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## Intersubband absorption in m-plane ZnO/ZnMgO MQWs

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### ABSTRACT

ZnO has great potential for devices in the mid IR and the THz range through the use of intersubband (ISB) transitions in multiple quantum wells (MQWs), although exploiting these transitions requires great control of the epitaxial layers as well as of the physics involved. In this work we present an analysis as ISB optical absorbers of non-polar ZnO quantum wells grown homoepitaxially by molecular beam epitaxy on m-plane ZnO substrates. The MQWs were characterized under a 45°-bevelled multi-pass waveguide configuration allowing the observation at room temperature of an ISB transition in the 4-6  $\mu\text{m}$  region for *p*-polarized incident light.

**Keywords:** ZnO, ZnMgO, intersubband, terahertz, infrared, homoepitaxy, non-polar, quantum well

### INTRODUCTION

Mid and far IR optoelectronic devices and THz electronic devices receive a great deal of attention from the semiconductor device research community, especially in terms of developing devices with extended operation frequency capable of bridging or reducing the so-called terahertz (THz) gap -roughly spanning from 0.1 to 10 THz (wavelengths from 3 mm to 30  $\mu\text{m}$ )- where there is a lack of efficient and compact semiconductor emitters and detectors of radiation. Devices making use of the intersubband transitions (ISBT) occurring between confined levels in the conduction band of quantum wells (QWs) are very attractive options to cover this gap from the high frequency (i.e. optical/IR wavelengths) side. Indeed, commercial devices exist that are based on such ISBTs between the confined levels in the conduction band of QWs based on GaAs and related alloys. This work is supported by the H2020-FET project ZOTERAC, which aims to demonstrate the potential of ZnO for these applications. Here, we discuss its advantages with respect to the established GaAs-based technology. We commence by reviewing the strong points of ZnO for its use in this field, and we finish showing some promising experimental results on absorption ISBTs in ZnO/ZnMgO QWs.

#### Photodetectors based on intersubband transitions

Examples of radiation detectors based on these transitions are the quantum well infrared photodetectors (QWIPs) used in some commercially available IR sensors<sup>1</sup>. These devices usually consist of a multiple quantum well structure (MQW), with typically tens of QW periods. Absorption of radiation by the QWs yields an electronic transition from the first or ground level to the excited levels, usually the second confined level of the QW. These transitions can be tuned in energy by varying the width and the barrier height of the QW. The electrons in these excited levels can escape the QWs and, by the application of an external potential, be collected at the device electrodes and counted in the outer device electronics. Note these are monopolar devices, i.e. only one type of charge carrier (electrons) is involved, as opposed to bipolar devices in which both electrons and holes participate. The frequency of operation of these devices has been extended in recent years to the THz range<sup>2</sup>. Unfortunately the operation temperatures of these devices based on GaAs/AlGaAs is limited to values below RT.

It has to be kept in mind that intersubband absorption must comply with the well-known light-polarization rule stating that only light polarized (even if it is only partially) perpendicularly to the planes of the quantum wells can be absorbed<sup>1,3</sup>. This

implies there is no absorption when the incident light is perpendicular to the QW planes and, therefore, at normal incidence with respect to the material surface, which coincides with the QW interfaces in the usual layer-by-layer deposition scheme used for the fabrication of these structures. Therefore, it becomes mandatory to make use of approaches so the light which arrives to the device surface at normal incidence (i.e. the simplest configuration for the devices in terms of both fabrication and packaging) gets deviated from its path so it arrives at the QWs at an arbitrary angle of incidence. The use of gratings inscribed on the top surface of the devices is a common strategy to achieve this goal.

Related to the QWIP is the concept of quantum cascade photodetector (QCD), which operates in a similar way to the former photodetector in terms of absorption of the light, but the photogenerated electrons are transferred to the next active QW in the MQW structure through a multi-quantum well extractor region, resulting in a photovoltage across the device. These are ultrafast devices that work without applied bias and are free from issues related to dark current. However, only one demonstration of GaAs-based QCDs in the THz has been reported so far<sup>4</sup>.

