

Identification of valence-band ordering in ZnO by using four-wave mixing

S. Adachi,* S. Muto, K. Hazu¹, T. Sota¹, K. Suzuki¹, S.F. Chichibu²,
G. Cantwell³, D. B. Eason³, D. C. Reynolds⁴, and C. W. Litton⁴

Department of Applied Physics, Hokkaido University, N13 W8, Kitaku, Sapporo 060-8628, Japan.

¹*Department of Electrical, Electronics, and Computer Engineering,
Waseda University, Shinjuku, Tokyo 169-8555, Japan.*

²*Institute of Applied Physics; Graduate School of Pure and Applied Sciences,
University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan.*

³*Eagle-Picher Ind., 200B. J. Tunnel Blvd., Miami, Oklahoma 74354. and*

⁴*Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio 45433.*

Time-integrated and spectrally resolved four-wave mixing (FWM) experiments have been performed to identify the valence-band ordering in ZnO. Clear FWM emission associated with the Γ_1 exciton from (110) cleaved surface has been observed in B exciton region, not in A exciton region. The presented data demonstrate that the Γ_1 state belongs to B exciton and therefore the valence-band ordering is $A - \Gamma_9$, $B - \Gamma_7$, and $C - \Gamma_7$.

Zinc oxide (ZnO) is one of direct-gap, II-VI semiconductor with a wurtzite structure. It has a large fundamental band-gap of ~ 3.37 eV at room temperature and strong excitonic absorption. Because of its large band-gap and large exciton binding energy, ZnO and its related materials are promising materials for short wavelength optical devices in blue to ultraviolet region such as laser diodes, as wells as for applications in optoelectronics such as transparent field effect transistors and transparent conducting electrodes. ZnO is also available as substrate material for homoepitaxy and promising for the fabrication of wurtzite group-III-nitride based device heterostructures due to its almost perfect lattice match to GaN.[1] Accompanying the above motivation, recent progress in epitaxial growth technique has again attracted a great deal of researchers to a study of ZnO.[2-5]

As a fundamental issue in ZnO, there has been a long standing controversy on the valence-band ordering for last four decades. It has been widely believed that the valence-band ordering is $A - \Gamma_7$, $B - \Gamma_9$, and $C - \Gamma_7$ [6-8]. The assignment is attributed to a negative spin-orbit interaction due to a rather strong admixture of d states. To the contrary, Park et al.[9] have first claimed that the ordering is $A - \Gamma_9$, $B - \Gamma_7$, and $C - \Gamma_7$ based on absorption and reflection spectra measured using four different samples. Recently, Reynolds et al. have again claimed the same assignment based on the polarized reflectance and magneto-photoluminescence spectra using a sample of rather high quality.[3] Gil has supported the assignment by calculating the oscillator strengths of excitons taking the short-range electron-hole exchange interaction into account.[2] Quite recently, Chichibu et al. have also supported the assignment based on polarized reflectance, photoluminescence, and photoreflectance spectra.[10] Conversely, Lambrecht et al. have claimed that the ordering is $A - \Gamma_7$, $B - \Gamma_9$, and

$C - \Gamma_7$ based on the first-principle calculations.[11]

In this work, in order to settle experimentally the controversy, we have performed time-integrated and spectrally resolved FWM signals of ZnO, where the FWM technique is aimed at measuring the simplest nontrivial coherent emission and is known to be very sensitive to the intrinsic nature of polarizations induced in the system.[12] A sample investigated herein was a insulating bulk ZnO with c -face, which was grown by the seeded vapor transport method. The sample size was $2 \text{ mm} \times 3 \text{ mm} \times 500 \text{ }\mu\text{m}$. The thickness allows us to measure various optical signals from a cleaved edge. Characterization of the sample using the polarized reflectance and photoreflectance have been seen in Ref. 10. The degenerate FWM experiments were performed on this ZnO sample by using the second harmonic of a passively mode-locked Ti:sapphire laser as an excitation source. The laser oscillator produced the 80-fs pulses at a repetition rate of 80 MHz. The frequency-doubled output was divided into two beams with equal intensities. These pulses with the wave vectors \mathbf{k}_1 and \mathbf{k}_2 , respectively, were superimposed on the sample surface and the FWM signal was measured in the $2\mathbf{k}_2 - \mathbf{k}_1$ backward direction. The reflection geometry prevents the FWM signals from distorting due to the polariton propagation effects. The FWM signals were detected time-integrated as a function of the delay time τ_{12} ($\tau_{12} > 0$ if \mathbf{k}_1 pulse precedes the \mathbf{k}_2 pulse) and/or spectrally resolved by a combination of a 0.35-m focal length spectrograph with a 2400 grooves/mm grating and a multi-channel CCD detector (the spectral resolution was ~ 0.45 meV). Throughout the measurements, the sample was held in a closed cycle helium cryostat and its temperature was kept to be 10 K. In the experiments, the presented data were measured from the (110) cleaved surface ($\mathbf{k} \perp \mathbf{c}$).

