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# Compensation mechanism for As donor in $Hg_{1-x}Cd_xTe$: The case of $As_{Hg}$–$V_{Hg}$ pair

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ABSTRACT

Using first-principles method we studied the compensation mechanism of As donor in $Hg_{1-x}Cd_x$ Te based on the model Berding et al. (1998, 1999) [1] of $As_{Hg}$–$V_{Hg}$ pair. We show that the binding of $As_{Hg}$ and $V_{Hg}$ results from donor-acceptor coupling, and the compensation of As donor can be clearly explained in terms of electronic deactivation by $V_{Hg}$. The pairing physics derived from this study confirm the available theoretical and experimental results.

## 1. Introduction

In $Hg_{1-x}Cd_xTe$-based infrared technology, arsenic (As) doped epitaxial layers grown by molecular beam epitaxy (MBE) are of special concern, as they are currently the most desirable choice for $p$ side of junction with well-controlled doping levels and profiles [2]. However, the doping process is complicated by the amphoteric behavior of As and the low-temperature, Te-rich growth mode of MBE [3]. For this reason, there are some unresolved issues to be addressed regarding the *in situ* As doping in MBE. The most challenging one is about the character of As impurity states in as-grown $Hg_{1-x}Cd_xTe$. As incorporated during the growth process has been found behaving as a highly compensated donor in as-grown MBE $Hg_{1-x}Cd_xTe$. Although this electrical compensation has been confirmed by several groups [4–6], experimental evidence is still lack as to the nature of the compensation and even the presence of the inactive, non-precipitated As, mainly because neutral and compensating defects are difficult to be measured electronically or optically. Fortunately, theoretical work has shed light upon the microscopic mechanism of the compensation of As donor in $Hg_{1-x}Cd_xTe$, and it is widely accepted the model [1] well established by Berding et al.

The model proposed by Berding et al. is derived from statistical thermodynamic theory and assumption that because of the typical Te-rich condition of MBE growth, As atoms are initially incorporated on Hg site ($As_{Hg}$), with each As atom inducing a vacancy on a neighboring Hg site ($V_{Hg}$) that compensates the As donor. Most of recent experiments (Hall measurements) [5–7] qualitatively favor the compensation mechanism induced by the $As_{Hg}$–$V_{Hg}$ pair, where $As_{Hg}$ is believed to give a deep donor level by forming a complex with $V_{Hg}$. In spite of this, little has been reported so far on experimental determination of this deep donor level, except for recent optical observations [8,9] by Yue et al., who found a deep level at $E_V + 34.0$ meV and ascribed it to the transition related to the $As_{Hg}$–$V_{Hg}$ pair. To identify the observed deep level necessitates further theoretical investigations on the nature of $As_{Hg}$–$V_{Hg}$ defect level. In addition, Berding et al. proposed [1] that the transfer of As from Hg to Te sublattice (the essential step in activation annealing) starts from the $As_{Hg}$–$V_{Hg}$ pair. Thus, a close examination of the $As_{Hg}$–$V_{Hg}$ pair is also necessary for modifying the activation annealing strategy.

In our previous work [10,11] we have studied the electronic structure of isolated $As_{Hg}$ and $V_{Hg}$ point defects. In this Letter, we will show that the pairing of $As_{Hg}$ and $V_{Hg}$ is energetically favored, and the underlying compensation mechanism in As-doped $Hg_{1-x}Cd_xTe$ is associated with the coupling of the $As_{Hg}$ and $V_{Hg}$ defect states.

## 2. Details of the calculations

The present calculations were performed within the general-gradient approximation (GGA) as implemented by the plane-wave total energy VASP code [12]. The technologically important $Hg_{1-x}Cd_xTe$ ($x = 0.25$) alloy was chosen as the host system. The cation $d$ electrons were treated as valence states [13] with the Vanderbilt ultrasoft pseudopotentials [14]. The corresponding pseudopotentials were checked with plane-wave cutoff up to 400 eV, at which the calculated lattice constant and cohesive energy of bulk $Hg_{0.75}Cd_{0.25}Te$ was 6.667 Å and 3.99 eV/molecule, respectively, in agreement with the experimental values of 6.466 Å [15] and 3.53 eV/molecule [16]. For defect calculations we used a 216-atom supercell and $2^3$ Monkhorst–Pack mesh for Brillouin zone integrations. All internal coordinates were fully relaxed un-

