

FIRST-PRINCIPLES PROPERTIES OF AN INTERMEDIATE BAND MATERIAL BASED ON TI-IMPLANTED SILICON

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ABSTRACT: A first-principles study is aimed to reveal the properties of a crystalline Ti-implanted Si compound obtained experimentally with a Ti concentration clearly above the corresponding equilibrium solubility limit and high enough to be capable of presenting an electronic intermediate band brought about by Ti *3d* electrons instead of the well-known impurity levels structure. Interstitial, substitutional and other Ti implantation processes are considered, as well as several possible mixtures of them, in order to clarify the origin of a donor-kind transition observed experimentally at about 0.36 eV. Also the possibility of obtaining an intermediate band from the studied compound is considered. When convenient, calculations of magnetic and optical properties were carried out to help to identify this potential intermediate band material.

Keywords: Intermediate Band, Silicon, Quantum Calculation

1 INTRODUCTION

In the recent years a number of intermediate band materials have been proposed for making highly-efficient photovoltaic devices [1-4]. Following the work of A. Luque and A. Martí [5], in order to approach the highest efficiency it is convenient to start from a host semiconductor with a bandgap around 2 eV.

Conventional Si, being not optimal for this purpose, allows to profit from a broad knowledge and therefore once obtained the active material the manufacture of the solar cell would be to some extent straight. There are well-known impurity levels originated from transition metal *3d* orbitals, as Ti. The main difficulty to achieve an intermediate band from these levels is to go beyond the Mott limit, which shows the minimum concentration to get an efficient band instead of an impurity level avoiding the existence of possible nonradiative recombination centers [6]. This may have been accomplished by J. Olea *et al.* [7] due to a crystalline sample of Ti-implanted Si with a Ti concentration of about $6 \times 10^{19} \text{ cm}^{-3}$, several orders of magnitude exceeding its solubility limit and above the approximated value of 10^{18} cm^{-3} shown by E. Antolin *et al.* [6]. Moreover a donor level sited 0.36 eV below the conduction band edge has been found in that compound [8].

In order to explain the foundations of this level, its possible relationship to an appropriate intermediate band, and to guess how the possible intermediate band can be confirmed through experimental measurements, several quantum calculations have been performed in order to get an idea of the structural, electronic, magnetic and optical properties of the compound [9].

2 METHOD

Calculations have been carried out at several concentrations and configurations of Ti species. Therefore compounds proposed are derived from 2x2x2, 3x3x3 and 4x4x4 supercells of conventional Si₈ cell which translates into 64, 216 and 512 Si atoms, respectively. In turn this enhances to decrease the Ti concentration down to 8×10^{20} , 2×10^{20} , and 10^{20} cm^{-3} ,

respectively.

The exchange-correlation potential was approached by means of the generalized gradient approximation (GGA) with the PW91 parameterization [10] implemented in the density functional theory [11,12] code, VASP [13,14]. The inner electrons were represented through projector augmented wave (PAW) potentials [15,16].

In the compounds derived from 2x2x2 and 3x3x3 supercells an optimization of the atomic structure was carried out reaching to lower the inter-atomic forces below 0.01 eV/Å. The possible presence of Jahn-Teller distortions was discarded due to slight deviations from high-symmetry configurations relaxed towards the symmetric structure.

The Brillouin zone has been sampled by means of the Monkhorst-Pack scheme, using 6x6x6, 4x4x4 and 2x2x2 Γ -centered meshes.

3 RESULTS

3.1 Formation energies

The mechanisms of several possibilities of a Ti implantation process have been studied. Amongst them, simple substitutional processes, tetrahedral and hexagonal type interstitial implantations, split dumbbell type configurations and some combinations and more complex situations have been considered.

One simple possibility consists on the substitution of one Si atom by one Ti (Ti_{Si}). As all the Si atoms are equivalent, there is only a possible substitutional implantation. Interstitial Ti can be placed both in tetrahedral (Ti_t), or, less likely, in hexagonal (Ti_{hi}) sites, without distorting drastically the host compound. The dumbbell split [110] configuration, which is common in Si self-interstitial defects, was unstable in the case of the Ti and the atomic structure relaxed into the previous interstitial case.