In the point symmetry of C_{6v} , the degeneracy of the valence bands at Γ -point is lift up due to the crystal field and spin-orbit splittings (if it is positive) and the valence-band ordering is $A - \Gamma_9$, $B - \Gamma_7$, and $C - \Gamma_7$, where Γ_9 level is the topmost level.[13] The valence bands are usually referred to as A , B , and C valence bands. The

*Electronic address: adachi-s@eng.hokudai.ac.jp

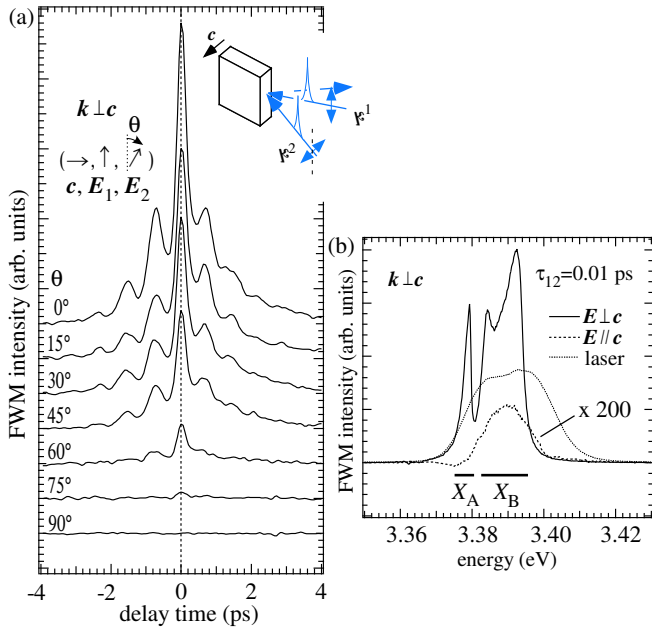


FIG. 1: (a) FWM traces as a function of τ_{12} for $k \perp c$ at the central excitation energy of 3.372 eV. θ denotes the angle between polarization vector of k_1 pulse and that of k_2 pulse. The former is fixed normal to the c axis ($E_1 \perp c$). The angle θ is varied from 0° ($E_2 \perp c$) to 90° ($E_2 \parallel c$). (b) FWM spectra in A - and B -exciton regions for colinear polarization with $E \perp c$ (solid line) and $E \parallel c$ (broken line), where E means E_i ($i=1, 2$). Note that the spectral intensity for $E \parallel c$ is magnified by 200. The excitation spectrum (dotted line) is also shown. Horizontal bars labeled as X_A and X_B indicate the energy regions of $A(\Gamma_5)$ and $B(\Gamma_5)$ excitons, which are obtained from the analysis of the polarized reflection spectra.

corresponding excitons are called as A , B , and C excitons in the lowest order approximation. The irreducible representation of the conduction band is Γ_7 . Thus, the possible representations are $\Gamma_9 \otimes \Gamma_7 = \Gamma_5 \oplus \Gamma_6$ for A exciton and $\Gamma_7 \otimes \Gamma_7 = \Gamma_1 \oplus \Gamma_2 \oplus \Gamma_5$ for B and C excitons. Excitons

with the Γ_1 and Γ_5 symmetry are dipole-allowed for the electric field polarized parallel and perpendicular to the c axis, i.e., $E \parallel c$ and $E \perp c$, respectively. The above relation is utilized in order to identify the observed excitons in the FWM measurements.

