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Intensity of Optical Absorption Close to the Band Edge in Strained ZnO Films

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Besides other one of the remarkable properties making wurtzite ZnO such an interesting material is its large exciton binding energy of about 60 meV, leading to stable excitons at room-temperature. Also, the Curie temperature of this wide-gap material has been predicted to lie above room temperature, making ZnO alloyed with magnetic ions a possible material for spintronics applications. One big challenge in the fabrication of ZnO-based heterostructure devices is the lattice mismatch between the ZnO films and the substrates and the different thermal expansion coefficients inducing biaxial strain. This work reports on the electronic band structure of biaxially strained ZnO for strains along the a- or the c-axis ranging from -1 % to 1 %, as calculated by means of the empirical pseudopotential method. Thereby, we also account for relativistic effects in the form of the spin-orbit interaction, as well as for the energy dependence of the crystal potential through the use of nonlocal model potentials. Moreover, the application of a variable plane wave basis set allows us to directly obtain the strain-induced variations of the electronic and the optical properties of wurtzite ZnO.

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I. INTRODUCTION

For uniaxial or biaxial materials, the diagonal components of the dielectric function are different and may be determined using generalized ellipsometry. Without loss of generality, the tensor of the dielectric function of an uniaxial material, for example ZnO, is given in the main axis representation [1] as

$$\begin{aligned}\tilde{\epsilon} &= \begin{pmatrix}\epsilon_\perp & 0 & 0\\ 0 & \epsilon_\perp & 0\\ 0 & 0 & \epsilon_\parallel\end{pmatrix}\\ &= \begin{pmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{pmatrix}\frac{1}{2}(\epsilon_\perp + \epsilon_\parallel)\end{aligned} \quad (1)$$

$$+ \begin{pmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & -1\end{pmatrix}\frac{1}{2}(\epsilon_\perp - \epsilon_\parallel)\,, \quad (2)$$

being subdivided into an isotropic term ($\frac{1}{2}(\epsilon_\perp+\epsilon_\parallel)$) and a strain/structural induced anisotropy ($\frac{1}{2}(\epsilon_\perp - \epsilon_\parallel)$) term. Therefore, strain effects have to be taken into account when interpreting an anisotropy probed, for example in magnetic ZnO. Also, for an interpretation of optical data probed in the band gap near the spectral range of magnetic ZnO, polarization-dependent transition probabilities between the three uppermost valence bands and the conduction band have to be known. The valence bands are labelled from higher to lower energies as A, B and C [2]. Because of the absence of data in the literature until now, the same probabilities have been assumed for the transitions between the A, B and C valence bands and the conduction band minimum (CBM). However, exper-

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iments where both optical transitions from the A valence band into the CBM and from the B valence band into the CBM have been excited have revealed a finite spin polarization in magnetic ZnO. This may be explained if the corresponding polarization-dependent optical transition probabilities are different. In this paper, we report on the effect of strain on the anisotropy ($\epsilon_\perp - \epsilon_\parallel$) in ZnO films grown on Al_2O_3 or on SiC substrates as determined by using empirical pseudopotential calculations.

II. EMPIRICAL PSEUDOPOTENTIAL METHOD

Within the empirical pseudopotential method (EPM), the crystal potential

$$V^{crystal}(r) = \sum_{\mathbf{G}} V_a(\mathbf{G}) S(\mathbf{G}) e^{i\mathbf{G}\mathbf{r}}\,, \tag{3}$$

is set up as a superposition of spherically symmetric model potentials placed at atomic positions within the crystal. In this work, we make use of the empty-core model potential introduced by Ashcroft [3]:

$$v_{ion}(r) = \begin{cases} 0 & \text{for } r < r_i \\ -\frac{2z_i}{r} & \text{for } r > r_i, \end{cases} \tag{4}$$

with z_i (effective ion charge) and r_i (effective ion radius) being adjustable parameters. These parameters are fitted to experimentally well-known low-temperature transition energies of ZnO, thereby reproducing the fundamental band gap and yielding the correct band dispersion. Additionally, nonlocal correction terms have been considered to take into account the energy dependence of the crystal potential and the relativistic spin-orbit interaction, which has been modeled due to Bloom and Bergstresser [4]. A more detailed description of the method and its implementation can be found elsewhere [5–8]. Since the EPM relies on a plane-wave basis set, which has to be determined by applying an energetic cut-off condition to restrict the number of allowed reciprocal lattice vectors in the expansion of Eq. (3), we have to be careful when calculating strain-related properties with such a basis set. Small changes in the lattice constants of the ZnO host material can lead to small shifts in the calculation of the reciprocal lattice vectors, leading to the addition or removal of some reciprocal lattice vectors from the basis set, which would immediately change the results for the electronic properties. We have applied a smooth variable basis set, which minimizes the effect of adding or removing reciprocal lattice vectors from the basis set [9].

