Coordination defects in a-Si and a-Si:H: a characterization from first principles calculations

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We study by means of first-principles pseudopotential method the coordination defects in a-Si and a-Si:H, also in their formation and their evolution upon hydrogen interaction. An accurate analysis of the valence charge distribution and of the “electron localization function” (ELF) allows to resolve possible ambiguities in the bonding configuration, and in particular to identify clearly three-fold ($T_3$) and five-fold ($T_5$) coordinated defects. We found that electronic states in the gap can be associated to both kind of defects, and that in both cases the interaction with hydrogen can reduce the density of states in the gap.

I. INTRODUCTION

Amorphous silicon (a-Si) and hydrogenated amorphous silicon (a-Si:H) are prototypes of disordered covalent semiconductors. Extensive work, both experimental and theoretical, has been done to study their topological and electronic structure. Although most of Si atoms are tetrahedrally coordinated, anomalously coordinated configurations can locally occur in pure and hydrogenated amorphous samples, but –at variance with the case of crystals where coordination defects can be easily recognized as deviations from the perfect ordered structure– their identification is not trivial. Hence, one of the most challenging problems in the amorphous systems is to localize the defects, to classify them and to identify their peculiar electronic features.

Traditionally, three-fold ($T_3$) defects have been considered as the most likely intrinsic defects in a-Si. The non vanishing density of states (DOS) observed in the gap has been commonly ascribed for a long time to the “dangling bonds” corresponding to these defects, and its lowering upon hydrogenation has been explained with the saturation of dangling bonds by hydrogen (Ley 1984, Fedders and Carlsson 1988, 1989, Biswas et al. 1989, Holender and Morgan 1993, Lee and Chang 1994, Davis 1996, Tuttle and Adams 1996).

More recently, this picture has been debated and revised. In particular the importance of five-fold coordinated ($T_5$ or “floating bonds”) in a-Si has been clearly stated in the theoretical works by Pantelides (1986, 1987) and Kelires and Tersoff (1988) a dozen of years ago, both in terms of their existence and their peculiar role in the electronic structure. The empirical simulation by Kelires and Tersoff (1988) has shown that $T_5$ atoms have lower energy than $T_3$ atoms, and therefore should be favoured in general. Also some ab-initio molecular dynamics simulations of a-Si structures show a predominance of $T_5$ defects with respect to $T_3$ (Buda et al. 1989, Stich et al. 1991, Buda et al. 1991). Pantelides (1986, 1987) argued that $T_3$ and $T_5$ are conjugated defects and must be considered on the same footing, since a bond elongation can transform a $T_5$ + $T_4$ structure into a $T_4$ + $T_3$ one, or vice versa an inward relaxation can transform a $T_4$ + $T_3$ structure into a $T_5$ + $T_4$ one; furthermore, he proposed a mechanism for H diffusion based on floating-bond switching and annihilation/formation of $T_5$’s through interaction with H (Pantelides 1987), which —at variance with the commonly accepted picture of dangling bonds hydrogenation—is compatible with the rapid decrease in the number of defects without any appreciable change in the density of Si–H bonds experimentally observed at low temperature.

Some of these ideas have been widely used in discussing the geometrical characterization of defects; their soundness in terms of electronic properties has been investigated mainly by model calculations (Fedders and Carlsson 1987,
1988, 1989, Fedders et al. 1992) and more recently by some first-principles calculations (Fedders et al. 1992, Lee and Chang 1994, Tuttle and Adams 1996, 1998, Fornari et al. 1999).

It remains the necessity of a simple tool going beyond purely geometrical criteria for a localization and an unambiguous characterization of defects. Recently the maximally-localized Wannier function approach has been applied to analyze the bonding properties in amorphous silicon ([Marzari and Vanderbilt 1997, Silvestrelli et al. 1998). We focus in the present work on a real-space analysis of the bonding pattern of a-Si and a-Si:H using the simplest tools provided by first-principles electronic structure calculations: a comparative analysis of the electronic charge density and the “electron localization function” (ELF) (Savin et al. 1992). We address the reader to another work (Fornari et al. 1999) for an accurate analysis using local or projected density of states (DOS) which completes the characterization of the coordination defects in terms of electronic properties, and we recall here only the main results.

