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Edge dislocation effect on optical properties in wurtzite ZnO

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ABSTRACT

The effect of edge dislocations on optical properties in wurtzite ZnO is studied using a $\boldsymbol{k}\cdot\boldsymbol{p}$ multiband Hamiltonian model. An edge dislocation is modeled as a negatively charged line due to its electron-acceptor nature with an elastic strain field due to the lattice distortion around the dislocation. The electrostatic potential strength of the negatively charged dislocation depends on the filling fraction, which describes the fraction of acceptor sites occupied by trapped electrons along the dislocation line. To understand the effect of electrostatic potential strength, the filling fraction has been varied in this work. Using the calculated energy levels and wave functions for electrons and holes from the $\boldsymbol{k}\cdot\boldsymbol{p}$ multiband Hamiltonian, the spontaneous emission spectrum has been obtained as a function of dislocation density and filling fraction. The calculated results are compared with available experimental photoluminescence data. The band edge peak intensity decreases significantly with increasing dislocation density. It is found that the electrostatic potential strength does not affect the band edge peak emission, but it generates deep level emissions. For low filling fractions, corresponding to high temperature, the most commonly observed green luminescence is found. For a high filling fraction, corresponding to low temperature, the green luminescence shifts to red luminescence, which is consistent with experimental observation.

1. Introduction

Wurtzite zinc oxide (ZnO) is a wide band gap semiconductor that has received much attention as a substitute to gallium nitride (GaN) in optoelectronic devices including solar cells, UV and blue light emitting diodes, and laser diodes [1–3]. It has a band gap of 3.37 eV [4], similar to 3.4 eV of GaN [5], and an exciton binding energy of 60 meV [6], which is much higher than GaN, 21–28 meV [5,7]. The high exciton binding energy of ZnO is an advantage over GaN, allowing for excitonic related emission at room temperature [8,9]. To take advantage of these ZnO properties in device application, it is critical to obtain a stable *p*-type ZnO [2]. However, due to the low solubility of *p*-type dopants and the intrinsic *n*-type impurities such as oxygen vacancy and zinc interstitial, it is difficult to produce a reliable *p*-type ZnO [10]. Even though there are some reports claiming success in *p*-type control on ZnO [11,12], the reliable formation of *p*-type conductivity still remains a challenge [13,14].

An alternative way has been taken by a number of research groups to use the advantages of ZnO in the form of heterojunctions where an *n*-type ZnO film is grown heteroepitaxially on *p*-type substrates such as *p*-GaAs [15], *p*-Si [16], *p*-diamond [17], *p*-GaN/Al_2O_3 [18], and *p*-6H-SiC [19]. In heteroepitaxial ZnO films, due to the large lattice mismatch with substrates, a high dislocation density between $n_{dis}=10^8-10^{10}\,cm^{-2}$ has been commonly observed [20–22]. Among three types of threading dislocations (i.e. edge, screw, and mixed types), it has been found that up to 94% of the total dislocation density are edge dislocations in ZnO thin films [21]. Using transmission electron microscopy [23] and scanning capacitance microscopy [21], edge dislocations have been found to act as electron acceptors, resulting in negatively charged lines. In ZnO, various line charge densities, which are determined by the filling fraction, have been reported [23,24]. The filling fraction is defined as the fraction of filled electron acceptor sites along dislocations [25]. Screw dislocations have been found to be electrically inactive [26].

The luminescence spectrum of ZnO consists of a strong band-edge emission (BE) at 3.37 eV [27–29] and a wide range of deep level emissions (DL) between 1.5 and 3.2 eV [30]. The BE peak intensity has been shown to decrease as dislocation density increases [22,27,31–34]. The most commonly reported DL emission is a green luminescence (GL) band ranging from 2.3 to 2.5 eV [27,32,35,36]. Its origins are still debated, with many studies indicating that GL is from various defects. Heo et al. [28] found that GL shifts to yellow luminescence (YL) when Zn vacancies are reduced, suggesting that GL is related to the deep-level acceptor [37]. Annealing of ZnO thin films in O_2 atmosphere quenches the GL indicating that it is from oxygen vacancies [35], which is a

