Clustering of boron into Si(100) vicinal surfaces: a quantum mechanical study at semiempirical level

2002 J. Phys.: Condens. Matter 14 12825

(http://iopscience.iop.org/0953-8984/14/48/322)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **14** (2002) 12825–12828 PII: S0953-8984(02)54038-8

Clustering of boron into Si(100) vicinal surfaces: a quantum mechanical study at semiempirical level

A M Mazzone

CNR Istituto IMM-sez.di, Bologna-via Gobetti 101, Bologna-40129, Italy

E-mail: mazzone@lamel.bo.cnr.it

Received 27 September 2002
Published 22 November 2002
Online at stacks.iop.org/JPhysCM/14/12825

Abstract

In this work the equilibrium configurations of boron impurities embedded into silicon surfaces, vicinal to (100), are studied using the Hartree–Fock method at semiempirical level. Clusters containing up to five boron atoms are considered. These impurities are either of a substitutional or of an interstitial type and are placed at the step edge. The most stable shape of the doped step is evaluated, relaxing the system to an energy minimum with a steepest-descent approach. The results indicate that the impurities are stabilized by the formation of bonds considerably shorter than the normal interatomic distance in crystalline silicon. However, clustered defects do not dissolve. Furthermore, the need to host defects of a remarkably different structure leads to an appreciable dependence of the relaxed step shape on the defect type and size.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

One of the main p-type dopants of silicon is boron. Boron atoms dissolve to the substitutional positions in the silicon lattice and act as acceptors. Furthermore, it is well known, from the use of molecular beam epitaxy, that boron exhibits segregation at the surface substituting for silicon atoms and this induces several kinds of surface reconstruction.

In recent years it has become increasingly evident that steps play an essential role in many surface processes. A relevant experimental finding is the discovery of a 'striped' phase on vicinal Si(001) [1, 2]. This structure consists of steps of variable width and is observed at high temperature in samples heavily doped with boron. Theories based on a continuum elasticity approach [1, 2] indicate that this extensive reconstruction can be attributed to the impurities provided that the step–boron coupling has the required strength. This coupling is a property of the electronic configuration and cannot be directly proved by models, such as the ones adopted in [1, 2], with a mesoscopic formulation.

The evaluation of the step–boron coupling at quantum mechanical level is therefore of some importance and has motivated this contribution. This study is based on the use of a simplified Hamiltonian and the reduced need for computer time allows one to tie together a realistic structure of the silicon surface with the quantum mechanical evaluation of the boron–silicon interactions.

2. The simulation method; the cluster approach and the AM1 Hamiltonian

It is common, especially in quantum chemistry, to find studies where extended systems are represented by cluster models (CM). In CM the system concerned is represented by a cluster of finite size and boundary effects are minimized by the use of passivating atoms. This approach has been adopted also in this study and the simulation cell consists of a cluster modelling one isolated step. The step structure reproduces the structures predicted by the Chadi's theory (see below) and the dangling bonds of the peripheral atoms are compensated with hydrogen atoms. In [4] an extensive testing was conducted on the cell size and composition. It was found that cells with approximately 100 silicon atoms and H compensation up to the subsurface atoms offer two advantages, i.e. the effects of a single deposited impurity are perceptible and the evaluation of the total energy E_t is not vitiated by size-dependent effects. Realistic and accurate results are therefore to be expected from the use of these clusters.

