

Relaxations and bonding mechanism of arsenic in-situ impurities in MCT: first-principles study

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Abstract: The structural and electronic properties of the arsenic in-situ impurity in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ (MCT) were studied by combining the full-potential linear augmented plane wave (FP-LAPW) and plane-wave pseudopotential methods base on the density functional theory. Structural relaxations, local charge density, densities of states are computed to investigate the effects of the impurity on the electronic structure. The bonding characteristics between the impurity and the host atoms are discussed by analysis of the valence charge density and the bonding charge density. The amphoteric behavior of arsenic impurity in MCT has been shown. The defect levels introduced by the in-situ arsenic impurities are determined by the single-particle electron energy calculations, which are in good agreement with the experimental results.

Key words: $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$; arsenic impurity; atom relaxation; bonding mechanism; first-principle study

1 Introduction

Mercury cadmium telluride ($\text{Hg}_{1-x}\text{Cd}_x\text{Te}$, MCT) is currently one of the most widely used semiconductor materials for infrared detector arrays. It is well known that the applications of the semiconductor materials, especially for II-VI compounds and alloys, mainly depend on whether they can be doped with donor or acceptor[1]. For infrared detectors fabricated by $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$, the p on n heterojunction is currently the preferred device design. In recent years, due to its low diffusivity in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ [2] compared with the native acceptor and the group I elements, attention has been focused on group V elements, especially arsenic, as the p-type dopant in heterojunction devices where a sharp doping profile is essential for device performance [3]. The experimental results indicate that arsenic can provide a shallow acceptor level in molecular beam epitaxy(MBE) $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ [4]. But the arsenic doping is strongly self-compensated, requiring annealing for its p-type electric activation[5]. At the same time, the amphoteric

behavior of arsenic in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ has been found in materials grown by bulk method[6], liquid phase epitaxy (LPE)[7], MBE[8], and MOCVD[9], with incorporation as a p-type dopant under Hg-rich conditions, and as an n-type dopant or un-active dopant under Te-rich conditions. Although MBE is done at much lower temperatures than LPE, and thus offers some distinct advantages, the group V impurities are still observed to incorporate as donors[4], self-compensating the p-type doping. HARMAN pointed out that there is a significant fraction of the arsenic residing on the cation sub-lattice even under cation-saturated conditions. According to the arsenic dopant incorporation model[11] and the quasichemical predictions[12], some of the doped arsenics in MCT grown by MBE are incorporated on the cation sublattice as isolated defects, As_{Hg} , unbound to vacancies, as donors. Although the arsenic incorporation can be switched from an n- to p-type through post-growth annealing, the electronic properties of in-situ As_{Hg} not only determine the material properties before annealing, but also mainly dominate the annealing activation process from n- to p-type. As we know that the

the annealing process not only affect the electronic properties but also affect the structural properties [13,14] which is worth studying thoroughly. Moreover, for doping levels above $5 \times 10^{18} \text{ cm}^{-3}$, the As activation efficiency drastically drops because of the As_{Hg} self-compensation [15,16]. Herein the complicated behavior of the arsenic impurities in MCT, we must study thoroughly the electronic properties of both As in-situ substitute Hg and As in-situ substitute Te in MCT. Although the models of the amphoteric behavior are suggested, there is not comprehensive consensus on the microscopic mechanism of group V impurity incorporation in MCT, which is essentially important for infrared focal plane array technology.

Some theoretical studies the arsenic doped MCT materials. However, the calculations reported with the ab initio method, to our knowledge, are lack. In our previous work [17], we have reported the relaxations, bonding mechanism and electronic structure of As_{Hg} in $\text{Hg}_{0.5}\text{Cd}_{0.5}\text{Te}$. In order to give full understanding of the electronic behaviors of the As in-situ impurities in MCT, we have performed the total energy calculations of full potential linear augmented plane wave (FP-LAPW) to systematically investigate the effect of the arsenic in-situ impurity on the electronic structure, the bonding mechanism with the host atoms, and the relaxation procedure in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$. In this paper, we choose $\text{Hg}_{0.5}\text{Cd}_{0.5}\text{Te}$ as the major prototype system. The reason why we choose such a mole fraction is that the computational results can be compared with that of the thoroughly studied II - VI semiconductors (CdTe and HgTe) to some extent. On the other hand, the results can be easily extrapolated to other mole fraction compositions. Furthermore, the results and conclusions of the calculations on $\text{Hg}_{0.5}\text{Cd}_{0.5}\text{Te}$ are confirmed, and also extended to the other mole fractions by using plane-wave pseudopotential calculations with larger supercells.

