

## INFLUENCE OF INTRAPORE PRESSURE ON ELECTROPHYSICAL PROPERTIES OF POROUS SILICON

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The influence of internal pressure, which appears due to the formation of ice in pores of porous silicon (PS), on the physical characteristics of metal-PS-Si structures has been studied. The maximum of accumulation capacitance was observed in the temperature range  $T = -4.0 \div 4.0$  °C. The nonmonotonic behavior of the capacitance is explained, first of all, by the increase of the intrapore pressure, when water becomes frozen in pores. Under the condition of the formation of an ice-like structure in pores with decrease in the temperature, the temperature behavior of the capacitance is also affected by both a jump-like reduction of the effective dielectric permittivity of the PS-ice system and the reconstruction of deep levels in the PS. The latter scenario was confirmed by the results of DLTS measurements of the capacitance relaxation curves of MIS structures with intrapore water in the vicinity of the ice-formation temperature. Making use of the Bruggeman effective medium approximation, the cylindrical pore model, and the approximation of isotropic extension of water, which was capillary adsorbed in pores, at its freezing, we, by analyzing the temperature dependences of the capacity-voltage characteristics, estimated the magnitude of local intrapore pressure, which turned out to be  $7 \times 10^9$  Pa. Such pressure gives rise to a reduction of the bandgap in porous silicon by 0.16 eV and induces a corresponding shift of the activation energy of deep levels in a porous semiconductor.

### 1. Introduction

Nowadays, electrochemical layers of PS are widely applied in sensor electronics. Various chemical, biological, and radiation sensor devices with different transducer mechanisms – electrical, optical, luminescent, and so on – have already been developed on their basis [1]. Less studied remain issues concerning the mechanical properties of this material. It is evident that internal stresses, which arise either in the course of electrochemical etching of single-crystalline silicon in fluoric acid solutions or when a liquid fills in the pores of functioning sensors, drastically change the electron structure of near-surface defects and, therefore, can provoke the sensor parameter instability [2, 3]. In addition, the internal pressures, which arise when the porous structure is formed, can be responsible for the

modulation of the band structure in silicon; they can even be regarded as an alternative mechanism of visible photoluminescence in PS [4]. However, the magnitude of internal stresses, which can arise in PS, remains still unknown.

While studying the influence of uniaxial pressure on the electroconductivity of heterostructures belonging to the type metal-nanoporous Si-*p*-Si, we revealed a negative tensoresistive effect [5]; i.e. the height of the potential barrier in the heterostructure and the band gap in PS decrease as the pressure grows. The tensoresistive effect coefficient for structures fabricated on the basis of thick PS films is approximately twice as high as that for a silicon wafer with a specific resistance of  $4.5 \Omega \times \text{cm}$ , subjected to the uniaxial squeezing along the axis [100]; as the thickness of the porous layer grows, this coefficient becomes larger. The latter phenomenon can be associated with the gradient of internal stresses which are created by nanopores and nanocrystallites in the porous layer, when porosity becomes lower in the direction from the surface to the interface with the Si substrate.

In this work, in order to study the influence of internal hydrostatic pressure on electric properties, we used water, which was capillary absorbed into pores and, when the whole structure was cooled, created an additional internal pressure owing to the increase of its volume at freezing.

Due to a small kinetic diameter  $d = 0.264$  nm and a small contact area ( $S_{\text{H}_2\text{O}} = 0.125 \text{ nm}^2$ ) of water molecules, they can readily penetrate into the pores of a hydrophilic film [6]. A hydrophilic film of PS can be easily prepared by keeping an as-fabricated material in the open air for a few days [7]. Since the low-frequency dielectric permittivity of water is much higher than that of silicon or air, the intrapore adsorption of H<sub>2</sub>O molecules substantially modifies the electrophysical parameters of MIS structure; in particular, the saturation capacity increases [8], and

the inflection point in the CVC becomes shifted owing to the fact that adsorbed water molecules possess a considerable dipole moment.

