Detection of Acetonitrile and Chloroform using Structures on the Base of Porous Silicon

S.M. Manakov, M.K. Ibraimov, Ye. Sagidolda*, Sh.A. Zhumatova, M.B. Darmenkulova

Al-Farabi Kazakh National University, 71 al-Farabi ave., Almaty, Kazakhstan

Article info

Abstract

In this work porous silicon samples obtained by electrochemical etching were investigated. Using scanning probe microscope the morphology of porous silicon samples was studied. To determine the thickness of the porous layer and the pore diameter, micrographs were obtained using a scanning electron microscope. The dimensions of the nanocrystallites were determined from the Raman spectra. For the detection of vapors of organic compounds, planar structures were used. The results of the study confirmed the possibility of using nanoporous silicon as a sensitive material for the determination of acetonitrile and chloroform vapors. It is shown that the adsorption phenomena in porous silicon depend on its structure and morphology. It is established that the humidity of the air when detecting the vapors of organic compounds under investigation has a significant effect on the sensitivity. It is also shown that such structures can be used as instruments for measuring air humidity.

1. Introduction

Porous silicon (Por-Si) is considered one of the promising materials for the manufacture of chemical sensors and attracts much attention of developers of various gas sensors on the base of it [1]. The attractive properties of Por-Si are associated not only with the large surface area of this material, but also with the ability to control its properties by selecting the type of impurity and its concentration in the original single-crystal silicon substrate. The effect of electrochemical etching regimes on the morphology of the Por-Si surface, the sizes of the pores and nanocrystallites and the physical properties were investigated in [2].

The authors of work [3] developed a gas sensor with improved selectivity on the base of a Por-Si, in which information on the concentration of detectable gases was recorded from a change in the value of the sensor capacitance and the reflection coefficient with respect to external adsorbents. A similar method of using a capacitive sensor for the detection of polar and nonpolar organic solvents is described in [4]. In [5] a simple method was described for detection of NO_2 at room temperature by measuring the resistance sensors using a programmable digital multimeter.

Another type of nanostructured silicon, silicon nanowires (SiNWs), which can be obtained with the inexpensive method of metal-stimulated chemical etching, are also an excellent material for manufacturing gas sensors. This was first shown in 2001 [6]. It is also proposed to use the SiNWs in the manufacture of economically advantageous, low-power and small-size gas hydrogen sensors, which has no odor, color, and is highly flammable at concentrations of just over 4% [7]. Harmful vapors of ammonia (NH_3), which may adversely affect the environment and can cause respiratory disease, also serves to detect by sensors on the base of SiNWs [8]. In [9], arrays of porous silicon nanowires were investigated as a sensitive element of an optical gas sensor. The authors of this paper showed that such porous nanowires have a huge specific surface area, due to which their physicochemical properties are highly sensitive to the molecular environment.

The purpose of this work is to study the structure and physical properties of nanoporous silicon and to assess the feasibility of creating gas sensors for polar and nonpolar organic compounds on the base of it.

2. Experimental

Nano- structured Por-Si films were used as research objects. Por-Si samples were obtained by electrochemical etching of n-type silicon wafers. The voltage and current density values were 10 V and 15 mA/cm^2, respectively. The etching time was 20 sec. As the initial substrate, monocrystalline silicon substrates were used with charge carrier concentration ~ 10^{19} cm^{-3} and crystallographic orientation (100).

To measure the electrical properties and impedance of gas-sensitive Por-Si structures, metal contacts of thickness ~ 250–390 nm were deposited exclusively on the surface of the samples. Then sensors were placed into a special chamber and different vapors of polar and nonpolar liquids were fed. The vapors were created by passing dry air (15% moisture) through the liquids and diluting the gas stream with dry air. The change in the capacitance of the sensors when the test gases were applied was recorded by the Agilent LCR meter.

3. Results and discussion

Images of the morphology of the samples were obtained with the Ntegra SmaxT: Ntegra Therma multifunctional scanning near-field probe microscope using a semi-contact method. The results of the study of the surface morphology of a Por-Si -based sensor are shown in Fig. 1. According to a 3D image obtained by a scanning probe microscope (SPM), a strong inhomogeneity is observed on the sensor surface (Fig. 1a).