Using the expansion coefficients c_i and c_j from plane wave band-structure calculations, we were able to calculate the transition matrix elements for polarizations parallel and perpendicular to the optical axis. The corresponding eigenfunctions with the plane wave expansion coefficients c_i and c_j have been used to calculate the polarization-dependent transition matrix elements, which follow from

$$M_{ij}(\mathbf{k}) = \sum_{\mathbf{G}} c_i^* c_j i\,[\mathbf{k} + \mathbf{G}]\,\hat{e}\,, \tag{5}$$

where $\mathbf{G}$ are the allowed reciprocal lattice vectors and $\hat{e}$ is the polarization vector. The optical matrix elements were calculated along high symmetry lines in the Brillouin zone to evaluate the dominant character of allowed band-to-band transitions, whether occurring for polarization parallel or perpendicular to the c-axis of ZnO. Finally, the imaginary part of the dielectric function of wurtzite ZnO was calculated according to

$$\varepsilon_2(\omega) = \left(\frac{2\pi e}{m\omega}\right)^2 \sum_{\mathbf{k}} |M_{ij}|^2\, \delta(E_c(\mathbf{k}) - E_v(\mathbf{k}) - \hbar\omega)\,, \tag{6}$$

where the integration over the Brillouin zone was performed by means of the linear tetrahedron method after Lehmann and Taut [10].

III. RESULTS

The Poisson ratio ν, *i.e.*, the ratio between the strain along the c-axis and a-axis,

$$\frac{c - c_0}{c_0} = -\nu \frac{a - a_0}{a_0}\,, \tag{7}$$

with $a_0 = 3.2490$ Å and $c_0 = 5.2042$ Å, amounts to $\nu = 0.5$ or $\nu = 0.38$ for ZnO on Al_2O_3 or ZnO on SiC, respectively. The imaginary part of the dielectric function of ZnO [2,5] has been calculated up to 14 eV above the band edge along the Poisson lines $\nu = 0.5$ and $\nu = 0.38$. In Figure 1, the polarization-dependent imaginary part of the dielectric function ϵ_2 of strained ZnO is presented as a function of the a-axis lattice parameter. For $a < 3.2490$ Å and for $a > 3.2490$ Å, the films have a biaxial compressive strain (Figure 1(b,d)) and a biaxial tensile strain (Figure 1(a,c)), respectively. We reveal a clear polarization dependence of the imaginary part of the dielectric function for ZnO under biaxial strain to be considered for the interpretation of anisotropy probed, for example, for magnetic ZnO.

We also investigated the electronic band structure of biaxially- strained ZnO in the near-band gap region by using the elaborated EPM for values of the a-axis lattice parameter ranging between 3.22 and 3.28 Å. The c-axis lattice parameter was determined using Eq. (7). The calculated strain-dependent energetical positions of the CBM and of the three uppermost valence bands A, B and C are represented in Figures 2(a,c) and allow us to determine the effect of the lattice mismatch and the thermal expansion on the optical absorption close to the band edge in strained ZnO films. In wurtzite ZnO, the crystal field and the relativistic spin-orbit interactions produce a valence band splitting. The splitting

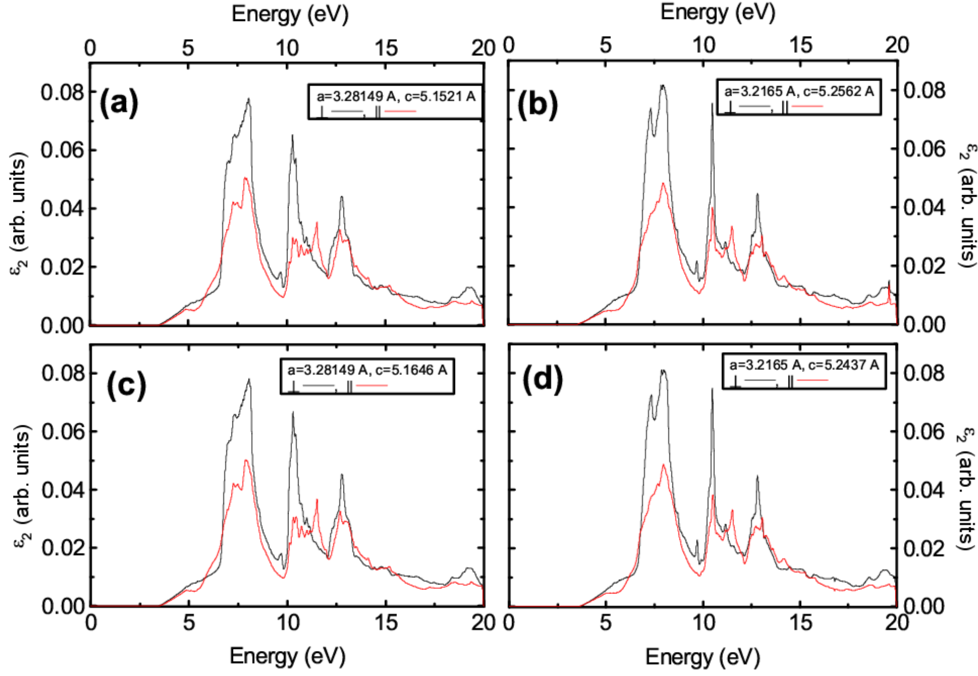

Fig. 1. Calculated imaginary part of the dielectric function of ZnO revealing clear anisotropy effects, namely $\epsilon_{\perp} - \epsilon_{\parallel} \neq 0$, for (a) $a = 3.28149$ Å and $c = 5.15215$ Å, (b) $a = 3.2165$ Å and $c = 5.25624$ Å, (c) $a = 3.28149$ Å and $c = 5.16465$ Å and (d) $a = 3.21651$ Å and $c = 5.24375$ Å.

