Experimental observation of glassy dynamics driven by gas adsorption on porous silicon

Experimental observation of glassy dynamics driven by gas adsorption on porous silicon

Stefano Borini

Electromagnetic Division, INRIM, Strada delle Cacce 91, I-10135 Torino, Italy

E-mail: s.borini@inrim.it

Abstract
We report on electrical resistance measurements of mesoporous silicon samples at room temperature, in the presence of various dosages of ammonia, showing very slow non-exponential responses of the system to any variation of ammonia pressure. Resistance always relaxes according to a stretched exponential law, independently of the sign of the variation. Moreover, the system remembers its own history, and memory effects can be accounted for in a very simple way in the framework of the same relaxation law. A possible extrinsic scenario based on rearrangement of trapped charges is proposed and discussed. These findings suggest that mesoporous silicon in the presence of polar molecules may be regarded as a suitable system for the study of glassy dynamics by means of electrical measurements at RT.

1. Introduction

Glassy systems, which evolve out of equilibrium in a sluggish way, have attracted a broad interest mainly due to their ubiquitous character in nature. Indeed, peculiar history dependent (non-ergodic) behavior is observable in very different systems, such as spin glasses (found in particular magnetic alloys) [1] and structural glasses (e.g. polymers) [2]. Very recently, some typical features of the glassy phase were even seen in the response of living cells to transient stretch [3]. Moreover, glassy behavior is particularly interesting because it is directly connected to the complexity of the systems, i.e. it is a manifestation of complexity in nature.

In a very few cases, glassy dynamics of charge carriers traveling through a solid has been observed, suggesting the existence of the theoretically predicted electron glass [4, 5]. Experimental reports on this topic mainly include electrical measurements on amorphous or granular materials (e.g. indium oxide [6] and Al [7]) and on 2-dimensional electron gases (2DEG) in Si devices [8], at cryogenic temperatures. Very recently, some typical glassy features, such as slow dynamics and simple ageing, were reported for mesoporous silicon (mesoPS) conductance at room temperature (RT) [9], under the stress ageing protocol [10], but the origin of glassiness remained unclear.

MesoPS is a disordered network of interconnected Si nanocrystals, whose average size is of the order of tens of nanometers [11]. In this material, charge carriers appear frozen out at RT, even though the starting bulk Si substrate is highly doped, giving rise to an almost insulating behavior. Moreover, adsorption of some 'acceptor' or 'donor' molecules (such as NO_2 and NH_3) can restore a high concentration level of free carriers in the nanocrystals [12, 13]. In particular, ammonia is known to alter the electronic properties of mesoPS, by injection of free electrons in the material and an increase of the carrier mobility [14, 15]. Therefore, the resistance of mesoPS samples can be lowered by the presence of ammonia molecules in a reproducible and reversible way.

Here we show that glassy dynamics of electrical conductivity may arise in porous silicon, as a consequence of the adsorption of ammonia molecules on the material surface. We report resistance measurements of mesoPS samples in the presence of various dosages of ammonia, showing very slow non-exponential responses of the system to any variation of ammonia pressure. Moreover, memory effects are clearly visible in the reported results as a hallmark of glassy dynamics.

2. Experimental details

MesoPS samples were produced by anodization of (100)-oriented B doped Si wafers (resistivity 0.008–0.012 Ω cm) in HF[50%wt]:EtOH solution 1:1 in volume, at a current density of 100 mA cm^{-2} (etch stops [16] 1:10) and controlled

temperature $T = 10\,°C$. This way, porous films were formed with a porosity of about 60% (estimated by a gravimetric method) and with a thickness of 50 μm. Then two Cr/Au pads, separated by a 50 μm gap, were evaporated on top of mesoPS immediately after the etching process.

