Diffusion and clustering of substitutional Mn in (Ga,Mn)As

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The Ga vacancy mediated microstructure evolution of (Ga,Mn)As during growth and post-growth annealing is studied using a multi-scale approach. The migration barriers for the Ga vacancies and substitutional Mn together with their interactions are calculated from first principles, and temporal evolution at temperatures ranging from 200 to 350°C is studied using Lattice Kinetic Monte Carlo simulations. We show that at the typical growth and annealing temperatures (i) gallium vacancies provide the diffusion mechanism for substitutional Mn and (ii) in 10–20 h the vacancy mediated diffusion of Mn promotes the formation of substitutional clusters. Clustering reduces the Curie temperature ($T_C$), and therefore the Mn clustering combined with the fast interstitial Mn diffusion explains the experimentally observed twofold annealing behavior of $T_C$.

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Understanding of microstructure evolution during growth and post-growth annealing is one of the key issues in materials science. The microstructure and its inhomogeneities largely determine the material properties, including the basic phase transition points for materials ranging from high temperature superconductors to diluted magnetic semiconductors. In the ongoing quest for room temperature semiconductor spintronics, diluted magnetic semiconductors have been one of the main candidates since the observation of the relatively high Curie temperature $T_C$ of 110 K. Typically the (Ga,Mn)As thin films, where Mn substitutionally replaces Ga atoms, are grown by means of low-temperature molecular beam epitaxy, which also leads to the formation of As antisites (As$_{Ga}$) and interstitial Mn (Mn$_i$). The substitutional Mn (Mn$_{Ga}$) act as acceptors, providing spin-polarized holes that mediate the ferromagnetic coupling, while the As$_{Ga}$ and Mn$_i$ as donors hamper the ferromagnetism by compensating holes. Post-growth annealing of a few hours is an efficient method to remove the interstitial Mn$_i$ and thus increase $T_C$. However, extended annealing at temperatures around 250°C for ten hours or longer reduces $T_C$ again, and annealing at higher temperatures leads to a more swift lowering of $T_C$. This twofold behavior clearly indicates that besides the Mn$_i$ out-diffusion another yet unknown microstructure evolution process takes place. At present, the nature of this process and the mechanism underlying this evolution is not understood.

In this Letter we show that the mechanism behind the long-term microstructure evolution is gallium vacancy (V$_{Ga}$) mediated Mn$_{Ga}$ diffusion on the Ga sublattice. We also show that this diffusion leads to Mn clustering, which reduces $T_C$. Although the formation of Mn$_{Ga}$ clusters has been shown to be energetically favorable, it requires an abundance of mobile gallium vacancies. The recent discovery of rather high gallium vacancy (V$_{Ga}$) concentrations in (Ga,Mn)As up to $10^{18}$ cm$^{-3}$ gives us good reason to consider this mechanism plausible, but the mobilities of V$_{Ga}$ and Mn$_{Ga}$ in (Ga,Mn)As are unknown. We calculate their migration and binding energies from first principles and use them as input data in lattice kinetic Monte Carlo simulations of microstructure evolution.

The vacancy mediated substitutional Mn migration over the Ga-sublattice consists of the following three steps: (1) the Mn$_{Ga}$ atom and a vacancy form a pair; (2) the Mn$_{Ga}$ and the vacancy switch places; and (3) the pair dissociates. This mechanism is henceforth called the pair formation–dissociation mechanism. The consideration of Mn diffusion via V$_{Ga}$ requires the knowledge of at least the following three energy quantities: the migration energy for V$_{Ga}$, the migration barrier for the Mn$_{Ga}$→V$_{Ga}$ transition, and the Mn$_{Ga}$–V$_{Ga}$ interaction potential (i.e. binding energy). These energies are calculated using first principles and the obtained values are used as input data in lattice kinetic Monte Carlo simulations of microstructure evolution.
We find that bringing a Mn$_{\text{Ga}}$V$_{\text{Ga}}$nism. However, in contrast to the Mn$_{\text{Ga}}$E barriers for direct Mn$_{\text{Ga}}$V$_{\text{Ga}}$nism.

The binding energies are calculated as the difference in total energy of the pairs located at nearest-neighbor and fifth-nearest-neighbor separations on the Ga fcc sublattice in 64 atom supercells that are fully relaxed, as described in Ref. [12]. In the 107 atom supercell we use a $4 \times 4 \times 3 \bar{k}$-point sampling mesh giving a similar $\bar{k}$-point density as that used in Ref. [12].

