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Influence of Growth Parameters on the Structural, Morphological and optical Properties of $Mg_xZn_{1-x}O$ Prepared by Metal Organic Chemical Vapor Deposition

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Abstract The influence of growth parameters on the structural, morphological and optical properties of $Mg_xZn_{1-x}O$ grown on sapphire substrate by metal organic chemical vapor deposition is studied. Pure oxygen gas is used as oxidant, bis-methyl-cyclopentadienyl magnesium ($(MeCp)_2Mg$) and diethyl zinc are used as Mg and Zn source, respectively. The growth temperature between and 320°C and 620°C, the VI/II (O/Mg, Zn) ratio ranging from 60 to 960 and the growth rate from 0.5 to 3.3 µm/h, are systematically varied to determine their effects upon the above mentioned physical properties. Structural, morphological and optical properties of the thin films are characterized by means of X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Photoluminescence (PL). Experimental results indicate that the growth conditions are essential for engineering the growth of $Mg_xZn_{1-x}O$. The optimum substrate temperature is found to be 420°C for the growth of $Mg_xZn_{1-x}O$ with a solid composition x below 30%, composition above which a phase segregation has been previously observed. With increasing temperature, strong parasitic reaction between $(MeCp)_2Mg$ and oxygen is found to occur before they rich the substrate.

Keywords: *MgZnO ternary alloys, MOCVD, bis-methyl-cyclopentadienyl magnesium ((MeCp)2Mg), Columnar growth*

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1. Introduction

ZnO and its related alloys are currently extensively investigated for applications in optoelectronic and microelectronic device fabrication. $Mg_xZn_{1-x}O$ alloys are in particular needed for the fabrication of optoelectronic devices in the blue to the UV spectral regions. It is widely used in optical devices, such as light-emitting diodes, transparent conductive oxide, solar cells, laser, optical detector, photocatalysis and photoelectrochemistry [1]. In the process of the research, most of the growth of $Mg_xZn_{1-x}O$ films has been carried out using molecular beam epitaxy [2] and pulsed laser deposition [3]; few have been prepared using metal organic chemical vapour deposition (MOCVD) [4] in particular using pure oxygen gas as oxidant(see Ref. [5]). In most cases, tertiary butanol (TBOH) has been mainly used in the growth of ZnO and MgZnO. It has been proven difficult to obtain high quality $Mg_xZn_{1-x}O$ thin films in part because of the phase segregation, which appears at certain percentage of Mg content. Indeed, by alloying ZnO with MgO, the films retain the ZnO hexagonal structure for up to ~0.3 using TBOH in our reactor [5], such result is found by Ohtomo *et al.* [6] using oxygen gas. We have reported that the optical band gap can be tailored from 3.3 eV to 3.75 eV keeping the hexagonal structure [5]. Consequently, it causes a little lattice mismatch for the small difference between the ionic radius of Zn^{2+} (0.60 Å) and Mg^{2+} (0.57 Å) [7]. Alloying ZnO with Mg disturbs the structural properties, the density of structural defects, and causes alloy disorder effects. Therefore, due to the compositional unstable nature of the alloy, the presence of phase segregation and the presence of various defects causing numerous changes in the structural, morphological and optical properties, it appears essential to always investigate the effect of the MOCVD growth parameters. Such will improve and give insight on the material properties, and mostly on the various possible applications.

In this paper, the effect of growth parameters using oxygen pure gas as oxidant is investigated. Using the same MOCVD reactor (two inlet reactor tube), the effect of growth using TBOH as oxidant has been published (see Ref. [5]). The growth temperature and VI/II ratio is varied in order to examine, their effects on the structure,

the morphology and optical properties. The effect of growth rate have been also studied. Suitable substrate would be chosen that favor growth orientation and optical properties of MgZnO itself to gain further improvement of crystal quality.

2. Experiments

$Mg_xZn_{1-x}O$ films were deposited on c-Al_2O_3 (0001) substrates using Ar as the carrier gas. $(MeCp)_2Mg$ and DEZn were used as Mg and Zn sources, respectively. The total flow of the group II reactants, as well as the flow of the oxidizing agent (O_2), was fixed to yield a VI/II ratio of 60 (optimum for ZnO growth in our reactor). The Mg/Mg+Zn ratio was varied in order to change the Mg content in the vapour phase. $Mg_xZn_{1-x}O$ was deposited for 45 min (around 1–2 μm thickness) at 320, 420, 520 and 620°C. The VI/II also was varied from 60 to 960.

