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Silicon Nano Structures for Hydrogen Detection

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ABSTRACT

Silicon nanostructures layer was formed by electrochemical anodization on p-type silicon surface. TiO and ZnO[Al] thin films were deposited onto silicon nanostructures surface by electron-beam evaporation. A Pt catalytic layer and Au electrical contacts for further electrical measurements were deposited by thermal evaporation. Changes in sensitivity versus time of obtained structures were examined for different concentrations of hydrogen gas and propane–butane mixture. High sensitivity and selectivity to hydrogen gas was detected. All measurements were carried out at 40 ℃

KEYWORDS : Optical sensing, gas sensor, Synthesis of Silicon Nanostructures

Introduction

In recent years many investigations are carrying out to obtain gas sensors which are characterizing with small size, low response and recovery time and working near room temperature. Large amounts of publications related to hydrogen gas sensors because hydrogen is one of the most dangerous and combustible gases. Besides hydrogen is used as energy carrier, and because of limited resources of coal and natural gas hydrogen will become one of the main energy carriers in the near future. Therefore there is growing interest to the explosive gas sensors for different application with industry development. Hydrogen sensors are preparing now mainly on metal oxide semiconductors (see, for example, [1–2]. High sensitivity to changes in the surrounding gas atmosphere of metal oxides SnO_2, In_2O_3, ZnO and TiO_2 are well known [3–6]. The number of papers reporting on the successful application of these oxides in gas sensing device is dramatically increasing each year. The shortcoming of majority of such gas sensors is the necessity in the remarkable heating of the work body of sensors (sometimes up to several hundred degree of Celsius) in order to provide the low response and recovery time and high sensitivity of the sensors. Many metal oxides are very stable in different gas media and atmosphere at low temperatures. To improve the interaction between hydrogen and semiconductor materials, Pt catalytic layers are used. Gas sensitive properties of silicon nano structures layer were also investigated. The interest to such a material is connected partly with their very large specific surface area (up to 1000m^2/cm^3 [7]), which can be easily realized by the rapid and cheap etching of silicon surface. It envisages an intensive interaction of silicon nano structures surface with gases. Unfortunately, silicon nano structures layer is easy to oxidize and degrades in short time, which is becoming the reason of unstable work of sensors made from silicon nano structures. Therefore, based on above mentioned properties of silicon nano structures and metal oxide layers, we attempt to develop hydrogen gas sensors made of silicon nano structures and covered with thin metal oxide film, which will combine high sensitivity and stability [8].

Experimental

Because the stoichio metric TiO_2 film is an insulator with resistivity 10^{13} Ωm, a thermal treatment of that layer was carried out in noble gas (He) atmosphere. In this case it is possible to obtain partially reduced samples with oxygen deficiency. In retile anion sub lattice, the vacant site of oxygen plays the same role as donor impurities. By the change in the concentration of vacant sites of oxygen, it is possible to vary the resistivity of samples in the range 10^2–10^7 Ω m. In our case (shown are results of chemical analysis) a composition of obtained samples was $TiO_{1.98}$. As shown in the results of the X-ray diffraction analysis, obtained samples were homogeneous and kept the structure of raw material. The resistance of obtained samples was about 10^3 Ω m. We prepared also ZnO ceramic. It is also well known that ZnO has rather high specific resistance; its value can be as high as 1012 Ω m.

