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# Low temperature reflectivity study of ZnO/(Zn,Mg)O quantum wells grown on M-plane ZnO substrates

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We report growth of high quality ZnO/Zn<sub>0.8</sub>Mg<sub>0.2</sub>O quantum well on M-plane oriented ZnO substrates. The optical properties of these quantum wells are studied by using reflectance spectroscopy. The optical spectra reveal strong in-plane optical anisotropies, as predicted by group theory, and marked reflectance structures, as an evidence of good interface morphologies. Signatures of confined excitons built from the spin-orbit split-off valence band, the analog of exciton C in bulk ZnO are detected in normal incidence reflectivity experiments using a photon polarized along the c axis of the wurtzite lattice. Experiments performed in the context of an orthogonal photon polarization, at 90° of this axis, reveal confined states analogs of A and B bulk excitons. Envelope function calculations which include excitonic interaction nicely account for the experimental report.

Wurtzite semiconductor heterostructures have been subject of intense investigations during the last two decades in correlation with the potential application of these materials [1, 2] for optoelectronic applications from the visible to ultraviolet portion of the electromagnetic spectrum. However, such structures grown along the c-axis exhibit a Quantum Confined Stark Effect (QCSE) due to the large internal electric fields along this direction. This is the case for ZnO heterostructure [3-6]. In order to annihilate the effect of the built-in electrical field on the excitons properties, one can growth them along non-polar orientations [7-9]. In this letter we report reflectance investigations performed on a series on ZnO/(Zn,Mg)O single quantum wells grown on M-plane oriented ZnO substrates. The observation of both ground state excitons and spin-orbit split-off excited state ones demonstrates a reasonable interface roughness as an evidence of a highly controlled growth procedure.

The samples have identical designs and all consist of a bulk ZnO carefully prepared so that its (10-10) plane can be used as a growth substrate. A 200 nm thick (Zn,Mg)O barrier layer is first deposited, then a ZnO confining layer, and finally a second (Zn,Mg)O barrier layer. Growth along the M-plane orientation leads to a strong anisotropy of the optical properties: in normal incidence reflectivity experiments,  $\Gamma_1$  excitons can be probed for example using a photon polarized along the [0001] direction and energies of  $\Gamma_5$  excitons are revealed if using a photon polarized orthogonally to [0001]. A detailed description of reflectivity properties of ZnO layers, including birefringence effects, or polariton fine structure effects is out of the scope of this letter but can be found in the ref. 10. We wish to outline here that, thanks to the large value of the crystal field splitting in ZnO, the topmost valence band states are built from  $p_x$  and  $p_y$  type wave functions (in a spinless description) whilst the crystal field split one is mainly built from  $p_z$  type states [11]. Thus, in case a reflectivity experiment is performed under normal incidence conditions, the electric field of the photon being parallel to the [0001] direction, the most intense optical transition will be the one which concern excitons built from states at the conduction band bottom and hole states built from this excited state hole. The corresponding excitonic transition (C line) is very strong in these experimental conditions. In contrast, in crossed polarization configuration, most of the oscillator strength is detected at the lower energies of

the A and B excitons (excitons built from states at the conduction band bottom and hole states built from top most valence band states). The intensity of line A is smaller than the intensity of line B which dominates the spectrum. The transition energies of these lines are typically 3.376 eV and 3.383 eV for  $\Gamma_{5T}$  A and B excitons, 3.425 eV for  $\Gamma_1$  C exciton at liquid helium temperature. When ZnO quantum wells are grown on a (10-10) oriented surface, electron and hole confinements are produced. Even in the case of a homoepitaxial quantum well the degeneracy of the  $p_x$  and  $p_y$  states in the bulk is lifted, due to the breaking of translational symmetry along the growth direction. The growth plane has orthorhombic symmetry; the optical response is anisotropic in this growth plane.