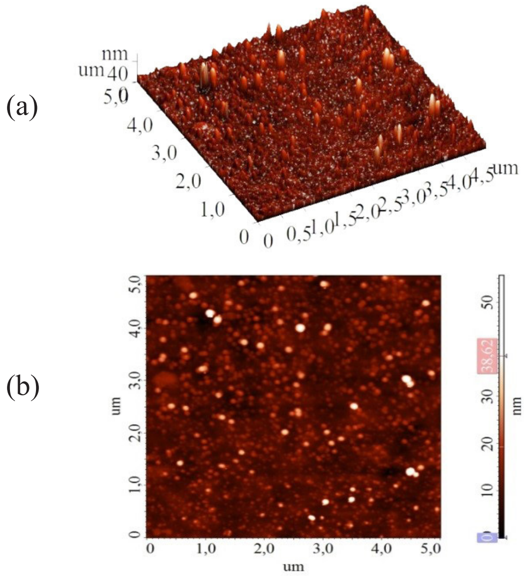


Fig. 1. SPM image of the surface of a gas sensor based on porous silicon.

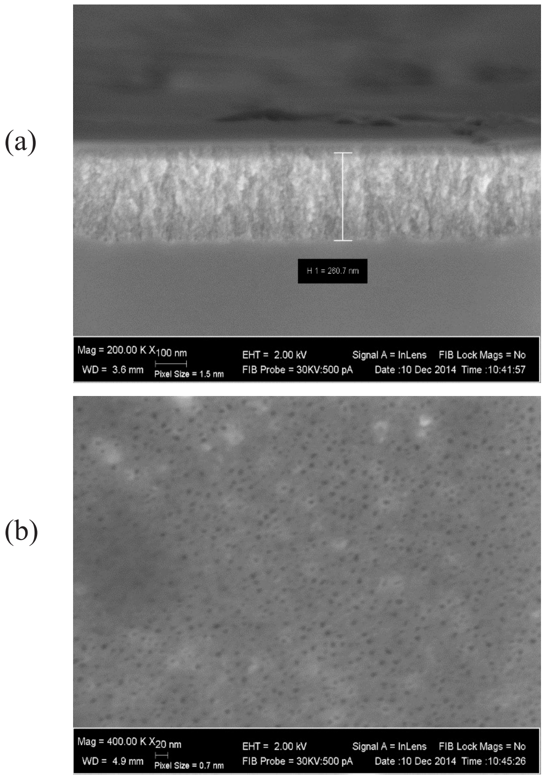


Fig. 2. Micrographs of porous silicon samples: (a) – side view; (b) – top view.

Non-uniformly distributed filamentary protrusions, which height reaches 40 nm, are also clearly visible. According to the 2D image, the degree of porosity is ~ 50% (Fig. 1b).

Figure 2 shows the micrographs of the samples studied using scanning electron microscope Quanta 200i 3D. It is seen from Fig. 2 that the thickness of the porous layer is ~ 250 nm, the pore diameter varies from 5 nm to 10 nm.

Raman spectra of porous silicon are a good diagnostic tool in the study of structural phases in a Por-Si and make it possible to estimate the characteristic sizes of nano-crystallites. For this purpose, the shift of the Raman peak to the low-energy region of the spectrum is measured with respect to a narrow peak at a frequency of 520 cm^{-1} in single-crystal silicon corresponding to longitudinal optical modes (LO). Raman spectra of the samples were determined using an NT-MDT-Ntegra Spectra spectrometer and are shown in Fig. 3.

The peak at 514 cm^{-1} (instead of 520 cm^{-1}) appears after etching of single-crystal silicon and is associated with the formation of a nanoporous structure [10]. The 465–485 cm^{-1} region is associated with transverse optical modes (TO) in amorphous silicon. For all Por-Si samples, a shift in the position of the Raman spectra peaks to the low-energy region was observed.

