Phase segregation in \( \text{Mg}_x\text{Zn}_{1-x}\text{O} \) probed by optical absorption and photoluminescence at high pressure

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The appearance of segregated wurtzite \( \text{Mg}_x\text{Zn}_{1-x}\text{O} \) with low Mg content in thin films with \( x > 0.3 \) affected by phase separation, cannot be reliably probed with crystallographic techniques owing to its embedded nanocrystalline configuration. Here we show a high-pressure approach which exploits the distinctive behaviors under pressure of wurtzite \( \text{Mg}_x\text{Zn}_{1-x}\text{O} \) thin films with different Mg contents to unveil phase segregation for \( x > 0.3 \). By using ambient conditions photoluminescence (PL), and with optical absorption and PL under high pressure for \( x = 0.3 \) we show that the appearance of a segregated wurtzite phase with a magnesium content of \( x \approx 0.1 \) is inherent to the wurtzite and rock-salt phase separation. We also show that the presence of segregated wurtzite phase in oversaturated thin films phase is responsible for the low-energy absorption tail observed above \( x = 0.3 \) in our \( \text{Mg}_x\text{Zn}_{1-x}\text{O} \) thin films. Our study has also allowed us to extend the concentration dependence of the pressure coefficient of the band gap from the previous limit of \( x = 0.13 \) to \( x \approx 0.3 \) obtaining \( dE_g/dP = 29 \text{ meV/GPa} \) for wurtzite with \( x \approx 0.3 \) and 25 meV/GPa for the segregated \( x \approx 0.09 \) wurtzite phase.

I. INTRODUCTION

With a deep excitonic binding energy of 59 meV \cite{1}, long-lived optical phonons \cite{2}, and a polar structure, zinc oxide (ZnO) has been extensively studied among others applications for stimulated light emission \cite{3,4}, as a second harmonic generation based O\(_2\) sensor \cite{5}, and as a matrix for diluted magnetic semiconductors \cite{6}. Alloying with magnesium its band gap widens from 3.37 eV to 7.8 eV \cite{7–10} reinforcing its use in solar-blind communication devices \cite{11}. ZnO crystallizes in the hexagonal wurtzite-type structure while MgO crystallizes in the cubic rock-salt-type structure. Therefore, once the solubility limit is reached in wurtzite-type \( \text{Mg}_x\text{Zn}_{1-x}\text{O} \) solid solution, \( \sim 4\% \) in bulk \cite{12} and \( \sim 30\% \) or \( \sim 50\% \) in thin films depending on the growth method \cite{8,13}, phase separation appears \cite{14} and both rock-salt and wurtzite type phases coexist. A lot of effort has been put on trying to reach the highest incorporation limit of Mg\(^{2+}\) in phase pure wurtzite-type \( \text{Mg}_x\text{Zn}_{1-x}\text{O} \). However, the study of the optical properties of \( \text{Mg}_x\text{Zn}_{1-x}\text{O} \) thin films with phase separation has been scarce \cite{15–17}. Those previous studies find with optical absorption spectroscopy \cite{15–17} a low-energy absorption tail overlapped to the main absorption edge for Mg concentrations above a critical concentration when phase separation occurs. The origin of this absorption tail observed in \( \text{Mg}_x\text{Zn}_{1-x}\text{O} \) thin films grown by different methods, has been tentatively explained by some authors \cite{17} as due to the beginning of the absorption edge of the coexisting rock-salt phase. However, the rock-salt MgO even alloyed with Zn remains transparent up to energies quite above 4.06 eV \cite{18}. Therefore, the origin of the observed low-energy absorption tail remains unclear. The study of Gries et al. \cite{14} has successfully employed transmitted electron microscopy (TEM) on thermally annealed \( \text{Mg}_{0.3}\text{Zn}_{0.7}\text{O} \) thin films grown by molecular beam epitaxy (MBE) to investigate the microscopic effect of having phase separation. They found that the coexistence of the wurtzite and rock-salt phases in \( \text{Mg}_x\text{Zn}_{1-x}\text{O} \) due to phase separation gives rise to the existence of a secondary wurtzite-type phase, with a reduced Mg content of \( x \approx 0.15 \) determined by TEM energy dispersive x-ray spectroscopy (EDX). The presence of some amount of this segregated wurtzite-type phase could explain the low-energy absorption tail observed by optical absorption studies on \( \text{Mg}_x\text{Zn}_{1-x}\text{O} \) thin films when phase separation occurs. However, neither x-ray diffraction (XRD) nor TEM are well suited for probing phase segregation in as grown \( \text{Mg}_x\text{Zn}_{1-x}\text{O} \) thin films with phase separation. The volume of this segregated wurtzite phase was too low to be detected by XRD and it was embedded in the thin film preventing selective access with TEM. For this reason, Gries et al. \cite{14} had to employ a buffer layer of MgO/ZnO to promote the growth of a segregated wurtzite phase in the \( \text{Mg}_x\text{Zn}_{1-x}\text{O} \) thin film, after annealing the sample at 950 °C, in order to detect the segregated wurtzite phase by means of TEM.

