Electrical Properties of Porous Silicon Nanocrystals in a Dielectric Matrix

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In this work, the porous silicon nanocrystals were obtained in a dielectric matrix. Porous silicon layers obtained by photoelectrochemical etching of single-crystalline wafers with the [100] and [111] crystallographic orientations were separated from the silicon substrate using epoxy resin. Systems of the porous silicon nanoparticles were characterized by scanning electron microscopy. The dimensions of the silicon nanocrystals varied from several to tens of nanometers in the cross-section. On the basis of comprehensive studies by impedance spectroscopy and thermal activation methods, processes of transfer and relaxation of non-equilibrium charge carriers have been studied. Impedance model of obtained nanosystems was constructed and its electrical parameters were determined. The internal resistance of free-standing porous silicon nanocrystals was more than 10 GOhms and was several orders of magnitude higher than the typical resistance of the porous layer on the silicon substrate. Activation mechanism of charge transport in the 270-350 K temperature range was found and the activation energy of the conductivity was determined. Based on the spectra of thermally stimulated depolarization current, the localized electron states that affect the charge transport in the porous silicon nanosystems were revealed. The calculated energy distribution of the filling density of states has a maximum in the 0.45-0.6 eV energy range. The found trap levels of nonequilibrium carriers are probably related to the electrically active defects at the interface between silicon nanocrystals and the epoxy resin.

Keywords: Porous silicon, Electrical conductivity, Impedance, Activation energy, Thermally stimulated depolarization, Charge traps.

1. INTRODUCTION

Silicon-based heterogeneous nanosystems attract the attention of researchers due to the wide range of possible applications. In particular, gas sensors [1], light emitting devices [2, 3] and photodetectors [4], lasers and active waveguides [5, 6] can be created on their basis. Besides, the possibility of silicon nanostructures use is considered for the creation of single-electron transistors [7] and memory elements [8] that are based on processes of transfer, capture and storage of charge carriers in such quantum dots.

A quite simple way to obtain the silicon nanocrystals system is a technology of the porous silicon (PS) formation. The PS nanostructures can be prepared as a result of the electrochemical etching of the narrow pores that are directed into a silicon wafer. Since the porous layer thickness and porosity, size and shape of the pores are determined by the etching parameters and initial silicon wafer [9, 10], the main structural properties of the PS can be easily controlled. That is why the PS is used as a convenient model object for the study of various optical and electrical properties of semiconductor nanostructures.

In order to eliminate the unwanted effect of the silicon substrate (e.g. injection extra charge carriers into the high-resistance silicon nanocrystals), it is necessary to use free-standing PS layers. However, the PS layer without a substrate has low mechanical strength and usually needs some reinforcing matrix. So technologies of incorporation of silicon nanocrystals into a dielectric matrix are often used. In addition, the dielectric environment improves the stability of the PS nanocrystals [11]. It should be noted that bottom-up nanotechnology makes it possible to effectively synthesize silicon nanocrystals with visible photoluminescence in the silicon-oxide matrix too [12, 13].

In general, the optical and luminescent properties of silicon-based nanosystems were studied more than their electrical properties. Therefore, the purpose of our work was to study the charge transport features in systems of the PS nanocrystals in the dielectric matrix. The study of electronic processes that occur in the silicon-based nanosystems opens new technological possibilities and constructive approaches for creating a new generation of electronic devices.

2. EXPERIMENT

In order to obtain the silicon-based nanosystems, the PS layers were prepared by electrochemical etching of n-Si wafers with [111] and [100] crystallographic orientation in a water-ethanol solution of hydrofluoric acid. The volume ratio of the electrolyte components was $HF:C_2H_5OH:H_2O = 1:1:1$. The anodic current density was 20-30 mA/cm² for different samples while the duration of the etching process was 10-20 min. The working surface of silicon wafers was irradiated by 500 W filament lamp to generate holes which were involved in chemical reactions and formation of the PS [10]. The electrochemical etching was finished after a short-time (about 30 s) increase in the anode current density to the 200-250 mA/cm². The increase in the anodic current facilitates to take off the porous layer

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from the silicon wafer due to high porosity at the boundary of the PS-silicon substrate. After the etching process, the PS layers were washed with distilled water and dried in air.

