

Optical properties of wurtzite and rock-salt ZnO under pressure

J.A. Sans^a, A. Segura^{a,*}, F.J. Manjón^b, B. Mari^b, A. Muñoz^c, M.J. Herrera-Cabrera^c

^a*Institut de Ciència dels Materials-Dpt. de Física Aplicada, Universitat de València, Ed. Investigació, E-46100 Burjassot (València), Spain*

^b*Dpt. de Física Aplicada, Universitat Politècnica de València, 46071 Valencia, Spain*

^c*Dpt. De Física Fundamental II, Universidad de la Laguna, 38204 La Laguna (Tenerife), Spain*

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Abstract

This paper reports on the pressure dependence of the optical absorption edge of ZnO in the wurtzite and rock-salt phase, up to 14 GPa. Both vapor-phase monocrystals and pulsed-laser-deposition thin films have been investigated. In both types of samples the wurtzite to rock-salt transition is observed at 9.7 ± 0.2 GPa. The absorption tail of the fundamental gap, as measured in monocrystals, exhibits a pressure coefficient of 24.5 ± 2 meV/GPa. The evolution under pressure of the full absorption edge of the wurtzite phase is studied with thin film samples, yielding a slightly lower pressure coefficient (23.0 ± 0.5 meV/GPa for the A–B exciton). Rock-salt ZnO is shown to be an indirect semiconductor with a bandgap of 2.7 ± 0.2 eV. At higher photon energy a direct transition ($E_{gd} \sim 4.5$ eV) can be also identified in thin films transitioned to the rock-salt phase. Results on the high-pressure phase are interpreted on the basis of density-functional-theory (DFT) electronic structure calculations.

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1. Introduction

Zinc Oxide (ZnO) is the object of a quickly growing attention in the last few years owing to its potential applications in ultraviolet optoelectronic devices [1].

High-pressure studies are a very efficient tool in understanding the electronic structure of semiconductors [2], but they have been scarcely used in the investigation of ZnO, compared to other II–VI semiconductors. The equation of state and phase diagram has been investigated through X-ray diffraction (XRD) under pressure [3–6]. The lattice dynamics has been studied through Raman [7,8] and Mossbauer [4] effect measurements under pressure. As regards the optical properties, the pressure coefficient of the wurtzite ZnO (W-ZnO) bandgap was determined through optical reflectance [9] and absorbance of smoke samples [10]. More recently, in a detailed investigation using two-photon absorption, Mang et al. [11] reported the pressure coefficients of the A, B and C band-gaps and the ones of the binding energies of the related excitons. Nevertheless, the evolution of the absorption edge under pressure has not been investigated.

The electronic properties of the high-pressure phase, that is known to have the rock-salt structure [3–6], have been investigated in theoretical papers [12,13], but there are no experimental reports on its optical properties. In this paper we report on the pressure dependence of the absorption edge of wurtzite and rock-salt ZnO (RS-ZnO). Experimental methods are described in Section 2. Results are presented in Section 3 and discussed in Section 4, on the basis of density-functional-theory (DFT) calculations.

2. Experimental and calculation methods

ZnO thin films were prepared by pulsed-laser deposition on fluorite, sapphire and mica monocrystalline substrates. The ZnO target was a compressed pellet of 5N ZnO powder annealed at 950 °C for six hours in air atmosphere. Films were prepared at relatively low temperature (400 °C) in a dynamically controlled atmosphere of 5N oxygen at 2×10^{-4} mbar and then subjected to 6 h annealing in air at higher temperatures (up to 800 °C). Their quality was checked by XRD and low temperature absorption and photoluminescence measurements. Photoluminescence was excited with a HeCd laser. In order to allow for an accurate measurement of the ZnO absorption edge, the thin film thickness was fixed at some 200 nm. Only samples on mica substrates could be studied under pressure as these

* Corresponding author.

