Charge storage, photoluminescence, and cluster statistics in ensembles of Si quantum dots

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(Received 30 November 2007; published 14 March 2008)

In this paper, we provide a framework for the description of the basic transport processes in ensembles of disordered semiconductor quantum dots by studying solid systems of Si nanocrystallites embedded in an insulating matrix. Our combined structural, transport, charge storage, and optical studies enable us to evaluate these processes as a function of the density of the quantum dots. In particular, we found a remarkable matching between the onset of the formation of quantum dot clusters, the above properties, percolation-clusters theory, and intracluster carrier migration.

DOI: 10.1103/PhysRevB.77.125318 PACS number(s): 73.22.−f, 64.60.F−, 78.60.−b, 78.67.Hc

I. INTRODUCTION

The understanding of the conduction mechanism in ensembles of Si quantum dots (QDs) is still at a rudimentary level in spite of the large interest in the physics of Si nanostructures in the past two decades.[1] This situation has not changed much in this period, probably since the emphasis in the study of these systems was on very dilute ensembles of Si QDs that included, in particular, charge storage (CS) in two-dimensional (2D) arrays and photoluminescence (PL) phenomena in essentially isolated QDs. In all these systems, the results obtained amounted, in general, to the simple sum of the contributions of the individual QDs. It was, however, noted already a decade ago by Burr *et al.*[2] that the transport in such and denser ensembles is governed by two types of mechanisms. One type is of a "topological-percolation" nature and the other is of an "electrical" nature. However, in that and later works, the first aspect was hardly discussed beyond some very general statements, while for the latter aspect, which was considered in quite a few works, the density of the QDs in the systems, $\tilde{N}$, has not been specified, thus yielding very different conclusions as to the electrical conduction mechanisms (for a short review, see Ref. 3).

In this paper, we try to derive *a self-consistent and comprehensive framework* for the basic physics of the transport phenomena and the related optical properties in ensembles of Si QDs by considering primarily the topological-percolation aspect of the problem, i.e., by applying cluster statistics as offered by percolation theory.[4] This is done here by combining detailed structural, transport, optical, and CS information[3,5] for the *same* ensembles of Si nanocrystallites (ncs). In our work, the Si QDs are embedded in an insulating matrix. Throughout this paper, $\tilde{N}$ (or the crystallite Si phase content) will be characterized by x, the vol % of the separate Si phase in that composite. The corresponding percolation threshold for Ohmic conduction will be denoted here by x_c.[3]

Before turning to the subject of this paper, let us point out that the connectivity between "touching" QDs in ensembles of semiconductor ncs is different than in granular metals[6] as in the former case; usually (and as in the system of interest here), there are narrow (no more than 0.3 nm wide) boundaries formed between the particles.[3] This quantum size "grain boundary" limit has not been studied thus far. We will call, however, the charge transfer process between such touching ncs, "migration," and we will refer to a connected group of such touching ncs as a QD cluster.

In a previous study,[3] we have emphasized the mutual exclusion of the PL and the transport, and suggested the dominance of the double barrier tunnel junction (DBTJ) like charging effects in the vicinity of the systems' x_c. This mutual exclusion of the PL and the photoconductivity is exhibited in Fig. 1 by a typical example that shows the intensity of the PL peak value (obtained in the 700–800 nm range[3]) and the magnitude of the photoconductivity as a function of x in the same sample. The fit of this dependence of the photoconductivity to the predictions of percolation theory yields that, in the case shown, x_c is at about 30 vol %.[3] Here, we are concerned with the very special features of the transport below and above x_c. These, as we show below, turn out to be quite unusual as they are markedly different from the most common findings on very dilute systems of Si QDs.[7–14] Moreover, we can now identify results reported in the

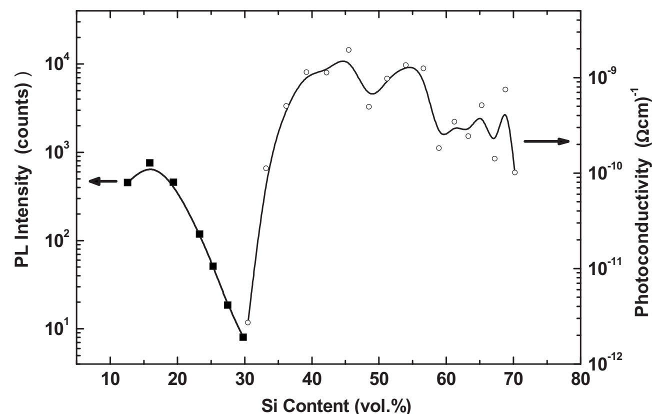

FIG. 1. The typical dependence of the PL intensity peak (full squares) and the photoconductivity (open circles) on the Si phase content in our cosputtered films.

