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THE SENSING PERFORMANCE OF SURFACE-MODIFIED POROUS SILICON GAS SENSORS FOR NON-POLAR GAS DETECTION

Abstract. Gas sensors are important devices in various industrial and environmental monitoring applications. Toluene and chloroform are harmful non-polar gases that are produced in various combustion processes and are associated with air pollution and respiratory diseases. Porous silicon (PS) has shown promising results as a material for ammonia and ethanol gas sensing applications. However, there is potential for further improvement by optimizing their surface properties for non-polar gas sensing applications. Chemical treatment has been widely utilized to modify the surface characteristics of materials, including semiconductors, for various applications. We have deposited nickel (Ni) layer on PS surface using chemical treatment. In comparison to the PS sample, it was discovered that the Ni-deposited PS sample was more sensitive to 0.1 ppm concentrations of non-polar toluene and chloroform vapours, increasing from 1% to 39% and 32.6%, respectively. This study provides valuable insights into the surface modification techniques for enhancing the performance of gas sensors, which can have a significant impact on the development of advanced sensing technologies for environmental and industrial applications.

Key words: gas sensor, porous silicon, nickel, chemical treatment, sensitivity.

Inroduction

Nowadays, the development of industrial technologies and automation of processes, increasing requirements for human health and environmental protection have led to a significant increase in the demand for gas sensors [1]. Control and monitoring systems used to analyze the composition of air in the environment and to accurately determine the concentration of a certain type of gas mainly consist of a gas sensor, an analog-to-digital converter, a microprocessor used for digital processing of information on the composition of air, and an electronic display. In addition, if necessary, such systems can be equipped with wireless communication systems for remote control and monitoring. The main areas of application of these devices include industrial enterprises, factories, mines, industrial security services and crowded places [2].

The primary measuring element of the electronic gas sensor is the sensitive element. As the primary sensitive component of gas sensors, metal-oxide semiconductors like ZnO, SnO2, TiO2, In2O3, and MoS2 are frequently utilised. [3]. In addition, many works have been published to study the possibilities of gas sensors based on organic compounds, optical sensors, materials based on carbon nanotubes and conductive nanostructures as various gas sensors. However, gas sensors based on metal-oxide semiconductors, which are widely used in practice, usually operate at high temperatures between 150-300°C, and therefore require high energy consumption and low selectivity and sensitivity to some types of gases [4]. In addition, poor compatibility with contemporary silicon-based electronic gadgets and increasingly complex manufacturing techniques. Thus, it can be considered a difficult task to monitor harmful gases using gas sensors based on metal oxide semiconductors at room temperature [5].

The large surface area due to the fractal structure, the chemical activity of the material surface, the uncomplicated production technology, as well as the unique optical, electrical and structural properties make porous silicon (PS) a promising material for use as a sensitive element in gas sensor technology [6].

In addition, another advantage of using silicon nanostructures as a gas sensor is compatibility with modern electronics. Although PS is highly sensitive to certain types of gases, it is less stable due to rapid acidification of its surface. Therefore, the sensitivity and selectivity characteristics of electronic gas sensors for difficult-to-detect gas species can be increased by using a surface-modified PS for solid-state electronics manufacturing applications [7]. The results of the experimental study showed that the tested samples can detect harmful gases at a concentration of 0.1 ppm at room temperature. These results demonstrate the possibility of developing highly sensitive and cost-effective electronic sensors for various harmful and hazardous gases. High-tech tools and processes of radio engineering and electronics were used to obtain sensitive elements and study their electrical, morphological and optical characteristics.

In this work, we investigate the impact of chemical treatment on the morphology of PS as well as on the gas sensing performance of surface modified PS-based gas sensors towards non-polar gases such as toluene and chloroform in order to enhance the device performance.

Main provisions

For the first time, surface-modified porous silicon with a nickel layer was used to detect non-polar gases with concentrations up to 0.1 ppm.