The formation energy of each implantation is obtained from the balance of total energies of the different stable compounds known. For example, after calculating the energy of pure Si (-1170.797 eV for the Si₂₁₆ cell) and the energy of hcp-Ti, (-15.486 eV for the primitive cell having two Ti atoms) it is possible to

extract the balance from the energy of the substitutional $\text{Ti}_{\text{Si}}\text{Si}_{215}$ compound (-1177.034 eV):

$$E^f[\text{Ti}_{\text{Si}}\text{Si}_{215}] = E[\text{Ti}_i\text{Si}_{216}] - (215/216)E[\text{Si}_{216}] - (1/2)E[\text{Ti}_2] = + 2.156 \text{ eV}$$

Additionally, the energetic balances of several combinations of these implantations were also studied. These include combination of two interstitial implantations, substitutional plus interstitial and substitutional plus Si autointerstitial. Energies were calculated both in the nearest (*N*) and in the remotest (*R*) configurations for this kind of combinations. The formation energy per Ti atom is shown in Table I.

Table I: Formation energies of different Ti implanted compounds.

Compound	E^f eV
$\text{Ti}_{\text{Si}}\text{Si}_{215}$	+ 2.156
$\text{Ti}_i\text{Si}_{216}$	+ 1.506
$\text{Ti}_{\text{Si}}\text{Si}_{216}$	+ 3.343
$\text{Ti}_i\text{Ti}_i\text{Si}_{216}$ (R)	+ 2.993
$\text{Ti}_i\text{Ti}_i\text{Si}_{216}$ (N)	+ 2.632
$\text{Ti}_i\text{Ti}_{\text{Si}}\text{Si}_{215}$ (R)	+ 3.629
$\text{Ti}_i\text{Ti}_{\text{Si}}\text{Si}_{215}$ (N)	+ 2.094
$\text{Ti}_{\text{Si}}\text{Si}_i\text{Si}_{215}$ (R)	+ 6.002
$\text{Ti}_{\text{Si}}\text{Si}_i\text{Si}_{215}$ (N)	+ 4.103

It can be seen from the positive sign of the energy balances that none of the individual Ti implantation processes are favored. However, amongst the three proposed mechanisms, it can be seen that the lower penalty corresponds to the interstitial Ti_i . The 0.66 eV difference between it and the substitutional implantation helps to understand that only the 2% of Ti atoms occupy substitutional sites. The hexagonal interstitial implantation is rather improbable to take place due to the difference from the formation energies regarding to the formers.

The combination of processes, when placed at the remotest sites of the supercell, shows formation energy nearly equal to the addition of both implantations, as it was expected. This formation energy is lowered when they get closer due to the tendency of Ti atoms to be grouped forming a cluster. Comparing the different possible combinations, the $\text{Ti}_i\text{Ti}_{\text{Si}}\text{Si}_{215}$ shows the smallest penalty. Its formation energy per Ti atom, +1.097 eV is even below that of $\text{Ti}_i\text{Si}_{216}$ compound. However, it must be noted that the concentration of Ti_{Si} atoms is 2% against 98% of Ti_i . Therefore, even in the case that every Ti_{Si} would appear together with an interstitial Ti forming a dimer, its concentration would be two orders of magnitude below $[\text{Ti}_i]$.

3.2 Atomic structure

The relaxed substitutional structure shows a Ti atom surrounded to four Si nearest neighbors, placed in tetrahedral coordination. The $\text{Ti}_{\text{Si}}\text{-Si}$ distance is 2.502 and 2.504 Å for the $\text{Ti}_{\text{Si}}\text{Si}_{63}$ and $\text{Ti}_{\text{Si}}\text{Si}_{215}$ compounds, respectively. The second nearest neighbors are placed further away, at distances of 3.902 and 3.901 Å for the $\text{Ti}_{\text{Si}}\text{Si}_{63}$ and $\text{Ti}_{\text{Si}}\text{Si}_{215}$ compounds, respectively.