An epoxy resin was used as the dielectric matrix for our nanosystems. The epoxy resin was deposited on the PS surface. Then the samples were treated in an ultrasonic bath for 10 min for more effective penetration of the epoxy resin into pores. After polymerization, the epoxy resin with the PS layer had been taken off from the wafer surface. As a result, PS nanocrystals that bordered with the substrate were used in our further experiments.

The PS nanocrystals in the epoxy matrix were characterized by a scanning electron microscope (SEM) JEOL 7600F. For the study of electrical properties of the PS-based nanosystems, silver contacts were thermally deposited onto the sample surface. The distance between the contacts was about 0.2 mm.
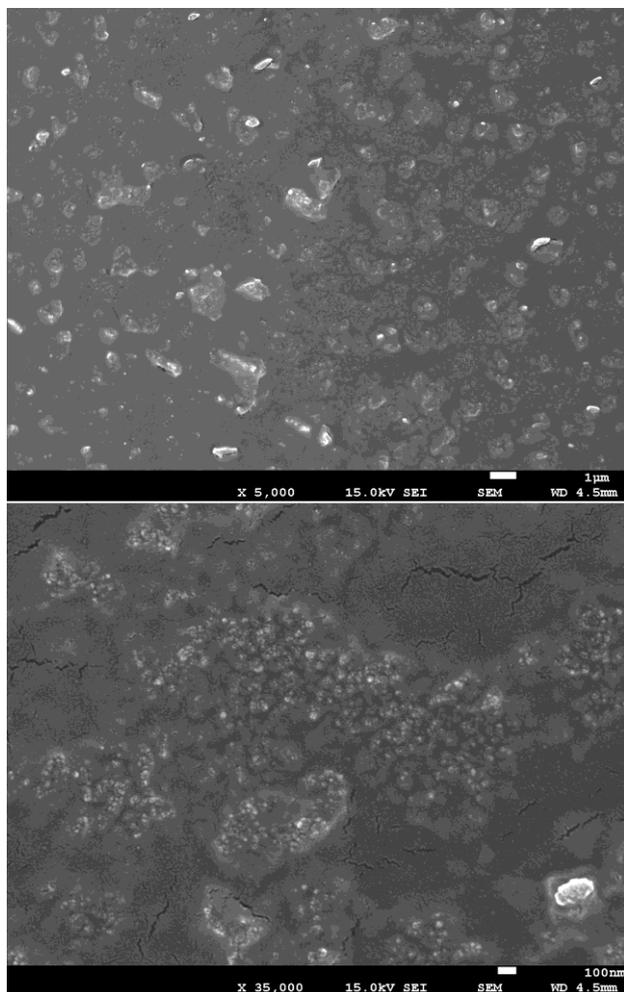
Fig. 1 – SEM images of the PS_{111} nanocrystals in the epoxy polymer at various magnifications

In the thermally stimulated depolarization (TSD) experiment, the PS-based nanosystems were initially polarized (polarization voltage was 5 V) at room temperature and cooled down to liquid nitrogen temperature. The TSD current was measured at heating in the absence of an external electric field using V7-30 electrometer.

The electrical parameters of the obtained nanosystems were investigated in both DC and AC regimes. Impedance spectroscopy of the experimental samples was performed using R, L, C measuring device E7-20 ("Kalibr", Belarus) at room temperature in the 25 Hz-1 MHz frequency range. The temperature dependences of the conductivity were measured in a vacuum (10-3 mm Hg) at linear heating from 90 to 350 K and a polarization voltage of 9 V.

3. RESULTS AND DISCUSSION

Analysis of the PS-based nanosystem surface was carried out using SEM method in secondary electron mode. As one can see from Fig. 1 and Fig. 2, the silicon nanostructures are well integrated into the epoxy resin matrix.

