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Gas adsorption on ZnO nanowires as studied by surface acoustic wave resonators

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The sensitivity of ZnO nanowires to gas adsorption has been studied by the surface acoustic wave resonance method. ZnO nanowire aggregates have been deposited on the surface of quartz two-port surface acoustic wave resonators with gold electrodes whose frequency output has been studied for gas sensing activity. High sensitivity combined with selectivity to specific analytes such as ammonia and acetic acid have been found. To exploit the maximum adsorption capacity of the wires, pretreatment with acetic acid has been found necessary. A considerable sensitivity to toxic pyridine and hexamethyleneimine has been separately established. The physical and chemical features of the adsorption processes have been discussed with focus on the inverse effect of gas adsorption on the nanowires sensing efficiency.

Keywords: ZnO nanowires, SAW resonator, gas, adsorption

INTRODUCTION

Recently, chemical gas sensing devices have been developed and studied at growing rates because of the increasing demands for control and monitoring in the atmosphere, food industry, medicine, agriculture, etc. Recent advance in nanotechnology has brought other means for improving the sensitivity by using specifically designed nanomaterials. Among various materials used in such nanostructures, metal oxides occupy a significant place nowadays. Within the extensive family of oxides explored and used in multiple microelectronic applications, ZnO is considered to be perhaps the most prospective one due to a number of advantages such as large exciton binding energy, high electromechanical coupling constant and resistivity to harsh environment. From the variety of ZnO nanoforms used, one-dimensional nanostructures (nanotubes, nanowires, nanofibers, etc.) have been demonstrated to be excellent candidates for chemical sensors because of the enhanced sensitivity that primarily derives from their very high surface to volume ratio [1]. Usually, these structures provide sensitivity several orders of magnitude better than that of thin films made of the same material [2]. Another advantage of this approach is that these nanoforms are produced by numerous methods, such as etching, wet chemistry, metal-organic chemical vapor deposition, physical vapor deposition, electrochemical method, molecular beam epitaxy, pulsed laser deposition, sputtering, flux, electrospinning, etc.

The priority role played by ZnO nanowires in gas adsorption raises the necessity for detailed investigation of the sorption mechanism. The specificity of the oxide reaction to irradiation with gas analytes involves two kinds of sorption. One is the physical sorption that allows the gas molecules to leave freely the substance surface after stoppage of the gas presence in its proximity.

The other mechanism is chemical sorption that leads to irreversible changes in the surface morphology and properties. It has been known, for example, that when the nanowire diameter becomes comparable to the Debye screening length, chemisorption induces surface states that effectively alter the electronic structure of the entire system [3]. One aspect of this irreversibility which, in our opinion, has not been given enough attention so far, concerns the evolution of the sensor material in time, produced by its action as a detector. It is not clear to what extent such sensors are reusable, and could there be some beneficial effect from gases previously applied or measured. Along with studying the response to various gases, the present contribution is also an effort to better understand this latter side of the ZnO nanowire sensing behavior and application. To follow the gas sensitivity of nanowires we have used the surface acoustic wave (SAW) method based on the change in the SAW velocity produced by gas molecules

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adsorbed by nanowires deposited on the wave propagation surface. In fact, there are a number of studies on gas sensors using ZnO nanostructures and SAW detection [4, 5]. However, the problem with those nanostructures is that, due to their semiconductor nature, they could have a shorting effect on the interdigital SAW electrodes (so called acoustoelectric effect [4]). This could lead to degradation of the resonance properties of the SAW device and to a considerably increased loss [5]. For this reason such gas sensor studies have been usually based on SAW delay-lines. SAW resonators have been scarcely mentioned, and, to our knowledge, they have not yet been used in the nanowire case. It is to mention that studies using bulk acoustic wave resonators have also provided positive results in studying the response to specific analytes such as, for example, NO_2 [6] and ammonia [7, 8]

In this study we use the SAW resonator method [9], as it fits well the task of studying the details of gas adsorption due to its high sensitivity. This sensitivity primarily derives from the high operating frequency and also from the strict phase conditions for establishing the main resonance. We use different types of VOCs family gases as active analytes (acetone, formalin, ammonia, acetic acid, pyridine and hexamethyleneimine (HMI). The latter two are specifically studied to reveal the effect of the molecule size on the adsorption features.