To increase the conductivity of ZnO samples, they were doped with Al. Porous silicon layers were formed in both single crystal n- and p-type Si surface. Before anodization, samples were boiled in isopropyl alcohol and immersed into HF aqueous solution to remove the native oxide from silicon surface. The samples were washed in distilled water and ethyl alcohol and finally dried in air. The anodization was carried out under the following conditions: current density and anodization time for p-type Si were varied in the range 10–50 mA/cm^2 and 10–600 s, respectively. Current density and anodization time for n-type Si were varied in the range 40–90 mA/cm^2 and 10–600 s, respectively. The following electrolyte HF (48%):C2H5OH (96%) in ratio 1:1 by volume was used for porous silicon formation. The anodization was carried out in a Teflon electrochemical cell with Pt cathode. Then obtained samples were immersed into ethyl alcohol and dried in air. Obtained p-type porous silicon samples were placed in the electron-beam evaporation chamber. n-type porous silicon samples were placed in magnetron sputtering chamber. Thereafter obtained n-type TiO_2 and n-type ZnO[Al] ceramic tablets were used as target for electron-beam evaporation and magnetron sputtering, respectively. Thin films of $TiO_{1.98}$ were evaporated on the p-type porous silicon surface by electron-beam evaporation under the following condition: electron-beam current was equal to 30 mA, target bias was 1.25 kV and process duration was 20 min. Thin films of ZnO[Al] were deposited from ceramic target on the n-type porous silicon surface by magnetron sputtering under the following condition: magnetron power was equal to 80 W and the process duration was 10–30 min. Then on the surface of obtained structures Pt catalytic layer and gold electrical contact through the metallic mask were deposited by ion-beam sputtering for further measurements. Five percent of H_2 in N_2 and propane–butane premixed gases were used for the sensitivity examination. Before gas entrance into measuring chamber, they passed through a moisture trap. Sensitivity of the obtained structure was examined in the gas concentration range (1000 to 5000) ppm at temperature of 40 °C.

Results and discussion

Changes of the sensitivity of PS/TiO1.98/Pt and PS/ZnO[Al]/Pt samples versus time at 1000–5000 ppm concentration of hydrogen at 40 °C are shown in Figs. 1 and 2, respectively. For clearness, in order to know how much the sensitivity of the obtained structures is, gas sensitivity was determined as the ratio Rgas/Rair of the resistance in hydrogen gas (Rgas) to that in air (Rair) for PS/TiO1.98/Pt structure. For PS/ZnO[Al]/Pt structure that value is defined as versa of PS/ $TiO_{1.98}$/Pt structure, i.e. Rair/Rgas. The measurements of samples sensitivity were carried out continuously during eight months. Obtained results repeated, which means that the samples did not degrade. It means that $TiO_{1.98}$ and ZnO[Al] layer effectively protecting the porous silicon layer form degradation. As can be clearly seen from Figures. 1 and 2, the sensitivity of PS/$TiO_{1.98}$/Pt structurewas changed 4 times and sensitivity of PS/ZnO [Al]/ Pt samples was changed 2 times. Both samples have relatively short response and recovery time, but PS/ZnO [Al] /Pt structures have short response time and have long recovery time in comparison with PS/ $TiO_{1.98}$/Pt structures. Generally in most cases, to ensure the fast recovery time, the gas sensors designing such a way that allow an additional heating of sensor body during its recovery and that temperature actually is high than the gas sensors working temperature (it can be up to several hundred degree).

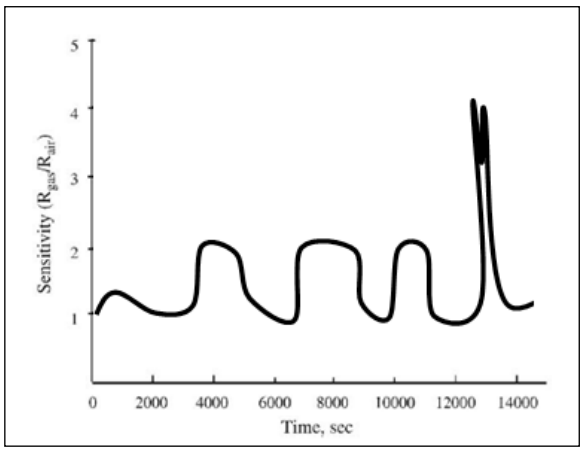

Figure 1. Sensitivity of PS/$TiO_{1.98}$/Pt structure to different concentrations of hydrogen gas at 40 °C.