E-mail address: alfredo.segura@uv.es (A. Segura).

substrates can be easily cleaved to a thickness below 30 μm , adapted to studies in a diamond anvil cell (DAC). Bulk ZnO crystals were grown by the vapor phase method [14]. Samples for DAC measurements were small splints with parallel faces resulting from breaking large crystals.

For optical measurements under pressure a sample was placed together with a ruby chip into a 200 μm diameter hole drilled on a 50 μm thick Inconel gasket and inserted between the diamonds of a membrane-type diamond anvil cell (MDAC) [15]. Methanol–ethanol–water (16:3:1) was used as pressure transmitting medium for absorption experiments in the visible/near infrared range. Pressure was determined through the ruby luminescence linear scale [16]. Transmission measurements were made in an optical set-up similar to the one described in Ref. [15]. The use of fused silica lenses, reflecting optics objectives and a visible–UV spectrometer allows for investigating the optical properties of materials under pressure up to the absorption edge of IIA diamonds (nearly 5 eV). All measurements were carried out at room temperature (RT).

The electronic structure at different pressures of RS-ZnO has been calculated through the total energy pseudopotential plane wave method using the density-functional-theory (DFT) in the framework of the local density approximation (LDA). The semi-core 3d electrons of Zn are treated as forming part of the valence states. Plane waves up to 130 Ry energy cut-off were used in order to have highly converged results. In spite of the well-known underestimation of the band gap in DFT methods, it is also well established that they yield very good results for the pressure evolution of the electronic transitions.

3. Results

XRD measurements show that the W-ZnO thin films are well crystallized and oriented in the (0001) direction.

Fig. 1 shows the temperature dependence of the absorption edge of a W-ZnO film deposited on fluorite. Three exciton-related peaks can be identified in the spectrum taken at 20 K. We will name them X_1 (3.393 eV), X_2 (3.466 eV) and X_3 (3.540 eV). The high intensity of these absorption peaks at low temperature reveals the good quality of the films [17,18]. The inset of Fig. 1 shows the temperature dependence of the photon energies corresponding to peaks X_1 and X_2 . The energy difference between X_2 and X_1 decreases with increasing temperature. At 20 K it is of the order of 73 meV, close to the energy of the E_1 LO polar phonon in W-ZnO [19,20]. At 300 K it is of the order of 56 meV, close to the energy difference between the C and A exciton peaks [11].

Fig. 2 shows the photoluminescence spectra at low temperature of two W-ZnO thin films deposited on fluorite and sapphire. The more intense peak in both spectra corresponds to the bound exciton peak and its

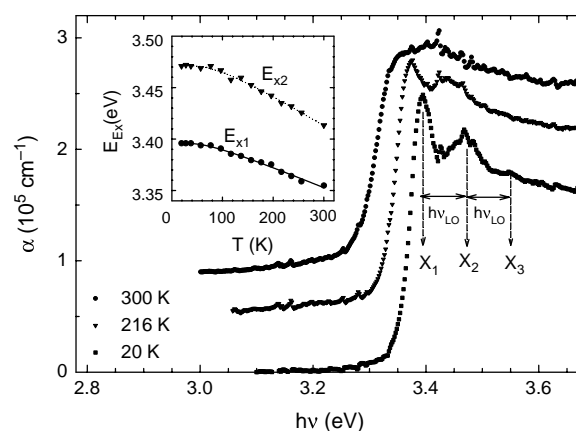


Fig. 1. Absorption edge of a W-ZnO film on fluorite at different temperatures. Spectra have been shifted vertically by regular amounts to avoid superposition. Inset: temperature dependence of the two exciton-related maxima observed in the absorption edge.

full-width-at-half-maximum (FWHM) is about 6 meV, which confirms the good quality of the films [17,18].