EXPERIMENTAL

Two identical two-port Rayleigh SAW resonators with gold electrodes structure on ST-quartz at 440 MHz (courtesy of Research Center Karlsruhe, Germany) have been used. ZnO nanowires have been synthesized by electrodeposition in aluminium oxide membranes – a widely used technique for the fabrication of metal or metal oxide nanowires [10]. The nanowires collected have been dispersed in isopropanol by ultrasonification. A single drop of the dispersion (20 μL) has been applied onto the substrate which has been placed on a hotplate (at approximately 60°C) for solvent evaporation.

SEM images of the actual resonator surface after deposition of the nanowires are shown in Fig. 1 for two magnifications. A cluster character of the coverage is clearly seen. The nanowire coating produces a decrease in the resonance frequency (about 1.5 MHz) and a heavy increase in the peak loss (about 30 dB). These changes in the resonator performance are related to two independent factors. One is the mass loading of the surface and the other is the electric shorting of the two electrode combs due to the finite conductance of the ZnO wires. For the moment, these two contributions are practically impossible to separate.

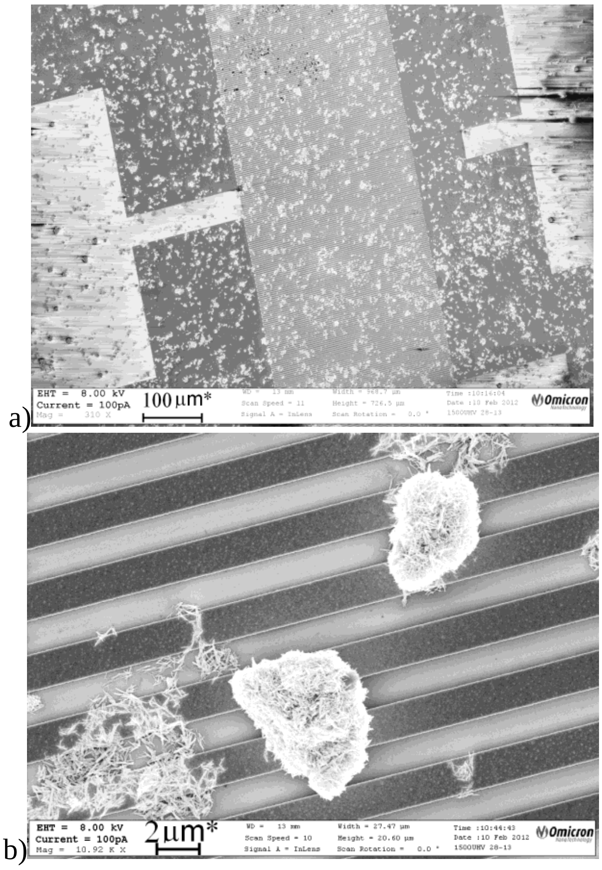

Fig. 1. The surface of Rayleigh SAW resonator after nanowire coating; a) scale 100 μm; b) scale 2 μm.

The large resonator damping and the resulting broad frequency peak do not allow the measurement of the resonance frequency on a resonator based oscillator and the readout of the spectrum analyzer should be exploited. However, because of the same reasons, the programmed direct usage of the peak function of the analyzer is insecure and leads to unjustified dispersion of the results. To get better confidence each resonance frequency has been determined as a mean of the two values obtained on the left and right slope of the response at 3.0 dB.

In a first series of measurements the coated surface of one of the samples (resonator 1) has been exposed to the action of vapors of volatile organic compounds. The experiments have been done in a gas cell using the non-flow method described in details in our previous paper [11]. The liquid to evaporate has been step-like introduced into the cell at definite quantities (typically 0.2 ml) and a corresponding time interval for achieving equilibrium before reading the frequency (usually about 2 min) has been followed. Because the response has been found to be generally reversible, different gases have been applied in a sequence. In a second series of experiments the surface of another coated resonator (2) has been exposed to the action of two highly toxic organic substances – pyridine (C_5H_5N) and hexamethyleneimine, HMI ($C_6H_{13}N$). Apart from the application side, another ground for this choice is the difference in the volumes (the kinetic diameters) and the basicity of these two heterocyclic organic molecules. To highly secure the ambient atmosphere we applied the gas flow cell method described in our earlier published paper [12]. The analyte molecules are carried by N_2 that is let through the liquid in a hermetically sealed system. Unfortunately, this method does not allow to precisely determine the gas concentration and what we present instead is the gas flow rate settled by a flow meter. This alternative, however, has the advantage of establishing the absorption behavior of the ZnO nanowires in a dynamic regime and to determine the concentration of their absorption centers.