II. RESULTS AND DISCUSSIONS

For studying the bonding properties in a-Si and a-Si:H we start from some selected samples generated by other authors (Buda et al. 1989, Štich et al. 1991, Buda et al. 1991) using Car-Parrinello first-principles molecular dynamics (CPMD). These structures reproduce quite well the experimental pair correlation function and bond angle distribution function using a reasonable number of atoms and hence they are suitable for accurate ab-initio studies. The configurations studied are cubic supercells of side \(a = 2a_0\), where \(a_0 = 10.17\) a.u. is the theoretical equilibrium lattice parameter of c-Si, which also corresponds —in our calculations— to the optimized density of a-Si and a-Si:H. The supercells contain respectively 64 Si atoms to describe a-Si (Buda et al. 1989, Štich et al. 1991) and 64 Si atoms plus 8 H atoms for a-Si:H (Buda et al. 1989, 1991).

We use state-of-the-art electronic structure methods based on DFT using norm-conserving pseudopotentials and plane-wave basis set (Fornari et al. 1999). The CPMD configurations, aiming mainly at reproducing the structural properties, have been obtained using a kinetic energy cutoff \(E_{\text{cut}} = 12\) Ry and the \(\Gamma\) point only for Brillouin Zone (BZ) sampling. We improve in our calculations the BZ sampling using 4 inequivalent special \(k\) points for self-consistency and 75 \(k\) points for DOS. These parameters have been chosen as a reasonable compromise between accuracy and computational cost. The optimization of the a-Si and a-Si:H structures with the new computational parameters is accompanied only by small structural rearrangements, and therefore the mean structural properties are very similar to those reported by Buda et al. (1989, 1991) and Štich et al. (1991) for the original configurations, and we do not discuss them in detail here. We only report that in a-Si the mean bond length is \(d \approx 4.47\) a.u., quite similar to the crystalline one which is 4.40 a.u.. The mean bond angle is \(\vartheta \approx 109^\circ\), close to the characteristic value of the perfect tetrahedral network. The location of the first minimum of the radial distribution function defines geometrically the cutoff distance for the nearest neighbours (NN), which turns out to be \(R_{NN} = 5.08\) a.u., giving an average coordination number of about 4.03. In a-Si:H the average Si-Si bond length is the same as in a-Si, but the first peak of the radial distribution function is more broadened and it is more appropriate to consider a larger NN cutoff distance, \(R_{NN} = 5.49\) a.u.. Each H is bound to one Si atom with an average distance \(d_H = 2.95\) a.u., very close to the corresponding value in SiH4 molecule.

The standard geometrical analysis based simply on counting the atoms lying inside a sphere of radius \(R_{NN}\) indicates that the starting configurations have a predominance of \(T_3\) defects and of distorted \(T_4\) sites. Moreover, the a-Si samples do not contain well defined \(T_4\) defects. This feature can be a consequence of the rapid quench from the liquid states which has been done in preparing the sample in the molecular dynamics process (since the liquid state is sixfold coordinated, a rapid quench typically favours overcooordination rather than undercoordination).