Figure 1 summarizes a series of reflectivity experiments carried out in normal incidence conditions. The electric field of the photon is parallel to the [0001] direction. Thus  $\Gamma_1$  excitons are probed by this experiment. From the low to the high energy regions one detects the strong signature of the 1s  $\Gamma_1$  C exciton in the bulk together with the weaker signature of the 2s state at higher energy. Note the phase differences between the reflectance features of the samples due to slight different thickness of the near surface barrier layer through the series of samples. The bulk exciton always occurs at the same energy and the full width at half maximum does not vary from sample to sample. Most interesting is the observation of a high energy feature, typical of these quantum wells which blue shifts when the thickness of the ZnO quantum well layer decreases. This structure is marked with vertical arrows. The radiative inhomogeneous broadening increases with decreasing the well width, due to the increase of the spreading of the wave functions into the barrier layers when the well width decreases and to the increased sensitivity of the transition energy to the roughness of the heterointerfaces. In case of the thinner well this transition could no longer be detected. The energy of this transition decreases and reaches the one of bulk ZnO with increasing well width as an evidence of the absence of QCSE in these samples, as expected from group theory [12].

Figure 2 summarizes a series of reflectivity experiments also carried out in normal incidence conditions. The electric field of the photon is now orthogonal to the [0001] direction. Thus bulk  $\Gamma_5$  excitons and their confined analogs are probed by this experiment. From the low to the high energy regions one detects the strong signatures of the  $\Gamma_5$  A and  $\Gamma_5$  B exciton in the bulk (note again the phase differences

from sample to sample). The energies of bulk excitons and their full widths at half maximum are not sample-dependent. Observation of 2s excited states excitons are also reported and are indicated in the figure. The high energy feature blue shifts when the thickness of the ZnO quantum well layer decreases. Its full width at half maximum prevents us to detect A-B splitting. The increase of the radiative inhomogeneous broadening is ruled by phenomena similar to those previously reported for  $\Gamma_1$  excitons. The energy of these quantum confined excitons also saturates with increasing well width, again, as an evidence of the absence of QCSE in these samples.

The evolution of the transition energies with well width are plotted in figure 3. The trend is similar to the one earlier reported by some of us in the case of homoepitaxial ZnO/(Zn,Mg)O quantum wells grown on a-plane oriented substrate [8]. To avoid bringing further complication in the figure, we omitted plotting the 2s states of the bulk A, B and C lines which energies overlap the energy of the unresolved (A, B) doublet and C confined states. The fit to the data has been achieved in the context of the one band envelope function calculation: this approximation is reasonable here due to the inhomogeneous broadening of the excitonic lines which does not leads to measuring A-B splitting in our quantum wells in the one hand and the little knowledge of the electronic structure of (Zn,Mg)O in another hand. The valence band orderings were taken identical to both ZnO and (Zn,Mg)O [13]. The fundamental band gaps of ZnMgO lattice matched to ZnO is settled at 3835 meV at 10 K and the distribution of conduction to valence band discontinuities is taken in the 0.8/0.2 ratio. Concerning the electron and (A, B) (resp. C) hole effective masses they are taken isotropic 0.28 [14] and 0.59 [14] (resp. 0.59) in units of the electron mass at rest. Both the calculation and the experiment are plotted in figure 3 (black lines). The band to band envelope function calculation was corrected from the evolution of the long range electron-hole Coulomb interaction which was here computed in the context of a one-band variational calculation. The excitonics transitions are labeled here as  $(e_1, X_1)$ , where 1 indicates the confined quantum number and X refers to the symmetry of the valence band of the bulk ( $X = A, B,$  and  $C$ ). The evolution of this excitonic binding energy estimated in this context for both C-plane oriented and M-plane oriented quantum wells are different as shown in figure 4 in the specific case of A and B

excitons. We note that this long-range interaction is not reduced in the case of our quantum wells by the quantum confined stark effect observed in case of C-plane grown structures as expected from previous studies on GaN/(Ga,Al)N quantum wells [15]. The variational calculation indicates that the exciton binding energy varies from 70 to 90 meV in these samples. This 10-30 meV enhancement with respect to the bulk value (60 meV) is slightly larger than the inhomogeneous broadening and this indicates the need for making this correction to the band to band calculation.