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literature[15] to be different from the conventional ones[8] as being so due to their association with particular (in that case, high) concentrations of the QDs.

II. EXPERIMENT

Our tool for the determination of the stored charge in the present study is the capacitance-voltage (C-V) measurement in the metal-oxide-semiconductor (MOS) configuration,[16,17] as this is the most developed and best understood method for this purpose. While such measurements were usually employed[8–11] for the study of 2D arrays of silicon QDs, in this paper, we present a systematic study of the charging of the dots as a function of their density in three-dimensional systems. In particular, we will show here that not only is there a mutual exclusion of CS and conductivity, which is reminiscent of the above mutual exclusion of PL and conductivity, but also that there is an exact matching between the CS and the PL, and that it is associated with the variations in the Si QD cluster sizes and concentrations upon the increase of $\tilde{\mathrm{N}}$.

The films used in the present study were deposited by the cosputtering technique that was used extensively in the study of granular metals.[6] We have previously described our films' deposition procedure and the corresponding transport and PL measurements, demonstrating[3,18,19] that the Si ncs that are embedded in a continuous matrix of an insulating SiO_2 phase constitute a composite of Si QDs. The great advantage of this preparation technique is that *under the very same conditions*, one can prepare a continuous series of samples that differ from each other only by the contents of the two phases. In the present study, we used, however (in order to enable transport, PL, and CS studies on simultaneously deposited films), two adjacent parallel substrates, one made of an elongated ($13.5\times 1\ \mathrm{cm}^2$) quartz slide, for the coplanar transport and PL studies, and the other of a series ($14\times 1\ \mathrm{cm}^2$) of (four) strips that were cut from a n-type Si wafer for the CS and high resolution transmission electron microscopy (HRTEM) studies.[19] After the deposition and annealing (40 min at 1150 °C under nitrogen flow), the films' thickness was found to vary from about 0.8 μm, at the low ($x=5$) Si (high SiO_2) end, to about 1.2 μm, at the high ($x=80$) Si end. This configuration enables then, as shown in Fig. 1, to conveniently characterize various physical properties with a high resolution of x.[3,6,18,19] Let us mention also, in particular, that for the set of samples studied in the present work, we found (from the conductivity dependence on x, as in Ref. 3) that x_c was at 36 ± 1.

The main structural characterization of the films that was applied in this study was cross sectional transmission electron microscopy (TEM). The corresponding images that are summarized in Fig. 2, as a function of x, have revealed that our films consist of Si ncs embedded in an amorphous (primarily SiO_2 with possible minute amorphous Si) phase. The size and the shape of the silicon crystallites were found to vary from 3 nm and perfectly spherical, at the $x\approx 5$ end, to distorted spheres (mainly due to the need to accommodate neighbor ncs) with an average size of 8 nm, at the $x\approx 80$ end. For $x<18$, we found always (and in accordance with works of others[7]) isolated crystallites. Here, we were interested, however, mainly in the $17\leq x\leq x_c$ regime, as the PL and the interesting CS phenomena occur there. The image that is shown here for $x=25$ demonstrates clearly that for this x, we have ncs with an average diameter of 5 nm, and that some of the ncs are touching their neighbors, showing that QDs clusters are formed for $x>17$. We will assume below that the conduction mechanism between touching QDs differs from tunneling between separated QDs and that x_c is associated with the onset of a continuous network of touching QDs.[3]