The structural differences between nanosystems on the basis of the PS nanocrystals with [111] initial substrate orientation (abbreviated hereafter as PS_{111}) and [100] orientation (PS_{100}) are probably due to selective pore etching mainly along the [100] crystallographic direction [10]. Study of the nanosystems surface at major magnification allows estimating the dimensions of the PS nanocrystals. They varied from several to tens of nanometers in the cross-section.
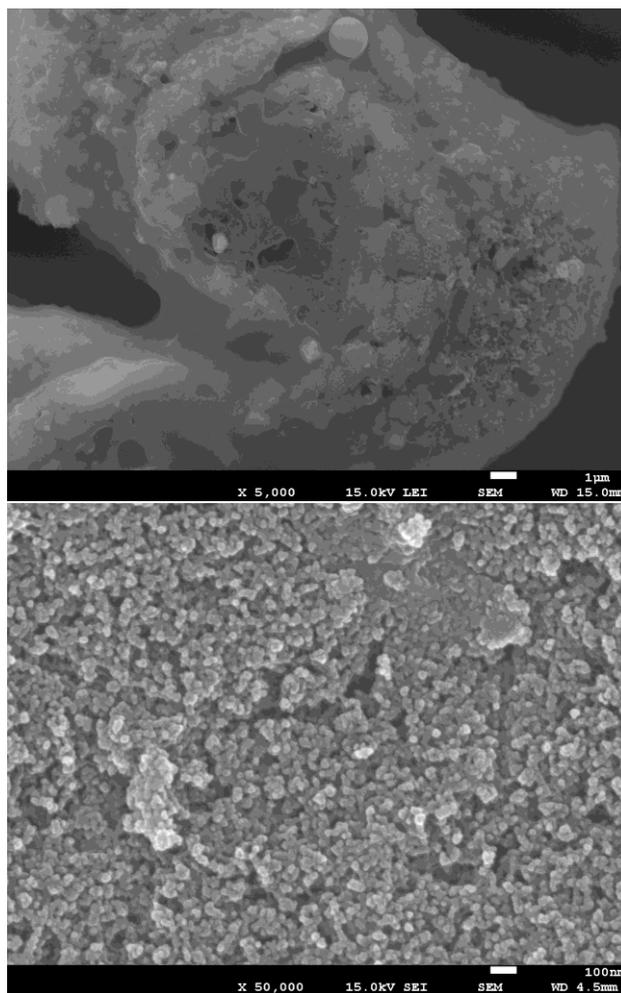
Fig. 2 – SEM images of the PS_{100} nanocrystals in the epoxy polymer at various magnifications
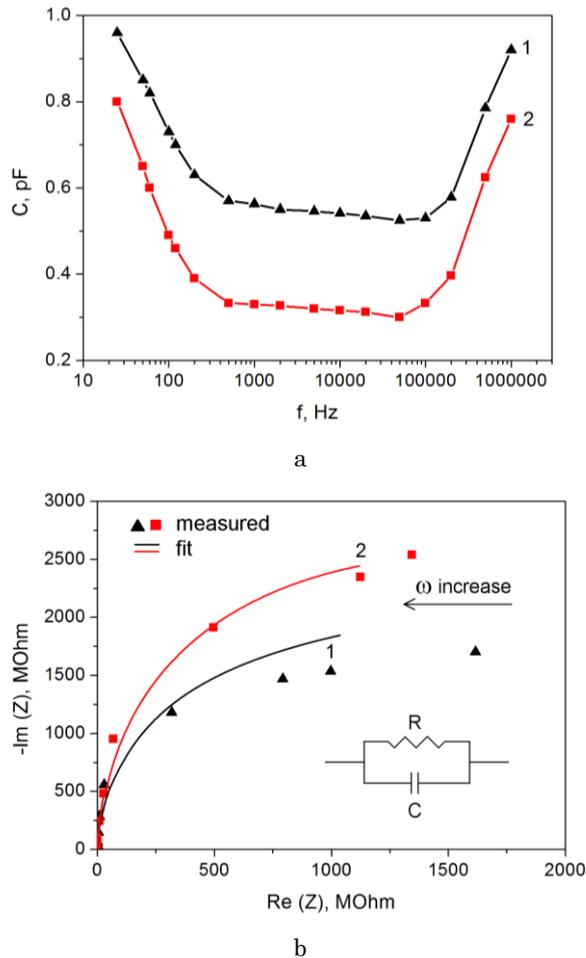
Fig. 3 – Frequency dependences of electrical capacitance (a) and Nyquist plots (b) of the PS$_{111}$ (1) and PS$_{100}$ (2) nanosystems. Inset: equivalent circuit diagram of the PS-based nanosystems

Impedance spectroscopy of the PS nanocrystals in the epoxy matrix has revealed nonmonotonic frequency dependences of the electrical parameters of our samples in the 25 Hz-1 MHz range (Fig. 3a). The obtained dependences indicate the different dispersion of the PS-based nanosystem capacitance in different frequency ranges. It was observed a decrease in capacitance at the 25-1000 Hz frequencies and its increase in the 0.1-1 MHz range. Low-frequency dispersion is probably related to the transport of charge carriers through the barriers between PS nanostructures, and high-frequency one is associated with transfer charge processes in nanocrystal volume. The observed features in the impedance spectra can be due to the hopping mechanism of the conductivity through localized states or recharging of trap levels in PS nanostructures [14, 15].

