' \frac{|\rho(\vec{G})|^2}{\vec{G}^2} + \sum_{G}\varepsilon_{xc}(\vec{G})\rho^*(\vec{G}) + \\ & + \sum_{\vec{k},\vec{G},\vec{G}',i,l,s} S_s(\vec{G}-\vec{G}')\Delta V_{l,S}^{NL}(\vec{k}+\vec{G},\vec{k}+\vec{G}')b_i(\vec{k}+\vec{G})b_i^*(\vec{k}+\vec{G}') + \sum_{\vec{G},S}{}' S_s(\vec{G})V_S^L(\vec{G})\rho^*(\vec{G}) + \left\{\sum_S a_s\right\}\left[\Omega^{-1}\gamma_{Ewald}\right]\end{aligned} \qquad (1)$$

where $\vec{k}$ matters from the first Brillouin zone of the superlattice, $\vec{G}$ – the reciprocal lattice vector, $b_i(\vec{k}+\vec{G})$ – the coefficient of the wave function expansion, $i$ denotes the occupied states for a certain $\vec{k}$, $\rho(\vec{G})$ is a coefficient of the valence electron density expansion, $s$ enumerates the atoms in the unit cell, $S_s(\vec{G})$ is a structural factor, $V_S^L$ is a local ($L$ – independent) spherically symmetric pseudopotential, $l$

denotes the quantum orbital number, $\Delta V^{NL}_{l,t}$ is a non-local ($L$ – dependent) contribution to the $V^L_S$, $Z_S$ is the charge of the ionic core, $\gamma_{Ewald}$ is the Madelung energy of point ionic framework.

$$q_\alpha = Z_\alpha - \int\limits_{V_\alpha} \rho(\vec{r}) d\vec{r} \qquad (2)$$

The atomic basis of the unit cell of the artificial lattice for reproducing object I consisted of 108 atoms, object II – 114 atoms, object III – 106 atoms, object IV – 112 atoms. For all objects, in addition to changing the position of water molecules and atomic vacancies (6 variants of location, Fig. 3), the distances between the nanowires also changed, which was equal or 0.33 nm, or 0.29 nm, or 0.25 nm.

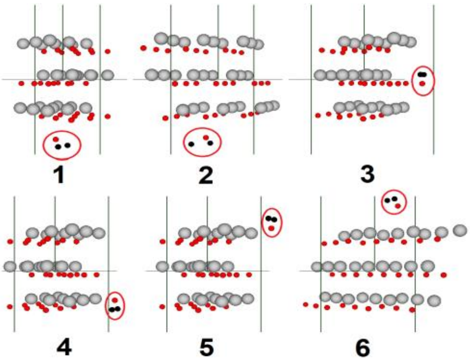

**Fig. 3** – Positions of the water molecule (circled in red ellipse) near the surface of the ZnO nanowire (object II), for which the calculations were performed. Large gray spheres represent zinc atoms; small red ones - oxygen atoms

The positions of the water molecule near the ZnO nanowire surface, labeled "1", "2", and "3", are the closest to the surface oxygen (O) atoms of the nanowire. Locations "1" and "2" are located on the $(000\bar{1})$ O polar surface, and location "3" is located on the (0100) non-polar surface. Positions "4", "5", and "6" are the closest to the surface zinc (Zn) atoms of the nanowire, with locations "5" and "6" on the (0001) polar surface Zn and location "4" on the (0100) non-polar surface. If the water molecule is removed in Fig. 3, an image of object I is obtained. If the water molecule and a specific surface atom of the nanowire are removed in Fig. 3, an image of object III is obtained. If the atom closest to the water molecule is absent in Fig. 3, i.e., a surface vacancy is created, then an image of object IV is obtained.

Fig. 4 shows all the positions of the atoms on the wire surface to which the water molecules were brought, i.e., the trajectory of the water molecule is indicated.