Materials and Methods

During the experiment, nanoscale PS samples were used as the research subject. By electrochemically etching p-type silicon wafers with a resistance of 10 Ohm/cm and a crystal orientation of 100, PS samples were produced. Fig. 1 shows a schematic illustration of the electrochemical etching procedure [8].

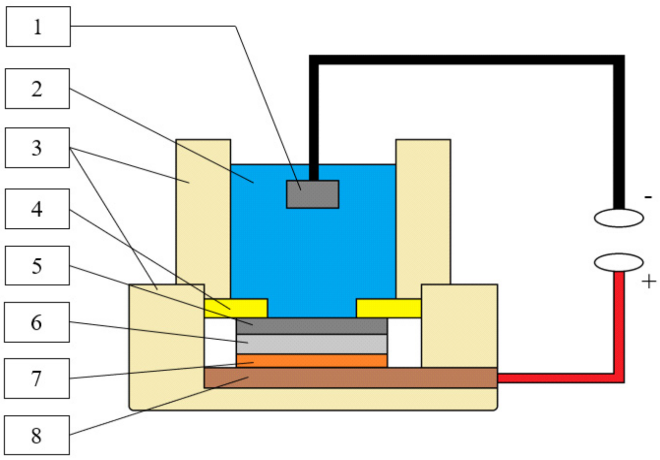

Figure 1 – Electrochemical etching procedure: 1 – platinum cathode; 2 – electrolyte; 3 – Teflon-like fluoroplastic cell; 4 – sealing ring; 5 – porous silicon; 6 – silicon; 7 – metal layer; 8 – anode [8].

In the beginning, thin films of PS were created by electrochemical etching in a 1:1 HF:C2H5OH solution electrolyte. Before being rinsed with deionized water, silicon wafers were first cleaned in HF solution. A metal layer needs to be deposited on the silicon wafer's bottom surface before it can be placed in the cell used for the electrochemical etching procedure. For this, a silicon wafer must be kept pre-covered in a nickel solution that has been heated to between 50 and 60 oC for five to seven minutes. The silicon wafer is placed in a cell constructed of fluoroplastic Teflon and an electrolyte is poured over it after the metal layer has been applied to the bottom surface. On the silicon's bottom surface, a sealing ring is put in place to prevent the electrolyte from passing through. Because platinum is one of the metals that does not change when exposed to the HF solvent acid, platinum is employed as the cathode. Anode is attached to the silicon surface where nickel has been deposited. Such a structure has an edge over other technologies due to its ease of use and affordable cost. At a current density of 5 mA/cm2, the electrochemical etching process was conducted for 40 minutes.

The gravimetric method was used to determine the porosity of the obtained PS sample in accordance with the expression (1) below. [9]:

$$P = \frac{m_1 - m_2}{m_1 - m_3} \times 100\%, \qquad (2.1)$$

where m_1 – mass of the sample before the PS layer is fabricated, m_2 – mass of the sample after the PS layer has been fabricated, m_3 – mass of the sample after the PS layer has been stripped off.

PS samples generated by electrochemical etching were placed in a nickel solution heated to a temperature of 50–60 °C for 5-7 minutes in order to deposit a nickel layer on the surface.

A scanning electron microscope, the Quanta 200i 3D, was used to examine the morphology of the materials. A 473 nm laser was used to excite the photoluminescence, which was examined using the NT-MDT Solver Spectrum system. In order to obtain electrical properties, two ohmic contacts of InGa alloy in a coplanar configuration were thermally installed on the surface of the samples. The samples' sensitivity to vapours of toluene and chloroform was determined using the formula in [10].

Results and Discussion

The PS substrate had a porosity of 72.7%.

Fig. 2 shows the cross section and top view SEM images of the obtained Ni/PS material. As shown in the figure, the Ni layer is deposited on the PS surface as a porous structure and a metal-conductor contact is formed.

