doi: 10.15407/ujpe62.02.0166

I.B. OLENYCH, L.S. MONASTYRSKYI, B.P. KOMAN
Ivan Franko National University of L'viv
(50, Dragomanov Str., Lviv 79005, Ukraine; e-mail: iolenych@gmail.com)

PACS 71.20.Nr, 72.20.Pa

ELECTRICAL PROPERTIES OF SILICON-OXIDE HETEROSTRUCTURES ON THE BASIS OF POROUS SILICON

The processes of charge-carrier transport and relaxation in silicon-oxide heterostructures based on porous silicon have been studied, by using voltammetric measurements and thermoactivation spectroscopy. The temperature dependences of the conductivity in experimental structures are measured in an interval of 80–325 K, and the activation energy of the electrical conductivity is determined. On the basis of the temperature dependences obtained for the depolarization current, the energy distribution of localized electron states, which affect the charge transport processes, is calculated. The influence of coating the porous silicon layer with a thin SiO_x film on the electrical properties of the layer is analyzed. The obtained results extend the application scope of silicon-oxide nanosystems.

Keywords: porous silicon, silicon-oxide film, current-voltage characteristic, conductivity activation energy, thermally stimulated depolarization.

1. Introduction

A number of fundamental physical principles impose restrictions on a decrease of the dimensions of functional elements created on the basis of silicon as a basic material for the microelectronic technology. In particular, these are quantum-size effects in nanostructures, the statistical uncertainty of the parameters of small elements, and the existence of a minimum operating voltage for semiconductors, which is associated with unavoidable thermal fluctuations in them. In the case of elements created on the basis of metal-insulator-semiconductor (MIS) structures, the problems of microminiaturization also include the charge carrier tunneling through a gate insulator, the injection of hot carriers into oxide, and the electric breakdown of an insulator. In essence, the solution of those problems depends on the level of development of a technology applied to the creation of high-quality insulator layers with high thermal stability, high dielectric permittivity, and wide spectral interval of optical transparency [1–3].

That is why the focus of attention in the researches of MIS structures has been lately shifted toward issues dealing with nano-sized objects and extremely thin insulators, for which the ballistic charge transport takes place [4–8]. This phenomenon can be either extremely undesirable (for example, in field-effect transistors) or necessary (as in the structures with MIS injector) for the devices to work. In the majority of technically important cases, it is necessary that the charge carriers should not simply move through an insulator or a set of barrier layers, but they should get with a definite energy into silicon. In particular, this is necessary for resonance-tunnel diodes and superlattices, as well as for devices on the basis of impact ionization.

Taking all this into account, the study of the charge transport processes through an insulator into semiconductor nanocrystals is a challenging problem. The most accessible cheap way to obtain a system of silicon nanostructures is the technology of porous silicon (por-Si) fabrication by etching small voids in a silicon single crystal. As a result, the thickness of walls between the pores can achieve a value of a few nanometers [9–11]. Porous Si is regarded as a convenient model object for studying a wide range of optical and electrophysical properties in nano-structured materials, because it can be produced rather easily, and its structural properties can be modified. The formation of a silicon oxide film on the surface of a por-Si layer provides a uniform highly effective passivation of the surface of silicon nanocrystals, which is crucial for their application to the optoluminescence, electronic, and photoelectronic domains [12, 13].

In order to form an oxide film on the por-Si surface, the thermal oxidation of silicon – a traditional technology in microelectronics – is usually applied [13–15]. However, this method results in a size reduction of silicon nanocrystals or in the complete oxidation of a porous layer. This can be avoided, by using the sol-gel technology of oxide film fabrication on por-Si from colloid solutions of organic silicon compounds [16]. Also promising are the methods of ionic-plasma and thermal deposition of thin SiO_x films, which are used to produce silicon nanocrystals in oxide layers [17, 18].

Therefore, the aim of this work was to create SiO_x/por-Si/Si heterostructures and study their electric parameters. For this purpose, the charging properties of silicon oxide nanosystems are studied by measuring and analyzing their current-voltage characteristics (CVCs), as well as the temperature dependences of the conductivity and current of thermally stimulated depolarization (TSD).

