High sensitive NH₃ sensor based on electrochemically etched porous silicon

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Abstract: In the current study, porous silicon (por-Si) samples were fabricated by electrochemical etching at different times (20 min, 40 min, 60 min). Scanning electron microscope (SEM) images of horizontal cross-sections of the samples showed the formation of pores. The etched samples’ porosity was determined by the gravimetric method and amounted to 59.5%, 72.7%, 83.3%, respectively. Optical characteristics such as Raman spectra and photoluminescence (PL) spectra were obtained. The current-voltage and capacitance-voltage characteristics were also measured to calculate the sensitivity of the samples. The study results show that sample, which is etched for 40 minutes has a maximum response value to ammonia (NH₃) gas than others, and the sensitivity is 33.25. The results demonstrated that it is possible to develop a high sensitive sensor device based on por-Si for determining NH₃ gas in concentrations below 0.1 ppm at room temperature.

Subjects: Physics; Matter & Solid State Physics; Semiconductors

Keywords: porous silicon; ammonia sensor; optical characteristics; electrical characteristics

1. Introduction

Nowadays environmental pollution with noxious gases negatively affects both the human body and the ecosystem as a whole (Desai et al., 2005). Therefore, it is important to monitor the excess of harmful gases and determine how many molecules of poisonous gases are contained in the environment (Kayahan, 2018; Yamazoe, 2005). The detection of ammonia (NH₃) gas is as of great importance.
interest in areas such as agriculture, industrial chemistry, environmental orientation, mechanical engineering, and medicine. Gaseous NH$_3$ is very dangerous, flammable, poisonous gas that can damage the skin, eyes, and respiratory system even in small concentrations. At present, metal oxide semiconductors are widely used as NH$_3$ and other gas sensors (ZnO, SnO$_2$, TiO$_2$, WO$_3$, etc. (Berger et al., 2009; Jeevitha & Mangalaraj, 2019; Karunagaran et al., 2007; Matsubara et al., 2005; X. Wang et al., 2006). Naderi et al. developed a high-stability sensor device capable of detecting NH$_3$ gas up to a concentration of 212 ppb at 150°C from the V$_2$O$_5$/CUWO$_3$ heterostructure, and also chemically explained sensitivity mechanism (Naderi et al., 2020). Bin Yang et al. showed that sensitivity and selectivity of the sensor device to NH$_3$ gas increase at high temperatures using the ZnFe$_2$O$_4$ structure as sensitive material and adding gold to it (Yang et al., 2020). Weiwei Gong et al. found that the structure Bi$_{0.95}$Ni$_{0.05}$VO$_{3.975}$ obtained by hydrothermal method is good at detecting NH$_3$ gas at a high temperature of 500–600°C (Meng et al., 2018). Although these sensors have a high coefficient of sensitivity to NH$_3$ gas, usually sensors based on metal oxides have a high operating temperature, which can increase the power consumption (Yuan et al., 2016), as well as have complex and expensive production technologies.

Due to the large surface area and the chemically active surface of the material, porous materials (Hoseinzadeh et al., 2019), namely, silicon (por-Si) can be used as a gas sensor (Baratto et al., 2000; H.J. Kim et al., 2010). Hee-Kyung Min et al. used por-Si for sensing the concentration of ethanol solutions (Min et al., 2000). S.M. Manakov et al. developed a structure based on por-Si for detecting of acetonitrile and chloroform (Manakov et al., 2019). In fact, por-Si can be obtained by electrochemical etching in an electrolyte with hydrofluoric (HF) acid by applying an electric current to the silicon wafer (Zhang & Braun, 2012). Such parameters as the current density of the electrochemical process, the etching time, and also the correctly selected concentration of liquids in the electrolyte make it possible to precisely control the structure of silicon and the thickness of the nanostructured layer (Ahmed & Mehaney, 2019; Zhanabaev et al., 2016).

The main purpose of this work is to determine the optimal parameters for preparing inexpensive sensor device based on por-Si, which is highly sensitive to ammonia gas and does not require complex technology of manufacturing, as well as to explain the reasons of changing the electrical characteristics of por-Si under the influence of the gas.

