

Lattice dynamical investigations on Zn diffusion in zinc oxide

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Abstract. Zinc self diffusion in bulk zinc oxide is studied by lattice dynamical approach here to get more insight into the diffusion in nano ZnO. The results reveal that only cationic self diffusion is dominant over anionic self diffusion and that too by single vacancy mechanism. The results are compared with the available experiments and discussed.

Keywords. Self diffusion; zinc oxide; lattice dynamics.

1. Introduction

Self-diffusion is the most fundamental and important transport property in solids. In recent years, various reports on diffusion from different groups are available for the most promising material, zinc oxide (ZnO). ZnO is a direct bandgap semiconductor with $E_g = 3.37$ eV and large exciton binding energy, 60 meV. Zinc oxide doped with magnetic impurities plays an important role in spintronics and is the most promising among all the diluted magnetic semiconductors (DMS) showing ferromagnetism at or above room temperature (Sharma *et al* 2003). The theory proposed by Dietl *et al* (2000) predicts room temperature ferromagnetism for Mn-doped (*p*-type) ZnO. In addition to Dietl's prediction, ferromagnetism in magnetically doped ZnO has been theoretically investigated by *ab initio* calculations based on the local density approximation. Recently, results are available for the enhancement of transport properties in nano ZnO (Serrano *et al* 2004) when compared to bulk.

Photodetectors, blue and ultraviolet laser diodes, transparent field effect transistors, etc. are the immediate applications of ZnO. The growth of ZnO in the zinc-blende structure could improve optoelectronic devices such as AlN and GaN (Raji *et al* 2005). A large number of experimental studies for the self diffusion of zinc in ZnO are available but no consensus on diffusion coefficient and migration mechanism could be achieved, as no two diffusion experiments have given the same results. For example, Tomlins *et al* (1998, 2000) recently reported an experimental study on the self diffusion in ZnO by tracer isotope technique in which both cationic (Tomlins *et al* 2000) and anionic diffusions (Tomlins *et al* 1998) were studied. Their results reveal that the Zn diffusion in ZnO is predominantly through single vacancy.

This has been echoed recently by Erhart and Albe (2006a, b) and so they carried out a theoretical study on diffusion. This is mostly by using VASP, a simulation software. So a systematic theoretical investigation is very much essential to understand the diffusion in ZnO. Still the theoretical understanding on many of the transport properties in ZnO is sparse. Erhart and Albe (2006a, b) have done first principle investigations in self diffusion of ZnO on both zinc and oxygen diffusion. In that report it has been clearly stated that the diffusion mechanism is assisted by single vacancy. But another experimental work by Secco and Moore (1957) clearly states that the diffusion may be through interstitial. In order to verify these results, a lattice dynamical investigation on diffusion in ZnO becomes very important. Also, since at present we study the particle and thermal diffusion in nano ZnO, it becomes necessary to study the atomic diffusion in bulk ZnO first, as theoretical works on this aspect is also very sparse in the literature. The experimental results reported by different groups also deviates from one another for the diffusion coefficient (Moore and Williams 1959; Kim 1971).

Shaw (1988) has brought out a review on diffusion process in II–VI systems, where the self diffusion is predominantly through single vacancy. Recently, Tomlins *et al* (1998, 2000) experimentally measured self diffusion in ZnO using isotopes ^{64}Zn and ^{66}Zn by radiotracer technique and the results are available for both cationic and anionic diffusions.

2. Theory

Atomic diffusion in solids occurs when any of the following defects are present (i) vacancy, (ii) interstitial, or (iii) substitutional. Diffusion in solids is the result of thermally activated hops of impurity atoms and defects which is governed by Fick's law,

$$J_N = -D\nabla N, \quad (1)$$

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where J_N is the number of atoms of one species in the solid crossing unit area in unit time, N the concentration of the species in the solid, D the diffusion coefficient. The diffusion coefficient varies with temperature, T as

$$D = D_0 \exp(-Q/K_B T), \quad (2)$$

where Q is the activation energy, K_B the Boltzmann constant. The diffusing atom should possess an energy atleast equal or greater than the activation energy and then only the diffusing atom can hop the barrier. The jump frequency Γ for diffusion is

$$\Gamma = \Gamma_0 \exp(-Q/KT), \quad (3)$$

where Γ_0 is the attempt frequency to cross the barrier, and the exponent term is the probability with which the atom crosses the barrier.