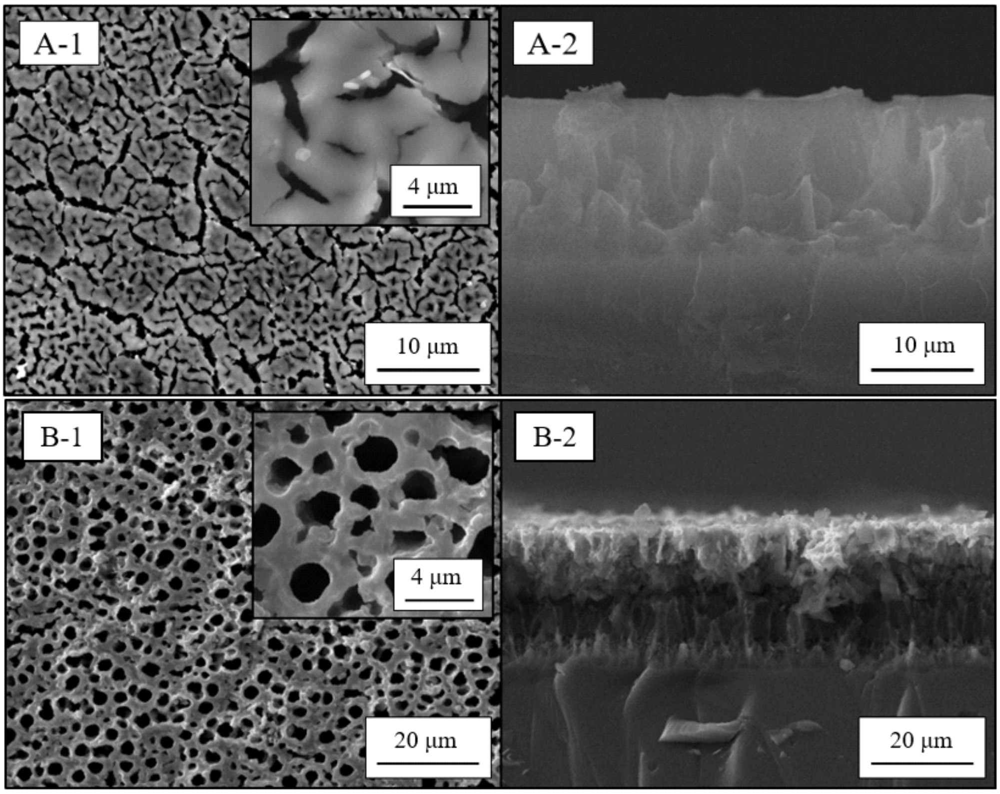

Figure 2 – SEM images of PS (A) and Ni/PS (B): 1 – top view; 2 – cross-section view.

Figure 3 shows that, as compared to PS, the Ni/PS sample's normalised photoluminescence (PL) intensity is displaced to the green area of the spectrum at wavelengths of 520 nm and 535 nm, respectively (photon energies are 2.38 eV and 2.32 eV).

Photoluminescence signals of semiconductor materials are generated by photoinduced recombination of charge carriers [10]. It is seen that the spectrum of the given material has the ability to radiate from the blue to the red region.

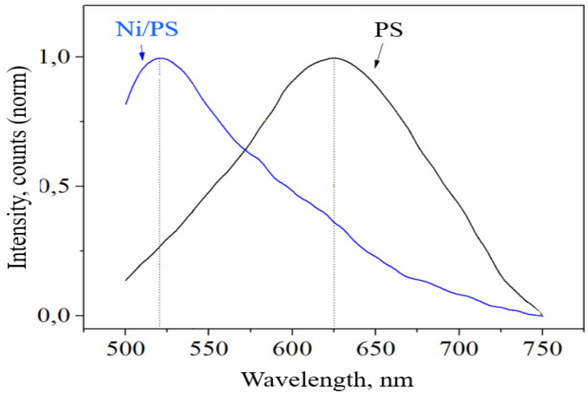

Figure 3 – Photoluminescence spectra of PS and Ni/PS samples

The defect states created from oxygen vacancies are responsible for the material's emission at various wavelengths. As the efficiency of electron transport at the border between the adsorbed molecule and the material's surface rises, such oxygen vacancies enable materials to be more sensitive.

