Monte Carlo Simulation of Atomic Diffusion: Gold into Silicon

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ABSTRACT Diffusion by vacancy mechanism, interstitial mechanism, kick-out mechanism and Frank-Turnbull mechanism in crystalline solids are analyzed through Monte Carlo simulation. These diffusion mechanisms are strongly dependent on the temperature. The simulation was done to find the dominant diffusion mechanism of Au into Si for temperatures ranging from 500K to 1800K. The result shows that the vacancy mechanism is the dominant diffusion, followed by kick-out, interstitial and Frank-Turnbull. Kick-out mechanism only appears at 670 K, interstitial at 850 K and Frank-Turnbull at 1500 K.

ABSTRAK Resapan melalui mekanisma kekosongan, interstis, tendang-keluar dan Frank-Turnbull dalam pepejal berhablur dianalisis secara simulasi Monte Carlo. Mekanisma-mekanisma ini bergantung kuat kepada suhu. Matlamat simulasi ini adalah untuk mencari mekanisma yang paling berpengaruh bagi resapan Au dalam Si bagi julat suhu diantara 500 K hingga 1800 K. Keputusan simulasi ini menunjukkan mekanisma kekosongan adalah yang paling berpengaruh diikuti dengan mekanisma tendang-keluar, interstis dan Frank-Turnbull. Mekanisma tendang-keluar hanya muncul pada suhu 670 K, interstis pada 850 K dan Frank-Turnbull pada 1500 K.

(Frank-Turnbull; interstitial; kick-out; vacancy)

INTRODUCTION

At present, our knowledge of atomic diffusion [1] is still not deep enough. A variety of diffusion models exist which try to explain the experimental data. However, most of the models are still highly controversial. Even some of the most fundamental questions concerning atomic diffusion like self-diffusion at high temperatures are highly contentious.

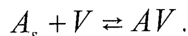
Until now most of our understanding on diffusion mechanisms are based on analytical or experimental methods. Understanding diffusion mechanism through these methods is quite difficult due to the complexity of the process.

Diffusion of gold into silicon was first studied by Struthers [2] to measure diffusion coefficients using radio tracers. In later studies, many other methods were used to measure diffusion coefficients. In all previous studies, diffusion coefficients were measured while the aim of this study is to find the diffusion mechanism that is most dominant in silicon via computer simulations. In this study, we have simulated the diffusion of gold in silicon [3, 4] at a variety of temperatures ranging from 500 K to 1800 K by using the Monte Carlo method.

THEORY

In order for atoms to diffuse, they need to have enough energy (thermal energy) to break the bonds and squeeze through their neighbours. The energy necessary for motion is called the activation energy (Figure 1).

In the vacancy [5-7] mechanism, atoms on substitutional sites A_s may meet with a vacancy, V. It can be explained by the following equation,



$$A_s + V \rightleftarrows AV.$$

The activation energy of diffusion for an AV is given as

$$Q_{AV} = H^{f}_{AV} + H^{m}_{AV} \qquad (1)$$

$$= H^{f}_{V} - E^{b}_{AV} + H^{m}_{AV} \qquad (2)$$

where H^{f}_{AV} is the formation enthalpy for the AV complex and H^{m}_{AV} the migration enthalpy. Here, H^{f}_{AV} is H^{f}_{V} i.e. the formation enthalpy of V, less the AV binding energy, E^{b}_{AV}. The size of the AV attraction when the vacancy is at the saddle point of the diffusion event is denoted by $\Delta E'_{AV}$. If H^{m}_{V} is the migration enthalpy of V we can then write

$$Q_{AV} = H^{f}_{V} - E^{b}_{AV} + H^{m}_{V} + E^{b}_{AV} - \Delta E'_{AV} \qquad (3)$$

$$= H^{f}_{V} + H^{m}_{V} - \Delta E'_{AV} \qquad (4)$$

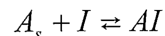
This equation shows the link between the activation energy of impurity diffusion and self-diffusion. The potential diagram (Figure 2) forms the basis of the lattice Monte-Carlo simulation.

In an interstitial mechanism, atoms on interstitial sites, A_i dissolved mainly as an interstitial defect hops from one interstitial site to another and performs a diffusion that is usually very fast and has low activation energy. The interstitial migration energy is described by

$$Q_{A_i} = H^{m}_{A_i} \qquad (5)$$

For interstitial mechanism, the diffusion rate depends on the kinetic energy of the interstitial energy. Hence the temperature plays the most important role in the diffusion rate of the interstitial mechanism.