Electrical measurements were performed by means of a Keithley 2410 source meter, at RT in a vacuum chamber equipped with a dry pumping unit (background vacuum 1×10^{-4} Torr), a gas inlet, a mass-flow meter and a MKS Baratron capacitance transducer, so that a fine adjustment of ammonia pressure under continuous flow conditions was possible. MesoPS resistance was monitored by measuring the current flowing between the two pads under a dc bias field of about 10 V cm^{-1}. At such a low bias field, we verified that the samples exhibit an ohmic behavior, visible in the I–V characteristics.

3. Results

The basic typical experimental procedure consists of a very simple protocol. First the sample was left to equilibrate overnight, under vacuum pumping and constant bias voltage, such that the resistance reached an almost constant value. Then a controlled flow of NH$_3$ gas was adjusted by the mass-flow meter, and the variation of resistance induced by gas adsorption was monitored for several hours, always keeping the same constant bias.

In figure 1 the typical response of the system to ammonia is visible. In this case, first the sample was left to equilibrate in vacuum (under pumping) at a bias electric field of 10 V cm^{-1}, then at $t = 0$ a constant gas flow was switched on, giving rise to a pressure of 0.20 Torr in the test chamber. It can immediately be seen that, as a consequence of the presence of ammonia, the resistance starts to drop, tending to a new smaller equilibrium value with a very slow non-exponential relaxation. We point out that such a slow dynamics cannot be a trivial result of adsorption kinetics, as will become very clear on the basis of further results on memory effects reported later on in this paper. Moreover, it is worth noting that the variation ΔR is referred to the asymptotic value R_{eq} the system is approaching and not to the starting value. Indeed, as we are interested in the transit of the system toward a new quasi-equilibrium condition, we have to look at the evolution of the 'distance' from such equilibrium. This way, taking the normalized variable $y = \Delta R/R_{eq}$, where $\Delta R = R(t) - R_{eq}$ and R_{eq} is the equilibrium value of the resistance for a given ammonia pressure value, we found that the relaxation curves can be very well fitted by the stretched exponential law:

$$y(t) = y(0) \cdot \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] \quad (1)$$

with the stretching exponent satisfying the condition $0 < \beta < 1$. The stretched exponential behavior shows very clearly in the log–log plot of $-\log(\frac{y(t)}{y(0)})$ versus t reported in figure 1(b), where β is the slope of the linear fit and τ is given by the abscissa at which the function is equal to 1. Therefore, each relaxation is fully characterized by two
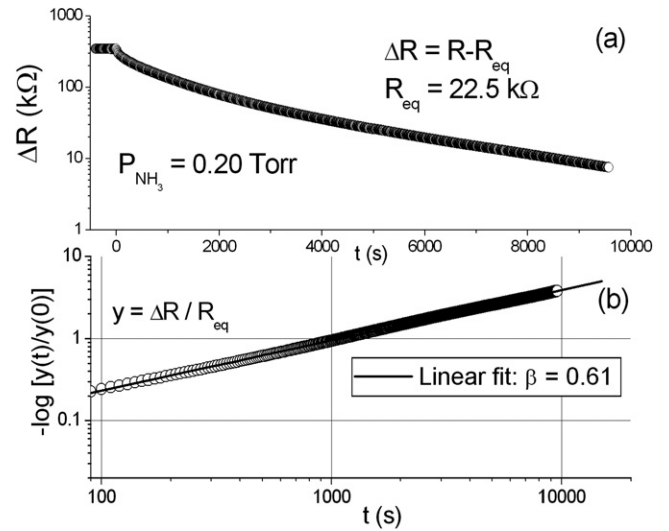

Figure 1. Non-exponential response of mesoPS resistance to dosage of ammonia (0.20 Torr). The stretched exponential behavior emerges in (b).

parameters, β (stretching exponent) and τ (time constant). Note that equation (1) holds for both signs of $y(0)$, i.e. even when $R_{eq} > R(0)$.

