

SUPERHYDROPHOBIC/SUPERHYDROPHILIC SWITCHING ON THE SURFACE OF ZnO MICROSTRUCTURES CAUSED BY UV IRRADIATION AND ARGON ION ETCHING PROCESS

V. B. Kapustianyk^{1,2}, B. I. Turko², Y. V. Rudyk¹, R. Y. Serkiz², U. R. Mostovyi¹

¹*Chair of Solid State Physics, Ivan Franko National University,
Lviv, Ukraine,*

²*Scientific-Technical and Educational Center of Low Temperature Studies,
Lviv, Ukraine*

Received 18.03.2016

ZnO microstructures of different morphology were investigated using the water contact angle (WCA) analysis. The as-grown ZnO microstructures were found to exhibit pure hydrophobic behavior, which is enhanced with the increase of their surface area. The most hydrophobic structures (WCA = 157°) were found to be the complex microoctapods, containing both the macro- and nanoscale features.

Keywords: zinc oxide, nanostructures, hydrophobicity.

СУПЕРГИДРОФОБНОЕ/СУПЕРГИДРОФИЛЬНОЕ ПЕРЕКЛЮЧЕНИЯ НА ПОВЕРХНОСТИ МИКРОСТРУКТУР ZnO, ВЫЗВАННОЕ УЛЬТРАФИОЛЕТОВЫМ ОБЛУЧЕНИЕМ И ТРАВЛЕНИЕМ ИОНАМИ АРГОНА

В. Б. Капустяник, Б. И. Турко, Ю. В. Рудык, Р. Я. Серкиз, У. Р. Мостовой

Микроструктуры ZnO различной морфологии были исследованы с помощью анализа угла контакта воды (УКВ). Было установлено, что выращенные непосредственно перед измерением микроструктуры ZnO проявляют гидрофобные свойства, которые усиливаются с увеличением площади их поверхности. Наилучшими гидрофобными свойствами (УКВ = 157°) владели микрооктаподы с микро- и наноразмерными составляющими структуры.

Ключевые слова: оксид цинка, наноструктуры, гидрофобность.

СУПЕРГИДРОФОБНЕ/СУПЕРГИДРОФИЛЬНЕ ПЕРЕМИКАННЯ НА ПОВЕРХНІ МІКРОСТРУКТУР ZnO, ВИКЛИКАНЕ УЛЬТРАФІОЛЕТОВИМ ОПРОМІНЕННЯМ І ТРАВЛЕННЯМ ІОНАМИ АРГОНУ

В. Б. Капустяник, Б. І. Турко, Ю. В. Рудик, Р. Я. Серкіз, У. Р. Мостовий

Мікроструктури ZnO різної морфології були досліджені за допомогою аналізу кута контакту води (ККВ). Було встановлено, що вирощені безпосередньо перед вимірюванням мікроструктури ZnO проявляють гідрофобні властивості, які посилюються зі збільшенням площі їхньої поверхні. Найкращими гідрофобними властивостями (ККВ = 157°) володіли мікрооктаподи з мікро- і нанорозмірними складовими структурами.

Ключові слова: оксид цинку, наноструктури, гідрофобність.

INTRODUCTION

The superhydrophobic materials cause significant interest among scientists in recent years because of their significant potential for application use. They can be used in the manufacturing of the devices and things with self-cleaning properties (solar panels, textiles, building materials, such as glass, tile, etc.), coatings with a low friction (such as vehicles), anti-corrosion anti-icing and anti-sticking coatings, lab-on-chip devices, drug delivery etc. [1–5]. The superhydrophobic

surfaces are inherent for the materials with the low surface free energy values, including ZnO micro- and nanostructures [3, 6, 7].

It is known, that the effect of switching from the hydrophobic to the hydrophilic surface condition of the material may be achieved via optical, magnetic, mechanical, chemical, thermal or electrical activations [2, 7]. There are a large number of publications, which describes a reversible light-controlled hydrophobic/hydrophilic transition for zinc oxide films, micro- and

nanostructures [1, 3, 7–13]. Other methods of obtaining of the switching effect, in particular ion etching, have been paid much less attention [14–17].

This paper presents the wettability properties of ZnO microstructures with a different surface morphology treated with UV illumination and argon ion bombardment for various periods of time.

EXPERIMENTAL

The granular-like ZnO microstructures (Fig. 1) were grown on the *n*-type silicon (100) substrate by thermal evaporation of the metallic zinc powder (99.99 % purity) at the temperature 700 °C [18, 19]. This temperature was maintained for 1 h. Afterwards the oven was shut off and cooled spontaneously to room temperature. This yielded an uniformly deposited, white layer of zinc oxide on the substrates.