Fig. 3 shows the optical absorption edge of a W-ZnO film on mica as a function of pressure up to 8.8 GPa. In W-ZnO/mica films only one broad maximum (corresponding to peak X_2) is clearly observable at ambient pressure (X_1 peak appears as an inflexion of the absorption edge, just below X_2). This situation does not basically change under pressure. A monotonous shift of the absorption edge towards higher energies is observed as pressure increases. The absorption edge can be interpreted through the Elliot–Toyozawa equation for excitonic absorption in semiconductors [21], including the contribution of two excitonic transitions (X_1 and X_2). The inset of Fig. 3 shows the pressure dependence of the energies of both excitons. The pressure coefficients are 23.0 ± 0.5 and 23.5 ± 0.6 meV/GPa, for the X_1 and X_2 excitons, respectively. These pressure coefficients are slightly lower than the one reported by Mang et al. [11] (23.6, 24.4 and 26.5 meV/GPa for excitons A, B and C, respectively).

The phase transition to the NaCl phase in ZnO/mica thin films is observed at about 9.7 GPa, as a decrease of

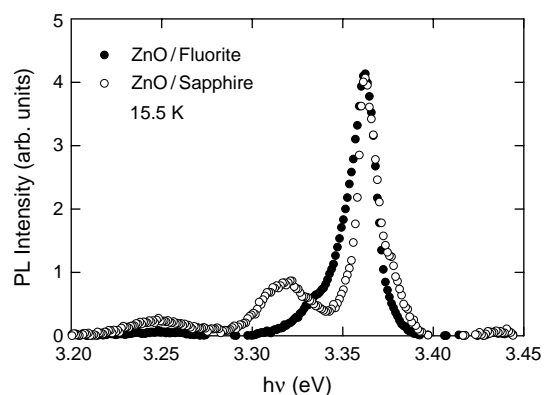


Fig. 2. Photoluminescence spectra at 15.5 K of two ZnO films on sapphire and fluorite substrates.

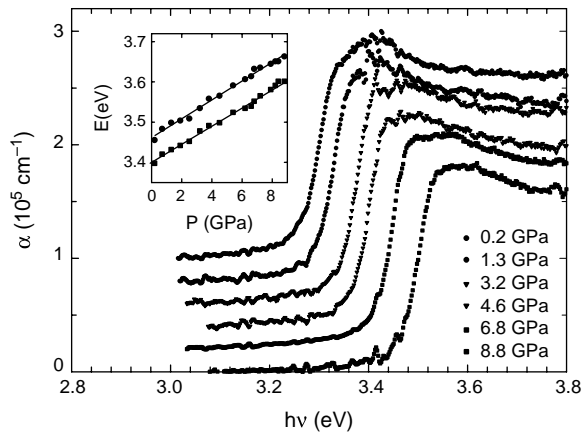


Fig. 3. Absorption edge of wurtzite ZnO, at different pressures, as measured in a thin film deposited on mica. Spectra have been shifted vertically by regular amounts to avoid superposition. Inset: pressure dependence of the A–B (■) and C (●) exciton peaks.

the absorption coefficient in the whole explored photon range, as illustrated in Fig. 4. This effect is coherent with the change of the gap nature in the phase transition. W-ZnO is a direct semiconductor with an absorption edge dominated by very intense excitonic peaks. RS-ZnO is an indirect semiconductor, with low absorption coefficient at the absorption edge [12,13]. Then the effect of indirect transitions in the thin film transmittance is not observable. Only intense direct absorption edges are detectable in transmission measurements in a 200 nm thick film. This is the case of the absorption edge observed at photon energies higher than 4.5 eV, that is most probably related to an allowed direct transition.

In the experiment with vapor-phase bulk W-ZnO samples, we used a 15 μm thick sample. Consequently, only the low-energy tail of the W-ZnO absorption edge is observable, as shown in Fig. 5. This absorption tail exhibits an exponential dependence on the photon energy, which is a typical feature of exciton absorption tails in polar semiconductors (Urbach tail). The pressure coefficient of this absorption edge (at a constant absorption coefficient) is a little higher than the one measured

