INFLUENCE OF POINT DEFECTS' CONCENTRATION ON THE ZnO MATRIX – A SIMULATION STUDY

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ABSTRACT

Numerical simulations of the effect of the presence of point defects in the matrix of ZnO were carried out using MATLAB computation procedure. The variation of impurity atom concentration with the energy gap was simulated. The plot obtained exhibited an exponential increase in energy gap with respect to the concentration of impurity atoms and corresponded to the theoretical solution of impurity modeling in ZnO. The computation procedures showed that oxygen vacancies and shallow donor nature of hydrogen impurities screen acceptor in ZnO. Oxygen interstitials were found to have high formation energies and were as such, unlikely to occur. The potentials and challenges of the application of ZnO for semiconductor devices were considered. Findings showed that recent studies of native point defects did not adequately explain the often observed n – type conductivity but that was rather accountable to the introduction of impurities at the processing stages.

Keywords: ZnO, Impurities, Oxygen Vacancies, Semiconductor Devices, Simulation

INTRODUCTION

Point defects include lattice defects such as interstitial atoms , vacant lattice sites and impurity atoms in substitutional or interstitial lattice sites. Deliberate or inadvertent insertion of the chemical defects into the matrix of an electronic material alters the electronic properties of the material and constitutes the basis for device fabrication and control. Point defects result in highly localized distortion of energy band structure in their vicinity, leading to the formation of trapping sites for free carriers. Consequently, carrier is inversely related to defect concentration (Ghandi, 1968).

Zinc oxide (ZnO) has shown great promise as n – type wide band gap semiconductor with a range of optical, electronic and mechanical applications. Its wide gap of 3.0eV at room temperature opens the possibility of creating UV light emitting diodes. A photoluminescence depending on substrate and post annealing temperature has been found to arise from the presence of oxygen vacancies in a layer just below the ZnO crystallite surface (Studenikin *et al.*, 1998) ZnO is relatively cheap, abundant and more chemically stable with low processing temperatures and readily available doping materials. Its high electron mobility, high thermal conductivity, direct band gap and large exciton binding energy make it suitable for a range of devices (Janotti and Van de Walle 2009).

Fouchet *et al.*, (2006) reported ferromagnetism associated with a large amount of defects close to the interface in - Codoped zinc oxide thin films. Similarly optical absorption studies by Zhao *et al.*, (2010) revealed that band energy of $Zn_{1-x}Ni_xCo$ powder decreases with increasing Ni concentrations. Also (Ga, Co) – codoped ZnO thin films have been reported to exhibit carrier concentration dependent Hall effect (Xue – Chao *et al.*, 2011). Consequently, an understanding of the role of donor impurities in the ZnO matrix will inspire novel procedures for introducing acceptor dopants to control its n-type conductivity.

Theoretical studies based on Density Functional Theory (DFT) have been helpful in providing insight into the role of lattice point defects and presence of impurities on its n-type conductivity. Petit *et al.* (2006) used self-interaction corrected local spin density approximation to investigate the ground state vacancy configuration of impurities in n- and p-type ZnO. The calculation indicated that the donor level is situated in the gap with Fermi energy close to the conduction band minimum. Using DFT, Van de Walle (2000) showed evidence that hydrogen could be a shallow donor in ZnO, capable of contributing p-type conductivity. Moreover, contrary to the common notion that oxygen vacancies and zinc interstitials are sources of n-type conductivity, experimental

finding and accurate DFT calculations by Van de Walle (2001) showed this to be inconsistent. Nevertheless, Oba *et al* (2001) found that only zinc antisites (i.e. Zn atoms in oxygen sites) or interstitials can explain the n-type conductivity of undoped ZnO. In addition Janotti and Van de Walle (2005; 2006) asserted that oxygen vacancy is not a shallow donor but deep level below the conduction band and that native point defects, are unlikely to cause n-type conductivity.

We investigate in this work, the influence of the presence of impurities in the ZnO matrix by simulation using DFT. In this procedure the structure of pure zinc oxide is modelled using classical molecular dynamics (MD) simulation. The effect of lattice defect or impurity on the pure ZnO matrix is then simulated using MATLAB.

