Phys. Status Solidi C **9**, No. 10–11, 1952–1954 (2012) / **DOI** 10.1002/pssc.201200256

physica status solidi c
www.pss-c.com
current topics in solid state physics

Ab initio modelling of boron related defects in amorphous silicon

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Received 18 June 2012, accepted 19 June 2012
Published online 6 September 2012

Keywords ab initio modelling, defects, boron, amorphous, silicon

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We have modeled boron related point defects in amorphous silicon, using an *ab initio* method, the Density functional theory-pseudopotential code AIMPRO. The boron atoms were embedded in 64 atom amorphous silicon cubic supercells. The calculations were performed using boron defects in 15 different supercells. These supercells were developed using a modified Wooten-Winer-Weaire bond switching mechanism. In average, the properties of the 15 supercells agree with the observed radial and bond angle distributions, as well the electronic and vibrational density of states and Raman spectra. In amorphous silicon it has been very hard to find real self-interstitials, since for almost all the tested configurations, the amorphous lattice relaxes overall. We found that substitutional boron prefers to be 4-fold coordinated. We find also an intrinsic hole-trap in the non-doped amorphous lattice, which may explain the low efficiency of boron doping. The local vibrational modes are, in average, higher than the correspondent crystalline values.

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1 Introduction Amorphous silicon (a-Si) plays a major role in microelectronics and, in particularly, in energy conversion technologies. a-Si can be prepared in large-area films onto a variety of subtracts at a far lower cost than its crystalline counterpart (c-Si) and, when nanocristals are incorporated in a-Si matrix, its optical properties are enhanced [1].

Many attempts have been made to model the structure of a-Si. Earlier models like Polk and Boudreaux [2,3] presented some concordance with experimental data, but were cluster-based, so they suffer from awkward problems posed by free surfaces. The models from Henderson [4] and Guttman [5] eliminate these problems by including boundary conditions, but the production of relatively large supercells was difficult. The Wooten-Winer-Weaire mechanism (also known as WWW bond-switching) [6] addresses the previous issues with a simple solution. From a diamond structure with periodic boundary conditions build in from start, two randomly chosen nearest neighbour atoms interchange one of their four nearest neighbours, rearranging simultaneously their position in order to preserve tetrahedral bonding. If this bond switch is repeated several times, it will destroy the crystalline features, but supercell periodicity is retained. In this paper, we present a study on the boron related defects (substitutional boron and boron-silicon pair) in 15 different 64 atom a-Si cubic supercells, which have been amorphised using a modified WWW bond switching. In average these 15 a-Si supercells reproduce very well the properties of a-Si and hydrogen passivated a-Si (a-Si:H) [7].

2 Method Density functional theory (DFT) calculations as implemented in the AIMPRO code [8] were performed along with the local density approximation (LDA) to the exchange correlation potential [9]. Explicit treatment of core electrons was avoided by using dual-space separable pseudopotentials by Hartwigsen, Goedecker and Hutter [10]. The valence structure of Si and B individual atoms is $3s^2 3p^2$ and $2s^2 2p^1$, respectively. Wave functions were expanded in Cartesian-Gaussian Bloch atom-centered functions with a kinetic energy cut-off of 80 Ha, and the electron density and potential terms are deal in reciprocal space by fast Fourier transformation (FFT). The Brillouin zone was sampled with help of a shifted 2×2×2 symmetry-folded special ***k***-point mesh, according to the recipe by Monkhorst and Pack [11].

The 15 a-Si supercells used were the same 64 atom cubic supercells from [7]. For each structure, after several

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WWW bond-switching to a crystalline supercell, volume and atomic positions were allowed to relax using a Simplex optimization, as implemented on the same code. The stop criterium for structural optimisation was an energy difference lower than 10^{-5} Ha. The radial distribution function agrees well with experiment, being the first peak at 0.230 nm. The first minimum at 0.275 nm is used as bond length cut-off for silicon and boron atomic coordination assessment. The averaged bond angle was at 109.4º. The electronic density of states, the phonon density of states and the reduced Raman spectra agree very well with experimental data [7].

For the substitutional boron defect modelling we picked several random Si atom sites from each pre-*relaxed* a-Si supercell and replaced by a B atom. We took special care to pick roughly 1/3 for each initial site coordination (3-, 4- and 5-fold Si atomic coordination) in order to assess the final preferable B atomic coordination.