2 Computational procedure

The density functional theory (DFT) [18] calculations are performed using the FP-LAPW method implemented in the WIEN2K package [19]. We adopt Perdew-Burke-Ernzerhof (PBE) functional [20] to describe the exchange-correlation interaction. We consider a $2 \times 2 \times 2$ supercell (SC) with totally 64 atoms, consisting of eight quasi-zinc-blende crystal structure of unit cells $\text{Hg}_{0.5}\text{Cd}_{0.5}\text{Te}$ (each unit cell contains eight atoms including 4 Te atoms, 2 Hg atoms, and 2 Cd atoms). In the SC model, one of the 16 mercury atoms or one of the 32 tellurium atoms, on the lattice site (0.5, 0.5, 0.5) of SC, is replaced by an arsenic atom. A $2 \times 2 \times 1$ SC with 32 atoms of no impurity has been chosen as reference system for comparison purpose, and the

computational parameters are set to be the same as the vacancy case. In order to ensure well convergence, the muffin-tin (MT) radius and the number of k-points for generating the final results have been carefully chosen after optimization. The states treated as valence are $\text{Hg}(5d^{10}6s^2)$, $\text{Cd}(4d^{10}5s^2)$, $\text{Te}(5s^25p^4)$, and $\text{As}(4s^24p^3)$. The muffin-tin radii are chosen to be 2.60 atomic unit (a.u.) for all the four kinds atoms. A satisfactory self-consistent convergence has been achieved by considering a number of FP-LAPW basis functions up to $R_{\text{MT}}K_{\text{max}}=6.0$ for the 64-atoms SC and $R_{\text{MT}}K_{\text{max}}=7.0$ for 32-atoms SC. The K_{max} is the maximum value of the planwave vector which determines the so called energy cutoff for the plane wave expansion. The self-consistent iteration is considered to be converged when both the total energy and the total charge in the atomic sphere are stable within 10^{-4} eV per unit cell and 10^{-4} electron charges per atom, respectively. The localized levels are deduced from the calculations of the single-electron energy levels at Γ point and are aligned using the energy levels of core electrons. The relaxation procedures are conducted following the damped Newton dynamic schemes. The criterion of the forces convergence for all atoms is set below 0.5 eV/nm. The relativistic effect of spin-orbit (SO) coupling is also included.

To confirm the results on the supercell of 64 atoms using FP-LAPW calculations and extend the conclusions to the other mole fractions of MCT, the plane-wave pseudopotential code Vienna ab initio simulation package (VASP) is also used in this paper. In the VASP calculations, the core-electron interaction is modeled by the ultrasoft pseudopotentials, which can yield reasonably precise results with relatively low cutoff energy. Thus, it is possible to deal with the larger supercell. In the present paper, supercells with 256 and 512 atoms have been chosen. The plane-wave cutoff energy is chosen as 300 eV, the standard ultrasoft pseudopotentials from the VASP package are employed for all the cases, and the Brillouin zone is sampled by using $5 \times 5 \times 5$ and $3 \times 3 \times 3$ Monkhorst-Pack grid for 256-atoms and 512-atoms supercells, respectively. The energy convergent criterion is 1×10^{-4} eV per unit cell, and forces on all relaxed atoms are less than 0.1 eV/nm.

3 Results and discussion

3.1 Structural relaxation

The appearance of arsenic impurity in MCT induces the structural relaxation of the host and modifies the electronic structure of the system. Before relaxation of atomic structures, from the calculated total energy versus five different volumes around the lattice constants given by Vegard's law, the equilibrium volumes have been obtained for MCT systems with and without impurities,

respectively. All the calculated values are fitted to the Murnaghan equation of state. In comparison with the experimental results, the computed bond lengths of $R(\text{Te}-\text{Cd})$ and $R(\text{Te}-\text{Hg})$ are about 1% larger than that of the experimental results of CdTe and HgTe. Geometry optimizations reveal that the arsenic impurity, either substituted Hg or Te lead to inward relaxation of the NN atoms around the impurity, the calculated results of the radial relaxation of the NN atoms around the impurity are shown in Table 1.

