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Strain effect on the diffusion of interstitial Mn in GaAs

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Abstract
The influence of external strain on the diffusion barriers of interstitial Mn in GaAs is studied using the first-principles calculations within the density functional theory. The diffusion barrier changes with strain in different manners: linear on the tensile strain and nonlinear on compressive strain, in contrast to the linear behavior of the continuum elastic model. The discrepancy between the continuum elastic model and the results of the first-principles method is attributed to the energy-level crossing caused by strain. Moreover, we find that the external strain can not only effectively change the diffusion barrier (even to zero, at certain strain), but also the position of saddle points along the migration path. Our finding provides an alternative way to reduce the population of interstitial Mn in GaAs, thus correspondingly to increase the Curie temperature of this system.

(Some figures may appear in colour only in the online journal)

1. Introduction

The discovery of III–V diluted magnetic semiconductors (DMS) has attracted significant technical and scientific interest during the last decade because of their large potential for the development of spintronic devices [1–3]. Mn-doped GaAs is one of the most promising candidates for an all-semiconductor spintronic device due to its relatively high Curie temperature T_c [4, 5]. Significant efforts have been put into the investigation of the mechanism of the ferromagnetism in Mn-doped GaAs, in the hope of finding ways to raise the T_c [6–9] to above room temperature. However, the measured Curie temperature is still too low for realistic applications. Extensive theoretical and experimental studies on Mn-doped GaAs indicate that the Curie temperature depends sensitively on the doping sites of the magnetic atoms, i.e. the substitutional or interstitial site [10–12]. Interstitial Mn atoms in GaAs would decrease T_c by acting as double donors and compensating the holes provided by the substitutional Mn atoms that induce the ferromagnetism. Therefore, it would be ideal to increase the substitutional Mn and reduce the interstitial Mn concentration in GaAs. To achieve high Curie temperature, besides growing the sample at, for example, Ga-poor conditions, other approaches have also been proposed. For example, the percentage of substitutional doping can be increased by co-doping with interstitial Li atoms during the crystal growth, which has been demonstrated from first-principles calculations recently by Bergqvist and co-workers [13]. Chen *et al* demonstrated that a Curie temperature as high as 200 K can be obtained by patterning a heavily Mn-doped (Ga, Mn) As thin film into nanostructures [14]. Patterning the (Ga, Mn) As film into nanowires increases the free surface and allows the Mn interstitials to diffuse out at the sidewalls, thus enhancing the efficiency of annealing [14].

The diffusion mechanisms of Mn impurities in GaAs have been studied extensively. For example, using atomistic modeling based on a first-principles approach, Raebiger *et al* and Hynninen *et al* had calculated the diffusion barrier of substitutional Mn in GaAs [15, 16]. Baykov *et al* had shown

that the diffusion barriers of an interstitial Mn impurity in the neutral and singly charged states are much lower than that in the doubly charged state [17], and the activation energy for interstitial Mn diffusion is within the range 0.55–0.95 eV.

Applying strain is a common approach in semiconductor technology to control the doping behavior. Zhang *et al* had shown that an applied pressure can stabilize the substitutional position of transition metal impurities in Si [18]. Shu *et al* showed that the effect of strain on surface diffusion is inherently correlated with the intrinsic surface stress induced by the adatom along its diffusion pathways [19]. Many first-principles studies had also been performed to investigate the effect of strain on surface diffusion. It is natural to expect that the diffusion of interstitial Mn can also be tuned by external stress. If the diffusion barrier of the interstitial Mn atom in GaAs is low enough, then it could be diffused out by an annealing treatment and thus the T_C of the system could be increased.

In this paper, we have calculated the diffusion barriers for interstitial Mn in GaAs using first-principles calculations. We find that the diffusion barrier of interstitial Mn depends sensitively on the applied strain. The linear dependence of the diffusion barriers on the tensile strain is observed. In contrast, under the compressive strain the linear dependence breaks down, which is found to be closely related to a band crossing [20].

The remainder of this paper is organized as follows. section 2 presents computational details, and the results are subsequently discussed in section 3. The conclusions drawn from this work are summarized in section 4.

2. Computational method

The first-principles calculations are carried out using Vienna *ab initio* simulation package (VASP) [21], based on the density functional theory with the projector augmented wave (PAW) pseudopotential [22] and the generalized gradient approximation (PBE-GGA) [23] to the exchange–correlation functional. For Mn-doped GaAs, GGA has been widely used in the past and the results are reasonable compared with experiments. The energy cutoff for the plane-wave basis functions is chosen to be 400 eV for all the calculations. The convergence test shows the change in energy per atom is less than 1 meV by increasing cutoff to 600 eV. The same cutoff was adopted in previous studies for Mn-doped GaAs systems [17, 24]. For pure zinc blende GaAs, the optimized lattice constant is 5.75 Å, which is in excellent agreement with the previous studies [25, 26].