2. Experimental details

Por-Si layers were formed by electrochemical etching of <100 > p-type boron-doped silicon wafers (10$^{15}$ cm$^{-3}$) having resistivity of 10 Ω·cm with dimensions of 1 × 1 cm$^2$. The electrochemical etching process was carried out in a special Teflon bath and was controlled by a special power source. The silicon wafers were immersed in HF acid for 5 seconds and then cleaned with ethanol. An aluminum plate, the silicon wafer, and the O-ring were collected horizontally in the Teflon bath in the form of a sandwich (Figure 1). The electrolyte solution used was consisted of HF acid and ethanol in 1:1 volume ratio. Formation current was chosen as 5 mA and etching time was set to be 20, 40, and 60 minutes for samples 1, 2 and 3, respectively. To obtain electrical characteristics, two ohmic contacts of InGa alloy were deposited on their surface by thermal installation. The etched samples’ porosity was determined by the gravimetric method using the formula (1):

$$p = \frac{m_1 - m_2}{m_1 - m_3} \times 100\%,$$

(1)

The current-voltage characteristics of por-Si samples were taken by the NI ELVIS II + module in the voltage range U = ±2.5–2.5 V and the capacitance-voltage characteristics were measured using the Agilent E4980A LCR-meter at 1 MHz frequency. Photoluminescence (PL) and Raman spectra were studied on NT-MDT Solver Spectrum and excited by a laser with a wavelength of 473 nm. The morphology of por-Si was investigated from images of the scanning electron microscope (SEM) Quanta 200i 3D. To determine the sensitivity of por-Si to NH$_3$, samples were placed in a cubic sealed
box with a volume of 19x19x19 cm$^3$ for 2 hours, and, finally, by measuring the current and capacity values at constant voltage and various gas concentrations, the sensitivity was calculated.

3. Results and discussion

SEM images were used to determine the size, the shape, and the thickness of the fabricated por-Si samples. Figure 2 shows cross-section SEM images of por-Si samples, which were etched for 20, 40, and 60 minutes, respectively. According to the theory of pore formation, the size, the porosity, and the thickness of the pores increase with increasing the etching time (Choi et al., 2019). In Figure 2 one can see that due to electrochemical etching in hydrofluoric acid, the pores were formed in the vertical direction and their thickness are 6.27 microns, 10.52 microns, 18.82 microns, respectively.

The porosity values of the samples were calculated by formula (1) and amounted to 59.5%, 72.7%, and 83.3% for three samples, respectively.

Figure 3 shows the Raman and PL spectra of the samples. In Figure 3A it can be noted that the Raman spectra of all three samples exhibit a peak intensity at 520 cm$^{-1}$ band. This is the main combination scattering band that occurs from the action of monochromatic light with a crystal lattice. Raman spectra indicate that the size of the crystal structures of sample 3 is larger compared to the others (Kadlečiková et al., 2018). The small spectral hump for all samples at the band of 940 cm$^{-1}$ is the result of the scattering of transverse optical phonons (Harraz et al., 2016).
As can be seen in Figure 3B, sample 2 has the highest PL intensity, with a porosity value of 72.7 (625 nm). High PL intensity is associated with an increase in the total volume of nanocrystallites on the surface of por-Si (D.A. Kim et al., 2004).

The current-voltage and the capacitance-voltage characteristics of the samples were measured at various concentrations of NH₃ gas at room temperature using the special sealed box. The desired concentration of gas in the sealed box is determined by the following formula (2):

\[
C = \frac{\rho \times T \times V_1 \times R}{M \times V_2 \times P},
\]

where \( C \) (ppm) is the concentration of gas, \( \rho \) (g/cm³) is the density of NH₃, \( T \) (K) is the absolute temperature, \( V_1 \) (μl) is the volume of liquid (NH₃), \( R \) (8.31 J/mol*K) is the universal gas constant, \( P \) (Pa) is the pressure inside the box, \( V_2 \) (L) is the volume of the box, \( M \) (g/mol) is the molecular weight of the liquid (Naderi et al., 2020).