The Crystalline quality of the ZnO films was determined by X-ray diffraction using $CuK_{\alpha 1}$ radiation (λ=0.154 nm). Surface morphology of the samples was studied using a Jeol JSM-7001F field emission scanning electron microscope (FESEM). Mg content in the solid was determined by energy dispersive X-ray (EDX) analysis. For low temperature (4.2 K) measurements, the samples were immersed in liquid He. The samples were excited with the 325 nm line of a HeCd laser at a typical excitation power of 7 mW.

3. Results and Discussion

Figure 1 shows normalized PL spectra of $Mg_xZn_{1-x}O$ grown at different growth temperatures (320°C to 620°C) on c-Al_2O_3 (0001), using pure oxygen gas as group VI source. The donor bound exciton (D^oX) position varies slightly probably due to small compositional non-uniformity in Mg incorporation. As was the case for growth using TBOH [1], stacking fault-related transitions are observed at energies below that of the D^oX line, labelled (e, A^o: free-to-bound). No obvious trend is observed in terms of Mg incorporation or strength of stacking faults-PL. The Mg content is higher at around 520°C, this is concluded repeating the experiment. It has been reported that the growth using $(MeCp)_2Mg$ can be performed up to 800˚C using either O_2 or N_2O [5]. However with TBOH, degradation of the films occurs above 500°C, as well as a weakness in strength of the luminescence intensity. This is mostly due to the low reactivity, low cracking temperature of the alcohols and the heavy incorporation of carbon in the film. Although, the reported growth temperature using metal alkyls range between 200°C and 400°C, $(MeCp)_2Mg$ seems useable up to higher temperatures, while still yielding good quality layers. The critical issue for growth at higher temperatures above 420°C, is the occurrence of a strong parasitic oxidation reaction between $(MeCp)_2Mg$/DEZn and the oxygen sources. This phenomenon occurs mostly at the inlet of the reactor tube and can cause an oxygen deficiency above the substrate. There is however a large disparity in published results with regards to higher temperature growth. This is most probably due to differences in the precursors used, but also due to the reactor setup (geometry and total pressure).

Figure 2 shows SEM images of the above mentioned thin films. The surface morphology changes significantly with substrate temperature. At ~320°C, uniform columnar crystals are obtained. This feature remains at 420°C, but the size of the columns increases. At 520°C, the surface exhibits faceted features with a variety of shapes. Some of these have the characteristic hexagonal symmetry. A further increase in temperature increases the size of the crystallites with no hexagonal columns observed. The growth temperature which seems to yield columnar growth is around 420°C. This temperature has also been found to be “optimum” for growth of ZnO using O_2. Energy Dispersive X-ray spectroscopy done on the sample grown at such optimized temperature allowed us to determine the Mg mole fraction of about 7%. In regard of this result, it can be concluded that the incorporation efficiency of the Mg within the use of $(MeCp)_2Mg$ is extremely low.

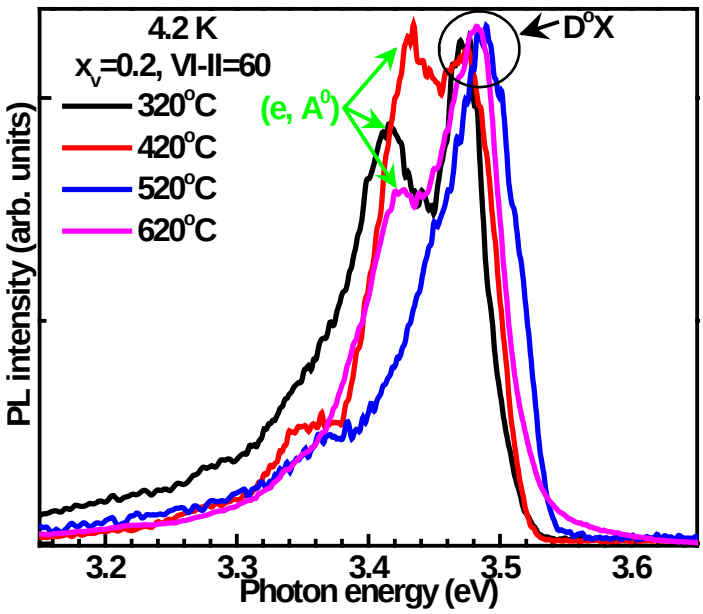

Figure 1. Low temperature (4.2 K) PL spectra of $Mg_xZn_{1-x}O$ films (x_v=0.2) grown on c-Al_2O_3 at temperatures of 320 ˚C to 620 ˚C using O_2 as oxygen source