## 2. Specimens and the of Heterostructure Model

Gas-sensitive MIS structures were fabricated on the basis of silicon of the  $p$ -type (100) ( $p_0 = 10^{15} \text{ cm}^{-3}$ ) with a PS interlayer. PS films were formed following a routine electrochemical etching of the silicon substrate surface in a 1:1 mixture of fluoric acid and ethanol, and in a direct current mode ( $20 \text{ mA/cm}^2$ ). The thickness of the PS layer obtained was 150 nm. A Ti rectifying contact was deposited by the thermal evaporation method; its thickness did not exceed 15 nm, and the contact area  $S$  was about  $1 \text{ mm}^2$ . The CVCs of the fabricated structures were measured by the bridge method at the frequency  $f = 1 \text{ MHz}$ . In order to study the variation of electrophysical properties of the structure at the time moment of the phase transition (water freezing), the specimen was placed into a cryostat. CVC measurements were carried out in the temperature range  $-10 \div +10 \text{ }^\circ\text{C}$ , as well as at room temperature. The cooling rate  $\Delta T/\Delta t$  was about  $0.2 \text{ K/min}$ , so that the measurements can be considered as carried on in the quasiequilibrium regime.

The equivalent circuit of the studied structures is depicted in Fig. 1. Here,  $C_{\text{cr}}$  is the capacity of the nanocrystalline matrix of the PS layer,  $C_{\text{por}}$  the capacity of the pores filled with air,  $C_{\text{H}_2\text{O}}$  the capacity of adsorbed and condensed water, and  $C_{\text{Si}}$  the capacity of the space charge region (SCR) in Si.

The total capacity of the porous layer in the water-vapor environment is  $C_{\text{eff}} = \varepsilon_0 \varepsilon_{\text{eff}} S/d$ . On the other hand,  $C_{\text{eff}} = C_{\text{cr}} + C_{\text{por}} + C_{\text{H}_2\text{O}}$ . The value of capacity  $C_{\text{eff}}$  is determined in the accumulation regime ( $C_{\text{Si}} \gg C_{\text{eff}}$ ), so that  $C_{\text{max}} \approx C_{\text{eff}}$ . On the relative humidity  $RH = 0$ , the capacity of the porous layer is  $C_{\text{eff}} = C_{\text{cr}} + C_{\text{por}}$ . In the framework of the Bruggeman effective medium approximation and the cylindrical pore model, the effective dielectric permeability of the porous layer is

$$\varepsilon_{\text{eff}} = (1 - \alpha)\varepsilon_{\text{cr}} + \alpha\varepsilon_{\text{air}}, \quad (1)$$

where  $\alpha = S_{\text{por}}/S$ ,  $S$  is the surface area of the metal electrode,  $S_{\text{por}}$  the area of pores under the electrode, and  $\varepsilon_{\text{cr}}$  and  $\varepsilon_{\text{air}}$  are the relative dielectric permittivities of the solid substrate and the air, respectively. Expression (1) makes it possible to determine – from the experimentally measured values for  $\varepsilon_{\text{eff}}$ , and adopting that  $\varepsilon_{\text{cr}} = \varepsilon_{\text{Si}} = 12$

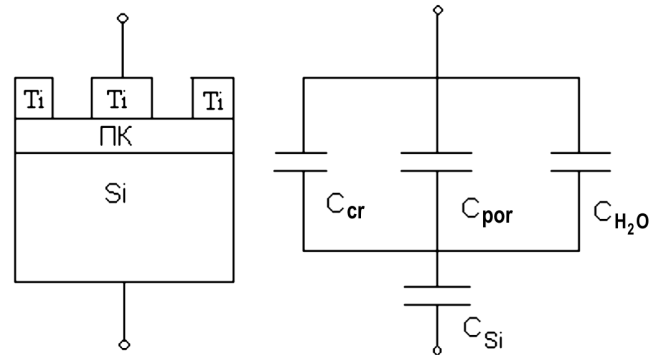


Fig. 1. Scheme and the equivalent circuit of Ti-PS-Si specimens. See notations in the text

and  $\varepsilon_{\text{air}} = 1$  – the interlayer porosity  $\alpha$ :

$$\alpha = \frac{\varepsilon_{\text{cr}} - \varepsilon_{\text{eff}}}{\varepsilon_{\text{cr}} - \varepsilon_{\text{air}}} \approx \frac{\varepsilon_{\text{Si}} - \varepsilon_{\text{eff}}}{\varepsilon_{\text{Si}} - 1}. \quad (2)$$