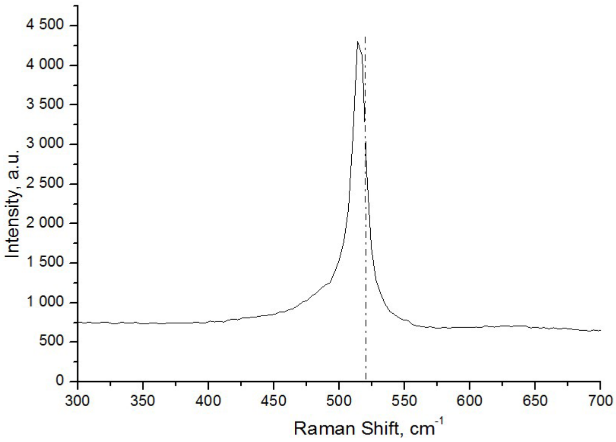


Fig. 3. Raman spectra of a sample of porous silicon.

Information on the average size of nanocrystallites in a Por-Si can be obtained from the Cardon equation [11]:

$$d = 2\pi\sqrt{\frac{B}{\Delta\omega}} \quad (nm), \tag{1}$$

where B = 2.24 cm^{-1} for silicon, Δω – is the shift of Raman peak in Por-Si relative to the peak of crystalline silicon. Accordingly, the sizes of crystallites in Por-Si samples were varied within 3.8 nm – 6.6 nm. The broadening of the Raman spectra with increasing etching time indicates a violation of the crystal structure of the original silicon, the appearance of an amorphous phase and nanocrystalline clusters located on the pore surface.

To study the sensitivity of the Por-Si to vapors of organic compounds, a planar configuration of the contacts was used (Fig. 4). Ohmic contacts were deposited on the surface of the samples in a “clean room” by magnetron sputtering. The total contact thickness was approximately 370 nm, of which the thickness of the titanium layer was 20 nm, the aluminum layer 300 nm and the nickel layer 50 nm. It should be noted that, given the ability to rapidly oxidize Por-Si surfaces, before applying the contacts, the samples were annealed in an inert gas atmosphere. The diameter of the contacts and the distance between them was 1 mm.

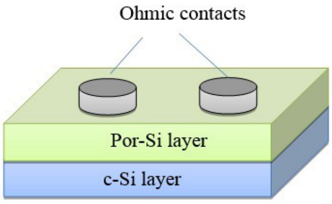


Fig. 4. Planar configuration of contacts on the surface of porous silicon.

Molecules that are adsorbed on the Por-Si surface change its dielectric constant, and, consequently, lead to a change in the capacitance and conductivity of the structures under study. The sensors were placed into a chamber and then vapors of organic substances were delivered.

The coplanar structure of the sensor can be considered as a flat capacitor in which the relative permittivity of the Por-Si with the adsorbed substance (ε_{eff}) depends not only on the structure, composition and morphology of the porous silicon, but also on the concentration of the vapor of the detected substance in the air (n). The capacity of such a structure is:

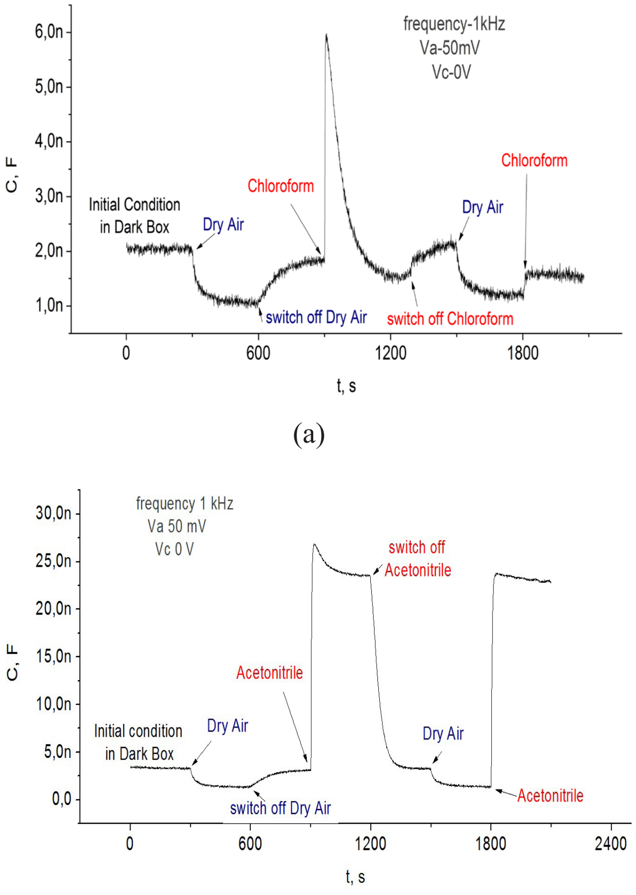
$$C(n) = \frac{\varepsilon_0 \varepsilon_{eff}(n) S}{d} \tag{2}$$

