Wannier-functions characterization of floating bonds in a-Si

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Abstract

We investigate the electronic structure of over-coordinated defects in amorphous silicon via density-functional total-energy calculations, with the aim of understanding the relationship between topological and electronic properties on a microscopic scale. Maximally-localized Wannier functions are computed in order to characterize the bonding and the electronic properties of these defects. The five-fold coordination defects give rise to delocalized states extending over several nearest neighbors, and therefore to very polarizable bonds and anomalously high Born effective charges for the defective atoms.

1 Introduction

Coordination is a well-defined concept in crystalline systems, where it is closely related to the concept of bonding. For instance, silicon atoms are tetrahedrally coordinated, and exhibit covalent bonds with their four nearest-neighbors (NNs) in the ordinary crystalline phase (c-Si). Whenever symmetry is broken, as in the case of amorphous silicon (a-Si) studied here, the link between coordination and bonding becomes less obvious. Even if atomic positions are intimately connected with the electronic ground state, we are usually unable to extract detailed informations about bonding from a purely geometrical investigation. Standard analytical tools based on coordination-number analysis are thus insufficient to characterize bonding properties, since they are insensitive to the details of the electronic charge distribution. Whenever strong topological disorder is present, as in the case of atoms with three or five nearest neighbors (T₃ or T₅ defects), the ionic potential and the charge distribution can be significantly different from the crystalline case, and great care should be used to identify the nature of bonding.

In this work we use density-functional theory in the local density approximation to calculate the electronic properties of over-coordinated defects in a-Si. Density-functional theory provides an accurate and parameter-free description of the electronic ground-state, and is equally capable of dealing with four-fold coordinated atoms and with more complex topologies. The characterization of defects is then based on the decomposition of the electronic ground state into localized orbitals, using the technique of maximally-localized Wannier functions (MLWF). In this approach, the extended Bloch orbitals are transformed via unitary transformations into a representation where
they are maximally localized. The role and importance of such localized Wannier functions in the study of disordered systems (amorphous silicon in particular) has been advocated by Silvestrelli and coworkers [2], who have shown that the coordination analysis is often insensitive to the electronic charge distribution and that similarly coordinated atoms can be surrounded by rather different bonding environments. Our present results support these findings.

The conjecture that over-coordination could play an important role in the formation of mid-gap electronic levels in amorphous silicon has been recently validated by some of us [3], using accurate density functional calculations. In that work we argued that $T_5$ defects can be responsible, as much as $T_3$ ones, for states close to the Fermi level. We also showed that in the case of $T_3$ defects the mid-gap electronic state originates from the dangling bond and is well localized on the $T_3$ defect itself. Conversely, in $T_5$ defects the midgap electronic state is delocalized over several NNs of the $T_5$ site, in agreement with the findings of tight-binding calculations reported in Ref. [4]. In this work we pursue further the study of the extended nature of $T_5$ defects. Our goal is to understand how many atoms can be actively involved in a defect, since this number influences the shape of the “super-hyperfine” structure of the D center in the electron-spin resonance (EPR) spectrum [5]. In turn, this should discriminate dangling bonds from floating ones. It should be noted that both $T_3$ and $T_5$ centers generate a D signal; it is the contributions of the secondary ions involved in the uncompensated spin distribution (the super-hyperfine structure) that should be very different in the case of a dangling or a floating bond.

The plan of the work is as follows: in Sec. 2 we describe our ab-initio calculations and we review the method used to compute the MLWFs. We also comment on the link with the dynamical Born effective charges $Z$. In Sec. 3 we discuss the results for our a-Si sample, in comparison with the results obtained using the “electron-localization function” (ELF) [6] and the “atomic-projected charge” (APC) analysis [3]. Sec. 4 is devoted to the conclusions.

## 2 Computational tools

The calculations performed here are based on density-functional theory in the local-density approximation, using a cubic super-cell containing 64 Si atoms [7], a plane wave basis set, and accurate norm-conserving pseudopotentials. The electronic ground-state is obtained using an all-bands conjugate gradient minimization [8]. The sampling in reciprocal space is performed with 8 $\mathbf{k}$ points in the full Brillouin zone.

The analysis of the Kohn-Sham orbitals and their charge density has been previously performed using the APC and the ELF analysis [3, 6]. APC is a measure of the contribution of the different atoms to the charge density, and it is obtained projecting the Bloch orbitals $\Psi_{nk}$ on localized atomic functions [3]. ELF, defined as in Ref. [9], is a measure of the conditional probability of having one electron close to another one with the same spin. It approaches its upper limit (1.0) when the electron density resembles a covalent bond or in the presence of unpaired electrons.

Both these approaches provide useful results in the characterization of the electronic distribution; still, there are several limitations that will be mentioned in the next section. The analysis based on localized Wannier functions overcomes these lim-
Figure 1: Left panel: structure of the “defect group” embedded in our a-Si sample. Atoms are labelled T\textsubscript{5} (T\textsubscript{4}) when they are five-fold (four-fold) coordinated. Atom I (interstitial) is the only four-fold atom that is a NN of both T\textsubscript{5}’s. Right panel: the “defect group” is shown together with the centers of the associated Wannier functions. C\textsubscript{1} and C\textsubscript{2} are the centers with the lowest symmetry, and exhibit the strongest deviations from the geometrical mid-bond positions.