A $(2 \times 2 \times 2)$ cubic supercell containing 32 Ga and 32 As host atoms is adopted for all the calculations (including the calculation for pure GaAs system and those with interstitial Mn). A reciprocal space k-point mesh of $4 \times 4 \times 4$ is employed. This k-point mesh is widely used in previous studies and the convergence test has shown that increasing the k-point mesh from $2 \times 2 \times 2$ to $4 \times 4 \times 4$ changed the formation energies by 20 meV [24]. The interatomic positions are allowed to relax until the atomic forces were smaller than 10^{-2} eV Å^{-1}.

The diffusion barrier of Mn in GaAs is calculated under external uniaxial strain (ϵ_{uni}), biaxial strain (ϵ_{bi}) and triaxial strain (ϵ_{tri}). Two interstitial sites are considered, i.e. the Ga-coordinated site (I:Ga) surrounded by four Ga atoms and the As-coordinated site (I:As) surrounded by four As atoms [27]. The diffusion path is from I:Ga to I:As, described as in [17].

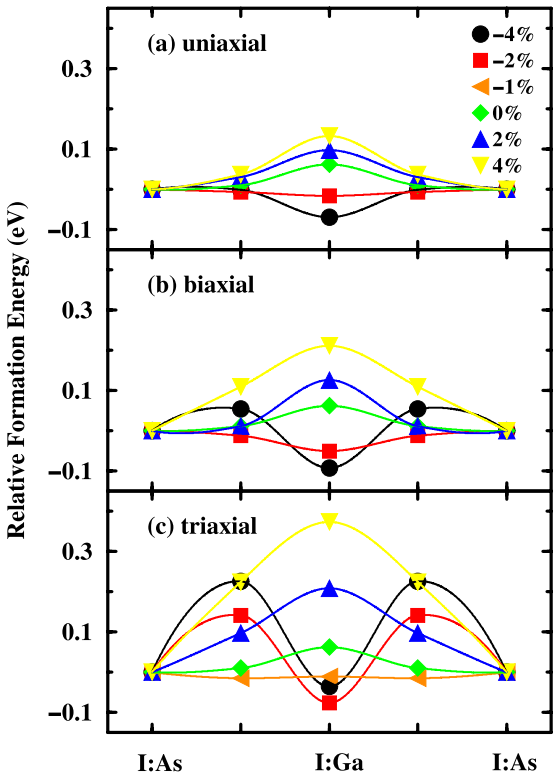

Figure 1. The relative formation energy of interstitial Mn along I:As–I:Ga–I:As path. Here the energy is referenced to that for Mn at I:As. (a) Uniaxial strain; (b) biaxial strain and (c) triaxial strain. The numbers in the figure are the strain.

3. Results and discussion

In figure 1, the formation energy of Mn along the migration path from I:As to I:Ga is plotted, where the energy is referenced to that for Mn at I:As. First, at $\epsilon = 0$, we find that the diffusion barrier is small, which is in good agreement with previous calculations [17]. Second, the effect of strain on the site preference is quite significant, and we can see obvious differences in the diffusion barrier under compressive and tensile strain. Our calculations show that the site preference of Mn can be changed by applying external strain. At zero strain, the I:As site has a lower energy than the I:Ga site due to a stronger Coulomb interaction. The energy difference increases under tensile strain ($\epsilon > 0$), so does the height of diffusion barrier. On the other hand, under compressive strain the energy difference decreases and even reverses the sign due to the relatively large open space at the I:Ga site. The saddle point shifts to an intermediate position. Interestingly, we find that the diffusion barrier almost disappears when the triaxial strain is around -0.01 (figure 1(c)). The diffusion barrier is also close to zero as the uniaxial or biaxial strain takes a certain value between $\epsilon = 0.0$ and -0.02. Therefore, the migration between these two sites appears much like kinetic

processes, i.e. Mn atoms swap relatively easily between two nearest-neighbor interstitial sites.

