Titanium Impurities in Silicon, Diamond, and Silicon Carbide

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Received on 31 March, 2003

We carried a theoretical investigation on the electronic and structural properties of titanium impurities in silicon, diamond, and silicon carbide. The calculations were performed using the spin-polarized full-potential linearized augmented plane wave method in the supercell approach. The atomic configurations and transition and formation energies of isolated Ti impurities were computed.

1 Introduction

Since transition metal impurities affect the electronic and optical properties of semiconductors [1], it is important to understand the role of such unavoidable impurities on those properties. At the same time, transition metals in semiconductors can be used in other unusual situations. The energy levels related to transition metal impurities are aligned with respect to each other for the same group of isovalent semiconducting compounds [2]. Therefore, this defect-related level could be used as a reference to determine an important property in semiconductors: the valence band offset in the interface between two compounds [3].

Titanium, vanadium and chromium are native impurities which are incorporated during growth of several type-IV and type IV-IV semiconductors [4, 5]. The properties of the titanium impurity in those materials are also interesting from a fundamental point of view, since it has a $3d^2 4s^2$ atomic configuration, being isoelectronic with the host atoms. In the specific case of silicon carbide, experimental data indicates that titanium is stable in a silicon site [6], and while it is electrically active in 4H-SiC, it is inactive in 3C-SiC [4]. Although the nearest-neighbor local structure for a substitutional Ti impurity is essentially the same in either hexagonal or cubic material, such distinction in the electrical activity behavior has been associated with the large difference in the materials bandgap ($\varepsilon_{\rm g}$) for the polytypes ($\varepsilon_{\rm g}$ ranging from 2.42 eV for the 3C-SiC to 3.33 eV for the 2H-SiC). Deep level transient spectroscopy (DLTS) experiments on Ti in 4H-SiC show that Ti introduces gap levels near the bottom of the conduction band [5]. Since $\varepsilon_{\rm g}$ is considerably smaller in 3C-SiC than in 4H-SiC, the Ti-related energy levels would be pinned in the conduction band for the 3C-SiC, and therefore they would be undetectable.

Here, we have carried a theoretical investigation on the electronic and the atomic structure, the spin state, and the stability of Ti impurities in silicon carbide, silicon, and diamond. We computed the Ti-related acceptor transition energies in all those materials, and using the model by Langer and Heinrich [2], we determined the valence band offset among Si, SiC, and diamond.

2 The FP-LAPW method

The calculations were performed within the framework of the density functional theory [7, 8], using the total energy full-potential linearized augmented plane wave (FP-LAPW) method, implemented in the WIEN97 package [9], combined with the exchange-correlation potential of Perdew-Burke-Ernzerhof [10]. We considered reference supercells of 54 atoms for the cubic crystals and of 56 atoms for the hexagonal (2H-SiC) crystal. For the bulk SiC, a convergence in total energy was achieved using 5.8/R (maximum length of the plane-waves), where R is the smallest radius of spheres which defines the host atoms. We used $\rm R_{Si} = 1.5$ a.u. and $\rm R_{C} = 1.2$ a.u. For bulk Si, the convergence criteria was 6.0/R, with $\rm R_{Si} = 1.8$ a.u., and for diamond, it was 7.0/R, with $\rm R_{C} = 1.2$ a.u. For simulations involving titanium impurities, $\rm R_{Ti} = 1.2$ a.u. was used.

The full Brillouin zone (BZ) was sampled by a 6^3 grid of k-points [11], which reduces to 16 k-points in the irreducible BZ (IBZ) in the primitive cell. Self-consistent interactions were performed until convergence on both the total energy (10^{-4} eV per unit cell) and total charge in the atomic spheres (10^{-5} electronic charges per atom) were achieved. Total energy minimizations, with respect to variations in the lattice parameters, lead to values of $a = 4.38$ Å ($a_{expt} = 4.360$ Å [12]) in 3C-SiC, $a = 3.09$ Å and $c = 5.05$ Å ($a_{expt} = 3.076$ Å and $c_{expt} = 5.035$ Å [12]) in 2H-SiC, $a = 5.46$ Å ($a_{expt} = 5.431$ Å [12]) in silicon, and $a = 3.57$ Å ($a_{expt} = 3.567$ Å [12]) in diamond.

