Slow conductivity relaxation and simple aging in nanostructured mesoporous silicon at room temperature

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Experimental observations of peculiar time-dependent charge transport phenomena, such as slow conductivity relaxation, nonergodicity, and simple aging, are reported here for mesoporous silicon at room temperature. These effects are discussed on the basis of the strong disorder in the nanocrystalline silicon network constituting the material. Taking into account various independent results reported in literature, the authors suggest that the observed behavior may reflect nonequilibrium glassy dynamics due to Anderson localization and Coulomb interactions.

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I. INTRODUCTION

The electron transport in disordered systems has been widely investigated[1] since Mott and Anderson started to develop their fundamental studies about 50 years ago. However, the nonequilibrium dynamics of electrons in such systems is still the object of intensive research in both theoretical and experimental fields due to the peculiar physical phenomena involved. Indeed, for instance, some universal characteristics of glassy systems, such as nonergodicity, very slow relaxation, and aging, can be found in the transport properties of Anderson insulators. Although the existence of the electron glass, where the interplay of disorder and Coulomb interactions gives rise to a sluggish response of free carriers to excitations out of equilibrium, was predicted more than 20 years ago,[2,3] experimental evidences for such a system have only been reported in the case of relatively few materials, including granular metals (Au,[4] Al,[5,6] Bi, and Pb[7]) and indium oxide films[8] at low temperature T. Among standard semiconductors, a similar behavior was only seen in capacitance measurements in doped GaAs.[9]

In this paper, we show that some peculiar time-dependent transport phenomena, such as slow logarithmic relaxation of conductivity and simple aging, can be observed in mesoporous silicon (mesoPS) at room temperature (RT). MesoPS is a disordered network of interconnected silicon nanocrystals fabricated by electrochemical etching of heavily doped silicon. The average size of nanocrystals is typically $\gtrsim 10$ nm,[10] so that quantum confinement is not effective as in the case of luminescent nanoporous silicon. Nevertheless, the conductivity of mesoPS is strongly suppressed as compared to the starting Si substrate,[11] and the free charge carriers appear frozen out at RT.[12] To interpret the time-dependent results reported here consistently with the previous literature, we suggest that the material may manifest nonequilibrium glassy dynamics arising from the interplay of disorder and Coulomb interactions within the nanocrystalline Si network.

II. EXPERIMENT

The samples measured in this study were obtained by anodization of (100)-oriented boron doped p^+-type Si (resistivity 0.008–0.012 Ω cm) in HF [50 wt %]:EtOH solution, 1:1 in volume, at a current density of 250 mA/cm^2 (etch stops[13] 1:10). This way, porous films were formed at an etch rate of 200 nm/s and with a porosity of about 60% (estimated by gravimetric method). Thickness ranged between 5 and 10 μm, depending on the etching time. Then, a Cr/Au pad (area=20 mm^2) was evaporated on top of mesoPS films immediately after the etching process, and a second electrode was given by the underlying Si substrate (a contact was made by silver paste on the backside of our devices). The samples were left to stabilize in ambient air for one month or more, and then inserted in a Janis ST-100 cryostat equipped with a heater, a thermocouple, and a Lakeshore 331 temperature controller. The electrical measurements were carried out in vacuum (1×10^{-5} mbar) by means of a Keithley 6430 source meter equipped with a remote preamplifier. No relevant differences were observed in the time-dependent behavior of the four samples considered in this study.

III. RESULTS AND DISCUSSION

We investigated the response of free carriers in mesoPS to excitations out of equilibrium by studying the relaxation dynamics of the dc conductance G measured at a bias voltage in the Ohmic regime, after biasing the sample by a larger non-Ohmic electric field. The backside contact was chosen to be the anode in order to use the p^+-type Si substrate as an efficient hole injecting contact. The experiment was carried out at constant temperature T=300 K. Two remarkable features are immediately visible in the graphs of Fig. 1. First, during the excitation induced by the non-Ohmic field F_1, the conductance continuously increases in a sluggish manner, and it can hardly reach an equilibrium value even after several hours. On the other hand, if the bias is switched to the lower value F_0, G starts to relax following a logarithmic dependence on time.