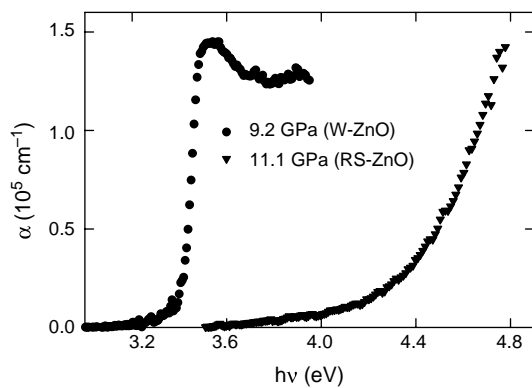


Fig. 4. Change of the absorption spectrum of a ZnO film on mica in the wurtzite to rock-salt phase transition.

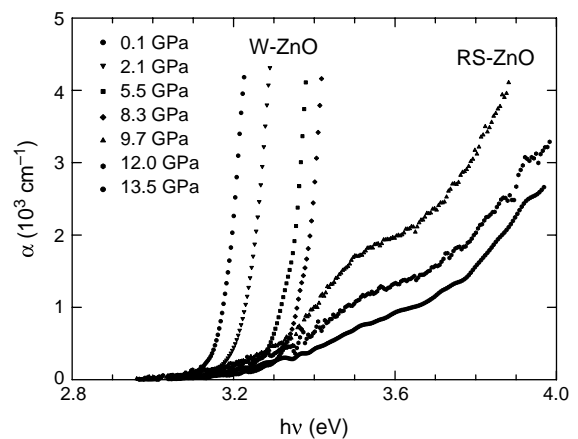


Fig. 5. Absorption edge of a bulk ZnO sample at different pressures below and above the wurtzite-to-rock-salt transition pressure.

in thin films (24.5 ± 2 meV/GPa) and nearly identical to the one reported by Mang et al. [11] for the B exciton.

The transition to the NaCl phase occurs at about 9.7 GPa, as in thin film samples. It is also observed as an overall increase of the sample transparency. The photon energy dependence of the absorption coefficient changes from the steep exponential dependence observed in W-ZnO to a much smoother quadratic dependence in RS-ZnO. Below 13.5 GPa, the absorption edge of RS-ZnO exhibits a structure, probably related to small regions of the sample remaining in the wurtzite phase. This interpretation is confirmed by the fact that the structure disappears at higher pressures, when the transition to the rock-salt phase is complete and is no longer observed in the pressure down-stroke [20]. This structure is very weak in the absorption spectrum taken at 13.5 GPa (see Fig. 5). At this pressure the absorption coefficient exhibits a fairly quadratic dependence on the photon energy, as illustrated in Fig. 6. If this quadratic tail is assigned to an indirect transition, the bandgap value would be 2.7 ± 0.2 eV. Let us notice that this estimation of the RS-ZnO indirect gap can be perturbed by the presence of some remains of the wurtzite phase in

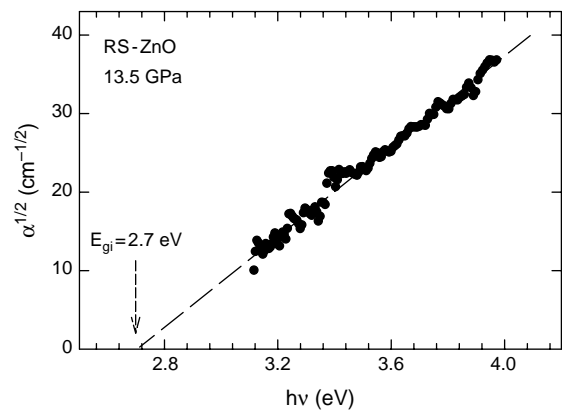


Fig. 6. Square root of the absorption coefficient of a bulk RS-ZnO sample versus the photon energy at 13.5 GPa.

the sample. Measurements at higher pressure, when the transition of the sample to the RS phase is complete, yield a slightly lower value of the RS-ZnO indirect bandgap (2.45 ± 0.15 eV at 14.5 GPa, in the pressure down-stroke) [22].

