# Si diffusion in GaAs

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**Abstract.** Theoretical studies are carried out to ascertain the dominant mechanism of Si diffusion in GaAs. Lattice dynamical model calculations have shown that the most probable diffusion mechanism is through a single vacancy even though several experiments cannot fix the mechanism as substitutional, substitutional–interstitial pair or neutral defect pair.

**Keywords.** Solid state diffusion; lattice dynamics; impurity diffusion.

## 1. Introduction

Impurity diffusion in semiconductors has the technological importance in the fabrication of junction devices, semi-insulating compounds and high temperature growth of materials (Mizoguchi *et al* 1999). The study on GaAs : Si diffusion has gained momentum in the last decade and over 25 papers have been published in various journals on the account of technological importance of the system (Fisher 1997). Persistent photoconductivity and the DX centres in this system are examples (Wolk *et al* 1991) for the interest in the system. Similarly, the LOPC (LO phonon–plasmon coupled) modes appear in such compounds (Dobal *et al* 1995). In addition, charge conversion takes place on $H^+$ ion implantation in this compound and this is manifested in the LOPC modes in Raman spectra (Murugan *et al* 2002). Si diffusion in GaAs has been experimentally studied by many techniques; among them, the measurements by secondary ion mass spectroscopy (SIMS) and capacitance–voltage method are important. In these methods, the diffusivity is obtained from the concentration profile and temperature.

Ahlgren *et al* (1997) have reported from their experimental studies on Si diffusion in GaAs, that concentration independent diffusion is mainly through interstitials, whereas concentration dependent diffusion is through vacancies. Greiner and Gibbons (1984) have also reported similar results from their experiments. Meanwhile, Lee *et al* (1990) reported that Si diffusion is through neutral defect pair, $Si_{Ga}^+ - V_{Ga}^-$, which is also supported by many of the experiments (Nutt *et al* 1991; Matsushita *et al* 1993) and theoretical first-principle calculations (Dabrowski and Northrup 1994) and molecular dynamics simulations (Chen *et al* 1994).

Herzog *et al* (1995) have reported, from SIMS, that Si diffusion in GaAs is through (i) interstitial and (ii) frank faulted loop and a kind of interstitial. Since different mechanisms for Si diffusion in GaAs are reported in literature and also no two diffusion experiments by the same technique could lead to identical results, we investigated by lattice dynamical approach the diffusion mechanism in this system, accounting for the experimental observations.

## 2. Theory

Diffusion of an atom in a crystal takes place through discrete jumps between the defect and the diffusing atom. In general, the role of these defects on diffusion also should be considered. Usually, only the passive role, considering the lattice relaxation to be negligible, due to the presence of defects when diffusion process takes place is considered to elucidate the diffusion process (Sadaiyandi and Ramachandran 1991). However, the active role taking into account the lattice relaxation for the defects is considered in our present approach (Sadaiyandi and Ramachandran 1992). When this jump is obstructed by a ring of neighbouring atoms, the diffusing atom should overcome the potential barrier for the jump to materialize. Instantaneous relative displacement of the diffusing atom with respect to the neighbours in the diffusion ring is expressed as reaction coordinate (Flynn 1968)

$$\mathbf{X} = \left[ \mathbf{U}^a - \frac{1}{n} \sum_i \mathbf{U}^i \right] \cdot \hat{\mathbf{X}}, \qquad (1)$$

where $\mathbf{U}^a$ is the displacement of the diffusing atom, $\mathbf{U}^i$ the displacement of the $i$th atom in the ring of $n$ neighbours obstructing the jump, and $\hat{\mathbf{X}}$, the unit vector along the jump direction.