It is known that a step-edge location represents a preferred adsorption site for deposited silicon atoms and also for dopant impurities. Accordingly, substitutional clusters are constructed by replacing step-edge silicon atoms with boron. Also interstitial clusters are placed at the step edge, in the space between the two terraces or between the dimer rows. According to experimental finding [3] the maximum size of N for both interstitial and substitutional impurities is five atoms. The shape of the interstitial clusters is constructed using an energy minimization for unsupported clusters, as reported in [4]. Optimized shapes of boron clusters with N in the range from 3 to 5 are reported in figure 1. These plots show that the cluster structure is small at all sizes. However, at $N = 5$ it changes from planar to three dimensional as a distorted bipyramid is the structure of the pentamer I_5. The stable shape of the doped step is obtained by relaxing the structure containing the defect by a steepest-descent method. In this minimization only boron and silicon atoms are allowed to move while the hydrogen atoms are immobile. The energy evaluation is based on the semiempirical Hartree–Fock AM1 method [5]. The detailed analysis performed in [4] indicates that the evaluation of the dimerization on Si(100) with this Hamiltonian is of comparable accuracy to LDA results available in the literature.

3. Interstitial and substitutional impurities attached at steps

Numerous experimental studies have shown that (100) surfaces with a miscut angle less than about 1° are formed by steps of a monolayer height. Such steps occur in two types, denoted by SA or SB after Chadi. In the case of SA the dimers on the upper terrace are perpendicular to the step edge and on SB they are parallel to the edge. Furthermore, the SB step may be terminated by either a rebonded or a nonrebonded edge (steps of this last type are therefore indicated as SBN). A lattice view of the flat surface and of SA and SBN steps is presented in figure 2 (these plots are constructed on the basis of the CM representation used in the following simulations).

Figures 3 and 4 report representative shapes of boron-doped steps. These figures refer to substitutional (figure 3) and interstitial (figure 4) impurities, respectively. The figures illustrate

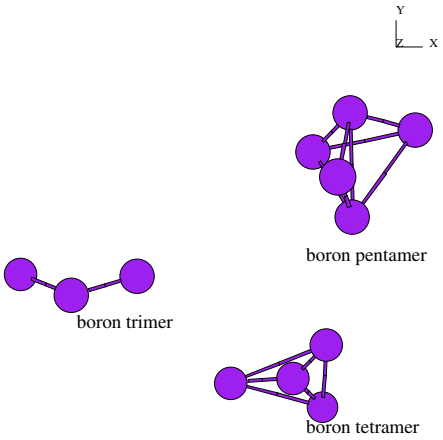

Figure 1. Free-standing boron clusters obtained from the minimization of the total, electronic and nuclear, energy.

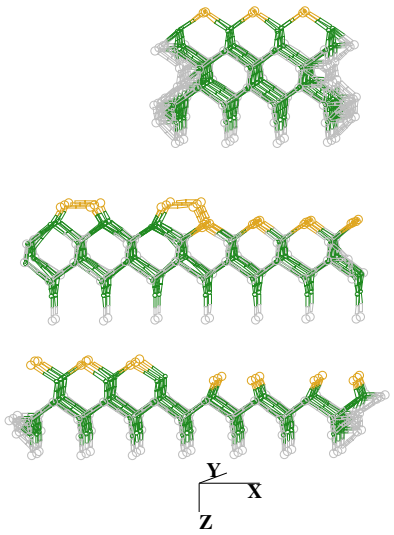

Figure 2. The flat surface and SA and SBN steps in the CM representation.

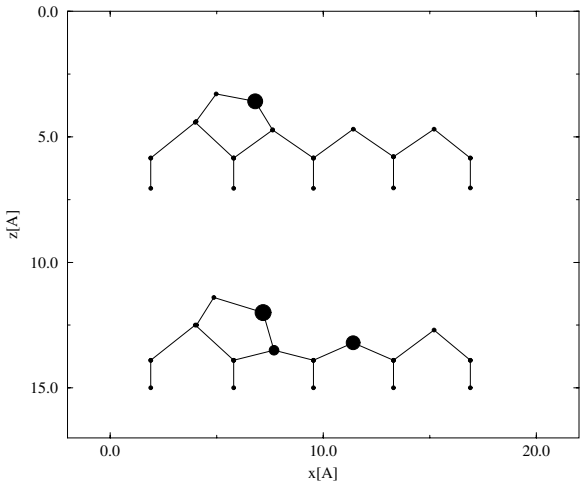

Figure 3. Substitutional boron on SA. The boron locations are indicated by the darker dots. Dots of a different size indicate a different coordinate along the y-direction perpendicular to the step edge.