Kick-out [8] mechanism can be represented by



$$A_s + I \rightleftarrows AI$$

or

$$A_s + I \rightleftarrows A_i \qquad (6)$$

where I is the interstitial impurity. The activation energy of AI pair is

$$Q_{AI} = H^{f}_{AI} + H^{m}_{AI} \qquad (7)$$

$$= H^{f}_{I} - E^{b}_{AI} + H^{m}_{AI} \qquad (8)$$

where H^{f}_{AI} is the formation enthalpy for the AI pair, H^{m}_{AI} the migration energy of the diffusing pair, H^{f}_{I} the formation enthalpy of I and E^{b}_{AI} the binding energy. Referring to the similar ness with the vacancy mechanism, we can write the equation as

$$Q_{AI} = H^{f}_{I} - E^{b}_{AI} + H^{m}_{I} + E^{b}_{AI} - \Delta E'_{AI} \qquad (9)$$

$$= H^{f}_{I} + H^{m}_{I} - \Delta E'_{AI} \qquad (10)$$

where H^{m}_{I} is the migration enthalpy of I and $\Delta E'_{AI} = E^{b}_{AI} + (H^{m}_{I} - H^{m}_{AI})$. For the interstitial kick-out mechanism via equation 6, the usual definition applies

$$Q_{A_i} = H^{f}_{A_i} + H^{m}_{A_i} \qquad (11)$$

Here we can see that the formation enthalpy $H^{f}_{A_i}$ of the interstitial impurity is not related to H^{f}_{I} by a simple binding-energy term, since $H^{f}_{A_i}$ accounts not only for the formation of self-interstitial, but also includes kick-out displacement of A_s into interstitial A_i. The migration energy $H^{m}_{A_i}$ is the activation energy that had to be overcome to move between interstices.

Frank-Turnbull [9] mechanism can be represented by

$$A_i + V \rightleftarrows A_s .$$

The activation energy of diffusion for A_s can be decomposed as

$$Q_{A_s} = H^{f}_{A_s} + H^{m}_{A_s} \qquad (12)$$

where $H^{f}_{A_s}$ and $H^{m}_{A_s}$ are the enthalpy of formation and migration respectively for A_s. Hence the activation energy for Frank-Turnbull mechanism is its kinetic energy for the interstitial type of occupant plus the sum of interstitial binding energy between the interstitial and its nearest lattice.

MONTE CARLO SIMULATION

The simulation starts by reading the input files. There are four input files. The files are the environment file, occupant file, inter-occupant file and defect placement file.

Environment file is the main control file of the simulation. It contains all the names of other files and controls the migration mechanisms of the program. In addition, it contains the conditions for terminating the simulation, the temperature, the diffusion mechanisms which are to be simulated, and the periodic boundaries of the simulated crystal, compound (diamond structure or zinc-blende structure) and the seed for the random number generator.

The occupant file contains all data about each particular type of defect. This file carries all the information about energy of the defects in the lattice. The number of defects is set to nine and hence this file contains nine energy values. For each occupant, there may be one interstitial type, although there may be different interstitial types for different occupant.

The inter-occupant file describes the interaction between the different occupants. It contains the bond energy between every possible pair occupant types and the interstitial-lattice binding energy between every interstitial type of one species and all other species.

The defect placement file contains all the defects and their coordinates of a simulation. This file defines the initial defect configuration of the simulated crystal. In this file, the position of the defects are listed in Cartesian coordinates (in units of the lattice constant a).

The program starts in the main routine by initializing a set of global data. After initializing the global data, the program then reads the information contained in the environment file. It keeps on setting up the configuration according to the desired mechanisms, modes with the occupants and interstitial types contained in the occupant and inter-occupant file. The next step is the processing of the defect placement file, which represents the initial defect configuration. The parameters from these files are used to create mobile list (vacancies and interstitials). All defects, the mobile and the static ones, are then entered into the defect list, which has been implemented as a hash-table that is chained in both directions to ensure a fast look-up of each defect. Then the neighbours of the mobiles are identified and the required data is collected.

After obtaining all the required data, the simulation starts. A major part of it is the calculation of the probability p_tot, that any of the mobile defects will hop, which is the sum of the hop probabilities of each mobile.