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The displacements of atoms due to the presence of impurity is considered as a perturbed term through the scattering matrix. When a lattice plane wave, $U_0$, passes through the defect space consisting of the defect and the neighbours in the diffusion ring, the situation can be treated as a scattering problem with $U$ as the displacement matrix consisting the displacement of the scattered wave $w$, following the theory of Maradudin *et al* (1971)

$$U = U_0 + w, \qquad (2)$$

where the matrix, $U_0$, corresponds to a perfect lattice and can be expressed as

$$U_0(\mathbf{q}, k) = \left[ \frac{\hbar}{2NM_k w(\mathbf{q}, k)} \right]^{1/2} \mathbf{e}(\mathbf{q}, k) \exp(i\mathbf{q} \cdot \mathbf{r}), \quad (3)$$

and

$$L U_0 = 0, \qquad (4)$$

where $\mathbf{e}(\mathbf{q}, k)$ is the polarization vector in the wave vector $\mathbf{q}$ for $k$th atom in the $l$th cell. $M_k$ is the mass of the $k$th atom. The matrix, $L$, is constructed from the force constants, $f$, as

$$L_{ab}(ll'; kk'; w^2) = M_k w^2 d_{ll'} d_{kk'} d_{ab} - f_{ab}^0(ll'; kk'), \quad (5)$$

$a$ and $b$ are the degrees of freedom. $w$ the scattered wave matrix is defined as

$$w = G \left( \frac{\partial L}{I - G \partial L} \right) U_0. \qquad (6)$$

The displacements of the host atoms in the defect space are given in the form of a column vector $U$, as

$$U = \left( I + \frac{G \partial L}{I - G \partial L} \right) U_0, \qquad (7)$$

where $I$ is the unit matrix, $G$ the Green's functions matrix, $L$ corresponds to the vibrations of the perfect host crystal and $\partial L$ the perturbation matrix, all matrices being of the order $3(n + 1) \times 3(n + 1)$.

The atomic jump rate then can be written as (Achar 1970)

$$\Gamma = \Gamma_0 \exp \left[ \frac{-X_c^2}{\sum\limits_{q,k} |X(\mathbf{q}, k)|^2} \right], \qquad (8)$$

where

$$\Gamma_0 = \sqrt{ \frac{\sum\limits_{q,k} w^2(\mathbf{q}, k) |X(\mathbf{q}, k)|^2}{\sum\limits_{q,k} |X(\mathbf{q}, k)|^2} }, \qquad (9)$$

and $\Gamma_0$ is called attempt frequency of the jump. $X_c$ is the critical value of $X$ above which only, the jump will materialize. Critical value of $X_c$ is obtained from

$$\frac{X_c^2}{\sum\limits_{q,k} |X(\mathbf{q}, k)|^2} = \frac{Q}{k_B T}, \qquad (10)$$

where $Q$ is the activation energy, $k_B$ the Boltzmann constant and $T$ the temperature.

Using the jump frequency, the diffusion constant, $D_0$, and diffusion coefficient, $D$, can be estimated from

$$D_0 = \frac{H \Gamma_0 d^2}{2ps}, \qquad (11)$$

$$D = D_0 \exp \left( \frac{-Q}{k_B T} \right), \qquad (12)$$

where $H$ is the Havan's ratio, $d$ the jump distance and $s$ the number of identical jumps. $Q$ is the activation energy for jump. For the vacancy mechanism, $H$ and $s$ are 0·78146 and 12, respectively, as GaAs belongs to zinc blende structure (Sadaiyandi 1992).

## 3. Diffusion mechanism

Three kinds of diffusion mechanisms are considered in our present work viz. single vacancy mechanism, vacancy assisted interstitial and neutral defect pair (divacancy) mechanism, since many of the experiments suggest these possible mechanisms.

### 3.1 *Single vacancy mechanism*

In this process the substitutional foreign- or host-atom diffuses by jumping into the nearby vacancy, which acts as the diffusion vehicle. Particularly, in the case of Si diffusion in GaAs, Si is initially assumed to occupy a positively charged substitutional site, $Si_{Ga}^+$ at (0 0 0). It diffuses by jumping into nearby negatively charged vacant site $V_{Ga}^-$ at (1 1 0). The ring of neighbours obstructing the jump is shown in figure 1 and has only three atoms in the ring at the positions Ga (0 1 1), Ga (0 $\bar{1}$ 1) and As ($\frac{1}{2} \frac{1}{2} \frac{1}{2}$), lying in a plane perpendicular to the jump direction [1 1 0].

