Electronic localization and optical absorption in embedded silicon nanograins

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(Received 19 December 2008; accepted 13 January 2009; published online 4 February 2009)

We study the spatial distribution of electron states in crystalline Si nanograins embedded into amorphous silicon. We prove that it is not possible to tune the absorption gap by only controlling the size of the grain, since no quantum confinement there occurs. The absorption properties of such a two-phase system are rather controlled by the population of localized electron states generated by large angular distortions of Si–Si bonds. © 2009 American Institute of Physics.

[DOI: 10.1063/1.3078281]

Nanocrystalline silicon (nc-Si) is currently under investigation for applications in optoelectronics and photovoltaics.1 It is a two-phase system (consisting of Si nanosized grains embedded into a Si amorphous matrix) combining the properties of the two separated phases to possibly provide improved optical absorption. In fact, while thick crystalline (c) Si solar cells achieve the highest photoconversion efficiency, amorphous (a) Si has a higher absorption coefficient. For these reasons, a-c Si systems are currently considered as a natural candidate for developing efficient but cheap thin film solar cells or low cost optoelectronics. The open question is whether the absorption properties of such silicon systems can be tailored by controlling the number and the size of the crystalline grains.

A first possible mechanism affecting absorption in nanostructured systems is quantum confinement (QC),2 occurring when the a-c boundaries act as efficient potential energy barriers for moving electrons. In case of QC, efficient tandem solar cells can be manufactured by modifying the average grain size in the nanocrystalline material, so as to stack layers with different absorption gaps on top of each other.4 As the average size of the nanograins is decreased, the energy gap increases, so that the absorption properties are accordingly affected.2 A clear evidence of QC effect is predicted and actually found in nanocrystals (or nanowires) in vacuum,2 as well as in nanocrystals embedded into a wide gap dielectric matrix (e.g., silicon dioxide). In this case, QC critically depends on the complex morphology of the grain-matrix boundary. Concerning nc-Si, QC is in principle possible since a sizeable band offset (about 0.4 eV) is provided by the different energy gap between c-Si and (hydrogenated, i.e., with very few dangling bonds) a-Si. Nevertheless, theoretical studies rather indicate a blue shift in the absorption peak,4 although a clear picture is still missing.

A second possibility to tailor the absorption properties of a-c layers is by modifying the number of intragap electron levels. It has been recently demonstrated that structural defects at the grain interface (rather than QC) can be responsible for the observed absorption properties of Si quantum dots in SiO2.5,6 In the case of nc-Si, localized electron states are similarly expected to affect absorption and to depend on the morphological features of the a-c boundaries, or on the actual occurrence of defects.7 In particular, localized states are known to contribute to the low energy absorption tails (i.e., Urbach tails) in a-Si.8 Their correlation to the atomic-scale structure has been recently readressed9,10 but not yet fully resolved. Finally, it is well known that such localized states fully control the absorption below the mobility edge.11

This picture clearly states that it is critical to correlate the number and the nature of defect-induced electron levels to the actual a-c microstructure.12 Unfortunately, this task is especially difficult since it is experimentally very hard to fully characterize the atomic-scale features of a-Si. The present work is aimed at improving our basic understanding about confinement and localization and at establishing a robust picture on their role in the absorption properties of a-c Si systems. To this aim, we calculate the optoelectronic properties of perfectly fourfold coordinated systems consisting of a cylindrical nanocrystal embedded into amorphous silicon and we study the spatial localization of electron states and its dependence on the actual grain size.

Our model nc-Si system consists of a single cylindrical nanograin (with diameter ranging from 0.4 to 4 nm) inserted into a a-Si matrix, previously generated by means of the Wooten, Winer, Weaire algorithm.13 We adopt the Tersoff force field14 to relax the nanostructure by means of damped dynamics. Overall the present computer-generated models contain 1024 atoms, placed within a periodically repeated orthogonal slab of dimensions 2d0 × 8d0 × 8d0, where d0 is the c-Si lattice constant. The perfect fourfold coordination was kept everywhere in the system, including the a-c boundaries. The enforced fourfold coordination mimics the typical experimental conditions, where dangling bonds are mostly suppressed by hydrogenation. We remark, however, that possible effects due to H decoration of nanograins are not discussed here and will be treated elsewhere. We also point out that while QCs in silicon nanocrystals have been already investigated extensively by using both first-principles and empirical methods,2 only a few studies3,15 focused so far on the case of embedded grains.

The electron states are calculated by means of a sp3s* orthogonal tight binding (TB) model,16 already successfully adopted to investigate the electronic properties of both c-Si and a-Si. In particular, this model correctly reproduces the...
indirect nature of the c-Si energy gap, as well as the gap value in a-Si and c-Si. Conduction tail states are therefore well reproduced. The absorption coefficient $a(E)$ is evaluated from the joint density of states within the constant matrix approximation. We calculate the integrated absorption coefficient as $\Omega = \int^E a(E) dE$, where $E$ is the energy range for absorbed photons. Once $E$ is fixed, it is possible to calculate the integrated absorption coefficient as a function of the grain diameter $D$ because $\Omega$ depends on the crystal-to-amorphous ratio $\chi$ (Ref. 19) or, equivalently, on the grain diameter. In this work we consider two different absorption energy ranges, namely, $E=3$ eV and $E=4$ eV. The results are reported as symbols in Fig. 1 (top panel). Interesting enough, our present atomistic calculations are well reproduced by a simple model that combines the integrated absorption of bulk a-Si ($\Omega^a$) and bulk c-Si ($\Omega^c$) into the following weighted average:

$$\Omega(D) = \chi \Omega^a + (1 - \chi) \Omega^c,$$

with $\chi = \pi D^2 L^2 / 4$, whereas $L^2$ and $\pi D^2 / 4$ represent the area of the simulation slab and of the cylindrical grain, respectively. We note that thereafter all absorption values are normalized to the c-Si one.