The program checks through the mobile list to see whether the hop probability for each mobile that has been calculated is still valid. If not, it will recalculate this value, depending on the mobile, its vicinity, and the simulation configuration. If the mobile defect under consideration is a vacancy, the bond energy of all its neighbours has to be added up to get the activation energy.

For an interstitial, we have to take not only the direct interstitial migration into account, but also the probability of a hop onto a nearest lattice neighbour, which could result in a Frank-Turnbull or a kick-out event. Last, but not least, the reverse Frank-Turnbull mechanism that is interstitial-vacancy mechanism is considered.

Having calculated p_tot, the average time until a hop occurs is

$$<T> = 1 / p_tot. \quad (13)$$

This virtual time is expressed in units of phonon periods. It can be divided by the Debye frequency of the crystal to convert it into the experimental time in seconds. Random number generator is used to decide which event is to occur after <T>. The random number generator provides a random number, r in the range $0 \leq r < 1$. The quantity

$$p_critical = p_tot \times r \quad (14)$$

determines which event is to take place. This is accomplished by adding up all partial probabilities of the possible mechanisms, until the sum becomes greater then p_critical. The event with the probabilities, which was added up last, is the chosen one. This also determines the direction of the hop.

After the chosen event is simulated, the neighbours will be "informed". The affected defects are moved and the mobile list is updated by tagging the atoms in the neighbourhood, resulting in a recalculation only of the hop probabilities in the next call of those defects which are located in the vicinity of the moving atom. The migration continues until one of the limit parameters, which are set in the environment file, is exceeded. The result is displayed on monitor as well as printed on an output file with updated defects, their coordinates and the virtual time in which the simulation was performed. The information about the diffusion on a microscopic level both in space and time is also included in the output file. The flowchart of this program is shown in Figure 3.

RESULTS AND DISCUSSIONS

Considering only the vacancy and interstitial mechanisms, Figure 4 shows that the vacancy mechanism dominates over the interstitial mechanisms. Interstitial mechanism starts to appear only when the temperature reaches 800 K. Only at this temperature the atoms have obtained enough energy to diffuse via interstitial mechanism. After that temperature, interstitial mechanism increases steadily with the temperature. Up to 1800 K, vacancy mechanism still dominates but the dominance decreases to 95% and tends to decrease further as the temperature increases. It is clear that the vacancy mechanism requires less energy to diffuse compared to interstitial mechanism.

When diffusion by kick-out mechanism is included, vacancy mechanism still dominates. Kick-out mechanism starts to appear at 670 K (Figure 5), much earlier than interstitial. Interstitial mechanism started to appear only at 850 K. Interstitial mechanism appears much later if kick-out mechanism is included because the atom that diffuses by interstitial mechanism earlier, now had diffused via kick-out. Break-even point between interstitial and kick-out appears at 1600 K. At this point the amount of atoms that diffuse via interstitial and kick-out are the same.

When all the major diffusion mechanisms (vacancy, interstitial, kick out, Frank-Turnbull and interstitial-vacancy) are considered, everything is the same as previously (Figure 6) till 1500 K because Frank-Turnbull and interstitial-vacancy mechanisms only appear at that temperature (Figure 7). In Frank-Turnbull and interstitial-vacancy mechanisms, the dominance of vacancy mechanism shows steep decrease from 1500 K to 1600 K while kick-out shows steep increase. The steep decrease in vacancy and increase in kick-out are due to interstitial-vacancy mechanism. Interstitial-vacancy mechanism is the opposite of Frank-Turnbull mechanism. This mechanism increases the amount of defects. The increase of interstitial of Au increases the kick-out mechanism. After that temperature, it does not show much increase. Frank-Turnbull and interstitial-vacancy mechanisms increase up to 1700 K and do not show much increase beyond that.

The dominance of vacancy diffusion decreases with temperature until 1700 K and remains unchanged beyond that temperature. Interstitial mechanism and kick-out mechanism increase with temperature until 1700 K and remains unchanged beyond that temperature. Frank-Turnbull and interstitial-vacancy mechanisms appear only at

1500 K, increase until 1700 K and remain the same as the temperature increases further.

CONCLUSIONS

Diffusion by vacancy mechanism is the only kind of diffusion to occur at temperatures below 800 K. When kick-out mechanism is included, the total dominance of vacancy mechanism is only at temperatures below 670 K. After 900 K, kick-out mechanism increases with the temperature. Interstitial mechanism appears only at 850 K. Frank-Turnbull mechanism occurs at 1500 K and increases up to 1700 K. Interstitial-vacancy mechanism correlates with Frank-Turnbull mechanism because they are the opposite of each other. After 1600 K, there is no change in the dominance of the vacancy mechanism.