Then, in further experiments, the basic experimental protocol was modified by adding a relatively short step in ammonia pressure P_H during the relaxation at a lower pressure P_L (see figure 2(a)).

We observed that, after the high pressure 'pulse', a new relaxation $y^{(1)}$ started, which carried a clear memory of the relaxation $y^{(0)}$ prior to the pulse. In particular, we have verified that even the new relaxation follows the stretched exponential law described in equation (1), provided that the equilibrium value $R_{eq}^{(1)}$ becomes time dependent, coinciding with the extrapolation of the previous relaxation $R^{(0)}$:

$$R_{eq}^{(1)} = R_{eq}^{(1)}(t) = R^{(0)}(t_0 + t) \quad (2)$$

where t_0 is the time interval during which the system relaxed according to the $R^{(0)}$ behavior, before being interrupted by the onset of the high pressure pulse. In other words, the system first relaxes toward the pristine relaxation curve, then continues its path to the final equilibrium value.

Such a behavior is displayed in figure 2, where typical experimental results are reported and analyzed. In this case, a relaxation at $P_L = 0.07$ Torr was interrupted by a higher ammonia dosage ($P_H = 0.67$ Torr) for 400 s, and the new relaxation $R^{(1)}$, starting after switching back to P_L, was considered and compared to the pristine relaxation $R^{(0)}$. Figure 3 shows that, after the proper normalization by $R_{eq}^{(1)}$ defined in equation (2), even the new relaxation displays the stretched exponential behavior of equation (1), with a stretching exponent close to the exponent of the previous relaxation, whereas the τ parameter tends to increase.

Moreover, the non-monotonic behavior of $R^{(1)}$, clearly visible in figure 2(c), indicates that the dynamics under study is not merely a result of standard gas adsorption kinetics. By the way, it is interesting to note that a non-exponential
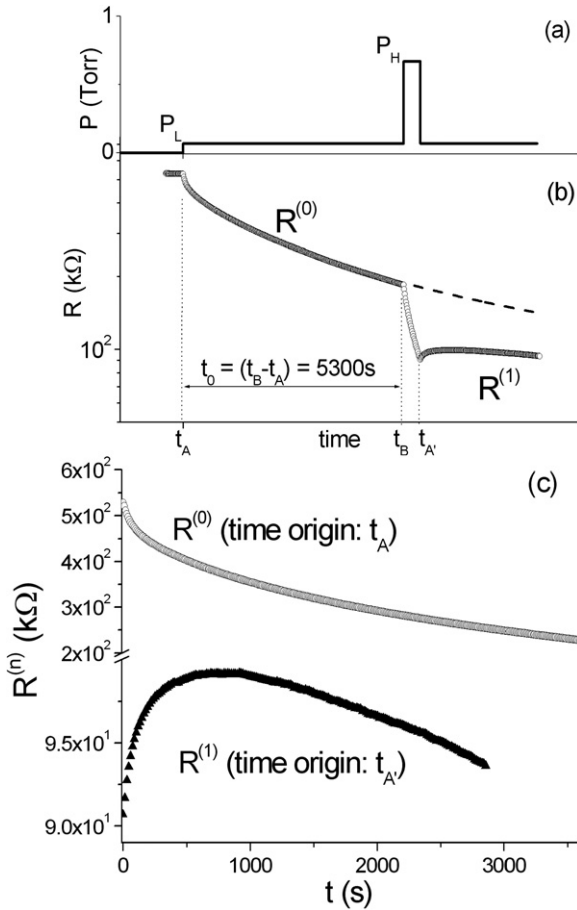
Figure 2. Response to a P_L dosage (0.07 Torr) with a momentary interruption (for 400 s) by a P_H dosage (0.67 Torr). The dashed line is the extrapolation of the stretched exponential decay for $R^{(0)}$. In (c) the two relaxations at P_L are compared.
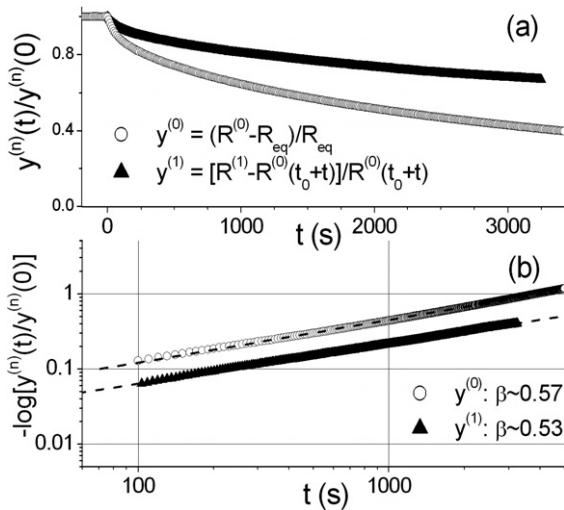