2.1 Achar's diffusion theory

Based on the theory developed by Achar (1970) for the diffusion in metals, jump frequency of the diffusing atoms are computed to find out the most probable mechanism.

Generally the diffusion of an atom in a crystal takes place through discrete jumps between the defect and the diffusing atom. According to the theory developed, a ring formed by the neighbours restricts the jump of the diffusing atom. This ring, in general, will be constructed from the neighbours lying in the same plane and perpendicular to the direction of jump of the diffusing atom. When a ring of neighbouring atoms obstructs it, the diffusing atom should overcome the barrier for the jump to materialize. Instantaneous relative displacement of the diffusing atom with respect to the neighbours in the diffusion ring is given as a reaction coordinate,

$$X = \left(u^\alpha - \frac{1}{n} \sum_i u^i \right) \hat{X}, \quad (4)$$

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

The reaction coordinate for all modes can be written as

$$X = \sum_{q,\lambda} X(q,\lambda), \quad (5)$$

where $X(q,\lambda)$ is the contribution to the fluctuation in the reaction coordinate due to the (q,λ) mode. The atomic jump occurs when the fluctuation in X exceeds a critical value X_c , given by

$$\left| \sum_{q,\lambda} X(q,\lambda) - X_c = 0 \right|. \quad (6)$$

The atomic jump frequencies are calculated from

$$\Gamma = \left[\frac{\sum_{q,\lambda} \omega^2(q,\lambda) |X(q,\lambda)|^2}{\sum_{q,\lambda} |X(q,\lambda)|^2} \right]^{1/2} \exp\left(-\frac{X_c^2}{\sum_{q,\lambda} |X(q,\lambda)|^2}\right), \quad (7)$$

where ω is the phonon frequency of the mode (q,λ) and the attempt frequency Γ_0 is

$$\Gamma_0 = \left[\frac{\sum_{q,\lambda} \omega^2(q,\lambda) |X(q,\lambda)|^2}{\sum_{q,\lambda} |X(q,\lambda)|^2} \right]^{1/2}. \quad (7a)$$

When diffusion takes place, the force constant is softened or strengthened depending upon the diffusing atom, due to relaxation. Based on the force constant changes, two kinds of contributions can be assumed for the defects: (i) passive role and (ii) active role for defects.

2.2 Passive role for defects

In the passive role, the change in force constant is considered small; when the diffusion process takes place, i.e. no change in force constants are assumed.

The displacement of the diffusing atom is given as

$$|u^\alpha(q,\lambda)|^2 = \frac{1}{nm_k} \left\{ [1 - \varepsilon \omega^2(q,\lambda) \tilde{G}_0(\omega^2)]^2 + \pi^2 \varepsilon^2 \omega^2(q,\lambda) G_0(\omega^2) \right\}^{-1}, \quad (8)$$

where $\varepsilon = 1 - (m_\alpha/m_k)$ is the mass defect parameter; $G_0(\omega^2)$ the Green's distribution function for squared frequencies and $\tilde{G}_0(\omega^2)$ the Hilbert transform of $G_0(\omega^2)$; m_k the mass of the host atom and n the number of atoms in the unit cell. The displacement of the other atoms in the diffusing ring is calculated using the harmonic approximation as

$$u_0(q,\lambda) = \left[\frac{\hbar}{2nm_k \omega(q,\lambda)} \right]^{1/2} e_k(q,\lambda) \exp(iq \cdot r), \quad (9)$$

where e is the polarization vector.

Phonon frequencies of the host lattice are calculated from the modified rigid ion model and the Green's functions are also obtained (Maradudin *et al* 1971), which are essential for the calculations of the displacements of the diffusing and other atoms and also the jump frequency.

Table 1. Rigid ion model parameters.

