

Studies on Sensitivity of Porous Silicon Surfaces to Environmental Gases

A.E. Aliev, Sh.U. Yuldashev, P.K. Khabibullaev, M.H. Khan, and F.A. Khalid

We have studied the electrophysical properties of porous silicon p-n junction in an atmosphere of various gases: moisture, ammonia, benzene, acetone, and ethanol. The high sensitivity of ac conductivity to the polar gas molecules is connected with an additional pathway through the opened surface of the p-n junction.

Keywords
ac conductivity, gas sensitivity, p-n junction, porous silicon

1. Introduction

THE ANODIZATION of silicon wafers at low-current densities in hydrogen-fluorine-base (HF-base) solutions can be used to generate an array of extremely small holes that run orthogonal to the surface (Ref 1). Bulk silicon can be made with different size and density of pores depending upon substrate resistivity and anodization conditions (Ref 2).

Much attention has been directed to porous silicon (PS) after the discovery of intense photoluminescence in the visible region of the electromagnetic spectrum (Ref 3). This discovery created the possibility of integrating the technology of integrated circuitry with emitting devices that operate in the visible light range. Therefore, many studies have been devoted to the optical properties of PS and to the origin of its wide-band gap (Ref 4-7). At the same time, relatively few studies of the effects of environmental atmospheres on the electrical properties of these porous materials have been made (Ref 8-12).

The porous surface, since it can be altered by etching and subsequent treatments, can also be used in applications that do not necessarily exploit the light emitting properties but rather the very unique surface of porous silicon. Possible applications include gas concentration sensors, capacitors, and electromagnetic radiation attenuators.

This work presents data on certain electrical properties of PS surface and the effect of various environmental gases such as moisture, ammonia, acetone, benzene, and ethanol on those electrical properties.

2. Experiment

The porous silicon samples are prepared from 100 oriented silicon wafers, which are usually used for solar cells. The p-n junction is made by standard diffusion of phosphorus into p-type boron-doped wafers with resistivities in the range 1 to 5 $\Omega \cdot$ cm.

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The depth of p-n junction is about 1 µm. The porous layers are prepared by electrochemical dissolution in an HF (50%) solution: ethanol (1:1) electrolyte under current density of 20 to 50 mA/cm^2 for the duration ranging from 3 to 10 min. The following etching is performed in the same solution for 30 min. This standard procedure of PS preparation is usually to produce the porous layers with thickness about 20 µm and porosity more than 80% (Ref 13). Before the deposition of the upper contacts, the samples are washed in an ultrasonic bath filled with ethanol ($P \sim 10$ W cm^{-2}, $t \sim 10$ s). After final drying in ambient air for 30 min at room temperature, a final check is made of the most important property of the new porous silicon layer, namely that it exhibits luminescence in the visible range. The samples do indeed emit intense yellow-red light under ultraviolet (UV) excitation.

Two different approaches are used to make electrodes. In the first, silver electrodes about 0.4 µm thick are evaporated on top of PS layers through a shadow mask. In the second approach, graphite electrodes are prepared by rubbing graphite powder onto the sample, and contacts are achieved by pressing wires to the graphite layers.

3. Results and Discussion

A current-voltage I (V) curve of PS samples with silver electrodes in the presence of air at room temperature and ambient pressure is shown in Fig. 1. Diode-like behavior is shown in curve 2 where the slope of I (V) increases drastically for voltages above approximately 2 V. The curves numbered 1 and 2 correspond to the first and fifth attempts to measure the I (V) characteristics of this particular sample. The values of the current in Fig. 1 are for tests in which the current has stabilized. The characteristics of curve 2 can be achieved in the same samples if they are conditioned for about 2 to 3 min at 10 V in ambient air.

If the voltage is increased to about 10 V (and the current through the sample is about 100 mA), intense electroluminescence in the form of visible yellow-red light is clearly seen by the naked eye.

The current through the sample is not steady. Figure 2 shows the decay in current over 300 s when the voltage is set and held constant at 1.6 V. The characteristic time to reach steady state is of the order of 500 s. This is for a sample in air. For samples in vacuum (<10^{-3} torr), the transient current is less than 10% of the initial current. This shows that the device could be used, in principle, to monitor the presence of ambient gases.