METHODOLOGY

Different approaches have been employed in investigating point defects in ZnO for the prediction of band gap, such as the local density approximation (LDA) and the generalized gradient approximation (GGA). However position of defect induced states with respect to the valence band maximum can be underestimated thus affecting the prediction of band gap (Janotti and Van de Walle, 2009).

The theoretical investigation is based on Density Functional Theory (DFT) in which the ZnO structure is simulated by classical molecular dynamics (MD). Molecular dynamics is a specialized discipline of molecular modelling and computer simulation based on statistical mechanics. In this work, statistical ensemble averages are assumed equal to time averages of the system, referred to as the ergodic hypothesis. It is often termed as Laplace's vision of Newtonian mechanics for predicting the future by animating nature's forces and allowing insight into molecular motion on an atomic scale. Molecular dynamics simulations generate information at the microscopic level, including atomic positions and velocities. These are convertible to macroscopic observables such as pressure, energy, heat capacities, etc. using statistical mechanics.

On the macroscopic scale, large number of atoms or molecules spanning vast configurations are represented by statistical averages defined in terms of ensemble averages, taken simultaneously over a large number of replicas of the system and corresponding to experimental observables. The ensemble average is defined by the equation:

$$\langle A \rangle_{ensemble} = \iint dP^N dr^N A(P^N, r^N) \rho(P^N, r^N) \quad (1)$$

where $A(P^N, rN)$ is the observable of interest expressed as function of momentum, P and position, r. The integration is over all possible variables of r and P. $\varrho(P^N, r^N)$ is the probability density of the ensemble, given by the equation:

$$\rho(P^N, r^N) = \frac{1}{Q} \exp \left[-\frac{H(P^N, r^N)}{k_B T} \right] \quad (2)$$

where H is the Hamiltonian, T is the absolute temperature, k_B is Boltzmann's constant and Q is the partition function given by:

$$Q = \iint dP^N dr^N exp[-H(P^N, r^N)/k_B T] \quad (3)$$

In this work, the points in the ensemble are calculated sequentially in time, passing through all possible states corresponding to particular thermodynamic constraints. For the time average of A, we have:

$$\langle A \rangle_{time} = \lim_{\tau \to \infty} \frac{1}{\tau} \int_{t=0}^{\tau} A(P^N(t), r^N(t)) dt = \frac{1}{M} \sum_{t=1}^{M} (P^N, r^N) \quad (4)$$

where t is the simulation time, M is the number of time steps in the simulation and $A(P^N, T^N)$ is the instantaneous value of A.

Considering defect concentrations and formation energies, it is shown that the presence of defects alters internal energy and entropy of the crystal: In the dilute regime where there is assumption of thermodynamic equilibrium and negligible defect-defect interaction, the concentration of a native defect C_s in a solid is determined by its formation energy E_f. If there are n defect sites per unit volume, we may-write the internal energy E as:

$$E = nE_f \quad (5)$$

In the dilute regime, volume change is negligible, so contributions to E_f from formation volume and formation entropy are small and can be neglected. Then the free energy may be written as:

$$F = E - TS \qquad (6)$$

Where S is the configurational entropy given by the equation:

$$S = k_B ln C_n^N \qquad (7)$$

And N is lattice sites per unit volume. Using Stirling's approximation in (7), we may write at equilibrium,

$$\left(\frac{\partial F}{\partial n}\right)_T = 0 \text{ and } E_f = k_B T \, ln \frac{N-n}{n} \qquad (8)$$

Hence

$$n = \frac{N}{1 + e^{E_f/K_B T}} \quad or \quad n = N e^{-E_f/k_B T} \qquad (9)$$

Equation (9) shows that defects with high formation energies occur in low concentrations and equilibrium concentration of defects changes with formation energy and temperature. The formation energy is computed from first principle and the density functional theory allows us to calculate the ground state total energy of systems of electrons subject to the Coulomb potential given by the nuclei or ions. In doing so, supercells containing up to several 100 atoms are periodically repeated in three dimensional space while interaction between defects in neighbouring supercells are assumed small.