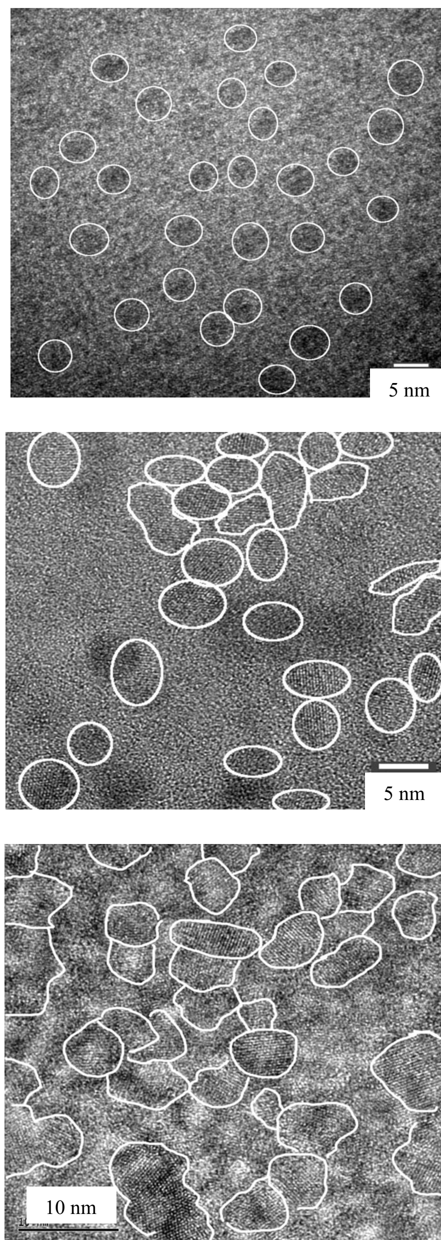

FIG. 2. HRTEM images of our cosputtered composites for three Si phase contents: 17, 25, and 80 vol %. The crystallites, detected by the Si lattice fringes, are marked by their border. Note that for $x<18$ vol %, the crystallites are geometrically isolated, nearly perfect spheres, and for $x=80$ vol %, they take the shapes needed for their high density accommodation.

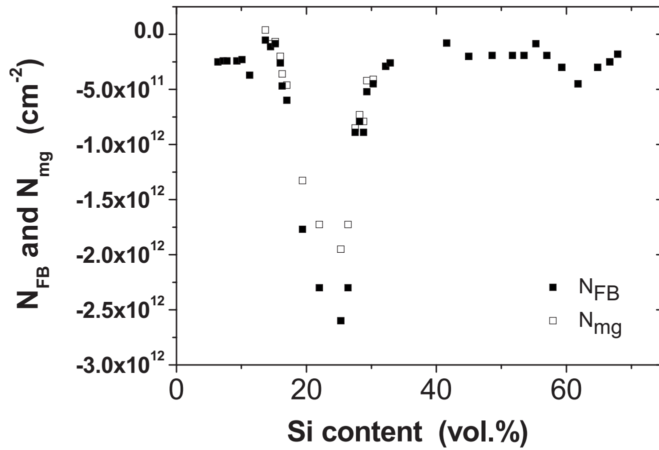

FIG. 3. The dependence of the Q_{FB} and Q_{mg} (given here by the corresponding densities of the stored, negative, elementary charges) on the silicon phase content in our cosputtered films. The fact that the stored charges are electrons is marked here by the sign of N_{FB} and N_{mg}.