### Wide band-gap semiconductors for intersubband transitions

Virtually all the devices mentioned in the previous sub-sections are based on the semiconductor gallium arsenide (GaAs) and its related alloys, such as the larger-band gap semiconductor aluminum gallium arsenide (AlGaAs), which is usually employed as barrier material in GaAs/AlGaAs QWs. The use of this material system has the advantage that GaAs is a very mature material and, therefore, the technology for the growth of the multiple quantum well structures and the fabrication technology for the devices is well established and widely deployed.

The use of wide-band gap alternatives to GaAs, such as GaN and ZnO, for the fabrication of devices based on intersubband transitions is receiving increasing attention. Actually, there has been a noticeable number of reports on devices based on GaN (see, for example, the review in Ref. 5 and references cited therein), and, more recently, absorption ISBTs in ZnO material have also been reported<sup>6,7</sup>. These semiconductors possess a number of interesting features that make them very interesting candidates for the next generation mid-IR and THz emitters and detectors. These features are described in the following paragraphs.

First, ZnO and GaN have longitudinal-optical phonon energies of  $\sim 72$ <sup>8</sup> and  $\sim 90$  meV<sup>9</sup>, respectively. These values are much larger than that of GaAs, of only  $\sim 36$  meV<sup>10</sup>. This has an interesting implication on the emission efficiency of ISBTs. Let us suppose we have an electron residing in the excited level of a GaAs/AlGaAs QW. This electron can relax to the ground level by the emission of a photon or by the non-radiative emission of phonons. If the longitudinal-optical phonon energy is comparable to the intersubband transition energy, the phonon-assisted non-radiative channel is very fast and the luminescence can be severely quenched. If the phonon energy is slightly larger than the intersubband transition energy (i.e. still within  $\sim kT$  of the transition energy, where  $T$  is the temperature and  $k$  is the Boltzmann's constant) the non-radiative channel still has an impact on the radiative efficiency of the transition as the intersubband transition can also occur at higher energies. One potential solution to this problem is the use of materials with a larger optical phonon energy, such as ZnO, so even the highest energies in the intersubband transition have an energy smaller than that of the phonon excitation. Thus, the non-radiative channel via emission of phonons is hindered, and the radiative efficiency of the devices will be improved<sup>11</sup>.

Another important advantage of ZnO is the availability of non-polar, native ZnO substrates. This has two implications. First, the use of native substrates allows ZnO to be grown homoepitaxially with a very low density of dislocations and other defects, which are obviously detrimental for the efficiency of light-emitting devices.<sup>12</sup> The second advantage of growing the ZnO structures on native, non-polar substrates is the cancellation of the internal electric field present in semiconductors with the wurtzite structure if they are grown along the c-axis. This internal field is responsible for the quantum-confined Stark effect (QCSE) which is detrimental for devices based on ISBTs because it can reduce the oscillator strength of the transitions involved. Growing the structures on a non-polar orientation can help thus improve the efficiency of the devices<sup>13</sup>.

As mentioned above, ISBT in ZnO have already been demonstrated by two groups. Belmoubarik *et al.*<sup>7</sup> reported on the photocurrent of ZnO/ZnMgO quantum wells at 18 K temperature. The structures were grown on c-plane ZnO substrates. They attributed the photocurrent peak to the  $E1-E3$  transitions which, although forbidden due to the wavefunctions involved having the same parity, is supposed to be allowed because the internal electric field breaks the symmetry of the wavefunctions. The second, more recent report on ISBT in ZnO was also from material grown on polar orientation, this time on c-plane sapphire. Zhao *et al.*<sup>6</sup> showed relatively wide absorption ISBTs bands at room temperature. Our group is the first to show room-temperature ISB absorption from m-plane ZnO/ZnMgO MQWs.