Wannier functions are an alternative representation of the electronic ground state, that classifies states using a spatial coordinate \( \mathbf{R} \) and a band index \( n \). Wannier functions are not eigenstates of the Kohn-Sham Hamiltonian, but are related to them via the unitary transformation

\[
|\mathbf{R}n\rangle = \frac{V}{(2\pi)^3} \int_{BZ} |\Psi_{nk}\rangle e^{-i\mathbf{R}\cdot \mathbf{k}} d\mathbf{k}.
\] (1)

In the electronic structure problem there are degrees of freedom that do not affect the self-consistent ground state, but determine the shape of the WFs obtained from Eq. (1). They consist of arbitrary unitary rotations \( U_{mn}(\mathbf{k}) \) that mix together at any given \( \mathbf{k} \) in the Brillouin zone fully occupied Bloch orbitals (in the case of a single band, these unitary matrices reduce to a phase factor \( \phi(\mathbf{k}) \)). It is of paramount importance, in order to provide a meaningful real-space representation, to choose these arbitrary matrices \( U_{mn}(\mathbf{k}) \) so that the resulting WFs are well localized. The approach used here follows the lines of Ref. [1], where the unitary rotations are refined until the resulting Wannier functions are maximally-localized, i.e. they have minimum spread

\[
\Omega = \sum_{n} \left[ \langle 0n|\mathbf{r}|0n\rangle - \langle 0n|\mathbf{r}|0n\rangle^2 \right].
\] (2)

Incidentally, the sum of the Wannier function centers (WFCs) \( \mathbf{r}_c^n = \langle 0n|\mathbf{r}|0n\rangle \) is directly related to the macroscopic polarization of the sample \([10]\), and this makes the Wannier function analysis attractive to study dielectric properties. In particular,
Figure 2: Wannier functions centered near crystal-like coordinated atoms in the a-Si supercell. In each case a covalent bond (light gray) exists between two four-fold coordinated atoms, and the WFC is close to the geometrical bond center. For each atom, clover back-bonds (dark gray) point towards the remaining three neighbors.

the change in polarization induced by the displacement $\Delta \tau_N$ of an atom $N$ is directly related to the electronic component of its Born dynamical-charge tensor $Z_N$ by

$$(Z_N)_{i,j} = -2 \sum_n \frac{\Delta r^c_n \cdot e_i}{\Delta \tau_N \cdot e_j}$$  \hspace{1cm} (3)$$

where $n$ runs over all the occupied WFs in the unit cell and $\Delta r^c_n$ are the displacements of the WFCs.

### 3 Results on a-Si

The presence of mid-gap states in a-Si is usually ascribed to the existence of T₃ defects in the system. Such conclusion relies on EPR experiments, which measure the unpaired spin oscillations of the electrons in the dangling bonds. Nevertheless, certain features of the EPR signals (the “super-hyperfine structure”) derive also from the ionic magnetic moment and the quadrupolar term of the secondary ions in the defect [3]. Thus, the
EPR signal is indirectly sensitive to the presence of complex geometries. $T_5$ defects are expected to give rise to more delocalized states involving several atoms $\ldots$, and could thus provide a distinctive shape to the EPR signal. Prompted by these considerations, we investigate in this work the electronic properties of over-coordinated defects in amorphous silicon.

Our samples have been obtained by annealing configurations spanned during a first-principles molecular dynamics simulation $\ldots$. In particular, we have selected for this study a sample presenting two $T_5$ coordination defects. Although this corresponds to a density of defects higher than that of experiments, it still results in a useful model to investigate the effects of local strain and topological disorder. The defects were first identified using a geometrical analysis: an atom is counted as a neighbor if it resides inside a sphere of radius $R_c = 2.6$ Å (to compare with the theoretical NN distance in c-Si $d_{NN} = 2.357$ Å). This radius is chosen as the first minimum in the correlation function $g(r)$, since the peaks correspond, intuitively, to the succession of shells surrounding the reference atom. The two $T_5$ defects (labelled $T_5^A$ and $T_5^B$ in Fig. 1) belong to a “defect group” (Fig. 1, left panel), mostly composed of bonds which are longer and weaker than four-fold ones. Such environment seems favorable to induce delocalization of the wavefunction over several neighbors; our previous APC analysis (see Ref. $\ldots$) supported this conjecture, as did a similar investigation (Ref. $\ldots$) based on the electronic localization function. Both approaches however suffer from inherent limitations: the projection technique used for the APC does not provide meaningful informations on the mid-bond region; on the other side, ELF (once it has been been used to unambiguously distinguish between a $T_3$ and a $T_5$ site) is not able to improve the qualitative description of the defect that can be obtained from the direct inspection of the charge density.