Here we show a spectroscopic approach to probe phase segregation in spray pyrolysis (SP) as grown \( \text{Mg}_{0.3}\text{Zn}_{0.7}\text{O} \) thin films by means of optical absorption spectroscopy and PL measurements under high pressure and ambient temperature along the composition-dependent pressure-induced wurtzite to rock-salt irreversible phase transition \cite{19,21} avoiding any postgrowth treatment on the grown sample.

II. EXPERIMENTAL DETAILS

Thin films of \( \text{Mg}_x\text{Zn}_{1-x}\text{O} \) with measured Mg content of \( x = 0, 0.06, 0.09, 0.15, 0.22, 0.3, 0.35, \) and 0.55 were grown by the SP method on c-plane oriented sapphire,
transmitting medium. and a mixture of methanol-ethanol (4:1) as pressure calibration in the center of a 250 \(\mu\)m hole made in an Inconel gasket we placed a ruby chip for pressure calibration. The samples were preindented to a thickness of 45 \(\mu\)m. Inside the pressure chamber we placed a ruby chip for pressure calibration. The presence of spinel (Mg,Zn)Al\(_2\)O\(_4\) known to appear as a spurious phase in some processes of synthesis was not detected neither by TEM [17] nor XRD.

The PL spectra of Mg\(_x\)Zn\(_{1-x}\)O thin films with different Mg content are shown in Fig. 2 together with the dependence of the peak maximum and the full width at half maximum (FWHM) with Mg concentration. For the optical absorption and the PL measurements we used a deuterium lamp and an all-solid-state pulsed laser at 266 nm with a maximum power of 10 mW, respectively. The transmitted or photoemitted light were detected with a multichannel UV-enhanced spectrometer. For the high-pressure experiments a confocal system with two cassegrain objectives was employed together with the same UV-Vis spectrometer. In the high-pressure experiments we used the Mg\(_{0.3}\)Zn\(_{0.7}\)O sample grown on the ScAlMgO\(_4\) substrate which was exfoliated to a thickness of around 10 \(\mu\)m. ScAlMgO\(_4\) has been shown to have the same compressibility [21, 22] as ZnO. The sample was loaded in a diamond anvil cell (DAC) equipped with two diamonds with 500 \(\mu\)m culets, in the center of a 250 \(\mu\)m hole made in an Inconel gasket preindented to a thickness of 45 \(\mu\)m. Inside the pressure chamber we placed a ruby chip for pressure calibration [23] and a mixture of methanol-ethanol (4:1) as pressure transmitting medium.

### III. RESULTS AND DISCUSSION

In Fig. 1(a) and (b) we show the SEM images of the top and cross-sectional views of the Mg\(_{0.3}\)Zn\(_{0.7}\)O thin film grown on the sapphire substrate. As expected, Mg incorporation results into a shift of the peak position corresponding to the hexagonal (0002) reflection towards higher 2\(\theta\) angles as the result of the contraction of the c lattice parameter observed before [8] [17]. Regarding the (10\(\bar{1}\)1) reflection peak position, since it is contributed by both lattice parameters and \(a\) expands differently to \(c\) with Mg incorporation, it remains almost unaffected by Mg incorporation. Above \(x = 0.3\) the peak corresponding to the (0002) reflection broadens as an indicative of compositional disorder and the cubic rock-salt reflection (111) peak emerges and grows with Mg incorporation. This confirms that our samples are phase pure wurtzite up to \(x = 0.3\) when the onset of the phase separation occurs. The presence of spinel (Mg,Zn)Al\(_2\)O\(_4\) known to appear as a spurious phase in some processes of synthesis was not detected neither by TEM [17] nor XRD.

