Paper

Adsorption properties of porous silicon

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Abstract — Porous silicon shows some interesting features for micromechanical applications. Some applications make use of its high surface-to-volume ratio. A capacitive gas or humidity sensor using the adsorption of gases on the porous surface can be easily fabricated. However an opportunity for more sensitive device is given by micromechanical structure. In this paper we report on the piezoresistive cantilever beam structure with porous silicon adsorbing spot as a gas sensor.

Keywords — porous silicon, cantilever beam, gas sensor.

1. Introduction - idea of the gas sensing microprobe

Both thermal heating and variations in relative humidity can significantly influence the deflection of a cantilever microbeam. Chemical sensor can be based on the detection of gas adsorption by monitoring the bending or resonance frequency shift of a cantilever beam [1]. The idea of the considered sensor structure is shown schematically in Fig. 1.

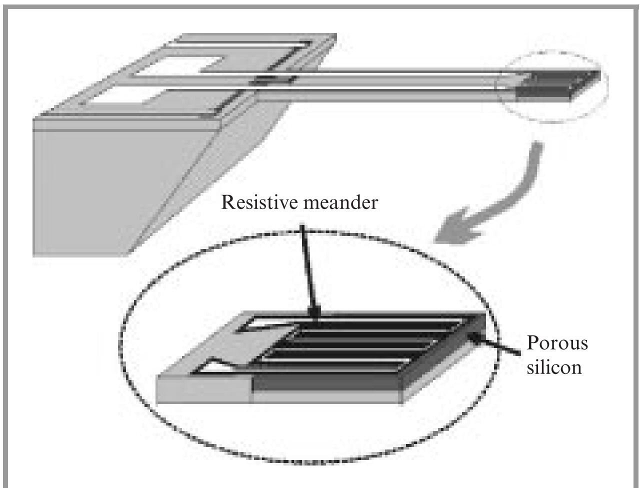

Fig. 1. The idea of piezoresistive cantilever gas sensor with a porous silicon adsorbing spot.

Piezoresistors, necessary for resonance measurement are placed at the support of the cantilever [2] while porous silicon spot is formed on the free end of the beam to obtain maximum sensitivity. Assuming simplified model (see Fig. 2) of the adsorption process on the porous silicon area of the cantilever, elementary calculations of device sensitivity have been performed. Decrease of the resonance frequency due to gas adsorption on the free end of the cantilever beam can be estimated using the formula:

$$\Delta f_0 = \frac{1}{2\pi}\left(\sqrt{\frac{k}{M+\Delta m}} - \sqrt{\frac{k}{M}}\right), \qquad (1)$$

where M is cantilever weight, Δm is weight of adsorbed substance and k is beam elasticity coefficient.

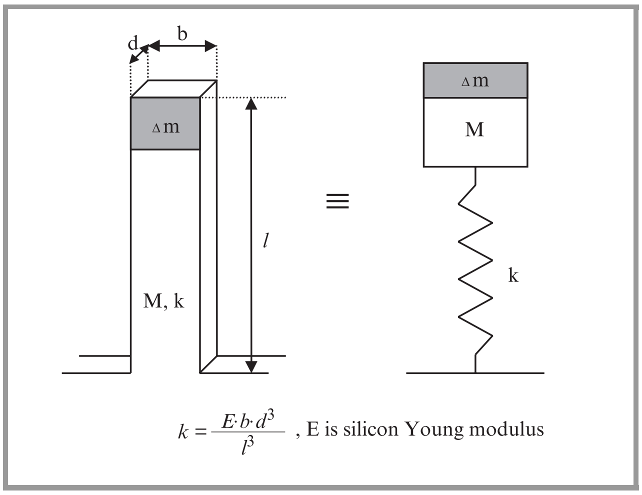

Fig. 2. Simplified model of adsorption process on the porous cantilever.

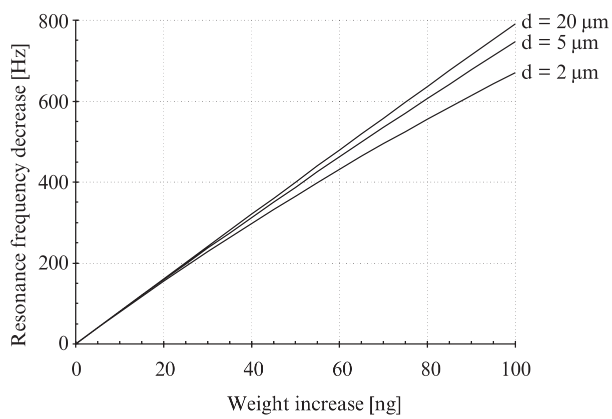

Fig. 3. Resonance frequency decreases due to adsorption for cantilevers (480 x 160 μm) and 2, 5 or 20 μm thick.