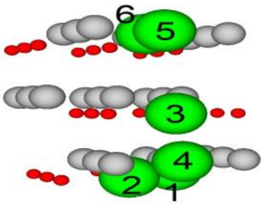

**Fig. 4** – Positions of atoms (marked with large green spheres) on the surface of the wire to which the water molecules were brought

## 3. RESULTS OF CALCULATION AND THEIR DISCUSSION

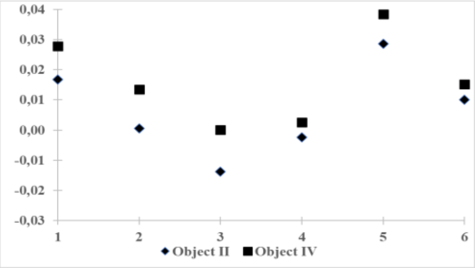

**Fig. 5** – Energy profiles of the water molecule motion along the trajectory consisting of locations "1" – "6" on the surface of ZnO nanowires at a distance of 0.33 nm between the wires for objects II and IV. The energy is given in eV

Fig. 5 through 7 present the energy profiles of the water molecule motion along a trajectory consisting of locations "1" through "6" on the surface of ZnO nanowires with inter-wire distances of 0.33 nm, 0.29 nm, or 0.25 nm for objects II and IV containing water molecules. The total energy values calculated using formula (1) were normalized to the volume of the unit cell and the number of atoms in the atomic basis and were referenced to the energies of atomic objects I and III that did not contain water.

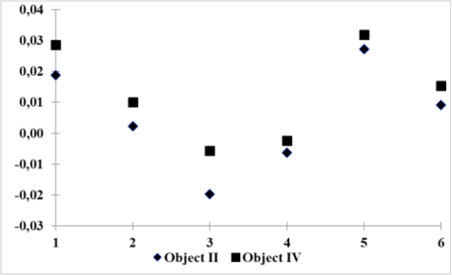

**Fig. 6** – Energy profiles of the water molecule motion along a trajectory consisting of locations "1" – "6" on the surface of ZnO nanowires at a distance of 0.29 nm between them for objects II and IV. The energy is given in eV

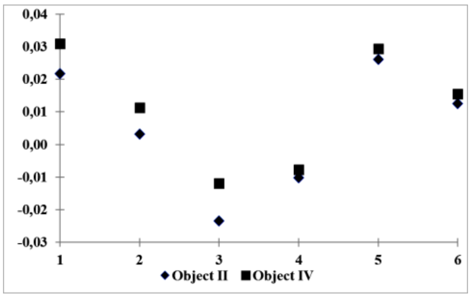

**Fig. 7** – Energy profiles of the water molecule motion along a trajectory consisting of locations "1" – "6" on the surface of ZnO nanowires at a distance of 0.25 nm between them for objects II and IV. Energy is given in eV

Guided by the analysis of the energy profiles of water molecule motion along the trajectory defined above by the criterion, which stated that the hydrophobic reaction (repulsion of water molecules) of the nanowire surface is characterized by an increase in the total energy of the atomic system (nanowires + water molecules), while the hydrophilic reaction (attraction of water molecules) is characterized by a decrease in the total energy, it was determined that different crystallographic orientations of the ZnO nanowire surface have different wettability.

In particular, the polar surfaces of the nanowires (locations "1", "2", "5" and "6") repelled water molecules, while the lateral surfaces (locations "3" and "4") exhibited hydrophilicity. Surface defects associated with both oxygen and zinc did not change the qualitative nature of the wettability of ZnO nanowire surfaces, but increased the energy of these processes.

The amount of space between nanowires, i.e. the density of nanowires in the array, which was varied in this numerical experiment by changing the distance between the wires, did not turn out to be a critically important parameter. Even if the surfaces of ZnO nanowires were additionally modified with defects, then in this case the qualitative nature of the wettability of ZnO nanowire surfaces did not change when the distance between the wires was reduced, but only the activation energies of these processes slightly increased.