Let's now think about the electrical properties of the Ni/PS sample under various gas exposures. The current-voltage characteristics of the PS sample with a Ni layer modification are shown in Fig. 4. The figure illustrates how the sample's current-voltage characteristics have a rectifier character under both ambient circumstances and gas impact. Additionally, when exposed to all of the gas utilised for the test, the current of the Ni/PS sample increases.

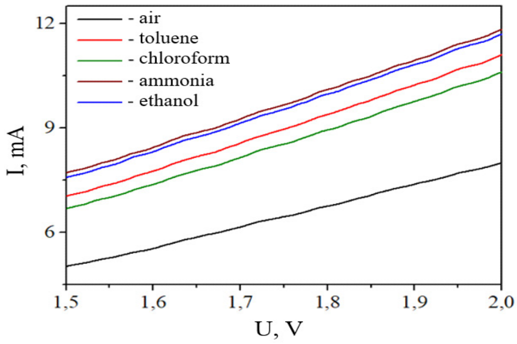

Figure 4 – Current-voltage characteristics of the Ni/PS-based gas sensor under different gas exposures

Figure 5 depicts diagrams of the Ni/PS sensitive element's sensitivity to vapours of ammonia, ethanol, toluene, and chloroform. The sensitivity is greater than 30% for all gas types.

Table 1 provides a summary of the examined properties of the materials employed as gas sensors. The table makes it evident that adding a metal layer to the PS surface can enhance the features of gas sensors.

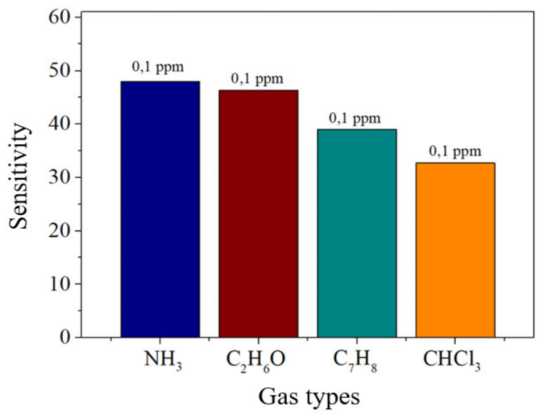

Figure 5 – Diagrams illustrating the gas sensors' sensitivity to various gas molecules based on PS modified with a Ni layer

Table 1 – Comparison of PS and Ni/PS-based gas sensors

No.	Sensitive material	Sensitivity				Response time / recovery rime, sec			
		NH_3	C_2H_6O	C_7H_8	$CHCl_3$	NH_3	C_2H_6O	C_7H_8	$CHCl_3$
1	PS	33.25	5.75	-	-	3 / 270	-	-	-
2	Ni/PS	47.97	46.3	39	32.68	3 / 360	15 / 15	20 / 10	50 / 60

As a result, as compared to the original PS, the Ni/PS gas sensor's sensitivity to non-polar toluene and chloroform vapour concentrations at 0.1 ppm ranges from 1% to 39% and 32.6%, respectively.

Conclusion

In this work, the non-polar gas sensor was constructed from a surface-modified porous silicon sample and given a chemical treatment to improve its performance. SEM analysis and PL spectra were used to examine the structure and morphology of the etched and sputtered nanomaterials, and they supported the deposition of Ni on the PS surface. According to the results of the gas sensing, Ni/PS outperformed PS in terms of toluene and chloroform sensitivity at ambient temperature. As a result, the Ni layer's alteration of the PS surface increased their sensitivity to vapours. This study demonstrates that a highly sensitive, low-cost gas sensor device based on a Ni/PS structure is feasible for detecting toluene and chloroform vapours at room temperature in concentrations up to 0.1 ppm.