### 3.2 *Vacancy assisted interstitial*

Since, it is reported that Si diffusion in GaAs by vacancy assisted interstitial mechanism may be possible, it is also considered in the present work and the mode of transport by this mechanism is shown in figure 2. The jumping Si atom is initially assumed to be at (0 0 0) site; first goes to the interstitial site at ($\frac{1}{2} \frac{1}{2} \frac{1}{\bar{2}}$) in [11 $\bar{1}$] direction and then

to Ga vacancy at (1 1 0) site in [1 1 1] direction. The resulting jump direction is same as [1 1 0]. The ring of neighbours obstructing these jumps is shown in figure 2.

### 3.3 *Neutral defect pair*

In this mechanism, substitutional foreign- or self-atom diffuses by jumping into one vacancy of the bound defect pair. The Si atom is assumed to occupy a Ga site first substitutionally. Because of the fluctuations due to lattice vibration, the Si atom jumps to the As site $(\frac{3}{2} \frac{1}{2} \frac{1}{2})$ which is purely a temporary site and the Si atom will occupy this intermediate metastable site for diffusion. Immediately it jumps to the next vacant Ga (2 1 1) site. Two vacancies are assumed, one at Ga site and other at As site, so that Si diffuses through these sites as these are the two possible vacancies through which the jump can occur. The system may be unstable for the two defects to occur in the same unit cell simultaneously, but the As vacancy is assumed only as an intermediate site and the present configuration of $[V_{Ga}-V_{As}]$ is postulated. The direction of first jump is [1 1 1] and for the second jump is along [1 $\bar{1}$ 1], the resultant jump direction is [1 0 1]. Figure 3 illustrates this mechanism of diffusion.

### 4. Isotope effect

Achar's (1970) theory gives the method of finding the most probable diffusion mechanism from isotope effect ($\Delta K$), which is defined as the ratio of kinetic energy of the moving atom, in the dissolution normal mode at the saddle point, to the total kinetic energy. The kinetic energy and the isotope effect are correlated by a factor, $f$, through the relation

$$\Delta E = f \Delta K. \tag{13}$$

The isotope effect is a measure of the dependence of the tracer diffusion rate on the isotope mass, and is given by

$$\Delta K = \frac{\dfrac{\Gamma_1}{\Gamma_2} - 1}{\sqrt{\dfrac{M_2}{M_1}} - 1}. \tag{14}$$
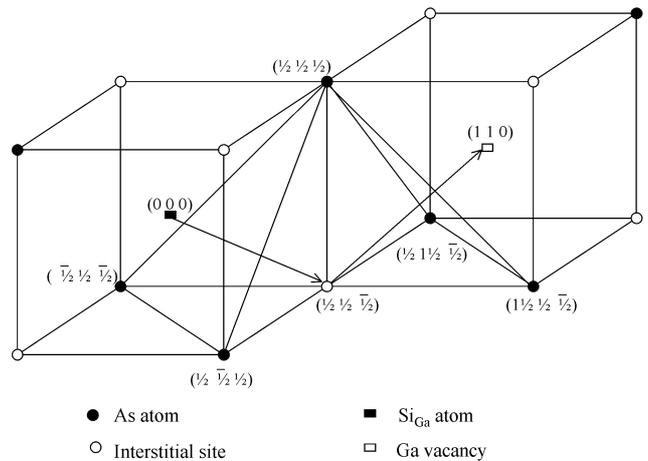
**Figure 2.** Vacancy assisted interstitial (positions are given in units of $r_0 = a/2$).
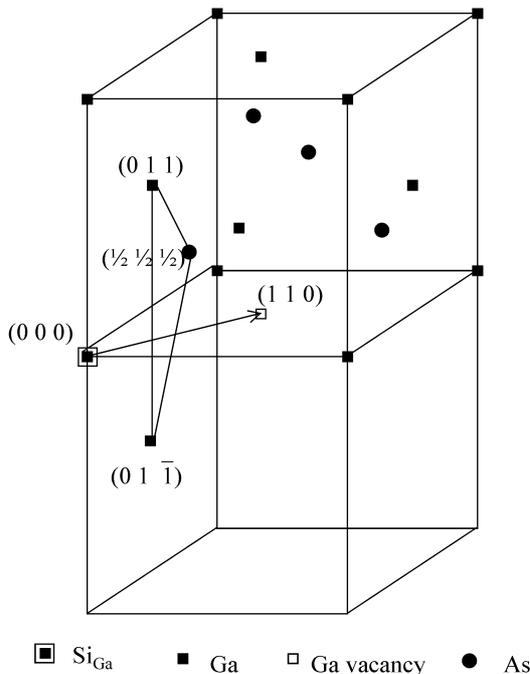
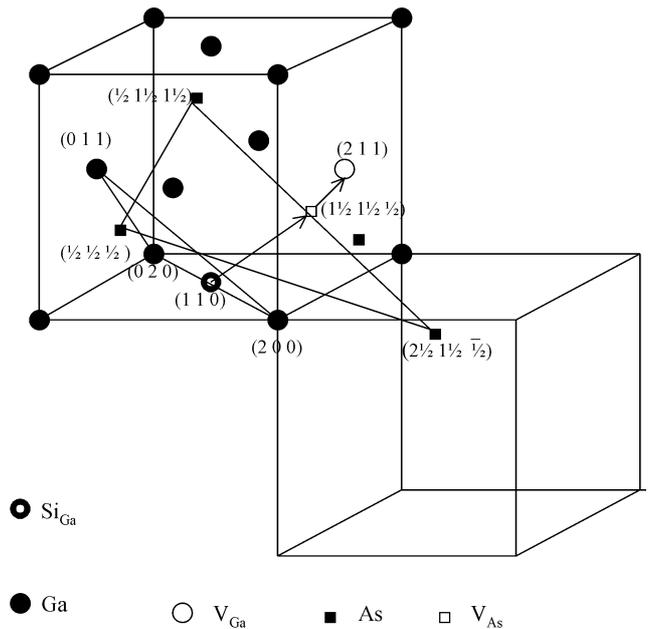**Figure 1.** Single vacancy mechanism (positions are given in units of $r_0 = a/2$).

