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DC conduction in free-standing porous silicon

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In this article, we have studied electrical conduction of free-standing porous silicon (FPS) and its comparison with porous silicon (PS). P-type unpolished silicon wafers are used for fabrication of the samples. Dimethylformamide (DMF) instead of ethanol, different current density and various anodization times are applied for preparation. Then, SEM images and morphology of the samples considered. Thickness and porosity of the samples are measured by gravimetric method and confirmed by SEM analysis. Electrical behavior of PS samples has been investigated in ambient air as a function of the temperature in the interval 200 – 300 K. In the next step, after preparation of PS, the porous layer is separated from substrate to get FPS. The dc electrical conduction of FPS filled with a polar dielectric liquid was investigated. The two contact I-V characteristic is determined by metal/PS rectifying interface, whereas, a linear dependence of the current vs. voltage was found for our FPS samples in the presence of polar liquids. Our results showed that with increasing or decreasing dielectric constants of polar liquids, dc conduction of FPS increased or decreased, respectively. The concentration of free holes is increased by condensation of dielectric liquids. A model of the dielectric confinement for charge carriers is applied to explain the dependence of dc conduction of FPS on the dielectric constant of the ambience of the Si nanostructures.

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1. Introduction

In recent years, porous silicon (PS) is one of the most actively researched materials for its possible use due to various applications like photoluminescence [1], optical emission [2], waveguide [3], and solar cell [4]. However, these applications require detailed knowledge on the electrical and optical properties of this material. Study on electric transport in porous materials is a challenging problem. In particular, an important issue in understanding the electrical transport of PS is how to interpret the PS dc conductivity behaviour [5].

On the other hand, the existence of free charge carriers in PS or Si nanostructures is a complex phenomenon, which concerns binding energy of a charge carrier in nanostructures with a dielectrically modified ambience. The importance of the dielectric confinement for the binding energy of hydrogenic impurities and excitons in semiconductor nanostructures was discussed by Keldysh [6].

Only recently the electrical conduction [7] and solar cells [8] in free-standing porous silicon (FPS) were reported. In fact the electrical characteristics of FPS are difficult to consider due to its fragility, environmental surface sensitivity, and critically structure dependence on process conditions. In addition, PS composes a disordered material, which is a network of Si nanostructures randomly connected.

In a previous work [9] surface resistivity and activation energy in FPS was investigated by using van der Pauw technique. It was found that surface resistivity and activation energy of PS samples increased for FPS samples. In this work the electrical behavior of PS samples in the range of 200 – 300 K employing a two contact technique and the dc electrical conduction of FPS samples filled with a polar dielectric liquid were investigated.

2. Experimental

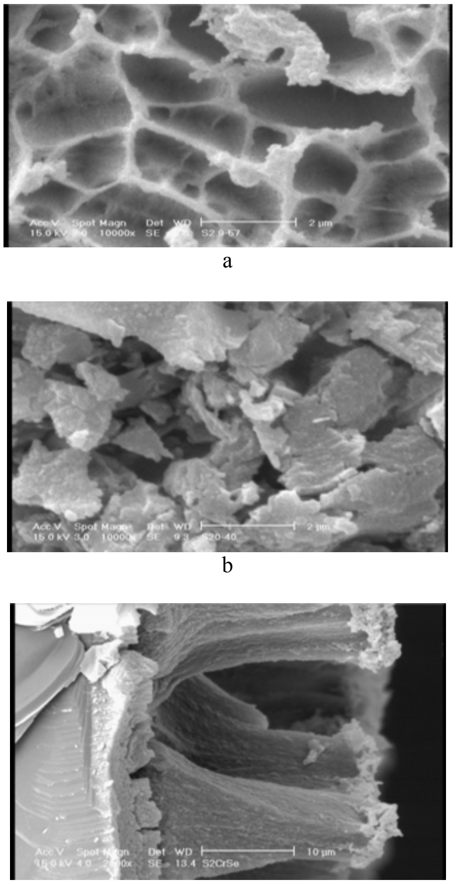
Free-standing films were obtained from p-type silicon substrate (100) oriented with resistivity of 0.3-0.4 Ω cm. Before anodization, an Al ohmic back layer is evaporated on the backside of the wafers followed by annealing process at 550ºC for 20 minutes. The wafer was anodized with different current densities of 20 and 40 mA/cm^2 and etching times of 20, 30, and 40 min. Two distinctly different electrolytes are used. In the first electrolyte, ethanol has been used and in the second, DMF. Characteristic of PS samples with various parameters is listed in Table 1. Porosity and thickness of the PS samples where measured by gravimetric method [10] and confirmed by SEM analysis.