For the simple beam (480 μm long, 160 μm wide and 20 μm thick) adsorption of 6 ng of substance causes resonance frequency decrease about 50 Hz. The comparison of resonance frequency shift for similar cantilever differing from each other only in the thickness is shown in Fig. 3.

2. Fabrication process

Fabrication of the piezoresistive cantilever based devices is based on double-side silicon bulk/surface micromachining combined with standard CMOS processing. In fabricating the gas sensing microprobe, schematically illustrated in Fig. 4, we start with double side polished <100>-oriented, n-type, $3 \div 7\ \Omega$cm silicon wafers. After initial cleaning 800 nm of thermal oxide is grown. Standard pho-

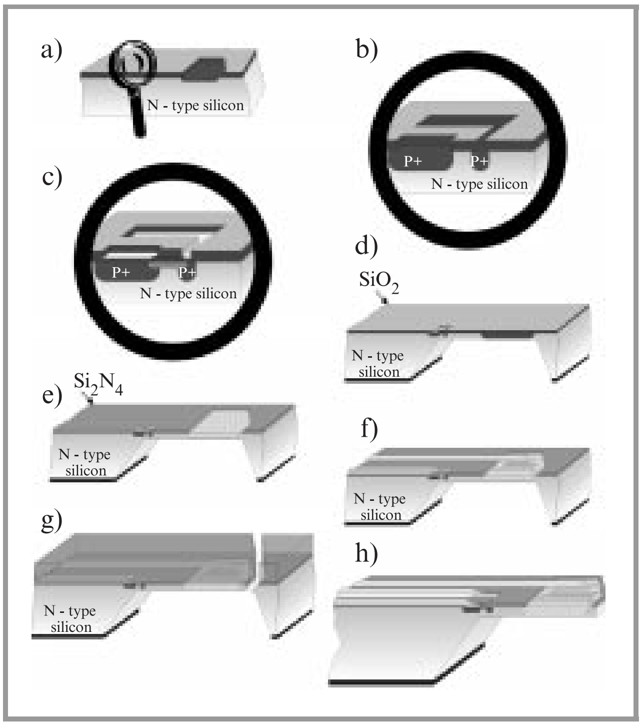

Fig. 4. Gas sensitive piezoresistive cantilever fabrication sequence: a) masking of Si wafer, boron diffusion, b) formation of diffusion paths, c) implantation of piezoresistors, d) bulk micromachining – membrane etching, e) anodization – porous silicon formation, f) formation of metal connections and microheater, g) surface micromachining – deep RIE etching, h) separation of devices.

tolithography defines mask for deep (30 μm) boron diffusion (Fig. 4a). During basic CMOS processing connecting diffusion paths are formed through boron diffusion from highly *in-situ* boron doped, CVD film (Fig. 4b) and piezoresistors are created through boron implantation (Fig. 4c). Phosphorous diffusion creates n^+-type regions, which serve as contacts to the substrate (Fig. 4d). Then backside photolithography with corner compensated pattern and deep silicon wet etching in KOH solution is performed to create $10 \div 20\ \mu$m thick membrane. The wafer mounted in a chuck for front side protection is etched from the back. Next 100 nm of LPCVD silicon nitride is deposited on front surface and selective anodization is performed in chuck to convert boron-doped spots into porous silicon (Fig. 4e). Full electrical circuit is completed with metal connection and resistive meander (Fig. 4f). Finally thick photoresist is deposited for circuit and tip protection and cantilevers shapes are defined in the membrane by last photolithography and dry plasma etching (Fig. 4g). Devices have to be separated from the wafer mechanically (Fig. 4h).

3. Microheater over porous silicon

Porous silicon is obtained by anodization of monocrystalline silicon in hydrofluoric acid solutions. The properties of this material are strongly dependent on the type and resistivity of the silicon and parameters used during the anodization process. Nevertheless, the porous silicon always exhibits extremely high chemical reactivity due to well-developed system of microscopic pores. Figure 5 shows AFM image of a typical porous silicon sur-

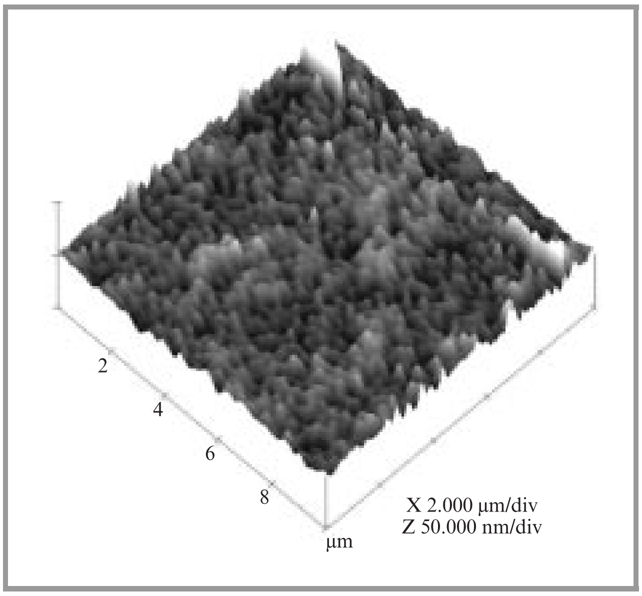

Fig. 5. AFM image of porous silicon surface.