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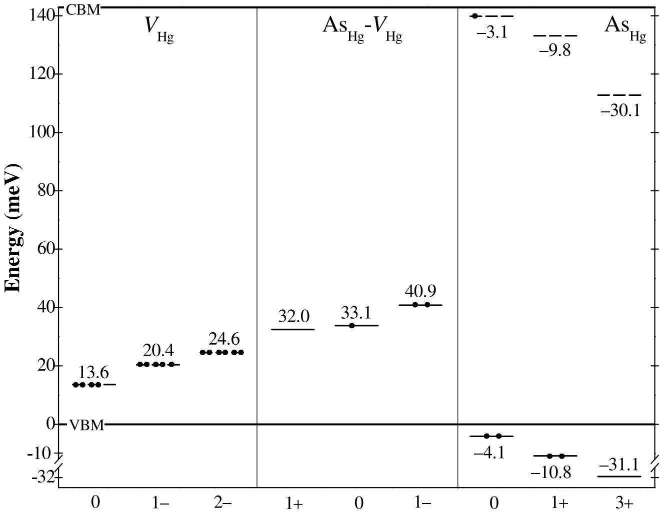

**Fig. 1.** Calculated single electron energy states for $V_{Hg}$, $As_{Hg}$, and $As_{Hg}$–$V_{Hg}$ pair in various charge states. The gap-state levels are measured from the VBM for $V_{Hg}$ and $As_{Hg}$–$V_{Hg}$ pair, and from the CBM for $As_{Hg}$, respectively. The solid dots depict the occupation of each defect state.

til the Hellmann–Feynman forces were less than 0.02 eV/Å. For charged defects, a jellium background charge was applied. We estimated with 512-atom supercell calculations, and the error in the band dispersions was within ±0.2 eV.

## 3. Results and discussion

### 3.1. Isolated point defects

Motivated by Berding's suggestion that $As_{Hg}$ tends to pair with its neighboring $V_{Hg}$, forming a $As_{Hg}$–$V_{Hg}$ diffusion pair, we calculated the $As_{Hg}$–$V_{Hg}$ complex binding energy defined as

$$E_b = E_{tot}(As_{Hg} - V_{Hg}) + E_{tot}(Hg_{0.75}Cd_{0.25}Te) - E_{tot}(As_{Hg}) - E_{tot}(V_{Hg}),$$

where $E_{tot}$ is the total energy calculated using the same supercell at the neutral state. The calculated binding energy is −1.27 eV, indicating that the pairing of $As_{Hg}$ and $V_{Hg}$ is favorable in energy with respect to the isolated point defects. To understand the origin of the strong binding of the $As_{Hg}$–$V_{Hg}$ pair, we first discuss the electronic properties of the isolated point defects.

Fig. 1 shows the single electron defect levels determined at $\Gamma$ point and aligned by core potential of the defect cell with the defect-free cell [17]. For the neutral $V_{Hg}$, the defect level is quite shallow, at about 13.6 meV above the VBM. Such a shallow level can be understood as follows: Due to the large Hg–Te bond length, and thus the weak coupling of Hg *p* with Te *p* orbitals [18], removing Hg and its *p* orbital causes a small perturbation at the VBM. Again, the VBM consists of mostly Te *p* orbital (with exceeding 70% character), so the absence of Hg *p* orbital doesn't affect the VBM' properties except for a small perturbation. For example, when two valence electrons of Hg are removed from the VBM, the partially occupied $t_2{}^{v}$ state moves upward in energy, forming a double acceptor level above the VBM, but the $V_{Hg}$ level remains the $t_2{}^{v}$ representation. The neutral $V_{Hg}$ is unstable against the formation of non-degenerate spin states because the threefold degenerated $t_2{}^{v}$ level is not fully occupied. According to our calculations, the electronic structure of $V_{Hg}$ derives from the four dangling bonds around vacancy, and the dangling bonds are strongly localized on the Te sites. The weak overlap of these dangling bonds and consequently significant correlation effects prefers to the formation of the multiplet states. When these states are filled by an increasing number of trapped electrons, the $V_{Hg}$ becomes increasingly stable, whereby the vacancy can adopt charge states −1 and −2. The behavior of $V_{Hg}$ defect state is consistent with the general chemical trend for cation vacancy dopant in II–VI semiconductors [19,20].