The PL spectra of Mg\(_x\)Zn\(_{1-x}\)O thin films with different measured Mg content are shown in Fig. 2 together with the dependence of the peak maximum and the full width at half maximum (FWHM) with Mg concentration. As expected, the PL peak of wurtzite-type Mg\(_x\)Zn\(_{1-x}\)O blueshifts from 3.27 eV for \(x = 0\) to 3.91 eV for \(x = 0.35\) [Fig. 2(b)]. Also, from \(x = 0.3\), under Mg incorporation the FWHM of the main PL peak [Fig. 2(c)] starts to broaden due to the disorder caused by the presence of the phase separation found with XRD [Fig. 1(c)]. According to Gries et al. [14] the presence of phase separation in Mg\(_x\)Zn\(_{1-x}\)O would give rise to the appearance of segregated wurtzite phase with less Mg content. This would result into the appearance of a second PL peak at lower energies. We do not observe the additional PL peak for \(x = 0.3\), when phase separation starts in our samples, but above \(x = 0.3\) an additional peak emerges at \(\approx 3.4\) eV. An energy that approximately corresponds to the PL of a wurtzite-type Mg\(_x\)Zn\(_{1-x}\)O sample with measured Mg content of \(x = 0.09\) [Fig. 2(a)]. Similarly to Gries et al. [14] we do not find within our resolution any energy change of the PL peak at 3.4 eV with Mg content indicating that in our thin films the equilibrium Mg concentration of the segregated wurtzite phase is \(x \approx 0.09\). However, the question that arises is why we only find the PL peak at \(\approx 3.4\) eV above \(x = 0.3\) if phase separation already starts at \(x = 0.3\) in our as grown thin films according to XRD [Fig. 1(c)]. We shall address this issue below.

As commented before, previous optical absorption spectroscopy studies [15] [17] on as grown wurtzite-type Mg\(_{0.3}\)Zn\(_{0.7}\)O thin films show that for this Mg concen-
wurtzite Mg$_{0.3}$Zn$_{0.7}$O sample by optical absorption spectroscopy and PL under high pressure we would be able to i) determine the pressure coefficient of the low-energy absorption tail and ii) isolate the segregated phase which having a lower Mg content would persist in the wurtzite phase when the wurtzite phase with $x = 0.3$ transforms to rock-salt. This would allow us to confirm in as grown Mg$_{0.3}$Zn$_{0.7}$O the origin of the low-energy absorption tail which should present a $dE_0/dP \approx 25$ meV/GPa if due to a segregated wurtzite phase with $x \approx 0.09$ and unveil the PL from the segregated phase that should be present as a consequence of the phase separation that exists for this Mg concentration [Fig. 1(c)].

The optical absorption spectra of the as grown Mg$_{0.3}$Zn$_{0.7}$O thin film are shown at different pressures in Fig. 3(a). Up to 7.3 GPa the shape of the absorption edge, including the low-energy tail, is kept while the absorption edge shifts to higher energies due to the volume contraction. This indicates that both the main absorption edge and the tail have a similar pressure dependence confirming that the origin of the low-energy absorption tail is due to a wurtzite phase with lower Mg content. At 7.8 GPa the absorbance of the main absorption edge decreases as a consequence of the onset of the wurtzite to rock-salt phase transition while the absorbance of the low-energy tail persists up to 10.3 GPa when only the absorption tail of the rock-salt band gap is observed indicating the end of the phase transition. The similar pressure dependence of the low-energy tail and the main absorption edge confirm that the origin of the absorption tail is related to the band gap absorption of a wurtzite phase with lower Mg content. However, the strong overlapping does not allow us to reliably quantify its band gap and thus estimate its Mg content. The energy derivative of the absorption spectra can provide an estimation of the relative proportions of both wurtzites with different Mg content and the pressure dependencies of their band gaps. In Fig. 3(c) we show a collection of $d\alpha/dE$ spectra at different pressures. At 0.3 GPa two Gaussian peaks can be clearly observed at $\sim 3.5$ and $\sim 4$ eV. These peaks in the derivative spectrum correspond to the inflection point of the absorption edge, which roughly occurs at the band gap minus the width of the electronic transition. With this reservation, we can reliably assign the derivative peaks to the absorption edges for $x = 0.09$ and $x = 0.3$ supporting our previous conclusion that the low-energy tail is due to the absorption edge of the segregated phase with $x \approx 0.09$. Under pressure, the peak due to $x \approx 0.3$ blueshifts faster than the peak due to $x \approx 0.09$ up to 7.8 GPa when the intensity of the high-energy peak drops until becoming comparable to the intensity of the low-energy peak which remains constant up to 9.3 GPa. This indicates that wurtzite with $x \approx 0.3$ starts transforming to rock-salt at around 7.8 GPa while the segregated wurtzite phase remains unaffected up to 9.3 GPa at least.

In Fig. 2 we have found that while the PL signal from the segregated wurtzite phase is clearly observed for sam-

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**FIG. 2:** (a) Photoluminescence (PL) spectra of Mg$_{x}$Zn$_{1-x}$O of some of our thin films with different Mg content $x$. (b) Dependence of the maximum of the PL peak and (c) FWHM of the PL peak with Mg content obtained from the fit to an asymmetric lorentzian function. Continuous lines are guides for the eye. The empty dots are the maximum of the extra PL peak that emerges at lower energy for $x > 0.3$ eV. All measurements were performed with the same integration time in transmittance mode.