Table 1 Radial relaxation results of nearest neighbor atoms around arsenic impurity(nm)

NN atom	$\Delta d(\text{As}-\text{Te}^{\text{I}})$	$\Delta d(\text{As}-\text{Hg}^{\text{I}})$	$\Delta d(\text{As}-\text{Cd}^{\text{I}})$
HgTe(PAW)	-0.003 8	-0.025 7	—
0.25(PAW)	-0.003 4	-0.026 4	-0.021 9
0.5(PAW)	-0.003 1	-0.027 4	-0.022 0
0.5(LAPW)	-0.001 0	—	—
0.75(PAW)	-0.002 1	-0.028 1	-0.022 5
CdTe(PAW)	-0.000 8	—	-0.023 4

Minus mean inward relaxaion (nm)

The relationship between the radial relaxation and mole fractions is also shown in Fig.1. The results indicate that the NN atoms around the impurity relax inward, either arsenic in-situ substitute Hg or Te. On the one hand, the inward radial relaxations due to the difference of the covalent radii between arsenic and host atoms, the covalent radii are 1.20, 1.36, 1.49, and 1.48 for As, Te, Hg, and Cd, respectively. On the other hand, the inward relaxation of the NN atoms around impurity is induced by the strong bonding mechanism between the arsenic and the host atoms, the detail will be discussed below. The relaxation also show that the As_{Te} impurity induce larger inward radial relaxations of the NN cations than that of the As_{Hg} . The results shown in Table 1 come from the calculations by using the PAW method with 64-atoms SC. In order to confirm the results of the FP-LAPW and PAW calculations on the supercell with 64 atoms, larger supercells have been used, such as supercells with 256 atoms and 512 atoms, respectively. The structural relaxations are conducted by using PAW method implemented in VASP. PAW calculations with 512-atoms supercells give the same relaxation trend of NN-atoms that of the 64 atoms SC calculations. The numerical results using two different methods both demonstrate the inward relaxations of NN-Te for $x=0.5$, as listed in Table 1. Larger radial relaxation of the PAW calculations comes from relatively small force criterion by comparison with that of FP-LAPW calculations. Considering the large calculated time consuming, full relaxation of atomic positions is used in PAW calculations, while symmetry constraint is applied in FP-LAPW calculations. Approximately linear relation-

ship between the inward relaxation of the NN atoms and the mole fractions of MCT is shown in Fig.1. But, the linear relationship is inversed for As_{Te} and As_{Hg} doping case. Namely, the inward relaxations of the NN atoms become smaller as the mole fractions become larger for As_{Hg} , and become larger as the mole fractions larger for As_{Te} doping case.

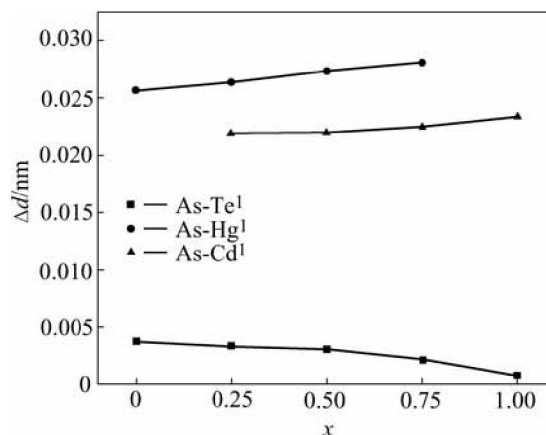


Fig.1 Relationship between inward radial relaxations of NN atoms and mole fraction of MCT

3.2 Bonding mechanism

In order to find out the reason of the NN atoms inward relaxation in MCT caused by arsenic impurity, the valence charge density and the bonding-charge density have been calculated. The bonding charge density is defined as the difference between the total charge density in the solid and the superpositions of neutral atomic charge densities placed at atomic sites, i.e.

$$\Delta\rho(r) = \rho_{\text{solid}}(r) - \sum_{\alpha} \rho_{\alpha}(r - r_{\alpha}) \quad (1)$$