As the result we find a binding energy of $E_b = 0.1$ eV for the Mn$_{\text{Ga}}$Ga dimer. We find further that the binding of a Mn$_{\text{Ga}}$ atom to a Mn$_{\text{Ga}}$ cluster can to good accuracy be estimated as $n \cdot E_b$, where $n$ is the number of nearest neighbor Mn$_{\text{Ga}}$ bonds formed. Consequently, the lowest energy microstructure can be expected to be composed of Mn clusters, i.e., a collection of Mn atoms occupying nearest neighbor Ga sites, instead of separated single Mn$_{\text{Ga}}$, or even of second phase precipitates for very high Mn concentrations. However, to approach the lowest energy microstructure within reasonable time requires an efficient diffusion mechanism for the substitutional Mn$_{\text{Ga}}$. Therefore we consider the plausible V$_{\text{Ga}}$ mechanism.

We consider migration of Mn/Ga in a Mn rich environment, i.e., migration in metallic (Ga,Mn)As. Thus, our supercells contain a Ga–V$_{\text{Ga}}$, or a Mn$_{\text{Ga}}$–V$_{\text{Ga}}$ pair and one inactive substitutional Mn$_{\text{Ga}}$ at the largest distance from this pair. The Ga $\rightarrow$ V$_{\text{Ga}}$ and Mn$_{\text{Ga}}$ $\rightarrow$ V$_{\text{Ga}}$ jumps take place along a path in the (110) plane (Fig. 1).

The migration barriers are calculated using the drag (GGA-PW91) for exchange-correlation implemented in the VASP code [19]. The binding energies are calculated as the difference in total energy of the pairs located at nearest-neighbor and fifth-nearest-neighbor separations on the Ga fcc sublattice in 64 atom supercells that are fully relaxed, as described in Ref. [12]. In the 107 atom supercell we use a $4 \times 4 \times 3 \bar{k}$-point sampling mesh giving a similar $\bar{k}$-point density as that used in Ref. [12].

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We also considered another scenario within the formation–dissociation diffusion mechanism, where the Mn–V$_{\text{Ga}}$ pair diffuses as an entity. The Mn$_{\text{Ga}}$, could kinetically trap vacancies enabling the pair to move for some sufficiently long distance before dissociating, if the migration barrier for the vacancy to jump past the Mn$_{\text{Ga}}$ to another neighboring site were significantly lower than the Mn$_{\text{Ga}}$–V$_{\text{Ga}}$ pair dissociation barrier. However, for this jump we find a non-relaxed activation barrier of $Q_b = 2.3$ eV, that is virtually the same value as for the pair Mn$_{\text{Ga}}$–V$_{\text{Ga}}$ dissociation. Thus such correlated diffusion will not occur and requires no special consideration.

We improve the estimated migration barriers by allowing constrained relaxations as follows. The migrating Ga/Mn atom is allowed to relax along the [001] axis, the As atoms 1-3 in Fig. 1 are allowed to relax in the (110) plane, and the As atoms 4-7 are allowed to relax in the (110) plane. This calculation is carried out for the initial and saddle point configurations of the non-relaxed calculations. For Mn we also calculate the local minimum point at the center of the migration path. The resulting energies are given in Fig. 2 (circles), and we obtain the improved barrier maxima of 1.6 eV and 0.8 eV for the Ga and Mn migration, respectively.

Although the Mn rich metallic environment studied in this work differs from pure GaAs, the migration barrier for the vacancy mediated Ga self-diffusion of 1.6 eV is well in agreement with the first principles calculation for a neutral vacancy [15], and also with the experimental values around 1.5-1.9 eV [20, 21, 22] in pure GaAs (Table I). We wish to remark that even the improved migration barriers given above may be overestimated because only
of the Mn nearest neighbor atoms are allowed to relax. Nevertheless, considering the calculated barriers, the probability of the $\text{Mn}_{\text{Ga}} \rightarrow \text{V}_{\text{Ga}}$ exchange vs. the $\text{V}_{\text{Ga}}$ migration jump differs at relevant temperatures by a factor of $10^7$. For the dissociation of a $\text{Mn}_{\text{Ga}} \rightarrow \text{V}_{\text{Ga}}$ we obtain an activation barrier of 1.4 eV by combining the $\text{V}_{\text{Ga}}$ migration barrier with the $\text{Mn}_{\text{Ga}} \rightarrow \text{V}_{\text{Ga}}$ negative binding energy. The Boltzmann factor for this dissociation barrier is 100 times smaller than the $\text{Mn}_{\text{Ga}} \rightarrow \text{V}_{\text{Ga}}$ migration barrier. This shows that the bottleneck for $\text{Mn}_{\text{Ga}}$ diffusion via the pair formation–dissociation mechanism is the mobility of $\text{V}_{\text{Ga}}$. However, at large $\text{Mn}_{\text{Ga}}$ concentrations, $\text{Mn}_{\text{Ga}} \rightarrow \text{V}_{\text{Ga}}$, pairs are formed more frequently, and due to the low pair dissociation and exchange barriers the $\text{V}_{\text{Ga}}$ diffusivity is expected to increase.