2. Experimental Part

Experimental por-Si structures were obtained, by using the method of photo-electrochemical etching of phosphorus-doped silicon single-crystals with conductivity of the n-type and a specific resistance of 45 Ω cm. The etching was carried out in an electrolyte on the basis of hydrofluoric acid with the volume ratio $HF : C_2H_5OH = 1 : 1$. The anodizing duration amounted to 10 min, and the anode current density was equal to 30 mA/cm^2. Under those technological conditions, layers of macro-porous silicon were formed. After the electrochemical treatment, the experimental specimens were washed out in distilled water.

A thin SiO_x film was deposited onto the por-Si surface by thermally evaporating a silicon powder on a vacuum installation VUP-5M in the air atmosphere at a residual pressure of about 10^{-1} mm Hg. Experimental por-Si specimens, which served as substrates in the course of deposition, were arranged at a distance of about 5 cm from a tungsten evaporator. Owing to the interaction between evaporated silicon and residual oxygen, a film of amorphous nonstoichiometric oxide SiO_x ($x < 2$) was condensed on the substrate. The application of macroporous silicon as a substrate promoted the penetration of the oxide film into pores. The thickness of the obtained SiO_x film was measured with the help of a microinterferometer and amounted to about 100 nm.

Electric contacts were deposited on the dielectric film surface and the rear side of the silicon substrate with the help of the thermal vacuum deposition of a metal film and a conducting varnish. The electric properties of experimental structures were studied in the geometry where the current through the structure was directed perpendicularly to its surface.

The current-voltage characteristics (CVCs) were measured by varying the bias voltage from −5 to 5 V and in the inverse direction. The measurements of the temperature dependences of the conductivity in silicon oxide nanosystems on the basis of por-Si were carried out in the ac mode, at a frequency of 1 MHz, and with the help of a digital LCR meter E7-12. The amplitude of the testing signal amounted to 250 mV. For this purpose, experimental specimens were arranged in a cryostat where a vacuum of 10^{-3} mm Hg was maintained. The temperature in the cryostat was measured with an accuracy of 1 K, and it could be varied from 80 to 325 K. The rate of specimen heating amounted to 0.1 K/s.

In the course of TSD researches, the experimental structures were preliminarily polarized (the polarization voltage $U = 5$ V) at room temperature and then cooled down to the liquid-nitrogen temperature. The temperature dependence of the depolarization current was studied with the use of an electrometer V7-30, by linearly heating up the specimens to 325 K in the absence of an external electric field.

3. Results and Their Discussion

The dark CVCs of experimental structures fabricated on the basis of por-Si were measured at room temper-