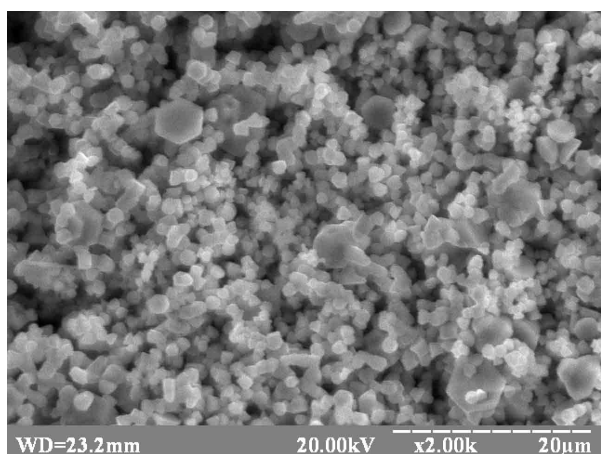


Fig. 1. SEM images of granular-like ZnO microstructures

ZnO microneedles (Fig. 2) and microoctapods (Fig. 3) were grown on the *n*-type silicon (100) substrates by the method of gas-transport reactions [11]. The mixture of the powdered high purity zinc oxide and graphite in the proportion of 1:2 was taken as an initial material for vaporization. This material and silicon substrates were placed into a quartz tube. The mixture of the powders was placed in a sealed end of the tube whereas the substrates - near the open end. The quartz tube was placed into a horizontal oven. The powder mixture was heated to the temperature of about 1050°C and the substrates were located into the zones with the temperatures of 850–900 °C (for the microrods) and 950–1000 °C (for the microoctapods). These temperature distributions

were maintained for 4 h. Afterwards the oven was shut off and cooled spontaneously to room temperature.

The morphology of the samples was examined using REMMA-102-02 Scanning Electron Microscope-Analyzer (JCS SELMI, Ukraine).

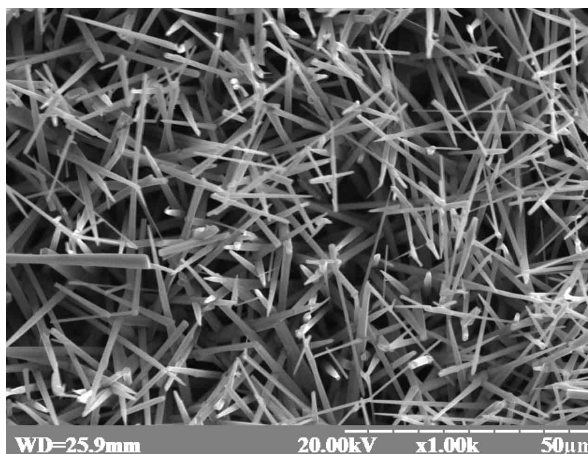


Fig. 2. SEM images of ZnO microneedles

A surface wettability of the ZnO experimental samples was evaluated by the water contact angle measurements performed by a sessile drop method. A 1 μ L de-ionized water droplet was gently positioned on a surface of the samples using a variable volume single channel pipette (Thermo Fisher Scientific, Waltham, Massachusetts, USA). A CCD camera-lens optical system (3.0 mPix, Ningbo Shengheng Optics & Electronics Co, LTD, Zhejiang, China) was used to capture the digital images of a droplet profile from a location parallel to a substrate. The images of the drops were analyzed with the TSview Version 6.2.4.5 software (Tucsen Imaging Technology Co., Ltd.,

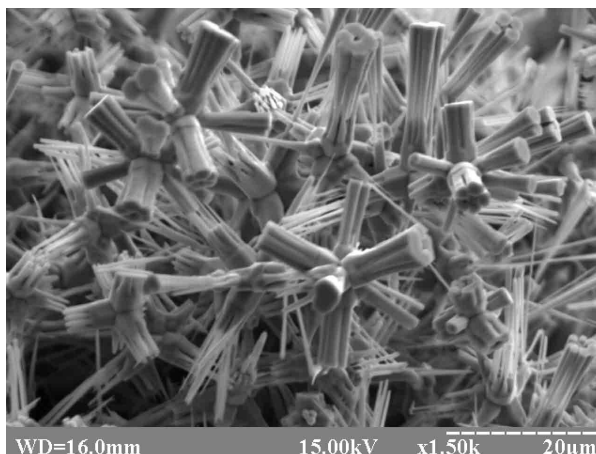


Fig. 3. SEM images of ZnO microoctapods

Fuzhou, China) to compute the contact angles. A mean value was calculated from at least five individual measurements.