The calculated binding energies $Q^b$ and the migration energies $Q^c$ (Table I) are used to study structural evolution with lattice kinetic Monte Carlo simulations using the Casino-LKMC code [24]. (Ga,Mn)As is studied in a supercell of more than 100,000 Ga atoms, where randomly picked Ga sites are either replaced with Mn representing a $\text{Mn}_{\text{Ga}}$ concentration of 5 % or 0.5 % ($\sim 10^{21}$ or $10^{20}$ cm$^{-3}$), or left empty representing a Ga vacancy concentration of $10^{18}$ cm$^{-3}$, mimicking the experimental samples of Ref. [18]. Here $[\text{Mn}]$ is defined as the proportion of the number of Mn atoms to the number of Ga sites.

We study the clustering due to Mn redistribution by evaluating the number of Mn atoms in clusters as a function of annealing time and temperature, given in Figs 3(a) and (b), where the clustering rate for $[\text{Mn}] = 5\%$ at 250°C is approximately the same as for $[\text{Mn}] = 0.5\%$ at 300°C. The clustering rate changes rapidly along the temperature, as seen for $[\text{Mn}] = 5\%$ in Figs 3(a) and (b), where the temperature is increased from 250°C to 300°C. We get a similar increase in clustering rate by increasing the Mn concentration from 5% to 8% e.g. at 250°C. The largest cluster size after annealing at 250°C for 24 h at $[\text{Mn}] = 5\%$ and 8% is 14 and 26 Mn atoms, respectively. The increasing number of large clusters may further indicate the formation of a secondary MnAs phase, as observed in growth of (Ga,Mn)As samples with Mn concentrations beyond 7 % [1].

The Curie temperature $T_C$ depends mainly on the concentration of Mn clusters [10] [defined as the proportion of the number of clusters (including monomers) to the number of Ga sites] [11, 12], i.e. $T_C \propto [\text{cl}]$. At the

| Process | $Q^b$ (eV) | $Q^c$ (eV) | PWPP (eV) | Expt (eV) |
|---------|-----------|-----------|-----------|-----------|
| Ga→$\text{V}_{\text{Ga}}$ | 2.4, 2.3$^b$ | 1.6 | 1.7$^b$ | 1.5-1.9$^c$ |
| Mn$_{\text{Ga}}$→$\text{V}_{\text{Ga}}$ | 1.1 | 0.8 | |

$^a$ Ga self-diffusion around a Mn$_{\text{Ga}}$. $^b$ [18], $^c$ [20, 21, 22].

FIG. 3: Percentage of Mn atoms included in clusters as a function of annealing time for the Mn concentrations of 0.5 % (a) and 5 % (b), and cluster portions for the Mn concentration of 5 % as a function of temperature at 250°C (c) and 300°C (d).
Mn concentration of [Mn] = 5% we find that [cl] evolves as follows: initially [cl] is 3.6%, and after annealing at 250°C or 300°C for 24 h [cl] drops to 3.3% or 1.5%, respectively. In Ref. [11] we show that [cl] values of 6.3 and 3.1% correspond to T_C values of 660 and 220 K, respectively, and using the mean field approximation for T_C, the drop in [cl] from 3.6 to 3.3% at 250°C corresponds to a drop in T_C of 40 K. Experimentally, annealing of samples with [Mn] = 6–8% at temperatures from 215 to 250°C for 24 h reduces T_C by 10–50 K [6,8], to which our result is in close agreement. Furthermore, Stanciu et al. find that annealing at 275°C induces a rapid drop in T_C of 20 K in 4 h [8], which is bracketed by our estimated drops in the same time at 250°C and 300°C.

To conclude, we have studied the redistribution of substitutional Mn_Ga in (Ga,Mn)As. The binding energies and migration barriers are calculated from first principles. We show that substitutional Mn atoms use Ga vacancies as a vessel for diffusion. Lattice kinetic Monte Carlo simulations yield that at annealing temperatures above 250°C the substitutional Mn redistribute into clusters, and that the clustering rate increases along temperature and/or Mn concentration [Mn]. This clustering on the other hand lowers the Curie temperature T_C, thus explaining quantitatively the drop in T_C observed in long-time annealing experiments. The increased clustering seems to impose a fundamental limit on T_C. Further, at large [Mn] beyond 8% clustering takes place already during sample growth, and formation of large Mn clusters indicates precipitation.

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