three constant features of the doped steps. First, the surface dimerization remains favourable and the step structure maintains, at least in its gross form, the structure of the undoped step. Second, the main mechanism stabilizing the impurities is the formation of reduced interatomic distances. The sketches of substitutional boron in figure 3 clearly show that this is achieved via a vertical downward-directed shift which enhances the coupling between the two terraces. Third, clustered defects do not dissolve. The simple energetic argument explaining this effect is that in the AM1 evaluation the binding energy of boron clusters falls in the range 2.4–3.3 eV/atom while the binding strength of the Si–B bond is 2.1 eV/atom. Therefore the

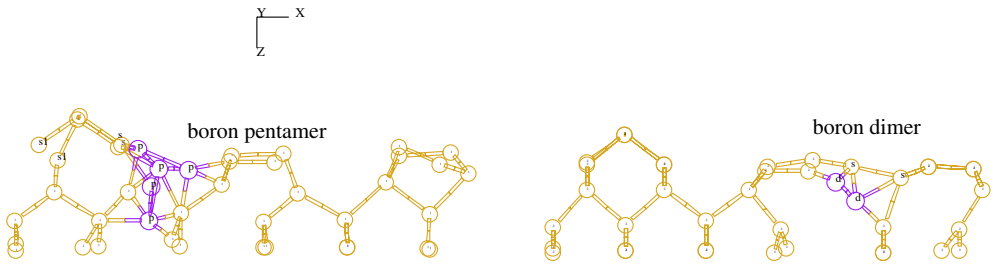

Figure 4. Interstitial boron clusters on SBN. The locations of boron atoms are indicated by the darker dots. The impurities are the boron pentamer and dimer whose atoms are labelled p and d, respectively. s and s1 indicate second-layer silicon atoms interacting with the boron clusters.

presence of a barrier to dissociation in the range 0.3 eV, or larger, has to be accounted for. In [4] it is also shown that softer Si–B bonds near the deposited cluster lead to a further increase of this barrier. In addition, the need for accommodating the defect may lead to a complex lattice reconstruction which depends on both the structure of the step and of the defect. This point is illustrated by the lattice views reported in figure 4. As shown in the figure, a large defect, the boron pentamer I_5 (the atoms are labelled p), pushes the second-layer atoms s and s1 sideways on the upper terrace and creates subsurface disorder. However, the shape of the lower terrace is fairly regular. In contrast, the interstitial dimer I_2 (the dimer atoms are labelled d) displaces two subsurface atoms (labelled s) to form a tetrahedrally connected network. While the lower terrace is highly irregular, the upper one has its undoped shape.

4. Conclusions

In conclusion, in this study a minimization of the total energy, evaluated at semiempirical level, has been used to illustrate the properties of (100) silicon steps doped with boron.

The results show that substitutional impurities are stabilized by reduced silicon–boron bond lengths. Interstitial impurities remain clustered and may produce an extensive lattice relaxation.

References

[1] Jones D E, Pelz J P, Hong Y, Bauer E and Tsong I S 1996 *Phys. Rev. Lett.* **77** 330
[2] Ebner C, Jones D E and Pelz J P 1997 *Phys. Rev.* B **56** 1581
[3] Jorke H and Kibbel H 1990 *Appl. Phys. Lett.* **57** 1763
[4] Mazzone A M 2001 *Comput. Mater. Sci.* **223** 213
[5] *MOPAC Quantum Chemistry Program Exchange* Program Number 571. For basic properties and testing of MOPAC, see
Dewar M S J and Thiel W J 1987 *J. Am. Chem. Soc.* 4899
Stewart J P 1989 *J. Comput. Chem.* **10** 209
Other information can be found at the Web site www.indiana.edu.