The change of diffusion barriers under external strain is shown in figure 2. There are several important and interesting observations. First, the influence of strain on diffusion is obvious in all three cases. At $\epsilon = 4\%$, the triaxial tensile strain can change the energy barrier as high as 380 meV (figure 2(c)). Second, the effect of strain on the diffusion barrier is nearly additive, i.e. $\Delta E_{\rm tri} \simeq 3\Delta E_{\rm uni} \simeq \Delta E_{\rm uni} + \Delta E_{\rm bi}$, where $\Delta E_{\rm tri}$, $\Delta E_{\rm uni}$ and $\Delta E_{\rm bi}$ are the change of diffusion barrier related to the value at zero strain, under triaxial, uniaxial and biaxial strain, respectively. To demonstrate the additivity, we have summed the changes of diffusion barrier (shown in figure 2(c) by open circles) under the uniaxial (figure 2(a)) and biaxial strains (figure 2(b)). It is clear that the change of diffusion barriers under triaxial strain (solid circles) agrees very well with the summation. Such additivity of the strain indicates that it is mainly contributed by the volume changes due to the strains. It also suggests that the diffusion barrier can be manipulated by applying only the uniaxial or biaxial strain, which might be easier to be realized experimentally [28]. Third, the diffusion barrier does not always exhibit a linear dependence on the external strain. Under tensile strain, the diffusion barrier exhibits a perfect linear behavior. However, the diffusion barrier has evidently nonlinear character under compressive strain.

Previous studies based on the continuum elastic model have shown that the diffusion barrier is a linear function of strain [19, 28–30]. In this model, it is assumed that the dopant induces a stress on the host crystal. When an external strain is applied, the diffusion barrier of the dopant, ΔE, as a function of strain can be written as

$$\Delta E = \Delta E_0 + V_0 \Delta P \epsilon \qquad (1)$$

where ΔE_0 is the energy barrier without strain and ΔP is the pressure difference of the intrinsic stress induced by the dopant at the saddle and minimum point. A similar relation between ΔE and external stress had also been proposed [30]. Some studies have found that the diffusion barrier can be well described by the elastic model, namely the predictions of the continuum elastic model are consistent with first-principles calculations [19, 28–30]. Some other works also suggest the elastic models may be questionable under certain conditions [31, 32]. Our studies show that, for tensile strain, the first-principles calculations are in good agreement with the prediction of equation (1) (dashed lines in figure 2), while the linear relationship fails under compressive strain. Recently, based on the quantum mechanical analysis, we have shown that, if the strain changes the occupation number of electrons on the levels, the continuum elastic model would fail [20]. In our theoretical model, the coefficient of the linear term $V_0\Delta P$ is proportional to the volume difference $\delta V_{\rm D} = V_{\rm D} - V_0$ [20]. It originates from the size difference between the dopant and the host elements. Under certain strains, electrons may jump from one level to another level with very different atomic wavefunction characters, thus causing nonlinear behavior in equation (1). This behavior usually happens when the defect level has a different origin

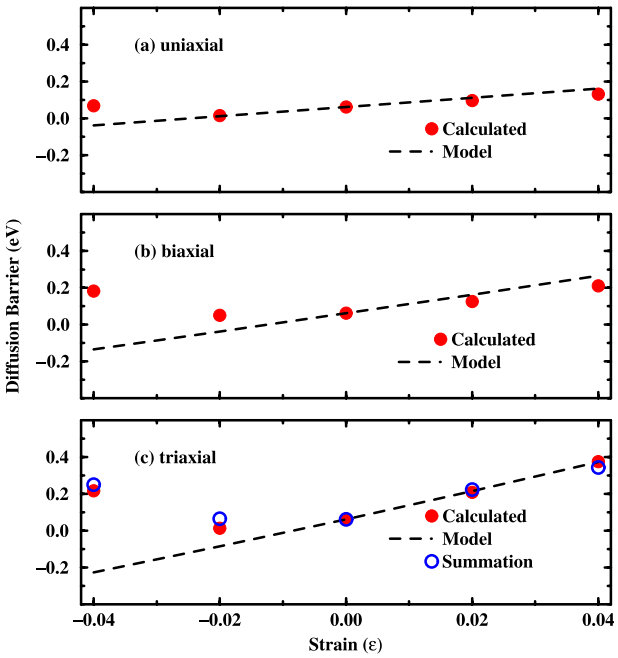

Figure 2. The diffusion barriers for an interstitial Mn in GaAs as functions of the (a) uniaxial strain, (b) biaxial strain and (c) triaxial strain. Filled circle: the first-principles results; dashed line: the predictions of equation (1); open circle: the energy barriers predicated by the additive relations (see text).

compared to the host energy level, e.g. the d orbital levels of a transition metal dopant are located close to the conduction band minimum (CBM) of a conventional semiconductor. If the charge transfers gradually, then there will be a graded transition region where the slope changes.

