Floating bonds and gap states in a-Si and a-Si:H from first principles calculations

M. Fornari, M. Peressi, S. de Gironcoli and A. Baldereschi

1 Istituto Nazionale di Fisica della Materia (INFM) and Dipartimento di Fisica Teorica Università di Trieste - Strada Costiera 11, I-34014 Trieste, Italy
2 Istituto Nazionale di Fisica della Materia (INFM) and Scuola Internazionale Superiore di Studi Avanzati (SISSA) - via Beirut 2-4, I-34014 Trieste, Italy
3 Institut de Physique Appliquée, Ecole Polytechnique Fédérale de Lausanne PHB-Ecublens, CH-1015 Lausanne, Switzerland

(received 13 April 1999; accepted in final form 12 June 1999)

PACS. 71.23−k – Electronic structure of disordered solids.
PACS. 71.23An – Theories and models; localized states.
PACS. 71.23Cq – Amorphous semiconductors, metallic glasses, glasses.

Abstract. – We study in detail by means of ab initio pseudopotential calculations the electronic structure of five-fold coordinated ($T_5$) defects in a-Si and a-Si:H, also during their formation and their evolution upon hydrogenation. The atom-projected densities of states (DOS) and an accurate analysis of the valence charge distribution clearly indicate the fundamental contribution of $T_5$ defects in originating gap states through their nearest neighbors. The interaction with hydrogen can reduce the DOS in the gap annihilating $T_5$ defects.

The atomic origin of the midgap energy levels in a-Si has been commonly ascribed to three-fold ($T_3$) coordinated atoms, and the observed reduction upon hydrogenation has been explained with the passivation of the “dangling bonds” by H [1]. This picture has been proposed in analogy with the well-known mechanism occurring in undercoordinated configurations such as at surfaces and vacancies in crystalline silicon (c-Si) [2].

The dangling bond picture for a-Si has been widely supported by many electronic structure calculations [3-7], although it has been recognized that gap states can be induced also by other coordination defects [4, 7], e.g., five-fold ($T_5$) coordinated “floating bonds” and anomalous four-fold ($T_4$) coordinated atoms.

We focus our attention here on the role of $T_5$ defects. Their importance in a-Si has been clearly stated by Pantelides [8, 9] and Kelires and Tersoff [10] some ten years ago. Pantelides [8, 9] suggested that the presence and the role of $T_5$ defects must be seriously reconsidered in order to explain some theoretical and experimental data (effective electron correlation [11],

(*) Present address: Naval Research Laboratory - Code 6391, Washington DC 20375-5345, USA.
E-mail: fornari@dave.nrl.navy.mil

© EDP Sciences
hyperfine structure from electron paramagnetic resonance data \[12\], relationship between intensity of paramagnetic signal and density of Si-H bonds \[13\]) that otherwise would remain unexplained in the common picture involving only dangling bonds, and he gave some arguments suggesting that $T_3$ defects could be predominant. He argued that $T_3$ and $T_5$ are conjugated defects, since a bond elongation can transform a $T_4 + T_5$ structure into a $T_3 + T_4$ one \[8\]; furthermore, he proposed a mechanism for H diffusion based on floating-bond switching and annihilation/formation of $T_5$’s through interaction with H \[9\]. The empirical simulation by Kelires and Tersoff \[10\] 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 indicate a predominance of $T_3$ defects with respect to $T_5$ \[14, 15\].

The ideas of Pantelides have then been applied mainly in discussing the geometrical characterization of defects \[6, 7, 16-18\]. Our aim is to discuss their soundness in terms of electronic properties, by analyzing charge distributions and atom-projected DOS obtained from accurate $ab\ initio$ calculations, also following some possible process of formation of $T_5$ defects and of evolution upon hydrogenation.

To this purpose, we start from some selected samples generated by other authors \[14, 15, 19\] using Car-Parrinello molecular dynamics (CPMD). These structures are a good starting point for this study, since they contain floating bonds; furthermore, they 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 small number of defects, which is however larger than in experiment, allows to easily single out effects associated to local features. The configurations studied are cubic supercells of side $a = 2 \, a_0$, where $a_0$ is the equilibrium lattice parameter of c-Si. With respect to the original configuration, where $a_0$ was fixed to the experimental value, we use the theoretical equilibrium lattice parameter $a_0 = 10.17$ a.u., which also corresponds —in our calculations— to the optimized density of a-Si and a-Si:H. The starting configurations contain, respectively, 64 Si atoms to describe a-Si \[14, 15\] and 64 Si atoms plus 8 H atoms for a-Si:H \[14, 19\].

