PHOTOVOLTAIC MATERIALS AND PHENOMENA SCELL - 2004

JOURNAL OF MATERIALS SCIENCE **40** (2005) 1383 – 1386

Ab-initio spin polarized electronic structure calculations for $Ti_xGa_nAs_m$ photovoltaic materials

P. WAHNÓN*,‡,§, P. PALACIOS‡,§, J. J. FERNÁNDEZ‡,§ AND C. TABLERO‡
‡*Instituto de Energía solar and* §*Departamento de Tecnologías Especiales Aplicadas a la Telecomunicación, ETSI Telecomunicación, Universidad Politécnica de Madrid, 28040 Madrid, Spain*
E-mail: perla@etsit.upm.es

A half-metallic isolated band in the band-gap of GaAs and GaP semiconductors has been found for Ti and Sc transition metal impurities and proposed as highly-efficient photovoltaic materials. In this paper, we have investigated by first principle calculations, the spin polarized and non-polarized dispersion band structures and lattice constants of Ga_3As_4Ti and Ga_4As_3Ti alloy semiconductor compounds. We have carried out a comparative study of these compounds in order to identify the basic features of the isolated intermediate band formation in the semiconductor band-gap. We use an ab-initio fully self-consistent density functional theory method in the local density approximation (LDA), with norm-conserving, non-local pseudopotentials for core electrons. To assess the results, we first determined the electronic properties of GaAs and compared them with the experimental results. We find that spin wave functions of the polarized Ga_nAs_mTi compounds noticeably modify the nature and properties of the intermediate band that have already shown in the corresponding paramagnetic compounds.

1. Introduction

Band structures of diluted semiconductor compounds of the Ga_4As_3X and Ga_4P_3X type, X being a transition metal, have been investigated recently in the cubic zinc-blende structure using an accurate ab-initio code based on the density functional theory [1, 2]. Results obtained for these compounds present in some of their structures an isolated intermediate half-filled band located in the semiconductor energy band-gap, showing both direct and indirect band gaps in their calculated band diagrams [3, 4]. The calculations have been made using both the local density LDA approach [5] and the semi-local generalized gradient approximation correction GGA [6]. The presence of this intermediate band allows these compounds to be predicted as high efficient photovoltaic materials with the possibility of providing enhanced efficiencies by low energy photon absorption [7]. Using the intermediate band to enhance the use of sub-band gap energy photons, direct optical absorption of the proposed half-metallic materials have been determined by means of quantum mechanic calculations of the transition matrix elements between the corresponding band states [8]. However, the major LDA and GGA failure is associated with excitation energies, mainly represented by band-gap problems in semiconductors. The ab-initio calculations of the optical properties for the GaAs and GaP semiconductors show several discrepancies with the experiments. To improve the results and correct the well-known band-gap problem, the exact exchange method (EXX) has been applied to GaP and GaAs [9] and more recently to the $TiGa_4P_3$ system and the half-metallic intermediate band have been confirmed in the non-polarized compounds [10].

On the other hand, the recent discovery of ferromagnetic behaviour of diluted magnetic III-V semiconductors containing small amounts of Mn atoms makes this kind of material very promising for developing new kinds of devices based in spintronic technology [11]. In particular, semiconductor materials in which carriers are spin-polarized also offer the possibility of realizing spin-polarized solar cells.

In the present work, first-principles theoretical investigations of spin polarized and non-spin polarized electronic band structure and the parameters of these Ga_nAs_mTi compound systems have been studied using the *ab-initio* self-consistent density functional theory (DFT) as implemented in the SIESTA program [2]. We use the LDA approach to determine the properties of these compounds to understand the effect of spin wave functions on the intermediate band properties. As a basic reference, to asses the validity of our results we compare first, equivalent ab-initio calculations for GaAs host semiconductors.

In Section 2, we describe the calculation methods and in Section 3, we present and discuss the results of our calculations. The conclusions are summarized in Section 4.