The sensitivity of por-Si samples at a constant voltage value (in our case \( U = 2 \) V) was calculated by the following formula (3):

\[
S_R = \frac{I_{\text{gas}} - I_{\text{air}}}{I_{\text{air}}},
\]

where \( I_{\text{air}} \) and \( I_{\text{gas}} \) are the currents of por-Si samples, measured in air and under the influence of NH₃ gas, respectively (Liu et al., 2019). All samples showed that they can react to NH₃ gas at room temperature even at concentrations below 0.1 ppm. As a result of the study, it was determined that the sensitivity of sample 2, obtained by etching for 40 minutes, the porosity of which is 72.7%, is higher compared to the other two samples, that is, the sensitivity was 33.25 for 0.1 ppm. In the reference (Zhang & Braun, 2012), the authors obtained similar results, and according to them, it is related to higher surface area and high enough initial resistance of the sample 2. The results are presented in Table 1.

A comparison of several reported NH₃ sensors on the sensing performance towards ammonia is summarized in Table 2.

Figure 4 shows the current-voltage and the capacitance-voltage characteristics of sample 2, measured after saturation of NH₃ gas of various concentrations in the sealed box (0.03 ppm, 0.06 ppm, 0.1 ppm). With the increase in the concentration of NH₃ gas, the resistance of the por-Si sample decreases, and the current increases. From Figure 4B one can see that with increasing the concentration of NH₃ gas, the capacity increases. The capacity has a high value if there is no NH₃ or presents in a low concentration at a low voltage, and increasing the voltage, it decreases.
Table 1. Sensitivity coefficients of por-Si samples at $U = 2\, \text{V}$

| Sample | $C$, ppm | $I_{\text{air}}$, mA | $I_{\text{gas}}$, mA | $C_{\text{air}}$, pF | $C_{\text{gas}}$, pF | Sensitivity |
|--------|---------|-----------------|-----------------|-----------------|-----------------|-------------|
| 1      | 0.1     | 0.003 ± 0.01%   | 0.057 ± 0.01%   | 1.67 ± 0.05%    | 5.1 ± 0.05%     | 18          |
| 2      | 0.1     | 0.004 ± 0.01%   | 0.137 ± 0.01%   | 6.81 ± 0.05%    | 36.94 ± 0.05%   | 33.25       |
| 3      | 0.1     | 0.005 ± 0.01%   | 0.135 ± 0.01%   | 4.4 ± 0.05%     | 24.25 ± 0.05%   | 26          |

Table 2. Comparison of ammonia gas sensors

| Sensing material | Sensitivity | Operating temperature (ºC) | Concentration (ppm) | Reference |
|------------------|-------------|-----------------------------|---------------------|-----------|
| Por-Si           | 33.25       | 26                          | 0.1                 | This work |
| Pt NP/WO3        | 26.86       | 250                         | 1                   | Liu et al. (2019) |
| TiO2/ZnO         | 32          | 573                         | 0.06                | Chen et al. (2018), Y. Wang et al. (2009) |
| CNFL/SnO2        | 71          | 400                         | 10                  | Chen et al. (2018), Lee et al. (2014) |

Figure 4. Current-voltage (A) and capacitance-voltage characteristics (B) at 1 MHz frequency of sample 2 at various gas concentrations.

Accordingly, then at a certain voltage value, it acquires a stable value. This behavior of the capacity is explained by the absorption of $\text{NH}_3$ molecules on the surface of por-Si, completely saturated with liquid vapors in the sealed box for 2 hours. As the concentration of $\text{NH}_3$ gas increases, its saturation time also increases. Therefore, capacitance values are small at low voltage for 0.06 ppm and 0.1 ppm in the figure, and as the voltage increases, the values will increase. At a constant voltage of 2 V, capacitance values in the air and under the influence of the $\text{NH}_3$ gas concentration of 0.1 ppm for all samples are shown in Table 1.