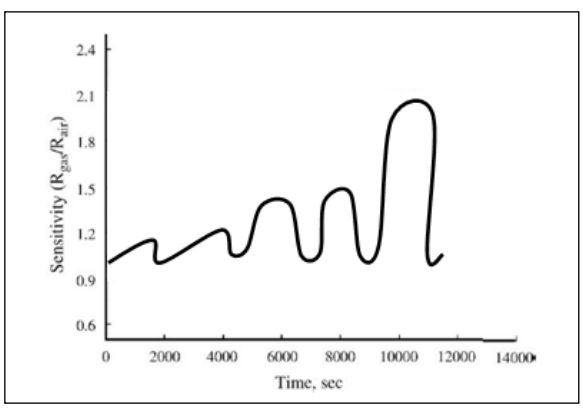

Figure 2. Sensitivity of PS/ZnO[Al]/Pt structure to different concentrations of hydrogen gas at 40 °C.

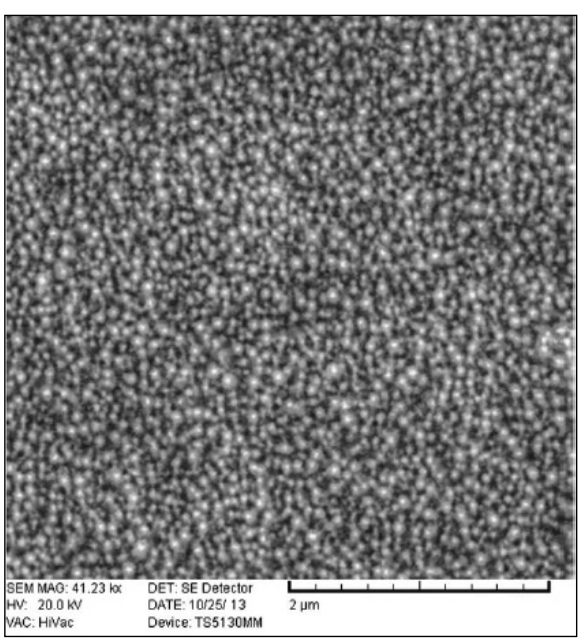

Figure 3. SEM image of TiO_2 – x/PS structure

And if the sensors work in explosive gas environment, high working temperature of gas sensors brings the additional troubles. Thus, the presence of $TiO_{1.98}$ and ZnO[Al] layers on the surface of porous silicon layer protects it from degradation and the presence of porous silicon layers provides low working temperature. But in comparison to ZnO[Al] layer application of $TiO_{1.98}$ ensures rather high sensitivity to hydrogen. Figure 3 represents the SEM images of PS/$TiO_{1.98}$/ Pt structure. As can be clearly seen from Fig. 3 the size of the porous silicon crystalline was about 70–90 nm. Note the sensitivity of samples also examined in propane–butane gas mixture environment at the concentration of 1000–5000 ppm and temperature of 40 °C. The samples' sensitivity did not change. That means that the obtained structures show selectivity to hydrogen gas. Probably the reason of such selectivity is the presence of Pt catalytic layer, not only because it appears as catalyst but also it appears in the selective layer. When sensor is placed in mixed gas environment, hydrogen separated from gas mixture absorbed on its surface and pass through the Pt layer. Therefore besides its catalytic properties, platinum layer has selective properties. One of the reasons of selectivity of obtained structure to hydrogen can be the fact that, in that temperature range, the interaction does not take place with other gases except hydrogen. Thus, we can suggest from obtained results that the presence of the metal oxide layer on the porous silicon surface protects such layer from the degradation simultaneously ensures rather high sensitivity. The samples were shown to have high selectivity to hydrogen gas in temperature as low as 40 °C.

Conclusions

Selective hydrogen gas sensor made of porous silicon layer covered by metal-oxide layer was realized. Change of the sensitivity to hydrogen gas and propane–butane gas mixture versus time was examined. Results of measurements that the obtained structures have high selectivity to hydrogen gas were shown.

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