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| Energy (eV) | Intensity |
|------------|-----------|
| 3.2        | 3         |
| 3.3        | 3         |
| 3.4        | 3         |
| 3.5        | 3         |
| 3.6        | 4         |

| Mg content | FWHM (eV) |
|------------|-----------|
| 0.09       | 4.0       |
| 0.30       | 3.0       |
| 0.35       | 2.8       |
| 0.55       | 2.4       |
Absorption Coefficient, $\alpha(x)$

$\alpha(x)$ at different pressures. Red continuous lines show the fit to two gaussians while the dots are the experimental data.

FIG. 3: (a) Absorption edge of the Mg$_{0.3}$Zn$_{0.7}$O sample deposited on ScAlMgO$_4$ at different pressures. (b) Simulated absorption spectrum (continuous line) of Mg$_{0.3}$Zn$_{0.7}$O at 0.3 GPa according to Elliot-Toyozawa theory [24–26] together with the experimental spectrum (black dots). (c) Energy derivative of the absorption spectra at different pressures. Red continuous lines are fits to the symbols are the band gap obtained by the energy derivative band gap obtained by Elliot-Toyozawa theory and the empty symbols are the band gap obtained by the optical absorption experiment performed on the as grown Mg$_{0.3}$Zn$_{0.7}$O sample we have demonstrated the existence of a segregated phase with a concentration of $x \approx 0.09$. All this indicates that the amount of segregated wurtzite phase in the as grown Mg$_{0.3}$Zn$_{0.7}$O sample, though visible with optical absorption, cannot be detected with PL. The reason why this occurs might be that the PL signal of the segregated phase is too weak and appears to be masked by the signal of the dominant peak corresponding to the wurtzite phase with $x \approx 0.3$. If this is the case, at around 7.3 GPa when, according to the optical absorption study the wurtzite phase with $x \approx 0.3$ starts to transform into the rock-salt phase, the signal from the segregated wurtzite phase should emerge. This is what can be seen in Fig. 3 (d). The PL peak of wurtzite with $x \approx 0.3$ blueshifts with pressure up to 7.4 GPa when the phase transition occurs and the intensity of the main PL peak drops. At this pressure a weak PL peak with an energy of 3.59 eV emerges. At 9.3 GPa the PL peak from the wurtzite with $x \approx 0.3$ vanishes while the PL peak at 3.59 eV stays up to 10.3 GPa when the phase transitions of both wurtzite phases with different Mg concentrations have finished and the rock-salt phase shows no PL signal. According to Sans and Segura [20] wurtzite Mg$_{0.09}$Zn$_{0.91}$O thin film has a pressure coefficient of 25 meV/GPa. Considering that our segregated wurtzite phase has a PL peak at

FIG. 4: Pressure dependence of the band gap $E_g$ (black) and PL peak (red) of Mg$_{0.3}$Zn$_{0.7}$O. Circles are from the wurtzite with higher Mg content and squares are from the segregated phase. The red square is the PL energy of the segregated phase ($x \approx 0.09$) only visible once wurtzite Mg$_{0.3}$Zn$_{0.7}$O has transformed to rock-salt. The solid symbols represent the band gap obtained by Elliot-Toyozawa theory and the empty symbols are the band gap obtained by the energy derivative of the absorption spectra. Red continuous lines are fits to the data points obtaining a $dE_g/dP$ of 25 meV/GPa for $x \approx 0.09$ in good agreement to [20] and 29 meV for $x \approx 0.3$. 
probed in as grown thin films of phase separated high-pressure approach that phase segregation can be due to certain compositional disorder. Under pressure the shift remains constant with pressure with both techniques providing a pressure coefficient for the band gap of \( dE_g/dP = 29 \text{ meV/GPa} (x = 0.3) \) and \( 25 \text{ meV/GPa} (x = 0.09) \). This value extends the dependence on \( x \) of \( dE_g/dP \) from \( x = 0.13 \) [20] to \( x = 0.3 \) and shows that \( dE_g/dP \) saturates for high magnesium contents.

IV. CONCLUSIONS

In conclusion, we have shown with a spectroscopic high-pressure approach that phase segregation can be probed in as grown thin films of phase separated Mg_{0.3}Zn_{0.7}O even for small embedded volumes not detected by x-ray diffraction and not accessible by transmission electron microscopy except with annealed samples [14]. We have solved the controversy about the low-energy absorption tail usually observed overlapping with the main absorption edge for \( x > 0.3 \). We have found that it is due to the band gap of the segregated wurtzite phase with \( x \approx 0.09 \) and not to the tail of the coexisting rock-salt phase [17]. The present work shows the usefulness of high pressure optical studies to obtain relevant information about phase separation effects in semiconductor alloys.

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