where ε_0 is the electric constant, S is the area of the electrodes, d is the thickness of the porous silicon. The structure of the porous silicon resembles a sponge with branched pores and is rather complicated. The study of porous silicon showed that the Por-Si samples under study are characterized by porosity in the range of 50–60%, contain nanocrystallites with characteristic sizes of 3.8–6.6 nm, regions of amorphous silicon and silicon dioxide. The detection of vapors of organic substances occurs in the process of replacing air, filling the pores with a detectable substance. The normal air humidity in the room is 40–60%. To exclude the effect of changes in air humidity on the change in capacity, samples of gas-sensitive structures were blown by dry air, the humidity of which was 15%.

Figure 5 shows the dynamic response of porous silicon by adding chloroform and acetonitrile vapors to a 0.5 m^3 measuring chamber. As an electrical characteristic, a capacitance was chosen with an alternating voltage of 50 mV at a frequency of 1 kHz, which was measured with the Agilent LCR meter.

Acetonitrile CH_3CN (methylcyanide) is a polar dielectric characterized by a relative permittivity $\varepsilon_1 = 38.8$. Chloroform $CHCl_3$ (trichloromethane) is a non-polar substance and its relative permittivity $\varepsilon_2 = 4.8$ [12]. The typical sizes of acetonitrile and chloroform molecules are 0.2 nm and 0.64 nm. Both substances are toxic, with chloroform being oxidized in the light to form phosgene.

As can be seen from Fig. 5, when the dry air is supplied to the working chamber, the capacitance of the sensor is approximately halved and the stationary capacitance value is reached after 100 s.



(a)

(b)

Fig. 5. Changing the capacity of the Por-Si sensor in time for the supply of various vapors of liquids: (a) – with chloroform; (b) – with acetonitrile.

After stopping the dry air supply, the initial capacity is set to 350 sec. Thus, capacitance measurements for dry and moist air show that the instrument being tested can be used as a humidity sensor.

The effective dielectric constant ε_{eff} of porous silicon with vapors of water and other substances as a multicomponent system can be determined proceeding from the theory of the effective medium approximation of Bruggeman [13]:

$$\sum_i \frac{f_i(\varepsilon_i - \varepsilon_{eff})}{\varepsilon_i + 2\varepsilon_{eff}} = 0 \qquad (3)$$

where ε_i is the relative permittivities of each component of the medium, f_i is the relative content of each component. The effective permeability of a Por-Si with a porosity of 50% is $\varepsilon_{PSi} \sim 2$, and for water at room temperature $\varepsilon = 80$, therefore, with increasing air humidity, the effective permeability of the Por-Si and the capacity of the sensor increase.

When the vapor of chloroform and acetonitrile are fed, a sharp increase in the capacitance of the sensor is observed (Fig. 5). The maximum capacity is reached within 10 sec for both substances, in the case of chloroform supply, capacity sharply increases threefold, and for acetonitrile, an eightfold increase in capacity was observed. Then, for chloroform, the capacity decreased during 150 s and its value was higher than for dry air, but lower than for moist air. When the supply of chloroform was cut off, the capacitance was increased to the initial value. After repeated supply of dry air and then chloroform, an abrupt increase in capacity was not observed, in this case the capacity reached a maximum value within 10 s.

After giving acetonitrile delivery, the steady-state value of the capacity was reached after 70 sec, with a decrease in capacity from the maximum value by ~10%. After stopping the supply of acetonitrile, the stationary value of the capacity was reached in 100 s. Repeated supply of acetonitrile after the supply of dry air led to a steady capacity of 10 sec after the supply, immediately and without a jump. The large value of the equilibrium capacity for a polar substance can be explained using the theory of an effective medium, taking into account the value of the relative permittivity of acetonitrile $\varepsilon_1 = 38.8$.

