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Manufacture and investigation of hydrogen sensitive TiO_{2-x} or ZnO<Al> film-porous silicon devices

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Abstract

Hydrogen sensor working at room and 40°C temperatures made of porous silicon covered by the TiO_{2-x} or ZnO<Al> thin film was realized. Porous silicon layer was formed by electrochemical anodization on a *p*- and *n*-type Si surface. Thereafter, *n*-type TiO_{2-x} and ZnO<Al> thin films were deposited onto the porous silicon surface by electron-beam evaporation and magnetron sputtering, respectively. Platinum catalytic layer and Au electric contacts were for further measurements deposited onto obtained structures by ion-beam sputtering. The sensitivity of manufactured structures to 1000–5000 ppm of hydrogen, propane–butane mixture, and humidity was studied. The sensitivity of obtained structures was determined as ratio of the resistivity of structures in the presence of investigated gas to that in air. Results of sensitivity measurements showed that it is possible to realize a hydrogen sensor, resistivity of which can be decreased up to 2.5 times at room temperature and 4 times at 40°C for the Pt/TiO_{2-x}/PS structure, as well as 2 times for the Pt/ZnO<Al>/PS structure at 40°C at 5000 ppm hydrogen concentration, respectively. Both structures have the recovery and response time of approximately 20 sec and rather high durability and selectivity to hydrogen gas.

1. Introduction

Requirements to gas sensitive devices increase at present because of their wide application in everyday life, industry, as well as for security and safety. High interest to gas sensors, especially to hydrogen sensors, is explained by the growing interest to hydrogen as a future energy carrier [1]. Extensive investigations in the field of gas sensors in order to obtain high-sensitivity, high-selectivity, and small-size gas sensors consuming low energy, are currently under way.

Silicon is now the basic material for electronics. Therefore it is very important to have silicon-based gas sensors. Much effort was made in this direction [2-8]. In particular, it was established that the active surface area of etched and textured Si interacting with gas increases significantly. This means that porous silicon-based gas sensors should have a high sensitivity.

Unfortunately, the parameters of porous silicon layers are often degrade with time which does not meet the requirement of durability of gas sensors. The main reason of degradation is that porous silicon reacts slowly with the ambient air and consequently its properties evolve continuously with time [9].

Thin film metal oxide ceramics has wide applications for gas sensors. Such gas sensors are small in size and cheap. In most cases their electrical conductivity dramatically changes under the influence of different gases. A relatively simple electric circuit suits for the fabrication of the final device. Note that metal oxide gas sensors need, as a rule, a remarkable pre-heating of working body of the sensor (up to 300–700^{0}C) [10–12]. It is necessary for an increase in removal of intense surface oxygen ions from the surface and decrease in the height of barrier between grains which leads to an increase in the conductivity. But high temperature of metal oxide leads to a decrease in the sensors stability, as well as there is a danger of explosion of hydrogen gas at high temperatures. To provide high working temperature of gas sensors, it is necessary to incorporate an additional heater and a power supply for that. In the first case a lithographic stage is added to the technological cycle of gas sensor preparation which leads to the rise in price of obtained structures and in the second case the size of gas sensors increases. Therefore it is necessary to develop gas sensors working at room temperature or without significant preheating. For example, such hydrogen sensors can be implementing into fuel cells.

So, the aim of reported investigations is to obtain structures sensitive to hydrogen which will be characterized by small size and work at reduced temperatures. Allowing for the above-mentioned properties of both porous silicon and metal-oxide materials, we investigate a possibility to realize a low-cost hydrogen sensor made of porous silicon layer covered with a metal oxide thin film, working at reduced temperatures [13, 14].

2. Experimental

Porous silicon films were obtained by electrochemical anodization on the *n*- and *p*-type Si surface with resistivity 0.3 kΩ·cm and 0.15 kΩ·cm, respectively. Before anodization the samples were boiled in isopropyl alcohol and immersed into HF aqueous solution to remove native oxide from the silicon surface, washed in distilled water, and finally dried in air. Anodization was carried out under the following conditions: the current density was varied from 10 to 50 mA/cm^2 and anodization time from 10 to 600 sec for the *p*-type Si, while for the *n*-type the current density was varied in the range 40–90 mA/cm^2 and anodization time in the range 10–600 sec. An electrolyte HF (48%):C_2H_5OH (96%) in proportion 1:1 by volume was used to produce porous silicon. Anodization was carried out in the Teflon electrochemical cell with a platinum cathode. The samples were then immersed into ethyl alcohol, dried in air, and placed in the electron-beam evaporation and magnetron sputtering chambers for deposition of the TiO_{2-x} and ZnO<Al> layers, respectively.