The dominance of the vacancy mechanism remains at around 92%, with the interstitial mechanism at about 2%, while the kick-out mechanism remains stable at above 5%.

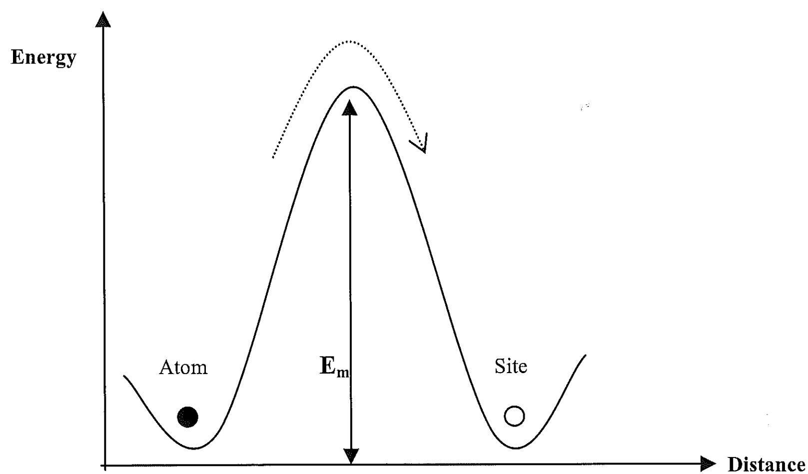


Figure 1. Order for atom to jump through activation energy

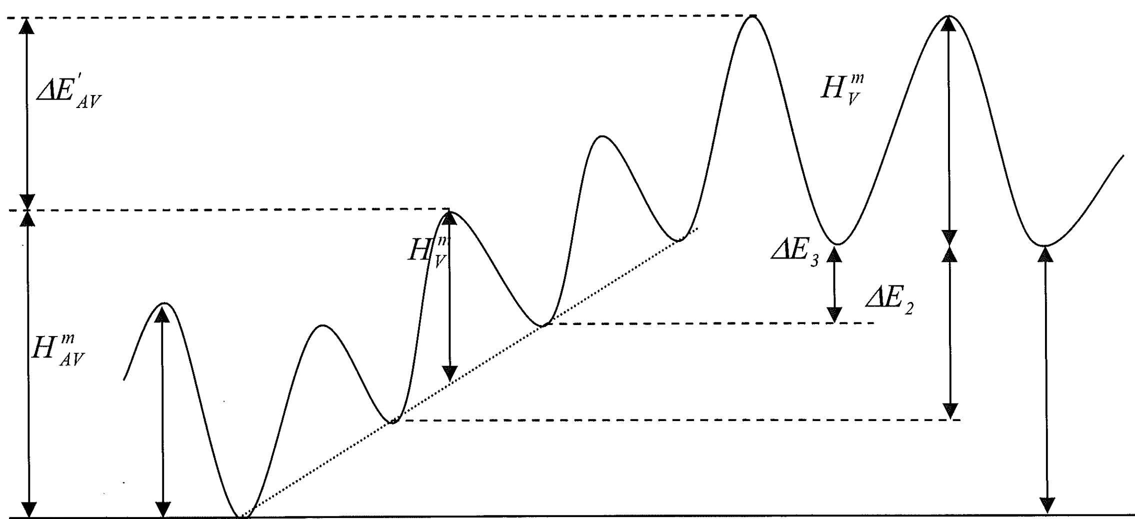


Figure 2. Vacancy potential as a function of neighbour distance from dopant atom, as assumed by Dunham and Wu [5]

