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Features of electrical charge transfer in porous silicon

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Abstract. The thermostimulated depolarization (TSD) spectra of porous silicon (PS) in the range of temperatures 77 – 450 K were investigated. Several wide bands of TSD current with different values referred to different types of PS charged defects were discovered. Comparative investigation of TSD spectra of PS layers and films of dioxide silicon on the silicon substrates were carried out. There was fixed the identification of low-temperature (77 – 300 K) parts of these spectra. Activation energies of defects and capture centers of PS were calculated. Low-temperature defects were identified as hydrogen – oxygen type ions. Infrared- and x-rays influence of PS on TSD spectra were fixed. An energy scheme of charge transport in PS based on changes in TSD spectra were proposed. Temperature changes of planar current – voltage characteristics and frequency dispersion of the capacity of porous silicon – silicon substrate heterostructures were investigated. The anomalous character of dependencies is explained by special features of ion transfer in PS.

Keywords: porous silicon, thermostimulated depolarization, capture centers.

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1. Introduction

In recent decade since the moment of its discovery, porous silicon has been attracting exceptional interest and attention of researchers due to unexpected luminescence properties in the visible region of spectrum [1]. But for these years porous silicon had enough time to cause certain disappointment which is associated with complexity of this object and processes what take place in it. Unfortunately, nature of light emitted from porous silicon is not realized in full volume, and this keeps its practical application off, specifically in creating light emitting and light detecting devices on its base. At first, usually, porous silicon surface presents itself as a material of very specific composition that includes conglomerates of different phase forms, namely fragments of silicon, small hydrogenated silicon particles, fragments of oxidized silicon, study of which will enable us to understand mechanisms of visible light emission. In forming the dielectric properties of porous silicon the least investigated is contribution of oxidized fragments. As a matter of fact the present work is devoted to liquidation of this flaw. Specifically, we investigated special features of migration processes of charge carriers in porous silicon under influence of fixed and changing electric fields at infrared, X-ray and temperature exposing.

2. Sample preparation

Porous silicon layers were formed by anodization of *p*-type monocrystalline silicon (*p*-Si) (4.5 Ω·cm) in electrolytical cell with platinum counterelectrode and hydroethanolic solution with HF concentration as electrolyte. The current density was maintained in time and fluctuated from 5 to 20 mA/cm^2 in different experiments. Duration of the electrolysis process was 10 – 60 min. Contacts on the porous silicon surface were traced by aquadag. Distance between contacts was ~6 mm. For isolation of the crystal from copper stock of the cryostat there were used mica plates.

Fig. 1 shows scheme of measurements. Samples previously were polarized by electrical field at room temperature and then were cooled to the temperature of liquid nitrogen. After that electrical field was switched off and turned on heating to investigate a dependence of depolarization current on temperature [2].

We used additional stimulus method for thermostimulated depolarization: infrared irradiation ($\lambda > 850$ nm) and exposing to X-rays (Mo anticathode, $I = 50$ mA, $U =$ $= 50$ kV).

Sample was settled in a vacuum cryostat, temperature was measured by copper – constantan thermocouple. Pressure in the cryostat was 10^{-1} Pa. Temperature in cryostat

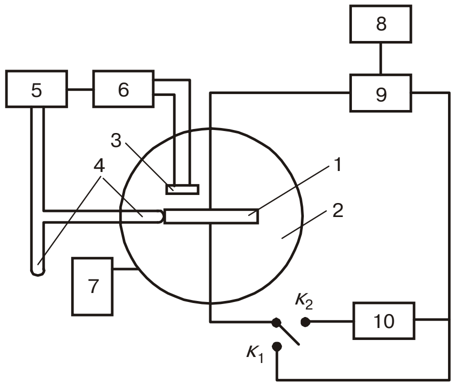

Fig. 1. Scheme of photothermestimulated depolarization method: 1 – sample; 2 – cryostate; 3 – copper stock, furnace; 4 – thermocouple; 5 – automatic system of temperature control; 6 – furnace feeding; 7 – forvacuum pump; 8 – registration device; 9 – voltmeter; 10 – stable tension source.

