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Nuclear Instruments and Methods in Physics Research B 230 (2005) 112–117
NIM B
Beam Interactions with Materials & Atoms
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Atomistic simulation of ion channeling in heavily doped Si:As

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Available online 21 January 2005

Abstract

The structure of vacancy–As complexes (V–As$_m$, with $m = 1,4$) is calculated by first-principles methods and implemented in Monte Carlo (MC) simulation of Rutherford backscattering-channeling (RBS-C) spectra. Using this procedure the atomic position of As, inferred from the model of the complex, is no longer treated as a free parameter of the simulation, as it usually occurs within MC fitting of RBS-C spectra. Moreover, physical effects which influence the backscattering and dechanneling yields of ions, such as the lattice distortion around the vacancy, are naturally taken into account in the simulation. We investigate the sensitivity of RBS-C to the different complex models and report an example of the application of the method to the case of heavily doped Si:As equilibrated at high temperature. The comparison of simulated and experimental angular scans shows that while the hypothesis of inactive As trapped in V–As$_4$ clusters is consistent with experimental observations, the presence of a significant amount of V–As clusters is unlikely.

PACS: 61.85.+p; 61.72.Tt; 82.80.Yc; 61.80.Jh
Keywords: Ion channeling; Atomic location of impurities; Vacancy–As complexes; Monte Carlo simulation

1. Introduction

Theoretical and experimental findings [1–9] suggest that the main mechanism of electrical deactivation of As in silicon is the formation of As–vacancy (V$_n$–As$_m$) complexes. The structural and electronic properties of these defects are a matter of current investigation [10,11]. The Rutherford backscattering channeling (RBS-C) technique has been used in the past to correlate the structural properties of heavily doped Si:As to the electrical deactivation process [1,4,9]. RBS-C results, in

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doi:10.1016/j.nimb.2004.12.027

agreement with other investigations based on different techniques (such as extended X-ray-absorption fine-structure EXAFS [2,12] and X-ray standing-wave spectroscopy (XSW) [7]), show that with decreasing carrier concentration an increasing amount of As is found in nearly-substitutional lattice positions. Although a direct interpretation of RBS-C measurements in terms of atomic-scale models of V_n–As_m clusters has not been reported so far, it appears that the experimentally estimated displacement of As from lattice sites (0.1–0.2 Å), is of the same order of the prediction by ab initio calculations [3,6].

In the present work RBS-C spectra of heavily doped Si:As are simulated by means of an atomistic approach similarly to our previous study [13,14] addressed to undoped Si lightly damaged by ion implantation. The geometry of V–As_m ($m = 1, 4$) clusters is calculated by means of the first-principles density functional theory (DFT) and implemented in the simulation of RBS-C spectra of Si:As. The sensitivity of the technique to the different cluster models is investigated and an example of comparison between simulations and measurements in the case of Si:As equilibrated at high temperature is reported.

2. The model

2.1. V–As_m complexes

The presence of the vacancy is crucial for the relaxation of the lattice nearby the defect, when dealing with the clustering of As atoms around a single vacancy to form V–As_m complexes. Both experimental measurements [15] and computer simulations [16] have shown, in fact, how a single vacancy in silicon produces a lowering in the tetrahedral symmetry due to the Jahn–Teller distortion. Early experiments [17] and recent theoretical results [10] have shown relevant Jahn–Teller effect also in the case of the V–As complex, in which relaxation comes out to be large and anisotropic along the $[1\,\bar{1}\,0]$ bond chains.

In order to obtain the fully relaxed geometries of both different V–As_m configurations and of the substitutional As (As–Si_4 cluster), supercells containing 64 and 216 lattice atoms have been considered. Calculations were performed according to the DFT approach [18], within the local density approximation (LDA), using norm-conserving [19] pseudopotentials for As and Si atoms. A kinetic energy cutoff of 18 *Ry* was used. The Brillouin zone was sampled using two special points, Γ and L, which ensure [20], together with the increasing size of the supercell, a negligible interaction between defect-images in periodically repeated supercells. The LDA calculated lattice parameter $a_0 = 5.403$ Å was used and the final relaxed cluster configurations were scaled to the experimental value of 5.431 Å.