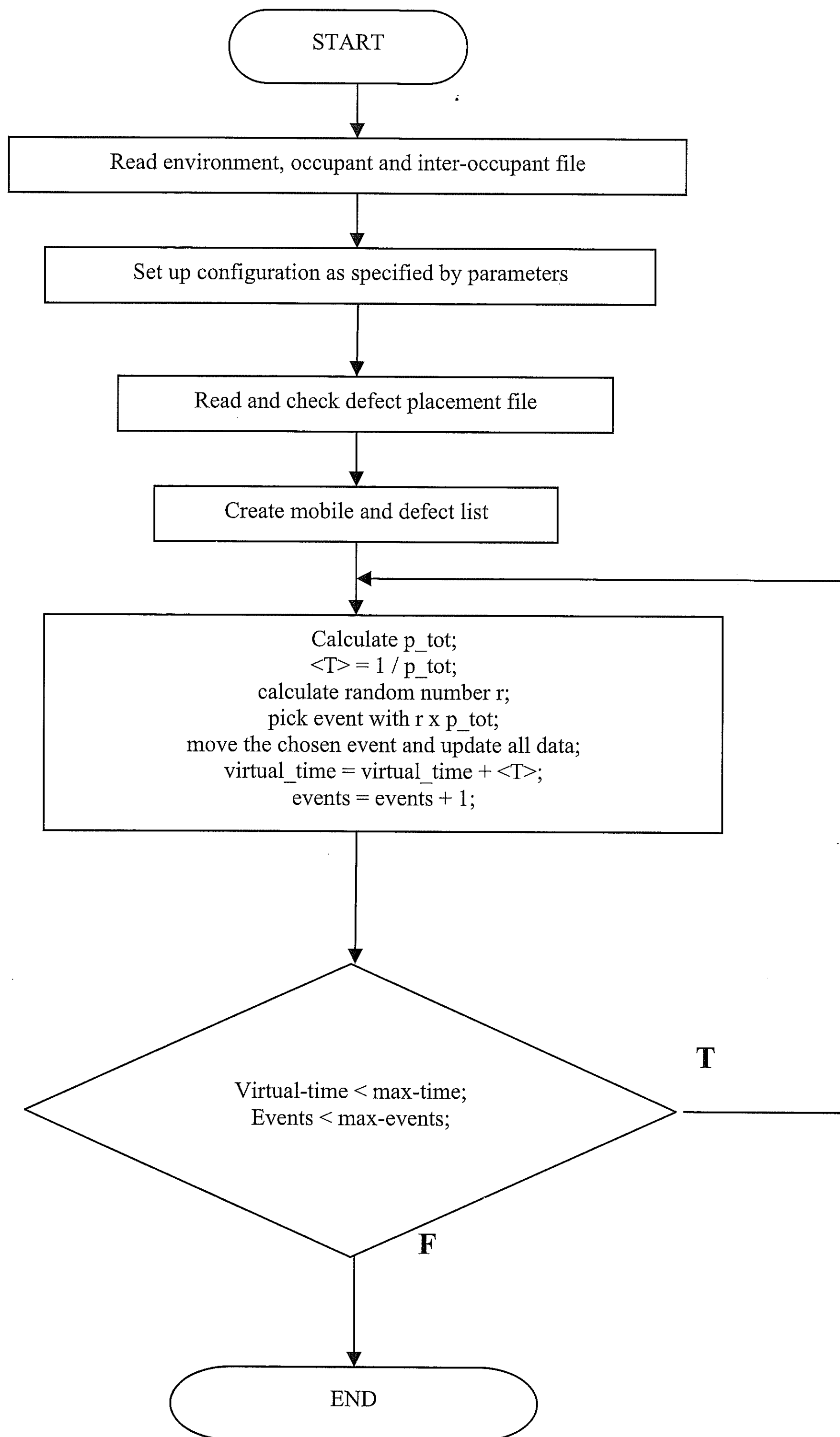


Figure 3. Flowchart of the program

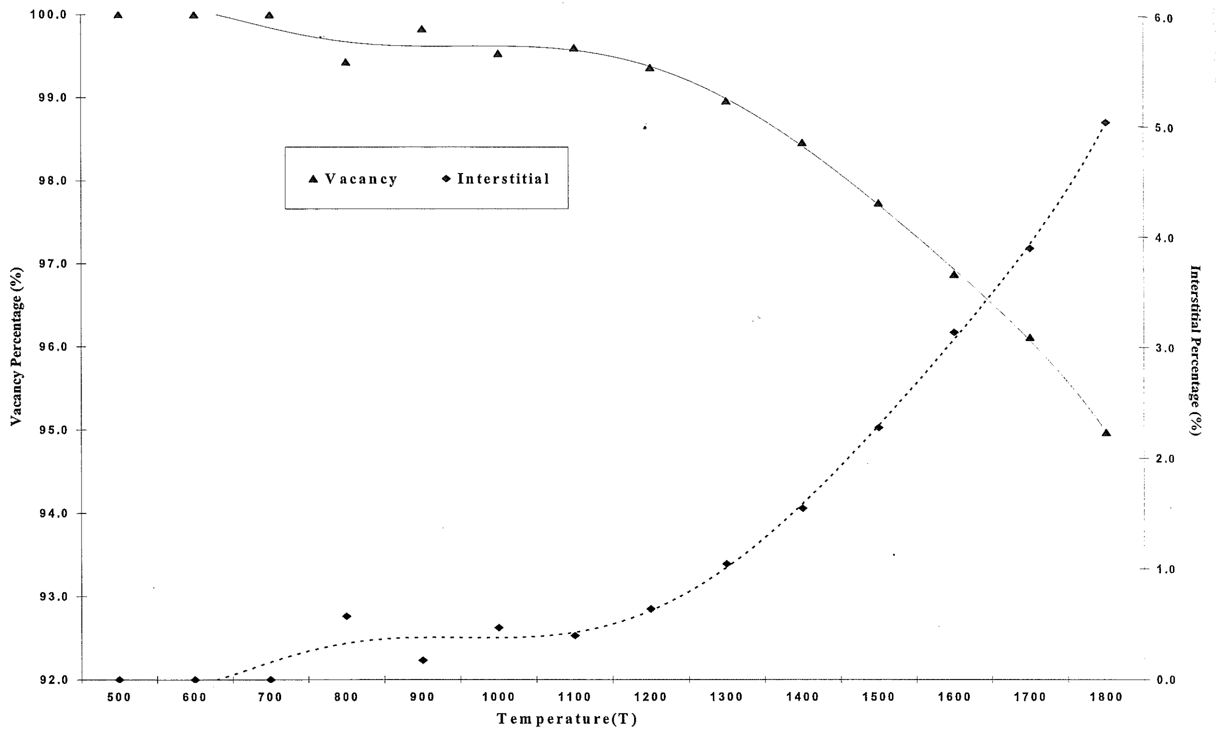


Figure 4. Graph Percentage(%) vs Temperature for Vacancy and Interstitial Mechanism