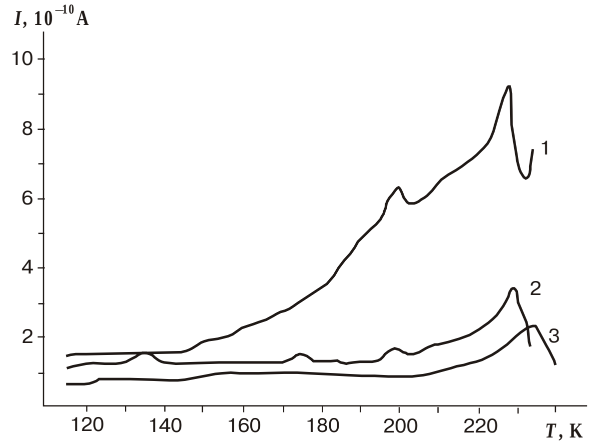

Fig. 2. TSD spectra of porous silicon, SiO_2 layers: 1 – porous silicon (×8); 2 – SiO_2 on silicon substrate (×20); 3 – porous silicon free layer.

in the region 80–400 K could be changed with ±1 K precision. Current was measured by electrometer B7-30 and over analogue converter was directed to the registration device. The rate of samples heating was 0.05 K/s. Thermocouple readings was controlled by voltmeter B7-21.

3. Experiment

Except the peaks of TSD at room and higher temperatures there were fixed peaks at 125 K, 175 K and then sharp peak at 225 K where sudden increase of TSD current took place.

Typical situation is characterized by TSD current curves by appearance of peaks of the same directions but also can realized a case of presenting in TSD spectra peaks of the different directions – so called inversion of TSD current. Alternating with each other directions and innovational peaks in dependence of the correlation of capture centers parameters for the positive or negative charges can change.

Analysis of low-temperature (to 300 K) parts of TSD spectra both for porous silicon and amorphous SiO_2 layers showed them as identical. It testifies in favor of their nature similarity and processes of transition carriers in these materials (Fig. 2) opposite to bulk silicon TSD spectra, which are presented as horizontal lines.

We have shown [3,4] that there are cluster features SiO_xC_y and bulk silicon on the PS surface. It served as a base for comparative investigations of TSD spectra of PS, SiO_x layers and bulk silicon.

The temperature dependence of the depolarization current was measured. The current increase at low temperatures as well as in 300–425 K and 450–525 K temperature ranges was observed. The energy assignment g(E) of the state filling up for identification of the electrically charged defect nature was calculated by us. All calculations were carried out basing on the phenomenological theory of the thermostimulated current depolarization for irregulate dielectrics by the way of numerical solution of the integral Fredholm equation using the regularization Tikhonov algorithm [2].

It is well known that heating of SiO_x leads to ion migration as a result of electrical field influence. Specifically, it was shown that mobility of ions, e.g., the negatively charged ones, is many times smaller then mobility of cations. So, anions should not play essential role in phenomena of electrotransfer. Among the positive ions, it is necessary to pay attention to hydrogen ions, single- and double-charged oxygen vacancies, alkali metal ions. Particularly, in a migration process, the activation energy value of the single-charged oxygen vacancy is about 0.44 eV. Hydrogen ions activation occurs at energies ~0.66 eV and 0.9–1.3 eV [5]. So, aforesaid ions form TSD spectra because their activation energies correlate with values of carrier energy barriers in PS. These ions, which have activation energy close to values of energy barriers, form TSD spectra.

We can confirm that 0.4–0.7 eV band is responsible for hydrogen ions activation energies. Transfer mechanism of hydrogen H^+ ions in PS must be the same in SiO_2 or else this is a transfer of OH^+ switching bonds. Activation energy of this process is about 0.73 eV. The transfer of switching bonds OH^+ is more probable than migration of H^+ or H_2 along junction due to its high reactional properties. There is hydrogen ion diffusion through the volume in amorphous SiO_x with activation energy ~0.66 eV. Most of ions are migrate on the surface in the case of small volume of globule SiO_x, that is responsible for high porousity or on boundary line of globules with less activation energy. So, energetical process of ions transfer in PS is the criterion of SiO_2 globules size valuation, in other words – porousity of Si.