In a simplified view the interstitial implantation could be considered as a tetrahedral as well, because the

first neighbors are located following this symmetry at 2.474 Å for the $\text{Ti}_i\text{Si}_{216}$ compound (2.481 Å for the $\text{Ti}_i\text{Si}_{64}$ cell). Actually the second nearest neighbors are worth to be considered, given that they are located at 2.774 Å (2.772 Å for $\text{Ti}_i\text{Si}_{64}$), only 0.3 Å further away. This will be analyzed again in the next sub-section. The environment of the Ti_i atom is shown in Fig. 1, from which it can be deduced that the second nearest neighbors form an octahedral configuration.

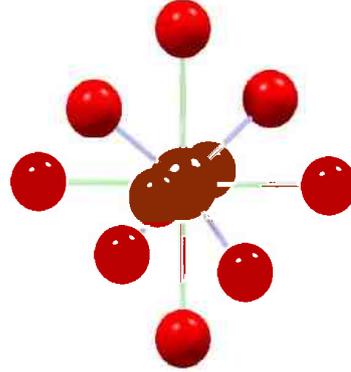


Figure 1: Environment of interstitial Ti implantation. Ti and Si atoms are colored in green and red, respectively. Tetrahedral and octahedral bonds are show also.

3.3 Electronic structure

In order to get a reference for the implanted compounds, the electronic structure of bulk-Si was obtained. The value calculated for the band-gap of the experimental lattice of the bulk structure was 0.60 eV for the different supercells. Otherwise, the gap found for the relaxed Si was 0.63 eV. Therefore the band gap calculated is around half of the experimental value (1.12 eV).

The band structure of the $\text{Ti}_{\text{Si}}\text{Si}_{63}$ compound is shown in Fig. 2. A band formed mainly by two states Ti $3d$, slightly overlapped to the conduction band of the host semiconductor, can be appreciated. These states have e_g symmetry and are split by the tetrahedral crystal field towards low energies in contrast to the t_{2g} states, which appear mixed with the conduction band.

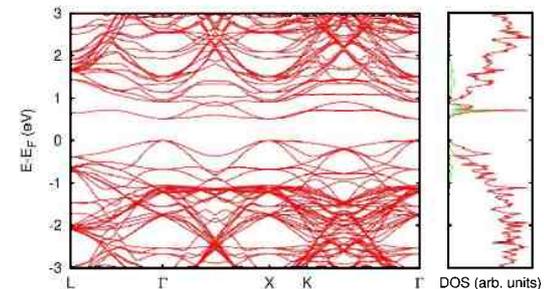


Figure 2: Electronic band structure (left) and density of states (DOS) (right) of the $\text{Ti}_{\text{Si}}\text{Si}_{63}$ compound. The projected DOS of the Ti $3d$ electrons is drawn in light green. In this case both spin states are degenerated.

A lower concentration of substitutional Ti results in a narrowing of the e_g band [4]. Indeed in the case of the $\text{Ti}_{\text{Si}}\text{Si}_{511}$ compound it appears completely isolated from the conduction band. However, in all the substitutional

compounds the band formed is empty and therefore does not fulfill with all the intermediate band requirements. Furthermore, an empty band is not compatible with the donor level found experimentally.

The properties of the interstitial compounds are rather different. The electronic structure corresponding to $\text{Ti}_i\text{Si}_{512}$ is represented in the Fig. 3. The splitting of a group of three Ti $3d$ low energy levels, which correspond to the well-known t_{2g} manifold in both spin channels contrasts with the previous case. This observation show that the crystal field caused by the six second nearest neighbors placed in octahedral positions overcomes the opposite, tetrahedral field caused by the four nearest neighbors, as it was aforementioned by G. W. Ludwig and H. H. Woodbury [15]. The probable cause may be that the increase in the coordinated ions of the octahedral environment be a more determining factor than the slight increase (0.3 Å) of the distance with regard to the tetrahedral one.