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deep donor [38]. By applying a direct electric field, the movement of GL from anode to cathode indicates that GL is due to complex defects involving zinc interstitials [39]. These point defects can be localized at dislocations due to the strain field, causing the negatively charged dislocations and introducing electronic states within the band gap [20,21,23,34]. Lin et al. [20] proposes that doubly charged Zn vacancies accumulated around dislocations contribute to conduction band bending, consistent with Read's model [25]. In addition to GL, red luminescence (RL) [27,36,40] at ~1.75 eV, and violet luminescence (VL) [36,41,42] at ~3.1 eV have also been observed. In samples grown under pure argon atmospheres, RL appears at low temperatures and then disappears as the temperature is increased, leaving GL observed alone [36]. Ozgur et al. [40] also found RL at low temperatures and GL emerges with increasing temperature. The appearance and increase of VL has been found to be directly related to dislocations. Cathodoluminescence studies have revealed that VL is more intense than BE emission at the center of dislocation pits [41].

In this work, the effect of threading edge dislocations on optical properties in wurtzite ZnO film is studied as a function of dislocation density and filling fraction. The spontaneous emission/absorption coefficients are calculated and compared with available experimental data. This paper is organized as follows: in Section 2 a $\boldsymbol{k\cdot p}$ Hamiltonian method has been applied to calculate the conduction and valence band bendings with presence of edge dislocations in ZnO films. In Section 3 the spontaneous emission/absorption coefficients have been calculated, and are compared with available experimental photoluminescence data. Conclusions are drawn in Section 4.

2. Conduction and valence band bending by edge dislocations

The system of interest is a ZnO film containing evenly distributed edge dislocations. To account for an extra half plane, the edge dislocations are paired with opposite Burgers vectors. Fig. 1 shows a calculation unit cell with a dipole of edge dislocations along the crystalline growth direction, $<0001>$. The thickness is set to be 1000 Å. A periodic boundary condition is applied in the x–y plane and the zero-valued Dirichlet boundary condition is applied along the z-axis. The desired dislocation density can be obtained by changing the area of the unit cell.

Due to its electron-acceptor nature and the lattice distortion by the extra half plane, the edge dislocation has been modeled as a negatively charged line with an elastic strain field. The electrostatic potential V_{dis} of the negatively charged dislocation line induces the band bending [25], which is modeled as [43]

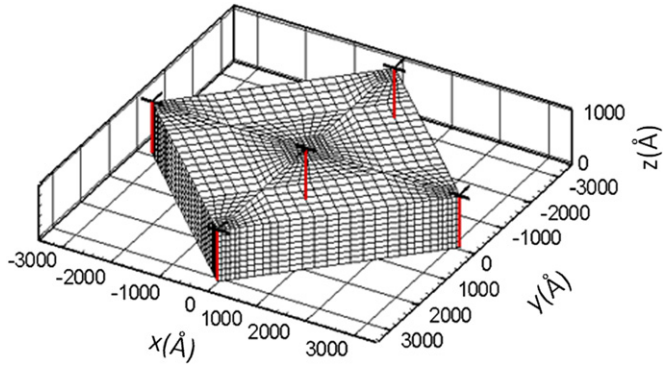

Fig. 1. A periodic calculation unit cell containing a dipole of edge dislocations with finite element mesh for dislocation density of $10^9\,cm^{-2}$. The periodic boundary condition in the x–y plane and the zero-valued Dirilecht boundary condition along the z direction have been applied. Threading edge dislocations have a dipole formation with opposite Burgers vectors and run through the film along the $<0001>$ growth direction.