III. EXPERIMENTAL RESULTS

Following our basic physical characterization of the above described films by PL[3,18] (excited by 488 nm photons) and electrical transport[3] measurements, we turned to the CS study by carrying out C-V measurements, such as we described previously[5] for various values of x. These were all taken at a frequency of 1 MHz, a voltage sweep rate of 0.5 V/s, and in the sweep direction from $V \leqslant 0$ to $V > 0$. For the derivation of the stored charge from the C-V data, we have employed, first, the rather standard maximum-minimum capacitance procedure[16,20] that yields the parameters of the corresponding ideal system, i.e., without the charge stored in the QDs (or the "oxide fixed charge"[16]), Q_f, and without the surface state charge, Q_{ss}, that are present at the Si substrate-composite interface. These parameters are the dopant density in the Si substrate and the "oxide" capacitance C_{ox}. The values of Q_f and Q_{ss} are derived then from the "flatband" (FB) charge $Q_{\mathrm{FB}} = -C_{\mathrm{ox}}\Delta V_{\mathrm{FB}}$ and the "midgap" (mg) charge $Q_{\mathrm{mg}} = -C_{\mathrm{ox}}\Delta V_{\mathrm{mg}}$, where the voltage deviations, ΔV_{FB} and ΔV_{mg}, are determined by the voltage shift between the experimentally found C-V characteristic and the corresponding, above mentioned, ideal C-V characteristic.[16,17] We have carried out both types (flatband and midgap) of analyses in order to check the self-consistency of the x dependencies of Q_{FB} and Q_{mg}. Indeed, as shown in Fig. 3, both quantities have the same dependence on x. A more detailed analysis of the "bulk" ($Q_{\mathrm{f}} \approx Q_{\mathrm{mg}}$) and surface stored charge ($Q_{\mathrm{ss}} \approx Q_{\mathrm{FB}} - Q_{\mathrm{mg}}$), which is not essential here, will be described elsewhere. The important and unexpected observation here is, however, that there is a relatively high density of stored electrons ($N_i = Q_i/q$, where N_i is the density of those charges per cm^2, i is FB or mg, and q is the elementary charge) for a particular x range, i.e., that the $Q_i(x)$ dependencies are peaked. The more striking finding is that this peak "happens" to be, within our experimental accuracy, *at exactly the same x value for which the PL intensity reaches its maximum*. For reasons to become apparent below, we call this x value the delocalization threshold of the ensemble, denoting it by x_d.

IV. DISCUSSION

Our above CS and PL results are summarized now in Fig. 4, in which we also show the expected theoretical prediction[4] of the dependence of ξ, the average cluster size, on x. The latter behavior is determined here by x_c (utilizing the above $x_c = 36$ result) and the TEM result that, as $x \to 0$, $\xi \approx d = 3$ nm, where d is the diameter of the individual QD. This yields then the average-cluster size dependence[3,4] $\xi = d[(x - x_c)/x_c]^{-\nu}$, where $\nu = 0.88$. The observed initial increase of the PL and the CS with x is obviously associated with the increase of the concentration of the QDs as reflected in Fig. 2. Similarly, the decrease of both the PL and the CS with the further increase of x is to be expected since as the QD density increases, the charge transfer between the QDs is facilitated and, thus, "eventually" (for high enough x) the delocalization of the carriers (from the QDs) will overcome the increase in the total concentration of the QDs, yielding the observed peaks. In particular, the formation and growth of the clusters for $x > 17$ (Figs. 2 and 4) appear to "accelerate" the "eventual" decrease of the PL and CS beyond the simple reduction of the average interdot distance (that in-

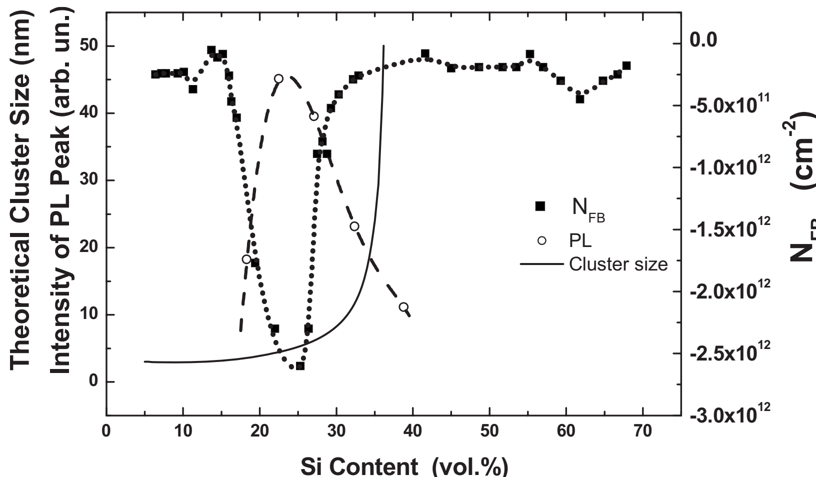

FIG. 4. The stored charge N_{FB} as a function of the Si phase content in our cosputtered samples as given in Fig. 3. Also shown for comparison are the corresponding electrical conductivity and the maximum intensity of the PL, as well as the theoretical prediction of the average cluster size of the QDs. The percolation threshold was derived from the fit of the electrical conductivity data to the prediction of percolation theory.

creases the interdot tunneling) with x. This is since the interdot migration is efficient enough for quenching the PL, which is determined[1,21] by the overlap of the electron and hole wave functions within the QD (needed for the efficient PL), as well as for the reduction of the CS, which follows the more efficient charge transfer by migration than by intercluster (including the nontouching ncs) tunneling[6,22]. In fact, the diffusive nature of the migration process is consistent with the increase in the dispersive nature of the PL[21] with the increase of x that we have found previously.[10] For the above reasons, beyond x_c, both the PL and the CS will diminish, and the relatively "free" inter-QD migration transport in the percolation cluster will yield the sharp increase of the conductivity.