The breakdown of a linear relationship under compressive strain can be understood as follows. The interstitial Mn acts as a donor, generating two electrons at the donor level (with As 4s and Ga 4s characters) near the CBM. The Mn spin minority d band is slightly higher than the donor level, so it is unoccupied when there is no strain. Therefore, at equilibrium lattice constant, interstitial Mn has high spin $d^{\uparrow 5} + 2e$ configuration. When a compressive strain is applied, the CBM and the donor level shift upwards in energy. If the strain is small, the diffusion barrier can be written as $\Delta E = \Delta E_0 + V_0 \Delta P \epsilon$, i.e. the linear relationship is valid. However, with the increasing compressive strain, the CBM shifts further upwards, even above the Mn spin minority d band. In this case, the electrons transfer from the derived donor level to the Mn spin minority d band, and the linearity breaks down. As shown in figure 2(a), the calculated values follow the linear relationship till the compressive strain up to 2% of $\epsilon_{\rm uni}$. Figures 2(b) and (c) show the same trends under large compressive strain of $\epsilon_{\rm bi}$ or $\epsilon_{\rm tri}$.

Under tensile strain, the CBM as well as the donor level shifts downwards, so there is no electron transfer from the CBM or the donor level to the Mn spin minority d band. In this case, the barrier depends linearly on the expansive strain, as shown in figure 2. The theoretical predictions, using the values of E_0 and ΔP obtained from the unstrained

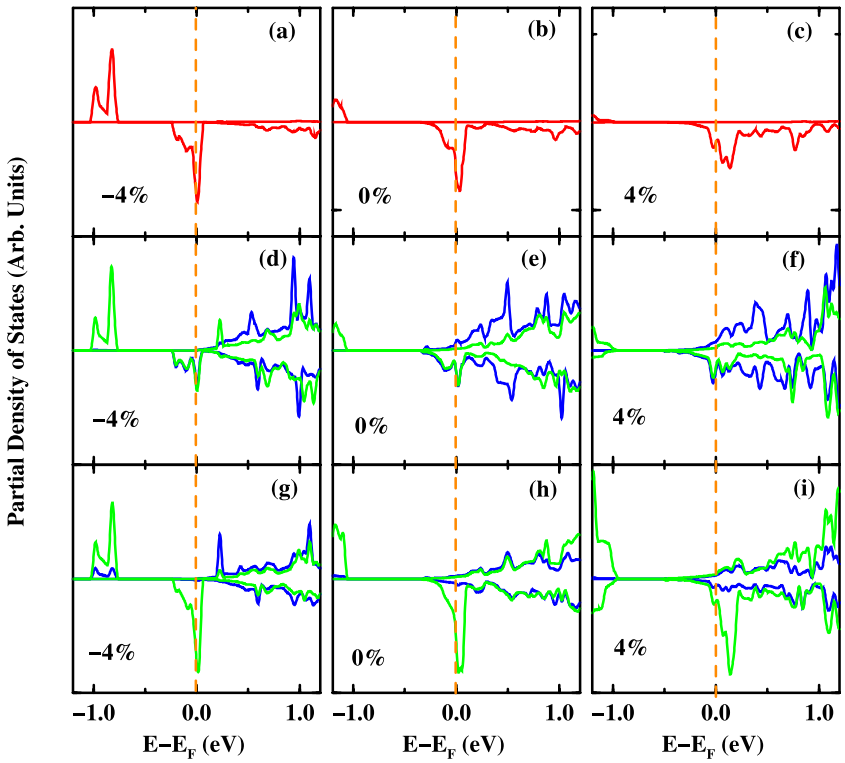

Figure 3. The spin-up and spin-down PDOS for neutral Mn on I:Ga site under triaxial strain. From left to right, they are the system at ϵ equal to −0.04, 0 and 0.04, respectively. Upper panel: Mn 3d states; middle panel: Ga s state (blue lines) and Ga p state (green lines); bottom panel: As s state (blue lines) and As p state (green lines). The vertical dashed lines in the figures indicate the Fermi level.

calculations (dashed lines), are in good agreement with our GGA calculations (filled circles).

To see these more specifically, we have presented the partial density of states (PDOS) of the Mn-doped GaAs for three different triaxial strains ($\epsilon = -0.04$, 0.00 and 0.04) in figure 3. It can be seen that, when a compressive triaxial strain ($\epsilon = -0.04$) is applied, the CBM, as well as the derived donor level, shifts upwards relative to the Mn spin minority d band and electrons transfer from the CBM to the Mn spin minority d band, so the electron configuration of the Mn dopant changes gradually from $d^{\uparrow 5}$ to $d^{\uparrow 5}d^{\downarrow 2}$ (see figures 3(a), (d) and (g)). In contrast, under the expansive strain ($\epsilon = 0.04$, see figures 3(c), (f) and (i)), the CBM shifts downwards relative to the Mn spin minority d band, so no electron transfers from the CBM to the Mn spin minority d band and the order of the occupied energy level does not change. This explains why the linear relationship between the diffusion barriers and strain is kept.