In conclusion, we have reported the observation of polarized excitonic structure in a series of homoepitaxial ZnO/(Zn,Mg)O quantum wells grown on M-plane bulk ZnO substrates. The evolution of the quantum confined exciton indicates the absence of Quantum Confined Stark Effect. In the limit of wide wells the splitting between anisotropically confined excitons asymptotically reaches the value of this splitting in the bulk. The interface roughness deduced from the inhomogeneous broadening of the reflectivity features does not indicate noticeable difference compared with quantum wells grown along the polar orientation, which is really a plus if optoelectronic applications are targeted using these quantum wells.

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## Figure captions

**Figure 1 (color online):** Normal incidence reflectivity spectra of a series of M-plane oriented ZnO/Zn<sub>0.8</sub>Mg<sub>0.2</sub>O single quantum well. The electric field of the photon is parallel to the [0001] direction of the crystal. Note the observation of 1s and 2s states of the C exciton in the bulk and the observation of confined excitons (transitions labeled e<sub>1</sub>-C<sub>1</sub>) at the energies marked by arrows.

**Figure 2 (color online):** Normal incidence reflectivity spectra of a series of M-plane oriented ZnO/Zn<sub>0.8</sub>Mg<sub>0.2</sub>O single quantum well. The electric field of the photon is orthogonal to the [0001] direction of the crystal. Note the observation of 1s of A exciton and 1s and 2s states of the B exciton in the bulk. The confined excitons (transitions labeled e<sub>1</sub>-(A,B)<sub>1</sub>) are also observed at the energies marked by arrows in this case the A-B splitting is not resolved experimentally.

**Figure 3 (color online):** Transitions energies plotted versus well width for a series of M-plane oriented ZnO/Zn<sub>0.8</sub>Mg<sub>0.2</sub>O single quantum well. The energies of the excitons in the bulk ZnO substrate is indicated using small dots. The red symbols represent energies of e<sub>1</sub>(A,B)<sub>1</sub> lines whilst blue ones correspond to e<sub>1</sub>-C<sub>1</sub> confined excitons. The result of the effective mass (excitonic) envelope function calculation is represented by black lines.

**Figure 4 (color online):** Result of the one parameter variational calculation of the exciton binding energies for M-plane (green) and C-plane (red) grown ZnO-Zn<sub>0.8</sub>Mg<sub>0.2</sub>O single quantum well. QCSE is included in the case of the C-plane orientation; the internal electric field is taken at 0.82 MV/cm in the calculation.