Table 1. Characterizations of PS samples with different parameters.

Sample	Current density (mA/cm^2)	Etching time (min)	Electrolyte Concentration (1:1:1)	Porosity (%)	Thickness (μm)
PS-1	20	30	$HF:C_2H_5OH:H_2O$	31	7.8
PS-2	20	40	$HF:C_2H_5OH:H_2O$	42	10.1
PS-3	40	20	$HF:C_2H_5OH:H_2O$	58	13.2
PS-4	20	30	$HF:DMF:H_2O$	55	17.8
PS-5	20	40	$HF:DMF:H_2O$	63	18
PS-6	40	20	$HF:DMF:H_2O$	73	18.5

3. Results and discussion

Fig. 1 shows SEM images of some typical samples which are taken by Philips XL30 model SEM. As shown in the figure, in the samples made by DMF (Fig. 1(a)), the better regularity of pores in comparison with made by ethanol (Fig. 1(b)) is seen. The measurements show that for samples with higher current density and etching time, higher porosity and thickness are achieved [11, 12]. Also, with more attention we understand that the role of the current density has been stronger than the etching time for increasing the porosity and thickness in the same electrolyte. The Fig. 1(c) is SEM verification for this issue.



a

b

c

Fig. 1. Typical SEM images: plain view of samples made by (a) DMF (2.9 mA/cm^2, 57 min, 2%:95%:3%) and (b) ethanol (PS-2), the scale bar is 2 µm. (c) Cross-section view of sample made by DMF (45 mA/cm^2, 55 min, 1:1:1), the scale bar is 10 µm.

In order to study electrical conduction behavior of PS samples, current-voltage characteristics are measured in a two contact technique. A circular spot metal contact on the sample is prepared by silver paste. The voltage is applied between the metal contact and the ohmic back contact. Forward bias means that the metal contact on the top of the PS layer is negative with respect to the ohmic back contact. There are two rectifying barriers, one could be in metal/PS contact and the other is PS/Si. The former is ignored because PS has high density of states at the Fermi level of the order of 10^{19} cm^{-3} eV^{-1} [13] that pins the Fermi level at the PS/Si interface, and then no depletion should occur at the metal/PS interface. This contact should almost behave in an ohmic manner. On the other hand, the high density of states might pin the Fermi level at the other heterojunction, the PS/Si boundary. The I-V characteristics of such structures are usually represented as a serial combination of a diode and a resistor [14]. For thin PS layers (of order 1µm or less [15,16]) the PS resistance is small therefore in reverse bias, the current will be limited by the diode resulting in rectifying characteristics. Thick PS samples (>10 µm) will have nearly symmetric I-V characteristics due to high resitance. The conduction behavior of PS layers in high electric fields (over thousand volts/cm) [17, 18] and in temperature range of 200-320 K (the selection of this temperature range is on the basis of self heating effects and instability of the hydride surfaces) is mostly suggested to analyze by the well known Poole-Frenkel relation which applies for transport via electric-field-enhanced thermal excitation of carriers from coulombic traps [14, 15, 16]. Measurements of 5 month aged samples are performed in the range of 200-300 K in air and day light. I-V curves exhibit diode like rectification, although we expect to observe nearly symmetric as shown in Figs. 2 and 3. This behavior is due to the aging problem. During 5 months after preparation of the samples, impurities like oxygen and hydrogen atoms existed in environment to form bonds with PS samples. These bonds decrease the PS density of states in PS/metal interface, and then the role of rectifying barrier isn't ignorable. It has been reported that, some phenomena such as sensing and photoluminescence show strong decrease for their intensities due to aging effect [19, 20].

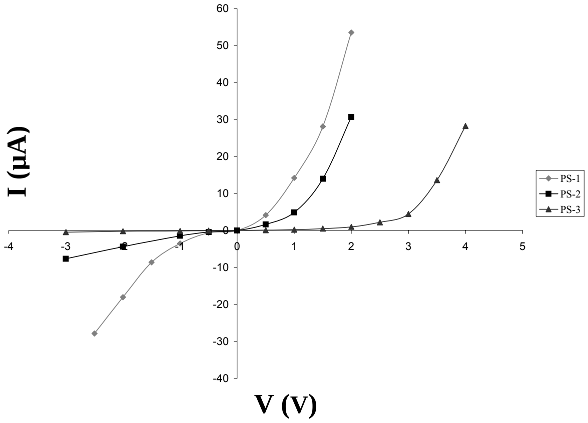


Fig. 2. I-V characteristics of PS-1, PS-2, and PS-3 are taken at room temperature. Ethanol is used in electrolyte.

