Intersubband absorption in ZnO/ZnMgO quantum wells grown by plasma-assisted molecular beam epitaxy on *c*-plane sapphire substrates

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The authors report the growth of ZnO/ZnMgO multiple quantum well (MQW) structures by plasma-assisted molecular beam epitaxy. A set of three MQW samples with different well thickness were grown on *c*-plane sapphire substrates. Structural and optical properties of the samples were characterized by reflection high-energy electron diffraction, high-resolution x-ray diffraction (XRD) and photoluminescence measurements. Clear superlattice satellite peaks and thickness fringes observed in XRD measurements indicate the formation of periodic structure with good interfacial quality and high crystalline quality. Mid infrared absorptions around 3 μm are observed from Fourier transform infrared spectroscopy measurement. The polarization-dependent absorption proves that the absorptions are originated from intersubband transitions.

Keywords:

A3. Molecular beam epitaxy A3. Quantum well B1. Oxides

B2. Semiconducting II-VI materials B3. Heterojunction semiconductor devices

1. Introduction

Although the challenges associated with p-type doping in ZnO have hindered the realization of efficient interband optical emitters, ZnO and related structures may find applications in intersubband devices [1, 2]. ISB devices are unipolar devices, in which electron (or hole) transitions happen between energy subbands within the conduction (or valence) band and only one kind of conduction carriers are needed. Since the observation of ISB transitions in semiconductor quantum wells (QWs) [3], various ISB devices such as quantum cascade lasers [4-6], quantum-well infrared photodetectors [7-11], and all-optical switches [12, 13] have been fabricated. The mature technology for achieving high n-type doping in ZnO makes it possible to employ ZnO-based heterostructures in ISB devices. The large band offset in ZnO-based heterostructures suggests a large conduction band offset (CBO), which makes the material system a very promising candidate for ISB devices working in the short wavelength infrared (IR) region. ZnO-based materials may find more applications in high speed devices due to their higher ionicity and thereby shorter carrier lifetime compared to their III-V counterparts.

Here we report the growth of ZnO/ZnMgO multiple QWs (MQWs) on *c*-plane sapphire substrates by plasma-assisted molecular beam epitaxy (MBE). The structural and optical properties were characterized by x-ray diffraction (XRD) and photoluminescence (PL) measurements. ISB absorptions were measured by Fourier-transform IR (FTIR) spectroscopy. At room temperature (RT), ISB absorptions at around 3 μm were observed in ZnO/ZnMgO MQWs.

2. Experiments

Three ZnO/ZnMgO MQW samples (samples A, B, and C) and a Ga-doped ZnO reference sample (samples D) are reported here. All these samples were grown on 2-inch *c*-plane sapphire substrates by plasma-assisted MBE in a modified DCA 350 system. Prior to the growth, the substrates were outgassed at 670°C for half an hour. After the outgassing, the substrate

temperature was ramped down to 650°C. At that temperature, the substrates were exposed to the active oxygen for another 30 minutes. The growth started with the growth of a thin (about 2 nm) MgO buffer (at 650°C). On the thin MgO buffer, a thick ZnO buffer layer (500 nm) was grown (at 650°C). After that the substrate temperature was lower down to 450°C to grow the ZnO/ZnMgO MQWs. The low growth temperature (450°C) is to avoid the phase separation in ZnMgO.

All growths were performed under group-II-rich (oxygen limited) conditions. Typical beam equivalent pressures for Zn, Mg, and Ga (used as n-type dopant) fluxes are 2.0×10^{-7} torr, 2.5×10^{-8} torr, and 0.3×10^{-9} torr, respectively. The oxygen flow rate was kept at 0.6 SCCM (standard cubic centimeter per minute). The RF source (OAR CARS25AI) was operated under a forward power of 350 W.

High-resolution XRD measurements were performed with a Bruker D8 Advance X-ray Diffractometer. PL measurements were carried out at room temperature (RT) using a 266 nm line of a solid-state laser as the excitation source. The ISB absorption was measured at RT with a parallel 45° multiple-pass waveguide geometry using a Nicolet Nexus-670 Fourier-transform IR (FTIR) spectrometer with a white light source, a CaF₂ beam splitter, a wire-grid polarizer, and a liquid-nitrogen-cooled HgCdTe detector. Hall Effect measurements were performed with Van der Pauw method in a Lake Shore 7604 Hall System.

3. Results and discussions

Samples A and B have 14 periods and sample C has 15 periods. The ZnO well thicknesses are 26.2 Å, 29.1 Å, and 31.2 Å for sample A, B, and C, respectively. The ZnMgO barrier thickness for sample A is 39.4 Å, for sample B is 43.7 Å, and that for sample C is 46.9 Å. Growth rates are obtained from dividing the film thicknesses by the growth time in separate calibration samples. The film thicknesses are calculated from thickness fringes in high-resolution

XRD curve. Figure 1 shows the XRD curve for sample D obtained with coupled $\theta/2\theta$ scan. Numerous thickness fringes were observed, indicating high crystalline quality and good surface/interface quality of the sample. From the angular spacing between the fringes, the thickness of the ZnO film was calculated. The growth rate thus determined is 0.28 Å/s. The ZnO well layers in Samples A, B, and C were doped with Ga with a carrier concentration of $1 \times 10^{19} \text{ cm}^{-3}$. The electron concentration is obtained from Hall Effect measurements on the reference sample (sample D). Bandgap energies of the ZnMgO barrier layers are 4.045 eV, 4.364 eV, and 4.364 eV for samples A, B, and C respectively, which are also obtained from separated calibration samples. According to the reported empirical formula [14], the corresponding Mg compositions are 28.4%, 39.7%, and 39.7% in samples A, B, and C, respectively.