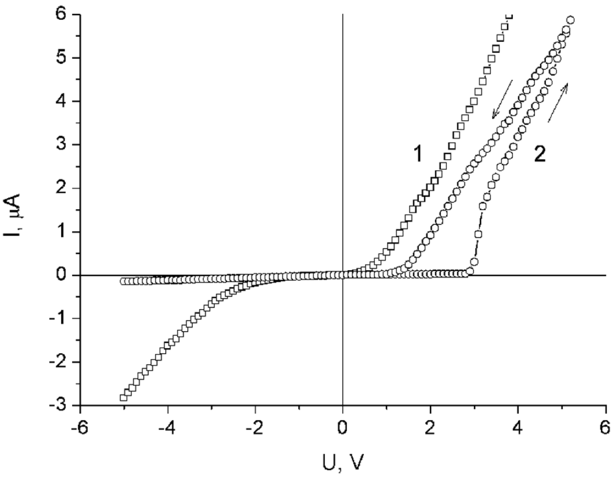

Fig. 1. CVCs of por-Si/Si (*1*) and SiO_x/por-Si/Si (*2*) structures

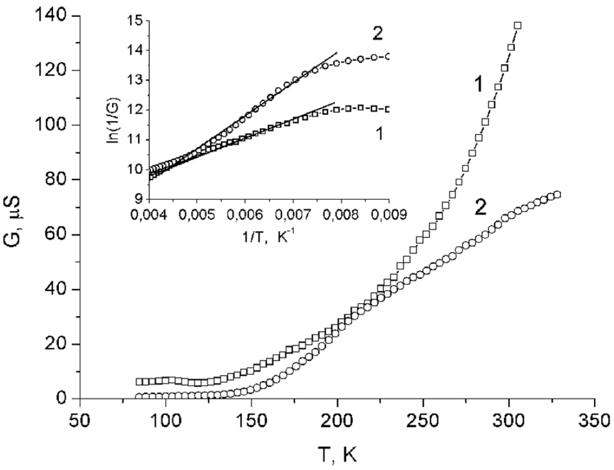

Fig. 2. Temperature dependences of the conductivity for por-Si/Si (*1*) and SiO_x/por-Si/Si (*2*) structures. The same dependences, but in the $\log G^{-1}$ versus T^{-1} coordinates, are shown in the inset

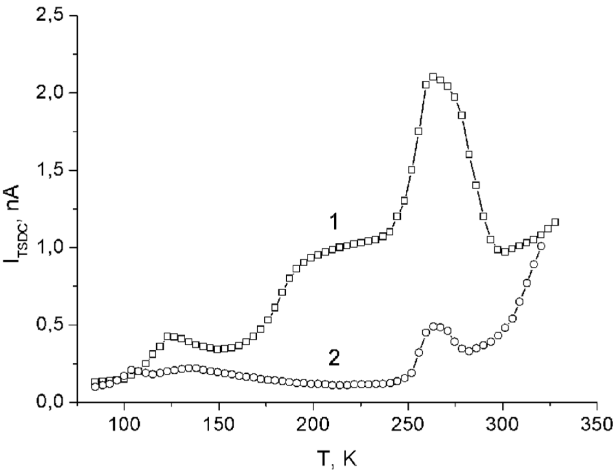

Fig. 3. Temperature dependences of the conductivity for por-Si/Si (*1*) and SiO_x/por-Si/Si (*2*) structures. The same dependences, but in the $\log G^{-1}$ versus T^{-1} coordinates, are shown in the inset

ature (see Fig. 1). The reference por-Si/Si specimen was characterized by a nonlinear CVC, which testified to the existence of several potential barriers in this structure. A nonlinear CVC can be a result of contact phenomena, electric barriers both in the porous layer and at the por-Si/silicon substrate interface, and the Poole–Frenkel effect [19, 20]. The deposition of a SiO_x film onto the por-Si surface gave rise to a modification of the CVC form, which acquired a rectifying profile typical of MIS structures.

During the measurements, we revealed a hysteresis in the direct CVC branch, when varying the voltage from negative to positive values and backwards. It should be noted that an increase in the current was observed at direct voltages above 3 V, which could be associated with the electric breakdown of the dielectric SiO_x film. The observable hysteresis could also be a result of the nonequilibrium filling of surface states in the film, which exchanged electrons with the semiconductor and, in such a way, stimulated complicated relaxation processes in the experimental structures [13, 21, 22].

In order to study the mechanisms of charge carrier transport in por-Si-based structures, the temperature dependences of the conductivity G in the interval 80–325 K were examined. They are shown in Fig. 2. The deposition of a SiO_x film onto the surface of a porous layer resulted in a reduction of the SiO_x/por-Si/Si heterostructure conductivity in comparison with the initial por-Si specimen in the whole indicated temperature interval. The temperature dependences of the conductivity are well described by the exponential dependence, which testifies to the activation mechanism of charge transfer in the experimental specimens. By analyzing the variation character of the $G(T)$-dependence for SiO_x/por-Si/Si heterostructures, two temperature sections can be distinguished: with approximate limits of 80–140 K and 140–290 K.

On the basis of the temperature dependences of the specific resistance for the experimental por-Si-based structures plotted in the $\log G^{-1}$ versus T^{-1} coordinates (see the inset in Fig. 2), the activation energy of conductivity can be evaluated. Calculated from the slope of the $\log G^{-1}(T^{-1})$-curve, the conductivity activation energy for por-Si was found to equal about 0.05 eV. In the case of SiO_x/por-Si/Si structure, the activation energy was equal to 0.11 eV in the temperature interval 140–290 K.