Figure 3. After the proper normalization, both the relaxations of figure 2(c) display a stretched exponential behavior, with very similar β exponents. Dashed lines are linear fits.

response of porous silicon conductivity to chemical vapor adsorption was reported in the literature some years ago but without being explained [17]. Indeed, even in that case, it was
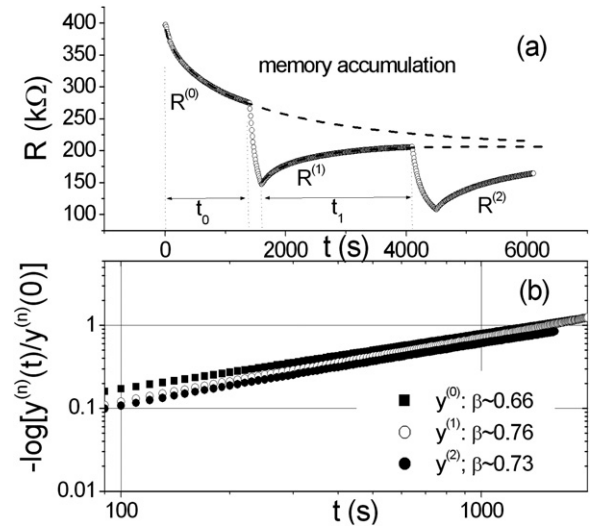

Figure 4. Response to an ammonia dosage of 0.07 Torr with two momentary higher pressure dosages (0.67 Torr). Dashed lines are extrapolations for $R^{(0)}$ and $R^{(1)}$. In (b) the stretched exponential behavior of all the three properly normalized relaxations at 0.07 Torr is highlighted.

found that such a sluggish relaxation was independent of the adsorption kinetics, because the recovery time of conductivity was much longer than the recovery time of photoluminescence upon chamber evacuation. We suggest that glassy dynamics of porous silicon conductivity relaxation may be at the basis of such experimental observation.

Taking into account the memory effects, the relaxation law can be rewritten in a more general form as:

$$y^{(n)}(t) = y^{(n)}(0) \cdot \exp\left[-\left(\frac{t}{\tau}\right)^{\beta} \right] \qquad (3)$$

where $y^{(n)}(t)$ is given by:

$$y^{(n)}(t) = \frac{R^{(n)}(t) - R^{(n-1)}(t_{n-1}+t)}{R^{(n-1)}(t_{n-1}+t)} \qquad (4)$$

and t_{n-1} is the time interval during which the system relaxation is described by $y^{(n-1)}(t)$. Moreover, $y^{(0)}(t)$ represents the initial 'memory-free' relaxation, when memory effects are absent, i.e.:

$$y^{(0)}(t) = \frac{R^{(0)}(t) - R_{eq}}{R_{eq}}. \qquad (5)$$

Therefore, we suggest that the repetition of pressure variation pulses, and the consequent memory accumulation, can be taken into account by an iterative use of equation (4), starting from the first relaxation $R^{(0)}$ where memory effects are not important, similarly to that reported by Struik [18] for structural glasses. This is shown in figure 4, where the results of an experiment involving two consecutive high pressure P_H pulses are reported. It can be appreciated that all the three relaxations at P_L are well described by the stretched exponential function of equation (3), with quite similar β exponents, after application of equation (4) for each $y^{(n)}$.

