SOLID MATTER

HUMIDITY SENSITIVE STRUCTURES ON THE BASIS OF POROUS SILICON

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The effect of adsorption-desorption processes of water vapors on the electric conductivity and high-frequency capacity of sensor structures based on porous silicon is investigated in the temperature range $15 \div 40$ °C. A significant variation of the electric conductivity and the capacity as functions of the water vapor concentration is registered. To estimate the sensor properties, the adsorption sensitivity of porous silicon structures and multilayer structures with a film of catalytic material were calculated. The kinetics of response of the structures to a change of the water vapor concentration is investigated. The obtained results allow one to optimize the processes of creation of humidity sensors on the basis of porous silicon.

1. Introduction

The creation of semiconductor chemical sensors is important for control of the environment, atmosphere of living and office spaces, quality of food and drinking water, in medicine and industry. Materials with a developed surface such as porous silicon (PS) and heterostructures on its basis are extremely perspective exactly in the field of sensor electronics. The adsorption of gas molecules on a semiconductor surface is accompanied by adsorption-electric effects consisting in the surface charging due to the electron exchange between adsorbed molecules and the substrate [1]. These effects can result in significant changes in the electrophysical parameters of the structure that are easily registered and can be used for the creation of gas-sensitive sensors [2–4]. Among various gas analyzers, an important place is occupied by humidity sensors. Humidity measurements in gas mixtures, particularly in air, is an urgent problem for a large number of scientific, industrial, and medical fields of application. The considerable attention is now paid to studying

PS-based adsorption humidity sensors, whose operation is based upon a variation of the electric parameters of a material (conductivity, capacity, and so on). A catalytic material (e.g., palladium or some conducting polymers) present on the PS surface can favor an increase of the adsorption sensitivity of such sensors.

2. Experiment

Experimental PS layers were formed by electrochemical anodization in the galvanostatic mode on substrates of single-crystal p- and n-silicon with specific resistances of 10.0 and 4.5 Ohm·cm, respectively. The anode current density was constant in time and amounted to $15 \div 20$ mA/cm^2 for different samples. The anodization process lasted for $20 \div 30$ min. An ethanol solution of hydrofluoric acid with the component ratio HF:C$_2$H$_5$OH=1:1 was used as an electrolyte at the anodization. The thickness of the obtained PS layers ranged from 10 to 30 μm for different samples. After the electrochemical treatment, the working surface was washed by distillated water.

Multilayer sensor structures were formed by the deposition of a catalytic palladium or polymer film on the PS surface. To obtain a palladium film, the thermal vacuum deposition of palladium (Pd 99.9%) was performed with the help of a VUP-5M vacuum assembly. The thickness of the deposited palladium film was 100 nm. A polymer film of polyepoxypropylcarbazole (PEPC) on the PS surface was obtained with the use of the electrochemical deposition from a monomer solution. It is worth expecting that, under the electrochemical polymerization conditions with an electroconducting polymer synthesized directly on the electrode surface, the monomer penetrated into silicon pores, where the further polymerization took

place [5, 6]. We performed 15 cycles of potential sweep with a sweep speed equal to 80 mV/s. The potential and the current ranged in the intervals 0.4÷1 V and −0.8÷1.5 mA, respectively.

In the case of multilayer sensor structures, point contacts were deposited onto the surface of a porous layer or a catalytic film of palladium or PEPC with the help of colloid carbon (aquadag). A metal (Ag) contact on the back (nonworking) surface of sensor structures was formed by thermal vacuum deposition of a silver layer ≈ 2 μm in thickness. The electric parameters of the PS-based sensor structures were investigated as the current passed through the structures normally to the surface (inset in Fig. 1). In the case of high specific resistance of a porous layer, almost all the voltage applied to the structure dropped across the PS layer. The use of structures with thick high-resistance PS layers and measurements of volt-ampere characteristics (VAC) in the low-current region (below 1 μA) allow one to assume that nonlinear phenomena will not appear at the contacts.