A common mechanism for determining the toxic gases of many gas sensors is a change in electrical conductivity or resistance as a result of the adsorption of gas particles (Ibraimov et al., 2016). When the gas sensor is in the air, oxygen molecules are adsorbed onto the surface of por-Si. Then, the adsorbed oxygen molecules are converted into oxygen ions by abstracting free electrons from the sensitive layer. The number of electrons decreases under the influence of electron abstraction in the outer region, and the number of holes increases, and a hole accumulation region is formed for sensitive p-type por-Si materials. Considering that the conductivity in semiconductors is formed by the action of holes, the resistance in the region of hole accumulation will be less than in other internal regions of the sensor.
When the por-Si-based sensor is exposed to NH$_3$ gas particles, it is adsorbed on the surface of por-Si and the electrons located on the sensor surface are attracted to gas molecules. Accordingly, the resistance of the p-type por-Si sensor is reduced, because the number of holes is increased, forming a hole accumulation layer. In fact, as the thickness of the hole accumulation layer increases, more holes are present in the silicon conductivity and the resistance decreases. The higher the gas concentration, the more the number of attracted electrons increases, and the higher sensitivity is observed (Choi et al., 2019; Mirzaei et al., 2018).

The sensitivity, determined by the change in the capacitance and conductivity of the por-Si-based sensor, depends on several factors (Harraz et al., 2020; Schechter et al., 1995). The combination of the dipole moment and polarization can provide complete information about the overall structural interaction (Baker & Gole, 2016; Harraz et al., 2020). The dipole moment of the gas induces a local zone, thus displacing the energy levels of surface states, as a result of which the space charge zones of the por-Si structure modify. This leads to a change in the conductivity of por-Si (Harraz et al., 2020; Schechter et al., 1995).

4. Conclusion
As a summary, the high sensitive por-Si-based gas sensor device was successfully fabricated by electrochemical etching method and applied for NH$_3$ gas detection at ambient temperature. Optical characteristics such as SEM, Raman spectra, PL spectra, and electrical characteristics were investigated. Research results revealed that a sample, which is etched for 40 min has the maximum sensitivity among all the three samples. The sensing mechanism of the por-Si-based gas sensor was proposed based on the resistance change as a result of the adsorption of gas particles. This study shows that it is possible to fabricate a high sensitive, inexpensive gas sensor device based on por-Si for determining NH$_3$ gas in concentrations below 0.1 ppm at a room temperature. However, it is obvious that many studies are needed before application of por-Si as a NH$_3$ sensor.

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References
Ahmed, A. M., & Mehoney, A. (2019). Ultra-high sensitive 3D porous silicon photonic crystal sensor based on the coupling of Tamam/Fano resonances in the mid-infrared region. Scientific Reports, 9(1), 1–9. https://doi.org/10.1038/s41598-019-43440-y

Baker, C., & Gole, J. L. (2016). Detection of liquid organic solvents on metal oxide nanostructure decorated porous silicon interfaces. ACS Sensors, 1(3), 235–242. https://doi.org/10.1021/acssensors.5b00075

Baratto, C., Comini, E., Faglia, G., Sberveglieri, G., Di Francia, G., De Filippo, F., La Ferrara, V., Quercia, L., & Lancellotti, L. (2020). Gas detection with a porous silicon based sensor. Sensors and Actuators. B, Chemical, 651(1–3), 257–259. https://doi.org/10.1016/S0925-4005(99)00297-X

Berger, F., Sanchez, J. B., & Heintz, O. (2009). Detection of hydrogen fluoride using SnO$_2$-based gas sensors: Understanding of the reactonal mechanism. Sensors and Actuators. B, Chemical, 143(1), 152–157. https://doi.org/10.1016/j.snb.2009.08.054

Chen, H. I., Hsiao, C. Y., Chen, W. C., Chang, C. H., Chou, T. C., Liu, I. P., Lin, K. W., & Liu, W. C. (2018). Characteristics of a Pt/NiO thin film-based ammonia gas sensor. Sensors and Actuators. B, Chemical, 256, 962–967. https://doi.org/10.1016/j.snb.2017.10.032

Choi, M. S., Na, H. G., Mirzaei, A., Bang, J. H., Oum, W., Han, S., Choi, S. W., Kim, M., Jin, C., Kim, S. S., & Kim, H. W. (2019). Room-temperature NO$_2$ sensor based on electrochemically etched porous silicon. Journal of Alloys and Compounds, 811, 151975. https://doi.org/10.1016/j.jallcom.2019.151975