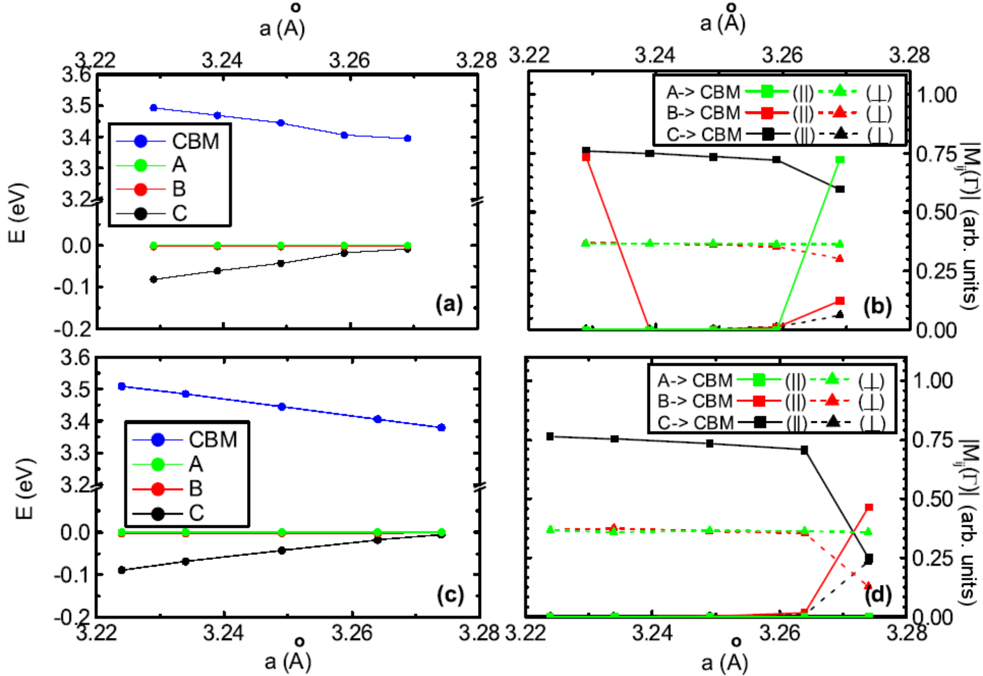

Fig. 2. Calculated (a),(c) strain-dependent fundamental band gap energy and valence band splitting and (b),(d) optical transition probabilities along the Poisson lines (a),(b) $\nu = 0.50$ (ZnO/Al_2O_3) and (c),(d) $\nu = 0.38$ (ZnO/SiC).

of the three uppermost valence bands A, B and C and the fundamental absorption edge decrease with increasing biaxial tensile strain. Larger biaxial tensile strain may reverse the ordering of the three uppermost valence bands. A valence band reversal becomes visible in the non-zero optical transition matrix elements $|M_{ij}(\Gamma)|$ for the C $\rightarrow$ CBM and for the B $\rightarrow$ CBM optical transitions for parallel polarization at large biaxial tensile strain (Figures 2(b,d)) and for the B $\rightarrow$ CBM optical transition for parallel polarization at large biaxial compressive strain (Figure 2(b)). Furthermore, for $\nu = 0.50$ and 3.24 Å $< a <$ 3.26 Å (Figure 2(b)) and for $\nu = 0.38$ and

$a < 3.26$ Å (Figure 2(d)), the optical transition probabilities for A $\rightarrow$ CBM and B $\rightarrow$ CBM are similar.

IV. CONCLUSIONS AND OUTLOOK

Using the polarization dependence of the dielectric function, we showed that the uniaxiality of ZnO has to be considered when discussing anisotropy effects in strained ZnO. This is of importance for the development of ZnO-based spintronic materials. Furthermore, we have shown that only for small biaxial strain are the optical transition probabilities similar for the A $\rightarrow$ CBM and the B $\rightarrow$ CBM transitions.

Because excitons in ZnO are stable at room temperature, one has to account for Coulomb-enhanced band-to-band transitions and discrete excitonic transitions. As shown by Shokhovets *et al.* [11], the band-to-band transitions calculated in the framework of a one-particle Schrödinger equation have to be weighted and discrete excitonic transitions have to be accounted for. We expect that due to the imposed selection rules for optical transitions, the corresponding A, B and C excitons possess a strain-field-dependent oscillator strength.

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