The investigations of adsorption processes in the PS-based structures were performed in a vacuum cryostat, whose gas medium can be changed. The water vapor concentration in air was determined experimentally by a "Honeywell"HIH-4000-004 humidity sensor that had a linear characteristic in the humidity range 0÷100% and temperatures lying in the interval −40÷85 °C. The electron parameters of the studied structures were measured by a V7-30 electrometer in the case of direct current and a digital E7-12 L, C, R meter at a frequency of 1 MHz.

3. Results and Their Discussion

To study gas sensors, we chose samples of p- and n-PS, as well as Pd/PS/p-Si and PEPC/PS/p-Si multilayer structures. The investigations of the PS electron characteristics demonstrate a dependence of the electric conductivity on the environmental conditions for practically all samples. The analysis of the PS VACs at various water vapor concentrations has revealed a number of peculiarities of the current passage. The VACs of the studied samples are of varistor character and can be described by the equation

$$I = BU^m,$$

where B is a constant, which is specific of each sample and depends on many factors: preparation, storage conditions and so on, and m is the coefficient of varistor nonlinearity. The varistor behavior of the VACs can be due to several reasons, particularly, currents restricted
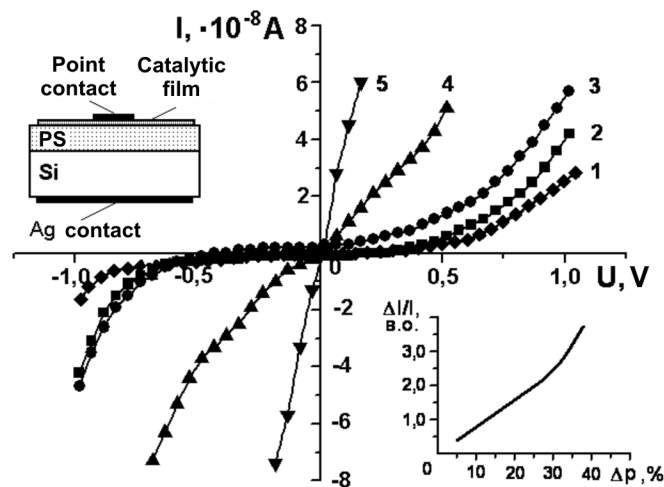

Fig. 1. VACs of the PS/Si structure in the atmosphere with water vapor concentrations of 46% (1), 55% (2), 60% (3), 80% (4), and 100% (5). In the insets – diagram of a miltilayer PS-based sensor structure and the relative change of the current through PS as a function of the relative air humidity

by the space charge, the existence of barriers between silicon nanocrystals of the porous layer, and the Poole–Frenkel effect [7, 8]. The inhomogeneity of PS layers complicated the unambiguous interpretation of charge transfer processes. The adsorption of water molecules by the PS surface results in an increase of the electric conductivity of porous layers and changes the parameters of the voltage-current dependence (Fig. 1). Analyzing the experimental VACs, a conclusion can be made that the electric conductivity of PS layers grows with increase in the water vapor concentration in the atmosphere. The adsorption of water vapor on the hydrophilic surface of silicon nanostructures changes the complex mechanism of electric conduction of the porous layer. The adsorption of polar water molecules can cause a decrease of the potential barriers and a growth of the charge carrier mobility and conductivity. At large water vapor concentrations (85÷100%), at which PS pores contain a large amount of condensed water, the proton charge transfer can take place in the network of hydrogen-bound water molecules [9], which induces a change of the VAC character from the varistor to linear one.