4. Discussion

The absorption edge of wurtzite-like semiconductors exhibits three exciton related peaks (named A, B and C) associated to three non-degenerate valence band maxima VBM at the Γ point of the Brillouin zone (B.z.). This VBM structure can be seen as derived from the triply degenerate VBM of zinc-blende-like semiconductors, when degeneracy is broken by the uniaxial wurtzite crystal field and spin-orbit interaction [23,24]. In bulk ZnO the photon energies of A, B and C peaks are 3.378, 3.393 and 3.433 eV at 5K, respectively [11]. Excitons A and B are allowed for light polarization perpendicular to the c -axis while exciton C is allowed for light polarization parallel to the c -axis [22]. As most W-ZnO thin films are oriented in the (0001) direction, the C-exciton peak is expected to be very weak.

In spite of these well-established results, the assignment of the maxima observed in the absorption edge of W-ZnO thin films is still controversial. Muth et al. [17] attribute the most intense peaks to excitons A (3.392 eV) and B (3.466 eV) and explain the large increase of the A–B splitting (with respect to bulk W-ZnO) as arising from biaxial stress in the film. This interpretation has been criticized by Makino et al. [18], by pointing out the unrealistically high biaxial stress that such a large splitting would imply. High quality ZnO films prepared by Makino et al. [18] exhibit two well-resolved absorption peaks (at 3.377 and 3.384 eV) and a broad maximum (at 3.450 eV) in the absorption spectrum at 5 K. The authors identify the peaks as excitons A and B, and the broad maximum as an exciton-LO phonon resonant absorption, following the classic assignment by Liang and Yoffe [24]. They also show that the intensity of the A exciton is much lower and more sensitive to defects than the one of the B exciton.

On the basis of the previous discussion, we are in conditions to assign peaks X_1 , X_2 and X_3 in Fig. 1. We think that the interpretation of Makino et al. [18] is physically well supported and, consequently, we assign the peak X_1 (3.393 eV) to exciton B (E_{XB}). Peaks X_1 and X_2 appear at photon energies very close to $E_{XB} + hv_{LO}$ and $E_{XB} + 2hv_{LO}$ ($hv_{LO} = 72$ meV is the energy of the E_1 LO polar phonon in W-ZnO) [19,20]. Then the main contribution to these peaks at low temperature is proposed to arise from exciton-LO phonon resonant absorption. Nevertheless, as we noticed in the previous paragraph (see inset of Fig. 1), the energy difference between peaks X_2 and X_1 decreases with increasing temperature and it is about 56 meV at room temperature. Even if this difference is larger than the difference between the C and A excitons (40 meV at 5 K)

[11], it is significantly lower than hv_{LO} and, consequently, we cannot exclude the presence of a partial contribution of exciton C to peak X_2 . This contribution would arise from residual stress in the film and from crystallites that are not oriented in the predominant (0001) direction.

The pressure dependence of the absorption edge of W-ZnO here reported is compatible with results of Mang et al. [11], even if we observe a slightly lower pressure coefficient for the exciton-related structures. Two factors can contribute to this small difference. On the one side, there is a large temperature difference between both experiments (6 K in Ref. [11] versus RT in our experiment). On the other side, there could be another contribution arising from strain in our thin film due to its differential compressibility with respect to the mica substrate. Let us also stress that the absorption edge shifts toward higher energies without dramatic changes (see Fig. 3). This result is also coherent with the small increase under pressure of the exciton binding energy reported in Ref. [11].

As regards the rock-salt phase, we will discuss our results on the basis of the calculated electronic structure. Fig. 7 shows the band structure of RS-ZnO, at 10.7 GPa, in high symmetry directions of the B.z., as calculated through an ab initio pseudopotential DFT–LDA method. RS-ZnO is correctly predicted to be an indirect semiconductor in which the conduction band minimum (CBM) (located at the Γ point) is about 1.1 eV above the valence band maxima (VBM) (located at the L point and midway in the ΓK direction).