Almost the same behavior has been observed by Orlyanchik *et al.*[14] when measuring insulating In_2O_3 samples immersed in liquid ^{4}He. In this case, the authors argued that a sufficiently large electric field is able to impart energy to charge carriers in hopping systems, so that the slow increase of G is due to the excitation of the electronic system throughout a landscape of local minima in the phase space, while the

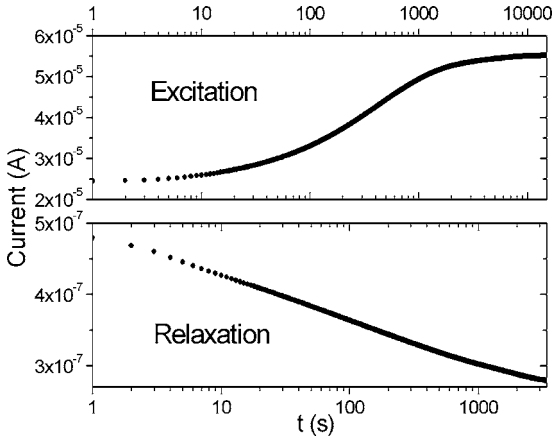

FIG. 1. Dynamics of mesoPS conductance during excitation by a non-Ohmic field (F_1=750 V/cm) and during relaxation at lower bias (F_0=50 V/cm).

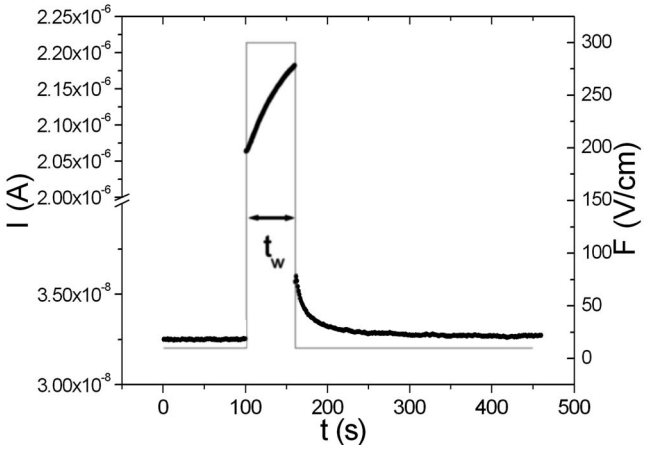

FIG. 2. Stress aging experiment. The temperature was kept constant at T=300 K.

lattice remains in thermal equilibrium. Therefore, applying a non-Ohmic electric field was found to be a method of exciting an electron glass out of equilibrium, producing the same result as the variation of the gate voltage in a field effect experiment.[15] Indeed, in both cases, after the excitation condition has been removed, a slow logarithmic relaxation takes place in the electronic system. The results described in Fig. 1 suggest that similar phenomena may manifest themselves even in mesoPS at room temperature. A minor difference with respect to what was observed with In_2O_3 is given by the departure from the pure logarithmic law in the first seconds of measurements. However, such feature may arise from competing space-charge effects which can be non-negligible in the first instants of experiment.

To gain insight into the slow relaxation phenomena in mesoPS, we have applied to our samples the stress aging protocol proposed by Orlyanchik and Ovadyahu.[16] Aging is a peculiar feature of glasses, related to the dependence of a given macroscopic property P on the history of the system. Moreover, after the application of an external excitation condition for a time t_w, P relaxes to equilibrium following a law which depends not only on time t but also on the interval t_w. Examples of this phenomenon can be found in very different materials, from polymers[17] to spin glasses.[18] In the stress aging protocol, the conductance G is the property observed after the system has been driven far from equilibrium by the application of a large electric field.

