Nonlinear electrical transport in porous silicon

M. Ben-Chorin, F. Möller, and F. Koch

Technische Universität München, Physik-Department E16, 85747 Garching, Germany

(Received 16 August 1993)

We present a study of the electrical transport in porous Si layers prepared by anodic etching of two different kinds of (100) p-type Si substrates. It is shown that by choosing a sufficiently thick layer, the problem of injection from the contacts can be eliminated. In this way we measure the intrinsic transport properties. The results suggest that a Poole-Frenkel type of mechanism accounts for the observed electric-field-enhanced conduction.

There is a great deal of current interest in the properties of porous Si (PS).[1,2] This material is known to be composed of a network of small Si particles with a typical size of a few nanometers.[2] PS has very efficient luminescence (in the visible regime), well above the band gap of crystalline Si.[1] This is attributed to carrier confinement by the crystallites, which leads to an increase of the band gap with respect to that of bulk Si.[1] In addition, a high density of surface states, e.g., dangling bonds,[3] has been observed in PS, due to the large internal surface area of the porous structure (~ 600 m^2/cm^3).[4] PS is insulating with a typical resistivity that is five orders of magnitude larger than that of intrinsic crystalline Si.[5] From the transport point of view the properties of this material are unique. PS cannot be regarded as a bulk wide-band-gap semiconductor since it has a granular structure on a length scale of nanometers. On the other hand, it is not amorphous either. The small crystallites retain the lattice structure and orientation of the bulk Si.[6] In a sense, PS can be viewed as a disordered assembly of three-dimensional quantum wells.

The main reason for the interest in PS lies in the challenge of using this material in Si-based light-emitting devices. Several groups have reported on such devices, but all of them have quite low efficiencies.[7] Whereas the existence of electroluminescence is now well established, its mechanism is not yet understood, because very little is known about the electrical transport properties of the material and the contacts. The usual structure of PS-based electroluminescent devices does not allow one to distinguish between contact and bulk contributions to the electrical properties. In this paper we present a study of the dc transport characteristics of PS. We show that bulk and contact properties can be separated, and we analyze the voltage and temperature-dependent conduction in PS.

Samples used in this work are prepared by anodization of (100) p-type Si with two distinctly different resistivities

in a 1:1 solution of HF acid (49% in water) and ethanol. Before anodization the specimens are provided with Ohmic back contacts, either by Al evaporation followed by annealing (550 °C, 20 min), or by Ga plating. Etch-current densities and substrate resistivities for the various sample types are listed in Table I. After anodization, the samples are removed from the etch cell, rinsed with propanol, and allowed to dry under ambient conditions. Al rectangular contacts (2×1 mm^2) are then evaporated. Au, NiCr, and In contacts are used for some of the samples without a major effect on the results. The structure of the samples is shown in Fig. 1.

Current-voltage characteristics are measured in a two-terminal configuration. The voltage is applied between the metal contact and the Ohmic back contact. The current is recorded using a Keithley 617 digital electrometer. These measurements are performed at different temperatures in the range 200–320 K. The upper temperature is limited in part by the instability of the hydrided surfaces of PS and self-heating effects. The high resistivity of the material below ~ 200 K, which results in a very long dielectric relaxation time, sets the lower bound.

Figure 1 shows the *I-V* dependences for type-*A* samples with different thicknesses. The preparation conditions are identical except for the anodization time that

TABLE I. Preparation conditions for the different types of samples.

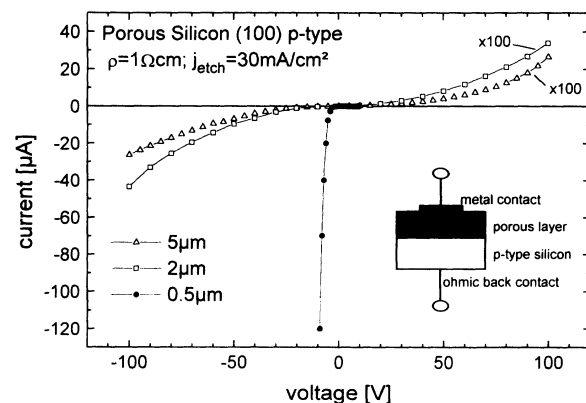| Type of sample	A	B
Substrate resistivity	5 Ω cm	75 mΩ cm
Etching current density	30 mA/cm^2	100 mA/cm^2

FIG. 1. The current-voltage characteristics of PS layers of type *A* with different thicknesses. The symmetrical behavior for the thick samples and the high resistance (note $\times 100$ is for both voltage polarities) show that the transport is limited by the bulk. Thin samples have contact-limited transport.