The processes of charge relaxation in por-Si-based structures were studied with the help of thermoactivation spectroscopy. In the case of disordered systems, including silicon oxide nanosystems, the levels of nonequilibrium charge carrier capture are arranged quasicontinuously according to the activation energy value. In order to determine the activation energies of electrically active defects in the experimental structures, TSD currents were measured. The temperature dependences of the depolarization current had a similar character for the por-Si/Si and SiO_x/por-Si/Si structures: they were characterized by the thermally stimulated charge emission starting from nitrogen temperatures and a wide band with the increasing current, when approaching room temperature (Fig. 3). In addition, the TSD spectrum of the initial por-Si/Si specimen demonstrated larger values of depolarization current in comparison with the spectrum registered for the SiO_x/por-Si/Si structure.

The TSD spectra were analyzed in the framework of the phenomenological theory for TSD currents in disordered insulators [23]. In Fig. 4, the calculation results obtained for the energy distribution of the state filling density are depicted. The calculations were carried out numerically on the basis of the Tikhonov regularization algorithm. The energy spectrum was not characterized by discrete energy values, but a definite distribution, which can be associated with the disordered character of the por-Si structure.

By analyzing the TSD spectrum, the energy distribution of the state filling density was determined. Levels of charge carrier capture, different by their nature and activation energy, were revealed in the intervals 0.2–0.3, 0.4–0.5, and 0.55–0.7 eV. By analogy with SiO_2, we may assume that the band at 0.2–0.3 eV corresponds to the activation energies of hydrogen ions H^+, and the capture levels at 0.4–0.5 and 0.55–0.7 eV are created by electrically active defects at the Si/SiO_x interface [11, 24]. The deposition of a SiO_x film onto the por-Si layer surface was acconpanied by a shift of the 0.4–0.5-eV-band toward

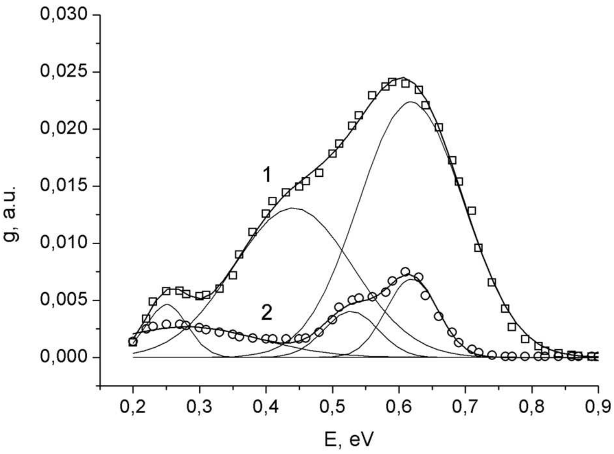

Fig. 4. Energy distributions of the state filling density in por-Si/Si (*1*) and SiO_x/por-Si/Si (*2*) structures

higher energies. This fact can be explained by a modification of the molecular composition of the surface coating on por-Si nanocrystals.

4. Conclusions

On the basis of the integrated study of the electric properties of SiO_x/por-Si/Si heterostructures, the processes of charge transport through the insulator into silicon nanocrystals and the relaxation of nonequilibrium charge carriers in those disordered nanosystems have been analyzed. A hysteresis in the direct CVC branch is revealed. It can be associated with the electric breakdown of the dielectric SiO_x film and the nonequilibrium filling of surface states.

The temperature dependences of the conductivity in por-Si-based structures are analyzed. The activation mechanism of charge transport in those nanosystems is established. On the basis of experimental results, the conductivity activation energy is determined in the temperature interval 140–290 K. Its value amounts to about 0.05 eV in the case of por-Si/Si structure and about 0.11 eV in the case of SiO_x/por-Si/Si heterostructure.

The energy distribution of the density of filling of nonequilibrium-charge-carrier capture levels, $g(E)$, which was calculated from the temperature dependences of the TSD current, is found to have maxima in the energy intervals 0.2–0.3, 0.4–0.5, and 0.55–0.7 eV. The deposition of an oxide film onto the por-Si surface resulted in a change of the state filling density in various energy intervals. Hence, the obtained results extend the application scope of silicon oxide nanosystems in optoelectronic devices, memory cells, and resonance tunneling diodes.