Based on the experimental VACs, we calculated the relative variation of the current running through PS as a function of the change in the relative air humidity at a constant voltage (inset in Fig. 1). The obtained dependence was linear at insignificant variations of the water vapor concentration, which is important for the creation of PS-based humidity sensors. However, at large varia-
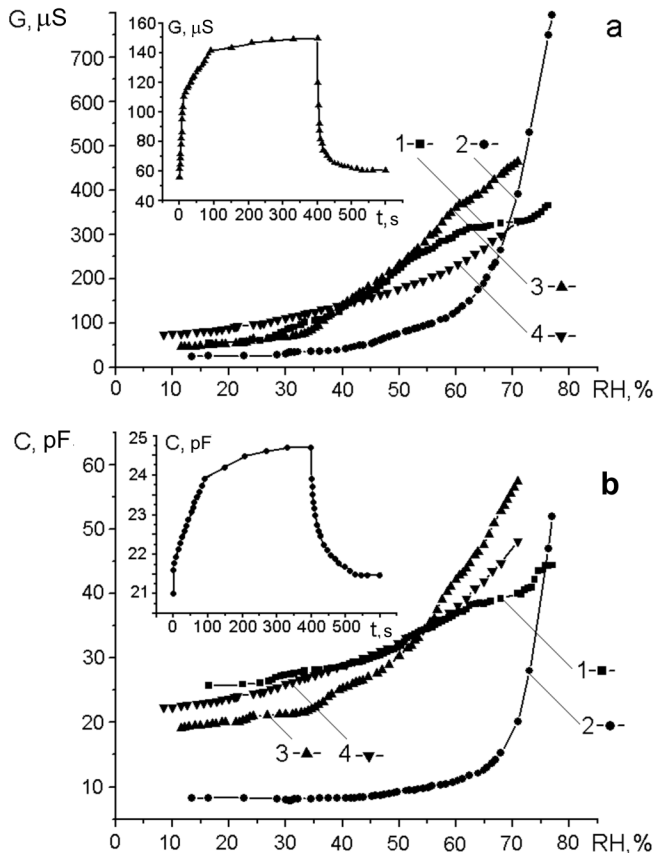
Fig. 2. Conductivity (a) and capacity (b) of the PS/p-Si (1), PS/n-Si (2), Pd/PS/p-Si (3), and PEPC/PS/p-Si (4) sensor structures as functions of the relative air humidity. In the inset – conductivity (a) and capacity (b) response of the PS/p-Si structure to the pulse of relative air humidity

tions of the water vapor concentration, the linearity of the dependence $\Delta I / I(\Delta p)$ was violated.

Along with the influence of water adsorption on the structure of the PS surface, it is worth noting a considerable (as compared to silicon and its oxide) value of the dielectric constant of water ($\epsilon = 81$), which results in a significant change of the permittivity of a porous layer due to the adsorption of water vapors. The increase of the relative humidity of the atmosphere surrounding PS must respectively result in a noticeable growth of its electric capacity. The change of the high-frequency (1 MHz) conductivity and capacity of such structures caused by the variation of the relative humidity in the interval 10÷80% is depicted in Fig. 2.

In the case where the relative humidity increases, a monotonous rise of the high-frequency conductivity and capacity of the samples was observed for various types of sensor structures. Experimental studies have revealed

an insignificant difference in the behavior of the dependences of the electric conductivity and the capacity on the air humidity for the structures formed on n- and p-silicon substrates. In particular, the variation of the relative humidity from 10 to 80% resulted in the growth of the conductivity from 20 to 800 μS for the PS/n-Si sensors, while the capacity grew from 8 to 54 pF (the rate of increase was larger in the humidity interval 60÷80%). For the PS/p-Si sensors, the conductivity and the capacity increased from 50 to 340 μS and from 26 to 43 pF, respectively. Such a behavior of the obtained dependences is explained by different morphologies of porous layers: the size of nanostructures formed on p-Si mainly does not exceed 5 nm (nanoporous silicon), whereas on n-Si, it ranges from ten to hundreds of nanometers (meso- or macroporous silicon) [10]. Nanoporous silicon is characterized by physical mono- and polymolecular adsorption. At low degrees of surface covering, the dominant role is played by intramolecular changes of the adsorbate, whereas, at high degrees of covering and at polymolecular adsorption, the intermolecular interaction in the adsorbed film is of major importance [11, 12]. For mesoporous silicon, the characteristic adsorption mechanism is the capillary condensation. It is technologically easy to form PS layers with different pore size distributions, which results in an increase of the selectivity and the sensitivity of a sensor in different humidity ranges, i.e., this allows one to control the PS functional properties.

The behavior of the high-frequency conductivity and capacity as functions of the relative air humidity for the Pd/PS/p-Si structure is related to the catalytic dissociation of water molecules at palladium nanoclusters. The formed atomic hydrogen has a high penetrability and passes into the depth of the porous layer, which results in an increase of the degree of variation of the conductivity or capacity of the structure under the water adsorption. A similar catalytic role is played by a polyepoxypropylcarbazole film.