Therefore, the bonding-charge density represents the net charge redistribution as atoms are brought together to form the crystal. The bond re-hybridization induced by the arsenic impurity also can be revealed clearly by the bonding charge density. The calculated valence charge density and the bonding charge density of $\text{Hg}_{0.5}\text{Cd}_{0.5}\text{Te}$ in the (110) plane, containing the arsenic impurity site are shown in the Figs.2 and 3. In which the dash lines mean the electrons move out relative to that of the atom superposition. From the Figs.2 and 3, we can see that the charge density distribution between the arsenic impurity and NN host atoms show the covalent characteristic either in the As_{Hg} or As_{Te} case. The valence charge density along the As-Te bond line in the case of As_{Hg} and As-Hg/Cd bond line in the case of As_{Te} have been picked up as shown in Figs.4 and 5. The figures indicate that As-Te bond and As-Hg/Cd bond are nearly perfect covalent bonds. Besides the smaller radius of arsenic than that of mercury and tellurium makes the NN

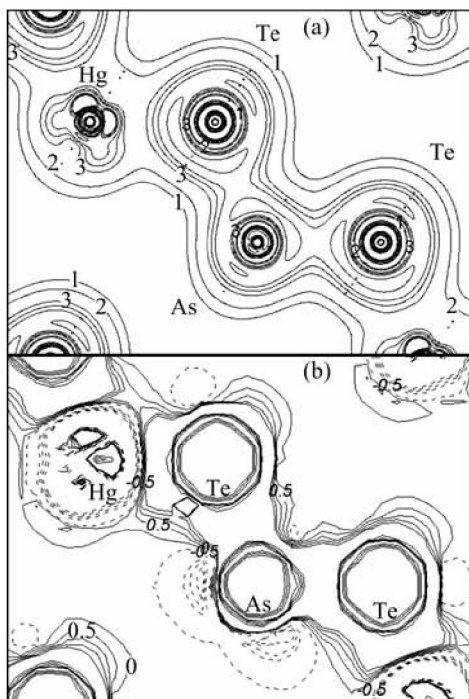


Fig.2 Total charge density bonding charge density in (110) plane for As_{Hg} (Contour step size is $6 \times 10^{-3} e/a.u.^3$ and $5 \times 10^{-3} e/a.u.^3$ for total charge density and bonding charge density, respectively.)

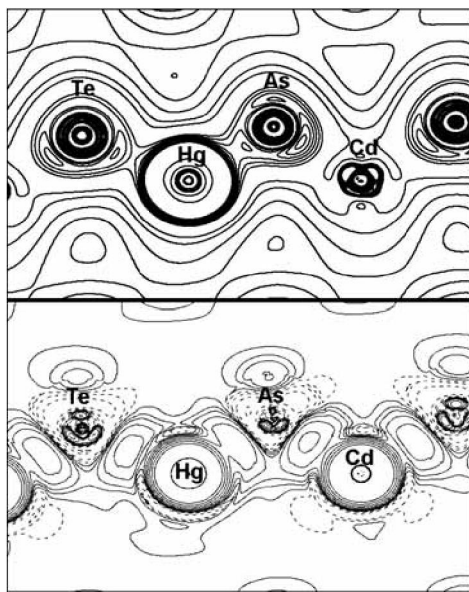


Fig.3 Total charge density bonding charge density in (110) plane for As_{Te} (Contour step size is $6 \times 10^{-3} e/a.u.^3$ and $5 \times 10^{-3} e/a.u.^3$ for total charge density and bonding charge density, respectively.)

tellurium inward relaxation, the stronger covalent bonding also results in NN host atoms inward relaxation. The bonding characteristics also give an explanation for the stably doping behavior of As in MCT.