Fig. 3b shows Nyquist plot of the PS-based nanosystems in coordinates of the complex plane Re(Z)-Im(Z). An equivalent circuit of our samples was built to interpret measured impedance spectra. Within this model, the PS-based nanosystems can be regarded as the composition of parallel-connected capacitor with capacitance C and resistor with resistance R [16]:

$$Z(\omega) = \frac{R}{1 + j\omega RC}.$$

Since the contribution of the contact resistance is negligibly small, we do not consider this resistance in the construction of impedance models for PS nanocrystals in epoxy resin. Based on the approximation of the impedance spectra, the values of the electrical parameters of our nanosystems were determined. The internal resistance was 10.5 GOhms for the PS$_{111}$ nanosystem and 12.6 GOhms for the PS$_{100}$ nanosystem. The values of electrical capacity were 0.57 pF and 0.33 pF respectively. The calculated values of the internal resistance of PS nanocrystals in the epoxy resin are several orders of magnitude higher than the resistance of the PS/silicon substrate structures. This fact indicates the significant influence of the silicon substrate on the electrical characteristics of the porous layer.

In order to elucidate the mechanism of charge carrier transport in PS-based nanosystems, the temperature dependence of electrical conductivity in the range of 90-350 K was studied. It was detected low conductivity of the PS-based nanosystems in the low-temperature region, a current rise band in the 250-270 K range and an exponential increase in the conductivity at elevating of temperatures (Fig. 4). We suppose that the current peak at 260 K is caused by the thermal release of charge carriers from the trap levels.

The exponential increase in the conductivity indicates the activation mechanism of charge transport in the temperature range of 270-350 K. On the basis of temperature dependence of the resistivity presented in ln R–T^{-1} coordinates one can estimate the activation energy for the conductivity by measuring the slope of ln R(T^{-1}) line (see inset in Fig. 4). In result, the calculated activation energy for PS nanocrystals in epoxy resin in the 270-350 K temperature range was within range 0.70-0.85 eV.

Impedance spectroscopy and temperature dependences of conductivity indicate the participation of localized states in the processes of transfer and relaxation of charge carriers in the PS nanostructures. It should be noted that the trap levels are distributed quasi-continuously on the activation energy in the PS and other disordered systems [17]. The TSD spectroscopy was used to find an energy distribution of the trap levels.

The TSD spectra of the PS nanocrystals in the epoxy matrix are characterized by a band with the maximum depolarization current in the 250-270 K range that corresponds to the increase in current on the temperature dependence of electrical conductivity (Fig. 4 and Fig. 5). This can serve as an argument in favor of the same nature of the higher current bands on the measured dependences.

The analysis of the temperature dependences of the depolarization current was performed based on the phenomenological theory of TSD currents for the disordered dielectrics and high-resistance semiconductors [17]. The calculation of the energy distribution of the density of states for nonequilibrium carriers g(E) was carried out by a numerical method based on Tikhonov's regularization algorithm. The calculation results are presented in the inset Fig. 5.
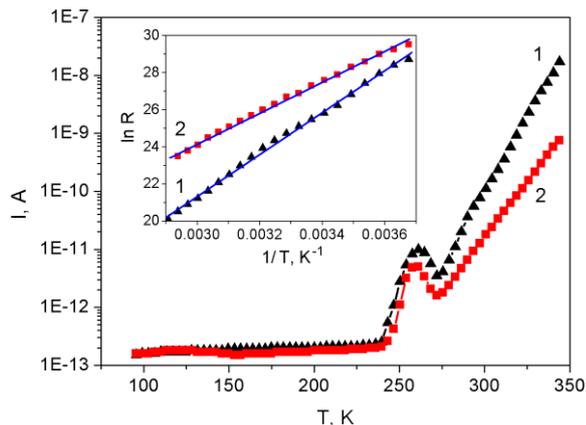
Fig. 4 – Temperature dependences of conductivity current for the PS_{111} (1) and PS_{100} (2) nanosystems. Inset shows the same temperature dependences in ln R–T^{-1} coordinates
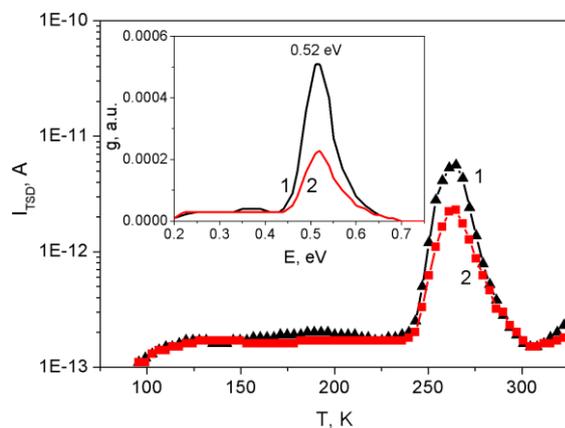
Fig. 5 – Temperature dependences of depolarization current and energy distribution of the density of states (inset) in the PS_{111} (1) and PS_{100} (2) nanosystems