Rutile TiO_2 metal-oxide tablet-target for electron-beam evaporation was formed from powder of this material undergone thermal annealing at the temperature 1100°C. Because the

stoichiometric TiO_2 is an insulator (with a specific resistance of 10^{13} Ω ·m), the thermal annealing has been carried out in the inert gas atmosphere resulting in obtaining partially substituted samples with oxygen vacancies. The free sites of the anion subsystem of rutile act as donor impurities in the semiconductor. Besides, by varying the concentration of free sites of oxygen, it is possible to vary the specific resistance of samples from 100 Ω ·m up to 10^7 Ω ·m.

Compact ZnO<Al> targets for magnetron sputtering were manufactured with the diameter ~40 mm and thickness ~ 3 mm. The semiconductor ceramic samples ZnO doped with 1 at % of Al were synthesized by the method of solid-phase reactions in air according to the following program: raising temperature from room up to 800°C for two hours, soaking at this temperature during 30 minutes, further increase in temperature for 2 hours up to 1200°C, soaking at this temperature during 3 hours, and subsequent slow cooling down to room temperature.

Thin films of TiO_{2-x} were obtained by the electron-beam evaporation onto the surface of the porous silicon layer under the following conditions: electron beam current of 30 mA, the target bias voltage of 1.25 kV, and the process duration of 10–30 min. Thin films of ZnO<Al> were obtained by rf magnetron sputtering under the following conditions: magnetron power of 80 W, process duration from 10 to 60 min.

Then, platinum catalytic film and gold electric contacts were deposited by the ion-beam-sputtering through a metallic mask on the top of obtained structures. The schematic diagram of obtained gas sensors is shown in Fig.1.

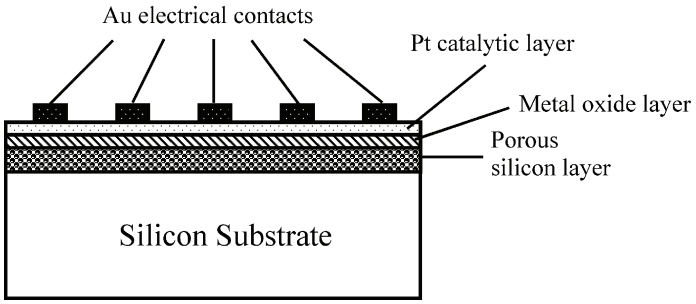

Fig. 1 Schematic diagram of gas sensor

Five percent of H_2 premixed in N_2, propane–butane mixture, and humidity were used in sensitivity examination. Sensitivity of the obtained structure to hydrogen gas and propane-butane mixture was examined in the range of concentrations from 1000 to 5000 ppm and for humidities from 50% to 80%. The PC control of the concentration of investigated gas is realized as follows: PC keeps open the gas valve until the gas concentration in the test chamber reaches the desired value. A special software is written for this purpose and the control is performed by DAQ card attached to PC and flow meter controller. All measurements were performed at room temperature and normal atmospheric pressure.

3. Results and Discussion

X-ray and chemical analysis were carried out by DRON-3 and EDX INCA Energy 300 setups in order to identify the structure and composition of deposited metal–oxide thin films. Results of measurements showed that the manufactured thin films had the following structure and composition: the value of x of grown TiO_{2-x} varied from 0.02 to 0.04 in the case of electron-beam evaporation; in the case of magnetron sputtered ZnO<Al> films, the grown films had the composition of the initial material. Both films were amorphous.

Sensitivity of obtained structures to the concentration of investigated gas was examined. The gas sensitivity was determined as a ratio (R_{gas}/R_{air}) of the resistance in investigated gas (R_{gas}) to that in air (R_{air}). All measurements were carried out in a test chamber at room temperature and 40°C using computer control system.

As mentioned above, the parameters of the porous silicon layer degrade in time. This phenomenon can be observed in Fig.2 where the sensitivity of as-prepared porous silicon samples to 5000 ppm hydrogen is shown versus time. It is evident from Fig.2 that the resistance of porous silicon changes sharply after injection of hydrogen into the test chamber, i.e. the obtained structure is sensitive. The resistance of porous silicon layer under influence of hydrogen increases first (Fig.2a), then, after the second injection no change in the resistance is observed (Fig.2 b), and finally the resistance decreases (Fig.2c). This means that the parameters of porous silicon layer degrade in time; therefore the sensors based on only porous silicon are not stable. In order to improve the stability of such gas sensors, it is necessary to protect the porous silicon layer from ambient. For this purpose, taking into account above mentioned properties of metal-oxide layers, we chose TiO_{2-x} or ZnO<Al> layer as protective one for porous silicon (PS).