To obtain a measure of the hybridization strength

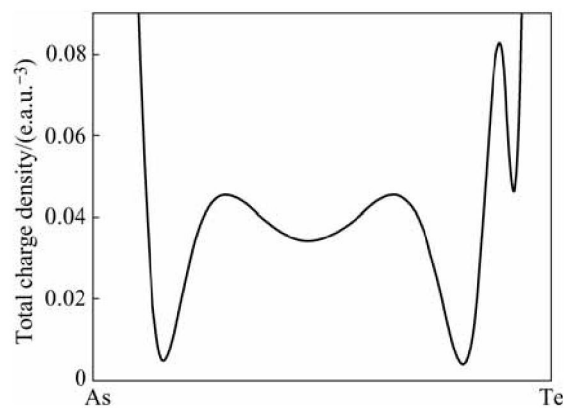


Fig.4 Total charge density along bond line of As-Te for case of As_{Hg}

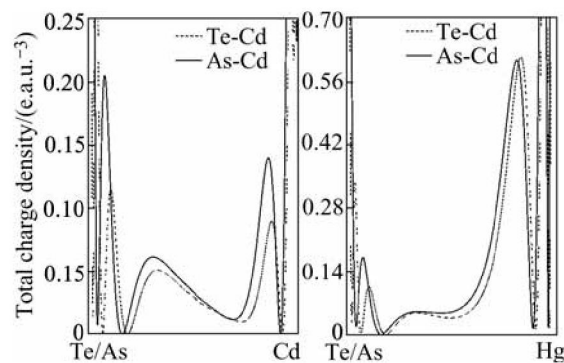


Fig.5 Total charge density along bond line of As-Hg/Cd for case of As_{Te} (Dash lines give charge density along Te-Hg/Cd bond line.)

between the orbital in the system, one can examine the density of states (DOS) and its partial density of states (p -DOS) which show how the “atomic” levels evolve into band states. The density of state (DOS) was calculated using the modified tetrahedron integration method and broadened using a Gaussian-like function with full width at half maximum (FWHM) equal to 0.1 eV. The total density of states (DOS) of un-doped and As_{Hg} - and As_{Te} -doped $Hg_{0.5}Cd_{0.5}Te$ are shown in Fig.6. Substitution of a mercury and tellurium by an arsenic atom makes the resulting system metallic because of one arsenic p state electrons fill up to the conduction band for As_{Te} doping and want of one valence electrons relative tellurium for As_{Te} doping. The Fermi level does not lie within the band gap, but it extends to conduction band and valence band for As_{Hg} and As_{Te} , respectively, as shown in Fig.6. The density of states (DOS) integrated from CBM to the Fermi level accommodates one electron in As_{Hg} doped material. And in As_{Hg} doped material the integration from Fermi level to the mid of band gap also accommodates one electron. The results mean that the impurity As_{Hg} and As_{Te} in $Hg_{0.5}Cd_{0.5}Te$ will behave as a single donor and a single acceptor,

respectively. The theoretical predications agree well with the experimental results[7,8].

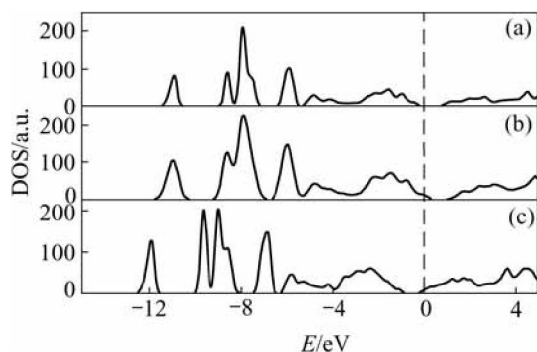


Fig.6 Total DOS of undoped-MCT-0.5(a), As_{Te}-MCT-0.5(b) and As_{Hg}-MCT-0.5(c) (Fermi level is set to zero)

For the case of charged neutral As_{Hg}, the defect center has total eleven electrons. Two of them occupy the a_1^V states, six of them occupy the t_2^V states and two of them occupy the a_1^C states which all locate in the valence band. The remaining one electron occupies the t_2^C which locates close to the conduction band as single donor. For the case of charged neutral As_{Te}, the defect center has total seven electrons. Two of them occupy the a_1^V states, five of them occupy the t_2^V states. One of unoccupied t_2^V state just above the VBM, behaves as single acceptor. The donor and acceptor levels for As_{Hg} and As_{Te} in MCT-0.5 determined by single-particle energy state are 19 meV above the VBM and 60 meV below the CBM which agree well with the experimental results[11].

4 Conclusions

The relaxations induced by the in-situ arsenic impurity have been given by combining FP-LAPW and PAW method. Both calculations give the same inward relaxation around the impurity. Through analysis of the charge density, nearly perfect covalent bond has been found between the impurity and host atoms. The bond characteristics between impurity and host atoms give the explanations for the stable doping behavior of arsenic in MCT. In the same time, the amphoteric behavior of arsenic impurity in MCT has been shown in the present paper.

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