In the presence of water ( $RH \neq 0$ ), the capacity of pores filled with a condensate with the dielectric permittivity  $\varepsilon_{\text{H}_2\text{O}}$  is to be taken into account. If the volume of condensed water is  $V_{\text{H}_2\text{O}}$ , then, under the assumptions made, the capacity of the porous interlayer is

$$C_{\text{eff}} = \frac{\varepsilon_0 S}{d} \left[ (1 - \alpha)\varepsilon_{\text{cr}} + \left( \alpha - \frac{V_{\text{H}_2\text{O}}}{dS} \right) \varepsilon_{\text{air}} + \frac{V_{\text{H}_2\text{O}}}{dS} \varepsilon_{\text{H}_2\text{O}} \right]. \quad (3)$$

Here,  $d$  is the effective thickness of the interlayer. The difference between the values of the interlayer capacity in humid ( $RH \neq 0$ ) and dry ( $RH = 0$ ,  $V_{\text{H}_2\text{O}} = 0$ ) environments is equal to

$$\Delta C_{\text{eff}} = \frac{\varepsilon_0 V_{\text{H}_2\text{O}}}{d^2} (\varepsilon_{\text{H}_2\text{O}} - \varepsilon_{\text{air}}). \quad (4)$$

The strong inequality  $\varepsilon_{\text{H}_2\text{O}} \ll \varepsilon_{\text{air}}$  should be taken into account; then, in the accumulation mode,  $\Delta C_{\text{eff}} \approx \Delta C_{\text{max}}$ . Therefore, according to Eq. (4), the measurements of the capacity of the junction structure allow the volumes of adsorbed and condensed water – and, hence, the value of relative humidity  $RH$  – to be determined in the general case. In our case, we determine only the volumes of adsorbed and condensed water (because a water droplet was deposited onto the structure).

One of the most informative and sensitive methods for monitoring the parameters of impurity and defect centers is DLTS. It is based on the measurements of temperature dependences of the capacity relaxation of a surface-barrier structure after the application of a pulse-like bias across it. This method allows the characteristics

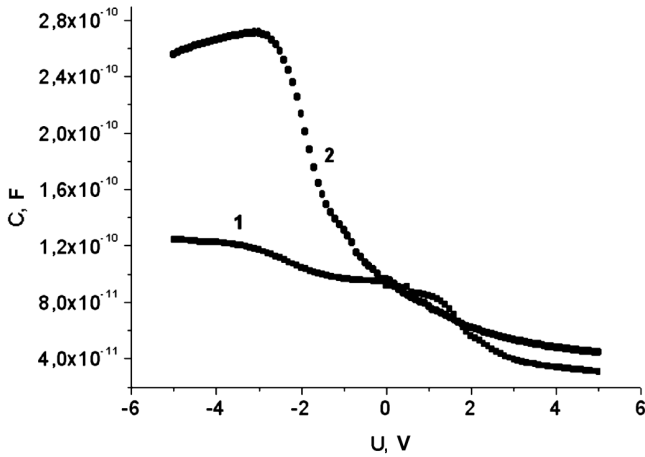


Fig. 2. CVCs of specimens free of water (1) and with water capillary absorbed in pores (2)

of deep levels – in particular, the activation energy or the capture cross-section – to be studied. Within a single temperature scanning, the spectra in four emission rate windows were registered. Having plotted the dependence of the spectrum maximum position  $T_m$  in the Arrhenius coordinates ( $\ln(\tau T_m^2)$  versus  $T_m^{-1}$ ), we obtain the sought parameters: the energy position of a deep level can be determined by the slope of the curve, and the capture cross-section by an interval, which is cut-off on the  $\ln(\tau T_m^2)$ -axis.

### 3. Experimental Results and Discussion

In Fig. 2, the specimen CVCs measured both at the relative humidity  $RH = 0$  and with water capillary deposited in pores are depicted. The curves look like CVCs typical of those for MIS structures. The analysis of these curves shows that, first, the saturation capacity grows due to the water adsorption on PS (the capacity  $C_{H_2O}$  in the equivalent circuit increases), and, second, the shifting of C-V is observed owing to the variation of the near-surface charge.