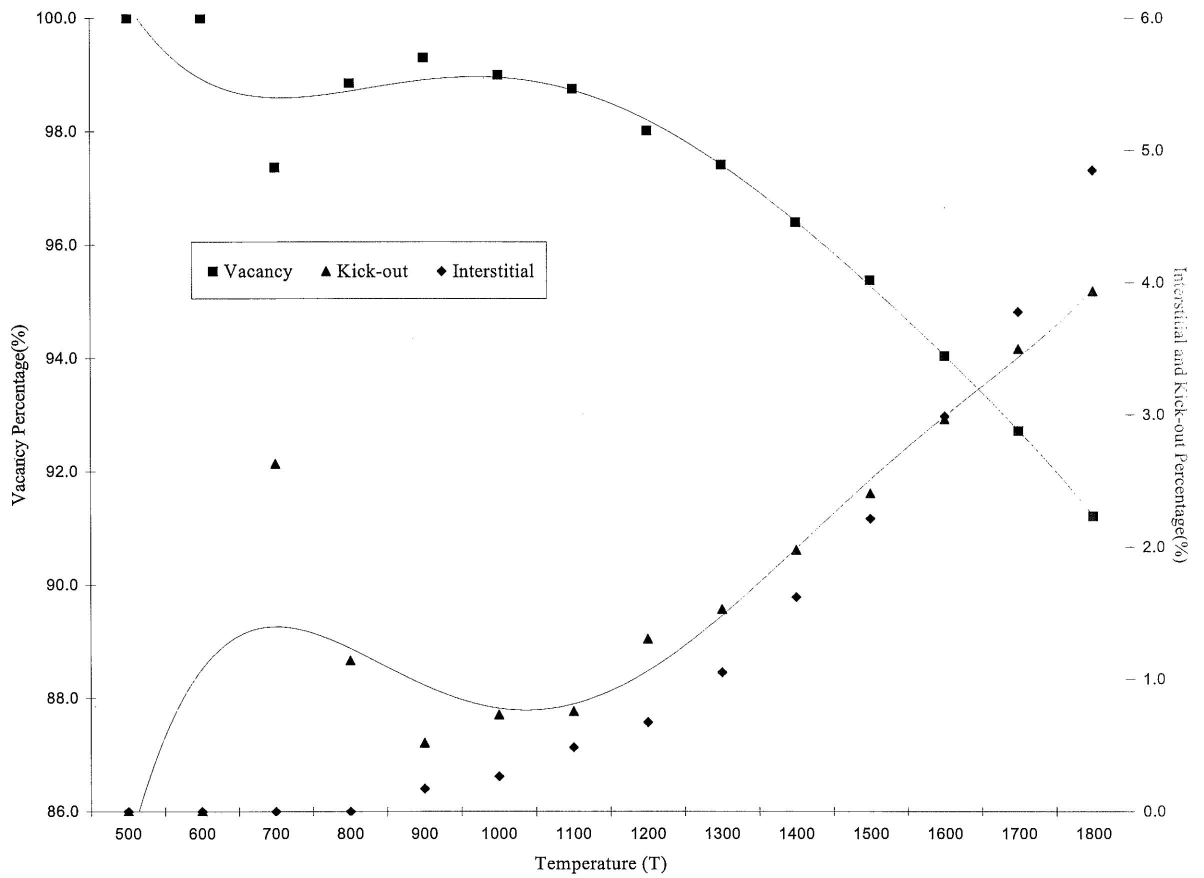


Figure 5. Graph Percentage(%) vs Temperature(T) for Vacancy, Kick-out and Interstitial Mechanism