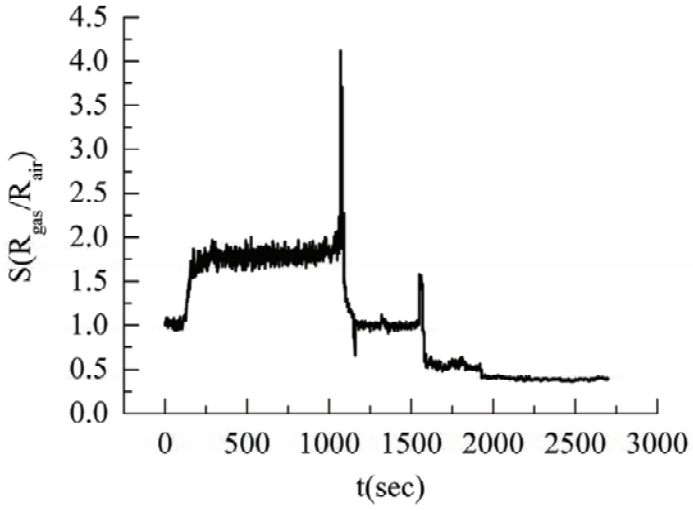

Fig. 2 Sensitivity of porous silicon structures to 5000 ppm hydrogen vs. time

Sensitivity of TiO_{2-x}/PS and ZnO<Al>/PS structures to 1000–5000 ppm of hydrogen was examined at two different temperatures. Results of measurements are shown in Figs.3–5. Only the TiO_{2-x}/PS structures were sensitive to 5000 ppm hydrogen at room temperature (Fig.3), while

the ZnO<Al>/PS structure was not. As clearly seen in Fig.3, the resistance of the TiO_{2-x}/PS structure changes 2.5 times, which means that it is possible to obtain hydrogen sensors working at room temperature without preheating of the working body of the sensor.

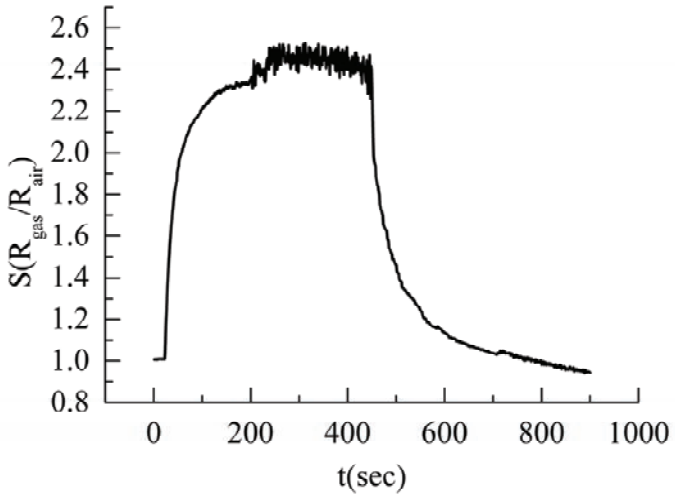

Fig. 3 Sensitivity of PS/TiO_{2-x}/Pt structures at room temperature

Further measurements of sensitivity to different concentrations of hydrogen were continued at 40°C in order to check possibilities of sensors to work close to room temperature with relatively high sensitivity.

Results of measurements of sensitivity of the TiO_{2-x}/PS and ZnO<Al>/PS structures to 1000–5000 ppm hydrogen at 40°C are shown in Fig.4 and Fig.5, respectively. As clearly seen in these two figures, the resistivity of structures to 1000–5000 ppm hydrogen was 1.5–4 times higher than that of TiO_{2-x}/PS structures and 1.1–2 times lower than for ZnO<Al>/PS structures. Both structures are characterized by short recovery and response times (~20 sec). In some cases, in order to realize low values of the response or recovery times of gas sensors, the working body of them was usually heated up to temperatures 2 times exceeding the working temperature. Therefore energy consumption and working temperature increased, which is commonly not suitable for gas sensor. In our case response and recovery times are relatively short even at 40°C. As mentioned above, we used platinum thin film as a catalytic layer. When hydrogen molecules pass through the Pt layer they dissociate into atoms or ions, which leads to better and stronger interaction between hydrogen atoms or ions with oxygen species adsorbed on the metal-oxide or porous silicon surface and thus to relatively high sensitivity and short response and recovery times of obtained structures [15]. Besides, as shown in [15], even if hydrogen is present in a mixture with other gases, presence of the Pt catalytic layer allows splitting and passing of primary hydrogen atoms, which means that the Pt catalytic layer plays always unambiguously positive role in the increase in selectivity of the fabricated structures to hydrogen. To ascertain correctness of the above-mentioned statement, the sensitivity of both obtained structures was checked in the propane–butane gas mixture and under humidity. The measurements carried out