We have studied both the mean configuration at room temperature and a snapshot of the CPMD run, in order to check for possible anomalies due to statistical average, and also to single out the effect on the electronic features of tiny structural variations. The CPMD configurations, aiming mainly at reproducing the structural properties, have been obtained using a kinetic energy cut-off $E_{\text{cut}} = 12$ Ry and the $\Gamma$ point only for Brillouin Zone (BZ) sampling \[14, 15, 19\]. Since electronic structure studies require better accuracy, 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, after tests with $E_{\text{cut}} = 16$ Ry and with the $\Gamma$ point or 32 special $k$ points for self-consistency. We have used for Si the pseudopotential by Gonze et al. \[20\] and for H a smoothed Coulomb potential.

The optimization of the a-Si and a-Si:H structures with the new computational parameters is accompanied only by small structural rearrangements. The results for the structural and electronic properties of the mean relaxed configurations that we present here are essentially valid also for the others (snapshot, unrelaxed).

The mean structural properties of these configurations are similar to those discussed in refs. \[14, 15, 19\]. We only report here 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 location of the first minimum of the radial distribution function defines geometrically the cut-off distance for the nearest neighbors (NN), which for Si-Si turns out to be $R_{\text{NN}} = 5.08$ a.u. and $R_{\text{NN}} = 5.49$ a.u. in a-Si and a-Si:H, respectively. In a-Si:H each H is bound to one Si atom with an average distance $d_H = 2.95$ a.u. With those values of $R_{\text{NN}}$, the resulting average coordination number for Si in a-Si
and a-Si:H is slightly larger than 4. For the purpose of the present work a classification of coordination defects based on a pure geometrical analysis is sufficient, but we point out that possible ambiguities in the bonding configuration can be resolved only by an accurate analysis of the valence charge distribution and of the “electron localization function” [21, 22].

Both our a-Si and a-Si:H configurations have a metallic character, with coordination-defect–induced gap states (the calculated total DOS is reported in the upper panel of fig. 1). The precise definition of the energy gap is one of the unresolved problems for an amorphous system. We have chosen to identify bottom \( E_{G}^{\text{bot}} \) and top \( E_{G}^{\text{top}} \) edges of the gap with the absolute minima of the DOS below and above the Fermi level \( E_{F} \). The occupied states in the gap are the most relevant for our discussion, even if their contribution to the charge density is small (less than 1% for a-Si and 0.5% for a-Si:H). Their atomic origin can be identified through the projection on LCAO pseudo wave functions. The accuracy of the projection, evaluated by means of the spilling parameter \( S \) [25] measuring the incompleteness of the LCAO basis set, is satisfactory \((S=0.03)\).

We focus now our attention on a-Si. The configuration considered here contains two \( T_5 \) sites close to each other, with an “interstitial” \((I)\) atom connecting them (see fig. 2), and no “true” \( T_3 \) defects. A charge density analysis helps in characterizing the different types of bonds [15,21].
We observe that $T_5$ sites are accompanied by a valence charge density depletion. In particular, those $T_5$-$T_4$ bonds which are about 10% longer than the average value ("long" bonds) and the bonds $T_3$-$I$ are characterized by a charge density distribution remarkably smaller (about 1/3) than the corresponding one in the crystalline phase, or than the average in the amorphous phase. These bonds are therefore weak and are the best candidates to break under a network distortion, giving raise to a $T_4 + T_5 \rightarrow T_3 + T_4$ transformation.

The middle panel of fig. 1 shows the DOS projected on different classes of atoms: $T_5$ atoms, atoms which are NN of $T_5$, and the remaining $T_4$ atoms. The peak of the DOS in the gap is unambiguously associated to the NNs of $T_5$ sites. In fig. 2 we show the atomic projection of the charge density of the gap states, obtained again from the LCAO coefficients. It is even clearer that the gap states are not located on $T_5$’s themselves but are delocalized on their NNs, and in particular on those connected by longer and weaker bonds. Evidence of a midgap state with these characteristics is also reported in ref. [18]. We argue that previous works ascribed the origin of gap states uniquely [6] or mainly [3, 4, 7, 17, 23, 24] to $T_3$, simply because they disregarded an accurate analysis of NN environments.