In order to further elaborate the above result, we make use of Eq. (1) where the $D$-dependent term $\Omega(D)$ is now obtained by an explicit TB calculation, while the $\Omega^a$ contribution is kept fixed at the a-Si bulk value. This allows to define an effective $\Omega^e(D)$ integrated absorption for the nanograin, which is reported in Fig. 1 (bottom) for the two selected photon energy ranges. We remark that when $D > 1$ nm, then $\Omega^e(D) \sim \Omega^c$, i.e., the nanograin absorbs similarly to bulk c-Si. This suggests that no QC actually occurs. At variance, when $D < 1$ nm, then $\Omega^e$ deviates from the crystalline value. The amplitude of the deviations is larger for smaller grains. We note, furthermore, that the largest deviation corresponds to a remarkable enhancement of the effective absorption with respect to $\Omega_c$. The case of a quantum wire in vacuum (calculated by using the data in Ref. 2) is reported in Fig. 1 (bottom) for the sake of comparison. The corresponding effective integrated absorption steadily decreases for small grains, following the increasing energy gap. In particular, it is found that for a wire diameter smaller than 0.8 nm no absorption takes place. Present calculations demonstrate that the absorption of an embedded cylindrical Si nanocrystal is not affected by QC, at variance with the case of a free-standing quantum wire (QW).

The observed deviations of $\Omega^e(D)$ with respect to the bulk value $\Omega_c$ are linked to fluctuations in the number of localized intragap levels of the a-c system. We will refer to an electron state as localized in a given point provided that no less than 50% of the electron charge is contained in a sphere of radius of 0.5 nm centered there. A careful analysis of the present a-c models shows that localized states are always associated to local angular distortions of Si–Si bonds, similar to what happens in bulk a-Si. A systematic investigation of the valence and conduction band tails leads us to identify two kinds of bond defects, namely, point ($P$-) and extended ($E$-) ones. $P$-defects are found when a single bond angle deviates from the perfect tetrahedral one by a $\Delta(\theta) > 27^\circ$; in such a case more than 50% of the electron charge is located at the defect core. E-defects, instead, involve a group of neighboring bonds for which $27^\circ < \Delta(\theta) < 22^\circ$. In this case the charge located nearby these bonds is always smaller than 16%. In Fig. 2 two examples of $P$-defects are shown for a very small (top) and a larger (bottom) grain, respectively.

In conclusion, we can also prove that $P$- and E-defects generate spatially overlapping states, both in the valence and conduction band tails, thus allowing for creation of geminate

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**Fig. 1.** Top: absorption coefficient integrated up to $E=3$ eV (open circles) and $E=4$ eV (full squares). Dashed and full line represents the corresponding predictions of Eq. (1). Bottom: effective absorption coefficient for a nanograin. Full and dashed lines are taken from Ref. 2 and correspond to an isolated quantum wire. Absorption of bulk c-Si is shown by a thin dotted line; its value is used to normalize the computed $\Omega(D)$ and $\Omega^e$.**

**Fig. 2.** (Color online) Spatial localization of two $P$-defects when the embedded nanocrystals have diameters $D=0.4$ nm (top) and $D=1.6$ nm (bottom). The color scale represents the degree of localization: the brighter is the color (yellow), the more localized is the represented electron state.
pairs. We quantify the spatial correlation between two \( n \) and \( m \) electron states (with energy \( e_n \) and \( e_m \), respectively) by calculating the quantity 

\[
C(\varepsilon) = \sum_{i,a} |c_{i,a}^n|^2 |c_{i,a}^m|^2,
\]

where \( c_{i,a}^n \) is the coefficient of the TB expansion for the \( n \)th state, \( i \) is the Löwdin orbital centered on atom \( \alpha \), and \( \varepsilon = e_n - e_m \). According to this definition, photon absorption induced transitions involving nearby localized states must correspond to a large \( C(\varepsilon) \) value. The spatial correlation function \( C(\varepsilon) \) is reported in Fig. 3 as a function of transition energy for a nanograin with diameter as large as \( D = 1.6 \) nm. By checking the spatial extension of the localized electron states for which \( C(\varepsilon) \) is larger, we found that they always correspond to neighboring band tail states, i.e., angular bond defects. We can therefore conclude that angular defects are both optically active and responsible for low energy absorption. Finally, we remark that optically active defects are found in the \( \alpha \)-Si phase. However, as shown in Fig. 2 (top panel), they also occur nearby (or just at) subnanometric crystalline grains. This result suggests that also subnanometric grains are indeed optically active defects.

This work was funded by EU under project “NANO-PHOTO” and by Italian MIUR under project “Cybersar.” We acknowledge S. Sanguinetti (University of Milano Bicocca, Italy) for useful discussions.