

BRIEF COMMUNICATIONS
SOLID-STATE PHYSICS

EFFECT OF WATER ADSORPTION ON THE IMPEDANCE OF
SILICON-POROUS SILICON-METAL STRUCTURES

S. N. Kozlov, A. N. Nevzorov, and A. A. Petrov

The effect of water adsorption on the conductivity and the capacity of silicon-porous silicon-metal structures has been studied in the frequency range from 10^2 to 2×10^3 Hz. It was demonstrated that the sensitivity (as regards the impedance) of the structures studied to the water adsorption effect is maximal in the frequency range from a few hundred Hz to 1 kHz.

In the past few years, porous silicon (PS) has attracted much attention throughout the world primarily because of the prospects for building optoelectronic devices (see reviews [1, 2]). At the same time, the vast specific surface area of this material, as well as the possibility to vary its fractional structure and micropore size over wide limits, form a good basis for the development of chemical sensors. Some promising progress has already been made along these lines (see, e. g., [3, 4]), but the potentialities of such structures are not yet fully revealed. Specifically the effect of water adsorption on the frequency dependence of the impedance of the structures containing PS layers is not completely understood. This work was aimed at elucidating how strongly the adsorption-induced change in the impedance of the structure under study depends on the frequency of the measuring signal and whether there exists an optimum signal frequency for the given adsorbate, at which it is advisable to register the "adsorption response" of the structure.

The Si-PS-metal structures of interest were fabricated on the basis of *p*-type Si with a resistivity of $12 \Omega \cdot \text{cm}$. The $7 \mu\text{m}$ -thick PS layers of about 70% in porosity were formed on the surface of Si (100) by way of anodizing, in a 1:1 mixture, a 48% HF solution and 96% ethyl alcohol at a current density of $20 \text{ mA} \cdot \text{cm}^{-2}$. Thereafter the structures were additionally oxidized in oxygen to stabilize the surface of the porous layer and make it hydrophilic. The gas-permeable metal contacts with the PS layer 1 mm^2 in surface area were formed by way of thermal atomization of first nichrome (layer thickness is 5 nm) and then silver ($3 \mu\text{m}$). The impedance of the structures was measured by means of an ac bridge over the frequency range from 100 Hz to 200 kHz. In our experiments water was used as the model adsorbate. The experiments were conducted at a temperature of 300 K.

Figure 1 shows (a) the conductivity and (b) the capacity of a silicon-PS-metal structures as a function of the measuring signal frequency in the starting condition after a thermal-vacuum treatment (TVT) at a temperature of 450 K and a pressure of 10^{-5} mm Hg for 2 h, and also after standing a few minutes in saturated water vapor. It can be seen that the TVT causes the conductivity and capacity of the structures to rise, especially in the low-frequency region. Following the exposure to saturated water vapor, the functions $G(\omega)$ and $C(\omega)$ gradually return to their initial form. In the course of the TVT the closely bound water molecules that provide a basis for slow donor-type electronic states are obviously removed from the surface of the silicon "filaments" [5]. As a result, the surface charge of the filaments shifts toward the negative side, and the "core" of the filaments becomes enriched in the majority carriers (holes), i. e., there takes

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place a "molecular doping" of the PS layer [6]. It is not only the conductivity, but also the capacity of the Si-PS-metal structure that rises in that case, because the number of conductive silicon filaments increases, and so does the effective area of the contacts at the Si-PS and PS-metal interfaces. The adsorption of water molecules in the PS layer brings about the reverse effect. Changes in the capacity and conductivity of the structure are most noticeable in the low-frequency region, because at higher frequencies the jump-type charge transport over the surface of silicon "wires" [7] plays a great role, which is apparently less sensitive to the effect of adsorption than the quasibulk electron transport.