The direct current (DC) ion etching of the sample surfaces was performed using a standard special equipment, which is a part of the vacuum universal station VUP-5M (SELM, Sumy, Ukraine). The etching was performed under the argon (the working gas) pressure of 0.1 Pa. The energy of argon ions was approximately equal 1keV.

UV light irradiation was realized in air ambient via exposure of the samples at certain time intervals by a low-pressure mercury lamp «DeLux» of 30 W power with a maxima at the wavelength $\lambda = 253.7$ nm (Shenzhen EUdelux Industrial Co. Ltd., Xixiang, China). The reverse transition from the hydrophilic to the hydrophobic state was performed via the storage in the dark conditions at room temperature over 24 hours.

RESULTS AND DISCUSSION

Figure 1 shows a SEM-image of the granular-like ZnO microstructures. The granules were found to possess the size of 1.5–2 μm . The morphology of ZnO microneedles and microoctapods are shown in Fig. 2 and Fig. 3, respectively. ZnO microneedles with a chaotic orientation were found to possess a length of 50 μm and diameter of about 4 μm near the base. The microoctapods possess the size in the range of 15 to 40 μm . The ZnO microoctapods consist of the eight arms branching from a single center, and the angles between the arms are the same. Each arm consists of a few hexagonal rods with a diameter of 0.5 to 3 μm and a length of 5 to 20 μm .

As it was expected, the as-grown structures represent a superhydrophobic surface: all the samples demonstrated the superhydrophobic behavior with a contact angle ranging from 154° to 157° . As it was predicted in [21, 22], due to the combination of the micro- and nanoscale structural parameters, the sample with ZnO microoctapods manifest the best superhydrophobic properties.

In order to change the wettability character of ZnO, the two methods were used. In the first case the experimental samples were irradiated by the ultraviolet light. The irradiation time was varied from 2.5 to 70 minutes. After a certain time of

UV irradiation the wetting transition from the superhydrophobic to the superhydrophilic state occurs for all the samples (Fig. 4).

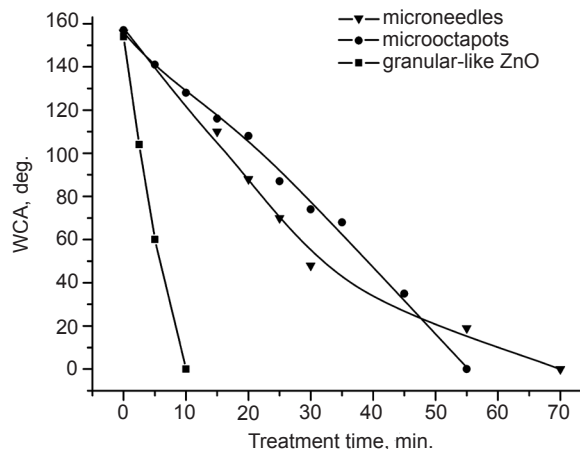
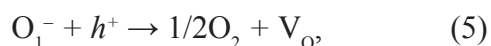
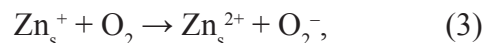
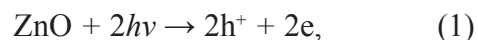


Fig. 4. Change of the water contact angle with time upon UV irradiation for ZnO of diverse morphology

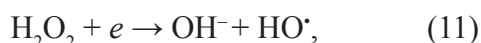
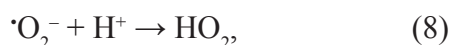
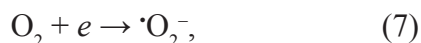
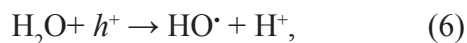
According to [3, 7, 9] the change of the wettability under irradiation with UV light with the photon energy, not lower than the band gap of ZnO can be described by the following expressions:



where h^+ , e , and V_O represent a hole, an electron, and the oxygen vacancy.