4. Discussion and conclusions

The stretched exponential relaxation (usually referred to as the Kohlrausch–Williams–Watts law [19, 20]) is a very common feature observed in various complex systems. In literature, such a behavior has been reported for a wide range of slow relaxations, and is usually ascribed to hierarchically constrained dynamics with a wide distribution of relaxation times [21]. For instance, it is very interesting to note that glass formers below the glass temperature exhibit a stretched exponential relaxation law like equation (1) and memory effects in dielectric ageing experiments [22]. In such a case, the ageing dynamics is determined by the structural relaxation process.

Trying to elucidate the origin of glassiness in the system under study, we ought to consider a possible electrical transport mechanism previously proposed for mesoPS. Already in 1995, Lehmann and co-workers [23] argued that the electrical resistivity of mesoPS may be determined by the constriction of conductive pathways produced by charged surface traps. Indeed, the free carriers freeze-out in mesoPS cannot be ascribed to quantum size effects (as in luminescent nanoporous silicon), due to the relatively large dimensions of the crystallites, so that a surface effect, involving Coulomb repulsion from trapped charges, is more likely to be the basis of the observed low conductivity. The mechanism proposed was analogous to the 'telegraph noise' in MOS devices, where a trapped charge can block part of the conductive channel by its electric field. This phenomenon can become very effective in PS, because of the huge specific surface (of the order of hundreds of $m^2\,cm^{-3}$) [24] and of the nanostructure of the material. In fact, the surface of PS is known to be rich in defects, typically Si dangling bonds at the Si/SiO_x interface, i.e. the so-called P_b centers [25]. P_b centers are electrically active amphoteric traps, so that they can easily localize both electrons and holes [26]. Therefore, these centers can strongly affect the conductivity of PS, by trapping free carriers and constricting the conductive pathways.

Recently, the model proposed by Lehmann has been corroborated by the experimental evidence of Coulomb blockade phenomena in mesoPS [27]. Indeed, the observation of a conductivity gap in the I–V characteristic has been ascribed to trapped charges in nanoconstrictions, which can inhibit the current flow by Coulomb repulsion, according to a transport mechanism predicted for nanocrystal arrays. A similar collective Coulomb blockade behavior was indeed observed in granular materials, such as Au nanocrystal arrays [28, 29], suggesting a phenomenological analogy between charge transport in mesoPS and in granular metallic films. Supporting this analogy, it is interesting to remember that non-equilibrium dynamics has been reported for the electrical conductance of granular metal films, and slow polarization processes were considered as a possible origin of glassiness by some authors [30–32]. Thus, the glassy behavior previously reported for mesoPS (stress ageing experiment [9]) may be interpreted in the framework of an extrinsic model, taking into account a rearrangement of charged traps induced by the external electric field. Finally, the morphological

disorder, i.e. the random variation of Si nanocrystallites shape and size within the PS network, may also influence the charge carrier transport [33], playing a role in the dynamics slow-down.