The presence of a significant supernormal excess of the equilibrium capacity for chloroform and a slight excess for acetonitrile in the case of their supply to a humid environment, and their absence, when organic vapors are fed into a dry medium, indicate that the excess capacitance is associated with a higher concentration of water vapor in moist air. During the adsorption of molecules by a porous structure, nanocapillary condensation and physical adsorption due to van der Waals forces play a decisive role. Therefore, the structure, composition and morphology of the surface of nanoporous silicon is the key factor for understanding adsorption phenomena in the Por-Si. It is possible that molecules of organic compounds, when introduced into a humid environment, stimulate an initial increase in the rate of surface and volume adsorption of water molecules, their filling with pores and their subsequent displacement by molecules of organic compounds.

4. Conclusions

The use of nanoporous silicon as a sensitive material for capacitive gas sensors has shown that the sensitivity of such a sensor for acetonitrile vapor, which is a polar compound, is significantly higher than its sensitivity for chloroform vapor, which is a nonpolar compound. Adsorption phenomena in Por-Si depend on its structure and morphology, which is determined by the technological parameters of the process of electrochemical etching.

The influence of air humidity is found when detecting the vapors of organic compounds. In the case of recording chloroform and acetonitrile vapors in moist air, the time to reach the equilibrium value of the capacitance was 150 s and 75 s, respectively. When these compounds were registered in dry air, the time to establish the equilibrium capacity was about 10 s for both chloroform and acetonitrile.

The humidity of the air, in which the admixtures of vapors of organic substances are determined, exerts a strong influence on the kinetics of the adsorption and desorption of the vapors of a detectable nonpolar compound, chloroform. For the polar compound of acetonitrile, this effect is much less. Therefore, for the development of sensors on the base of a Por-Si, it is necessary to take into account the effect of water vapor. Moreover, such structures can be used as devices for measuring air humidity.

Acknowledgments

The work was carried out with the financial support of the Science Committee of the Ministry of Education and Science under the grant program No. AP05132854.

References

[1]. I.A. Levitsky, *Sensors* 15 (2015) 19968–19991. DOI: 10.3390/s150819968

[2]. S.M. Manakov, Ye. Sagidolda, Investigation of the physical properties of nanoscale porous silicon films, Physical Sciences and Technology (1) (2015) 4–8.

[3]. T. Jalkanen, J. Tuura, E. Mäkilä, J. Salonen, *Sensor. Actuat. B-Chem.* 147 (2010) 100–104. DOI: 10.1016/j.snb.2010.03.005

[4]. F.A. Harraz, A.A. Ismail, H. Bouzid, S.A. Al-Sayari, A. Al-Hajry, M.S Al-Assiri, *Appl. Surf. Sci.* 307 (2014) 704–711. DOI: 10.1016/j.apsusc.2014.04.106

[5]. D. Yan, M. Hu, S. Li, J. Liang, Y. Wu, S. Ma, *Electrochim. Acta* 115 (2014) 297–305. DOI: 10.1016/j.electacta.2013.10.007

[6]. Y. Cui, C.M. Lieber, *Science* 291 (2001) 851–853. DOI: 10.1126/science.291.5505.851

[7]. G. Korotcenkov, S.D. Han, J.R. Stetter, *Chem. Rev.* 109 (2009) 1402–1433. DOI: 10.1021/cr800339k

[8]. L.J.M. van der Eerdena, P.H.B. de Visserb, C.J. van Dijk, *Environ. Pollut.* 102 (1998) 49–53. DOI: 10.1016/S0269-7491(98)80014-6

[9]. V.A. Georgobiani, K.A. Gonchar, E.A. Zvereva, L.A. Osminkina, *Phys. Status Solidi A* 215 (2017) 1700565-1-1700565-5. DOI: 10.1002/pssa.201700565

[10]. B. Bulakh, N. Korsunska, L. Khomenkova, T. Stara, Ye. Venger, T. Krystab, A. Kryvko, *J. Mater. Sci. Mater. Electron.* 20 (2009) 226–229. DOI: 10.1007/s10854-007-9550-8

[11]. Z.C. Feng, R. Tsu, Porous Silicon (World Scientific, Singapore, 1994) 488 p. DOI: 10.1142/2241

[12]. J. Workmans. Handbook of organic compound. Academic Press, 3 (2000) 1493.

[13]. V. Lucarini J.J. Saarinen K.-E. Peiponen E.M. Vartiainen. Kramers-Kronig Relations in Optical Materials Research, Optical Sciences. 110 (2005) 165.