Desai, R. R., Lakshminarayana, D., Patel, P. B., & Panchal, C. J. (2005). Indium sesquiphosphate (In$_3$Te$_4$) thin film gas sensor for detection of carbon dioxide. Sensors and Actuators. B, Chemical, 107(2), 523–527. https://doi.org/10.1016/j.snb.2004.11.011

Harraz, F. A., Ismail, A. A., Al-Sayari, S. A., Al-Hajy, A., & Al-Assiri, M. S. (2016). A highly sensitive and durable electrical sensor for liquid ethanol using thermally-oxidized mesoporous silicon. Superlattices and Microstructures, 100, 1064–1072. https://doi.org/10.1016/j.spmi.2016.10.074

Harraz, F. A., Ismail, A. A., Faisal, M., Al-Sayari, S. A., Al-Hajy, A., & Al-Assiri, M. S. (2020). Organic analytes sensitivity in meso-porous silicon electrical sensor
with front side and backside contacts. Arabian Journal of Chemistry, 13(1), 444–452. https://doi.org/10.1016/j.arabjc.2017.05.015

Hoseinzadeh, S., Heyns, P. S., Chakmaha, A. J., & Shirkani, A. (2019). Thermal analysis of porous fins enclosure with the comparison of analytical and numerical methods. Journal of Thermal Analysis and Calorimetry, 138(1), 727–735. https://doi.org/10.1007/s10973-019-08203-x

Ibrahimov, M. K., Sagidulova, Y., Rumyantsev, S. L., Zhanabaev, Z. Z., & Shur, M. S. (2019). Selective gas sensor using porous silicon. Sensor Letters, 14(6), 588–591. https://doi.org/10.1166/sl.2016.3657

Jeevitha, G., & Mangalaraj, D. (2019). Ammonia sensing at ambient temperature using tungsten oxide (WO3) nanoparticles. Materials Today: Proceedings, 18, 1602–1609. https://doi.org/10.1016/j.matpr.2019.05.254

Kadiškavová, M., Breza, J., Vanoč, E., Mäkelä, M., Hubereck, M., Rachko, J., & Gregus, J. (2018). Raman spectroscopy of porous silicon substrates. Optik, 174, 347–353. https://doi.org/10.1016/j.ijleo.2018.08.084

Karunagaran, U., Uthirakumar, P., Chung, S. J., Velumani, S., & Suh, E. K. (2007). TiO2 thin film gas sensor for monitoring ammonia. Materials Characterization, 58(8–9), 680–684. https://doi.org/10.1016/j.matchar.2006.11.007

Kayahan, E. (2018). Porous silicon based CO2 sensors with high sensitivity. Optik, 164, 271–276. https://doi.org/10.1016/j.ijleo.2018.03.024

Kim, D. A., Shim, J. H., & Cho, N. H. (2004). PL and EL features of p-type porous silicon prepared by electrochemical anodic etching. Applied Surface Science, 234(1–4), 256–261. https://doi.org/10.1016/j.apsusc.2004.05.028

Kim, H. J., Kim, Y. Y., & Lee, K. W. (2010). Multiparametric sensor based on DBR porous silicon for detection of ethanol gas. Current Applied Physics, 10(1), 181–183. https://doi.org/10.1016/j.cap.2009.04.020

Lee, S.-K., Chang, D., & Kim, S. W. (2014). Gas sensors based on carbon nanoflake/ tin oxide composites for ammonia detection. Journal of Hazardous Materials, 268, 110–114. https://doi.org/10.1016/j.jhazmat.2013.12.049

Liu, I. P., Chang, C. H., Chou, T. C., & Lin, K. W. (2019). Ammonia sensing performance of a platinum nanoparticle-decorated tungsten trioxide gas sensor. Sensors and Actuators B: Chemical, 291, 148–154. https://doi.org/10.1016/j.snb.2019.04.046