We should now consider how can ammonia intervenes in this scenario. *Ab initio* calculations have already shown that a positively charged P_b center $P_b^{(+)}$ (i.e. where a hole has been trapped) is a favorable adsorption site for ammonia [13]. Indeed, the NH_3 molecule can bind to the $P_b^{(+)}$, releasing an electron toward the mesoPS surface. Moreover, charge–dipole interactions are likely to occur between localized charges and adsorbed molecules, due to the dipole moment of ammonia. In fact, the evolution of the I–V characteristics in the presence of ammonia is consistent with such a scenario [15]. The conductivity gap is gradually canceled upon ammonia adsorption, revealing the interaction between adsorbed molecules and charged traps responsible for Coulomb blockade. Thus, preferential adsorption sites are likely to be directly related to the trapping centers, so that a rearrangement of trapped charges may induce a redistribution of adsorbed molecules, and vice versa. In other words, on one hand, charged defects are favorable adsorption sites, and on the other hand, ammonia, through its interaction with mesoPS surface, can alter the electronic distribution in the surface states. This kind of correlated dynamics may produce a situation typical for glasses, where the characteristic time to drive the system out of equilibrium (i.e., in this case the time to reach a new ammonia pressure value) is much shorter than the time needed for equilibrating at the new condition.

In summary, in the experiments reported in the present paper, gas adsorption can induce a rearrangement of trapped charges. Such a rearrangement directly influences the charge transport in the material, and it is likely to be a sluggish phenomenon. Indeed, there is likely to be a most favorable configuration for both the density and the occupation of surface states at each external condition, i.e. adsorbate amount. To reach such a configuration the system needs a long time, due to the correlation between the charge distribution in the surface states and the adsorbate distribution on the surface. The effect of charge rearrangement and the associated Coulomb interactions may interact with the strong morphological disorder in the porous network, giving rise to glassy dynamics. The causal mechanism may be somewhat similar to that recently observed in Al–AlO_x–Al glassy tunnel junctions, where off-equilibrium dynamics and stretched exponential relaxation of conductance were found to be related to the charge distribution in the interface states [34]. Moreover, such an extrinsic scenario may be close to the model recently proposed by Burin and co-workers to interpret the slow dynamics of amorphous hopping insulators [35], where the origin of glassiness was ascribed to slow rearrangements of structural defects.

In conclusion, the experimental observation of the stretched exponential relaxation of mesoPS resistance upon ammonia adsorption has been reported. Moreover, memory effects—a typical hallmark for glassy systems—are shown, and a simple method to account for them is proposed. Such

a method is based on the following main assumptions:

- the normalized variable y is the proper parameter to describe the out-of-equilibrium dynamics, because it represents the normalized distance from equilibrium;
- when the system is 'aged' (i.e. not at equilibrium before the excitation), the relaxation occurs toward the previous relaxation curve, which was interrupted by excitation.

A possible mechanism underlying the glassy behavior, involving a major role of trapped charges, has been proposed, yielding to a description of the material as an extrinsic electronic glass, where a slow rearrangement of the potential landscape seen by free carriers is reflected in conductivity measurements. However, a deep understanding of the origin of these phenomena obviously requires further study. In particular, the physical meaning of the relaxation parameters β and τ and their dependence on the external conditions (ammonia pressure) should be clarified. Experiments to investigate the T dependence of dynamics are in progress, and will certainly help to elucidate the mechanisms at the basis of the observed glassy behavior, clarifying the extrinsic or intrinsic nature of glassiness. Anyhow, the reported results may be a further important element to gain insight into the non-equilibrium dynamics of porous silicon, indicating this material as a suitable candidate for studying peculiar glassy dynamics by means of electrical measurements at room temperature. Moreover, people working on PS-based devices should be aware of the extremely slow relaxation processes involved in the electrical transport phenomena in this material.