<u>49</u>   2981

controls the thickness. There are obvious differences. While the thin sample exhibits diodelike rectification, the thick PS layers have nearly symmetric *I-V* characteristics. The observations suggest that the layered structure consisting of the metal contact, the PS layer, and the doped Si substrate should be understood qualitatively in terms of a series combination of a voltage-dependent resistance and a rectifying barrier. The latter could be the metal-PS contact, or the boundary layer between PS and the substrate. From the curves in the figure it is clear that the sample should be sufficiently thick and that it is preferred to use the data for negative *V* for a quantitative study of transport in the bulk of the PS layer. In this way we can be sure that current flow through the sample is limited by the PS resistance. For thin layers, of order 1 μm or less, the samples begin to act like a diode (cf. Fig. 1) from which the resistance of the PS is not easily identified.

Figure 2 shows the dependence of the conductance I/V on the voltage for a typical, thick PS layer (type *B*, 12 μm) at various temperatures. At high temperatures *T* the conductance depends exponentially on $\sqrt{V}$ over a large range of applied voltages. With decreasing *T* there is clearly an additional Ohmic contribution that is independent of the voltage. By extrapolating in each case the square-root dependence to $V=0$ we arrive at the set of values given by the open points in Fig. 2. These values obey a thermally activated dependence plotted in Fig. 3 with an activation energy E_A of 0.5 eV. The overall dependence on temperature and voltage is of the form

$$G(V,T)=G_0 \exp\left[\frac{-E_A}{k_B T}\right]\exp\left[\frac{V}{V^*}\right]^{1/2}.$$

This suggests the well-known Poole-Frenkel relation, which applies for transport via electric-field-enhanced thermal excitation of carriers from Coulombic traps.[8] The Ohmic part of the conduction process becomes prominent at lower temperatures. This is the hopping type of transport to which we have referred in previous work.[9]
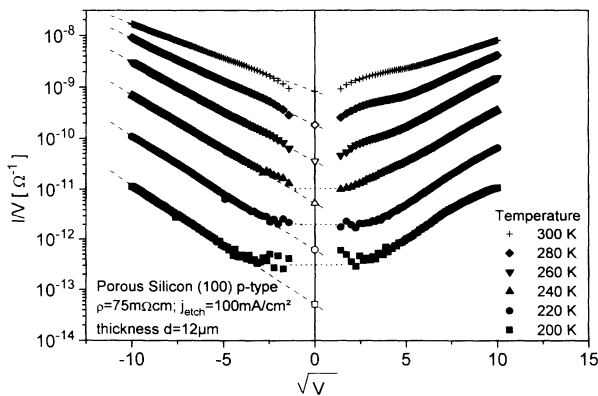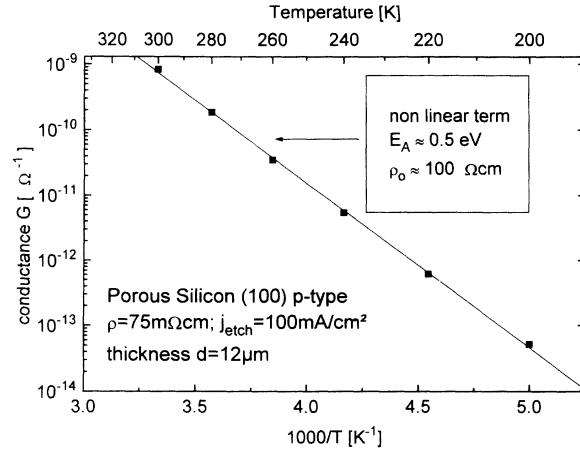

FIG. 3. Temperature dependence of the nonlinear conductances at $V=0$ for the data in Fig. 2

For conduction via the Poole-Frenkel mechanism there applies a specific expression for V^*. Another test, therefore, is provided by checking out and verifying the experimental dependences of this quantity. It is required that[8]

$$\sqrt{V^*}=\frac{kT}{e} \left/ \left[\frac{e}{\pi\epsilon_0\epsilon_r d}\right]^{1/2}\right.,$$

where ϵ_r is the relative dielectric constant and *d* is the layer thickness.