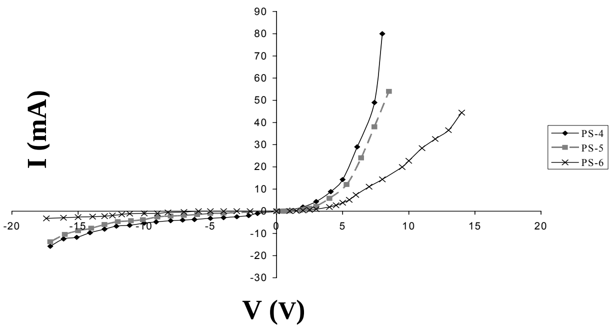


Fig. 3. I-V characteristics of PS-4, PS-5, and PS-6 are taken at room temperature. DMF is used instead of ethanol in electrolyte.

The PS conduction depends on the applied voltage because the electric field reduces the barrier energy and thus enhances conduction. The irregulare structure of PS disturbs the electric-field distribution at the trapping site, and then an excited carrier doesn't move freely because of the strong disorder [15]. If we prepare more regular and larger PS structure, the disturbance in electric-field distribution at the trapping site becomes less, thus the excited carrier moves more freely.

The samples prepared with DMF flows more current than the ones made by ethanol in the same voltage range. The result can be seen in Fig. 2 that current scale is μA whereas in Fig. 3 is mA. In DMF prepared samples, the PS crystallites with respect to those of the ethanol prepared samples are larger, more regular and homogenous SEM images, as it reported in Ref. 9, confirm this issue. Increase in dimensions of PS crystallites causes that charge carriers have more PS environment to move. Thus we continued our measurements on the DMF made samples at temperatures of 200, 230, and 255 K which have been shown in Figs. 4, 5, and 6, respectively. The reason for choosing the mentioned temperature interval is that the temperature in this range can release carriers from traps which are almost impurities here. As shown in the figures, in each temperature, the flowing current decreases with increasing porosity for the same voltage. Because with increasing porosity there will be more pores, smaller PS crystallites, more disorder and less PS environment for move, therefore the resistivity of samples increase.

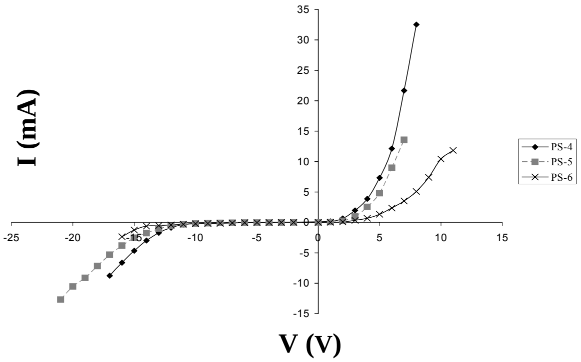


Fig. 4. The I-V characteristics of PS-4, PS-5, and PS-6 at 200 K.

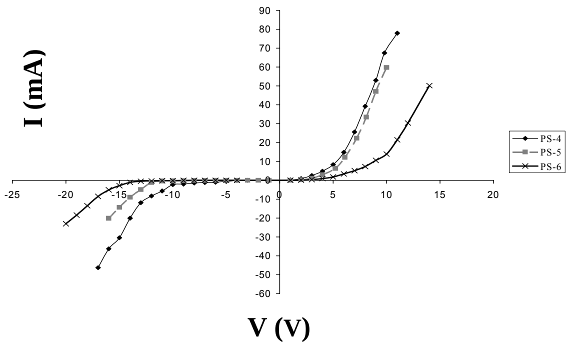


Fig. 5. I-V characteristics of PS-4, PS-5, and PS-6 at 230 K.

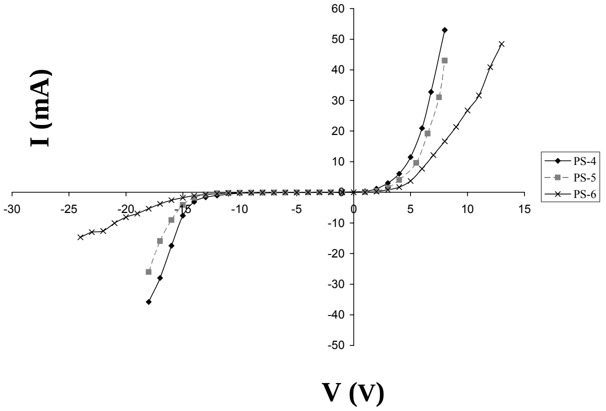


Fig. 6. I-V characteristics of PS-4, PS-5, and PS-6 at 255 K.