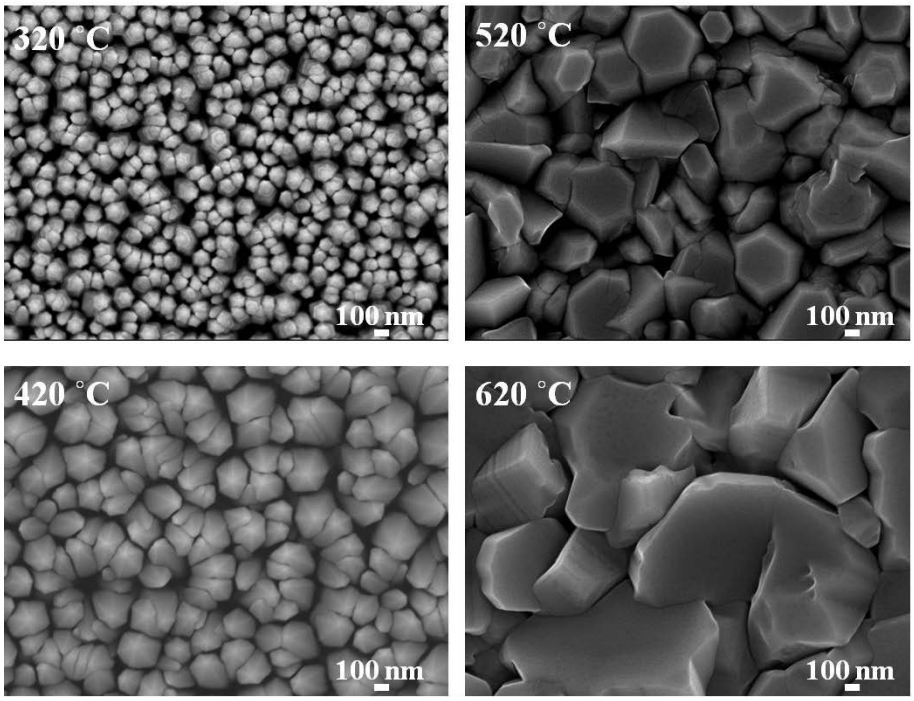

Figure 2. SEM images of the $Mg_xZn_{1-x}O$ films grown on c-Al_2O_3 at various temperatures using O_2

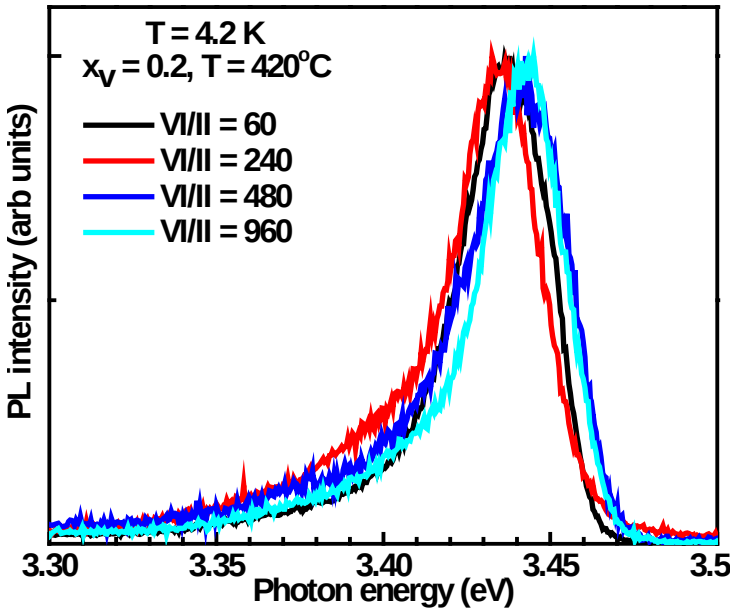

Figure 3. Low temperature (4.2 K) PL spectra of $Mg_xZn_{1-x}O$ films (x_v=0.2) grown on c-Al_2O_3 with different VI/II ratios and using O_2 as oxygen source

Figure 3 shows the PL spectra (4.2 K) of $Mg_xZn_{1-x}O$ (x_v=0.2) grown with different VI/II ratio on c-Al_2O_3 at 420°C. The spectra are dominated by the same D^oX as for the sample above. In this case the stacking fault related transition is very small, this confirms the nonuniformity of the sample. No obvious change in Mg incorporation is detected. The VI/II ratio has no major effect in the Mg incorporation when using $(MeCp)_2Mg$. Increasing oxygen gas has no effect in the Mg incorporation efficiency.