According to [3, 7, 9] the water molecules may be dissociatively adsorbed at the V_O site. These defect sites are kinetically more favorable for the hydroxyl group (OH^-) adsorption than oxygen adsorption, and hence promote an increased water adsorption at the UV light irradiated areas. However, the adsorption of OH^- on the defect sites is followed by distortion of the electronic structure of the surface and makes its state energetically unfavorable. Therefore, after termination of the UV illumination the surface tries to recover to its original hydrophobic state by replacing of the adsorbed OH^- with the atmospheric oxygen. During this process, OH^- and atmospheric oxygen tend to be dissociatively adsorbed on the defect sites [9].

At the same time, it would be convenient to consider the photocatalytic properties of zinc oxide [23–25]. Since ZnO microstructures are exposed to air, their surface adsorbs water from the environment. Therefore, when a ZnO surface is irradiated with UV light, an electron-hole pair is generated in the valence and conduction bands of ZnO, which could react with absorbed H_2O and O_2 molecules on the ZnO surface [24–27]:



where HO^\bullet — is the hydroxyl radicals, $\cdot\text{O}_2^-$ — the superoxide anions.

Under such circumstances due to the ultraviolet illumination the number of the hydroxyl groups on a ZnO surface will increase. Such an increase was observed using X-ray photoelectron spectroscopy [28]. The hydroxyl groups are adsorbed on the zinc ions and become the centers for further water adsorption [29].

In the second case the ion etching of ZnO samples' surface was used in order to change their wettability. Fig. 5 shows the measured water contact angle as a function of the time of the argon ion bombardment of ZnO microstructures.

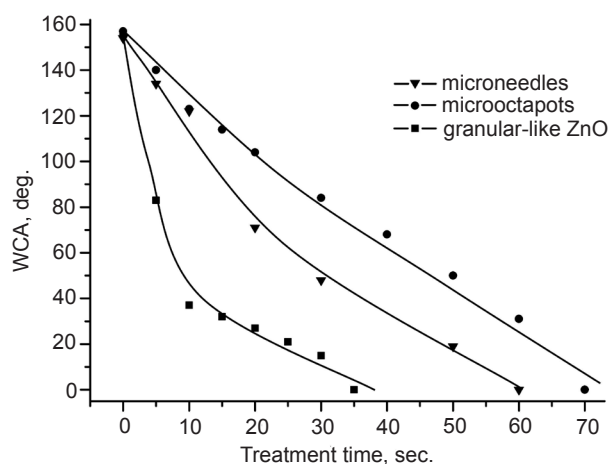


Fig. 5. Change of the water contact angle with time upon low energy argon ion bombardment for ZnO of diverse morphology

During the bombardment of the microstructures by the low energy Ar^+ ions in a vacuum there occurs a cleaning of a surface from contaminants and a sputtering of ZnO due to the destruction of the chemical bonds between zinc and oxygen in the crystal lattice. The atomic mass of argon (39.948 u) is larger than the atomic mass of oxygen (15.999 u) and smaller than the atomic mass of zinc (65.409 u). Therefore, the momentum transfer from an argon atom to an oxygen atom is much larger than that from an argon atom to a zinc atom. Therefore, the oxygen atoms are removed more easily. The number of oxygen vacancies on the ZnO surface will increase as a result of ion bombardment [30–33]. Since water vapor is always present even at high level of vacuum, the hydroxyl groups are immediately adsorbed on these surface defects introduced by Ar ion bombardment [34, 35].

Reducing of the WCA is slower in the case of UV irradiation than under the plasma treatment, probably due to differences in the energy level delivered during treatment and the subsequent surface alteration. The differences between the three samples in times of transition from the superhydrophobic to the superhydrophilic state (fig. 4, fig. 5) would be associated with different surface area of ZnO structures (roughness or surface-to-volume ratio).

CONCLUSION

The effect of a surface morphology on the argon ion bombardment or UV light-controlled wettability of ZnO microstructures was investigated. The samples with a larger surface roughness and surface-to-volume ratio were found to possess a considerably higher water contact angle and a time of transition from the superhydrophobic to the superhydrophilic state. The highest degree of hydrophobicity is exhibited by the complex ZnO structures, containing both micro- and nanoscaled surface features.

The obtained results would be useful for designing of the surfaces with a controlled wettability.