We thus start analyzing in detail an overcoordinated environment. For the sake of clarity, we will consider the case of a-Si (in a-Si:H overcoordination can be due to five Si neighbours, or to four Si and one H, and so on).
FIG. 1. The inset shows a snapshot from the a-Si configuration including two \( T_5 \) defects with an intermediate four-fold coordinated atom (I) and other \( T_4 \) atoms (not individually labelled). The curves are the profile of the valence charge density along some bonds shown in the snapshot, connecting: two normally four-fold coordinated atoms (dotted line), a \( T_5 \) with a \( T_4 \) at “normal” distance (short-dashed line), a \( T_5 \) with a \( T_4 \) at “longer” distance (long-dashed line), a \( T_5 \) with I (dashed-dotted line). “Normal” and “longer” are with respect to the average bond length. For comparison also the perfect crystalline bond is shown (solid line). In order to filter out possible unrelevant local fluctuations, the charge distribution is filtered averaging over small spheres of radius \( R = 0.6 \) a.u. moving along the bond. The distance is along the geometrical bond, calculated from one of the two atoms connected; note the different bond lengths. At variance with the crystalline case, the charge profiles are asymmetric with respect to the bond centre, indicating a partially ionic character of the bond.

In our a-Si sample there are two \( T_5 \) sites close one to each other (labelled A and B in the upper snapshot in figure 1), with a sort of interstitial (I) atom connecting them. A charge density analysis confirms for this configuration the bonding pattern predicted by the geometrical criteria, and helps in characterizing the different types of bonds (Stich et al. 1991). We observe that \( T_5 \) sites are accompanied by a valence charge density depletion. The charge density profiles reported in figure 1 show in particular that some \( T_5-T_4 \) “long” bonds and the bonds \( T_5-I \) are characterized by a very small charge density; hence, they are “weak” and therefore those \( T_5 \) defects are the best candidates to transform into \( T_3 \) sites after a bond elongation. The asymmetry in the bond charge profiles indicates that, at variance with the perfect crystalline environment, the bonds are not perfectly homopolar but have a certain degree of ionicity.

It is useful to investigate the bonding pattern using a different kind of real-space analysis, i.e. the study of the “electron localization function”. The ELF was originally defined as a scalar function \( \mathcal{E}(\mathbf{r}) \) measuring the conditional probability of finding an electron in the neighbourhood of another electron with the same spin. In the reformulation due to Savin et al. (1992) it is expressed as:

\[
\mathcal{E}(\mathbf{r}) = \frac{1}{1 + [D(\mathbf{r})/D_h(\mathbf{r})]^2},
\]

where \( D(\mathbf{r}) \) is the Pauli excess energy density, i.e. the difference between the kinetic energy density of the system and the kinetic energy of a non-interacting system of bosons at the same density. \( D_h(\mathbf{r}) \) is the same quantity for the
homogeneous electron gas at a density equal to the local density. With this definition, a value of $\mathcal{E}(r)$ close to 0.5 in the bonding regions indicates a metallic character; a value close to one is characteristic of regions where the electrons are paired to form a covalent bond, but also of regions with an unpaired lone electron localized, thus corresponding to a dangling bond. The ELF has been originally proposed in the all-electron formalism, and only very recently it has been successfully applied in the framework of the density functional theory (DFT) within the pseudopotential method (De Santis and Resta 1999). Whereas charge density plots are a standard tool in the first-principles theoretical studies of real materials, ELF investigations are still lacking, and this is, to our knowledge, the first application to disordered solid state systems.

In the case of normal or floating bonds, the ELF does not add much more informations with respect to the standard charge density analysis. In the left upper panel of figure 2 we show the ELF=0.85 isosurfaces for the overcoordinated environment in a-Si described before. High-value charge density (not show here) and ELF isosurfaces are almost similar in their extension and shape. The ELF isosurface in correspondence to the A–I bond clearly visualizes its bowing (the isosurface is not perfectly centred on the geometrical bond) and its weakness (the isosurface is smaller than those on the other bonds).