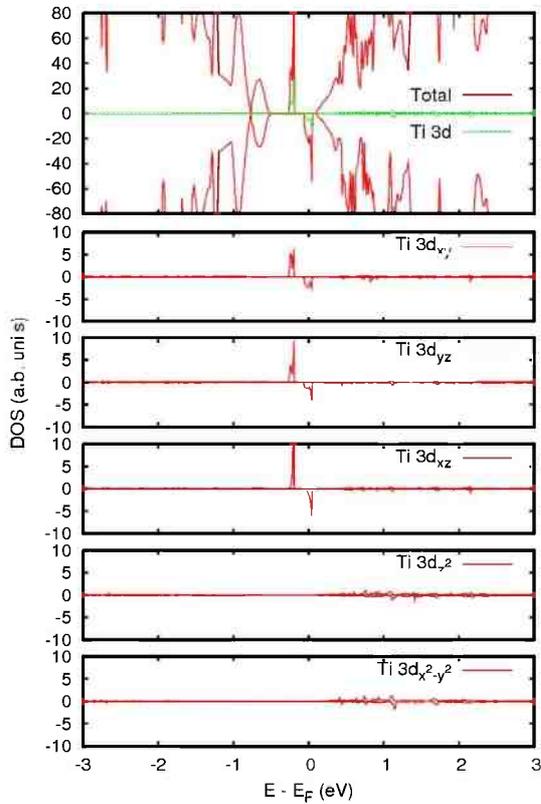


Figure 3: Total, Ti $3d$ projected and different orbital projected density of states. Majority and minority spin channels are represented in the upper and lower part of each chart. It can be seen that $3d_{xy}$, $3d_{yz}$ and $3d_{xz}$ form exclusively the states of the intermediate band, according to a t_{2g} type orbital.

In summary, predominant octahedral splitting causes the appearing of two narrow, isolated bands inside the host semiconductor band-gap of the $\text{Ti}_i\text{Si}_{512}$ compound. Both are populated with electrons and therefore any of them could originate the experimental donor level. However, after correcting the band-gap subestimation, the closest excitation energy to the donor level found (estimated in 0.36 eV [8]) corresponds to the minority band [9]. Furthermore, the minority manifold has is

partially (1/3) occupied and therefore fulfills all the requirements of an intermediate band.

3.3 Magnetic properties of interstitially Ti implanted Si

From now on only the properties corresponding to interstitially implanted compounds will be analyzed, given that 98% of implanted Ti atoms in the sample arrange in this configuration and that is the most plausible cause of the donor level found experimentally.

It has been addressed above that Ti atoms implanted interstitially in a homogeneous way show preference for ferromagnetic (FM) alignment, which is more stable than paramagnetic (PM) or antiferromagnetic (AF) configuration. In order to guess if this preference persists at different interatomic distances for a pair of Ti atoms, several calculations for the total energy of relaxed compounds with formula $\text{Ti}_2\text{Si}_{216}$ have been carried out considering different $\text{Ti}_i\text{-Ti}_j$ configurations. The magnetic moments used as starting condition were chosen including both FM and AF alignments for Ti atoms in every case.

A summary of the calculations is presented in Table II. It can be seen that for the shortest distances the most stable phase is the paramagnetic one. However, at distances longer than 9 Å, the FM alignment has the lower energy.

Table II: Distance between Ti atoms, more stable magnetic behavior, total magnetic moment per cell, and energetic difference between FM and AF phases (when convenient) of the $\text{Ti}_2\text{Si}_{216}$ compounds.

$d[\text{Ti-Ti}]$ (Å)	Stable phase	m (μ_B)	$E_{AF}-E_{FM}$ (meV)
2.49	PM	0	-
3.49	PM	0	-
5.20	PM	0	-
7.74	AF	0	-28
9.47	FM	4.03	11
11.84	FM	4.23	32
12.82	FM	4.02	3

The magnetic coupling constant, J , can be related to the energetic difference shown in table II, at least in the order of magnitude, although is possible that the disorder in the arrangement of the Ti atoms cause a lowering in the value. Therefore, the numbers suggest that at room temperature would not be rather probable to find long range magnetic ordering.

However, it seems possible that at low temperatures some magnetic order could be found in the material. Indeed, if ferromagnetic behavior were found in the experimental compounds that would be an argument pointing towards that the Ti atoms are implanted in an interstitial configuration.

3.4 Optical properties of interstitially Ti implanted Si

The dilution level $\text{Ti}_i\text{Si}_{216}$ was chosen to study the effect of the interstitial Ti on the absorption coefficient and reflectance, since it corresponds to the relaxed structure with the concentration closer to the experiment. These properties were obtained from the dielectric function that was calculated using the Fermi's golden rule, as a sum over independent transitions between the Kohn-Sham states.