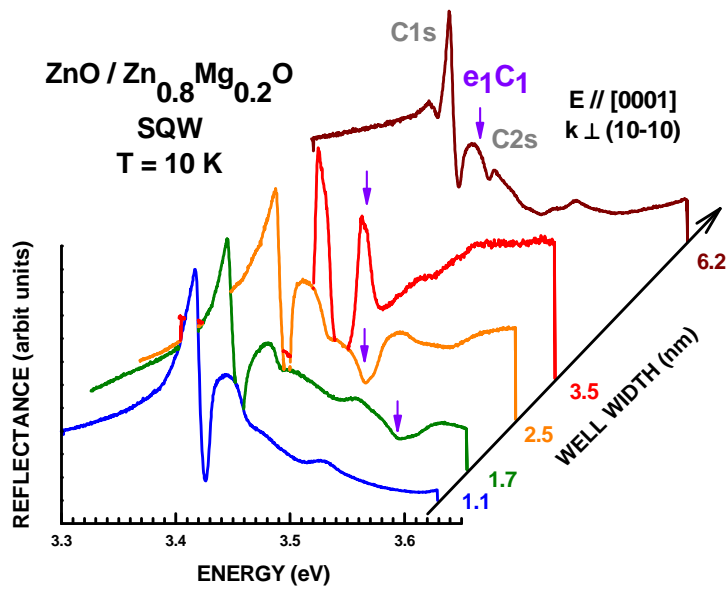


Figure 1

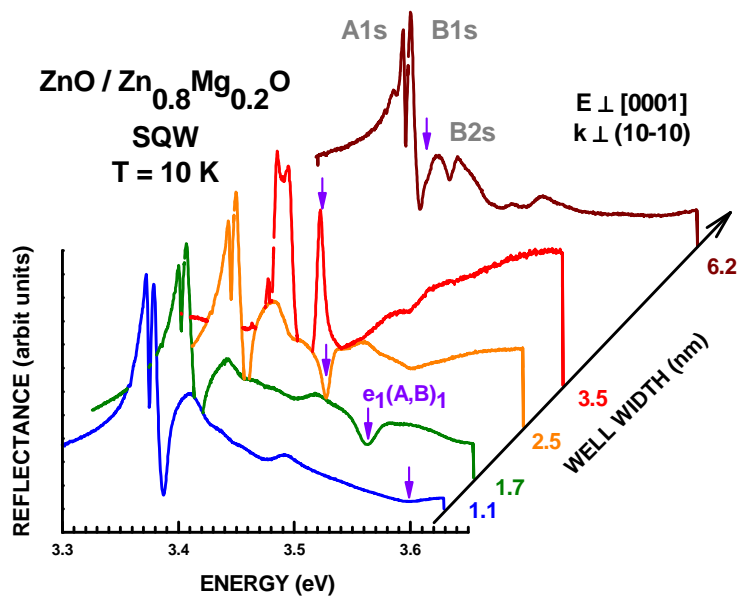


Figure 1

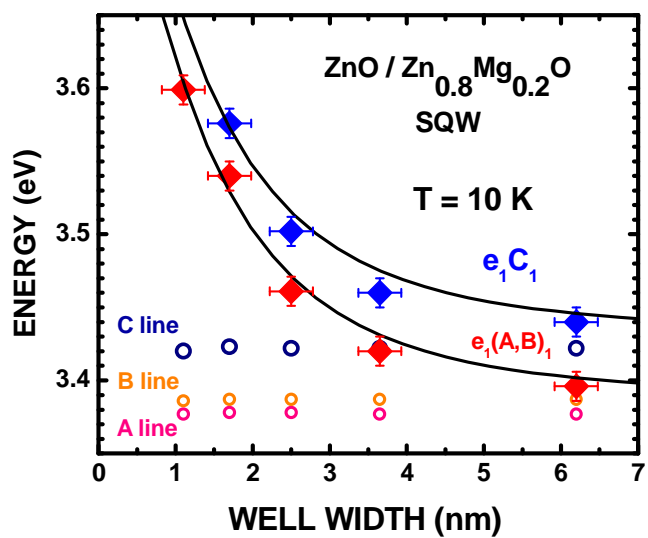


Figure 3

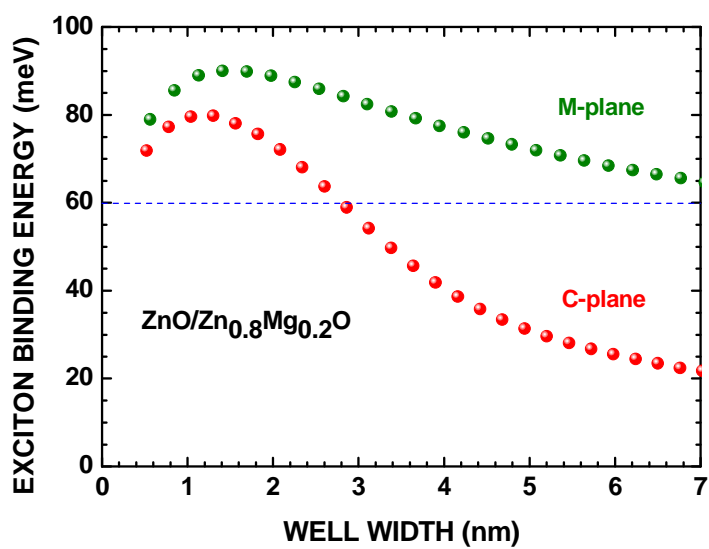


Figure 4