For the case of an oxygen vacancy in *ZnO*, the formation energy is obtained from the equation:

$$E_f(V_O) = E_{tot}(V_q O) - E_{tot}(ZnO) + \mu_O + q(E_f + E_{VBM}) \quad (10)$$

where $E_{tot}(V_q O)$ is the total energy of a supercell containing the oxygen vacancy in the charge state *q*, $E_{tot}(ZnO)$ is the total energy of a *ZnO* perfect crystal in the same supercell, μ_o is the chemical potential and *VBM* is the valence band maximum. Expression (10) is applicable to all native point defects. The chemical potential μ_o can be related to experimental conditions that are either *Zn — rich* or *O — rich* or anything in between the two extremes.

The thermodynamic equilibrium and stability of *ZnO*, however, impose upper bound given by $\mu_{max\,O}$ = ½$E_{tot}(O_2)$, corresponding to *O — rich* condition and a lower bound $\mu_{max\,Zn} = E_{tot}(Zn)$, corresponding

to extreme *Zn — rich* condition. The upper bounds lead to lower bounds given by thermodynamic stability condition:

$$\mu_{zn} + \mu_o = -H_f(ZnO) \qquad (11)$$

where $-H_f(ZnO)$ is the enthalpy of formation of bulk *ZnO* (negative for a stable compound). Usually $H_f(ZnO)$ is $-3.5eV$ (theoretical) or $-3.6eV$ (experimental).

The fermi level in equation (10) is determined by the condition of charge neutrality. In principle, equation (5) can be formulated for every defect or impurity. The complete problem including free carrier concentration in valence and conduction bands can then be solved self-consistently by imposing the charge neutrality condition.

The plot of formation energies as a function of E_f helps to examine the behaviour of defects when doping concentration changes. The fermi level is taken with respect to the valence band maximum and can vary from 0 to *4,* where E_g is the fundamental band gap. E_{VBM} in equation (10) is taken from a calculation for the perfect crystal, corrected by aligning the averaged electrostatic potential in the perfect crystal and a bulk region of the supercell containing the defect. Formation energies of charged defects or impurities are corrected for the effects of finite size supercells. Defect-defect interactions in neighbouring supercells converge slowly with the supercell size and are proportional to q^2, where *q* is the charge state of the defect. The assumption of a dilute regime *(n << N)* is exigent as the sample will cease to show intrinsic behaviour when the impurity concentration N_D is large compared with carrier concentration *Nc* (Hall, 1985) i.e. when