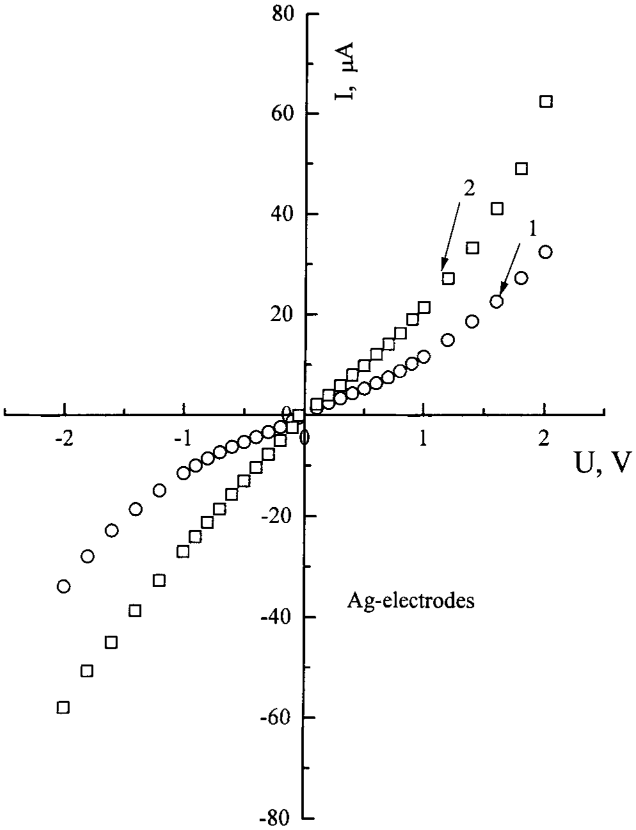

Fig. 1 *I* (V) characteristics of PS with silver electrodes in presence of air at room temperature and ambient pressure

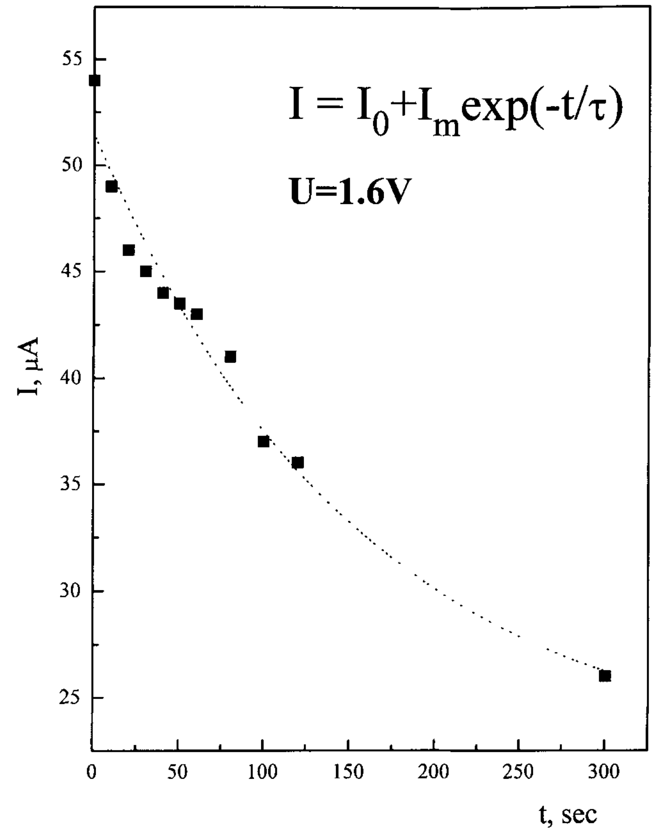

Fig. 2 Typical current transient behavior under the application of a direct voltage of 1.6 V

Table 1 Some physical properties of used gases

Type of gas	Dielectric constant ε	Temperature, °C	Dipole momentum μ, Debye	Saturated vapor pressure *p*, mm	Temperature, °C	σ, Ω^{-1} *f* = 10 kHz tgδ = 0.1
Ammonia, NH_3	16.9	25	1.48	7500	25	3×10^{-4}
Water, H_2O	78.3	25	1.84	23.7	25	1.3×10^{-4}
Acetone, CH_3COCH_3	20.9	...	2.84	177	20	5.8×10^{-5}
Benzene, C_6H_6	2.284	...	0	75	20	2.4×10^{-5}
Ethanol, C_2H_5OH	25	20	1.69	40	20	1.1×10^{-4}

Source: Ref 15

The sensitivity of the porous silicon surface to various gases is investigated by placing a sample in a glass vacuum chamber of internal volume 6×10^3 cm^3. For these tests, the investigated atmosphere is produced by evaporation at room temperature of the different liquids from a 10 mL pot placed into the chamber. The direct current (dc) response of an aluminum-porous p^+ silicon junction to various gases as versus time has been published (Ref 12). But as is mentioned above, the dc current through samples is not steady in air. Therefore, the ac characteristics of the silicon sample are used in this work. The alternating current (ac) conductivity response of PS structures to various gases (ammonia, moisture, ethanol, and acetone) versus the concentration of gas molecules is shown in Fig. 3. The value of the molecule concentration is obtained by measuring the capacitance change of an air capacitor that is placed in the chamber near the sample. The initial pressure is 10^{-3} torr, and the capacitance is practically the same for all gases. When the evaporation of the liquid is started, the capacitance is changed because of a difference of the gas permittivities. The concentration of gas molecules can be calculated using the equation (Ref 14):

$$(\varepsilon - 1) = N\mu^2/3kT$$

where ε is the dielectric constant of a gas, *N* is the concentration of gas molecules, *p* is the dipole momentum of the molecule, *k* is the Boltzmann constant, and *T* is the temperature.