In contrast with the above, the fact that x_d is *just the same* for the two different (PL and CS) properties is quite surprising since the effective delocalization due to the two processes as well as its consequences (e.g., the competition between the radiative and nonradiative processes which is relevant to the PL[10] but irrelevant to the CS) may be very different for the two properties. However, we can explain this common x_d by noting that the formation of clusters that are made of as few as two QDs is relatively much more effective in the cluster extent per mass, in comparison with the growth of isolated ncs or the formation of larger clusters (that tend to be spherical-like), yielding then simultaneously a considerable reduction of both the quantum confinement (i.e., the PL[1,21]) and the charge retention.[22] In particular, the formation of a two-QD cluster yields for our 5 nm QDs a cluster that is, in one direction, larger than the excitonic Bohr diameter in Si [8.6 nm (Ref. 1)], and for the CS, it yields the increase by a factor of 2 in the "aspect ratio" of the cluster, which is known[23] to increase efficiently the connectivity of the network. From the common peak, we conclude then that our *x dependencies of the PL and the CS* simply *reflect the concentration* of the essentially isolated single QDs. This conclusion is strongly supported by the fact that the value we found for x_d is at about $2x_c/3$, in excellent agreement with the prediction of percolation theory[4] for the peak in the concentration of the single-particle clusters. Also, the d-independent PL decay with x, which we found previously,[3] further suggests that we observe here a simple percolation effect.

The gross features of the complete transport scenario of the system for the three x regimes shown in Fig. 2 can be followed now. For $x<17$, we have isolated QDs and the communication between them can only be by sequential tunneling under Coulomb blockade as in granular metals in the dielectric regime.[6] This is to be contrasted with the common 2D (vertical-sandwich, MOS) configuration,[8,14] where only a single QD is involved in the transport and the injection of a carrier from the electrodes may be (unlike here) the high-field Fowler-Nordheim process.[12] The regime of greater interest in the present work is, however, the one between $x \approx 17$ and x_c, as there (see Fig. 2 for $x=25$) we have the intracluster migration transport as well as the intercluster tunneling transport. Finally, the conduction above x_c is quite different from the one in granular metals since there are still boundaries between touching QDs. In fact, the corresponding migration process is similar to that in polycrystalline semiconductors, but now the boundaries are in the quantum size regime. This scenario has not been discussed thus far and deserves a study in its own right. We note, however, that in the very close vicinity of x_c, we encounter the special situation that is reminiscent of the DBTJ.[3,24]

In conclusion, we have shown that, in ensembles of Si quantum dots, the mutual exclusion of the conductivity and the charge storage is very similar to the mutual exclusion of the former and the photoluminescence, and we argued that both are due to the formation of QD clusters. Correspondingly, we have introduced here the concept of the delocalization threshold of the ensemble, x_d, associating it with the onset of substantial migration of carriers within these clusters. We established here that the gross picture of transport in Si QD ensembles is reminiscent of that of granular metals, but the details are quite different. Here, below x_d, both carrier migration and intercluster tunneling are important; around x_c, quantum confinement as well as Coulomb blockade determine the electrical conductivity; and above x_c, the migration dominates the transport properties.

ACKNOWLEDGMENTS

This study was supported in part by the Russian Foundation for Basic Research (Project Nos. 04-02-16655, 05-02-16479, 05-02-16455) and in part by the Israel Science Foundation (ISF) and the Israeli Ministry of Science and Technology. The authors would like to thank I. Popov and M. Dovrat for the TEM images, and Y. Goldstein and O. Millo for very helpful discussions. I.B. acknowledges the support of the Enrique Berman chair in Solar Energy Research at the HU.

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