Besides TSD spectra, we have investigated electromagnetic radiation influence on charged defects moving in low dimension structures of PS. There were observed lowest values of TSD current under influence of infrared rays. We were observed two peaks: at 200 K and 225 K (I_{max}~ 2×10^{-9} A) (Fig. 3).

The highest values of TSD current were observed in a case without irradiation of samples. But we had two low-temperature peaks in 200 K and small peak in ~230 K.

Under irradiation of X-rays there were observed a maximum values of TSD currents (I_{max}~ 2×10^{-6} A) (Fig. 3). In this case all parts of low-temperature TSD spectra were demolished at temperature range T > 250 K.

We proposed the energy scheme of carrier thermostimulated motion under irradiation of PS by different types of electromagnetic flows using type identification of ions which transfer a charge in PS, calculated activation levels parameters that form TSD current spectra (Fig. 4).

Under exposing to infrared rays TSD current was decreased. We guess those currents are formed by additional positive ions, so infrared light generates charges of the opposite sign. In this case general TSD current became lower at the expense of infrared generated negative charges. Probably, there electrons are such charges which fall into a trap of >1.1 eV depth and particularly neutralize positive ions. If PS is exposed to high energy X-quanta then electrons and holes are generated in C- and V-bands of porous silicon. Attached to these electrons are completely neutralized positive ions with small activation energy. Holes fall into traps with deeper energy levels. Under heating to higher temperatures positive ions are liberated. A high temperature part of TSD spectrum appears.

Spectrum of PS had low- and high-temperature parts of the spectrum in absence of irradiation, these are related to two bands of activation energies and have different origin. Probably, hydrogen and oxygen ions are responsible for these features.

Presence of hydrogen and oxygen ions in porous silicon have essential influence on charge carrier transfer, which can be seen via-current – voltage dependencies observed in our experiments. Planar current-voltage characteristics were registered using the linear in time change of the external voltage with the rate close to 1 V/min and fixed on the registration devices. Measurements were performed using pumped out vacuum cryostat in the range of temperatures from the liquid nitrogen to room ones. We obtained characteristics that looked as non-linear, symmetrical curves relatively to the current axis. We can approximate these curves by hyperbolical functions.

Current stabilization through these structures that follows the increase of external voltage is connected with formation of the inner electret field having the direction opposite to the external field. Those fields can form ion – dipole structures in porous silicon (Fig. 5).

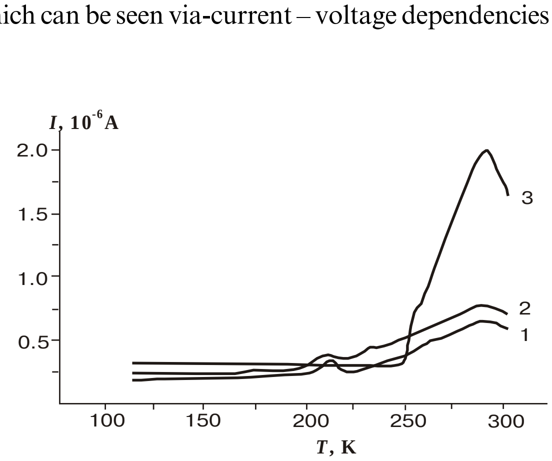

Fig. 3. The change of porous silicon TSD spectra under exposing to IR – (1), X-rays – (3); (2) – starting spectrum of porous silicon.