To improve our understanding of the electronic structure of the defect group, we calculated the MLWFs for this configuration. In crystalline Si each WF is centered in the middle of the bond and oriented along the bond $\ldots$; a covalent “barrel” of charge is shared between the two bonded atoms, while some back-bonding charge is distributed between each of these atoms and its remaining three NNs. We expect that in a slightly distorted environment, where short range order is conserved, the shape of the WFs would not drastically change. This is clearly confirmed by our calculations (see Fig. 2). Small deviations from the crystalline case are due to the bending and stretching of bonds, but no doubt exists on the nature of the bond, that resembles closely to the bond of crystalline silicon. Such “regular” bonds are clearly related to their crystalline counterparts by having a very peaked distribution in their spreads, with a maximum around 2.30 Å$^2$ (vs. 2.04 Å$^2$ for crystalline silicon, using the same 8 $k$-point sampling).

We started our analysis focusing on the position of the WFC, as suggested by Silvestrelli et al. $\ldots$. In that work it was observed that the centers of charge for anomalous WFs tend to be closer to one specific atom than those of regular WFs, which are instead equally distant from two bonded atoms. In Fig. 1 we show the WFCs belonging to our “defect group”; it can be seen that around the interstitial atom I the Wannier centers depart strongly from their ideal mid-bond positions. Similarly, the shape of the corresponding Wannier functions is clearly anomalous, with a delocalization extending over more than two atoms and with a much larger spread than average, of the order of 4 to 8 Å$^2$. This confirms our conjecture of delocalized orbitals connecting different
atoms inside the “defect group”; an inspection of the shape of the WF clearly confirms the delocalization of the electronic states. In Fig. 3 the left panel shows the WF with the center close to the $T_5^B$ defect (C1); its shape suggest a bond shared between two NN. In the right panel of Fig. 3 the delocalized orbital centered at C2 is shown. The shape of this orbital is also influenced by the additional interaction between the two $T_5$ defects.

The anomalous shape and spread of some WFs present in our sample suggest that unusual polarization properties could be present, and could be related to topological disorder. For this reason, we investigated the dynamical charge tensor $Z$, to quantify the local anisotropy and deviation from the crystalline order. Our preliminary results suggest that disorder plays a considerable effect on the dynamical charges of a-Si.

Following Ref. [11], we decompose the $Z$ tensor into an isotropic contribution (corresponding to the $l = 0$ spatial rotation representation), a $l = 1$ antisymmetric one, and a $l = 2$ traceless symmetric contribution. In crystalline Si the effective charges are zero, and the electronic contribution (-4 times the identity matrix) cancels exactly the ionic contribution (+4 times the identity matrix). This is not the case in amorphous silicon, and we find that atoms belonging to topological defects exhibit a very different behavior. To this purpose it is instructive to inspect Table 1, where the electronic effective charge tensors of some selected atoms are given, together with their decompositions. Even for regular $T_4$ atoms ($T_4^A$ and $T_4^B$), the effective charges can show strong anomalies, although this could be an artifact of the high density of defects in the sample. The anisotropy around atom $T_5^B$ on the other hand is clearly shown in Fig. 3 (right panel): $Z$ reflects the directionality in the polarization of this floating bond. Even if our results are still preliminary, they clearly show that the deviations of the effective charges from the crystalline value are noteworthy, and much larger than expected.
Table 1: Born effective charges (electronic) for some selected atoms in the a-Si supercell. The effective charge tensor has been decomposed into an $l = 0$ isotropic part $(Z_{ii}^l = \text{Tr}(Z)/3)$, a $l = 1$ antisymmetric part $(Z^A = (Z-Z^T)/2)$, and a $l = 2$ traceless symmetric part $(Z^S = (Z+Z^T)/2-Z^I)$. The superscript $T$ indicates transpose; atoms are labeled as in Fig. 1.

|      | $Z_{11}^T$ | $Z_{12}^T$ | $Z_{13}^T$ | $Z_{21}^T$ | $Z_{22}^T$ | $Z_{23}^T$ | $Z_{31}^T$ | $Z_{32}^T$ | $Z_{33}^T$ |
|------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| $T_{4}^A$ | -3.860     | -1.118     | 0.559      | 2.193      | -1.264     | -1.646     | -0.368     | -0.493     | -0.330     | 1.758   |
| $T_{4}^B$ | -5.732     | -1.734     | 0.213      | 1.882      | 0.564      | -1.903     | -0.271     | -2.582     | -2.385     | -2.018  |
| I    | -3.850     | 1.089      | -0.706     | 0.418      | -1.403     | 0.765      | 0.493      | -0.018     | 0.254      | 1.421   |
| $T_{5}^B$ | -5.544     | -1.831     | 0.646      | 2.261      | 3.735      | -1.059     | -0.374     | 4.120      | -2.647     | 0.385   |

4 Conclusions

We have presented our results on the microscopic features of floating bonds in a-Si, which have been obtained with a maximally-localized Wannier functions approach. We confirm the conjecture that $T_5$ defects are accompanied by well-defined delocalized states. Such states can be accurately characterized in terms of Wannier functions; a quantitative measure of delocalization is then provided by the the corresponding spreads. The delocalized states correspond to anomalous covalent bonds expanding over more than two atoms. The dielectric properties are readily available as a byproduct of the Wannier analysis; we find strongly anisotropic effective charges that are significantly different from zero.

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