$$N_D \geq N_C \exp\left[-E_g/2k_B T\right] \qquad (12)$$

RESULTS AND DISCUSSION

The simulation of the presence of impurities in varying percentage concentrations in the matrix of ZnO reveals corresponding changes in the value of the simulated energy gap. The plot of the energy gap (eV) against impurity concentration (%) is shown in Figure 1 while the presence of the impurity atoms in the ZnO matrix is as shown in Figure 2.
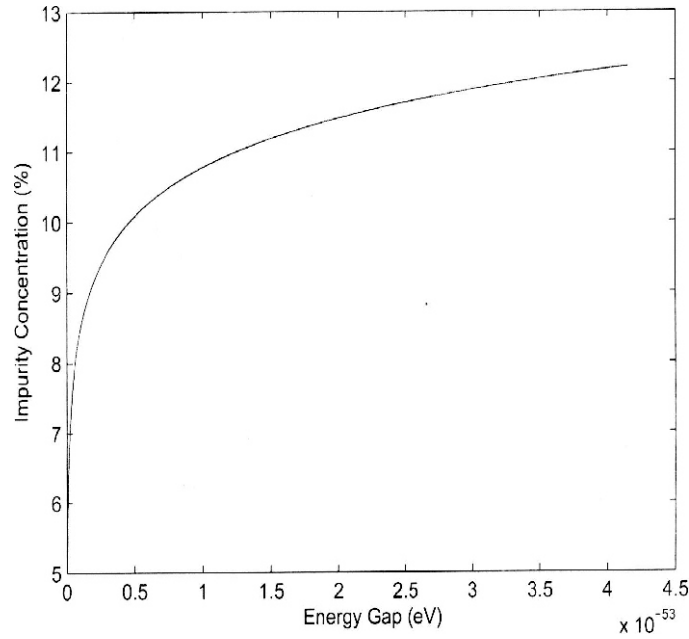
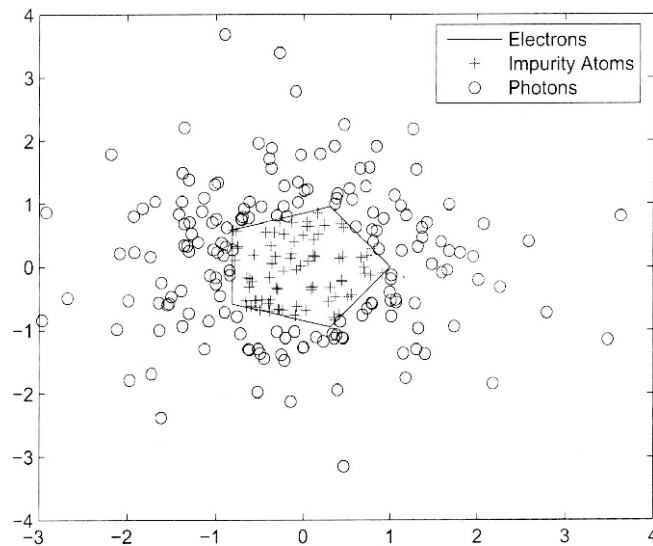Figure 1: Plot of the Energy Gap (eV) against Impurity Concentration

Figure 2: Impurity Atoms in ZnO Matrix

The plot (Figure 1) shows that there is no significant change in the value of the energy gap when the variation in impurity concentration was between 6 and 8 %. However, critical changes were observed for impurity concentrations between 9 and 10 %. An exponential increase in energy gap begins to occur at about 10.5 % impurity concentration, culminating in a threshold value of 11% and subsequently tends towards an asymptotic value.

Point defects induce occupied states in band gaps. Several calculations agree that oxygen and zinc vacancies are the lowest energy defects, followed by zinc interstitials and zinc in oxygen antisites, while oxygen interstitials and oxygen in zinc antisites are high in energy. Defects favoured by Zn-rich conditions are thought to act as donors while those favoured by oxygen-rich conditions act as acceptors (Janotti and Van de Walle, 2009). The oxygen vacancy related state in the energy gap has considerable contributions from Zn states. Oba *et al.* (2001) indicated that oxygen vacancy in the neutral charge state induces a doubly occupied single particle state and they submitted that only zinc antisites or zinc interstitials can explain the n-

type conductivity. Janotti and Van de Walle (2005) further established that oxygen vacancies in ZnO do not constitute shallow donors but deep levels. They confirmed that n-type conductivity could not be due to high formation energies of oxygen vacancies (Janotti and Van de Walle, 2006). Van de Walle (2000; 2001) earlier revealed impurities such as hydrogen as shallow donors.

Indeed the formation energy of point defects can vary over a wide range based on the formation enthalpy of ZnO as a function of the chemical potential. As such, the addition of hydrogen as impurity can raise the Fermi level above the valence band maximum.

CONCLUSION

In spite of the challenges of achieving p - *type* conductivity, *ZnO* remains a promising material for electronic and optoelectronic device applications. The availability of better thin film growth techniques and the high quality of *ZnO* substrates for group III nitrides spur further improvements.

Computational procedures have made major contributions to the understanding of the electronic and structural properties of native defects and impurities. Oxygen vacancies and shallow donor nature of hydrogen impurities screen 161 acceptors in *ZnO*. Recent studies have shown that native point defects do not explain the often observed *n–type* conductivity but may be adduced to the incorporation of impurities during growth or annealing. Computational studies show that oxygen interstitials are high energy defects that are unlikely to occur.

Reliable and reproducible p-*type* impurity incorporation into *ZnO* would boost *ZnO* application as incorporation of hydrogen increases carrier density, since hydrogen acts as a donor.

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