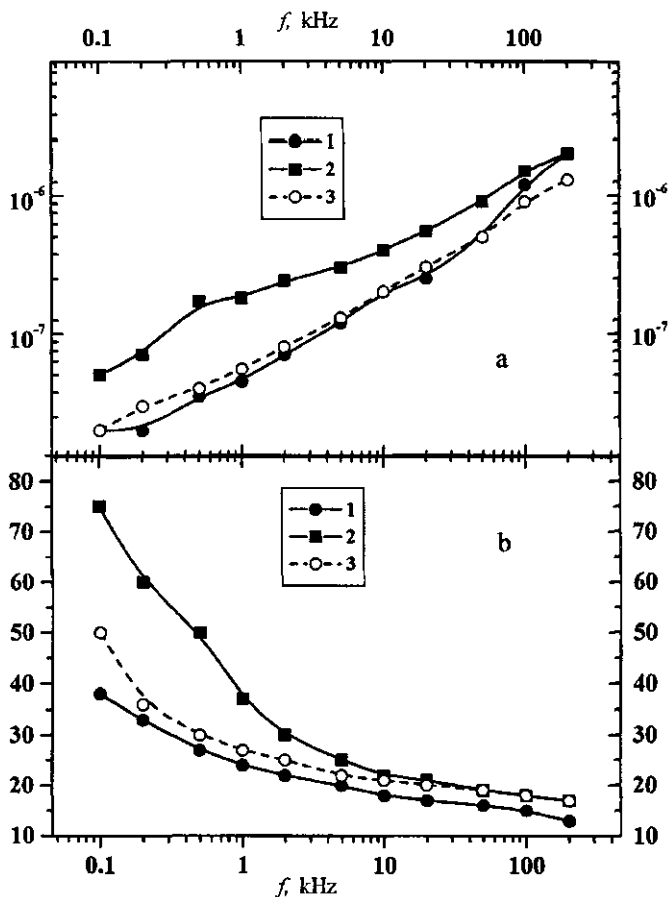


Fig. 1

Frequency dependences of (a) the conductivity and (b) the capacity of a Si-PS-metal structure in (1) the starting condition, (2) after thermal-vacuum treatment, (3) after standing in saturated water vapors.

The maximum relative sensitivity of the structures being studied to the adsorption of water vapor, as regards both conductivity and capacity, was attained in the frequency range from a few hundred Hz to 1 kHz (see Fig. 2a). The existence of the optimum signal frequency for measuring the adsorption response (as regards the impedance) of Si-PS-metal structures is apparently due to the fact that adsorption may simultaneously have an effect on a number of factors governing the charge transport conditions therein, namely, the quasibulk transport over the core of silicon filaments, jump-type transport over their surface, and also the rate of overcoming the potential barriers at the Si-PS and PS-metal interfaces. The frequency dependences of the corresponding effects may be different, and it is precisely their combination that determines the nonmonotonic character of the functions $\Delta C/C(\omega)$ and $\Delta G/G(\omega)$. Note in conclusion that our experimental data (see Fig. 2b) fail to support the intriguing conclusion drawn by Motohashi et

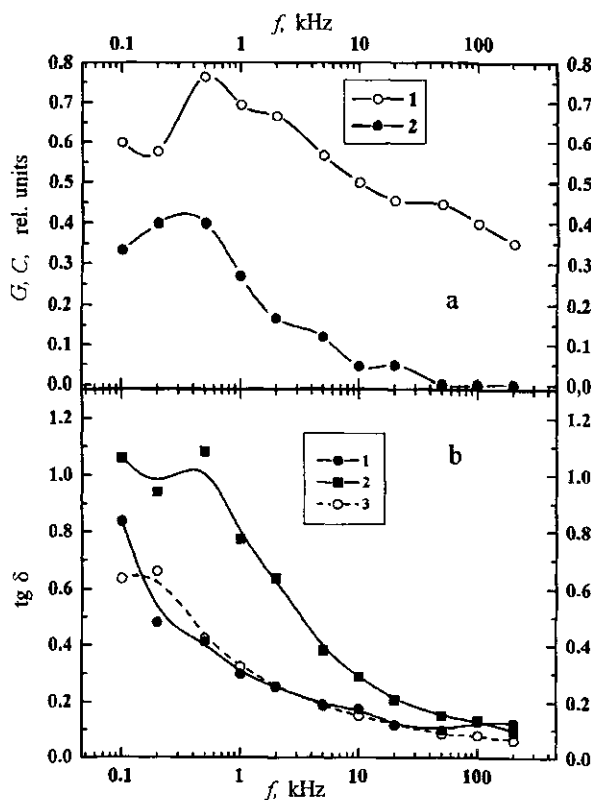


Fig. 2

(a) Relative changes in (1) the conductivity and (2) in the capacity of a Si-PS-metal structure at various frequencies as a result of saturated water vapor action and (b) frequency dependence of the loss angle tangent of this structure: 1 — in a vacuum; 2 — after thermal-vacuum treatment; 3 — and on standing in saturated water vapors.

al. [8] about the existence of dielectric loss maxima in the frequency range of 1–10 kHz associated with the relaxation specifics of liquid adsorbates in the micropores of porous silicon.

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