Two Meyer-Neldel Rules in Porous Silicon

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We observe two Meyer-Neldel rules for the dc conductivity in porous silicon. One rule corresponds to extended-states transport and the other to transport by thermally activated hopping. The quantitative resemblance of the first rule to the one found in hydrogenated amorphous silicon (*a*-Si:H) indicates that in samples in which it is observed the conduction takes place in an *a*-Si:H–like tissue that wraps the luminescent crystallites. In samples where the second rule is observed the conduction appears to be either by activated hopping in this disordered tissue, or by intercrystallite hopping. [S0031-9007(97)02616-1]

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Since the discovery that porous silicon (PS) may exhibit efficient visible photoluminescence (PL), there has been an extensive study of this material [1]. At present, it seems to be quite generally accepted that the PL is due to the quantum confinement effect in the small silicon crystallites [2,3]. It thus appears that the next fundamental issue concerning light emitting PS is the transport mechanism. This issue is of a quite general interest due to its obvious relation to electroluminescence and thus to the practical applications of this system [1]. Unlike the PL issue there is no agreement concerning the conduction path or the transport mechanism in PS. Present suggestions for the paths range from transport in the crystallites [4], diffusion [5], or tunneling [6] between the crystallites or on their surface [6–8]. Transport in a disordered silicon tissue (such as hydrogenated amorphous silicon, *a*-Si:H) which wraps the crystallites has also been suggested [9,10]. The proposed mechanisms include band conduction [11], activated hopping in the tails [9], activated deep states hopping [12], a Pool-Frenkel process [13], and activated hopping in a fractal network [14].

In this Letter we attempt to examine whether this rather large number of suggested paths and mechanisms can be narrowed down. For this purpose we use the Meyer-Neldel rule (MNR), which in the present context correlates the conductivity prefactor and the conductivity activation energy [15,16] (see below). We find quite convincingly that only two kinds of transport take place in PS, and that there is no need to introduce quantum confinement [17] effects.

Before turning to the conductivity data let us briefly review the established structure of PS [1]. This system has a coral-like structure, the members of which include individual crystallites. The typical width of these members, d, is a few nanometers. The crystallites form then a network of either continuous "quantum wires" [18] or disconnected "quantum dots" [4]. It is well known that as d decreases the peak of the PL curve is blueshifted [18]. The crystallites were argued [10,11,19–21] to be wrapped by a continuous "shell," which consists of disordered silicon [21] and related compounds [20] (such as SiO_xH_y).

For understanding the MNR approach taken in this Letter, consider a *p*-type semiconductor in which the conductivity is activated with temperature and can be written as

$$\sigma = \sigma_{00} \exp\left(-\frac{E_F - E_V}{kT}\right). \tag{1}$$

Here E_F and E_V are the energies of the Fermi level and the valence band edge, respectively, kT is the thermal energy, and σ_{00} is the microscopic prefactor [22]. On the other hand, one obtains the activation energy E_a and a prefactor σ_0 by fitting the experimental data to

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right). \tag{2}$$

Examination of this prefactor on PS layers, which have a luminescence peak centered around a photon energy, $h\nu$, of 2 eV, has yielded [9] σ_0 values lower than 10^{-3} (ohm cm)$^{-1}$. The interpretation given [9], based on theoretical expectations [22], was that the transport is due to activated band tail hopping rather than to transport above the mobility edge.

In order to examine the generality of this conclusion, we have carried out measurements of the temperature dependence of the dc conductivity on two sets of "free standing" (or "self supporting" [9]) PS samples, the preparation of which has been described elsewhere [10,21]. The PL of one set of samples was centered (at low temperatures) around $h\nu \approx 1.1$ eV, and the PL of the other set was centered around $h\nu \approx 1.7$ eV. Considering the correlation suggested [23] between the average diameter of the crystallites, the measured Raman spectra and the $h\nu$ values, we found [21] that the corresponding d values were 10 and 4 nm. This is in agreement with the quantum confinement interpretation of the luminescence data [1–3,18]. Correspondingly, we refer to the samples of the first set as mesoporous silicon and to samples of the other set as nanoporous silicon.