---

*Author to whom all correspondence should be addressed.

2. Calculation methods

The calculations of the fully self-consistent non-polarised and polarised Schroedinger equation have been carried out in this work, with the direct diagonalization method of the *ab-initio* SIESTA [2] code program. The code makes all the calculations by projecting electron wave functions and density onto a real space grid. The basis set used to describe valence electrons was a double zeta plus polarization DZP (2 s and 6p orbitals for Ga, and As, and 2 s and 10 d orbitals for Ti adding 5 d orbitals more for Ga, and As and 3 p orbitals more for Ti for the polarization) with different cut-off radius for s, s', p, p' and d orbitals.

An 8-atom simple cubic cell, where a single Ti atom replaces one atom of Ga or one atom of As respectively have been used for the two compounds. The model is assumed to have the smallest possible unit cell and retain the highest symmetry. In this work, we use the local-density approximation (LDA) in the Ceperley-Alder form [12] with the parameterisation fitting given by Perdew and Zunger [5] for the exchange-correlation potential. The core electrons were replaced by Troullier-Martins norm-conserving pseudopotentials [13] in the Kleinman-Bylander form [14] and were taken to be the 3p electrons and below for Ti, and 3 d and below for Ga and As. We tested the convergence with respect to the basis set and k-point samplings in the calculations for all systems. The equivalent cut-off energy in a real space grid from the transformed charge density was approximately 80 Ry. This relatively large mesh cut-off is needed to describe the localized d states of titanium. We used a Monkhorst Pack grid of $8 \times 8 \times 8$ k-points for the simple cubic unit cell. To determine the equilibrium structure of the systems studied, all the atomic positions and the unit cell were allowed to relax by the minimization of the total energy until the largest force components were below 0.001 eV/Å and the stress tolerance were less than 0.1 GPa.

The calculations were made first for the paramagnetic Ga_4As_3Ti and Ga_3As_4Ti alloy systems in two main directions of high symmetry of the Brillouin zone to identify and analyze the existence of the intermediate band in both systems. LDA approximation for the exchange and correlation potential were used in all calculations and compared the non polarized results to the exact exchange EXX calculations in order to get more accurate band-gaps analysis. Then we have calculated the spin polarized band states with the spin local density (LSDA) for the two aforementioned compounds with the same degree of accuracy and in the same directions of symmetry.

3. Results of calculations

In the absence of experimental data for the Ga_4As_3Ti and Ga_3As_4Ti alloy systems, we have calculated first both the LDA and GGA exchange and correlation potential of the pure binary GaAs compound in the two-atom zinc-blende structure with a DZP basis for the two atoms, in order to compare our results, as a basic reference, with the available experimental data in the crystals. GaAs is a well-known band semiconductor. Our ab-initio calculations are in very good agreements with the experimental data and with other more sophisticated calculations made with the exact exchange (EXX) method [6].

In this calculation, the optimized lattice parameter constants for GaAs for LDA and for GGA approximation using the DZP basis and after dynamical relaxation are 5.68 and 5.85 Å respectively, compared to the experimental data 5.65 Å [15]. LDA lattice constant calculations agree very well with the experimental ones whereas the theoretical GGA lattice constants show a lattice expansion of 3.3 (3.5)% respectively. Moreover, for the same calculation, the LDA band gap of GaAs is 0.968 eV which it is larger than the band gap obtained by the GGA approximation, 0.446 eV. In both choices the width of the band gap remains underestimated with respect to those calculated with the exact exchange EXX method, 1.49 eV [9] and to the experimental value, 1.53 eV [15]. A comparable relationship between the calculated and real values of the band gap can be expected also for the Ga_nAs_mTi systems.