RESULTS AND DISCUSSION

Particular interest has been paid to the response to ammonia since other studies have revealed considerable sensitivity to this analyte [8]. The obtained concentration dependences are shown in Fig. 2

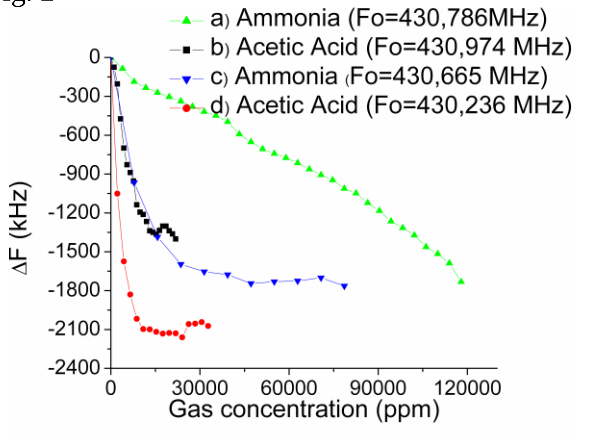

Fig. 2. Responses of resonator 1 to ammonia and acetic acid applied in chronological order. F_0 – starting resonance frequency. ΔF – difference between F_0 and current resonance frequency.

First ammonia response (a) is close to linear overall, revealing sensitivity of 40 Hz/ppm (all sensitivity data presented hereafter concern the initial linear part of the dependence; a 10000 ppm interval has been chosen to allow comparison). Then the resonator is exposed to acetic acid (b) resulting in the high sensitivity of 120 Hz/ppm. Expectedly, this response exhibits saturation behavior at higher concentration levels. The next exposure again to ammonia (c) results in a differently shaped characteristic with a sharp downfall at the beginning and a tendency for saturation thereafter (similar to previous one). Again a sensitivity of 120 Hz/ppm is achieved. Finally, another experiment with acetic acid reveals the extremely high sensitivity of 400 Hz/ppm. The results of all experiments in a chronological order are summarized in Table 1. Two additional facts should be noticed: i) the lack of response to acetone and formalin, and ii) the weakening of the response to ammonia with time. In fact, the last result in the table was obtained three months after the second exposure to acetic acid presented by curve (d) of Fig. 2. It is to note that this relaxed response is almost identical to that shown at the start of the ammonia/acetic acid series.

In all these experiments the resonator loss has been found, as expected, to increase with gas concentration but the increasing rate appears to be less pronounced compared to the rate of decreasing frequency. For example, a 1 MHz frequency shift (similar to that produced by the presence of the layer) is now accompanied with only 3 dB loss increase, as evident from Fig. 3.

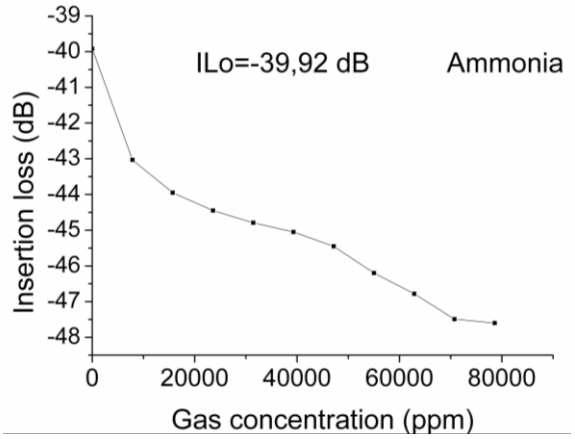

Fig 3. Resonator 1 insertion loss versus gas concentration. IL_0 – starting insertion loss. Corresponds to the frequency behavior of curve (c) on Fig. 2.

Table 1. Chronology of experiments on gas response of resonator 1.

Analyte	F_0, MHz	ΔF, kHz	Gas concentration, ppm	Date
Acetone	430.766	10	7500	09.02
Ammonia	430.786	250	10000	09.02
Acetic acid	430.974	1200	10000	11.02
Formalin	430.641	0	Up to 75000	16.02
Ammonia	430.665	1200	10000	29.03
Acetic acid	430.236	1600	4000 [a]	05.05
Ammonia	430.261	1250	7500 [a]	10.05
Ammonia	430.519	300	10000	05.07

[a] 10000 ppm out of linearity scope

The relaxation behavior of the strongest response to ammonia is given in Fig. 4a together with the frequency shift versus gas concentration (4b).