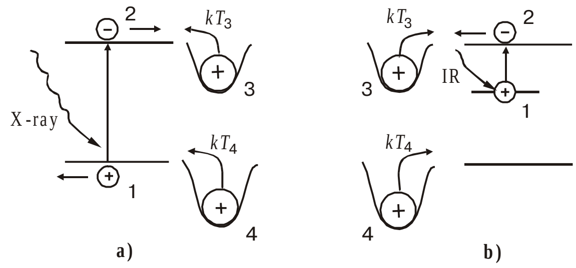

Fig. 4. PS charged defects activation energy scheme under thermostimulation (1), under thermostimulation and X-ray influence (2), under thermostimulation and infrared influence (3).

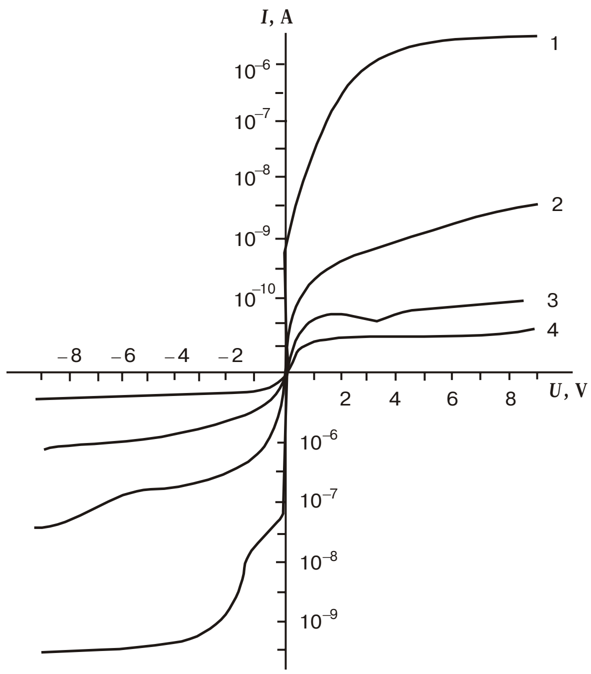

Fig. 5. Planar volt – current characteristic of porous silicon – silicon substrate heterostructures at temperatures: 1 – 300; 2 –211; 3 – 158; 4 – 80 K.