**Figure 3.** Neutral defect pair mechanism (position of atoms are given in units of $a/2$).

Here $M_1$ and $M_2$ are the masses of the two most abundant isotopes of diffusing atoms. Jump frequencies of isotopes are computed from the reaction coordinate and the mechanism yielding the isotope effect exceeding 50% is generally considered as the most probable.

## 5. Results

The jump frequency and diffusion coefficient for different temperatures are computed by employing the scattering matrix theory for the three different mechanisms viz. single vacancy, vacancy assisted interstitial and neutral defect pair mechanism.

In all the above cases, most abundant isotopes of Si, namely $^{28}$Si and $^{29}$Si are considered for diffusion. Green's functions are obtained from phonon frequencies and eigen vectors of GaAs for entire Brillouin zone from the modified rigid ion model (Plumelle and Vandevyver 1976). For constructing the scattering matrix, the lattice relaxation is considered through the force constant change (Pothiraj and Ramachandran 1995). Reaction coordinate of diffusing atom is calculated from (1), considering all the equivalent symmetry points. Initially, attempt frequencies are estimated for various diffusion processes. From the attempt frequency, $X_c$, the critical values of $X$ and diffusion constant are estimated. The jump frequency is estimated from (8) and the isotope effect is evaluated from the jump frequencies for all diffusion mechanisms at various temperatures from (14). Necessary software have been developed and the jump frequency and diffusion constant are computed.

The $X_c$, critical value of reaction coordinate, jump frequencies and the isotope effect for single vacancy mechanism are reported in table 1. It is found that the isotope effect, $\Delta K$, at all temperatures is well above 87% and the mean value of $X_c$ is around 1·345% of the ionic radius of $Ga^{3+}$.

In the vacancy assisted interstitial mechanism, two jumps are separately considered, one jump to interstitial site and another to vacant site. Jump frequency is estimated from the geometric mean of the two jump frequencies. Isotope effect (table 2) demonstrates that the $\Delta K$ is around 58% and the mean $X_c$ around 1·69% of ionic radius of $Ga^{3+}$.