Manakov, S. M., Ibrahimov, M. K., Sagidulova, Y., Zhumatsova, S. A., & Darmenkulova, M. B. (2019). Detection of acetaminamide and chloroform using structures on the base of porous silicon. Eurasian Chemico-Technological Journal, 21(1), 89–93. https://doi.org/10.18321/jetc796

Matsumura, I., Hosono, K., Murayama, N., Shin, W., & Izu, N. (2003). Organically hybridized SnO2 gas sensors. Sensors and Actuators B: Chemical, 89(1–2), 143–147. https://doi.org/10.1016/sbn.2004.10.051

Meng, W., Wang, L., Li, Y., Dai, L., Zhu, J., Zhou, H., & He, Z. (2018). Enhanced sensing performance of mixed potential ammonia gas sensor based on Bi85Sn0.05 VO3O2 by silver. Sensors and Actuators B: Chemical, 259, 668–676. https://doi.org/10.1016/j.snb.2017.12.120

Min, H.-K., Yang, H.-S., & Cho, S. M. (2000). Extremely sensitive optical sensing of ethanol using porous silicon. Sensors and Actuators B: Chemical, 67(1–2), 199–202. https://doi.org/10.1016/s0925-6470(00)00399-3

Mirzaei, A., Kang, S. Y., Choi, S. W., Kwon, Y. J., Choi, M. S., Bang, J. H., Kim, S. S., & Kim, H. W. (2018). Fabrication and gas sensing properties of vertically aligned Si nanowires. Applied Surface Science, 427, 215–226. https://doi.org/10.1016/j.apsusc.2017.08.182

Naderi, H., Hojati, S., Ghaedi, M., Dashitian, K., & Sabzehei, Mohammad. M. (2020). Sensitive, selective and rapid ammonia-sensing by gold nanoparticle-sensitized V2O5/Cu2O, heterojunctions for exhaled breath analysis. Langmuir, 36(4), 144270. https://doi.org/10.1021/acs.langmuir.0c02470

Schechter, I., Ben-Chorin, M., & Kux, A. (1995). Gas sensing properties of porous silicon. Analytical Chemistry, 67(20), 3727–3732. https://doi.org/10.1021/ ac00116a018

Wang, X., Zhang, J., & Zhu, Z. (2006). Ammonia sensing characteristics of ZnO nanowires studied by quartz crystal microbalance. Applied Surface Science, 252(6), 2404–2411. https://doi.org/10.1016/j.apsusc.2005.04.047

Wang, Y., Jia, W., Stout, T., Schepf, F., Zhang, H., Li, B., Cui, J., & Lei, Y. (2009). Ammonia gas sensor using polypropylene-coated TiO2/ZnO nanocomposites. Electroanalysis: An International Journal Devoted to Fundamental and Practical Aspects of Electroanalysis, 21(12), 1432–1438. https://doi.org/10.1002/ealan.200904584

Yamao, N. (2005). Toward innovations in gas sensor technology. Sensors and Actuators B: Chemical, 108(1–2), 2–14. https://doi.org/10.1016/j.snb.2004.12.075

Yang, B., Wang, C., Xiao, R., Yu, H., Wang, J., Liu, H., Xiao, F., & Xiao, J. (2020). High sensitivity and fast response sensor based on sputtering Au tuned ZnFe2O4-SE for low concentration NH3 detection. Materials Chemistry and Physics, 239, 122302. https://doi.org/10.1016/j.matchemphys.2019.122302

Yuan, L., Hu, M., Wei, Y., & Ma, W. (2016). Enhanced NO2 sensing characteristics of Au modified porous silicon/thorn-sphere-like tungsten oxide composites. Applied Surface Science, 389, 824–834. https://doi.org/10.1016/j.apsusc.2016.07.068

Zhanabaev, Z., Greveleva, T., & Ibrahimov, M. K. (2016). Morphology and electrical properties of silicon films with vertical nanowires. Journal of Computational and Theoretical Nanoscience, 13(1), 615–618. https://doi.org/10.1166/jctn.2016.6849

Zhang, H., & Braun, P. V. (2012). Three-dimensional metal scaffold supported bicontinuous silicon battery anodes. Nano Letters, 12(6), 2778–2783. https://doi.org/10.1021/nl204551m