Figure 1 (a) shows the dependence of the angle between E_1 and E_2 (the polarizations of k_1 and k_2 pulses) on the FWM signal from (110) cleaved surface ($k \perp c$). We fixed as $E_1 \perp c$ and varied the polarization of E_2 from $E_2 \parallel E_1$ ($\theta = 0^\circ$) to $E_2 \perp E_1$ ($\theta = 90^\circ$). If A valence band belongs to Γ_7 , the FWM emission is expected even for the condition that $E_2 \perp E_1$ ($\theta = 90^\circ$) because A exciton has both Γ_1 and Γ_5 states in the case. The central excitation energy was chosen as 3.372 eV to excite A excitons mainly. The pronounced beating (the period 0.79 ps) for $\tau_{12} < 0$ is due to interference induced by the created two-photon coherence of $G - XX_{AA}$ and $G - XX_{AB}$. The fact that the FWM emission becomes weaker increasing θ and vanished for $\theta = 90^\circ$ indicates that the Γ_1 state is not involved in A exciton.

Figure 1(b) shows the FWM spectra from A and B excitons for $E \perp c$ ($E \parallel c$). The resonance energies of the transverse and longitudinal A and B excitons locate within the energy region indicated by the horizontal bars labeled as X_A and X_B . They have been obtained from the polarized reflectance spectra.[10] Note that the spectrum for $E \parallel c$ is multiplied by 200 and appears only in the B exciton energy region. This clearly indicates the Γ_1 state belongs to the B exciton. Consequently, both data in Fig. 1 are clear evidence that the valence-band ordering in ZnO is $A - \Gamma_9$, $B - \Gamma_7$, and $C - \Gamma_7$ as well as CdS, CdSe, and GaN.

Acknowledgments

S. A. acknowledges the support by NSGF, SCAT, and CREST.

- [1] S. Nakamura, M. Senoh, N. Iwasa, S. I. Nagahama, T. Yamada, T. Matsushita, H. Kiyoku, and Y. Sugimoto, Appl. Phys. Lett. **68**, 2105 (1996).
- [2] B. Gil, Phys. Rev. B **64**, R201310 1 (2001).
- [3] D. C. Reynolds, D. C. Look, B. Jogai, C. W. Litton, G. Cantwell, and W. C. Harsch, Phys. Rev. B **60**, 2340 (1999).
- [4] D. C. Reynolds, D. C. Look, B. Jogai, , and T. C. Collins, Appl. Phys. Lett. **79**, 3794 (2001).
- [5] N. Ashkenov, B. N. Mbenkum, C. Bundesmann, V. Riede, M. Lorenz, D. Spemann, E. M. Kaidashev, A. Kasic, M. Schubert, M. Grundmann, et al., J. Appl. Phys. **93**, 126 (2003).
- [6] D. G. Thomas, J. Phys. Chem. Solids **15**, 86 (1960).
- [7] J. J. Hopfield, J. Phys. Chem. Solids **15**, 97 (1960).
- [8] B. Hönerlage, S. Lévy, J. B. Grum, C. Klingshirn, and K. Bohnert, Phys. Reports **124**, 161 (1985).
- [9] Y. S. Park, C. W. Litton, T. C. Collins, and D. C. Reynolds, Phys. Rev. **143**, 512 (1966).
- [10] S. Chichibu, T. Sota, G. Cantwell, D. B. Eason, and C. W. Litton, J. Appl. Phys. **93**, 756 (2003).
- [11] W. R. L. Lambrecht, A. V. Rodina, S. Limpijumnong, B. Segall, and B. K. Meyer, Phys. Rev. B **65**, 075207 1 (2002).
- [12] J. Shah, *Ultrafast Spectroscopy of Semiconductors and Semiconductor Nanostructures* (Springer-Verlag, New York, 1998).
- [13] G. L. Bir and G. E. Pikus, *Symmetry and Strain-Induced Effects in Semiconductors* (Wiley, New York, 1974).