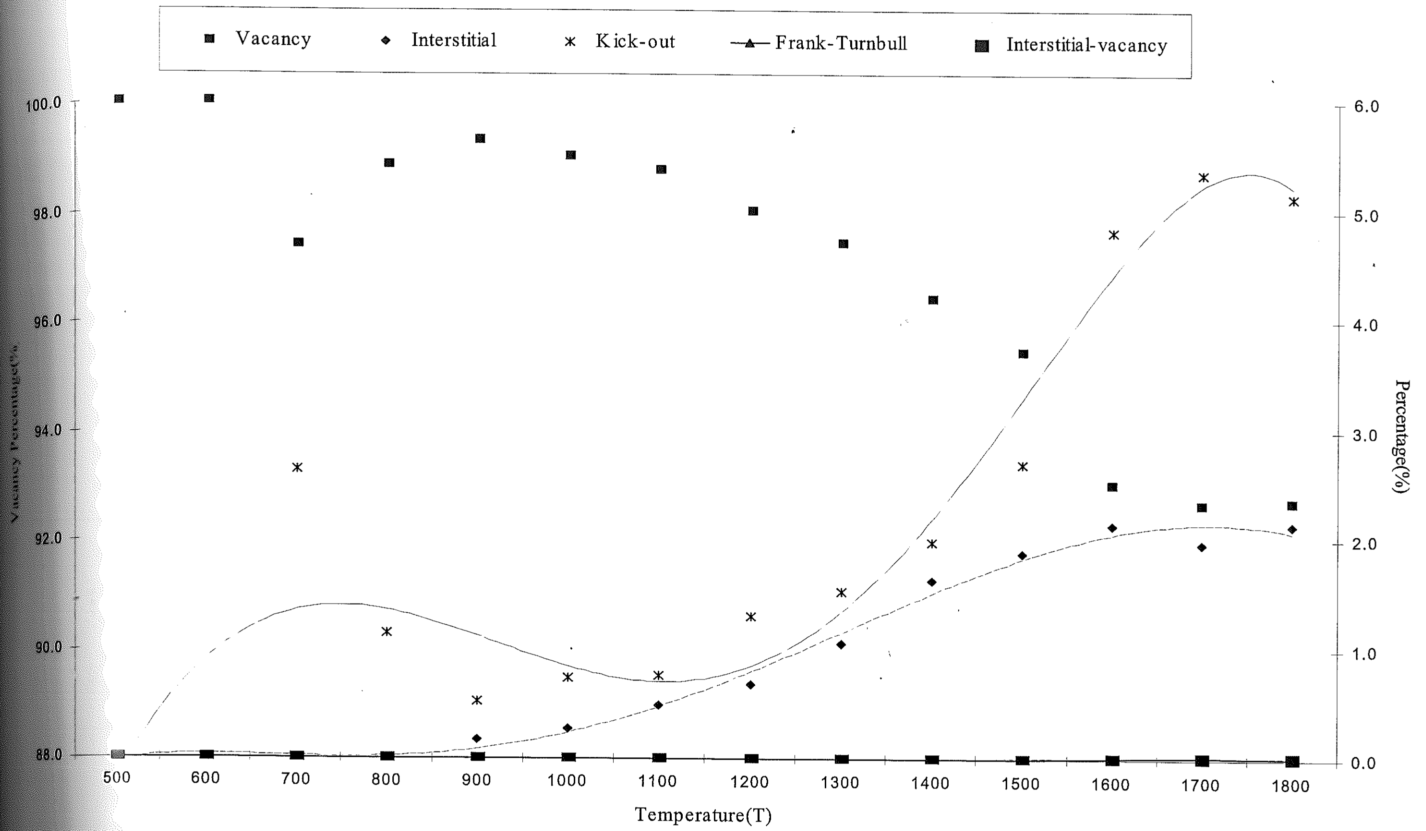


Figure 6. Graph Percentage(%) vs Temperature(T) for all Diffusion Mechanism

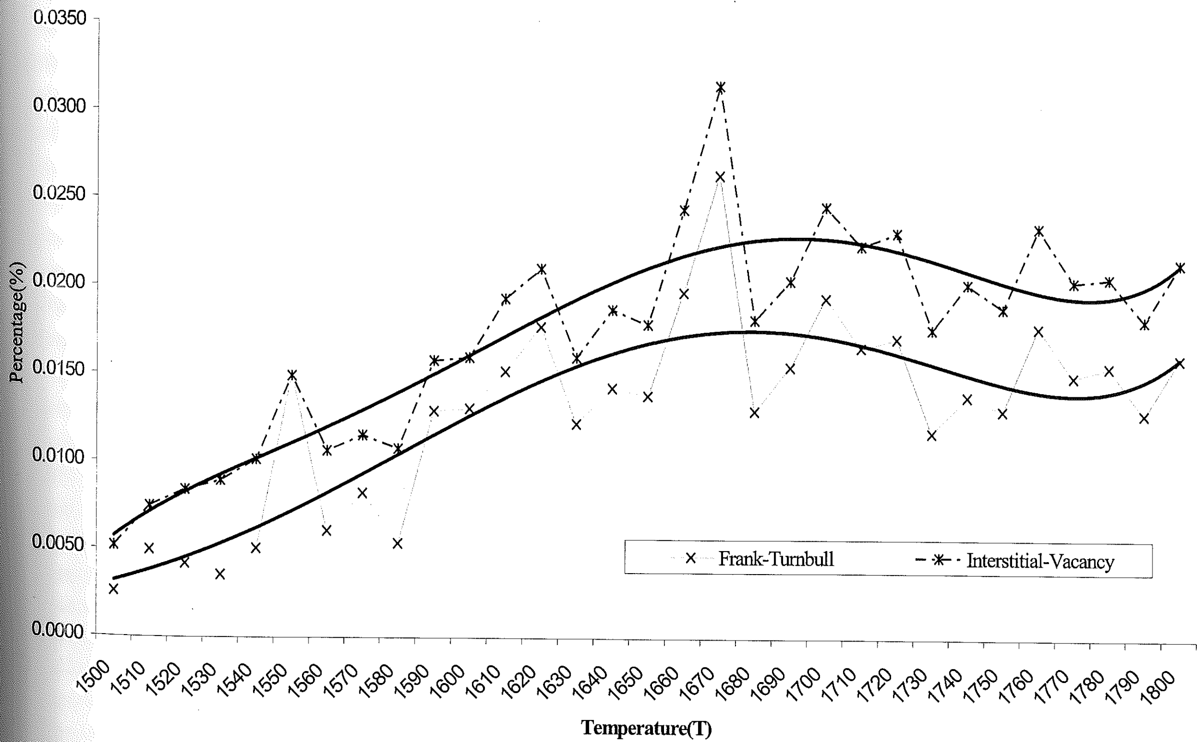


Figure 7. Graph Percentage(%) vs Temperature(T) for Frank-Turnbull and Interstitial-Vacancy Mechanism

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