References

[1] Lundgren L, Svedlindh P, Nordblad P and Beckman O 1983 *Phys. Rev. Lett.* **51** 911
[2] Hodge I M 1995 *Science* **267** 1945
[3] Trepat X, Deng L, An S S, Navajas D, Tschumperlin D J, Gerthoffer W T, Butler J P and Fredberg J J 2007 *Nature* **447** 592
[4] Davies J H, Lee P A and Rice T M 1982 *Phys. Rev. Lett.* **49** 758
[5] Pollak M 1984 *Phil. Mag.* B **50** 265
[6] Ben-Chorin M, Ovadyahu Z and Pollak M 1993 *Phys. Rev.* B **48** 15025
[7] Grenet T 2003 *Eur. Phys. J.* B **32** 275
[8] Bogdanovich S and Popovic D 2002 *Phys. Rev. Lett.* **88** 236401
[9] Borini S, Boarino L and Amato G 2007 *Phys. Rev.* B **75** 165205
[10] Orlyanchik V and Ovadyahu Z 2004 *Phys. Rev. Lett.* **92** 066801
[11] Münder H, Berger M G, Frohnhoff S, Thonissen M and Luth H 1993 *J. Lumin.* **57** 5
[12] Boarino L, Baratto C, Geobaldo F, Amato G, Comini E, Rossi A M, Faglia G, Lerondel G and Sberveglieri G 2000 *Mater. Sci. Eng.* B **69/70** 210
[13] Garrone E, Geobaldo F, Rivolo P, Amato G, Boarino L, Chiesa M, Giamello E, Gobetto R, Ugliengo P and Viale A 2005 *Adv. Mater.* **17** 528
[14] Chiesa M, Amato G, Boarino L, Garrone E, Geobaldo F and Giamello E 2003 *Angew. Chem. Int. Edn* **42** 5032
[15] Borini S 2007 *J. Appl. Phys.* **102** 93709
[16] Billat S, Thönissen M, Arens-Fischer R, Berger M G, Krüger M and Lüth H 1997 *Thin Solid Films* **297** 22
[17] Ben-Chorin M, Kux A and Schechter I 1994 *Appl. Phys. Lett.* **64** 481
[18] Struik L C E 1978 *Physical Aging in Polymers and Other Amorphous Material* (Amsterdam: Elsevier)
[19] Kohlrausch R 1874 *Ann. Phys. Chem.* **91** 179
[20] Williams G and Watts D C 1970 *Trans. Faraday Soc.* **66** 80
[21] Palmer R G, Stein D L, Abrahams E and Anderson P W 1984 *Phys. Rev. Lett.* **53** 958
[22] Lunkenheimer P, Wehn R, Schneider U and Loidl A 2005 *Phys. Rev. Lett.* **95** 055702
[23] Lehmann V, Hofmann F, Möller F and Grüning U 1995 *Thin Solid Films* **255** 20
[24] Hérino R, Bomchil G, Barla K, Bertrand C and Ginoux J L 1987 *J. Electrochem. Soc.* **134** 1994
[25] von Bardeleben H J, Stievenard D, Grosman A, Ortega C and Siejka J 1993 *Phys. Rev.* B **47** 10899
[26] Gerardi G J, Poindexter E H, Caplan P J and Johnson N M 1986 *Appl. Phys. Lett.* **49** 348
[27] Borini S, Boarino L and Amato G 2006 *Adv. Mater.* **18** 2422
[28] Fan H, Yang K, Boye D M, Sigmon T, Malloy K J, Xu H, Lopez G P and Brinker C J 2004 *Science* **304** 567
[29] Parthasarathy R, Lin X-M, Elteto K, Rosenbaum T F and Jaeger H M 2004 *Phys. Rev. Lett.* **92** 76801
[30] Adkins C J, Benjamin J D, Thomas J M D, Gardner J W and McGeown A J 1984 *J. Phys. C: Solid State Phys.* **17** 4633
[31] Cavicchi R E and Silsbee R H 1988 *Phys. Rev.* B **38** 6407
[32] Grenet T, Delahaye J, Sabra M and Gay F 2007 *Eur. Phys. J.* B **56** 183
[33] Parascandolo G, Cantele G, Ninno D and Iadonisi G 2003 *Phys. Rev.* B **68** 245318
[34] Nesbitt J R and Hebard A F 2007 *Phys. Rev.* B **75** 195441
[35] Burin A L, Kozub V I, Galperin Y M and Vinokur V 2007 *Preprint* 0705.2565v2