We first examine the linear dependence on *T* by plotting in Fig. 4 the experimental $\sqrt{V^*}$ values, which are the inverse slope of the straight-line fits in Fig. 2. For the *A* series of the materials we have made use of the thicknesses 15 μm$\pm$10% and 5 μm$\pm$10%. The *A* points are entered in Fig. 4 as closed and open circles after applying the $\sqrt{\frac{15}{5}}$ thickness scaling. The result is not inconsistent with a straight-line relation through the origin. Within the accuracy of the experiments we conclude that the required dependences on *T* and $\sqrt{d}$ are demonstrated. For *A*-type samples and the straight line in Fig. 4 the
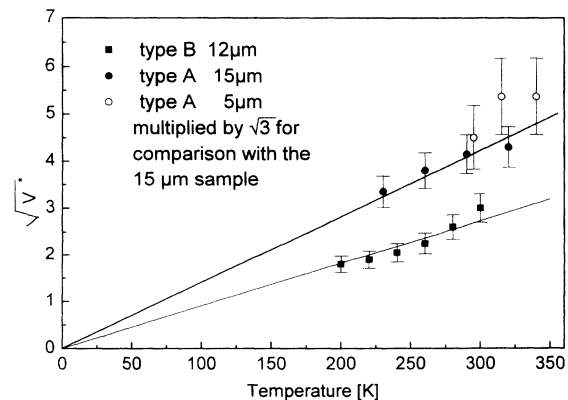

FIG. 2. The conductance vs square root of the applied voltage for a type-*B* sample at various temperatures. The dashed lines mark the fits for the extrapolation to $V=0$ in the forward direction. The Ohmic contribution is the difference between the dotted line and the open symbols.

FIG. 4. Temperature dependence of the $V^{*0.5}$ parameter of the Poole-Frenkel mechanism. The two *A* samples with 15- and 5-μm thickness are entered as solid and open circles, with the latter scaled according to the thickness. Error bars are confidence limits for the slope values.

ϵ_r value is ~ 10. For the B material it is $\epsilon_r \sim 5$.

There is a difficulty in the interpretation of the experimental results via the Poole-Frenkel mechanism. The use of this model for an inhomogeneous system like PS is questionable because there is no clear-cut meaning of ϵ_r for the microscopic trapping level. Nevertheless it is interesting to compare our estimated numbers with those obtained by optical experiments. These methods involve a shape-dependent effective medium averaging over regions of the order of μm, and lead to values of order $2-3$.[10] For transport in the Poole-Frenkel sense, a local electric field on the scale of a few tens of angstroms is relevant. This length is comparable with that of the structural features. The expected crystallite grain sizes for the A and B materials is $3-5$ nm, with the smaller values applying for A. For such small crystallites the notion of dielectric constant is not applicable. Therefore the ϵ values extracted from the Poole-Frenkel formula are proably not reflecting directly any physical feature of the material.

Before arguing for Poole-Frenkel behavior, we should reconsider the surface contact problems. For highly insulating substances, there could occur the space-charge-limited current transport. This leads to highly inhomogeneous fields and different I-V characteristics.[11] Our observations that the conductivity scales correctly with the thickness indicate that this mechanism is unlikely. The other possibility is an injection of carriers over a Schottky barrier at the contacts. This would lead to a dependence on $\sqrt{V}$, if the screening length is much larger than the sample thickness.[11] However, Schottky emission depends on the barrier heights at the metallic contact and at the PS-Si substrate interface. Thus, it is asymmetric with regard to the polarity. This mechanism does not appear reasonable in view of what has been obtained in Figs. 1 and 2.

We now return to the question of how the Poole-Frenkel mechanism can be applied to PS. It is generally accepted that PS is constructed from crystalline grains of a size of order $3-5$ nm which are connected in a random network by more or less insulating regions. These regions are narrow bridges of Si with high confinement energies. A strict application of the conventional Poole-Frenkel mechanism to this system is not reasonable. For this mode of conduction, the current is carried by charges which are thermally excited from traps to some transport band. The electric field reduces the barrier energy and thus enhances conduction. The simple $\sqrt{V}$ dependence applies only for Coulombic traps. This is wrong for PS, since the granular structure on the scale of $3-5$ nm will disturb the electric-field distribution at the trapping site. In addition, an excited carrier does not move freely (as it is supposed in the simple model) because of the strong disorder. These problems have been recognized when the Poole-Frenkel mechanism was applied to the interpretation of conductivity measurements in other disordered materials (e.g., a-Si). Pai[12] has addressed this question using a model developed by Onsager. This model incorporates disorder by assuming the excited carriers diffuse by Brownian motion under the influence of the long-range field of the Coulomb center. The results obtained by Pai show that the conductivity will have the same temperature dependence and a very similar field dependence to that predicted by the simple Poole-Frenkel case. The reason for this is that carriers move a long way under the influence of the Coulombic potential before they are able to escape and thus the details of the short-range disorder do not affect the general behavior. An escape of a carrier occurs when it reaches a critical distance R_c from the Coulombic center, for which the thermal energy kT is larger than the Coulombic energy, $e^2/\epsilon_0 \epsilon_r R_c$. For room temperature R_c can be as large as 1000 Å and for lower temperatures it will be even longer. Since this length scale is much larger than that of the porous structure, it is not surprising that the experimental results may be fitted using an effective dielectric constant. However, the value of ϵ_r obtained from the experimental data should be regarded more like a fitting parameter rather than an accurate measurement of the dielectric properties.