An important factor of studying the mechanisms of variation of the physical parameters of sensor materials under adsorption-desorption interactions with a gas medium is the determination of the adsorption sensitivity of the material. To estimate the sensor (gas-sensitive) properties of PS layers, we calculated the adsorption sensitivity using the relation [1]:

$$\gamma_G = \frac{1}{G} \frac{\Delta G}{\Delta p},$$

where $\Delta G / G$ denotes the relative change of the conductivity or capacity of the structure, and Δp is the change
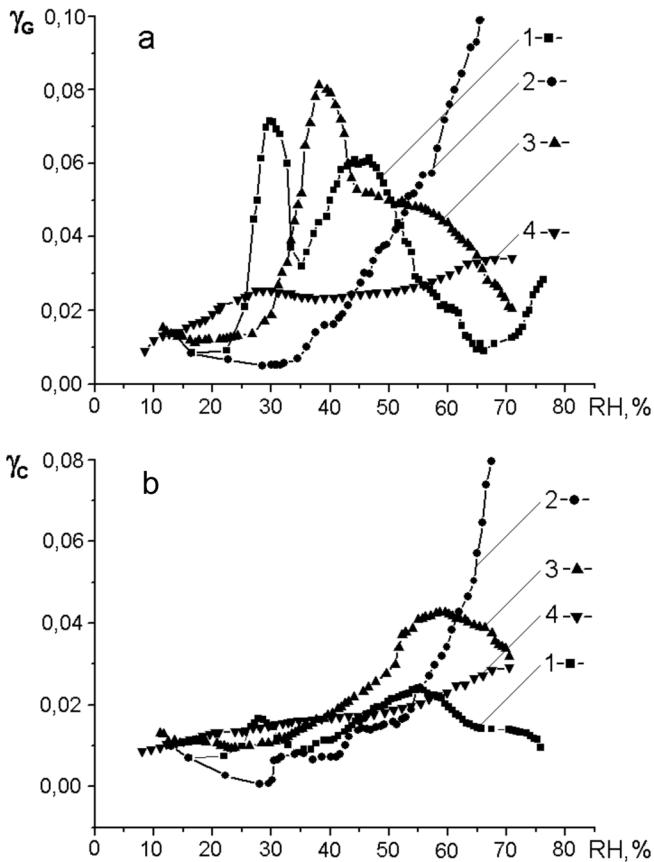
Fig. 3. Adsorption sensitivity in the resistive (*a*) and capacitive (*b*) sensor structures PS/*p*-Si (*1*), PS/*n*-Si (*2*), Pd/PS/*p*-Si (*3*), and PEPC/PS/*p*-Si (*4*) as a function of the relative air humidity

Fig. 4. Conductivity (*a*) and capacity (*b*) of the PS/*p*-Si structure as a function of the relative air humidity at various temperatures of the medium

in the relative air humidity. The calculated humidity dependences of the sensitivity of the PS-based sensor structures are shown in Fig. 3.

The dependences of the adsorption sensitivity for the PS/*p*-Si structure had extrema in the ranges of relative humidity 20÷35% and 40÷55%. Such extrema can be caused by a change of the mechanism of water adsorption. An abrupt increase of the sensitivity was observed for the PS/*n*-Si samples at relative humidities exceeding 60%. The catalytic action of palladium manifested itself in a rise of the adsorption sensitivity of the Pd/PS/*p*-Si structure in the humidity range 30÷70%. A PEPC film on the PS surface provided a more uniform sensitivity in the whole humidity interval.