Typical $\sigma(T)$ data, obtained in the coplanar contacts configuration for these free standing "meso" and "nano" PS layers, are presented in Fig. 1. It can be seen that the measured activation energies are 0.71 and 1.03 eV, and the associated prefactors are extremely high [5×10^5 and 1.4×10^9 (ohm cm)$^{-1}$, respectively]. These values are in apparent contrast to the results and conclusions derived in Ref. [9], indicating that the dominant conduction mechanism is different here. On the other hand, the correlation we found between the high values of the activation energies and the corresponding high values of the prefactors suggests the existence of a MNR in PS. Since the determination of a MNR requires many data, and because of the above disagreement between our results and those of Ref. [9], we turned to an examination of the data available in the literature and presented them within the framework of the MNR.

Before considering the data, let us give a short introduction to the relation between the MNR and dc conductivity and briefly review the two models that were proposed to explain the observation of the MNR in the dc conductivity of semiconductors. In one model, known as the kinetic model [15], the MNR was suggested to be a result of the many possible ways to collect the many excitations required for a kinetic process. In this picture the characteristic energy of the MNR (E_{MNR}, see below) is that of the excitations, which in the present context should be typical of optical phonons. This model has also been applied [15] to a material which is closely related [19] to PS, i.e., *a*-Si:H. The model, while very appealing because of its generality and applicability to many processes in *a*-Si:H, has not been shown to explain the more detailed behavior of the dc conductivity of this material [16,24]. In particular, it did not explain the observation [24] of E_{MNR} values, which are much larger than the optical phonon energy, in *a*-Si:H materials of high defect concentration. On the other hand, the other, more traditional, model for *a*-Si:H was able to account for the more detailed behavior of the MNR parameters in this material [16,24,25]. This model, known as the "statistical shift" model, is based on the fact that $E_F - E_V$ is temperature dependent due to both the shrinking of the gap and the well known receding of E_F towards midgap with increasing temperature. The rate of the E_F shift was argued to depend then on the density of states (DOS) gradient towards midgap [16,24,25].

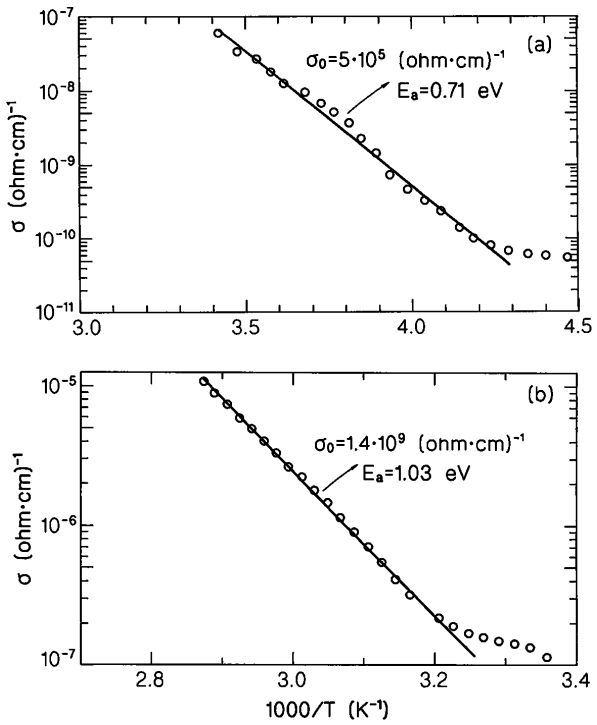

FIG. 1. Our measured temperature dependence of the dark conductivity in (a) mesoporous and (b) nanoporous silicon.

While at present the question of which of the above models is more appropriate for *a*-Si:H is not settled, the above discussion and the results found here for PS (see below) seem to indicate that the statistical shift model provides the more likely scenario for these materials. Accordingly, we present the MNR parameters using this model.