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БЕЙПОЛЯРЛЫ ГАЗДЫ АНЫҚТАУҒА АРНАЛҒАН БЕТІ ӨЗГЕРТІЛГЕН КЕУЕКТІ КРЕМНИЙЛІ ГАЗ СЕНСОРЛАРЫНЫҢ СЕЗУ ӨНІМДІЛІГІ

Аңдатпа. Газ датчиктері – өнеркәсіптік және экологиялық бақылаудың әртүрлі қосымшаларындағы маңызды құрылғылар. Толуол мен хлороформ – әртүрлі жану процестерінде пайда болатын және ауаның ластануымен, тыныс алу органдарының ауруларымен байланысты зиянды бейполярлы газдар. Кеуекті кремний (КК) аммиак пен этанол газын анықтауға арналған материал ретінде перспективалы нәтижелерді көрсетті. Дегенмен, бейполярлық газды сезіну қолданбалары үшін олардың беттік қасиеттерін оңтайландыру арқылы оны одан әрі жақсарту мүмкіндігі бар. Химиялық өңдеу материалдардың, соның ішінде жартылай өткізгіштердің беткі сипаттамаларын әртүрлі қолданбалар үшін өзгертуде кеңінен қолданылды. Біз химиялық өңдеу арқылы КК бетіне никель (Ni) қабатын қойдық. Ni-тұндырылған КК үлгісінің бейполярлы толуол мен хлороформ буларының 0,1 ppm концентрациясына сезімталдығы КК-мен салыстырғанда тиісінше <1%-дан 39%-ға және 32,6%-ға дейін жоғарылағаны анықталды. Бұл зерттеу қоршаған орта мен өнеркәсіптік қолданбалар үшін алдыңғы қатарлы зондтау технологияларын дамытуға айтарлықтай әсер етуі мүмкін газ датчиктерінің өнімділігін арттыру үшін бетті модификациялау әдістері туралы құнды түсініктерді береді.

Тірек сөздер: газ сенсоры, кеуекті кремний, никель, химиялық өңдеу, сезімталдық.

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ИЗМЕРИТЕЛЬНЫЕ ХАРАКТЕРИСТИКИ МОДИФИЦИРОВАННЫХ ПОВЕРХНОСТЕЙ ГАЗОВЫХ СЕНСОРОВ НА ПОРИСТОМ КРЕМНИИ ДЛЯ ОБНАРУЖЕНИЯ НЕПОЛЯРНОГО ГАЗА

Аннотация. Датчики газа являются важными устройствами в различных приложениях промышленного и экологического мониторинга. Толуол и хлороформ – вредные неполярные газы, образующиеся в различных процессах горения и связанные с загрязнением воздуха и респираторными заболеваниями. Пористый кремний (ПС) показал многообещающие результаты в качестве материала для измерения газов аммиака и этанола. Однако существует потенциал для дальнейшего улучшения за счет оптимизации свойств их поверхности для приложений, связанных с измерением неполярного газа. Химическая обработка широко используется для модификации характеристик поверхности материалов, в том числе полупроводников, для различных применений. Мы нанесли слой никеля (Ni) на поверхность ПК с помощью химической обработки. Установлено, что чувствительность образца ПС, осажденного Ni, к концентрации 0,1 ppm паров неполярного толуола и хлороформа увеличилась с <1 % до 39 % и 32,6 % соответственно по сравнению с ПС. Это исследование дает ценную информацию о методах модификации поверхности для повышения производительности газовых датчиков, что может оказать существенное влияние на разработку передовых сенсорных технологий для экологических и промышленных применений.

Ключевые слова: газовый сенсор, пористый кремний, никель, химическая обработка, чувствительность.