Figure 4 shows SEM images of the same films. As for growth using TBOH, there is no significant change in the morphology of the film. The VI/II ratio does not affect the size or the shape of the column or crystals. In cross-sectional views (not shown), the columnar structures are observed grow normally to the substrate, which indicates, a preferred growth along the c-axis, as seen with XRD measurement. The availability (amount) of oxygen does not influence the initial nucleation stage at the interface. The temperature is the main driving force for the growth with oxygen pure gas.

Figure 5 shows cross sectional SEM images of $Mg_xZn_{1-x}O$ grown on c-Al_2O_3 substrate at different growth rates 3.3 μm/h, 2.8 μm/h, 1.4 μm/h and 0.5 μm/h using oxygen as group VI source and x_v=0.2. The growth temperature was 420°C. For all growth rates, the films reveal columnar growth with cone shape ends. The size of the columns varies depending of the growth rate. For low growth rate (0.5 μm/h), the film appears denser compare to high growth rate (3.3 μm/h). The variations in thicknesses are within experimental error. The deposition rate strongly influences the initial nucleation and coalescence of the films. It seems likely that a decrease in growth rate

increases the coalescence of crystallite/grains formed during the initial deposition. The increase the group precursors strongly affect the film properties.

Figure 6 shows the surfaces of the films. For growth rates of 3.3 μm/h and 2.8 μm/h, the surface features are similar to those of ZnO films. The films comprise dense columnar crystals with the films grown at 2.8 μm/h having the smallest columns. For growth rates of 1.4 μm/h and 0.5 μm/h, the surface features are comparable to those of $Mg_xZn_{1-x}O$ film with $x \geq 0.2$. The surfaces of the films drastically differ from these grown at higher growth rates and are considerably rougher. The lower growth rates seem enhance the formation of cubic structure (see inserts). Similar results have been observed by Kim *et al.* [8] when growing $Mg_xZn_{1-x}O$.

The lower growth rates possibly enhance the Mg deposition at the interface, causing the formation of an MgO rich layer/region, which has been observed by AES measurements on other films. The same effect was seen when growing higher Mg content films. Low growth rates seems to favor/force the cubic structure instead of the wurtzite structure, which is supported by XRD spectra in Figure 7, which shows the presence of MgO (111) peaks for film grown with lower growth rates. One can suggest therefore that lower growth rate accelerate the formation of phase segregation in the films.

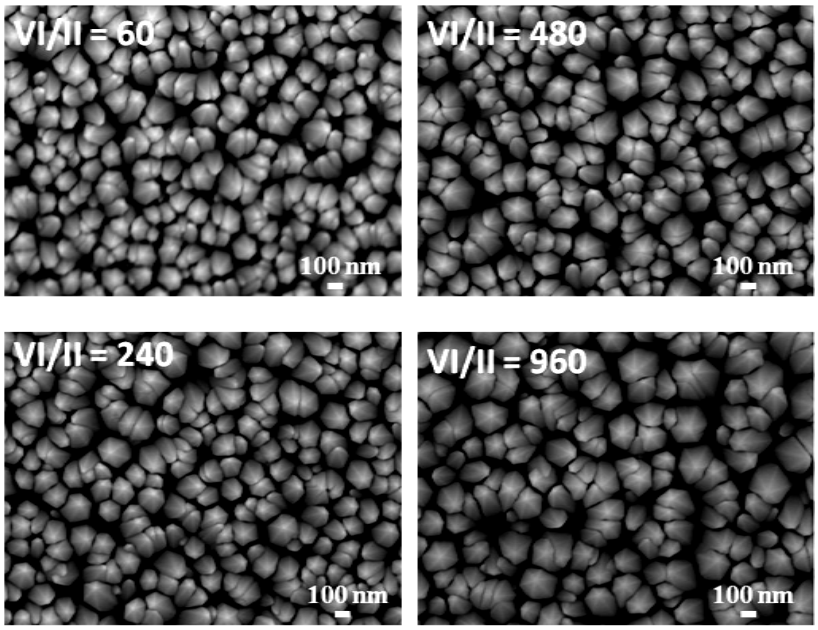

Figure 4. SEM images of $Mg_xZn_{1-x}O$ films grown on c-Al_2O_3 with different VI/II ratios (60-960) using O_2.