A typical experiment is depicted in Fig. 2. In this case, the sample was first equilibrated for a long time at a low bias F_0=10 V/cm, and then excited by a larger field F_1 =300 V/cm for a time t_w. Finally, the bias was switched back to the initial value, and the system was allowed to relax toward equilibrium. During the experiment, the temperature was kept constant at 300 K. The relaxation curves are plotted in Fig. 3(a) for different values of t_w. An aging effect is clearly visible, as the dynamics of the excess conductance ΔG following the excitation strongly depends on t_w. Moreover, as shown in Fig. 3(b), it is sufficient to renormalize the time variable by the t_w parameter to obtain the collapse of all curves in a universal function $\Delta G(t/t_w)$. Such scaling property is known as *simple aging*, and is a typical signature of electron glasses. In fact, the same results were obtained by Orlyanchik and Ovadyahu[16] by applying the stress aging protocol to In_2O_3 samples at T=4 K, and by various authors by using the gate protocol on different materials (In_2O_3 and granular Al).[6,15] However, it is worth reminding that the aging phenomenon is a necessary but not sufficient condition for the electron glass state, as recently pointed out by Muller.[19] Actually, as discussed by Grenet *et al.* in a very recent paper,[20] experimentally observed slow nonequilibrium dynamics can be interpreted either in the framework of an intrinsic glassiness of charge carriers or as a result of a collection of independent extrinsic degrees of freedom in the material, so that no conclusion on the existence of the electron glass state in mesoPS can be reached at this stage of the investigation.

The nonergodicity of the system, implicitly contained in the aging phenomenon, clearly emerges in Fig. 4. Here, the stress aging protocol was applied, but both F_0 (1000 V/cm)

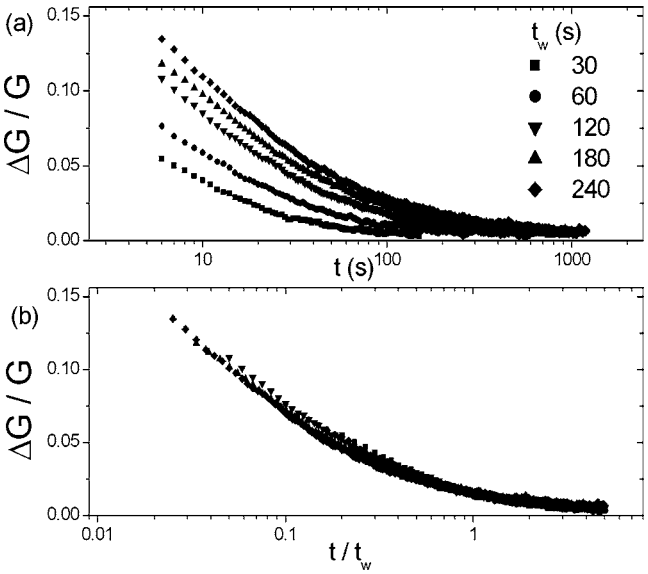

FIG. 3. Simple aging observed by applying the stress aging protocol to mesoPS at T=300 K (F_0=10 V/cm and F_1 =300 V/cm).

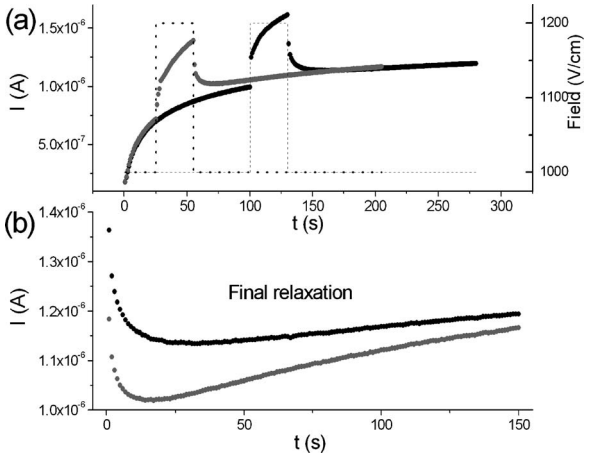

FIG. 4. Nonergodic behavior of mesoPS. The sample was biased at $F_0=1000$ V/cm for a time t_0, then at $F_1=1200$ V/cm for 30 s, and finally at F_0 for 150 s. The final step at F_0 is plotted in (b) in the case of two different values of t_0: gray dots correspond to 25 s and black dots to 100 s.

and F_1 (1200 V/cm) were chosen in the non-Ohmic regime. It can be seen that the final relaxation depends not only on the duration of the excitation at F_1, but also on the initial time spent at F_0. In other words, the system carries a memory of all the events constituting its history. Before each measurement cycle the sample was left to equilibrate at 0 bias, so that the origin of the time scale for the observed memory effects is given by the instant at which the system starts to be excited by F_0, i.e., the history begins at that point. Moreover, a very clean manifestation of simple aging is clearly visible even in this case where two non-Ohmic fields are employed (Fig. 5). Here, the sample was initially biased at 1000 V/cm (non-Ohmic) for a time $t_0=100$ s, and $G(t_0)$ was taken as the "quasiequilibrium" reference value for the relaxation step, after the excitation carried out by a higher non-Ohmic bias (3000 V/cm).