In Fig. 3, the temperature dependences of the heterostructure saturation capacity, which were measured when the temperature was either decreased or increased, are presented. The dependences are nonmonotonic and have a maximum in the temperature range  $-4 \div +4$  °C. The plot shape depends on measurement conditions, and the maximum is most pronounced when measurements are carried on at decrease in the temperature. Consider the physical processes, which underlie such a C-V-curve behavior.

It is well known that, when water freezes, its initial volume  $V_{H_2O}$  grows to  $V'_{H_2O}$ . Let us introduce the

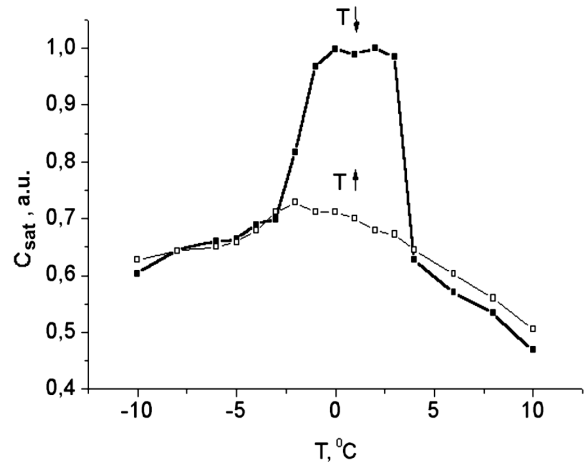


Fig. 3. Temperature dependences of the Ti-PS-p-Si-Al heterostructure capacity in the accumulation mode registered at the elevation (□) and the reduction (■) of the temperature

expansion coefficient  $\beta = V'_{H_2O}/V_{H_2O}$ . Then formula (3) reads

$$C_{\text{eff}} = \frac{\varepsilon_0 S}{d} \left[ (1 - \alpha) \varepsilon_{\text{cr}} + \left( \alpha - \frac{\beta V_{H_2O}}{d S} \right) \varepsilon_{\text{air}} + \frac{\beta V_{H_2O}}{d S} \varepsilon_{H_2O} \right]. \quad (5)$$

The last two summands depend on the temperature of water (or ice) in pores. In addition, while considering formula (5), the temperature dependence of  $\varepsilon_{H_2O}$  has to be taken into account. When the temperature approaches 0 °C, the dielectric permittivity first grows from 81.0 (at  $T = 20$  °C) to 88.3 (at  $T = +0$  °C); afterwards, when water starts to crystallize into ice, this parameter decreases in a jump-like manner from 74.6 (at  $T = -0$  °C) to 3.2 (at  $T = -10$  °C) [10]. However, the temperature dependence of the capacity in the saturation mode, which has been theoretically calculated in the framework of our model, differs from the experimental one. We suppose that there is one more factor which affects the saturation capacity, but in an implicit way. This is the pressure which emerges when water becomes transformed into ice, and stimulates the modification of the energy structure of PS, in particular, a reduction of either the energy band gap or the total potential barrier [5], which gives rise, in its turn, to a reduction of SCR in silicon. All that brings about an increase of the  $C_{\text{cr}}$  capacity [11] which is described by the formula

$$C = \sqrt{\frac{\varepsilon_0 \varepsilon e^2 n_0}{2(\varphi_0 - eV_2)}}. \quad (6)$$