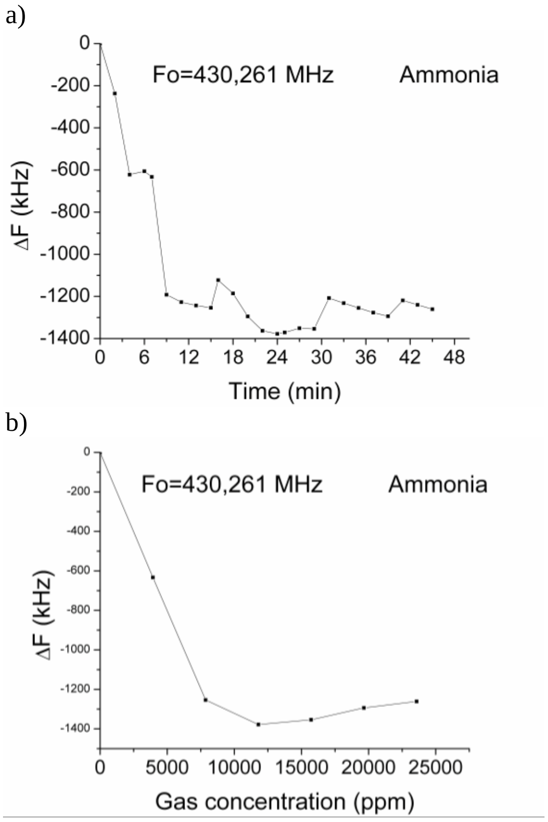

Fig.4. Frequency shifts with time a) versus corresponding gas concentration dynamics b) (ΔF – the difference between F_0 and current resonance frequency).

The obtained results for pyridine and HMI are presented in Fig.5 for a flow rate of 20 ml/min.

With HMI the resonator needs more time to reach equilibrium than with pyridine. The measurements with pyridine have been repeated at flow rates of 40 ml/min and 60 ml/min. At the higher rate the resonator demonstrated a clear tendency for saturation. After ending the experiments the surfaces of both resonators were studied by scanning electron microscopy. (Fig. 6 a,b). A rather peculiar shape of the aggregates is observed as the individual wires appear lost overall.

EDX-spectra of the two resonator surfaces indicate the presence of carbon and nitrogen which have obviously remained chemically bound to the surface.

It is known that ZnO behaves as an n-type semiconductor even without donor doping due to oxygen deficiency induced during processing [13]. This type of deficiency largely controls the adsorption at the surface and thus the reaction to different gaseous analytes [14]. The adsorbed molecules affect the properties of the space charge layer especially in thin films where the width of the layer becomes comparable to the thickness dimension. This principle lies in the performance of the widely exploited resistance sensors. In the nanowires case, the large surface to volume ratio enhances the sensitivity to the analyte molecules by offering larger amount of adsorbing centers. As seen from Table 1 and the related Figure 2, the attained sensitivity to ammonia and acetic acid has varied with time during the experiments, the highest values reaching 160 Hz/ppm for ammonia and 400 Hz/ppm for acetic acid, respectively. The detection limit is estimated by the short term stability of the resonator, i. e., the spontaneous departure of the resonance frequency over gate time corresponding to the time interval between consecutive read-outs, which is also the time elapsed to the first read-out following the introduction of the first analyte amount in the cell. Making a series of read-outs on the used resonator 1 by a step of 2 min over a time interval of 30 min we calculate a standard frequency deviation of 3.8 kHz. This corresponds to a detection limit of 24 ppm for ammonia and 9 ppm for acetic acid, respectively.