The boron-interstitial silicon pair was modelled by randomly picking a substitutional site of the amorphous sample and replacing with a B atom. An interstitial Si atom was placed in the vicinity of the picked substitutional site, so the majority of its neighbours became 5-fold coordinated. We also tested maintaining a Si atom in the picked random site and placing a B atom in the vicinity [see Fig. 1 (a)]. The results were identical taking both approaches.

3 Results

3.1 Boron related defects For the substitutional boron defect we made 43 analysis runs, and after structural relaxation, 72% of B atoms took final 4-fold atomic coordination. Only 17% and 11% became 3- and 5-fold coordinated, respectively. The overall supercell rearrangement for the B atom accommodation was localized and not widespread. These results are in agreement with the preferred atomic coordination of B in c-Si but in contradiction to what may be expected since B has only 3 valence electrons.

We have calculated the local frequencies (LVM) for 4-fold coordinated B, resulting in LVM's as higher as 840 cm^{-1} and spread by a 250 cm^{-1} range. The isotopic LVM shift from ^{10}B to ^{11}B are in average 28 cm^{-1}, 27% higher than in c-Si.

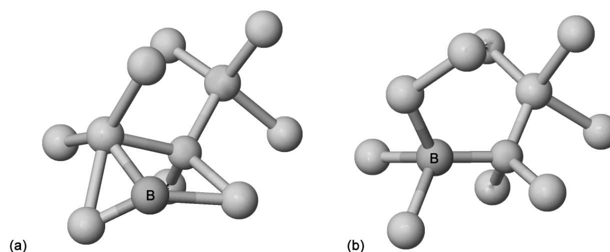

Figure 1 (a) Initial and (b) final *relaxed* structure of the boron-silicon pair simulations.

For the boron-silicon pair modelling we took about a total of 200 *relaxations* runs. A kind of kick-out mechanism (see Fig. 1) was observed in the majority of the runs.

During structure *relaxation*, the interstitial atom (whether Si or B) kicked-out an atom from its substitutional site. A widespread structural *relaxation* allowed that all atoms involved became once again 4-fold coordinated, but in less than 10% of the runs, the kicked-out atom became 3-fold coordinated instead. Also was not uncommon a final 5-fold coordination to the B atom (less than 20%). In the final structure the bond length between the B and the Si atom was smaller than other bonds (less than 0.20 nm). We intend to continue this B-Si pair study, in order to achieve a better understanding and a more quantitative analysis of this kick-out mechanism and its consequences concerning boron diffusion.

3.2 Low efficiency B doping As reported in the previous subsection, the B atom prefers to be 4-fold coordination, so it is expected that substitutional boron will provide one hole. However B doped a-Si has very low efficiency [12]. It has been recently proposed that this low doping efficiency is intrinsic to the deformed a-Si lattice, being the hole trapped in distorted-angles region [13].

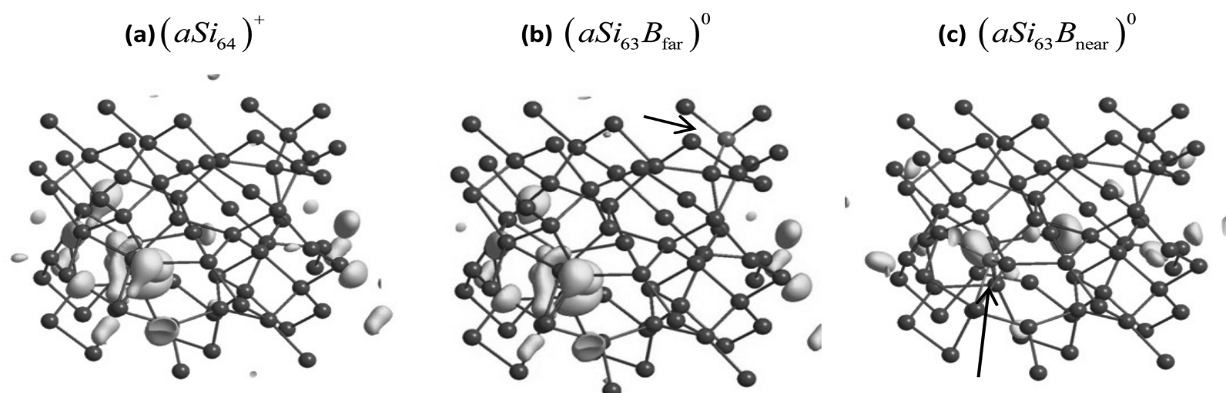

Figure 2 (a) Localized trapping states in an a-Si sample. Effect over the localized trapping states by the substitutional boron defect (in light grey) if the defect is far from the hole-trap region (b) and if the defect is close to the hole-trap region (c).