On the basis of the obtained energy distributions, one can conclude that in the bandgap of the PS nanocrystals in the epoxy polymer there is a group of trap levels with activation energies in the 0.45-0.6 eV range. Drawing the correlations with PS structures [15], we suggest that these localized electron states are probably related to the electrically active defects at the interface between silicon nanocrystals and the epoxy resin.

4. CONCLUSIONS

The PS nanocrystals were obtained by a simple method of the photoelectrochemical etching of silicon wafers with the [100] and [111] crystallographic orientation and separation of the porous layer from silicon substrate with epoxy resin. On the basis of SEM-images, we have found that silicon nanocrystals are well integrated into the polymer. Their dimensions varied from several to tens of nanometers in the cross-section.

The electrical parameters of the PS-based nanosystems were investigated in both DC and AC regimes. Using impedance spectroscopy, an equivalent circuit of obtained nanosystems was constructed and the internal resistance and capacitance of the PS nanocrystals in the epoxy matrix were determined. Values of the electrical parameters were 10.5 GOhms and 0.57 pF for the PS_{111} nanosystem and 12.6 GOhms and 0.33 pF for the PS_{100} nanosystem respectively.

By means of studies of the conductivity and depolarization current in the 90-350 K range, charge transport in PS-based nanosystems was analyzed. Activation mechanism of conductivity with the activation energy of 0.70-0.85 eV in the 270-350 K temperature range was found. The energy distribution of the density of localized electron states in our nanosystems was calculated. Energy distribution of the filling density of states has a maximum in the 0.45-0.6 eV energy range. Such localized electronic states affect electron transport in PS nanocrystals.

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Електричні властивості нанокристалів поруватого кремнію в діелектричній матриці

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У роботі отримано нанокристали поруватого кремнію в епоксидній матриці. Отримані фотоелектрохімічним травленням монокристалічних пластин з кристалографічними орієнтаціями [100] та [111] шари поруватого кремнію відокремлювали від кремнієвої підкладки за допомогою епоксидної смоли. Системи на основі наночастинок поруватого кремнію характеризувалися скануючою електронною мікроскопією. Розмір кремнієвих нанокристалів у перерізі становив від одиниць до декількох десятків нанометрів. На основі комплексних досліджень методами імпедансної та термоактиваційної спектроскопії досліджено процеси перенесення та релаксації нерівноважних носіїв заряду. Побудовано імпедансну модель отриманих наносистем і визначено її електричні параметри. Внутрішній опір відокремлених нанокристалів поруватого кремнію становив понад 10 ГОм і на декілька порядків перевищував типовий опір поруватого шару на кремнієвій підкладці. Встановлено активаційний механізм перенесення зарядів у температурному діапазоні 270-350 К та визначено енергію активації електропровідності. На основі спектрів термостимульованої деполяризації виявлено локалізовані електронні стани, які впливають на перенесення зарядів у наносистемах поруватого кремнію. Розрахований енергетичний розподіл густини заповнення станів володіє максимумом у діапазоні 0,45-0,6 еВ. Виявлені рівні захоплення нерівноважних носіїв заряду ймовірно пов'язані з електрично активними дефектами на межі розділу між нанокристалами кремнію та епоксидною смолою.

Ключові слова: Поруватий кремній, Електропровідність, Імпеданс, Енергія активації, Термостимульована деполяризація, Рівні захоплення.