A	B	C1	D1	E1	F1	C2	D2	E2	F2	Z
-4.45	-3.0	-1.2	-5.4	0	-1.44	-0.8	1.15	0.0	0.05	0.65

(All parameters except Z are in the units of 10^{-4} dynes/cm)

2.3 Active role for defects

The presence of defects causes relaxation of the neighbours with the appearance of new modes. The displacements of the atoms due to the presence of impurity is considered as a perturbation in the form of matrix called scattering matrix (Plumelle and Vandevyuer 1976). When a plane wave u_0 passes through the defect space consisting of the defect and the neighbours in the diffusion ring, the defect problem has to be treated as scattering mechanism with u as the displacement matrix giving the displacement of the scattered wave w , as $u = u_{(0)} + w$, where the matrix u_0 corresponds to the displacement matrix of a perfect lattice to be obtained from the solution of the time independent equation (9) and the solution is $Lu_0 = 0$, where the matrix L is defined in terms of the force constants, Φ , as

$$L_{\alpha\beta}(ll'; kk'; \omega^2) = m_k \omega^2 \delta_{ll'} \delta_{kk'} \delta_{\alpha\beta} - \Phi_{\alpha\beta}^0(ll'; kk'). \quad (10)$$

The scattered wave matrix is given as

$$w = G \left(\frac{\partial L}{I - G \partial L} \right) u_0,$$

where I is the unit matrix, G the Green's functions matrix, L corresponds to the vibrations of the perfect host crystal and

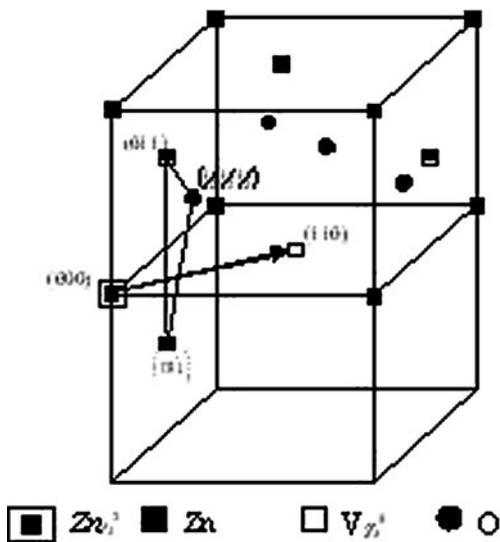


Figure 1. Single vacancy mechanism (atomic positions are given in units of $x = a/2$).

∂L the perturbation matrix, all matrix being of the order of $3(n+1) \times 3(n+1)$, where n is the number of neighbours in the ring which obstructs the jump and additional 3 degrees of freedom corresponds to the defect atom. The Green function is written as

$$G_{\alpha\beta} \left(\begin{matrix} l & l' \\ k & k' \end{matrix}; \omega^2 \right) = \frac{1}{N \sqrt{m_k m_{k'}}} \sum_{qj} \left[\frac{e_{\alpha} \left[(k|\bar{q}j) e_{\alpha}^* \left[2\pi i \bar{q} \cdot \bar{r} \left(\begin{matrix} l & l' \\ k & k' \end{matrix} \right) \right] \right]}{\left[\omega^2 - \omega_j^2(\bar{q}) \right]} \right]. \quad (11)$$

Using the displacements of the diffusing atoms and the neighbours in the ring, the jump frequencies are calculated from (7).

2.4 Isotope effect

The isotope effect, a measure of the diffusion rate is given by

$$\Delta K = \frac{(\Gamma_1/\Gamma_2) - 1}{\sqrt{m_2/m_1} - 1}, \quad (12)$$

where Γ_1, Γ_2 are the jump frequencies of the isotopes 1 and 2 with masses m_1 and m_2 , respectively.

With the attempt jump frequency, the pre-exponential factor $D_0, D = D_0 \exp(-Q/KT)$ is estimated where, $D_0 = (H\Gamma_0 d^2/2s\pi)$, where H is the Haven's ratio, s the number of identical jumps, d the jump distance. H and s are 0.78146 and 12, respectively for the zinc blende structure.

Table 2. Attempt frequencies at various temperatures isotopic Zn diffusion via single vacancy (passive role).