By comparing Figs. 4, 5, and 6, we observed that the flowing current decreases with decreasing temperature for the same voltage. The reduction of electrical conduction in our PS samples mentioned in the above experiments is due to the reduction of the concentration and mobility of charge carriers'.

There are different methods for producing FPS, our method was mechanical method [21-25]. Therefore, after the growth of porous layer, a stainless and clean razor was used for detaching the porous layers. In such a way free-standing fragments with an average of some millimeters were obtained. With more attention to I-V curves for PS samples, it can be concluded that voltage in spite of temperature has major role to creating carriers in PS samples. So, I-V characteristics for FPS samples have done only at room temperature.

I-V characteristics of FPS are measured by a two contact technique with filling polar dielectric liquids such as ethanol, methanol and cyclohexane. The contacts were checked by other measurement to insure that they are ohmic contacts. We neglected injection- or ionization-related phenomena for these measurements because the electric field was smaller than 10^2 V/cm [24], then the conduction of holes with increasing the voltage doesn't reduce. Before using the liquids, we didn't have any current by applying voltage because there was no connection among PS crystallites. The liquids interconnect the PS crystallites and cause the flowing current. Fig. 7, 8, and 9 show I–V curves in the presence of ethanol, methanol, and cyclohexane, respectively. Almost linear dependence of the current vs. voltage was found for our FPS samples in the presence of polar liquids. The reason could be due to elimination of PS/Si contact for the FPS samples.

The electrical conduction of FPS samples is the slope of the I-V curves in the presence of the liquids. The I-V curves show that the electrical conduction of FPS sample decreases with the same trend of PS sample. Since the porosity of PS samples increases, consequently the surface of PS crystallites increases. Then, absorbance of polar liquids to the surface of Si crystallites becomes more leading to increase in donor like states which result in higher conduction of low porous samples compared with high porous ones for the same dielectric liquid. This indicated that FPS samples keep similar texture with PS samples. The Si nanocrystal is approximated as an infinite cylinder. Because diameter of Si nanocrystal is much larger than the Si lattice constant, the dielectric constant inside the cylinder is ε_s =11.9 like for bulk Si. However, some papers are proposed the dielectric constant of PS in the range of 5-11.9 [15, 26, 27] whereas it is ε_d =25 for ethanol, ε_d =33 for methanol and ε_d =2 for cyclohexane. Therefore PS crystallites decrease electrical conduction of ethanol and methanol, and increase electrical conduction of cyclohexane. The effect of dielectric ambience for the free-carrier concentration in Si nanocrystals is examined by filling the pores in FPS with the polar dielectric liquids. The liquids are chosen because they have a large dielectric constant and their condensation in the pores influences in the effective dielectric constant of PS, significantly.

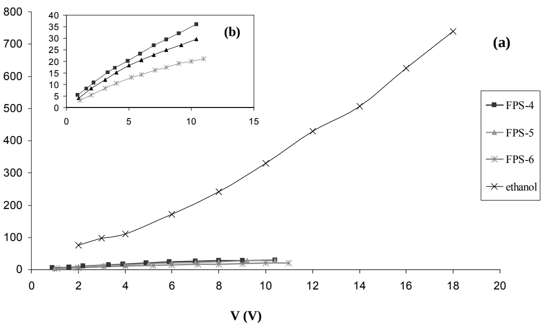


Fig. 7. (a) The I-V characteristics of FPS-4, FPS-5, and FPS - 6 in the presence of ethanol (b). For better comparison ethanol curve has been removed.

When we use liquid of dielectric constant (ε_d) which $\varepsilon_s \neq \varepsilon_d$, surrounded by a dielectric medium. The self-image effect due to different ε_s and ε_d causes dielectric confinement which leads to an increase or decrease of the binding energy of a charge carrier in the Coulomb potential of another one depending on whether $\varepsilon_s > \varepsilon_d$ or $\varepsilon_s < \varepsilon_d$, respectively [6]. Mobility (μ) is also affected by the dielectric confinement. If $\varepsilon_s < \varepsilon_d$, surrounding Si crystallites screens the potential fluctuations related to the self-image effect and therefore μ increases [26]. The presence of dielectric liquids activate the boron acceptors in PS made from Si (p-type doped by boron), then the concentration of holes increases. Our experimental results show that the liquid with larger dielectric constant has more roles in activation of such boron acceptors.