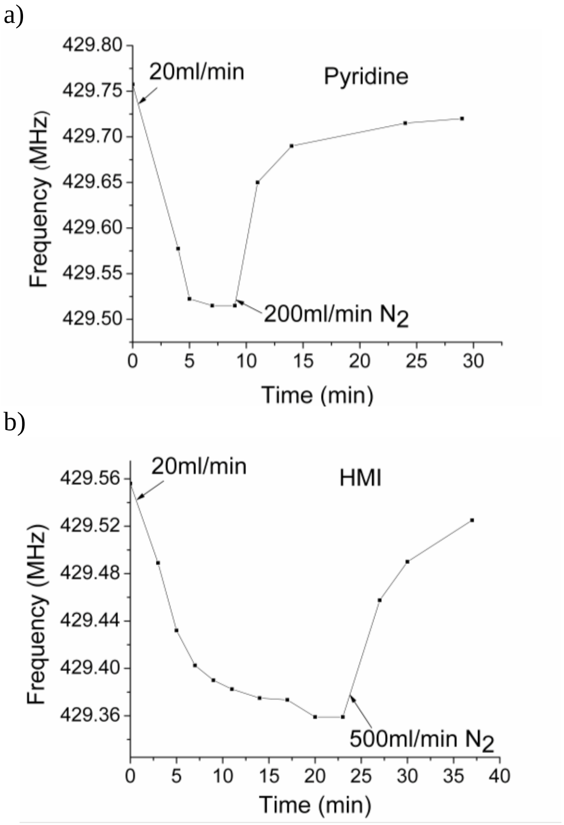

Fig.5. Response of resonator 2 to pyridine a) and HMI b), both at 20 ml/min carrying gas flow and air-flush at 200 ml/min and 500 ml/min carrying gas flow, respectively.

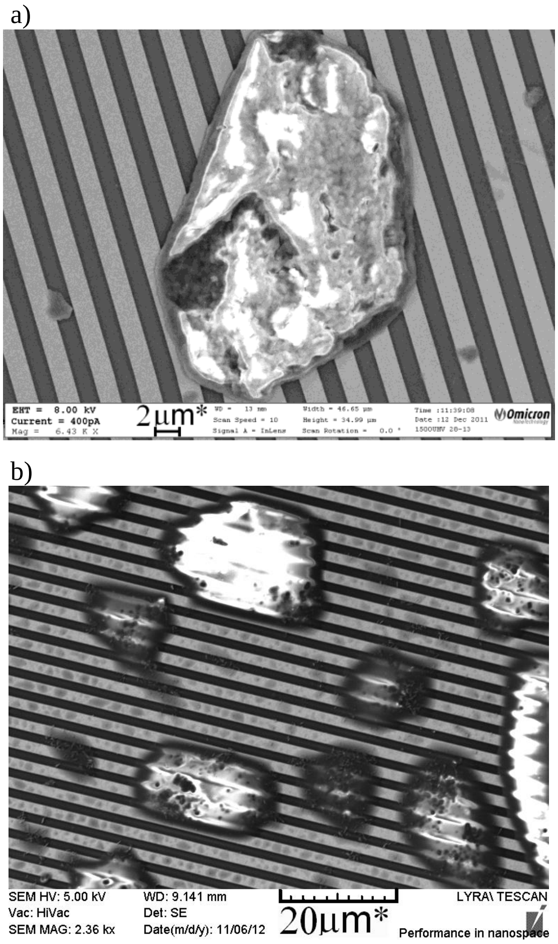

Fig.6. a) SEM image of a fragment of the material left on resonator 1 (scale 2 μm) after gas; b) SEM image of resonator 2 nanowire surface after exposure to pyridine and HMI.

Concerning ammonia, these data outperform the results obtained using the quartz microbalance method (40-1000 ppm; nanowires synthesized by thermal evaporation) [1, 8]. Compared with other gas sensing devices based on nanostructured ZnO obtained by magnetron sputtering and electrochemical deposition [7, 15], the studied SAW sensor device demonstrates increased adsorption capacity to NH_3 molecules. Although the density of the particles on the surface of the SAW resonator is much smaller compared to that in the referred works, the increased adsorption capacity probably comes from casual space distribution of scattered aggregations of ZnO nanowires offering a larger open adsorption area to the sorbate molecules (Fig. 6a). Acetic acid data are, to our knowledge, presented for the first time here.

The adsorption results obtained with ammonia and acetic acid reveal the considerable affinity of the studied configuration to these analytes at a low level of reproducibility. The adsorption capacity variation, as well as the unstable behavior of the starting resonance frequency should be related to the irreversible chemical reaction between the used sorbates. The reaction takes place between molecules of the actual analyte and those of the other analyte left on the surface of the ZnO nanowires from the previous experiment. Taking into account the chemical nature of these molecules it seems logical to assume that the undesorbed molecules act as sorption centers for the newcomers during the following cycle. The product of this artifact reaction is ammonium acetate - an organic salt that accumulates on the surface leading to downshift in the resonance frequency. Taking into consideration the complicated cascade of chemical reactions running on the resonator surface, we assume that the adhesion of this material to the surface of the nanowires (and also the gold electrode surface) is poor and results in subsequent mechanically produced material loss (long term upward shift of the resonance frequency). In parallel, the obtained maximum sensitivity to ammonia cannot be preserved unless new treatment with the acid is done. As for the lack of response of the resonator to acetone and formalin, it indicates indifference of the nanowires to these two sorbates at room temperature.