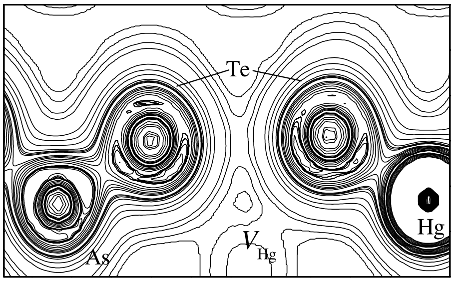

**Fig. 2.** Contour plot of total valence charge density on a plane passing the Te atom, the As atom, and the Hg vacancy for neutral $As_{Hg}$–$V_{Hg}$ pair.

For neutral $As_{Hg}$ with $T_d$ symmetry (i.e., in unrelaxed structure), As adopts $sp^3$ coordination, whereupon its extra three valence electrons (associated with As 4*p* orbitals) are tightly bound to the states created from the conduction band: two of them fully occupy the $a_1{}^{c}$ level and the remaining one occupies the higher $t_2{}^{c}$ level. Because the As 4*s* orbitals are higher in energy than the Hg 6*s* orbitals, the $As_{Hg}$ donor level is expected to be shallow. Our calculations show that the $a_1{}^{c}$ level moves deep into the valence band whereas the $t_2{}^{c}$ level indeed lies slightly above the CBM. However, the occupation of the $t_2{}^{c}$ level with a single electron will destabilized this level through a strong electron-phonon interaction [21]. Thus Jahn–Teller distortion around $As_{Hg}$ site is induced upon relaxation, which lowers the symmetry to $C_{3v}$. By the $C_{3v}$ symmetry the $t_2{}^{c}$ level splits into a single occupied $a_1$ level below the CBM and an empty *e* level above the CBM.

The $a_1$ level is fairly shallow, located 3.1 meV below the CBM, which thus suggests that $As_{Hg}$ could be a desired *n*-type dopant. Unfortunately, the unpaired electron at the $a_1$ level is rather delocalized and easily be bound by some trap center, whereby a deactivation of As donor occurs. Actually, the $T_d$ to $C_{3v}$ distortion causes large local tensile strain around $As_{Hg}$ site, which promotes the outward movement of the nearest-neighbor (NN) Te atoms. The $V_{Hg}$ is a natural candidate to release the tensile strain, regarding its remarkably high concentration in MBE as-grown $Hg_{1-x}Cd_xTe$. The open space by an adjacent $V_{Hg}$ leaves the 1NN Te move away from the As atom. In this way, the binding of $As_{Hg}$ and $V_{Hg}$ leads to large strain reduction and large binding energy. The binding energy of $As_{Hg}{}^{0}$–$V_{Hg}{}^{-}$ is thus expected to be much larger than that of $As_{Hg}{}^{+}$–$V_{Hg}{}^{0}$. Our calculations show that indeed, the binding energy between $As_{Hg}{}^{0}$ and $V_{Hg}{}^{-}$ is −1.29 eV, while when the $a_1$ level is unoccupied, and then the $T_d$ to $C_{3v}$ distortion is absent, the binding energy of $As_{Hg}{}^{+}$ and $V_{Hg}{}^{0}$ is reduced to −0.56 eV.

### 3.2. The pairing physics of $As_{Hg}$–$V_{Hg}$ complex

Now we turn to the interaction between the isolated $As_{Hg}$ and $V_{Hg}$ in forming the $As_{Hg}$–$V_{Hg}$ complex. As can be seen in Fig. 2, the wave function of the neutral $As_{Hg}$–$V_{Hg}$ pair clearly exhibits charge flow from the As atom into the vacancy site, indicating the bonding character mixed into the $V_{Hg}$ acceptor state; at the same time, the wave function exhibits depletion of charge around the As site, indicating the antibonding combination with the $As_{Hg}$ donor state. Therefore, the pairing of $As_{Hg}$ and $V_{Hg}$ is not through Coulomb interaction and thus the neutral configure should be thought of as $As_{Hg}{}^{0}$–$V_{Hg}{}^{0}$ rather than $As_{Hg}{}^{+}$–$V_{Hg}{}^{-}$.

For the neutral $As_{Hg}$–$V_{Hg}$ pair, the interaction between $As_{Hg}{}^{0}$ and $V_{Hg}{}^{0}$ can be understood from the fact that the donor and acceptor levels have the same atomic character (i.e., both consist of