In the case of neutral defect pair mechanism, two jumps are involved similar to the above case, viz. first jump to vacant As site and then subsequently to a vacant

**Table 1.** The jump frequencies and isotope effect for Si diffusion in GaAs (Active role – single vacancy mechanism).

| Temp. (K) | Isotope (Si) | $X_c$ (%) | $\Gamma$ (rad/sec) | $\Delta K$ (%) |
|---|---|---|---|---|
| 700 | 28 | 1·358 | $0·4655 \times 10^{-4}$ | 87·3 |
|  | 29 | 1·339 | $0·4728 \times 10^{-4}$ |  |
| 900 | 28 | 1·357 | 0·3861 | 87·5 |
|  | 29 | 1·338 | 0·3922 |  |
| 1100 | 28 | 1·356 | $0·1204 \times 10^{3}$ | 87·3 |
|  | 29 | 1·336 | $0·1229 \times 10^{3}$ |  |
| 1300 | 28 | 1·356 | $0·6414 \times 10^{4}$ | 87·7 |
|  | 29 | 1·336 | $0·6515 \times 10^{4}$ |  |

$X_c$ values are given in % of atomic radius of cation atom (Ga).

**Table 2.** The jump frequencies and isotope effect for Si diffusion in GaAs (Active role – vacancy assisted interstitial).

| Temp. (K) | Isotope (Si) | Jumps | $X_c$ (%) | Jump frequencies (rad/sec) | $\Gamma$ (rad/sec) | $\Delta K$ (%) |
|---|---|---|---|---|---|---|
| 700 | 28 | I | 2·019 | $0·3761 \times 10^{-4}$ | $0·4343 \times 10^{-4}$ | 59·7 |
|  |  | II | 1·478 | $0·5014 \times 10^{-4}$ |  |  |
|  | 29 | I | 1·926 | $0·3787 \times 10^{-4}$ | $0·4389 \times 10^{-4}$ |  |
|  |  | II | 1·421 | $0·5087 \times 10^{-4}$ |  |  |
| 900 | 28 | I | 2·018 | 0·3094 | 0·3574 | 59·1 |
|  |  | II | 1·477 | 0·4128 |  |  |
|  | 29 | I | 1·925 | 0·3115 | 0·3612 |  |
|  |  | II | 1·420 | 0·4188 |  |  |
| 1100 | 28 | I | 2·017 | $0·9597 \times 10^{2}$ | $1·1088 \times 10^{2}$ | 58·9 |
|  |  | II | 1·476 | $1·2811 \times 10^{2}$ |  |  |
|  | 29 | I | 1·925 | $0·9662 \times 10^{2}$ | $1·1205 \times 10^{2}$ |  |
|  |  | II | 1·419 | $1·2995 \times 10^{2}$ |  |  |
| 1300 | 28 | I | 2·017 | $0·5095 \times 10^{4}$ | $0·5889 \times 10^{4}$ | 58·7 |
|  |  | II | 1·476 | $0·6804 \times 10^{4}$ |  |  |
|  | 29 | I | 1·924 | $0·5130 \times 10^{4}$ | $0·5950 \times 10^{4}$ |  |
|  |  | II | 1·419 | $0·6901 \times 10^{4}$ |  |  |

Ga site. Jump frequency and isotope effect are computed (table 3) and it is found that the isotope effect for this case is about 52% and the $X_c$ is around 1·63% of ionic radius of $Ga^{3+}$.

## 6. Conclusions

Even though extensive experimental results are available for Si diffusion in GaAs, there is no clear-cut conclusion on the mechanism of diffusion i.e. the single vacancy and

neutral defect pair are some of the possibilities reported. In order to understand the exact mode of Si diffusion in GaAs, we have investigated theoretically all the possible mechanisms.

The values of $\Delta K$, a measure of the kinetic energy necessary for overcoming the potential barrier so that diffusion is possible, for the single vacancy mechanism are about 87% for all temperatures from 700–1300 K, whereas in vacancy assisted interstitial process, $\Delta K$ values are only about 59%. By comparison of $\Delta K$ values obtained with the two prominent mechanisms, single