The greatest variation of conductivity is observed for acetone and the lowest for ammonia molecules. In order to explain the electrical behavior of the sensor, the schematic representation of the structure given in Fig. 4 is proposed. The high sensitivity of ac conductivity of PS surface to the presence of

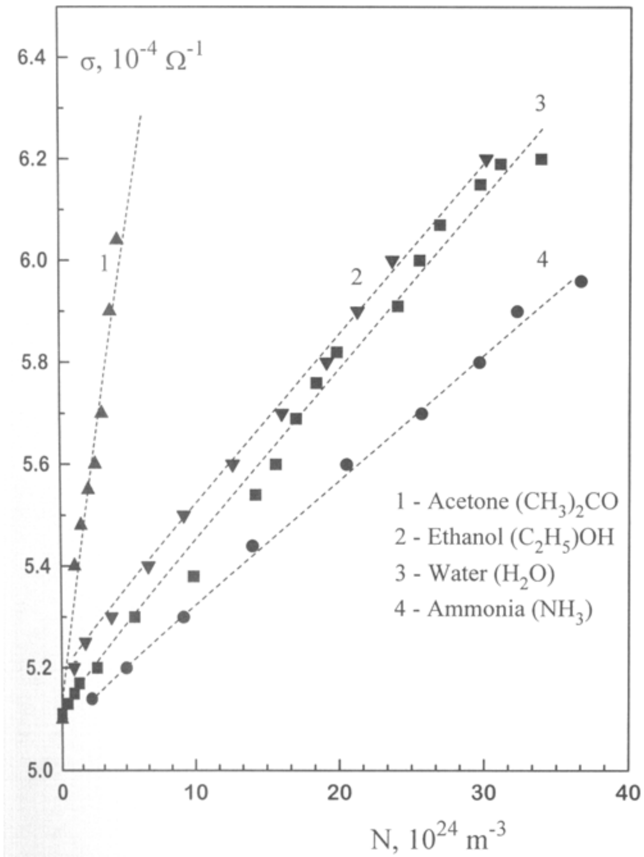

Fig. 3 AC conductivity of PS structure versus concentration of gas molecules: 1, acetone; 2, ethanol; 3, moisture; 4, ammonia

various gases is observed due to the appearance of an additional pathway through the opened surface of the p-n junction located at the edge of the electrodes. So far as increasing the current in the accepted geometry of the experiment is observed only for ac, that additional conductivity is caused by polarization effects. Therefore, the greatest variation of conductivity should be expected for polar molecules with high dipole momentum. Indeed, the greatest sensitivity has been observed for acetone (see Table 1). The absence of influence of benzene to the PS surface is associated with the zero dipole momentum ($m = 0$) of benzene molecules.

4. Conclusions

In conclusion, the variation of the ac current of a PS surface versus various adsorbed gases has been studied. A simple model mainly based on the appearance of an additional pathway through the opened edge surface of p-n junction was proposed.

The present studies of ac conductivity of porous silicon structure can be summarized as follows:

- The greatest sensitivity to polar molecules is obtained in the samples with p-n junction.

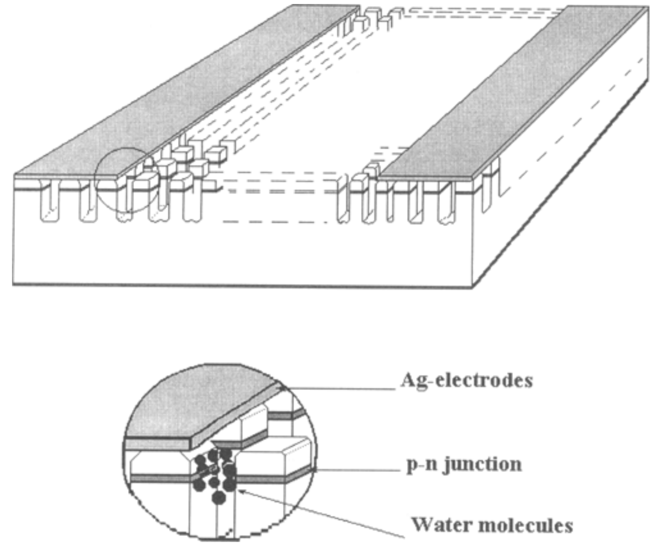

Fig. 4 Schematic representation of PS sample with electrodes and probable mechanism of the variation of the ac current

- The variation of capacitance, a part of the impedance by the excitation of the gas molecules, considerably exceeded the variation of dc conductivity.
- Increasing the concentration of the gas molecules results in increasing capacitance and decreasing conductivity.
- In the charge transfer process, only the regions closely disposed to electrodes are involved. Isolation of the central part of the cell surface has no influence on the variation of conductivity.

Acknowledgments

The authors thank Dr. I.A. Qazi (National Institute of Silicon Technology, Islamabad) for providing the silicon wafers. They are grateful to Prof. Zafar Iqbal (Quaid-i-Azam University, Islamabad) for helpful discussion. This work was performed within the framework of a scientific agreement between the Heat Physics Department of the Academy of Sciences of Uzbekistan and the GIK Institute of Engineering Science and Technology, Pakistan.

Sh.U. Yuldashev is also grateful to the Fundamental Researches Foundation of the Academy of Sciences of Uzbekistan for partial financial support of this work (Grant N4-96).

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