Then, we have first made calculations for non-polarized Ga_4As_3Ti and Ga_3As_4Ti using the accurate LDA approach. After total dynamical relaxation, the equilibrium total energies for both systems are -854.21 and -969.55 eV and optimized lattice parameters of the cubic supercells are 5.78 and 5.70 Å respectively. These values show that the substitution of one Ga atom for a Ti gives rise to a more stable semi-metallic compound and less distorted crystalline structure compared to the AsGa host with the same type of calculation (LDA lattice parameter, 5.68 Å). The non-polarized band dispersions along the high-symmetry lines are shown in Fig. 1 in the fcc structure for the two semi-metallic

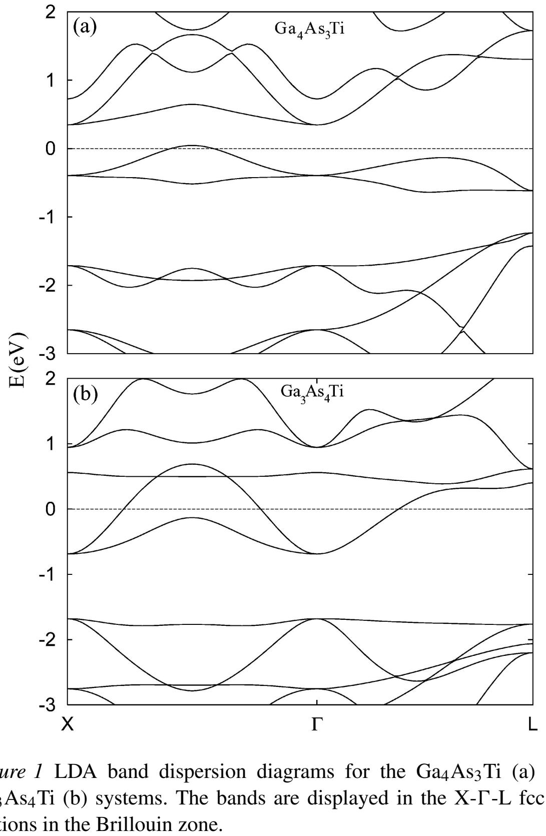

Figure 1 LDA band dispersion diagrams for the Ga_4As_3Ti (a) and Ga_3As_4Ti (b) systems. The bands are displayed in the X-Γ-L fcc directions in the Brillouin zone.

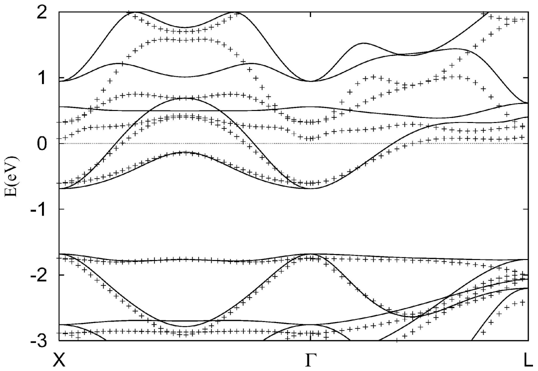

Figure 2 LDA band dispersion diagram for the Ga_3As_4Ti system (solid lines) compared to the EXX calculation (crosses). The bands are displayed in the X-Γ-L fcc directions in the Brillouin zone.

materials. The isolated intermediate band appears only for the Ga_4As_3Ti system as shown in Fig. 1a, where the substitution of one As atom for a Ti creates a hole related to the GaAs host. The Fermi level appears to be close to the top of the intermediate band. There are two energy gaps separating the intermediate band from the conduction and valence bands of the host semiconductor, fully consistent with the recent work [3, 4]. On the other hand, as shown in Fig. 1b for Ga_3As_4Ti, the intermediate band is mostly composed of Ti *d* states as in the other compound however it is much wider and does not appear to be isolated. In these LDA calculations, an empty Ti *d* band coming from the conduction band interacts with the upper part of the intermediate band in the Γ – X direction. However, the Fermi level lies close to the center of the intermediate band. A comparison with a calculation using only the exact exchange in the EXX method is shown in Fig. 2. The empty band of Ti is located now at higher energy separated from the intermediate band. It is expected that this empty state will appear in reality at a much higher energy.