**Table 3.** The jump frequencies and isotope effect for Si diffusion in GaAs (Active role – neutral defect pair).

| Temp. (K) | Isotope (Si) | Jumps | $X_c$ (%) | Jump frequencies (rad/sec) | $\Gamma$ (rad/sec) | $\Delta K$ (%) |
|---|---|---|---|---|---|---|
| 700 | 28 | I | 1·8077 | $0·4653 \times 10^{-4}$ | $0·4798 \times 10^{-4}$ | |
| | | II | 1·5529 | $0·4947 \times 10^{-4}$ | | |
| | 29 | I | 1·7350 | $0·4699 \times 10^{-4}$ | $0·4843 \times 10^{-4}$ | 52·5 |
| | | II | 1·4825 | $0·4991 \times 10^{-4}$ | | |
| 900 | 28 | I | 1·8064 | 0·3832 | 0·3950 | |
| | | II | 1·5516 | 0·4071 | | |
| | 29 | I | 1·7337 | 0·3869 | 0·3987 | 52·4 |
| | | II | 1·4812 | 0·4108 | | |
| 1100 | 28 | I | 1·8057 | $1·1892 \times 10^2$ | $1·2256 \times 10^2$ | |
| | | II | 1·5510 | $1·2632 \times 10^2$ | | |
| | 29 | I | 1·7330 | $1·2008 \times 10^2$ | $1·2371 \times 10^2$ | 52·5 |
| | | II | 1·4806 | $1·2746 \times 10^2$ | | |
| 1300 | 28 | I | 1·8053 | $0·6316 \times 10^4$ | $0·6509 \times 10^4$ | |
| | | II | 1·5506 | $0·6708 \times 10^4$ | | |
| | 29 | I | 1·7327 | $0·6377 \times 10^4$ | $0·6570 \times 10^4$ | 52·5 |
| | | II | 1·4802 | $0·6768 \times 10^4$ | | |

**Table 4.** Diffusivity, $D$ ($cm^2$/sec) of $^{28}$Si in GaAs for various mechanisms with experimental results.

| Temperature (K) | D (Present calculation) | | | Experiment |
|---|---|---|---|---|
| | I | II | III | |
| 700 | $0·799 \times 10^{-19}$ | $0·721 \times 10^{-19}$ | $0·797 \times 10^{-19}$ | $\mathbf{0·521 \times 10^{-19}}$(a) $0·222 \times 10^{-21}$(b) |
| 900 | $0·658 \times 10^{-15}$ | $0·593 \times 10^{-15}$ | $0·656 \times 10^{-15}$ | $\mathbf{0·293 \times 10^{-16}}$(a) $0·537 \times 10^{-17}$(b) |
| 1100 | $0·204 \times 10^{-12}$ | $0·184 \times 10^{-12}$ | $0·203 \times 10^{-12}$ | $\mathbf{0·165 \times 10^{-14}}$(a) $0·327 \times 10^{-14}$(b) |
| 1300 | $0·108 \times 10^{-10}$ | $0·978 \times 10^{-11}$ | $0·108 \times 10^{-10}$ | $0·268 \times 10^{-13}$(a) $\mathbf{0·278 \times 10^{-12}}$(b) |

I. Single vacancy mechanism;
II. Vacancy assisted interstitial, resultant diffusivity has been taken from the geometric mean of two jumps diffusivity;
III. Neutral defect pair mechanism, resultant diffusivity has been taken from the geometric mean of two jumps diffusivity;
(a) Laikhtman *et al* 1991; (b) Hirai *et al* 1995;
Bold values are close to our results.

vacancy is found to be the most dominant mechanism. Since neutral defect pair mechanism is also reported from experiments, we have worked out this mechanism also theoretically and the $\Delta K$ values are found to be about 52%.

In conclusion, we have calculated the isotope effect for (i) single vacancy, (ii) single vacancy assisted interstitial and (iii) neutral defect pair mechanisms to be 87%, 59%, 52%, respectively for active role of the defects. These results indicate that the most dominant mechanism for Si diffusion in GaAs is through single vacancy compared to the other two mechanisms under normal condition. The other mechanisms may also be possible under specific conditions, either at elevated pressure or temperature or higher doping concentrations.

In fact, most possible mechanism can also be understood from $X_c$, the critical value of reaction coordinate $X$. In case of single vacancy mechanism, this has a lower value compared to the other mechanisms, as shown in tables 1–3.

The results of the diffusivity for these mechanisms are given in table 4, where we could find a reasonable agreement with the experimental values (Laikhtman *et al* 1991; Hirai *et al* 1995). Diffusivity of Si in GaAs has nearly identical values for both single vacancy and neutral defect pair mechanisms and it is lesser in vacancy assisted interstitials mechanism.

## Acknowledgements

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