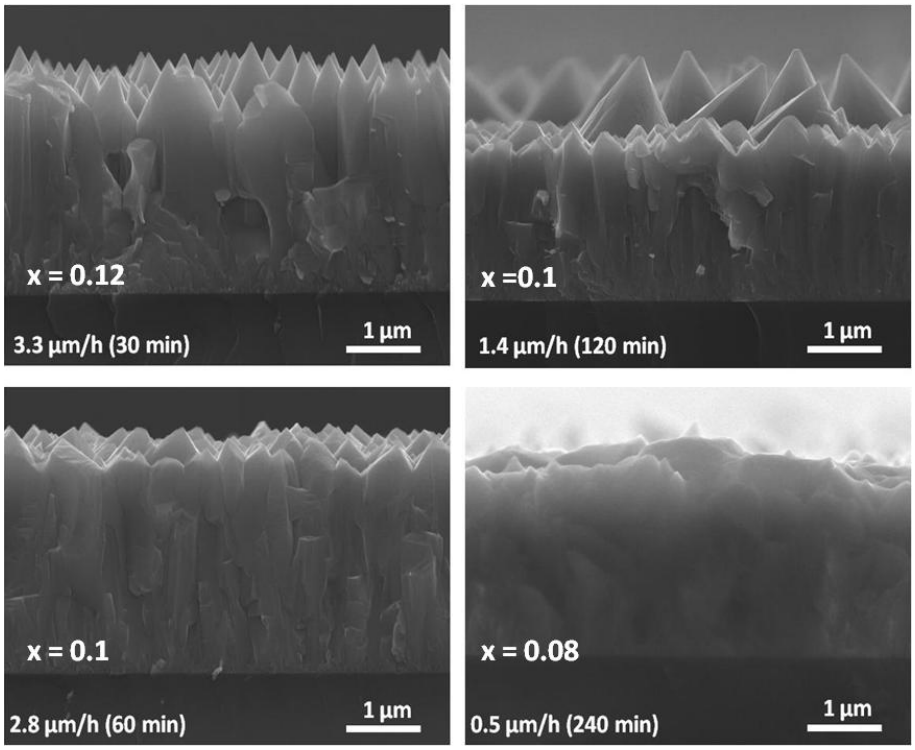

Figure 5. Cross sectional SEM images of $Mg_xZn_{1-x}O$ thin films grown on c-Al_2O_3 substrate at different growth rates: 3.3 μm/h, 2.8 μm/h, 1.4 μm/h and 0.5 μm/h using oxygen as oxidant

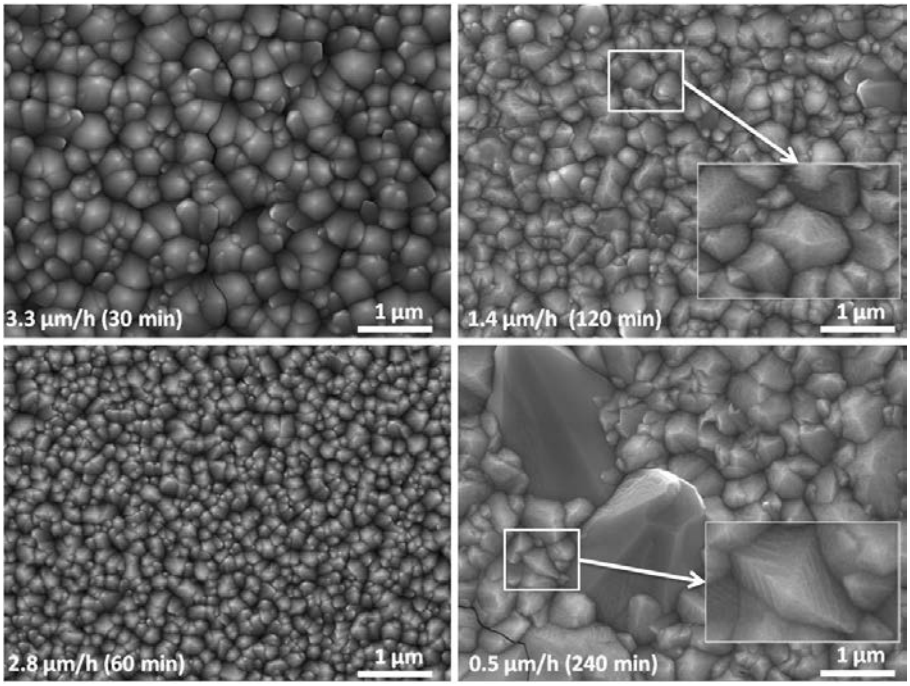

Figure 6. SEM images of $Mg_xZn_{1-x}O$ grown on c-Al_2O_3 at different growth rate grown using oxygen at 420 ˚C and VI/II ratio=60