Temp. (K)	Attempt frequency (10^{14} rad/s)		ΔK (%)
	Γ_1 (Zn^{64})	Γ_1 (Zn^{66})	
700	0.45568	0.45191	53.7
900	0.42731	0.42375	54.1
1100	0.40652	0.40314	54.0
1200	0.39822	0.39493	53.7

Table 3. Attempt frequencies at various temperatures of Zn diffusion via single interstitials (passive role).

Temp. (K)	Attempt frequency (10^{14} rad/s)				ΔK (%)
	Γ_I (Zn^{64})	Γ_{II} (Zn^{64})	Γ_I (Zn^{66})	Γ_{II} (Zn^{66})	
700	0.453238	0.315009	0.448204	0.312514	62.0
900	0.425261	0.313936	0.420478	0.311465	62.3
1100	0.404838	0.313386	0.400266	0.310927	62.4
1200	0.396706	0.313207	0.392224	0.310752	62.5

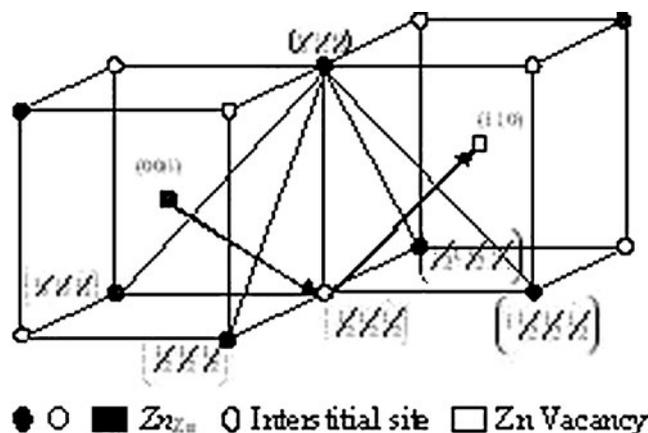
3. Results and discussion

The phonon frequencies and eigen displacements for ZnO are first estimated for the entire Brillouin zone with 48 allowed wave vectors, by employing the rigid ion model and the parameters listed in table 1. This is first compared with the experimental phonons. The agreement was good and so the Green functions are computed from the phonon frequencies and displacements of ZnO. This is also verified by computing the Debye–Waller factor.

3.1 Single vacancy mechanism

In this mechanism, a substitutional foreign or self-atom diffusing by jumping into the nearby vacancy, acts as the diffusion vehicle. In our case of self-diffusion of Zn, the most abundant isotopes, ^{64}Zn and ^{66}Zn , are considered. The Zn isotope will be initially assumed to occupy a positively charged substitutional site Zn_{Zn}^+ at (0 0 0). It diffuses by jumping into a nearby negatively charged vacant site V_{Zn}^- at (1 1 0). The ring of neighbours obstructing the jump is given in figure 1. It has only three atoms in positions $Zn(0\ 1\ 1)$, $Zn(0\ \bar{1}\ 1)$ and $O(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, which lie in a plane perpendicular to the jump direction (1 1 0).

First the single-vacancy mechanism for passive role is considered, using the Green's distribution function and

**Figure 2.** Vacancy assisted interstitial (atomic positions are given in units of $x = a/2$).

displacements of atoms, the attempt jump frequency for ^{64}Zn is computed using (7a) for various temperatures between 700 K and 1500 K. Same procedure is repeated for the other most abundant ^{66}Zn and from the two attempt frequencies of these isotopes; the isotope effect is computed and is given in table 2 which is around 54%.

3.2 Vacancy assisted interstitial mechanism

Considering the possibility of interstitial diffusion mechanism, we have attempted this computation also; the mode of transport is given in figure 2. The jumping Zn atom is initially assumed at (0 0 0) site; it first goes to the interstitial site at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ in $[1\ 1\ \bar{1}]$ direction and then to Zn vacancy at (1 1 0) site in $[1\ 1\ 1]$ direction. The resulting jump is $[1\ 1\ 0]$.

For Zn self diffusion in ZnO, the jump frequencies of two jumps are estimated for the passive role of defects in the temperature range 700–1500 K. The resultant jump frequency is taken as the geometric mean of the two jump frequencies. The same procedure is repeated for the other isotope. The results are listed in table 3 and the isotope effect is around 62%.