(Fig. 1/6 single column)

Figure 2a shows the reflection high-energy electron diffraction (RHEED) pattern after the thick ZnO buffer growth for sample C. A streaky (3x3) pattern with bright Kikuchi lines indicates the high crystalline quality and good surface morphology of the ZnO buffer layer. The streaky pattern maintained until the growth of the complete structure is finished, as shown in Figure 2b. Similar RHEED patterns were observed for other samples.

(Fig. 2/6 single column)

Clear satellite peaks were observed in the MQW samples (samples A, B, and C), indicating the formation of periodic structure and good interfacial quality in the samples. Figure 3 shows the XRD curve obtained with coupled $\theta/2\theta$ scan for sample B. The periodicity thus determined for sample B is 72.8 Å, very close to the designed value of 72 Å. A large number of thickness fringes from the thick ZnO buffer layers were observed around the ZnO (0002) peaks (see the inset of Figure 3). The observation of thickness fringes is an indication of excellent

crystalline quality of the sample. Thickness fringes corresponding to the total MQWs thickness are also observed around the satellite peaks (indicated by the downwards arrows in Figure 3). The periodicities of samples A and C determined from XRD measurements are 65.6 Å and 78.1 Å, respectively. These results demonstrate that ZnO/ZnMgO MQWs can be grown on *c*-plane sapphire substrates with high structural quality.

(Fig. 3/6 single column)

The emission energies of the MQW samples obtained from PL measurements are higher than that of the reference sample (Sample D – a Ga-doped ZnO thin film). The higher emission energy (blue shift) is the result of quantum confinement effect in the MQWs. At RT, the emission energies are 3.410 eV, 3.350 eV, and 3.332 eV for samples A, B, and C respectively. Figure 4 shows the PL spectra for the samples B in reference to sample D. The inset of Figure 4 shows the

emission energy as a function of ZnO well thickness. The blue shift in the MQW samples is also an indication of moderate electric field in the ZnO well, since a significantly high field can cause the red shift due to the strong quantum-confined Stark effect.

(Fig. 4/6 single column)

Figure 5 shows the absorbance of the MQW samples obtained by FTIR measurements at RT. The absorbance was obtained by taking the negative natural logarithm of the ratio between the p-polarized light and the s-polarized light. Due to the ISB transition selection rule, only the p-polarized light is absorbed by the QWs. Clear ISB absorptions in the mid IR spectral region are observed at 2.84 μm for sample A, 3.11 μm for sample B, and 3.46 μm for sample C. The difference in absorption wavelength (energy) is mainly due to different well width of the samples. All spectra have the Lorentzian line shapes. The full width at half maximum (FWHM) of absorption spectra for sample A is 180 meV ($\Delta E/E = 41\%$), for B is 158 meV ($\Delta E/E = 40\%$), and

for C is 146 meV ($\Delta E/E = 40.7\%$). The large FWHM may result from the very thin wells used. With such thin wells (~ 3 nm), a fluctuation of one monolayer in well thickness (about $3 \text{ \AA}$) can cause the change of ISB transition energy of more than 40 meV. We note that non-uniformity exists across the wafer. Both the layer thickness and the alloy composition decrease from the center to the edge of the wafer.

(Fig. 5/6 single column)

The absorptions observed in all the MQW samples are strongly polarization dependent. Figure 6 shows the absorbance spectra of sample C measured at different polarization angles, with 0° corresponding to p-polarized light and 90° s-polarized light. The strongly polarization-dependent absorptions are clear signatures of ISB absorption. The result is a direct proof that the observed absorptions are originated from ISB transitions in ZnO/ZnMgO QWs.

(Fig. 6/6 single column)

4. Summary

In summary, ZnO/ZnMgO MQW structures have been grown on *c*-plan sapphire by plasma-assisted MBE with high structural quality and good interfacial quality. Formation of high quality MQW structures was demonstrated by the observation of satellite peaks in high-resolution XRD measurements. PL measurements demonstrated the expected quantum confinement effect of these samples. Clear mid IR absorptions at 2.84 μm , 3.11 μm , and 3.46 μm have been observed. Polarization-dependent FTIR measurement results indicate that these absorptions were originated from ISB transitions. The observation of ISB absorptions demonstrates the potential to use the ZnO/ZnMgO heterostructures for ISB devices.

Acknowledgments

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Figure captions

Figure 1. High-resolution XRD curves obtained with couple $\theta/2\theta$ scans for sample D. The observation of clear thickness fringes is an indication of high structural quality of the ZnO film. The thickness of the ZnO layer can be determined from the angular spacing between the fringes.

Figure 2. (Color online) RHEED pattern of sample C took (a) after the growth of ZnO buffer layer; and (b) after the MQW structure is finished.

Figure 3. High-resolution XRD curves obtained with couple $\theta/2\theta$ scans for sample B. Satellite peaks originated from periodic QW structures were observed. Inset shows the magnified view around the ZnO (0002) peak and the 0th superlattice peak.

Figure 4. PL spectra of samples B and D measured at RT. Inset shows the emission energy as a function of ZnO well thickness.

Figure 5. Absorbance spectra obtained with FTIR measurements at RT for samples A, B, and C.

Figure 6. (Color online) Absorbance spectra of sample C measured at different polarization angles, with 0° (the topmost curve) corresponding to p-polarized light and 90° s-polarized light.