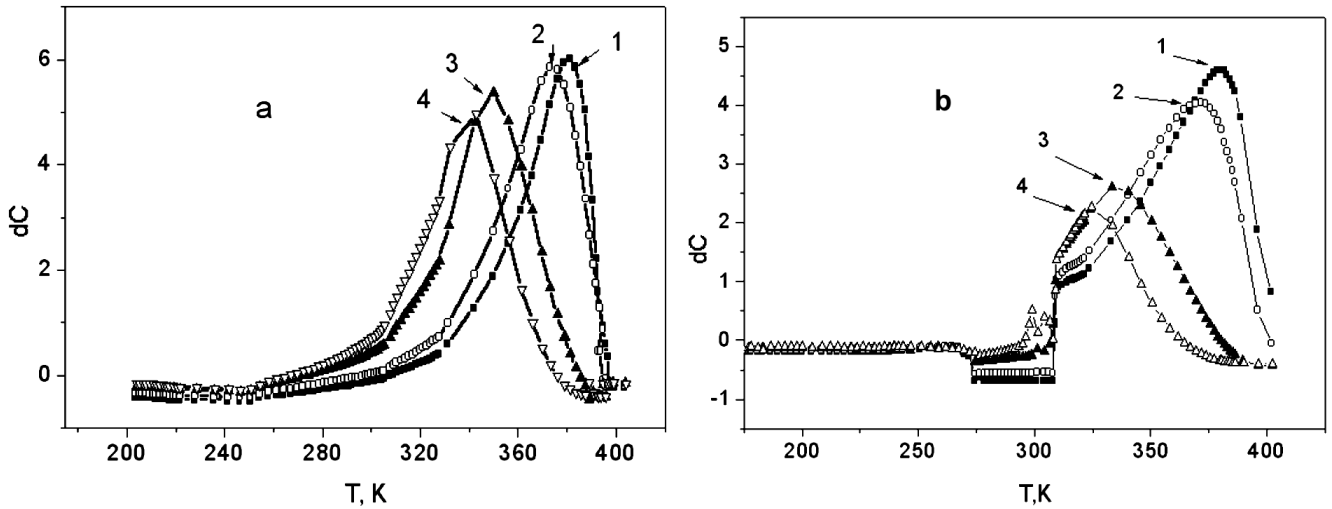


Fig. 4. DLTS spectra of the specimens free of water (a) and with intrapore water (b) measured at various emission windows: 98 (1), 294 (2), 487 (3), and 997  $\mu\text{s}$  (4)

Here,  $\varepsilon_0$  is the dielectric permittivity of vacuum,  $\varepsilon$  the dielectric constant of silicon,  $e$  the electron charge,  $n_0$  the concentration of free charge carriers,  $\varphi_0$  the potential barrier height, and  $eV_2$  the voltage drop across the SCR in PS.

We are going to evaluate the internal pressure which arises in the pores, when water becomes frozen. For this purpose, we take advantage of a few approximations. First, these are the Bruggeman effective medium approximation and the cylindrical pore model. Second, we suppose that water freezes quickly enough. Third, we assume that water expands isotropically. Since the ice volume  $V_{\text{ice}} = \beta V_{\text{H}_2\text{O}}$ , we obtain:

$$P = \frac{1}{\chi_{\text{Si}}} \frac{\Delta V}{V} = \frac{1}{\chi_{\text{Si}}} \left( \frac{V_{\text{ice}} - V_{\text{H}_2\text{O}}}{V_{\text{H}_2\text{O}}} \right) = \frac{1}{\chi_{\text{Si}}} (\beta - 1), \quad (7)$$

where  $\chi_{\text{Si}} = 0.98 \times 10^{-12} \text{ cm}^2/\text{dyn}$  [12] is the compressibility coefficient for silicon.

Taking all the above-mentioned into account, we obtain that the pressure amounts to  $7 \times 10^9 \text{ Pa}$ . Note that this extremal value agrees with the value obtained for the internal tension of about 2 GPa in a silicon film that is formed on a PS substrate and becomes oxidized at thermal annealing at  $600 \text{ }^\circ\text{C}$  [13].

Now, let us evaluate – in the framework of the model proposed in work [5] – the change of  $E_g$ . In that work, the influence of the squeezing on the CVCs of MIS structures with a PS interlayer was examined. The CVC modification under the action of pressure was explained by a reduction of the energy band gap which can be

described by the formula

$$\Delta E_g \sim \alpha P, \quad (8)$$

where  $\alpha = 2.3 \times 10^{-11} \text{ eV/Pa}$  is the tensorial coefficient. Substituting the pressure value of  $7 \times 10^9 \text{ Pa}$  into Eq. (8), we obtain that the variation of the energy band gap equals 0.16 eV. At such internal pressures, the position of the maximum in the photoluminescence spectrum must be shifted from 650 to 710 nm. It is worth noting that the change of  $E_g$  depends on the parameters of the porous layer, because, as was shown in work [5], the tensorial coefficient  $\alpha$  depends on the PS thickness ( $\alpha$  grows with the increase of the PS layer thickness). This circumstance evidences for the variation of the tensorial effect across the PS thickness, which testifies, in its turn, to the corresponding variation of PS properties across the interlayer.