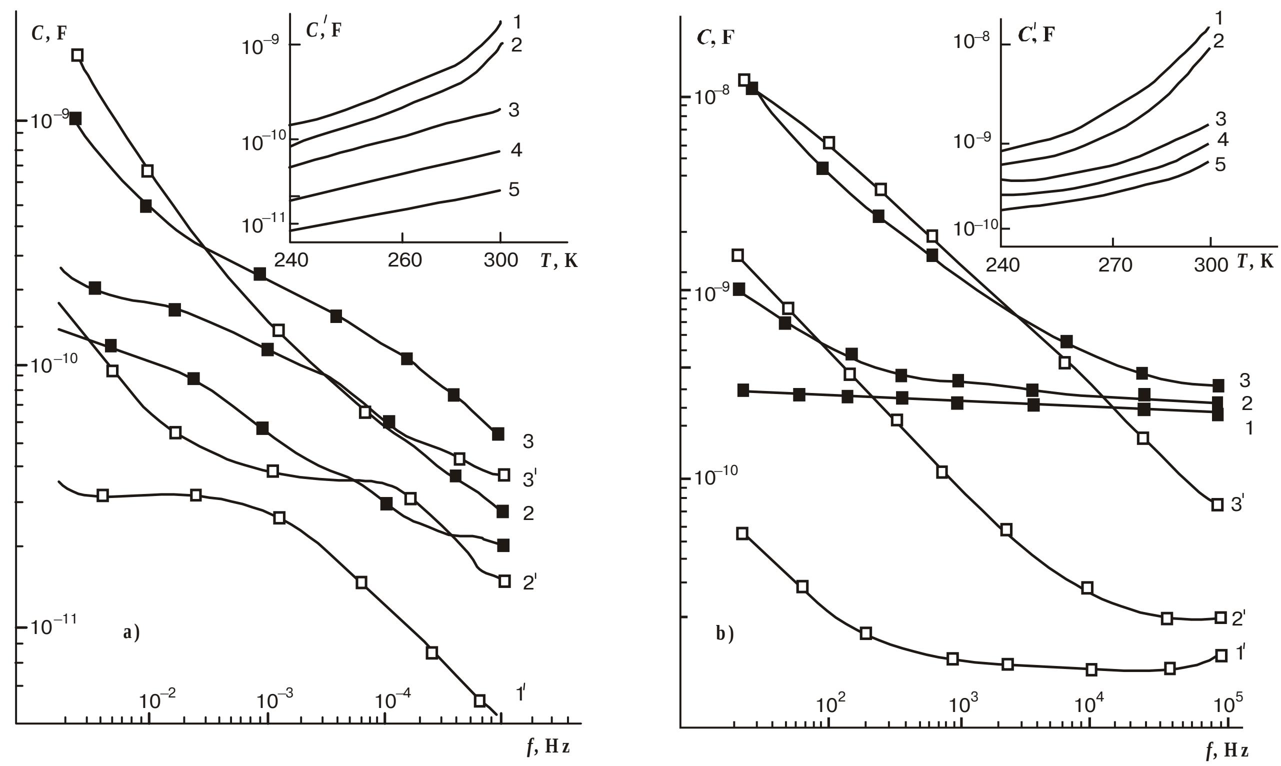

Fig. 6. Frequency dependencies of the capacity of porous silicon – silicon substrate (a – *p*-type, *b* – *n*-type) heterostructures: (1,2,3) – real;(1',2',3'); imagine part of the capacity (1,1'– 240 K, 2,2'– 266 K, 3,3'– 295 K). Insertion – temperature dependencies of capacity at different frequencies: 1 – 10; 2 – 100; 3 – 1000; 4 – 10000; 5 – 100000 Hz.

Presence of ions in porous silicon can manifest themselves under influence of external electrical fields changing in time and, also, must influence on the frequency dependencies of capacitance parameters of the material.

In connection with aforesaid, a frequency dispersion of real and imaginary parts of the PS – Si-substrate capacitance were investigated in the range of 1–10^6 Hz. Dependencies were investigated in the temperature range from liquid nitrogen to the room temperatures. As shown by experimental results, accordingly to the proposed model, that dependence is typical for semiconductors near low temperatures, and any frequency dependence is absent.

But near the room temperature the capacitance increases exponentially with decreasing frequency, in other words, it has an anomalous character. We can explain this dependence by movement of massive electro-active particles in this region, for example, hydrogen and oxygen ions. At low temperatures and high frequencies these particles have no considerable movement, and they are not present in capacitance dependencies (Fig. 6).

Conclusions

Possibility to observe the TSD phenomenon in studied structures testifies to thermoelectret properties of PS. Complicated TSD spectrum gave a possibility to find the existence of different type charged defects in PS. Specifically, the low-temperature part of TSD spectra of PS is practically similar to that of TSD spectra in amorphous SiO_x, which tells us about a presence of silicon oxides on the PS surface and their role in formation of PS thermoelectric properties.

Using TSD spectra we calculated activation energies and filling up degree of capture levels for PS ionized defects. Maxima are situated in the energy ranges 0.4 – – 0.7 eV and 1.1 – 1.3 eV. According to activation energies, it was determined that oxygen – hydrogen complexes are these defects.

It has shown in this paper that porous silicon in polarized state is sensitive to infrared- and X-ray irradiation. On the basis of changing of TSD spectra under influence of such irradiation there were suggested the energy scheme of capture, and discharge, interaction and movement of ionized defects in PS.

Current-voltage characteristic of PS manifest clearly pronounced nonlinear character and have a section of saturation with increasing temperature. It testifies to formation of inner built-in electric field equal in its value but with opposite direction to the external field, that is to formation of an electret state in PS.

The anomalous frequency dispersion of the capacitance of PS is also tightly bound with charge carrier transfer in the low dimensional structures and with ion/dipole activations under heating as well as influences of low frequency electric fields (10 – 100 Hz).

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