As a first step the structure of the neutral vacancy was calculated. An atom was removed and the positions of atoms neighbor to the vacant site perturbed, in order to eliminate any symmetry which could be preserved during the relaxation procedure. The whole supercell was then allowed to relax until the Hellmann–Feynman forces on the atoms were less than 10^{-3} eV/Å. The final configuration appears to be Jahn–Teller distorted, as expected [15]. The initial configurations for the calculation of neutral V–As_m complexes were then obtained by replacing m ($m = 1$–4) Si nearest-neighbor of the vacancy with As atoms. All the optimized cluster configurations show inward relaxation towards the vacancy. The amount of relaxation is sensitive to the size of the supercell: the distances d(V–X) between the vacant site V and the four nearest neighbors X ($X = \mathrm{Si}, \mathrm{As}$) decrease with increasing the size of the supercell from 64 to 216 atoms by an amount varying in the range 2–8%, depending on the cluster and on the type of the neighbor. RBS-C simulations (see next section) were found to be sensitive to these variations: we will therefore refer to the results obtained in the larger supercells, as they are expected to be less affected by artifacts due to the finite boundary.

Fig. 1 reports the ball and stick models of the V–As and V–As_4 complexes, as calculated by DFT-LDA. In agreement with previous findings [10,15] the cluster V–As shows the C_{1h} symmetry, in which two Si atoms facing in the $[1\,\bar{1}\,0]$ direction approach each other, by displacing towards the vacancy (d(V–Si) = 1.93 Å) more than the two atoms of As and Si belonging to the opposite chain

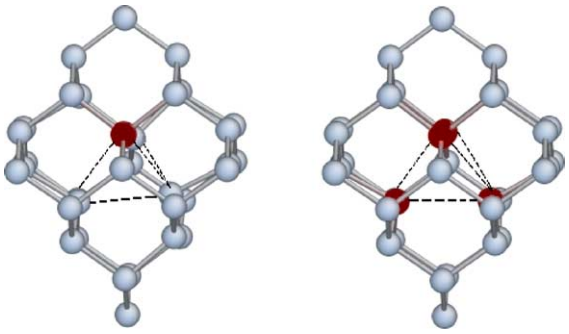

Fig. 1. Ball and stick models of the V–As (left) and V–As_4 (right) complexes calculated by DFT-LDA. Light atoms are Si, dark atoms are As. Thin dashed lines have been drawn, as a guide for the eye, to connect first neighbors of the vacant site. For the V–As complex the distances between these atoms are: As–Si = 3.55 Å and 3.43 Å for the long and the two short distances, respectively, and Si–Si = 2.83 Å and 3.39 Å for the short and the two long distances, respectively. For the V–As_4 complex all six As–As distances are equal to 3.45 Å.

(d(V–As) = 2.15 Å and d(V–Si) = 2.18 Å, respectively). This rebonding effect, due to the pairing of Si atoms, is responsible for a quite large distortion of the Si lattice around the cluster. Conversely, the V–As_4 complex relaxes isotropically, and d(V–As) appears to be the same (2.11 Å) for all the four atoms. As for the other two clusters, V–As_2 and V–As_3, a rebonding effect is still present in the former one (d(V–Si) = 1.97 Å and d(V–As) = 2.15 Å), while in the latter all the three As atoms are equally distant (d(V–As) = 2.09 Å) from the vacancy, whereas the Si neighbor lies at d(V–Si) = 2.22 Å. In turn, the calculated structure of the substitutional As, shows slightly outward relaxation of the four first neighbor Si atoms (d(As–Si) = 2.43 Å).

2.2. Atomistic RBS-channeling simulation

A large ($\sim 10^6$ atoms) Si supercell is populated with a constant concentration of 8×10^{20} cm^{-3} (1.6 at.%) As, which can be either in the form of substitutional atoms or V–As_m complexes. The selected concentration corresponds to the value measured in the experimental sample analyzed in Section 3.2. A lattice site is chosen at random within the host lattice and the Si atom is then replaced by an As or removed to generate the vacancy, depending whether a substitutional As or a V–As_m defect is to be inserted. Atoms up to the second neighbors of the site are replaced by As and Si atoms whose positions are inferred from the DFT-LDA geometry of the complex, scaled to the experimental lattice parameter of Si. The procedure is carried out taking care that no overlapping between complexes occurs.