FIG. 2. Upper panels: a snapshot from the starting a-Si configuration including two $T_5$ defects (A and B) with an intermediate $T_4$ atom (I). The ELF=0.85 isosurfaces are plotted: it is clearly visible the off-centered position and the small distorted shape between atoms A and I, indicating the bowing and the weakness of the bond. The total DOS of the a-Si sample is shown on the right, with electronic states close to the Fermi energy $E_F$. Lower panels: the structure evolved after addition of two H atoms (small white balls, H1 and H2) which have annihilated the $T_5$ defects. All the Si atoms of our sample are now “normal” $T_4$ sites, as shown by the more regular shape of the ELF isosurfaces and by the vanishing DOS in the gap.
Adding two hydrogen atoms in the neighbourhood of the $T_5$ sites and allowing the system to relax, two Si–Si bonds are broken so that the atoms A and B become normally tetrahedrally coordinated, and their fifth NN atoms connect with the additional hydrogens (see the snapshot in the lower panel of figure 2). In this configuration all the Si–Si bonds are rather strong (the ELF isosurface between A and I is more extended with respect to the previous case) and more bulk-like (all the isosurfaces are more regular in shape). The plots of the density of states (right panels in figure 2) show that, at variance with the starting configuration having a metallic character evidently due to defect induced states in the gap, the final one is clearly semiconducting.

FIG. 3. Upper panels: a snapshot from a-Si:H with a $T_4 + T_3$ structure (atom A and B respectively). Charge density isosurfaces ($n=0.06$ a.u.) and ELF=0.85 isosurfaces are plotted respectively in panels (a) and (b). The dangling bond on atom B is evident by comparison of the two plots as a region of low charge density but high ELF. The total DOS of the sample is reported in panel (c): the sizeable DOS around $E_f$ is due to the $T_3$ defect and other defects in the sample. Lower panels: a snapshot containing the same atoms after relaxation, with a new bond formed between A and B atoms giving rise to a $T_5 + T_4$ structure. Charge density and ELF isosurfaces are plotted in panels (d) and (e) respectively, as in the previous case. The new A–B bond is characterized as a region of high charge density and ELF. The total DOS of the sample is reported in panel (f): gap states are still present.

The combined charge-density and ELF analysis is necessary to identify unambiguously the dangling bonds and to distinguish for instance a $T_5 + T_4$ configuration from a $T_4 + T_3$. Whereas the presence of a covalent bond is indicated by a region of local maxima of both ELF and charge density, a dangling bond is identified by a region with high values of ELF but low electronic charge density. This is evident in figure 3 (upper panels), where we show a snapshot from a a-Si:H sample with a $T_4$ (labelled A) and a $T_3$ (labelled B) atoms (we have created a dangling bond by removing an hydrogen initially bond to the silicon atom B). Panel (a) shows charge density isosurfaces, and panel (b) ELF isosurfaces. The absence of high-value charge density isosurface together with the presence of high-value ELF isosurfaces in the region between atoms A and B clearly indicate the presence of a dangling bond originated from atom B. As expected, this configurations has a metallic character, with electronic states around the Fermi energy $E_f$ (panel (c) of figure 3).

When the system is allowed to relax, a new bond is formed between the silicon atoms A and B, as it clear from the
panels (d) (charge density) and (e) (ELF). The final system has still gap states, both because of the $T_5$ defect B which is now formed and because other coordination defects are present in the rest of the a-Si:H sample. The evolution of this structure from a $T_4 + T_3$ into a $T_5 + T_4$ is consistent with the picture of Pantelides (1986) of the conjugated $T_3$ and $T_5$ sites.

III. SUMMARY

In conclusion, we have presented the results of accurate ab initio self-consistent pseudopotential calculations of a-Si and a-Si:H samples with different coordination defects starting from some configurations generated via CPMD, and we have followed some possible processes of defect formation, annihilation by H, and transformation of one defect into the other. Those techniques allowing to identify the defects in real space are suitable for their localization in disordered structures. In particular, we have shown that a combined analysis of the electronic charge density distribution and ELF allows to unambiguously classify the different kind of defects. We have clearly identified $T_3$ and $T_5$ defects, and comparing the DOS in the different configurations we have shown that they both can induce states in the gap, whose density is reduced in both cases by interaction with H.

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