We have mentioned that $E_F - E_V$ is temperature dependent, and one can assume then that their relative position can be approximated by the linear dependence [16,25]

$$E_F(T) - E_V(T) = E_0 - \delta T\,, \tag{3}$$

where E_0 is the extrapolation, at $T = 0$, of the linear fit to the temperature dependence of $E_F - E_V$. If the conductivity takes place in extended states one finds that [16]

$$\sigma(T) = \left[\sigma_{00} \exp\left(\frac{\delta}{k}\right)\right] \exp\left(-\frac{E_0}{kT}\right). \tag{4}$$

A comparison of Eqs. (2) and (4) indicates that E_a will have the value of E_0, rather than $E_F - E_V$. Consequently, σ_0 will not be the microscopic prefactor σ_{00} associated with transport in extended states. For an amorphous semiconductor one expects [16] that the smaller the ratio between the density of band tail states and the density of deep (e.g., dangling bonds) states, the smaller the magnitude of δ. We further note that for such a material Eq. (4) will also be obeyed by the transport of activated hopping. In this case [26], however, the relevant level is not E_V, but the transport energy, E_t, where the dominant hopping transport in the band tails takes place.

Following the above explanation, one further expects that variations in δ will take place as E_F scans through a band gap region where the DOS changes [16,24,25]. In particular, one may get a linear relationship between δ and E_a. Following Eqs. (1)–(4), this means that the MNR will manifest itself by the relation

$$\ln(\sigma_0) = B_{\mathrm{MNR}} + \frac{E_a}{E_{\mathrm{MNR}}}\,, \tag{5}$$

where B_{MNR} and E_{MNR} are constants which are the *signature* of a specific system [16,24].

Returning to PS, we note that if the conduction in PS takes place through the disordered silicon tissue one would expect to observe the transport mechanisms known for disordered materials [16,22]. In particular, for extended-states transport one expects [16,22] relatively high σ_0 values. As mentioned above, relatively low conductivity prefactors [10^{-3} (ohm cm)$^{-1}$] have been reported for PS [9]. However, the present results and those of other workers [17,27,28] indicate much higher prefactors [larger than 10^3 (ohm cm)$^{-1}$; see below]. A very interesting finding in this context is the temperature dependence of the dc conductivity found by Lee and Lee [29]. They reported a change of the activation energy and the corresponding prefactor with temperature. Below 330 K they found that $E_a = 0.25$ eV with a low prefactor, while above this temperature they found that $E_a = 0.93$ eV with a high prefactor. Following the above discussion, one should interpret this transition as due to the existence of two temperature regions in each of which the transport is dominated by another mechanism. Moreover, this is a clear indication that two transport mechanisms can coexist in the same PS network.

Let us turn now to the analysis of the conductivity data within the framework of the MNR. In Fig. 2 we present all the prefactors and activation energies that we could derive by fitting Arrhenius plots to all available published $\sigma(T)$ results on PS that we could find [30]. Examining the data shown in this figure we note that there is an enormous spread of the measured activation energies, between 0.2 and 1 eV, and that the prefactors cover some 14 orders of magnitude. We can also see a general trend of an increase of the prefactor with increasing activation energy in agreement with the MNR [Eq. (5)]. The striking observation is, however, that all the data points belong to two well-separated groups, so that the results can be summarized by two MNRs, each relating to a group of data points. Accordingly, we have plotted in Fig. 2 the two best-fit (solid) lines that match the two groups of points. The fact that the two groups of PS data points are *well separated* clearly indicates that there are *two different* distinguishable transport mechanisms in PS. Following the above discussion, we attribute the lower line to one transport mechanism and the upper line to another transport mechanism. The fact that the data points of the various research groups mix around the two MNR lines indicates that the conclusions to be derived below are general for the PS system, and that they are not limited to a specific laboratory or particular preparation conditions. We also note in passing that data points obtained for samples in the sandwich configuration [9,11,14] mix well with data points found on samples in the coplanar configuration [10,17,27]. This provides probably the first indication that PS is an isotropic system, at least as far as the transport mechanism is concerned. All this leads to the important conclusion that there are *only* two transport mechanisms that are operative in PS. Also, the above-mentioned observation [29], of the increase of E_a with increasing temperature, indicates that these two transport mechanisms can coexist in the same sample, and only the details of the PS network structure and the ambient temperature determine which of them is the dominant one.