Simulation of RBS-C spectra are performed with the computer code BISIC [21,22], based on the Monte Carlo binary collision approximation (MC-BCA) method. Using the concept of close encounter probability [23] and approximating the path of a backscattered ion with a straight trajectory in a random medium, the program determines the yield at the detector as a function of backscattering energy. A description of the program and of the physical parameters of the BCA calculation can be found in [22]. We assume for As (both substitutional and in the complexes) a 1D thermal vibration amplitude equal to the one used for the host Si lattice (0.077 Å [24]).

3. Results

3.1. Sensitivity of RBS-C to the models of V–As_m complexes

Keeping the As concentration fixed, we performed different RBS-C simulations, each assuming the presence of one type of complex only. Spectra were calculated for three axial alignments: ⟨1 0 0⟩, ⟨1 1 0⟩ and ⟨1 1 1⟩. Fig. 2 shows the spectra simulated according to the V–As and V–As_4 DFT models. Spectra simulated assuming fully substitutional As are reported for comparison. From the analysis of Fig. 2 we can deduce the following: (i) the small displacements of As in either V–As or V–As_4 complexes increase significantly the dopant yield above the one expected for substitutional As; (ii) the increase in As yield is quantitatively similar for both complexes; (iii) due to Jahn–Teller effect, the V–As introduces significant deformation in the Si atoms surrounding the vacancy, and this increases the yield of Si well above the one observed in the case of fully substitutional As; (iv) the V–As_4 complex does not distort in a

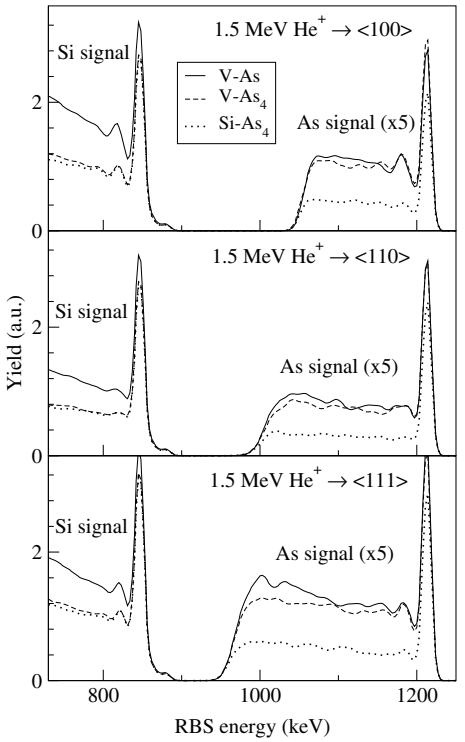

Fig. 2. RBS-C spectra of heavily doped bulk Si:As (constant concentration of 8×10^{20} cm^{-3}) simulated under three different axial alignment conditions, and according to three different assumptions on the atomic-scale arrangement of As atoms. The As signal is magnified by a factor of 5.

significant way Si atoms, and the Si signal remains close to the one observed for substitutional As; (v) all the above trends do not show any significant dependence on the alignment conditions investigated.

According to these observations we conclude that RBS-C can actually discriminate between the two complex models, the relevant difference being in the amount of deformation induced in the surrounding Si lattice.

3.2. Comparison with experiment: heavily doped Si:As equilibrated at high temperature

The experimental sample considered here consists of a (1 0 0) Silicon on insulator (SOI) wafer, implanted with 100 keV As^+ ions at a fluence of 3×10^{16} cm^{-2} and thermally equilibrated at 1100 °C for 120 min in slightly oxidizing ambient to prevent As out-diffusion. This treatment produces a 28 nm thick surface layer of thermal SiO_2, followed by a 335 nm thick Si layer with a nearly constant concentration of As, equal to 8×10^{20} As cm^{-3}, as determined by RBS. Electrical activation, obtained by sheet resistivity and Hall measurements, shows that 44% of As in the layer is electrically active [9].