The spin polarized bands calculated with LSDA exchange and correlation potential along high symmetry directions in the fcc structure for the two semi-metallic compounds are shown in Figs 3 and 4 in the spin-up channel (Figs a) and in the spin-down channel (Figs b). In the case of the Ga_4As_3Ti compound, the isolated intermediate band displayed in the non polarized system at the Fermi level, is split into two bands for the spin-up and in other one for the spin-down as shown in Fig. 3a and b. It means that both the spin-up and spin-down bands at Fermi level appear in the LSDA. One of the spin-up bands located deeply inside the gap is fully occupied by 3*d* Ti electrons and weakly mixed with the valence band of GaAs. Our calculations also show that the total 3*d* electron population in the Ga_4As_3Ti is around 3.35, i.e., the atomic configuration of Ti is compatible with both $3d^3$ and $3d^4$. However, in the case of the more stable Ga_3As_4Ti compound, the spin wave functions modify the electronic structure at the Fermi level as shown in Fig. 4. The spin-up channels (Fig. 4a) show a well-isolated band at the Fermi level of the 3*d* majority-spin with two narrow band-gaps meanwhile the spin-down electrons (Fig. 4b) present one wider band-gap.

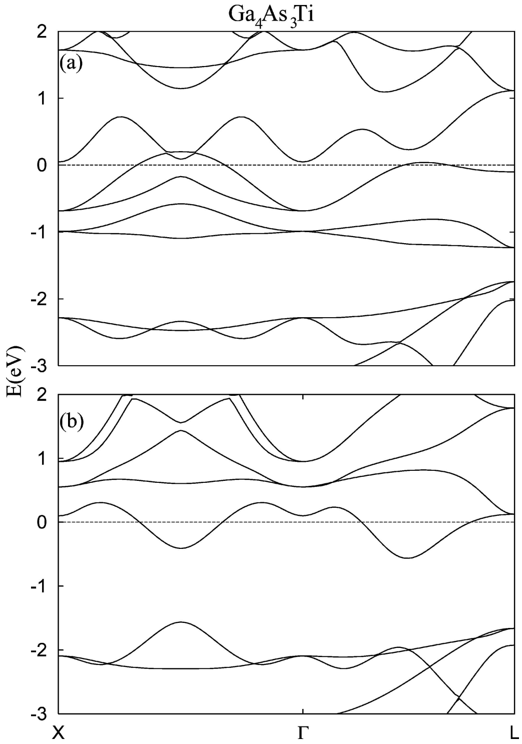

Figure 3 LSDA band dispersion diagrams for the Ga_4As_3Ti system: (a) spin-up and (b) spin-down. The bands are displayed in the X-Γ-L fcc directions in the Brillouin zone.

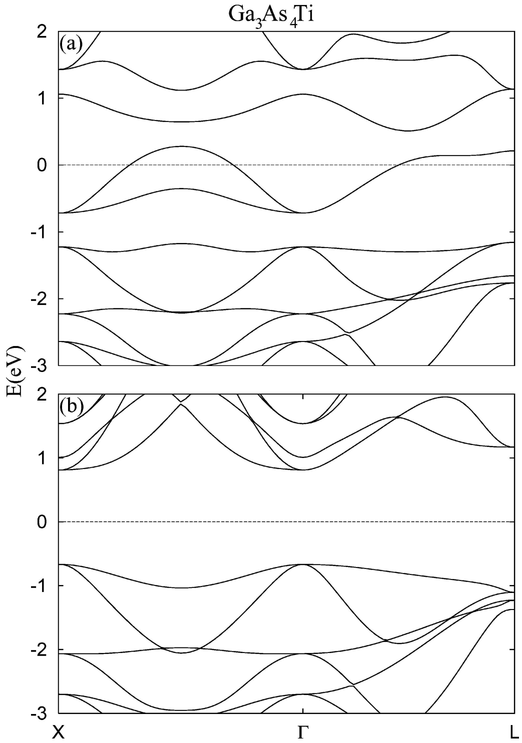

Figure 4 LSDA band dispersion diagrams for the Ga_3As_4Ti system. (a) spin-up and (b) spin-down. The bands are displayed in the X-Γ-L fcc directions in the Brillouin zone.