Our discussions above show that the site preference and diffusion barrier of the interstitial Mn in GaAs depends sensitively on the applied strain and does not follow the simple linear relation under external strain. This is because the Mn atom has two electrons near the CBM, and when the strain changes the occupation number of electrons on the level, the linear relation fails. In other words, if no change in the occupation number of electrons occurs, the site preference may not be sensitive to strain and the diffusion barriers will depend linearly on the strain. To further check this role played by the electronic occupation, we have performed a similar calculation by removing two electrons from Mn to make the system doubly charged [24]. In this case, when $\epsilon = 0.00$, there is a gap between the occupied and unoccupied states. Because no extra electron is located close to the CBM, the strain does not change the occupation of the electronic states. According to the above discussion, for the doubly charged system, the linear dependence of the diffusion barrier on the strain will be obeyed not only under tensile strain, but also under compressive strain. In other words, the continuum elastic model works for both kinds of strain.

Figure 4(a) shows the relative binding energy (left panel) of interstitial Mn along the I:As–I:Ga–I:As path and the diffusion barrier (right panel) of Mn in the doubly charged state as a function of the triaxial strains, which is indeed different from that in the neutral state (figure 1(c)). In figure 4(a), all the minima and saddle points are located at the As-coordinated and the intermediate positions, respectively. Under zero strain, the diffusion barrier in the doubly charged state is much higher than that in the neutral state, which is due to increased Coulomb interaction at the saddle point. Our results are consistent with the previous calculations [17]. Meanwhile, unlike the behavior in the neutral state, the diffusion barrier increases with increasing compressive strain and follows approximately the linear relation of equation (1), i.e. $\Delta E = \Delta E_0 + V_0 \Delta P \epsilon$, as shown in figure 4(b). In figure 4(b), we show the confirmation of our theory by taking the values of ΔE_0 and ΔP from the calculations of the unstrained system (dashed line), and the results from strained calculations (filled circles).

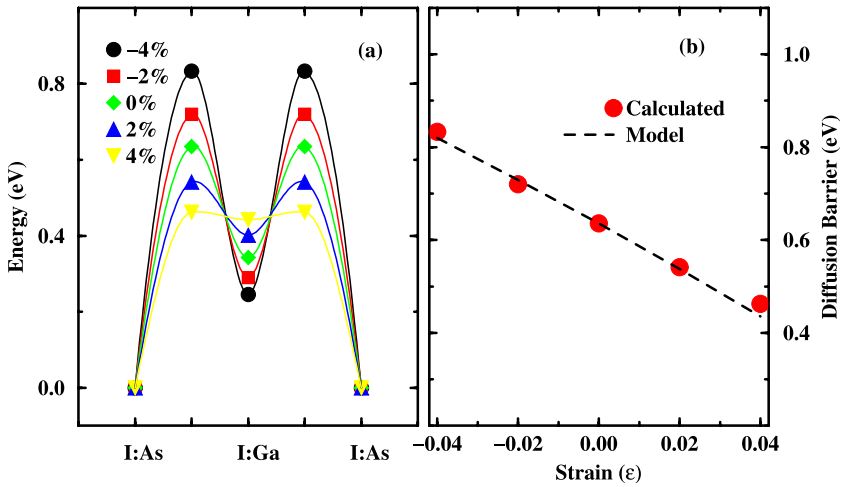

Figure 4. The relative formation energy of interstitial Mn along I:As–I:Ga–I:As path (left panel) and the diffusion barrier (right panel) as a function of triaxial strain for the +2 charged Mn interstitial. The per cent numbers in the left panel are the strain.

4. Conclusions

The strain influence on the diffusion of interstitial Mn in GaAs is analyzed by applying the first-principles calculations and elastic model. It is found that the shape of migration energies strongly depends on strain: the minimum and saddle-point positions change significantly with increasing external strain. The migration barrier is very low when the triaxial strain is close to −0.01. Our first-principles calculations demonstrate that the diffusion barrier is a nonlinear function of the applied strain, if the occupation number of electrons on the level has changed. We also show that the diffusion barrier can be tuned by changing the charge state of the dopant. We believe that our finding of tuning the diffusion barrier through strain can be very useful in controlling the diffusion of Mn in GaAs and, in general, diffusion of dopants in semiconductors.

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