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Grown-in beryllium diffusion in indium gallium arsenide: An *ab initio*, continuum theory and kinetic Monte Carlo study

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ABSTRACT

A roadblock in utilizing InGaAs for scaled-down electronic devices is its anomalous dopant diffusion behavior; specifically, existing models are not able to explain available experimental data on beryllium diffusion consistently. In this paper, we propose a more comprehensive model, taking self-interstitial migration and Be interaction with Ga and In into account. Density functional theory (DFT) calculations are first used to calculate the energy parameters and charge states of possible diffusion mechanisms. Based on the DFT results, continuum modeling and kinetic Monte Carlo simulations are then performed. The model is able to reproduce experimental Be concentration profiles. Our results suggest that the Frank-Turnbull mechanism is not likely, instead, kick-out reactions are the dominant mechanism. Due to a large reaction energy difference, the Ga interstitial and the In interstitial play different roles in the kick-out reactions, contrary to what is usually assumed. The DFT calculations also suggest that the influence of As on Be diffusion may not be negligible.

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1. Introduction

There is significant research interest in InGaAs as a promising candidate for future generation CMOS (complementary metal-oxide semiconductor) devices (specifically, for very advanced technologies e.g. 5 nm node and below) due to its considerably higher electron mobility compared to silicon. The high electron mobility and a lattice constant that matches with InP make $In_{0.53}Ga_{0.47}As$ an ideal candidate for such devices [1]. Beryllium has been considered to be an important and attractive p-type dopant due to a high activation ratio and the existence of well-developed and controllable doping methods [2]. However, Be diffusion in InGaAs is extremely fast, with a diffusivity five orders of magnitude larger than in GaAs at the same temperature [3]. Therefore, much effort has been devoted to investigate and understand the Be diffusion behavior, including experiments and simulations. Nevertheless, many questions are still unresolved. In particular, there is still no

agreement on the mechanism and particles' charge states for Be diffusion in InGaAs [4—6].

The mechanism that governs Be diffusion was widely assumed to be the kick-out mechanism ($Be_{III} + I_{III} \rightleftharpoons Be_i$) [2,5]. Be_{III} denotes a Be atom in a group-III sublattice position that is considered to be immobile while Be_i is a Be atom in an interstitial position that has a high mobility; I_{III} represents Ga and In interstitials. Usually, local thermodynamic equilibrium of the diffusion process is also assumed. With this model assumption, some works were able to match experimental data. However, further clarifications about these works need to be made: (i) samples grown under similar conditions have quite different diffusion parameters in these models; (ii) although the local thermodynamic equilibrium assumption makes the model simple and tractable, it is not a very reasonable one, considering that Be diffusion is very fast; (iii) the parameters used in these models, such as the reaction energy and diffusion parameters, are not extracted from or validated by other independent self-diffusion and in-diffusion experiments or *ab initio* calculations, but are merely fitting parameters, making these models less predictive; and (iv) these models treated In and Ga as effectively the same kind of atom and assumed that As is not involved in Be diffusion. Such assumptions are not intuitive.

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Some modified models have been proposed in order to overcome the above limitations [6]. Recently, Koumetz et al. proposed a combined diffusion mechanism, which removes the local thermodynamic equilibrium assumption and also takes the Frank-Turnbull (dissociative) mechanism ($Be_i + V_{III} \rightleftharpoons Be_{III}$) into account, in which V_{III} represents Ga and In vacancies, to explain the experimental data. Their simulation results suggested that the temperature dependence of group-III self-interstitial and of group-III vacancy effective diffusion coefficients are different. Specifically, for temperatures above 780 °C, group-III interstitial diffusion dominates the group-III vacancy diffusion, while below 780 °C the situation is reversed. Even though this model dispenses with the local thermodynamical equilibrium assumption and is more realistic than previous models that only considered the kick-out mechanism, it remains a purely phenomenological model: the choice of the mechanism and parameters is only based on fitting.

A number of authors have also proposed different charge states for the diffusion mechanism: specifically, the charge states of +1, +2 for Ga and In self-interstitials, 0, −1 for Ga and In vacancies, 0, +1 for Be interstitial and −1 for Be substitutional were proposed [4–16]. These charge states are either inferred from works on GaAs or chosen to fit experiments. Some of these proposed charge states are also counter-intuitive. For example, it is known that p dopants in group IV semiconductors such as Mg interstitials in Si are positively charged, and thus a similar charge state should be expected for Be [17]. This discrepancy provides the motivation for an independent *ab initio* determination of the charge state of Be in the InGaAs system, which we will describe in Section 3.3. A realistic model should explain experimental data obtained under different annealing conditions in one consistent way and based on as few assumptions as possible. To the best of our knowledge, such a model is still lacking.