face. Nanoporous layers made from lightly p-doped silicon present the highest porosity $(60 \div 80\%)$ and the highest value of the specific surface area (up to 600 m^2/cm^3) [3]. These unique properties make the material interesting for gas sensors applications. Usually porous silicon gas sensors make use of the influence of the gas adsorption on the electrical properties (e.g. resistivity) of the porous layer. Complex relation between amount of adsorbed substance and determined electrical parameter as well as rather small sensitivity is the main disadvantages of such sensors. Micromechanical structures give an opportunity for more direct relationships between measured and determined quantities. We have considered possibility of gas adsorption sensing on the basis of weight increase of piezoresistive cantilever beam. In contrast to the bulk structure consisting of the relatively thin porous silicon layer and huge volume of the silicon, the mass of the cantilever beam can be small enough to detect weight change, caused by adsorp-

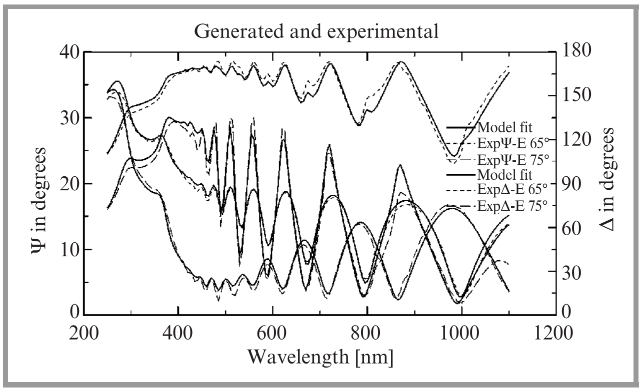

Fig. 6. Elipsometric measurement of porous silicon.

tion of gases on the large internal surface of porous silicon. Particularly sensitive measurements of the cantilever resonance frequency are the only way to observe so small changes (below 1%) of the beam weight. Porous silicon shows various forms of appearance. Porous layer can be characterized with variable angle spectroscopic ellipsometry (Fig. 6). This technique is sensitive to capillary condensation of water in the porous material [4]. Well-developed porous silicon surface is not thermodynamically stable and thus the reduction of the specific area occurs during high temperature process. Therefore thermal budget should be limited after porous silicon formation and anodization process should be arranged at the end of whole processing sequence, e.g. just after membrane etching.

Fig. 7. Cantilever beam integrated with piezoresistors and microheater.

Microheater made of resistive metal meander placed over porous silicon area is integrated with the sensor to outgas the porous area after each measurement, thus enabling a permanent monitoring of rapid changes of the atmosphere. It should be pointed out that different expansion coefficients of two layers (silicon beam coated with oxide) cause the cantilever deflection induced by the adsorption of infrared radiation or electrical power supplied to the microheater [5] (Figs. 7 and 8).

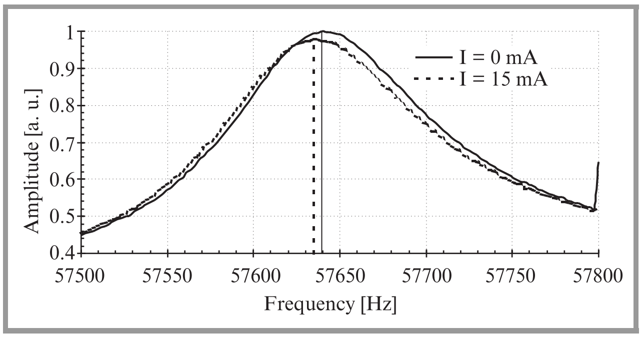

Fig. 8. Shift in the cantilever resonance frequency due to the power supplied to the microheater.

4. Conclusions

In this paper, we present a novel piezoresistive cantilever beam sensor with porous silicon spot enabling measurements of the adsorbed substance weight. We have also described the essentials of its fabrication process. The sensitivity of the shift in the cantilever resonance frequency allows estimating amount of adsorbed substance with single nanogram resolution. It suggests applications of such microprobes for humidity and gas detection.

Acknowledgement

This work was supported by the State Committee for Scientific Research under contract 8T11B00817.

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Tomasz Dębski – for biography, see this issue, p. 38.

Krzysztof Domański – for biography, see this issue, p. 39.