For transport the origin of the carriers is of great importance. It has been argued that the etching of PS is a self-limiting process, since in the small crystallites no free holes are available due to increased band gap.[2] On the other hand, the dopant atoms (in our case B), which are the source of the free carriers in the bulk material, are still present in the Si skeleton. One must expect that holes contributed by the doping levels are depleted by surface states. There are optical-absorption data available[13] that demonstrate the existence of both shallow and deep surface states on the Si grains. ac-conductivity measurements show that PS, unlike crystalline semiconductors, has a high density of states around the Fermi level.[9] Since the experimentally measured depth of the traps is ~ 0.5 eV below the transport band, it is reasonable to assume that the Fermi level is pinned in the energy region of surface states. This is supported by the fact that the activation energy is very similar to the width of the luminescence line (≈ 0.4 eV), which is a measure of the disorder in the energy spectrum. In addition, estimates of typical trap energies that are thought to participate in the optical-emission processes according to the surface-state model[14] are also of order 0.5 eV.

Keeping in mind the possible role of the surface in the transport, we realize that carriers can move both on the grains and between the grains. The conductance will register the larger of the two barrier types for a series addition of the resistances. For intergrain transport barriers an interesting fact should be noted. A single point charge e leaving a neutral grain and transferring to the neighboring one, which is of order of 30 Å away, requires a "Coulomb blockade" type of energy of order $e^2/\epsilon_0 \epsilon_r a$, where $a \sim 30$ Å. Depending on the choice of ϵ_r, this is as much as 0.5 eV. If the carrier is bound to a state inside the grain, the same order of magnitude applies.

Vial and co-workers have discussed extensively models in which the typical energy for an escape from a luminescing quantum particle of Si is modeled by an energy barrier of 0.3 eV. It is reasonable to expect that the barrier energy for a particle at the Fermi level is even larger.[15]

As a final point, we remind the reader that dc transport

in a random planar structure like PS is a highly selective process. Charges will move along special paths with the lowest barrier energies, those which offer the lowest resistance. A comparison with optical results, which represent a very different kind of average, is difficult to make in detail. However, the transport mechanism in high fields involves field-enhanced thermal excitation from traps. Although the microscopic nature of the Coulomb traps cannot be identified uniquely from transport data, it might be a deep level on the surface of the crystallites.

[1] L. T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).

[2] V. Lehmann and U. Gösele, Appl. Phys. Lett. **58**, 856 (1991).

[3] S. M. Prokes, W. E. Carlos, and V. M. Bermudez, Appl. Phys. Lett. **61**, 1447 (1992); M. S. Brandt and M. Stutzmann, *ibid.* **61**, 2569 (1992).

[4] R. Henrino, G. Bomchil, K. Barla, C. Bertrand, and J. L. Ginoux, J. Electrochem. Soc. **134**, 1994 (1987).

[5] R. C. Anderson, R. S. Muller, and C. W. Tobias, J. Electrochem. Soc. **138**, 3406 (1991).

[6] A. G. Cullis and L. T. Canham, Nature **353**, 335 (1991).

[7] A. Richter, P. Steiner, F. Kozlowski, and W. Lang, IEEE Electron Device Lett. **12**, 691 (1991); N. Koshida and H. Koyama, Appl. Phys. Lett. **60**, 347 (1992).

[8] J. Frenkel, Phys. Rev. **54**, 647 (1938).

[9] M. Ben-Chorin, F. Möller, and F. Koch, J. Lumin. (to be published).

[10] F. Müller, Ph.D. thesis, Technische Universität München, 1993.

[11] S. M. Sze, *Physics of Semiconductor Devices,* 2nd ed. (Wiley, New York, 1981), p. 432.

[12] D. M. Pai, J. Appl. Phys. **46**, 5122 (1975).

[13] F. Koch, V. Petrova-Koch, T. Muschik, A. Nikolov, and V. Gavrilenko, in *Microcrystalline Semiconductors: Material Science and Devices,* edited by F. M. Fauchet, C. C. Tsai, L. T. Canham, I. Shimizu, and Y. Aoyagi, MRS Symposia Proceedings No. 283 (Materials Research Society, Pittsburgh, 1992), p. 197.

[14] F. Koch, in *Silicon Based Optoelectronic Devices,* edited by M. A. Tischler, R. T. Collins, M. L. W. Thewalt, and G. Abstreiter, MRS Symposia Proceedings No. 298 (Materials Research Society, Pittsburgh, 1993), p. 319.

[15] J. C. Vial, A. Bsiesy, F. Gaspard, R. Herino, M. Ligeon, F. Muller, R. Romestain, and R. M. Macfarlane, Phys. Rev. B **45**, 14 171 (1992).