So far, we presented experimental evidences of peculiar time-dependent charge transport phenomena, such as slow relaxation, nonergodicity, and simple aging, in mesoPS. At this point, we would like to discuss the possible origin of this behavior, also taking into account other various independent observations reported in literature.

As a starting point, we consider the origin of the material, coming from a heavily doped bulk crystalline silicon where pores are formed by etching. The electrochemical process breaks the translational symmetry within the bulk crystal, and localized states must originate. From the point of view of charge carriers, the random variations of nanocrystallite shape and size in the porous network may render the potential distribution highly disordered, giving rise to Anderson localization. Importantly, the effect usually dominant in transport through a nanoporous matrix, i.e., quantum confinement, cannot be so relevant in mesoPS due to the relatively large size of nanocrystallites. Moreover, it should be recalled that a localizing effect induced by the morphology (i.e., by the disorder due to nanostructuration) has been argued by various authors in the description of transport in porous silicon.[21–24]

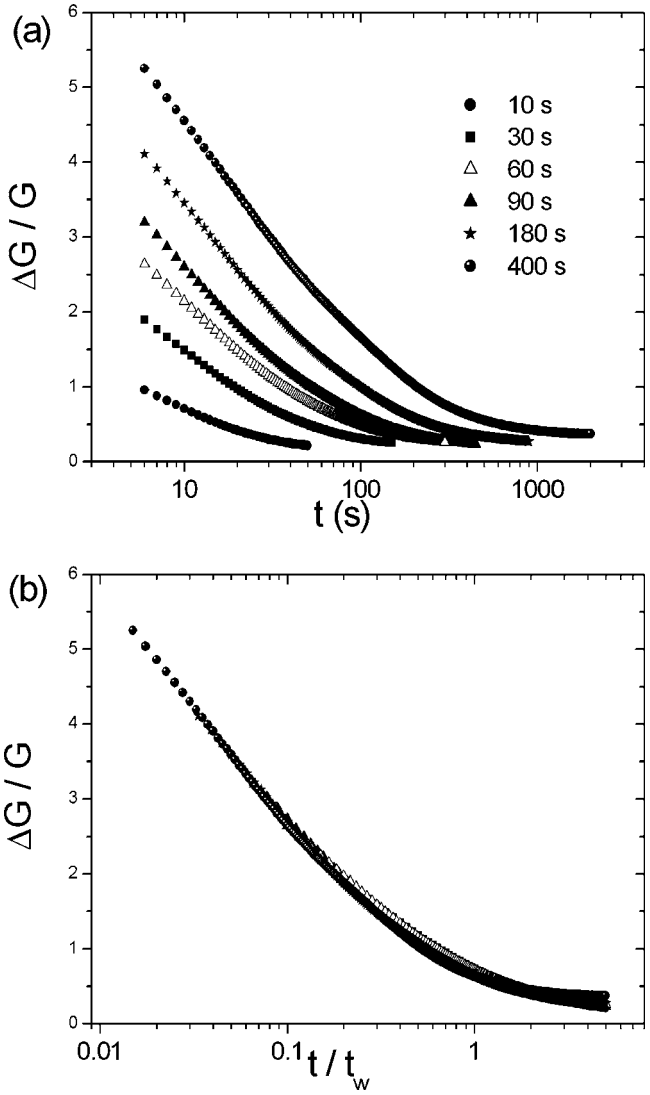

FIG. 5. Simple aging observed by applying the stress aging protocol with two non-Ohmic field values ($F_0=1000$ V/cm and $F_1=3000$ V/cm).