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In the case of an ideal acceptor in c-Si, the hole would be in a shallow state locally extended around the dopant impurity [14]. We have looked at a shallow state around the substitutional boron. Our findings show boron in a-Si does not create a hole as in c-Si. This conclusion is in line with results reported by Santos et al [13]. In Fig. 2 we pictured the hole trap location for different B configurations. For the configuration shown in Fig. 2(b) the hole is far from the B atom. In fact the hole location is independently of the B position. When the B atom is near the hole [Fig. 2(c)] the hole-localization is even stronger.

To determine whether the hole-localization region is induced by the B atoms or it exists even in the absence of acceptors, we analysed the same non doped 64-atom amorphous cell with positive charge [Fig. 2(a)], i.e., with the same number of electrons than the neutral B configuration. The resulting hole-localization is very similar to that of Fig. 2(b). Therefore, the region of interest is not induced by the B atoms but is inherent to the a-Si matrix. Its origin is not yet quite understood: Pan et al. [15] suggest that this hole traps occur in regions were the bond length are slightly smaller than the overall bond length in the supercell, while Bagalini et al. [16] and Wagner and Grosmann [17] attribute to slightly localized trapping states to distorted small bond angles. In our samples both previous characteristics occurs in the hole-trap region, were an average bond angle of ~80º was observed and slightly small bonds (smaller by ~0.02 nm).

4 Conclusions

In this work we present an ab initio study of boron related defects in volume and atomic relaxated 64 atom cubic supercell, amorphised from crystalline silicon by several WWW bond switchings. The physical properties of the used 15 a-Si supercells are in good agreement with experimental data [7].

We have found that the substitutional boron defect prefers to be 4-fold coordinated. We also found the existence of intrinsic localized hole-traps in our samples. We observed all features that had been indicated previously by other authors as causes for this phenomenon: localized small bonds and distorted angles. We confirm the presence of a substitutional B atom near the vicinity of these traps further enhances its localized effect. These trapping states lower the doping efficiency, which is a major drawback in the practical use of a-Si.

The boron-silicon pair was also modelled and some kind of a kick-out mechanism was observed during structure relaxation. In the majority of the computational runs, the interstitial atom kicks-out a substitutional atom, occupies its place, but the kicked-out atom will occupy a near non-substitutional site but in a way that its 4-fold atomic coordination prevails as well as the atomic coordination of its neighbours. These defects require further understanding.

Acknowledgements This work was partially supported by Fundação para a Ciência e a Tecnologia (FCT), Portugal, under contract PEst-C/CTM/LA0025/2011.

References

[1] L. Pavesi, L. D. Negro, C. Mazzoleni, G. Franzo, and F. Priolo, Nature **408**, 440 (2000).
[2] D. Polk, J. Non-Cryst. Solids **5**, 365 (1971).
[3] D. Polk and D. Boudreaux, Phys. Rev. Lett. **31**, 92 (1973).
[4] D. Henderson, J. Non-Cryst. Solids **16**, 317 (1974).
[5] L. Guttman, Phys. Rev. B **23**, 1866 (1981).
[6] F. Wooten, K. Winer, and D. Weaire, Phys. Rev. Lett. **54**, 1392 (1985).
[7] R. M. Ribeiro, V. J. B. Torres, M. I. Vasilevskiy, A. Barros, and P. R. Briddon, Phys. Status Solidi C **7**, 1432 (2010).
[8] M. Rayson and P. Briddon, Comput. Phys. Commun. **178**, 128 (2008).
[9] S. Goedecker, M. Teter, and J. Hutter, Phys. Rev. B **54**, 1703 (1996).
[10] C. Hartwigsen, S. Goedecker, and J. Hutter, Phys. Rev. B **58**, 3641 (1998).
[11] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[12] M. Stutzmann, D. K. Biegelsen, and R. A. Street, Phys. Rev. B **35**, 5666 (1987).
[13] I. Santos, P. Castrillo, W. Windl, D. A. Drabold, L. Pelaz, and L. A. Marqués, Phys. Rev. B **81**, 033203 (2010).
[14] L.-W. Wang, J. Appl. Phys. **105**, 123712 (2009).
[15] Y. Pan, F. Inam, M. Zhang, and D. A. Drabold, Phys. Rev. Lett. **100**, 206403 (2008).
[16] L. Bagalini, A. Mattoni, and L. Colombo, Appl. Phys. Lett. **94**, 053115 (2009).
[17] L. K. Wagner and J. C. Grossman, Phys. Rev. Lett. **101**, 265501 (2008).

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