4. Conclusions

We have calculated accurate ab-initio LDA and LSDA band dispersion diagrams for Ga_4As_3Ti and Ga_3As_4Ti alloy semiconductor systems in an eight-atom simple cubic cell using the SIESTA program. We have calculated first the exact exchange in EXX method and compared the results to the non-polarised Ga_3As_4Ti system. We showed that the first $3d$empty band of Ti that in the LDA calculations crosses the intermediate band must be located at higher energy. For the corresponding polarised LSDA calculations, it was found that the spin wave functions substantially modify the structure of the intermediate band in both compounds. Meanwhile for the diluted Ga_4As_3Ti compound both the spin-up and the spin-down bands appear at the Fermi level, the half metallic Ga_3As_4Ti presents only a well separated spin-up band at the Fermi level and a wide band-gap for the spin-down bands. Further systematic theoretical analysis is highly desirable for a deeper insight into the nature and composition of these spin polarize compounds.

Acknowledgements

This work has been partially supported by Plan Nacional de I+D of Spain program Ref. N: MAT2002-01076 and by the European Commission project FULL-SPECTRUM Ref. N: SES6-CT-2003-502620. P.P. acknowledges an F.P.I. grant from the Spanish Ministry of Science and Technology.

References

1. P. HOHENBERG and W. KOHN, *Phys. Rev. B* **136** (1964) 864; W. KOHN and L. J. SHAM, *Phys. Rev.* **140** (1965) 1133.
2. J. M. SOLER, E. ARTACHO, J. D. GALE, A. GARCIA, J. JUNQUERA, P. ORDEJÓN and D. SÁNCHEZ-PORTAL, *J. Phys.: Cond. Matt.* **14** (2002) 2745.
3. P. WAHNÓN and C. TABLERO, *Phys. Rev. B* **65** (2002) 165115.
4. C. TABLERO and P. WAHNÓN, *Appl. Phys. Lett.* **82** (2003) 151.
5. J. P PERDEW and A. ZUNGER, *Phys. Rev. B* **23** (1981) 5048.
6. J. P. PERDEW, K. BURKE and M. ERNZERHOF, *Phys. Rev. Lett.* **77** (1996) 3865; **78** (1997) 1396.
7. A. LUQUE and A. MARTÍ, *ibid.* **78** (1997) 5014.
8. C. TABLERO, A. GARCÍA, J. J. FERNÁNDEZ, P. PALACIOS and P. WAHNÓN, *Comp. Mat. Sci.* **27** (2003) 58.
9. J. J. FERNÁNDEZ, C. TABLERO and P. WAHNÓN, *ibid.* **28** (2003) 274.
10. *Idem.*, *J. Chem. Phys.* **120** (2004) 10780.
11. T. DIETL, H. OHNO and F. MATSUKURA, *Phys. Rev. B* **63** (2001) 195205.
12. D. M. CEPERLEY and B. J. ALDER, *Phys. Rev. Lett.* **45** (1980) 566.
13. N. TROULLIER and J. L. MARTINS, *Phys. Rev. B* **43** (1991) 1993.
14. L. KLEINMAN and D. M. BYLANDER, *Phys. Rev. Lett.* **48** (1982) 1425.
15. "CRC Handbook of Chemistry and Physics," 80th edn., edited by D. R. Lide (CRC Press, New York, 2000).