For the supercell calculations, the BZ was sampled by a $2 \times 2 \times 2$ grid [11], corresponding to a unique point to integrate the IBZ. For such calculations, the convergence cri-

teria for total energy and electronic charge were the same as described earlier [13, 14, 15]. The atomic positions were relaxed until the forces were smaller than 1mRy/a.u. Here, we investigated only substitutional Ti, since it has been recently shown by total energy calculations that the interstitial Ti is considerably less stable than the substitutional one in silicon carbide [13, 14].

3 Substitutional Ti in SiC, Si, and diamond

Figure 1 displays the impurity induced energy levels, based on the Kohn-Sham eigenvalues, for the neutral substitutional Ti impurity in Si, in diamond, in 3C- and 2H-SiC at the Γ point. In the T_d crystal field, the Ti 3d-derived states split into two energy levels with t_2 and e symmetries.

In silicon, the Ti_s impurity (fig. 1a) introduces a fully-occupied t_2 level in the valence band and an unoccupied e level in the bandgap. The center presents an effective spin S=0, and has a T_d point symmetry. This result is fully consistent with a previous theoretical investigation [16], although such investigation did not take atomic relaxations into account. Here, the four nearest-neighboring atoms undergo an outward relaxation of 6.0 % (with respect to the crystalline interatomic distance).

In 3C-SiC, the Ti_s^{Si} center (substitutional Ti in the Si site) introduces no energy levels in the band gap (fig. 1b). The center also shows an effective spin S=0 and a T_d point symmetry. The four nearest-neighbors undergo an outward relaxation of 6.6 %. The Ti-related energy levels are unoccupied resonant levels in the conduction band, where the e level lies below the t_2 level. Therefore, when a Ti atom replaces a Si atom, it undergoes a p-d hybridization, binding to the four nearest-neighboring carbon atoms. The Ti impurity reconstructs the Si vacancy dangling bonds, affecting only slightly the crystalline band structure. Since the Ti-related energy levels of Ti_s^{Si} center lie outside the bandgap, we could not compute the transition energies of this center. This center is very similar to the substitutional Ti impurity in silicon.

In 2H-SiC, the Ti_s^{Si} center (fig. 1c) shows an effective spin S=0 and relaxation only in the breathing mode. The four nearest-neighbors undergo an outward relaxation of 7.0 %. Although this center resembles the one presented in fig. 1b, here the Ti-related energy levels lie inside the gap, in contrast to that in 3C-SiC.

In the 3C-SiC, the Ti_s^C center (substitutional Ti impurity in the C site) has an effective spin S=0 in a T_d point symmetry (fig. 1d). The four nearest-neighboring Si atoms relax outward by 23 %. The impurity introduces a fully occupied t_2 energy level in the band gap and an unoccupied e level near the bottom of the conduction band. In this defect, binding between Ti and its Si neighbors is very weak, considerably different from all the previous cases. Here, the C vacancy dangling-bonds essentially are not reconstructed.

Finally in diamond, the Ti_s center has an effective spin S=0 in a T_d point symmetry (fig. 1e) and the four nearest-neighboring carbon atoms relax outward by 19 %. The impurity introduces a fully occupied t_2 energy level and a pair of unoccupied levels (e plus t_2) in the gap. The results for this center are similar to those of the Ti_s^C center in 3C-SiC.