Fig. 8 through 10 show the electric charges in the vicinity of a spherical volume with a radius of 0.1 nm around the surface atoms of a ZnO nanowire or their vacancies located along the trajectory of the water molecule motion in locations "1" through "6" for inter-wire distances of 0.33 nm, 0.29 nm, or 0.25 nm for objects I (without water), II (with water), III (without water), and IV (with water).

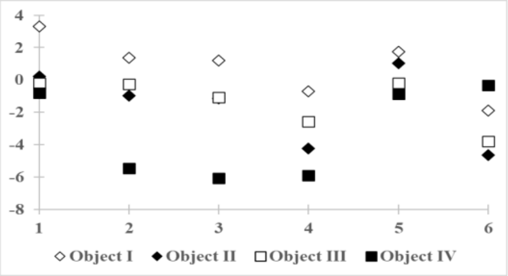

**Fig. 8** – Electric charges in the vicinity of the same volume of surface atoms of ZnO nanowire or their vacancies located along the trajectory of the water molecule motion in locations "1" – "6", at a distance between the wires of 0.33 nm, for objects I (without water), II (with water), III (without water), IV (with water). The charges are given in units of electron charge

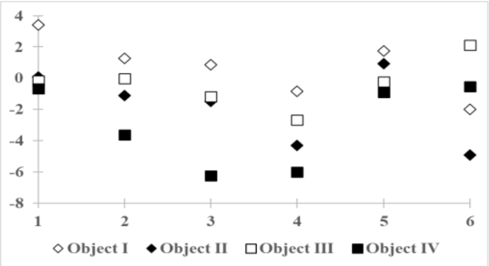

**Fig. 9** – Electric charges in the vicinity of the same volume of surface atoms of ZnO nanowire or their vacancies located along the trajectory of the water molecule motion in locations "1" – "6", at a distance between the wires of 0.29 nm, for objects I (without water), II (with water), III (without water), IV (with water). The charges are given in units of electron charge

Analysis of the sign and absolute value of the electric charge that entered the selected volume of the vicinity of the studied locations "1"-"6" allows us to conclude that the presence of water molecules near the locations leads to the accumulation of electronic charge, as evidenced by the "-" sign of the total charge, while in the absence of water molecules, these areas are characterized by the departure of valence electrons from them, as evidenced by the "+" sign of the total charge.

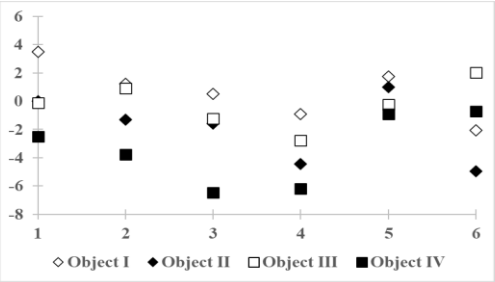

**Fig. 10** – Electric charges in the vicinity of the same volume of surface atoms of ZnO nanowire or their vacancies located along the trajectory of the water molecule motion in locations "1" – "6", at a distance between the wires of 0.25 nm, for objects I (without water), II (with water), III (without water), IV (with water). The charges are given in units of electron charge

The limiting distances between the water molecule and the polar surfaces of the nanowires (Zn or O) at which water begins to interact with the corresponding surfaces of the nanowires were also estimated: for the $Zn^{2+}$ surface this distance is 0.28 nm, for the $O^{2-}$ surface – 0.29 nm. The spatial distributions of the valence electron density within one nanowire in the such state of its surfaces, namely, with water, without defects (object II) shown in Fig. 11. They demonstrate their different configurations at distances when the interaction of the water molecule with the polar surfaces of the nanowire is observed or not. In Fig. 11a, one can see a common electron cloud of the water molecule and the surface of the nanowire, in Fig. 11b there is no common electron cloud.