Fig. 3 reports the ⟨1 0 0⟩ to {1 1 0} angular scans of the sample, performed with 1.5 MeV He^+ ions. Experimental As and Si dips are compared with dips simulated under the assumption of electrically inactive As being in the form of either V–As or V–As_4 clusters. In both cases to fit the experiment it is necessary to introduce a small fraction (few %) of As located incoherently in the lattice, whereas the 44% electrically active As is always put in substitutional positions, according to the As–Si_4 cluster model obtained from DFT calculations. In a previous work [9] the same angular dips were fitted by MC-BCA simulation, but in that case inactive As was described considering the atoms slightly displaced from the regular lattice sites, with 1-D value of displacement treated as a fitting parameter. Using first-principle models of V–As_m clusters, As location is no longer a free parameter. Since carrier concentration measurement fixes the

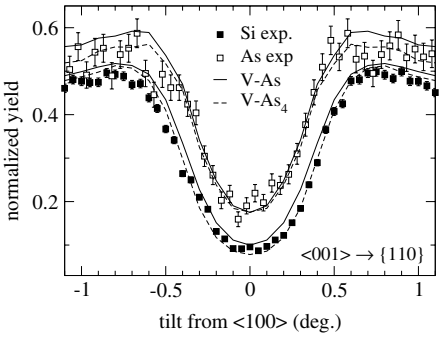

Fig. 3. Comparison between experimental and simulated As and Si angular scans of a SOI sample (thickness of the Si layer = 335 nm) doped with As and thermally equilibrated for 2 h at 1100 °C in order to produce a constant concentration of 8×10^{20} As cm^{-3}. To reproduce experimental As scan it was necessary to assume a small fraction of incoherently distributed dopant (5% and 6% for the cases of V–As and V–As_4 complexes, respectively) in the simulation.

amount of substitutional dopant, the only adjustable parameter is the fraction of incoherent As, as opposed to As trapped in the clusters. Results indicate that: (i) the hypothesis of inactive As being trapped in V–As_4 clusters, with the exception of a small (~6%) fraction placed in incoherent lattice position, is in agreement with the experiment; (ii) the assumption of inactive As being trapped in V–As complexes seems instead very unlikely. In fact, the latter reproduces the As angular dip, but at the same time the Si dip is appreciably overestimated. This is a consequence of the Jahn–Teller effect, which introduces a relatively large distortion in the Si lattice. It is worth noting that the hypothesis of dominant V–As_4 for a sample equilibrated at high-temperature is consistent with the energy of this configuration, which is the lowest among all the V–As_m investigated here.

More extensive simulations and comparisons with experiments, using also other models of V–As_m clusters, are in progress and will be the subject of future work.

4. Conclusions

We have reported the implementation of ab initio structural models of V–As_m complexes in MCBCA simulation of RBS-C spectra of heavily doped Si:As. Within this approach the atomic location of As is no longer a free parameter of the simulation and physical effects such as defect-induced lattice distortion, usually disregarded in the interpretation of RBS-C measurements, can be naturally taken into account. It becomes therefore possible to verify physical models concerning the atomic scale configuration of defect-dopant complexes and the mechanisms of electrical deactivation. First results reported here have shown that RBS-C can discriminate among different cluster models, due to the fact that some of them (such as V–As) introduce significant distortion in the neighbor Si atoms and are therefore expected to increase the Si yield appreciably above the one of a perfect crystal. Comparison of simulated and experimental angular scans of heavily doped Si:As equilibrated at high temperature demonstrates that the hypothesis of inactive As trapped in V–As_4 clusters is consistent with experimental observations, whereas a significant presence of V–As clusters is unlikely.

Acknowledgements

Thanks are due to R. Lotti and S. Cristiani for technical assistance in RBS-C measurements and for As ion-implantation. This work has been done within the *Iniziativa Trasversale Calcolo Parallelo* of INFM. This work was supported by MIUR, under the FIRB national project (contract RBAU01LLX2).

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