

SOLID-STATE PHYSICS

ELECTROPHYSICAL METHOD OF PORE SIZE DETERMINATION IN POROUS SILICON

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A method of pore size determination in a porous system based on its conductivity measurement with pores filled with a liquid conducting adsorbate is proposed. To evaluate the method, the silicon pore size is estimated using the data on the system conductivity in vapors of water and alcohol. The obtained results are in good agreement with pore size estimates obtained by adsorption methods.

INTRODUCTION

In recent years, crystalline nanoporous silicon, a material of considerable promise for optoelectronics and sensor devices [1, 2], has been a subject of intensive studies in many laboratories of the world. Its properties depend to a considerable extent on structural factors, in particular, on the size of nanopores penetrating it. A direct and most reliable method of pore size determination in microporous objects is to obtain low-temperature isotherms of inert gas adsorption [3]. However, this technique is rather labor-consuming and requires considerable amount of porous silicon to maintain necessary accuracy. In this paper, we propose a new method of estimating the size of nanopores in porous silicon based on investigation of silicon conductivity dependence on the pressure of water or alcohol vapors.

EXPERIMENTAL

In our work we used crystalline porous silicon films obtained on the (100) surface of monocrystalline *p*-Si with the resistivity of 12 Ω cm. A porous layer on a crystalline substrate was formed by anodizing in a 1:1 electrolyte containing a 48% HF solution and 96% ethyl alcohol. At the current density 20 mA/cm², a 1 μ m-thick porous silicon (PS) film with the specific surface to 6 m²/g was formed during 5 min. Then the samples were thoroughly rinsed with distilled water and placed into a vacuum chamber for deposition of metal contacts permeable to gas molecules. The 1-mm dia contacts were formed on the porous layer by thermal sputtering of nichrome (to form a 2-4 nm layer), and then silver (20-nm layer). All measurements were carried out at room temperature.

RESULTS AND DISCUSSION

The current-voltage characteristics of silicon-PS-metal structures had the form typical of Schottky diodes; negative voltage across the metal electrode corresponded to the current forward direction. Upon admission of water or ethanol vapors to an experimental cell pre-evacuated to 10⁻⁵ torr, the backward current increase through the structure was observed. Figure 1a illustrates typical dependences of backward current value at constant voltage across the metal electrode ($V_g = +5$ V) on the relative pressure p/p_s of water and ethanol vapors. In the course of measurements, the vapor pressure was gradually increased; the

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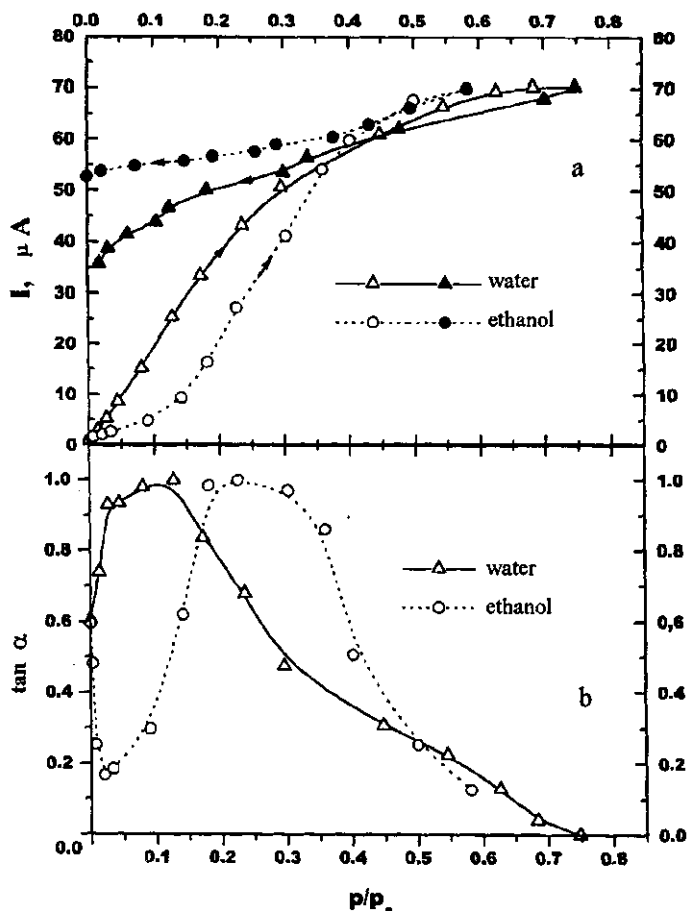


Fig. 1

(a) Curve of backward current through the silicon-PS-metal structure and (b) its slope upon gradual increase (circles) and decrease (dots) of pressure of water and ethanol vapors.