## DESCRIPTION OF THE SAMPLES

The material presented in this work was grown by molecular beam epitaxy at the facilities of the *Centre de Recherche sur l'Hétéro-Epitaxie et ses Applications*, in France. The samples were grown on m-plane ZnO substrates, and consist of a ZnMgO (30% Mg) buffer layer on top of which a set of 20 ZnO/ZnMgO QWs was grown. The barrier thickness is 15 nm and the QW thickness presented here is 3.7 nm. The QWs are doped at  $1 \times 10^{19} \text{ cm}^{-3}$  to populate the first level of the quantum well, leaving the first excited level mostly unpopulated to facilitate absorption. The sample was prepared as a multipass waveguide 3 mm wide and 6 mm long, with the short edge cut parallel to the c-axis, and then mechanically polished to optical quality at  $45^\circ$  to allow for *p*-polarized light to be coupled into the sample and thus have a component of the electric field perpendicular to the structures, fulfilling the polarization selection rule described above.

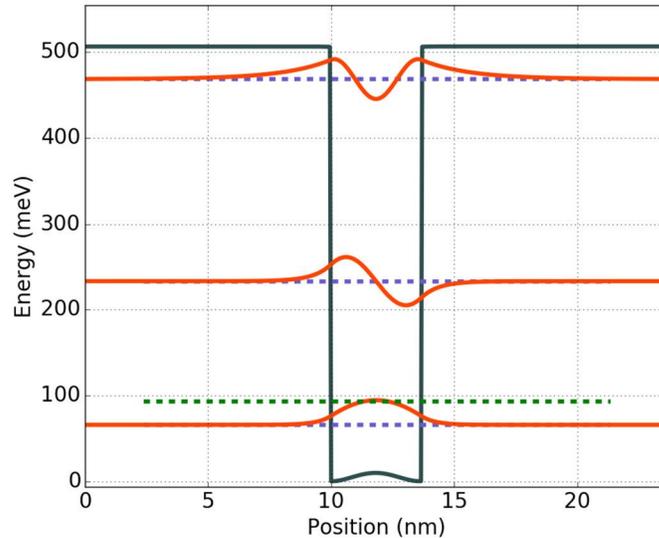


Figure 1. Schematic of one quantum well of the sample presented in this work as calculated from self-consistent solving of the Schrödinger and Poisson calculations. Only the first three levels are shown. The wavefunctions have been offset to their corresponding energy for clarity. The green line indicates de Fermi energy.

## MODELS AND CALCULATIONS

In order to predict the frequency of the absorption ISBTs we calculate the energy difference between the first and second confined levels in the QWs,  $E_{12} = E_2 - E_1$ , solving self-consistently the Schrödinger and Poisson equations to account for the modifications to the potential profile due to the inhomogeneous distribution of carriers in the QW. The nominal QW and barrier widths were employed in the calculation. The effective mass for ZnO and ZnMgO was taken as  $0.28m_0$ <sup>14</sup>, with  $m_0$  the mass of the free electron. The band-offset between well and barrier was 0.675 times the bandgap difference between ZnO and ZnMgO. This is the mid-point between the previously reported values of 0.65 and 0.7<sup>6,7</sup>. Finally, the band gap of ZnMgO was calculated as in Ref. 15 by increasing the band gap of ZnO on 25 meV for each % of Mg. The conduction band diagram thus calculated for a QW of our sample is shown in Figure 1.