for 1000–5000 ppm concentration of the propane-butane mixtures in rather wide temperature range (up to 70°C) and humidity range from 50% to 80% showed that the sensitivity to those ambient has not been observed.

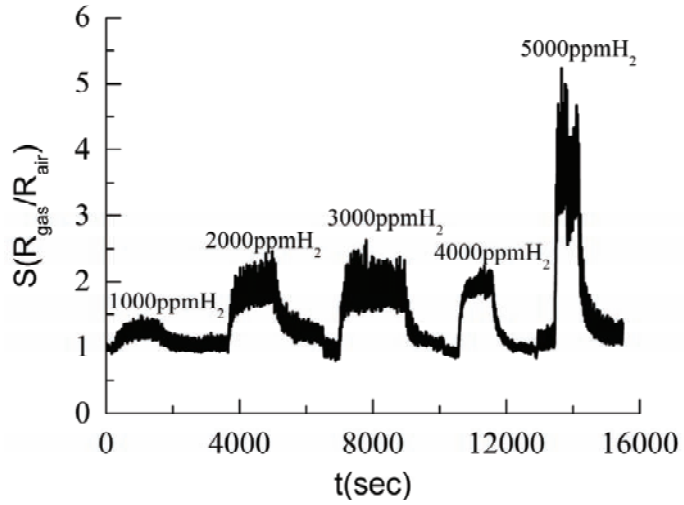

Fig. 4 Sensitivity of PS/TiO_{2-x}/Pt structures to different concentration of hydrogen at 40°C

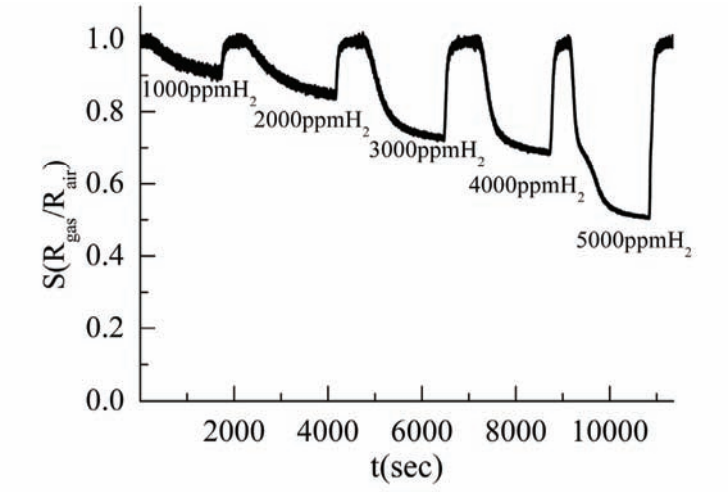

Fig. 5 Sensitivity of PS/ZnO<Al>/Pt structures to different concentration of hydrogen at 40°C

To ensure that degradation processes in porous silicon layer are very weak, when it is covered by a TiO_{2-x} or ZnO<Al> layer, we carried out continuous measurements of current–voltage characteristics and sensitivity of samples during 10 months and did not observe any change in parameters. This means that deposited metal-oxide layers protect effectively the PS layer.

Note that the reported gas sensors made on a silicon substrate, consist of hydrogen-sensitive thin layers of porous silicon and metal oxide and were manufactured by the technology traditional for the integral circuits (electrochemical anodization, electron-beam evaporation, and rf magnetron sputtering). Such sensors are characterized by durability, hydrogen-selectivity, and

relatively short recovery and response times, and they can operate at and close to room temperature, which is typical for many important devices (including fuel cells).

4. Conclusion

Hydrogen sensors working at and close to room temperature and made of porous silicon covered by the TiO_{2-x} or ZnO<Al> thin film have been realized. The sensitivity of manufactured structures to 1000–5000 ppm hydrogen was studied. Results of measurements showed that it is possible to realize a hydrogen sensor which has relatively high sensitivity and selectivity to hydrogen, durability, and relatively short times of recovery and response. Such sensors can also be a part of a silicon integral circuit.

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