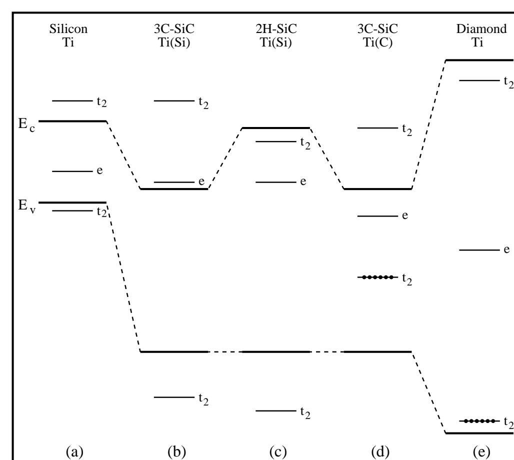

Figure 1. The Kohn-Sham energy eigenvalues representing the 3d-related impurity levels of substitutional Ti for the neutral charge state: (a) Si:Ti, (b) 3C-SiC:Ti^{Si}, (c) 2H-SiC:Ti^{Si}, (d) 3C-SiC:Ti^{C}, and (e) C:Ti centers. The top of the valence band (E_v) and the bottom of the conduction band (E_c) were adjusted according to the Langer-Heinrich rule [2], as explained in the text.

To analyse the stability of each center, we computed the defect formation energies. For those calculations, we used the chemical potentials of silicon, diamond, Ti (hcp structure), SiC, and TiC (sodium-chloride structure) crystals. In 3C-SiC, the formation energy of the Ti_s^C center is 7.2 eV and 8.3 eV higher than the Ti_s^{Si} center for Si-rich and C-rich conditions, respectively. This shows that it is energetically favorable for titanium to occupy the Si site. This gives a reasonable explanation why experiments have only identified the Ti impurity occupying the silicon site in silicon carbide [4, 6].

In Si, we found that the Ti impurity is more stable in an interstitial site than replacing a Si atom, in agreement with experimental evidences [16]. However, we computed the electronic structure of the substitutional Ti to calculate the acceptor transition energy in order to use the model by Langer and Heinrich [2], and determine the valence band offset among Si, SiC, and diamond. In diamond, on the other hand, it is energetically favorable for Ti to occupy a lattice site than an interstitial one, being fully justified our approach.

By computing the acceptor transition (0/-) energies of a substitutional titanium impurity (in SiC, Si, and diamond), we could extract the valence band offsets. These offsets are presented in figure 1. We find transition energies, above the top of the valence band, of 0.5 eV in silicon, 2.7 eV in 2H-SiC, 2.0 in 3C-SiC (Ti_s^C), and 3.2 eV in diamond. Using the model by Langer and Heinrich [2], we predict a valence band offset of 2.2 eV between Si and SiC, 1.2 eV between diamond and SiC, and 3.4 eV between silicon and diamond.

4 Summary

In summary, we performed an *ab-initio* investigation of titanium impurities in silicon, silicon carbide, and diamond. The Ti_s^{Si} center, which is the most stable configuration for Ti in 3C-SiC, presents no energy levels in the bandgap. Therefore, this center would not be detectable in 3C-SiC by EPR or DLTS measurements. By using the Langer-Heinrich rule [2], it has been proposed [4, 5] that the energy location of the Ti-related levels in the silicon carbide polytypes remains fixed with relation to the top of the valence band. Therefore, the positions of the levels do not depend on the polytype parameters, depending only on the gap magnitude. In 4H-SiC, DLTS experiments found an acceptor transition at E_c - 0.16 eV, which has been related to a substitutional Ti impurity in a cubic silicon site. Considering that this level is pinned with relation to the E_v for any polytype, this level would lie at E_c + 0.7 eV in 3C-SiC. This could explain why titanium is not detectable in cubic silicon carbide. Our result for the energy level of neutral Ti_s^{Si} center, at E_c + 0.3 eV is consistent with that experimental interpretation. Additionally, the electronic structure results show that the substitutional Ti impurity in SiC in the silicon site is very similar to that of Ti in silicon and that the substitutional Ti impurity in SiC in the carbon site is very similar to that of Ti in diamond. By using the acceptor transition energy of substitutional Ti impurity in SiC, Si, and diamond we predicted the valence band offset among all those compounds.

Acknowledgments

The authors acknowledge support from FAPESP and CNPq. The calculations were performed at the LCCA-CCE of the Universidade de São Paulo.

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