From inspection of fig. 2 we observe the large contribution to the DOS in the gap coming from the atom $I$ which is NN of two $T_5$’s. We observe that also some normally coordinated sites (labelled 18 and 44), characterized by having "long" bonds, partially contribute to gap states, in agreement with similar findings reported in refs. [4, 7, 23].

The a-Si:H [19] structure studied here is more complex. Well-defined $T_5$ sites are present and are the predominant kind of defect (we do not address in this paper the discussion of other more complicated defects which could require a better characterization beyond the pure geometrical analysis [21,22]). Overcoordination arises from five Si atoms, or from four Si atoms and one hydrogen as NN. The main features of the electronic structure are not very different from those of a-Si. As we found in a-Si, those atoms which are NNs of some $T_5$ sites give a large contribution to the DOS in the gap (fig. 1, lower panel).

In order to get further insight onto the characterization of the electronic properties of $T_5$ defects and to recover the ideas of Pantelides, we want to follow in terms of electronic states some possible processes of a) $T_3 \rightarrow T_5$ transformation and b) annihilation of $T_5$ by H. To this purpose, we follow two "computational experiments" starting from the CPMD configurations described before.

In the first one, we start from a-Si:H sample. We focus our attention on a normally coordinated cluster of atoms (fig. 3, upper panel) containing two $T_4$ Si (labelled 1 and 4) close to each other —but not directly connected— and their NNs which include two H atoms. This structure $T_4 + T_3$ has an almost negligible DOS in the gap. We first create artificially a $T_3$ site by removing one H atom and leaving all the other atoms fixed, so that the structure is now $T_3 + T_4$ (fig. 3, central panel). This configuration corresponds to a huge DOS in the gap, almost entirely originating from the dangling bond. After relaxation of the atomic positions the distance between atoms 1 and 4 is reduced from 5.63 a.u. to 4.48 a.u. and a new bond is formed, so that the structure is now $T_5 + T_4$ (fig. 3, lower panel). This process (removal of one H followed by bond reconstruction) is similar to that studied in ref. [18], with the difference that the other H atom in our configuration is replaced there by one Si atom. We observe that in the final configuration ($T_5 + T_4$) there are still midgap states, but now they are delocalized on the NNs of the atom 4 and pushed towards lower energies. Our findings support the picture of conjugated $T_3$ and $T_5$ defects. Moreover, the spontaneous evolution from $T_4 + T_3$ to $T_5 + T_4$, which is in agreement with the findings of ref. [16], confirms —although in a particular case—that the $T_5$’s can be energetically favoured with respect to the $T_3$’s, as indicated in ref. [10].

The inverse process, that may occur in real systems as proposed in ref. [9], indicates a possible mechanism of annihilation of $T_5$ defects by H. But this can be better studied following...
in terms of electronic states our second computational experiment. We start from the a-Si configuration and we focus our attention on the cluster with the two $T_5$ sites (fig. 4, upper panel). We add one H atom nearby a $T_5$. Relaxing the whole structure, a $T_4$-$T_5$ “long” bond breaks, so that a new Si-H bond is formed and the $T_5$ becomes a normal $T_4$ site (fig. 4, middle panel). This is accompanied by a lowering of the DOS in the gap. Adding another H atom, also the second $T_5$ is annihilated and the final structure has a vanishing DOS in the gap (fig. 4, lower panel).

A variety of other structural models have been proposed in the literature for a-Si and a-Si:H, describing even better some global properties, but we are confident that our findings concerning local environments are not much affected by the particular choice of the structural model. In fact preliminary results of another work in progress [22] using a larger sample of a-Si:H generated by L. Colombo using tight-binding molecular dynamics [26] confirm the validity of the present findings.