Important parameters of sensors are the response and recovery times. The interaction with water vapor has a character of physical adsorption and represents an inverse activationless process. In the dynamic dependences depicted in the inset of Fig. 2, one can see that
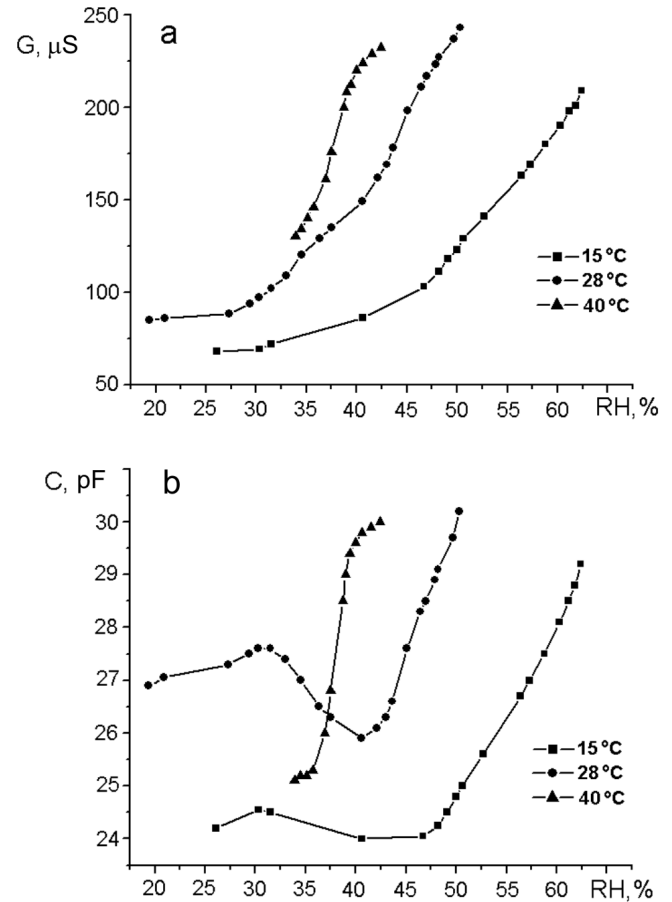
the conductivity sensors operate faster than the capacity ones, while the response and recovery times are equal to 50 and 150 s, respectively.

The kinetics of the response of a sensor to a variation of the relative air humidity has a two-stage character. The fast reaction is related to the adsorption (desorption) of water vapor on the available PS surface, whereas the slow one is determined by the diffusion transfer of water molecules in the bulk of the porous layer. As a whole, the response time approximates 2 min and is small enough for microelectronic humidity sensors.

The processes of water vapor adsorption were investigated in the temperature range $15 \div 40$ °C. As was expected, changes in the temperature of the medium resulted in the variation of the high-frequency conductivity and capacity of the PS-based sensors (Fig. 4).

In the case where the dependence of the initial parameters of sensor structures on the water vapor concentra-

tion did not change its character, it was found out that an increase of the temperature resulted in a noticeable growth of the variation in the conductivity under the water vapor adsorption, i.e. the intensification of the "adsorption effect".

4. Conclusions

Sensor structures based on porous silicon of n- and p-types and multilayer structures with a film of a catalytic material are created. It is experimentally established that the gas adsorption changes the electrophysical parameters of such structures. The analysis of the high-frequency conductivity and capacity, as well as the adsorption sensitivity of sensor structures as functions of the water vapor concentration, has demonstrated that the sensitivity maxima for the PS/p-Si and PS/n-Si structures belong to different ranges of the relative air humidity. Such a selectivity is explained by different mechanisms of water adsorption by structures with different surface morphologies. It is shown that the sensitivity of sensors to water-containing molecules can be increased due to the deposition of a palladium catalyst. The kinetics of response of the structures to a variation of the water vapor concentration is fast enough for microelectronic humidity sensors. The obtained results allow one to optimize the processes of formation of PS-based humidity sensors.

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ВОЛОГОЧУТЛИВІ СТРУКТУРИ НА ОСНОВІ ПОРУВАТОГО КРЕМНІЮ

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Р е з ю м е

Вивчено вплив адсорбційно-десорбційних процесів водяної пари на електричну провідність і високочастотну ємність сенсорних структур на основі поруватого кремнію в температурному діапазоні 15–40 °C. Зареєстровано суттєву зміну електричної провідності та ємності залежно від концентрації водяної пари. Для оцінки сенсорних властивостей було розраховано адсорбційну чутливість структур на основі поруватого кремнію та багатошарових структур з плівкою каталітичного матеріалу. Досліджено кінетику відгуку структур на зміну концентрації водяної пари. Отримані результати дозволяють оптимізувати процеси формування сенсорів вологості на основі поруватого кремнію.