This simple model is consistent with various independent observations reported in literature. First of all, it is well known that the electrical conductivity σ of mesoPS is thermally activated $\left[\sigma(T)\propto\exp\left(-\frac{E_A}{kT}\right)\right]$ in relatively high T ranges (close to RT), with an activation energy E_A on the order of hundreds of meV.[25–28] This is compatible with the hypothesis of a mobility edge whose distance from the Fermi level is greater than the thermal energy at RT, i.e., with the localization of charge carriers at RT. It is interesting to note that, for instance, indium oxide films exhibiting glassy behavior show an activation energy of a few meV,[29] so that carriers are localized only at very low T. Furthermore, in a recent paper, Zimin reported the 1/4 Mott hopping exponent for low porosity mesoPS samples at relatively high T (up to 200 K).[30] Such behavior reflects the existence of a finite density of states at the Fermi level and the presence of a mobility edge. Thus, even this result may be consistent with the Anderson localization hypothesis and the Fermi glass picture. Moreover, slow conductivity relaxation at high temperature was

observed even in porous amorphous Si exhibiting hopping transport.[31] Although, as mentioned before, the relaxation phenomena reported here are not sufficient to demonstrate the electron glass state in our samples, nevertheless, the strong disorder in the nanocrystalline Si network is likely to play a fundamental role in the observed behavior. Indeed, for instance, Ben-Chorin *et al.*[8] observed slow electron dynamics in indium oxide samples even at RT in the case of sufficiently high resistance and strong disorder.

Finally, it is worthy to recall what happens to mesoPS in the presence of NO_2 and NH_3 molecules. It has been shown by Fourier transform infrared spectroscopy that such molecules are able to inject free holes (in the case of NO_2) or electrons (in the case of NH_3) in mesoPS, augmenting the free carrier concentration by a maximum factor of about 10, depending on the gas pressure.[32] On the other hand, the electrical conductivity in the presence of NO_2 can increase by up to several orders of magnitude,[33] implying that even the diffusion constant varies over a broad range, as the free carrier increase is limited. This fact may be explained in the framework of the Anderson localization model, assuming that carrier injection pushes the Fermi level toward the mobility edge, thus reducing the localization at a given T. The same mechanism may be at the basis of the metal-insulator transition observed by Chiesa *et al.* by the electron paramagnetic resonance technique for mesoPS in the presence of ammonia.[34] In this case, it may be assumed that electrons are injected until the Fermi level crosses the mobility edge in the conduction band, giving rise to the reported sudden transition at a particular NH_3 pressure. Thus, different studies of the effect of NO_2 and NH_3 can support the hypothesis of mesoPS as an Anderson localized insulator.

Eventually, it has to be mentioned that the possible contribution of Coulomb interactions, so far neglected in our discussion, would increase the temperature limit to observe nonergodic behavior,[3] consistent with our results. Actually, Coulomb interactions have been shown to be important in mesoPS transport phenomena.[27,35,36] Indeed, it was recently reported that collective Coulomb blockade behavior can emerge at RT in the I-V characteristics of mesoPS samples tested in a particular guarded measurement configuration, due to the presence of nanoconstrictions and oxide barriers linking the Si nanocrystals in the porous network.[36,37] Therefore, the effect of trapped charges may interplay with the strong morphological disorder coming from the nanostructuring process, favoring the observation of glassy dynamics at high temperature.

IV. CONCLUSIONS

In summary, we have reported some experimental observations of anomalous time-dependent transport properties of mesoPS, such as slow conductivity relaxation, nonergodicity, and simple aging. These phenomena are likely to be related to the interplay of Coulomb interactions and the strong disorder introduced in the bulk crystalline Si by the electrochemical etching process. Taking into account various independent observations in literature, the dynamics reported in this paper can be inserted within a reasonable qualitative picture for the material, which may be useful for the comprehension of some peculiar phenomena previously observed. Indeed, we suggest that unclear experimental results, such as the sluggish electrical response of mesoPS sensors,[38] may be a manifestation of nonequilibrium dynamics in the nanostructured material. On the basis of these preliminary results, we think that further investigation on time-dependent charge transport phenomena in mesoPS may be very useful for the study of disordered electronic systems.

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