$$V_{dis}(r)=\frac{2fq^2}{4\pi\varepsilon_\perp c}K_0\left(\frac{r}{\lambda_D}\right) \tag{1}$$

where q is the magnitude of the electron charge, $\varepsilon_\perp$ is the dielectric constant in the x–y plane, c is the lattice constant along $<0001>$, and the filling fraction f describes the fraction of electron acceptor sites along the dislocation line that are occupied by trapped electrons, and the factor of 2 is due to the two electron acceptor sites per structural unit length c for dislocations in wurtzite ZnO [26]. If all of these acceptor sites are filled by electrons, the electrostatic potential in Eq. (1) has maximum strength at $f=1$. If half of the sites are filled, $f=0.5$. If no acceptor sites are filled by electrons, the electrostatic potential diminishes at $f=0$. $K_0(r/\lambda_D)$ is the modified Bessel function of the second kind of order 0 evaluated at r/λ_D. The radial distance from the dislocation line is r, and the Debye screening length is given as $\lambda_D=\sqrt{\varepsilon_\perp k_BT/q^2n'}$. The effective screening concentration n' is given as $n'=n_{carr}+(n_{carr}+N_A^-)[1-(n_{carr}+N_A^-)/N_D^+]$, where N_A^- and N_D^+ are the chemical acceptor and donor, respectively. For n-doped ZnO, N_A^- is assumed to be zero. Due to the electron acceptor nature of dislocations, the charge balance of $N_D^+=n_{carr}+2fn_{dis}/c$ is required.

The strain field ε_{ij} around the dislocation is given [44]

$$\varepsilon_{xx}=\frac{C_{11}\sigma_{xx}-C_{12}\sigma_{yy}}{C_{11}^2-C_{12}^2},\quad \varepsilon_{yy}=\frac{C_{11}\sigma_{yy}-C_{12}\sigma_{xx}}{C_{11}^2-C_{12}^2}$$

$$\varepsilon_{xy}=\varepsilon_{yx}=\frac{\sigma_{xy}}{2C_{66}},\quad \varepsilon_{zz}=\varepsilon_{xz}=\varepsilon_{yz}=0 \tag{2}$$

where σ_{ij} are the stress components given as,

$$\sigma_{xx}=-\frac{C_{66}b}{2\pi(1-\nu)}\frac{y(3x^2+y^2)}{(x^2+y^2)^2},\quad \sigma_{yy}=\frac{C_{66}b}{2\pi(1-\nu)}\frac{y(x^2-y^2)}{(x^2+y^2)^2}$$

$$\sigma_{xy}=\frac{C_{66}b}{2\pi(1-\nu)}\frac{x(x^2-y^2)}{(x^2+y^2)^2},\quad \sigma_{zz}=\nu(\sigma_{xx}+\sigma_{yy}),\quad \sigma_{xz}=\sigma_{yz}=0 \tag{3}$$

C_{ij} are elastic stiffness constants listed in Table 1, the magnitude of the Burgers vector is $b=1/3<11\bar{2}0>$, the Poisson ratio is $\nu=C_{12}/(C_{12}+C_{11})$, and $C_{66}=(C_{11}-C_{12})/2$.

The energy levels and wave functions with the presence of edge dislocations have been obtained by solving the Schrödinger equation as

$$H|\psi>=E|\psi> \tag{4}$$

The total Hamiltonian, H, includes contributions from kinetic energy, deformation potential energy, and electrostatic potential energy. Being a wide band-gap semiconductor, the valence and conduction bands can be solved independently of each other. For the conduction band, the Hamiltonian is given as [45]

$$H^C=E_C-\frac{\hbar^2\nabla^2}{2m_e}+a_{C1}\varepsilon_{zz}+a_{C2}(\varepsilon_{xx}+\varepsilon_{yy})+V_{dis} \tag{5}$$

where E_C is the conduction band minimum for unstrained bulk ZnO, and a_{C1} and a_{C2} are conduction band deformation potentials listed in Table 1. For the valence band, a 6×6 $\boldsymbol{k\cdot p}$ Hamiltonian [44] that includes the interaction between subbands and the kinetic and deformation potential energies is used in addition to a 6×6 matrix expansion of the electrostatic potential energy as [45]

$$H^V=\left[H^V_{\boldsymbol{k\cdot p}}\right]_{6\times6}+V_{dis}I_{6\times6} \tag{6}$$