In conclusion, we have presented the results of accurate \textit{ab initio} self-consistent pseudopotential calculations of the electronic properties of $T_5$ defects in a-Si and a-Si:H starting from some configurations generated via \textit{ab initio} molecular dynamics, and we have followed in terms of electronic density of states some possible processes of their formation and annihilation by H. Our calculations clearly indicate that i) $T_5$ sites give a \textit{fundamental} contribution to gap states through their NNs (figs. 1, 2); ii) in some circumstances the evolution from $T_5$ to $T_3$ is favoured, and this is accompanied by a delocalization of the corresponding electronic states with a shift.
towards lower energies (fig. 3); iii) the DOS in the gap can be reduced by the interaction of $H$ with the $T_3$'s (fig. 4). These results support Pantelides' proposals, and suggest that $T_3$ and $T_5$ in a-Si not only are “structurally” conjugated, but they also play a similar role in originating gap states, which can be in both cases passivated by hydrogen. This pictures reconcile those experimental findings that a description uniquely emphasizing the dangling bonds would not explain.

This work has been done within the “Iniziativa Trasversale di Calcolo Parallelo” of INFM using the parallel version of the PWSCF (Plane-Wave Self-Consistent Field) code. One of us (SdG) acknowledges support from the MURST within the initiative “Progetti di ricerca di rilevante interesse nazionale”. We would like to thank L. Colombo and G. L. Chiarotti for useful discussions and suggestions.

REFERENCES

[1] Davis E.A., J. Non-Cryst. Sol., 198-200 (1996) 1; LEY L., in The Physics of Hydrogenated Amorphous Silicon II edited by JOANNOPoulos J. D. and LUCOVSKY G. (Springer) 1984, p. 61.
[2] Pickett W. E., Phys. Rev. B, 23 (1981) 6603.
[3] Fedders P. A. and Carlsson A. E., Phys. Rev. B, 37 (1988) 8506; Phys. Rev. B, 39 (1989) 1134.
[4] Biswas R., Wang C., Chan C., Ho K. and Soukoulis C., Phys. Rev. Lett., 63 (1989) 1491.
[5] Holender J., Morgan G. and Jones R., Phys. Rev. B, 47 (1993) 3991.
[6] Lee In-Ho and Chang K. J., Phys. Rev. B, 47 (1994) 18083.
[7] Tuttle B. and Adams J. B., Phys. Rev. B, 53 (1996) 16265.
[8] Pantelides S. T., Phys. Rev. Lett., 57 (1986) 2979.
[9] Pantelides S. T., Phys. Rev. Lett., 58 (1987) 1344.
[10] Kelires P. C. and Tersoff J., Phys. Rev. Lett., 61 (1988) 562.
[11] Bar-Yam Y. and Joannopoulos J. D., J. Electron. Mater., 14 (1985) 261.
[12] Biegelsen D. K. and Stutzmann M., Phys. Rev. B, 33 (1986) 3006; Stathis J. H., Phys. Rev. B, 40 (1989) 1232.
[13] Biegelsen D. K., Street R. A., Tsai C. C. and Knights J. C., Phys. Rev. B, 20 (1979) 4839; Kumeda M. and Shimizu T., Jpn. J. Appl. Phys., 19 (1980) L197.
[14] Buda F., Chiarotti G. L., Štich I., Car R. and Parrinello M., J. Non-Cryst. Sol., 114 (1989) 7.
[15] Štich I., Car R. and Parrinello M., Phys. Rev. B, 44 (1991) 11092.
[16] Fedders P. A. and Carlsson A. E., Phys. Rev. Lett., 58 (1987) 1156.
[17] Fedders P. A, Drabold D. A. and Klemm S., Phys. Rev. B, 45 (1992) 4048.
[18] Tuttle B. and Adams J. B., Phys. Rev. B, 57 (1998) 12859.
[19] Buda F., Chiarotti G. L., Car R. and Parrinello M., Phys. Rev. B, 44 (1991) 5908.
[20] Gonze X., Stumpf R. and Scheffler M., Phys. Rev. B, 44 (1991) 8503.
[21] Peressi M., Fornari M., de Gironcoli S., De Santis L. and Baldereschi A., to be published in Philos. Mag. B.
[22] Fornari M., Peressi M., de Gironcoli S. and Baldereschi A., unpublished.
[23] Drabold D., Fedders P., Sankey O. and Dow J., Phys. Rev. B, 42 (1990) 5135.
[24] Holender J. and Morgan G., J. Phys. Condens. Matter, 4 (1992) 4473.
[25] Sanchez-Portal D., Artacho E. and Soler M., J. Phys. Condens. Matter, 8 (1996) 3859.
[26] Colombo L., in Annu. Rev. Comput. Phys., IV, edited by D. Stauffer, (World Scientific, Singapore) 1996, p. 147.