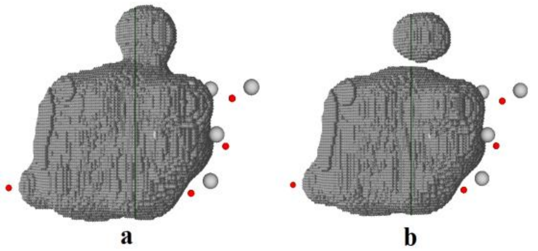

**Fig. 11** – Spatial distributions of the valence electron density for isovalues (0.2-0.1 from maximum) within a single defect-free ZnO nanowire with a water molecule, object II, water molecule location "6". The distance between the nanowire and the water molecule is 0.27 nm (a) and 0.29 nm (b)

## 4. CONCLUSIONS

Using the methods of the electron density functional and pseudopotential, the energy profiles of the water molecule migration along various surfaces of the defect-free ZnO nanowires and with surface oxygen or zinc vacancies were obtained from first principles.

It has been determined that the polar surfaces of nanowires repel water molecules, while the lateral nonpolar surfaces exhibit the property of hydrophilicity.

Surface defects associated with both oxygen and zinc does not change the qualitative nature of the wettability of the ZnO nanowire surfaces, but they increase the energy of these processes.

It was found that the density of nanowires in the array, which was controlled in this numerical experiment by changing the distance between the wires, did not turn out to be a critical parameter, even if the surfaces of the ZnO nanowires were additionally modified by defects. It was determined that the qualitative character of the wettability of ZnO nanowire surfaces does not change with decreasing distance between the wires, but only the activation energies of these processes slightly increase.

It was estimated critical distances between the water molecules and the polar surfaces (Zn or O) of nanowires at which the molecules begin to interact with these surfaces.

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# Керування за допомогою дефектів перемикання поверхні масиву нанодротів ZnO з гідрофобної на гідрофільну: розрахунки із перших принципів

О.М. Степанюк, Р.М. Балабай

*Криворізький державний педагогічний університет, пр. Університетський, 54, 50086 Кривий Ріг, Україна*

Одним з перспективних напрямків застосування нанодротів є контроль їхньої гідрофобності. Цього можна досягти шляхом модифікації структури та хімічного складу поверхні нанодротів. Одновимірні кристалічні наноструктури, такі як нанодроти, є особливо цікавими для контролю змочуваності, оскільки за допомогою точного налаштування висоти та відстані між нанодротами можна створити ідеальні супергідрофобні поверхні. Нанодроти оксиду цинку ZnO привертають значну увагу завдяки своїм унікальним властивостям для супергідрофобних застосувань. Розуміння взаємодії між молекулами води та поверхнями нанодротів ZnO є ключовим для дослідження їхніх змочувальних властивостей та потенційного використання у гідрофобних або гідрофільних покриттях. У цьому дослідженні за допомогою розрахунків із перших принципів вивчено вплив кристалографічної орієнтації та дефектів на змочуваність нанодротів ZnO, енергетичні рельєфи міграції молекул води по поверхнях нанодротів ZnO. Результати показали, що полярні поверхні нанодротів ZnO проявляють гідрофобні властивості, тоді як неполярні бокові поверхні є гідрофільними. Наявність поверхневих дефектів нанодротів ZnO, таких як вакансії кисню або цинку, не змінює якісно змочуваність поверхонь, але підвищує енергетичні бар'єри цих процесів. Варто відзначити, що щільність нанодротів у масиві, яка регулювалася шляхом зміни відстані між дротами, не є критично важливим параметром, навіть за умови модифікації поверхонь нанодротів ZnO дефектами. Якісний характер змочуваності поверхонь залишається незмінним при зменшенні відстані між дротами, спостерігається лише незначне зростання активаційних енергій. Визначено граничні відстані, на яких молекули води починають взаємодіяти з полярними поверхнями нанодротів ZnO. Результати дослідження поглиблюють розуміння механізмів реверсивної змочуваності нанодротів ZnO.

**Ключові слова:** Нанодроти ZnO, Гідрофобність, Гідрофільність, Поверхневі дефекти, Енергетичні рельєфи, Полярні та неполярні поверхні, Вакансії кисню та цинку, Розрахунки із перших принципів, Електричний заряд.