1. J. Robertson. High dielectric constant gate oxides for metal oxide Si transistors. *Rep. Prog. Phys.* **69**, 327 (2006) [DOI: 10.1088/0034-4885/69/2/R02].
2. A. Dutta, S. Oda, Y. Fu, M. Willander. Electron transport in nanocrystalline Si-based single electron transistors. *Jpn. J. Appl. Phys.* **39**, 4647 (2000) [DOI: 10.1143/JJAP.39.4647].
3. G.G. Kareva, M.I. Vexler. Electrical phenomena in a metal/nanooxide/p^+-silicon structure during its transformation to a resonant-tunneling diode. *Semiconductors* **47**, 1084 (2013) [DOI: 10.1134/S1063782613080083].
4. V.A. Gritsenko, K.A. Nasyrov, Yu.N. Novikov, A.L. Aseev, S.Y. Yoon, Jo-Won Lee, E.-H. Lee, C.W. Kim. A new low voltage fast SONOS memory with high-k dielectric. *Solid-State Electron.* **47**, 1651 (2003) [DOI: 10.1016/S0038-1101(03)00174-6].
5. S. Watanabe, M. Maeda, T. Sugisaki, K. Tsutsui. Fluoride resonant tunneling diodes on Si substrates improved by additional thermal oxidation process. *Jpn. J. Appl. Phys.* **44**, 2637 (2005) [DOI: 10.1143/JJAP.44.2637].
6. V.D. Kalganov, N.V. Mileshkina, E.V. Ostroumova. Tunnel emission of electrons in photo-field detectors and in an Auger transistor in very strong electric fields. *Semiconductors* **37**, 354 (2003) [DOI: 10.1134/1.1561532].
7. N. Asli, M.I. Vexler, A.F. Shulekin, P.D. Yoder, I.V. Grekhov, P. Seegebrecht. Threshold energies in the light emission characteristics of silicon MOS tunnel diodes. *Microelect. Reliability* **41**, 1071 (2001) [DOI: 10.1016/S0026-2714(01)00079-8].
8. K. Yano, T. Ishi, T. Hashimoto, T. Kobayashi, F. Murai, K. Seki. Room-temperature single-electron memory. *IEEE Trans. Electron. Dev.* **41**, 1628 (1994) [DOI: 10.1109/16.310117].
9. A.G. Cullis, L.T. Canham, P.D.J. Calcott. The structural and luminescence properties of porous silicon. *J. Appl. Phys.* **82**, 909 (1997) [DOI: 10.1063/1.366536].
10. O. Bisi, S. Ossicini, L. Pavesi. Porous silicon: a quantum sponge structure for silicon based optoelectronics. *Surf. Sci. Rep.* **38**, 1 (2000) [DOI: 10.1016/S0167-5729(99)00012-6].
11. L.S. Monastyrskii, T.I. Lesiv, I.B. Olenych. Composition and properties of thin solid films on porous silicon surface. *Thin Solid Films* **343–344**, 335 (1999) [DOI: 10.1016/S0040-6090(98)01597-1].
12. I.B. Olenych. Stabilisation of surface and photoluminescent properties of porous silicon. *Ukr. J. Phys. Opt.* **12**, 54 (2011) [DOI: 10.3116/16091833/12/2/54/2011].
13. L.M. Sorokin, L.V. Grigor'ev, A.E. Kalmykov, V.I. Sokolov. Structural properties and current transport in a nanocomposite formed on a silicon surface by oxidation of the porous layer. *Phys. Solid State* **47**, 1365 (2005) [DOI: 10.1134/1.1992619].
14. A.E. Pap, K. Kordas, G. Toth, J. Levoska, A. Uusimaki, J. Vahakangas, S. Leppavuor. Thermal oxidation of porous silicon: Study on structure. *Appl. Phys. Lett.* **86**, 041501 (2005) [DOI: 10.1063/1.1853519].