We also carried out measurements for specimens – both free of water and with it – following the DLTS method, which is described in work [14] in detail. The spectra, which were obtained at various emission windows, are presented in Fig. 4. Jumps at  $T \approx 270 \text{ K}$  in the curves depicted in panel b are explained by the fact that water, which was frozen in the pores, thaws, and this phenomenon changes the capacity of MIS structure in a jump-like manner. As the temperature increases, water becomes partially desorbed, which gives rise to the appearance of DLTS spectra similar to those obtained in the case  $RH \neq 0$ .

We also calculated the activation energy in those two cases. Their corresponding values are 0.54 and 0.44 eV.

On the basis of these results, we may suggest that, under the condition when an ice-like structure emerges in the pores, there occurs a reconstruction of the energy configuration of deep levels in PS. This phenomenon becomes possible, if either the energy band gap or the potential barrier varies, which stimulates, in its turn, the relocation of the energy level with respect to the vacuum level. The difference between the values of deep level activation energy in those two cases amounts to 0.1 eV, which correlates, by the order of magnitude, with the variation of the energy band gap calculated above (0.16 eV). This difference can be explained, first, by the overestimated value of intrapore pressure and, second, by accuracy of DLTS measurements. At last, the shift of the activation energy may not coincide with the variation of  $E_g$ , because other factors can exert their influence as well.

#### 4. Conclusions

Our studies of the CVCs of Ti-PS-Si MIS structures under conditions when PS pores are filled with water have revealed a maximum in the dependence of the saturation capacity on the temperature. The maximum was observed at temperatures close to 0 °C. Its emergence can be explained, first, by the variation of the water dielectric permittivity with change in the temperature; second, by the growth of the intrapore pressure when water freezes in pores; and third, by the reconstruction of the energy configuration of deep levels in PS, when an ice-like structure emerges in pores, which is confirmed by the DLTS measurements. In the framework of the Bruggeman effective medium approximation, the cylindrical pore model, and the approximation of the isotropic extension of freezing water that was capillary adsorbed in pores, we, by analyzing the temperature dependences of the CVCs, have evaluated the maximal value of intrapore pressure which turned out to be  $7 \times 10^9$  Pa. Such extremal pressure gives rise to a reduction of the energy band gap in porous silicon by 0.16 eV and a corresponding shift of the activation energy of deep levels in a porous semiconductor.

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#### ВПЛИВ ВНУТРІШНЬОГО ТИСКУ В ПОРАХ НА ЕЛЕКТРОФІЗИЧНІ ВЛАСТИВОСТІ ПОРУВАТОГО КРЕМНІЮ

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#### Резюме

Досліджувався вплив внутрішнього тиску, який виникає при утворенні льоду в порах поруватого кремнію (ПК), на електрофізичні властивості МДН-структури метал-ПК-Si. У температурному діапазоні  $T = -4, 0 \div 4, 0$  °C спостерігається максимум на залежності ємності акумуляції структури від температури. Немонотонна поведінка ємності пояснюється, в першу чергу, зростанням внутрішнього тиску при замерзанні води в порах. У процесі зниження температури, в умовах виникнення льодо-подібної структури в порах, на температурну поведінку ємності також впливає стрибкоподібне зменшення ефективної діелектричної проникності системи "ПК - лід" та перебудова енергетичної структури глибоких рівнів ПК. Останній факт підтверджується вимірюваннями методом релаксаційної спектроскопії глибоких рівнів кривих релаксації ємності МДН-структури з адсорбованою водою в порах в околі температури утворення льоду. В наближеннях ефективного середовища Бругемана, циліндричної моделі пор та ізотропного розширення при замерзанні капілярно адсорбованої води в порах з температурних залежностей вольт-фарадних характеристик оцінено величину локального внутрішнього тиску, яка досягає  $7 \cdot 10^9$  Па. Такий екстремальний тиск спричинює зменшення ширини забороненої зони ПК на 0,16 eV та відповідний зсув енергії активації глибоких рівнів у поруватому напівпровіднику.