REFERENCES

1. Frysali M. A., Papoutsakis L., Kenanakis G., Anastasiadis S. H., Functional Surfaces with Photocatalytic Behavior and Reversible Wettability: ZnO Coating on Silicon Spikes // *J. Phys. Chem. C.* — 2015. — Vol. 119. —

- P. 25401–25407.
2. Verplanck N., Coffinier Y., Thomy V., Boukherroub R., Wettability Switching Techniques on Superhydrophobic Surfaces // *Nanoscale Res. Lett.* — 2007. — Vol. 2. — P. 577–596.
 3. Barshilia H. C., Sai Tej K. R., Devi L. M., Rajam K. S., Nanometric multiscale rough Zn–ZnO superhydrophobic thin films: Self-diffusion of zinc and effect of UV irradiation // *J. Appl. Phys.* — 2010. — Vol. 108. — P. 074315.
 4. Tarwal N. L., Khot V. M., Harale N. S., Pawar S. A., Pawar S. B., Patil V. B., Patil P. S., Spray deposited superhydrophobic ZnO coatings via seed assisted growth // *Surface & Coatings Technology.* — 2011. — Vol. 206. — P. 1336–1341.
 5. Hu H., Ji H. -F., Sun Y., The effect of oxygen vacancies on water wettability of a ZnO surface // *Phys. Chem. Chem. Phys.* — 2013. — Vol. 15. — P. 16557–16565.
 6. Gurav A. B., Lathe S. S., Vhatkar R. S., Lee J. G., Kim D. Y., Park J. J., Yoon S. S., Superhydrophobic surface decorated with vertical ZnO nanorods modified by stearic acid // *Ceramics International.* — 2014. — Vol. 40 — P. 7151–7160.
 7. Khranovskyy V., Ekblad T., Yakimova R., Hultman L., Surface morphology effects on the light-controlled wettability of ZnO nanostructures // *Applied Surface Science.* — 2012. — Vol. 20. — P. 8146–8152.
 8. Yao L., Zheng M., Li C., Ma L., Shen W., Facile synthesis of superhydrophobic surface of ZnO nanoflakes: chemical coating and UV-induced wettability conversion // *Nanoscale Research Letters.* — 2012. — Vol. 7. — P. 216–224.
 9. Bhavsar K., Ross D., Prabhu R., Pollard P., LED-controlled tuning of ZnO nanowires' wettability for biosensing applications // *Nano Reviews.* — 2015. — Vol. 6. — P. 26711–26717.
 10. Chi P. W., Su C. W., Jhuo B. H., Wei D. H., Photoirradiation Caused Controllable Wettability Switching of Sputtered Highly Aligned c-Axis-Oriented Zinc Oxide Columnar Films // *International Journal of Photoenergy.* — 2014. — Vol. 2014. — P. 765209–765219.
 11. Kenanakisa G., Vernardou D., Katsarakis N., Light-induced self-cleaning properties of ZnO nanowires grown at low temperatures // *Applied Catalysis A: General.* — 2012. — Vol. 411. — P. 7–14.
 12. Feng X., Feng L., Jin M., Zhai J., Jiang L., Zhu D., Reversible Super-hydrophobicity to Superhydrophilicity Transition of Aligned ZnO Nanorod Films // *J. Am. Chem. Soc.* — 2004. — Vol. 126. — P. 62–63.
 13. Myint M. T. Z., Kumar N. S., Hornyaka G. L., Dutta J., Hydrophobic/hydrophilic switching on zinc oxide micro-textured surface // *Applied Surface Science.* — 2013. — Vol. 264. — P. 344–348.
 14. Subedi D. P., Madhup D. K., Sharma A., Joshi U. M., Huczko A., Study of the wettability of ZnO nanofilms // *International Nano Letters.* — 2012. — Vol. 2. — P. 1–5.
 15. Meng X. Q., Zhao D. X., Zhang J. Y., Shen D. Z., Lu Y. M., Dong L., Xiao Z. Y., Liu Y. C., Fan X. W., Wettability conversion on ZnO nanowire arrays surface modified by oxygen plasma treatment and annealing // *Chemical Physics Letters.* — 2005. — Vol. 413. — P. 450–453.
 16. Sliz R., Suzuki Y., Nathan A., Myllyla R., Jabbour G., Organic solvent wetting properties of UV and plasma treated ZnO nanorods-printed electronics approach // *Proc. of SPIE.* — 2012. — Vol. 6. — P. 8471–8477.
 17. Li J., Wan H., Liu X., Yinping Ye, Zhou H., Chen J., Facile fabrication of superhydrophobic ZnO nanoparticle surfaces with erasable and rewritable wettability // *Applied Surface Science.* — 2012. — Vol. 258. — P. 8585–8589.
 18. Fan H. J., Scholz R., Kolb F. M., Zacharias M., Gosele U., Growth mechanism and characterization of zinc oxide microcages, *Solid State Communications.* — 2004. — Vol. 130. — P. 517–521.
 19. Lu H., Liao L., Li J., Wang D., High Surface-to-Volume Ratio ZnO Microberets: Low Temperature Synthesis, Characterization, and Photoluminescence // *J. Phys. Chem. B.* — 2006. — Vol. 110. — P. 23211–23214.
 20. Panasiuk M. R., Turko B. I., Kapustianyk V. B., Stanko O. P., Mandryka A. V., Serkiz R. Y., Dubov Y. H., Photo- and thermostimulated luminescence of ZnO nanowires // *J. Appl. Spectrosc.* — 2013. — Vol. 80. — P. 240–243.
 21. Zhang J., Huang W, Han T., Wettability of Zinc Oxide Surfaces with Controllable Structures // *Langmuir.* — 2006. — Vol. 22. — P. 2946–2950.