15. G. Maiello, S. La Monica, A. Ferrari, G. Masini, V.P. Bondarenko, A.M. Dorofeev, N.M. Kazuchits. Light guiding in oxidised porous silicon optical waveguides. *Thin Solid Films* **297**, 311 (1997) [DOI: 10.1016/S0040-6090(96)09488-6].
16. A.M. Dorofeev, N.V. Gaponenko, V.P. Bondarenko, E.E. Bachilo, N.M. Kazuchits, A.A. Leshok, G.N. Troyanova, N.N. Vorosov, V.E. Borisenko, H. Gnaser, W. Bock, P. Becker, H. Oechsner. Erbium luminescence in porous silicon doped from spin-on films. *J. Appl. Phys.* **77**, 2679 (1995) [DOI: 10.1063/1.358735].
17. T. Nikitin, L. Khriachtchev. Optical and structural properties of Si nanocrystals in SiO_2 films. *Nanomaterials* **5**, 614 (2015) [DOI: 10.3390/nano5020614].
18. D. Nesheva, C. Raptis, A. Perakis, I. Bineva, Z. Aneva, Z. Levi, S. Alexandrova, H. Hofmeister. Raman scattering and photoluminescence from Si nanoparticles in annealed SiO_x thin films. *J. Appl. Phys.* **92**, 4678 (2002) [DOI: 10.1063/1.1504176].
19. N.S. Averkiev, L.P. Kazakova, N.N. Smirnova. Carrier transport in porous silicon. *Semiconductors* **36**, 336 (2002) [DOI: 10.1134/1.1461413].
20. O.V. Vakulenko, S.V. Kondratenko, B.M. Shutov. Varistor-like current-voltage characteristic of porous silicon. *Semicond. Phys. Quant. Electron. Optoelectron.* **2**, 88 (1999).
21. D.I. Bilenko, O.Ya. Belobrovaya, E.A. Zharkova, I.B. Mysenko, E.I. Khasina. The effect of adsorption on the electrical properties of structures based on oxidized porous silicon. *Semiconductors* **36**, 466 (2002) [DOI: 10.1134/1.1469197].
22. L.V. Grigor'ev, A.E. Kalmykov, V.I. Sokolov, L.M. Sorokin. Transport properties of a heterogeneous composite: Thermally oxidized silicon micropowder. *Tech. Phys. Lett.* **33**, 199 (2007) [DOI: 10.1134/S1063785007030054].
23. Yu.A. Gorokhovatskii, G.A. Bordovskii. *Thermally Stimulated Current Spectroscopy of High-Impedance Semiconductors and Insulators* (Nauka, 1991) (in Russian).
24. I. Olenych, B. Tsizh, L. Monastyrskii, O. Aksimentyeva, B. Sokolovskii. Preparation and properties of nanocomposites of silicon oxide in porous silicon. *Solid State Phenom.* **230**, 127 (2015) [DOI: 10.4028/www.scientific.net/SSP.230.127].

Received 08.08.15
Translated from Ukrainian by O.I. Voitenko

І.Б. Оленич, Л.С. Монастирський, Б.П. Коман

ЕЛЕКТРИЧНІ ВЛАСТИВОСТІ
ОКСИДОКРЕМНІЄВИХ ГЕТЕРОСТРУКТУР
НА ОСНОВІ ПОРУВАТОГО КРЕМНІЮ

Р е з ю м е

Методами вольт-амперних характеристик і термоактиваційної спектроскопії вивчено процеси перенесення та релаксації носіїв заряду в оксидокремнієвих гетероструктурах на основі поруватого кремнію. Досліджено температурні залежності провідності експериментальних структур в інтервалі 80–325 К та визначено енергію активації електропровідності. На основі температурних залежностей струму деполяризації розраховано енергетичний розподіл локалізованих електронних станів, які впливають на процеси перенесення заряду у структурах на основі поруватого кремнію. Проаналізовано вплив поверхневого покриття поруватого шару тонкою плівкою SiO_x на його електричні характеристики. Отримані результати розширюють перспективу застосування оксидокремнієвих наносистем.