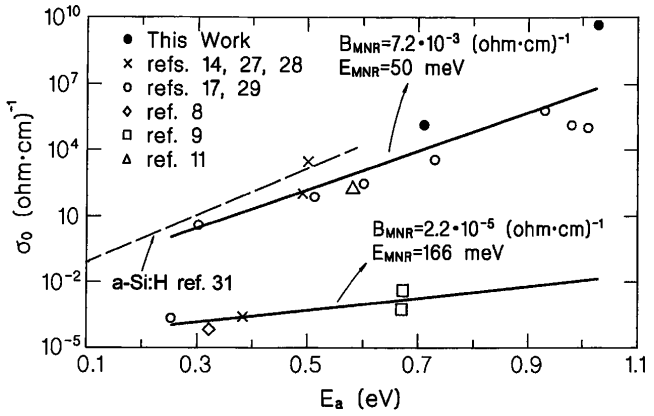

FIG. 2. The experimentally determined values of the dc conductivity prefactors as a function of the corresponding activation energies in a variety of porous silicon samples. The sources of the data are indicated in the figure. The solid lines represent the best fit to a MNR for transport in extended states (upper line), and for transport by activated hopping (lower line). The dashed line represents the data obtained in Ref. [31] for *a*-Si:H.

Let us try now to suggest which transport mechanism is represented by each of the lines in Fig. 2. As mentioned above the MNR is well known to exist in *a*-Si:H and to represent transport in extended states [16]. Also, quite a few workers have used the results of the MNR analysis of the dc conductivity of this material for the derivation of the DOS in the mobility gap [16,24,25,31]. Typical [25,31] *a*-Si:H data are presented by the dashed line [31] in Fig. 2. The similarity between this dashed line and our upper MNR line for PS indicates that transport in many PS systems does not only resemble that of *a*-Si:H, but that the DOS of its conductive network may be similar to that of *a*-Si:H. This conclusion is supported by the many studies that showed similarities between the electronic structure of the conducting networks of PS and *a*-Si:H, in particular, the similar existence of band tails [32] and deep (dangling bond) defects [20,33].

Turning to the lower MNR line in Fig. 2, we find that its values [$B_{\mathrm{MNR}} = 2.2 \times 10^{-5}$ (ohm cm)$^{-1}$, $E_{\mathrm{MNR}} = 166$ meV] are in clear disagreement with these of *a*-Si:H [16,24]. This gives further support to our suggestion that this MNR is related to a different transport mechanism. If we try to explain the lower MNR line within the framework of the kinetic model [15] mentioned above, we must assume, in view of the very high E_{MNR}, that this line is associated with ionic or atomic transport. This is very unlikely, since while such high E_{MNR} values have been observed in *a*-Si:H [24], no such dc transport has been reported. As for PS, probably the most convincing evidence against ionic conduction is the fact

that, as mentioned above, the results of Ref. [29] show a transition from the lower line behavior to the upper line behavior with increasing temperature. If interpreted according to the kinetic model this would imply a transition from ionic transport to electronic transport with increasing temperature, a very unlikely scenario.

On the other hand, the high E_{MNR} value and the low B_{MNR} value are consistent with the expectations from activated band tail hopping. The high value of the E_{MNR} is consistent with a statistical shift of $E_F - E_t$, which is expected [26] to be weaker than that of $E_F - E_V$, while the low value of the B_{MNR} is expected [9] from Mott's theory [22] of activated hopping in band tails.

We note in passing that in their effort to determine the transport mechanism in PS, the authors of Refs. [14,27,28] found an *a*-Si:H–like frequency dependence in the ac conductivity for samples where the dc conductivity yielded the behavior of our upper MNR line [14]. For other samples they found a different frequency dependence which they interpreted [14] as due to hopping over a scale of a few nm. The MNR analysis of the dc conductivity on the latter materials yielded a point on our lower MNR line. These findings are consistent then with the above interpretation of the upper line as representing extended-states transport and the lower line as representing intercrystallite hopping transport. We note that our present MNR analysis cannot distinguish between the two hopping mechanics. However, the analysis carried out in Ref. [14] provides, at present, more support to the latter mechanism.

In conclusion, the main finding of this work is that all the available dc conductivity data on PS indicate the presence of *only two* different conduction mechanisms. One is associated with extended-states transport (which is similar to the one found in *a*-Si:H), and the other is associated with activated hopping. We thus conclude that usually the dc conductivity in PS is taking place in an *a*-Si-H–like tissue but that in some PS samples the transport is dominated by activated hopping which appears to take place by intercrystallite hopping.

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