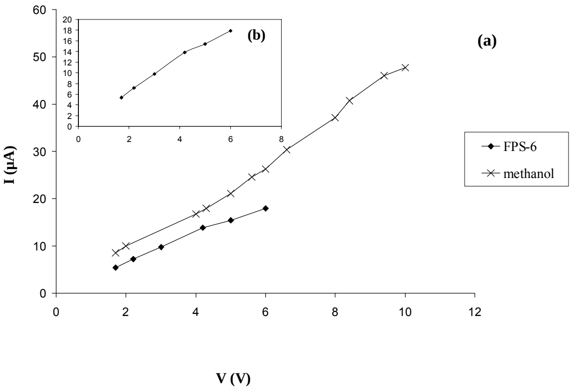


Fig. 8. (a) The I-V characteristic of FPS-6 in the presence of methanol (b). For better comparison methanol curve has been removed.

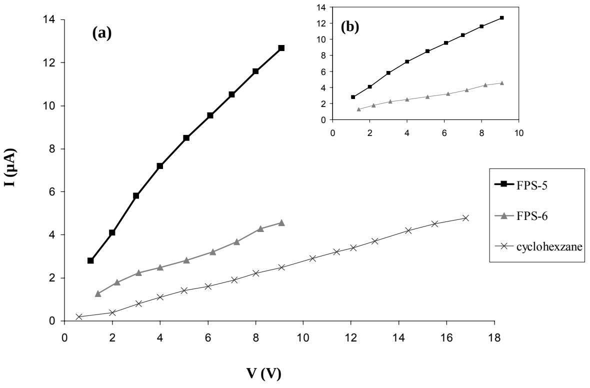


Fig. 9. (a) The I-V characteristics of FPS-5 and FPS-6 in the presence of cyclohexane (b). For better comparison cyclohexane curve has been removed.

The dependence of the electrical conduction of PS crystallites with polar dielectric liquids on the ambient dielectric constant is shown in Fig. 10 (solid circles). The error bars correspond to the accuracy of measurements. As it is explained, this can be understood if considering an increase or decrease of hole concentration and mobility in PS crystallites after using a polar dielectric liquid whether $\varepsilon_s < \varepsilon_d$ or $\varepsilon_s > \varepsilon_d$, respectively.

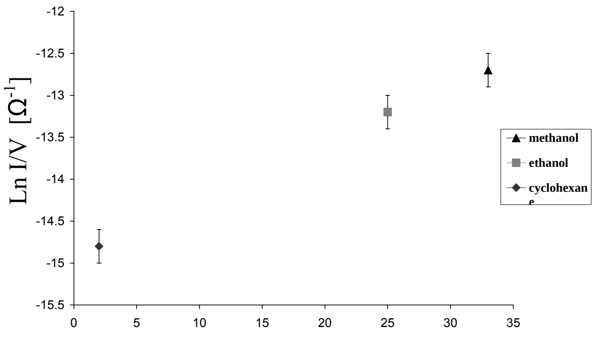


Fig. 10. Dependence of dc conduction of FPS-6 with polar dielectric liquids.

4. Conclusion

In this work, we have fabricated different porous silicon samples which showed different properties according to various anodization parameters. Then the samples which are made by electrolyte contained DMF are chosen because their morphology revealed ordered column like structure. The I-V characteristics of PS samples are measured in the temperature interval 200-300 K after 5 months which showed a diode like behavior. It is understood that Si atoms on the surface make bonds with impurity atoms like hydrogen and oxygen. These bonds give the PS/metal barrier a dominant contribution in electrical conduction of these samples.

It is observed that, in each temperature, the flowing current decreases with increasing porosity for the same voltage. Also the flowing current decreases with decreasing temperature for the same voltage. Moreover, it is found that decreasing temperature keeps similar behavior for I-V characteristics but in lower flowing current.

With attention to the results and avoiding from condensation of polar liquids in the low temperatures, we measured I-V curves of FPS fragment of the samples just in the room temperature. The dc electrical conduction of FPS was revealed only in the presence of polar liquids because these liquids activate the boron acceptors and make interconnections among PS crystallites then hole carriers increase whereas they have some ways for move. The most important reason for choosing polar liquids is that they don't make effective influence in the structure of PS crystallites.

The dependence of the electrical conduction of PS crystallites in presence of polar dielectric liquids on the ambient dielectric constant is related to increase or decrease of hole concentration and mobility in PS crystallites after using a polar dielectric liquid. Dielectric confinement causes an increase or decrease of the binding energy of a charge carrier in Coulomb potential whether $\varepsilon_s > \varepsilon_d$ or $\varepsilon_s < \varepsilon_d$, respectively. The mobility is also affected by the dielectric confinement which is important for the screening of potential fluctuations. The electrical conduction of PS crystallites decreases with the same trend of increasing porosity for PS samples. This shows that by separating PS layer, the structure of PS crystallites hasn't still changed.

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