The experiments with pyridine and HMI also show considerable sensitivity although, as commented above, we are unable to define it quantitatively. With regard to the highly toxic character of these analytes the obtained results offer serious potential for practical use. The adsorption capacity of the sorbent toward the two N-containing heterocyclic molecules is approximately the same which indicates that the two processes involve approximately the same amount of adsorption centers. The insignificant differences observed are most probably linked to a difference between the Van der Waals‘ volumes of the two organic molecules (steric factors) rather than to their basicity [16, 17]. It should be also noted that pKa of pyridine is 5.23 [18] and that of HMI is 11.07 [19]. The steric factor could also control the rate of attaining adsorption equilibrium in the studied systems (ZnO-pyridine and ZnO-HMI) [20]. In view of the planarity of pyridine molecules and the possibility of forming considerably denser adsorption monolayers on a solid sorbent surface [21, 22], the saturation of the polar ZnO adsorption centers with pyridine molecules would require considerably less time than with HMI (Fig. 5b).

A reasonable explication of the morphology changes of the ZnO nanoparticles after irradiation with acetic acid (Fig. 6a) can be found in their reactivity to this analyte [23]. The observed amorphization is probably due to a zinc acetate film formed on the sample surface that gives the ZnO aggregates a melt-like appearance. The obtained EDX-data came to support this understanding. After exposure to ammonia and acetic acid, the surface of the ZnO coated resonator is loaded with carbon atoms belonging to the acetate groups of a $Zn(OOCCH_3)_2$ layer. On the other hand, although appearing similar, the morphology changes of the nanowires after treating with pyridine and HMI (Fig. 6b) are difficult to assign to the same type of analyte action. It has been recently found that pyridine has the property of shaping the ZnO crystallites – a particle-to-rod transformation mechanism that appears different from mere amorphization [24]. Still, the carbon content left in this case is found even higher than with the acetic acid, indicating a chemical reaction again. These results appear to need further attention.

From the results obtained in this study two principal features can be outlined. One is the possibility of considerably increasing the sensitivity of the nanowires to ammonia by pretreatment with acetic acid. This increase varies in time and vanishes on the long run, with the sensitivity returning to its initial value found at the beginning of the gas experiment. As a whole, the response of the nanowire assembly remains slightly changed, despite the serious chemical transformations occurring during the experimental cycle. The other feature is the considerable sensitivity to pyridine and HMI combined with relaxation time difference due to difference in the basicity of these nitrogen-containing organic adsorbates.

CONCLUSIONS

The adsorption properties of ZnO nanowire aggregates on quartz surface acoustic wave resonators with gold electrodes submitted to gas exposure have been studied. High sensitivity combined with selectivity to specific analytes has been found. The response to ammonia outperforms previous data obtained with quartz microbalance sensors. To exploit the maximum adsorption capacity of the layer, pretreatment with acetic acid, to which the wires are also very sensitive, is required. The chemical reaction of nanowires with acetic acid and its effect on the sensitivity has been discussed. A considerable sensitivity to toxic pyridine and hexamethyleneimine has also been proved. The differences in the kinetics of the adsorption process are linked to steric factors in the latter two cases.

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ИЗСЛЕДВАНЕ НА ГАЗОВА АДСОРБЦИЯ ВЪРХУ НАНОЖИЧКИ ОТ ZnO С РЕЗОНАТОРИ С ПОВЪРХНИННИ АКУСТИЧНИ ВЪЛНИ

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(Резюме)

С помощта на резонансен метод, базиран на повърхнинни акустични вълни, е изследвана чувствителността на наножички от ZnO към адсорбция на газове. Върху повърхността на двувходов кварцов резонатор с повърхнинни акустични вълни със златни електроди са отложени агрегати на наножички от ZnO като са следени промените в резонансната му честота с оглед изследване на сензорни свойства към газове. Установени са висока чувствителност комбинирана със селективност към специфични аналити като амоняк и оцетна киселина. Показано е, че за постигане на максимален адсорбционен капацитет на наножичките е необходимо предварително третиране с оцетна киселина. Независимо е установена значителна чувствителност към токсичните пиридин и хексаметиленимин. Дискутирани се физичните и химичните особености на адсорбционния процес с акцент върху обратимия ефект на газова адсорбция по отношение на сензорната ефективност на наножичките.