As we have previously noticed, the bandgap nature changes from direct to indirect in the W to RS phase transition in ZnO. This is also the case of many II–VI semiconductors (even those crystallizing in the zinc-blende

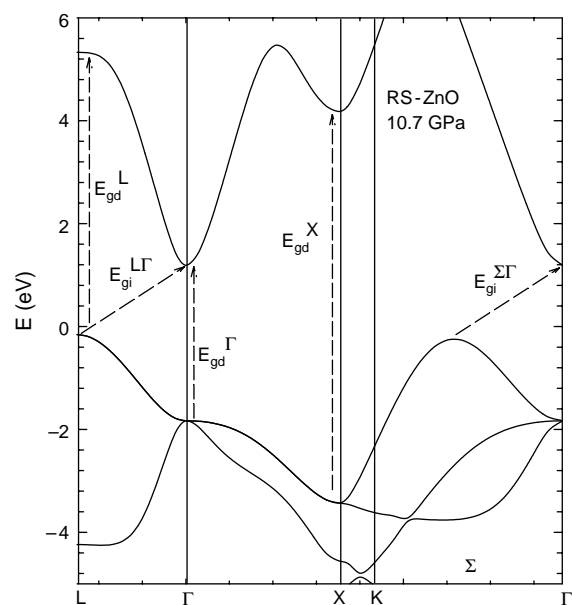


Fig. 7. Band structure of rock-salt ZnO at 11.1 GPa as calculated through ab initio DFT–LDA pseudo-potential method.

phase at ambient pressure). This change can be understood on the basis of the symmetry dependence of the interaction between the anion p states and the cation d states. In the zinc-blende and wurtzite structures, whose point groups (T_d or C_{6v}) do not contain an inversion center, anion p states and cation d states can mix at any point of the B.z., because there are always p or d states belonging to the same representation [25]. Then the p–d interaction results in a fairly uniform upward shift of the upper valence bands (with predominant anion p character) in the whole B.z. (p–d repulsion). On the opposite, the point group of the RS structure in the Γ point of the B.z. (O_h point group) includes inversion. In the O_h group p and d states belong to different representations and do not mix, which means that p–d repulsion vanishes at the Γ point. In other points of the B.z, with lower symmetry, p and d states mix. The p–d interaction depends on the electron wave-vector and the resulting p–d repulsion leads to an upwards dispersion of the upper valence bands (p bands) in directions $\Gamma-K$ (Σ) and $\Gamma-L$ (Δ) of the B.z. Consequently, the VBM occurs away from the Γ point and the material has indirect character.

As regards the predicted value of the indirect bandgap, it is underestimated in our calculation (1.1 eV versus an experimental value of about 2.6 eV), as expected in DFT–LDA methods. We must also stress that the calculation does not allow for an unambiguous assignment of the fundamental transition, as there are two sets of degenerate VBM (at the L point and in the S direction), virtually at the same energy. A more accurate determination of the indirect bandgap and further calculations of the electron-phonon deformation potentials associated to each indirect transition would be necessary to elucidate that point.

The direct transition at higher photon energy at about 4.5 eV (see Fig. 4) can be reasonably assigned on the basis of DFT–LDA band structure calculations. Direct transitions at X and L points are predicted at very large energies (about 5.6 and 7.6 eV respectively) (see Fig. 7). The direct transition at the Γ point is predicted at about 3 eV. Taking into account the DFT–LDA gap underestimation, the most likely assignment of the intense 4.5 eV transition seems to be the lowest direct transition at the Γ point, as indicated in Fig. 7.

5. Conclusions

The pressure behaviour of the absorption edge of W–ZnO thin films on mica have been shown to be very close to the one of bulk W–ZnO, which suggest that mica substrates do not introduce large strains in ZnO thin films, even under pressure. The electronic structure of RS–ZnO has also been investigated, showing that it is an indirect semiconductor,

with a bandgap around 2.7 eV, and a direct transition at a higher photon energy (about 4.5 eV at 11 GPa).

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