As there is not much difference between the isotope effects of single vacancy and interstitial mechanisms, we refined the calculations by assuming an active role of defects.

By applying the principles of active role of defects discussed above, the isotope effects are calculated for both the single vacancy and interstitial mechanisms and now a clear distinction could be made between the different diffusion mechanisms. The isotopic effect for the single vacancy mechanism by active role is around 65%, whereas for the interstitial mechanism it is just around 33%, which are given in tables 4 and 5, respectively.

Table 4. Attempt frequencies at various temperatures of Zn diffusion via single vacancy (active role).

Temp. (K)	Attempt frequency (10^{14} rad/s)		ΔK (%)
	Γ_I (Zn^{64})	Γ_I (Zn^{66})	
700	0.65030	0.64376	65.5
900	0.64599	0.63941	66.3
1100	0.64372	0.63713	66.7
1200	0.64297	0.63637	66.8

Table 5. Attempt frequencies at various temperatures of Zn diffusion via single interstitials (active role).

Temp. (K)	Attempt frequency (10^{14} rad/s)				ΔK (%)
	Γ_I (Zn ⁶⁴)	Γ_{II} (Zn ⁶⁴)	Γ_I (Zn ⁶⁶)	Γ_{II} (Zn ⁶⁶)	
700	0.05336	0.05342	0.85007	0.84054	32.5
900	0.05335	0.05342	0.84374	0.83410	32.9
1100	0.05335	0.05341	0.84036	0.83065	33.6
1200	0.05334	0.05341	0.83924	0.82949	33.3

The same procedure is repeated for anionic isotopic diffusion too, but this case has been ruled out as the isotopic effects are less than 50% in both the single vacancy and interstitial mechanisms. As one considers all the changes in the force constants, it is better to rely on the active role of defects, as the ΔK values of both single vacancy and interstitial in the passive role is close by. Our results on the active role of defects shows clearly that the single vacancy mechanism is the most probable mechanism for the isotopic Zn diffusion in ZnO agreeing well with the experiment.

The pre-exponential factor for cation diffusion for ZnO is found to be 4.54×10^{-4} . Since no other experimental works on this ZnO are available, this is compared with other metal oxides like Cr₂O₃ and FeO, where it is 10^{-9} and 10^{-5} , respectively. This also supports that the self diffusion in ZnO is mainly through single vacancy and hence the diffusivity is given as $D(\text{cm}^2/\text{s}) = 4.54 \times 10^{-3} \exp[(-2.84)\text{eV}/\text{kT}]$ and this agrees fairly well with the value of $D(\text{cm}^2/\text{s}) = 1.57 \times 10^{-3} \exp[(-2.66 \pm 0.26)\text{eV}/\text{kT}]$ (Serrano *et al* 2004).

4. Conclusions

The interpretation of diffusion experiments is becoming more and more difficult because of the availability of vast number of diffusion results by various groups but with less reliability. This has been again stressed recently by Erhart and Albe (2006a, b), even though in 1988, Shaw had tried to correlate the different results available at the time for diffusion. Since ZnO is being studied now both in bulk and nano forms for its outstanding uses in various fields of optoelectronics, and also the lattice imperfections and defects in ZnO affect drastically all the material properties, a theoretical investigation on the diffusion in ZnO becomes inevitable. Erhart and Albe (2006a) have brought out a theoretical calculation on this and concluded that at temperatures below room temperature, the self diffusion is through interstitial and above room temperatures, this diffusion is mainly through single vacancy.

Here, in our work, employing Achar's theory and scattering matrix formalism, various diffusion mechanisms for self

diffusion in ZnO are analyzed for passive and active role of defects by lattice dynamical investigations. From the investigations it is concluded that the cationic self diffusion mechanism is most likely through single vacancy at temperatures above room temperature. This agrees fairly with the result of Erhart and Albe (and their calculations are not on the basis of lattice dynamics). The experiment by Nogueira *et al* (2003) for diffusivity agrees with our calculations, even though there is a scatter of data with other experiments available.

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