In this sum, only interband and direct transitions

were taken into account, since we expect the contribution of the indirect transitions to be much lower than that of the direct ones, as they involve three particles.

In Fig. 4, the absorption coefficient of $\text{Ti}_i\text{Si}_{216}$ is shown and compared with that of the pure silicon. Due to the DFT underestimation of the conduction band eigenvalues, a rigid shift of the conduction band has been applied for the determination of the optical properties in order to match the experimental gap of Si. In this comparison, we can see the enhancement in the absorption of the $\text{Ti}_i\text{Si}_{216}$ with respect to that of bulk silicon in the range of higher solar emission. This increase in the absorption is due to the contribution of the new transition involving the Ti intermediate levels. The peak around 0.8 eV is resulting from transitions from the minority-spin intermediate band to the conduction band; the one around 1.4 eV is due to excitations from the majority-spin intermediate band to the conduction band; finally there is a component originated by the transitions from the valence band to the minority intermediate band that is modest in comparison to the others.

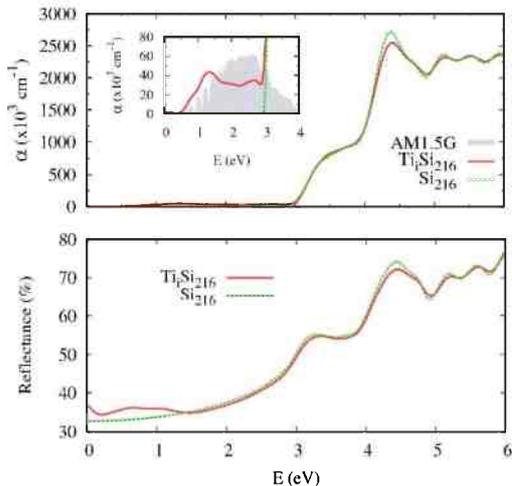


Figure 4: Optical absorption (top) and reflectance (bottom) calculated for the $\text{Ti}_i\text{Si}_{216}$ compound. The values corresponding to bulk Si_{216} are included for comparison. The inset of the top curve shows the enhancement of the absorption in the range of the solar spectrum, which is included as a shade.

In the quest of an efficient photovoltaic material, its reflectance plays also an important role. When combined with the absorption coefficient, it would allow us to study, among other properties, refractive indexes, extinction coefficients, transmittances and absorptivities. The reflectance spectra in Fig. 4 show the same behavior as the absorption coefficient. The main differences between the doped and the pure semiconductor spectra happen at the low-energy transitions range. An experimental result of reflectance combined with this theoretical spectrum could help in reinforcing the conclusion that the experimental sample has mainly interstitial Ti.

4 CONCLUSIONS

Calculations carried out help to explain that the concentration of experimentally implanted Ti on Si

corresponding to the interstitial implantation be much higher than the substitutional one, given the difference between both formation energies.

Furthermore, contrary to the case of Ti_{Si} atoms, interstitial implantation is coherent with the observation of an experimental donor level. Moreover, this level could represent one of the possible transitions in which an intermediate band formed by the Ti 3d states with t_{2g} symmetry would take part.

In principle, the experiment that would manifest the fact above would involve an increasing of photo-absorption at energies below the threshold marked by bulk Si absorption. The differences obtained theoretically from the reflectance could also help to identify an intermediate band material from interstitially implanted Ti.

Analysis of the energetic difference between FM and AF arrangements at different inter-atomic distances shows that if the Ti_i atoms are homogeneously distributed some alignment could be found at low temperatures conversely to Ti_{Si} atoms which show paramagnetic behavior.

ACKNOWLEDGEMENTS

This work was funded by the GENESIS-FV (CSD2006-0004) and PHOTOMAT (MAT2009-14625-C03-01) Projects of the Spanish Ministry of Science and from the NUMANCIA-MA (S-05050/ENE/0310) project of Comunidad de Madrid. K. S. acknowledges a grant from Consejería de Educación of Comunidad de Madrid and European Social Fund (E. S. F.). I. A. would like to acknowledge the MEC for a FPU grant. We acknowledge the computer resources and assistance provided by Centro de Supercomputación y Visualización de Madrid (CeSViMa).

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