22. Latthe S. S., Terashima C., Nakata K., Fujishima A., Superhydrophobic Surfaces Developed by Mimicking Hierarchical Surface Morphology of Lotus Leaf // *Molecules*. — 2014. — Vol. 19. — P. 4256–4283.
23. Kołodziejczak-Radzimska A., Jesionowski T., Zinc Oxide -From Synthesis to Application: A Review, *Materials*. — 2014. — Vol. 7. — P. 2833–2881.
24. Dodd A. C., McKinley A. J., Saunders M., Tsuzuki T., Effect of particle size on the photocatalytic activity of nanoparticulate zinc oxide // *Journal of Nanoparticle Research*. — 2006. — Vol. 8. — P. 43–51.
25. Sirelkhatim A., Mahmud S., Seeni A., Kasus N. H. M., Ann L. C., Bakhori S. K. M., Hasan H., Mohamad D., Review on Zinc Oxide Nanoparticles: Antibacterial Activity and Toxicity Mechanism // *Nano-Micro Lett.* — 2015. — Vol. 7, No. 3. — P. 219–242.
26. Soboleva N. M., Nosovich A. A., Goncharuk V. V., The Heterogenic Photocatalysis in Water Treatment Processes // *J. Water Chem. Tech.* — 2007. — Vol. 29, No. 2. — P. 72–89.
27. Baruah S., Pal S. K., Dutta J., Nanostructured Zinc Oxide for Water Treatment // *Nanoscience & Nanotechnology-Asia*. — 2012. — Vol. 2, No. 2. — P. 90–102.
28. Zhu X., Zhang Z., Men X., Yang J., Xu X., Fabrication of an intelligent superhydrophobic surface based on ZnO nanorod arrays with switchable adhesion property // *Applied Surface Science*. — 2010. — Vol. 256. — P. 7619–7622.
29. Farahani H., Wagiran R., Hamidon M. N., Humidity Sensors Principle, Mechanism, and Fabrication Technologies: A Comprehensive Review // *Sensors*. — 2014. — Vol. 14. — P. 7881–7939.
30. Lee J.-M., Kim K. -K., Park S. -J., Choi W. -K., Low-resistance and nonalloyed ohmic contacts to plasma treated ZnO // *Appl. Phys. Lett.* — 2001. — Vol. 78, No. 24. — P. 3842–3844.
31. Sulyok A., Menyhard M., Malherbe J. B., Stability of ZnO{0001} against low energy ion bombardment // *Surface Science*. — 2007. — Vol. 601. — P. 1857–1861.
32. Ra H. W., Choi K. S., Ok C. W., Jo S. Y., Bai K. H., Im Y. H., Ion bombardment effects on ZnO nanowires during plasma treatment // *Appl. Phys.* — 2008. — Vol. 93. — P.033112.
33. Park J. S., Jeong J. K., Mo Y. G., Kim H. D., Kim S. I., Improvements in the device characteristics of amorphous indium gallium zinc oxide thin-film transistors by Ar plasma treatment // *Appl. Phys. Lett.* — 2007. — Vol. 90. — P. 262106.
34. Sun R., Nakajima A., Fujishima A., Watanabe T., Hashimoto K., Photoinduced Surface Wettability Conversion of ZnO and TiO₂ Thin Films // *J. Phys. Chem.* — 2001. — Vol. 105. — P. 1984–1990.
35. Yamada T., Kuroda Y., Fukuoka A., Ichikawa M., Tanaka K., Reactivity of Surface Hydroxyl Groups with Metal Complex Compounds // *Journal of Electron Spectroscopy and Related Phenomena*. — 1990. — Vol. 54–55. — P. 845–854.