structure was kept in the vapors for 10 min at each pressure value. Then a +5 V voltage was fed to the metal electrode, the current flowing through the structure was measured, and the vapor pressure was increased again. The sharpest increase of backward current was observed at $p/p_s \sim 0.1-0.2$ for water and $\sim 0.2-0.4$ for ethanol (Fig. 1b). The increase of backward current through the structure in vapors of dissociating substances is apparently connected with an increase of ionic conductivity in the bulk of liquid condensed in nanoporous layer capillaries. It should be borne in mind, however, that the system conductivity increase in this range of relative pressures may be caused not only by an increase of the volume of conducting liquid in the PS nanopores, but also by the ions mobility growth [4]. We think that the most adequate information on the nanopore size can be derived from the relative pressure value at which the backward current vs. p/p_s dependence "saturation" sets in. Apparently, in this case the main micropore volume is already filled. In our experiments for water and ethanol, this takes place at $p/p_s \sim 0.6-0.7$ (see Fig. 1).

As is known, the radius r_m of pores filled at the given p/p_s and temperature T is defined by the Kelvin-Thomson formula

$$r_m = -\frac{2\gamma V_L}{RT \ln(p/p_s)}, \quad (1)$$

where γ is the surface tension of liquid adsorbate, V_L is its molar volume, $R = 8.314 \times 10^7$ erg/(mole deg) is the universal gas constant.

In particular, at room temperature $\gamma^{(w)} = 73$ dyne/cm, $V_L^{(w)} = 18$ cm³/mole for water and $\gamma^{(s)} = 22.8$ dyne/cm, $V_L^{(s)} = 57.6$ cm³/mole for ethanol. Since $\gamma^{(w)}V^{(w)} \cong \gamma^{(s)}V^{(s)}$, for both these substances a

general relation follows from (1),

$$\frac{1}{r_m} = -K \log(p/p_s), \quad (2)$$

where $K \cong 2.2 \text{ nm}^{-1}$.

Dependence (2) is shown in Fig. 2. It is seen that to the values $p/p_s \sim 0.6-0.7$ there corresponds the pore radius of 2-3 nm. This value is in good agreement with the results obtained by the "classical" adsorption method on PS samples prepared under similar conditions [3, 5]. From the presented data it follows also that pores even smaller in size occur in the PS layer. This conclusion does not contradict the literature data either [5]. We point out that the nanopore size determination from the data on the structure conductivity variation under gradual vapor pressure decrease proved to be difficult because the process of desorption of vapors from PS nanocapillaries was long-run (see Fig. 1).

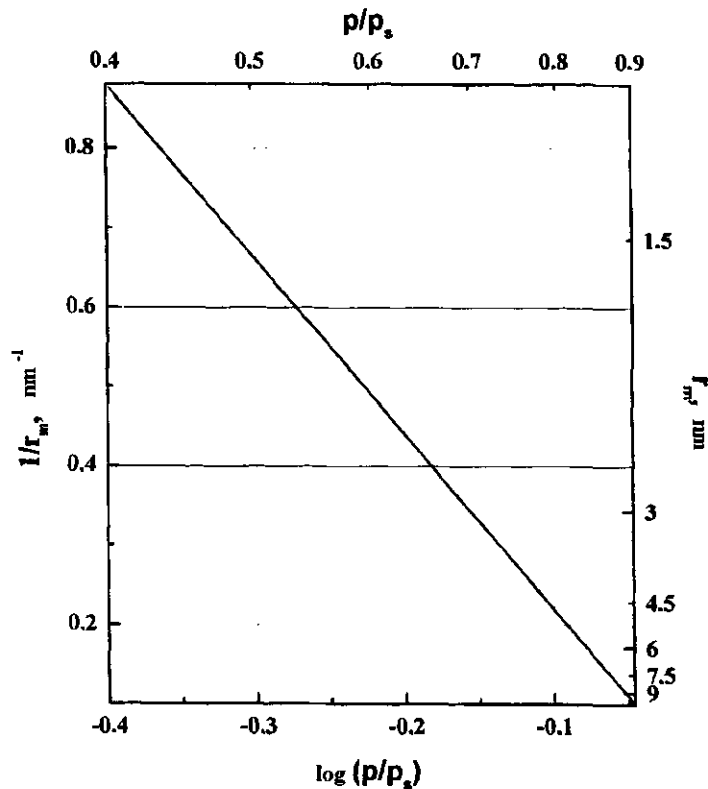


Fig. 2

Theoretical dependence of filled pores radius on the relative pressure of water or ethanol vapors.

Therefore, our investigation of the silicon-PS-metal structure conductivity as a function of water or ethanol vapor pressure makes it possible to estimate the pore size in the PS layer. The method is advantageous in that measurements can be carried out on samples of however small dimensions. The procedure can basically be used in the investigation of any nanoporous objects with low intrinsic conductivity, as well as of any condensing adsorbates with detectable conductivity.

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