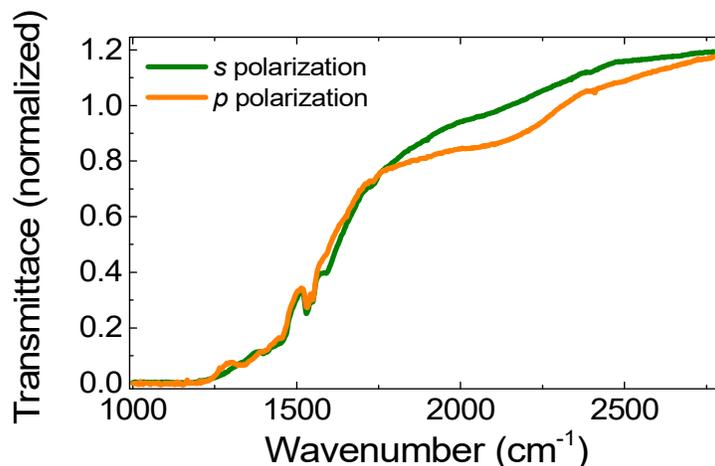


Figure 2. Normalized transmittance spectra of the multipass waveguide under  $p$  (orange) and  $s$  (green) polarizations of the incident light.

### ISBT RESULTS

Figure 2 shows the absorbance spectra of the MQW structure under  $p$  and  $s$  polarization of the incident light. At low wavenumbers the absorbance grows very rapidly because of free-electron absorption. Note in the multipass waveguide configuration the light travels across the whole length of the sample and, therefore, absorption by the substrate becomes large. It is clear from the figure that there is a feature in the absorbance spectrum, in the range from 1700 to 2500  $\text{cm}^{-1}$ , i.e. from 6 to 4  $\mu\text{m}$ , only present in the spectrum taken under  $p$ -polarization. This is an ISB absorption transition since it fulfills the selection rule for polarization.

It is easier to visualize the absorption ISBT if the ratio between the  $s$ -polarization and the  $p$ -polarization transmittance is plotted. Such a plot can be seen in Figure 3, from which we can extract a peak wavenumber of around 2200  $\text{cm}^{-1}$  for the ISBT as well as a full width at half maximum (FWHM) of around 800  $\text{cm}^{-1}$ . In relative terms, this peak width represents 36% of the peak energy (i.e.  $\Delta E_{12}/E_{12} = 0.36$ , with  $\Delta E_{12}$  the FWHM of the peak), comparable to what was obtained by Belmoubarik *et al.*<sup>7</sup> and much lower than reported by Zhao *et al.*<sup>6</sup>

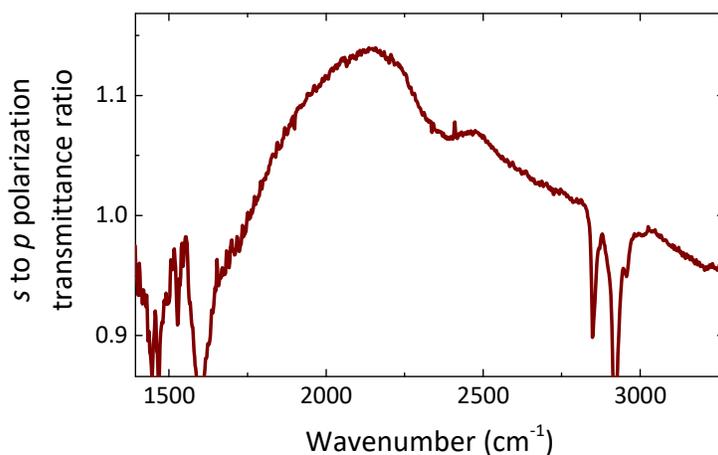


Figure 3. Ratio of the  $s$  to  $p$  transmittance polarization spectra of Figure 2.

## CONCLUSIONS

To conclude, we have presented the wide band-gap oxide semiconductor ZnO as a suitable candidate for the development of ISBT devices in the mid-IR. Its advantages with respect to the more established GaAs have been discussed. As an example of the suitability of this material for its use on ISBT-based devices, room-temperature ISBT absorption at  $2200\text{ cm}^{-1}$  has been demonstrated from a ZnO/ZnMgO multiple quantum well structure grown by MBE on m-plane, non-polar, native ZnO substrate. The absorption has a relative width of  $\Delta E_{12}/E_{12} = 0.36$ , which is comparable or better than the two previous reports on ISBT in polar ZnO material. All this proves ZnO is a very suitable candidate to play a main role in the next generation of ISBT-based devices.

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