In this work, a more comprehensive and physically-based model of diffusion behavior of grown-in Be in InGaAs is presented. To select possible mechanisms for Be diffusion, we calculated the reaction energies and diffusion barriers of a variety of possible mechanisms using density functional theory. The results suggest that the energies required for the Frank-Turnbull mechanism are much higher than for the kick-out mechanism, and so in the temperature range relevant to experiments, the Frank-Turnbull mechanism can be safely ignored. Furthermore, among the kick-out reactions, the energies required for reactions involving Ga and In are quite different. Contrary to the previous models, the roles of Ga and In in Be diffusion are different, and these elements ideally should not be lumped together. The influence of As on Be diffusion may not be negligible since the reaction energies for As being kicked out by Be are comparable with Ga/In being kicked out. We then build a diffusion model which is based on reaction energies and diffusion barriers calculated from first principles. By implementing this model in the Object Kinetic Monte Carlo (OKMC) simulator MMonCa [18], we are able to reproduce experimental data under different annealing temperatures and durations in a consistent way.

2. Methodology

2.1. Density functional theory

The calculations were performed using density functional theory [19,20] with the generalized gradient approximation and the Perdew-Burke-Eznerhof functional (GGA-PBE) [21] as implemented in Vienna *ab initio* simulation package (VASP) [22–24]. The projector augmented wave method (PAW) [25,26] was used to describe the interaction between the atomic cores and electrons. The valence configurations of the atoms were: Arsenic (As) $4s^2 4p^3$,

Gallium (Ga) $4s^2 4p^1$, Indium (In) $5s^2 5p^1$ and Beryllium (Be) $2s^2 2p^0$. A $2 \times 2 \times 2$ Monkhorst-Pack [27] k-point mesh and a cutoff of 400 eV were used for structure optimization. Atomic positions and cell vectors, where applicable, were relaxed using the conjugate gradient (CG) algorithm until all force components were less than 0.01 eV Å^{-1}. The single-point energy calculations on the structures, relaxed using the cutoff of 400 eV and $2 \times 2 \times 2$ k-points, were performed with $6 \times 6 \times 6$ k-points to achieve converged defect formation energies and diffusion barriers. A tetrahedron method with Blöchl [25] corrections was used for the partial occupancies. The density-of-state (DOS) calculations were performed using $5 \times 5 \times 5$ k-points meshes. The energy barrier for Be, Ga and In-atom diffusion were calculated using the climbing-image nudged elastic band (CI-NEB) method [28,29]; the force tolerance in the CI-NEB calculations was 0.05 eV Å^{-1}.

To ensure that the simulation cell is of size amenable to the calculations, we used the stoichiometry $In_{0.5} Ga_{0.5} As_1$ (abbreviated in the following as InGaAs), as was done in previous works [30,31]. The simulation cell size of about $12.0 \times 12.0 \times 11.9$ Å was used and is sufficient to neglect inter-cell interactions of the defects. The geometries of doped-InGaAs are fully relaxed. The CI-NEB calculations are performed under fixed cell. The charges on atoms of pure and doped InGaAs crystal are calculated using Bader analysis [32].

2.2. Kinetic Monte Carlo simulation

The Be diffusion process was modeled by OKMC modeling. In the framework of OKMC, the diffusion process is composed of succeeding events, either reaction or migration, which occur at different rates. In this study, we consider only kick-out reactions, surface trappings or injections, migrations and transitions between charge states. Once reactants approach each other within the reaction distance, the reaction will occur with the probability

$$P = \exp\left(-\frac{E_{re}}{k_B T} \right) \qquad (1)$$

when E_{re} is positive, otherwise the probability is 1. E_{re} is the reaction barrier, k_B is the Boltzmann constant and T is the temperature. In this study, such values are calculated according to the transition state theory. The interface between air and the InGaAs sample is the sink and the source of all self-interstitials: Ga_i, In_i; the trapping rate and injection rate are also determined by Eq. (1).

Self-interstitials and the Be interstitial can migrate in random directions with a fixed migration distance λ, while substitutional Be atoms are assumed to be immobile. The use of a fixed migration distance is justified by the crystal structure of InGaAs where elementary diffusion steps have all similar lengths. The migration rate is computed as

$$\nu_m = \nu_m^0 \exp\left(-\frac{E_m}{k_B T} \right), \qquad (2)$$

where ν_m^0 is the migration attempt frequency; E_m is the migration barrier.

Point defects in semiconductors usually have various electronic states. If we assume that a point defect X can be in three different charge states for example, singly negative, neutral, singly positive, we will denote this point defect as X^j, with $j = -, 0, +$. Then the relative concentrations are

$$\frac{[X^j]}{[X^{j+1}]} = \frac{g^j}{g^{j+1}} \exp\left(\frac{e_F - e(j+1, j)}{k_B T} \right), \qquad (3)$$