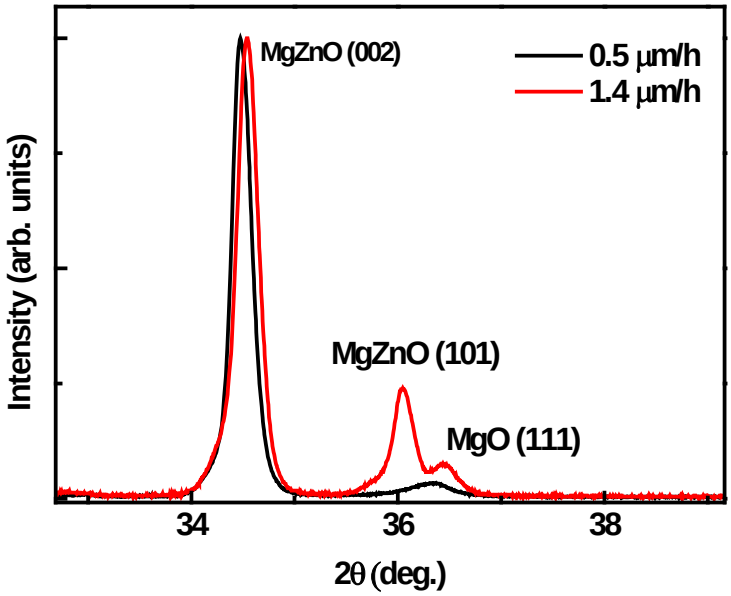

Figure 7. XRD spectra of $Mg_xZn_{1-x}O$ grown on c-Al_2O_3 at growth rate of 1.4 µm/h and 0.5 µm/h using oxygen, a growth temperature of 420 ˚C and VI/II ratio of 60

Figure 8 shows low temperature (4.2 K) normalized PL spectra of the films. It seems reasonable to assume that the dominating peak in each spectrum is the stacking fault-related transition (e, A^0). D^oX transitions appear as shoulders on the high energy side of the stacking fault PL. The sample grown at a growth rate of 0.5 µm/h seems to have two D^oX bands. For the sample grown at a rate of 1.4 µm/h, a shoulder at the lower energy side of the stacking fault PL is observed. This line is suggested to be another D^oX transition. For all samples ZnO is present in a small amount as illustrated by the presence of NBE emission at ~3.36 eV. The sample grown with the lowest growth rate (0.5 µm/h) shows the lowest Mg incorporation. The presence of two D^oX bands for the two lowest growth rates would indicate the existence of two bang gaps in the films. This would correlate with the deduction made from the morphologies in Figure 6.

In MOCVD technique, the growth rate is proportional to the flux of atoms being transported, usually by diffusion, in the gas phase to the interface, which is identical to the flux of atoms crossing the interface into the solid [9]. The growth rate is mainly mass transport limited. Since the growth rate depends on the flow rate of species, then the source type of material will strongly influence the growth process. For example, Leys *et al.* [10] explained the cause of the lower incorporation efficiency of P in $GaAs_xP_{1-x}$ to be dependent on growth rate, which influences the dwell time of As and P species on the surface. They attributed the lower incorporation efficiency of P to differences in the adsorption/desorption rate constants of the As and P

species on the surface. InGaN, because of the higher desorption rate of In, the In incorporation efficiency is relatively low in the low growth rate region. As the growth rate increases the desorption rate of In is significantly reduced, due to the faster completion of the next layer, and consequently a higher In incorporation efficiency will be obtained [11]. Similar behaviour for Mg is suspected. From the results there is a trend in increased efficiency of Mg incorporation for higher DEZn flow rates. It is believed that during the growth of $Mg_xZn_{1-x}O$ the transport of $(MeCp)_2Mg$ in the growth front depends strongly on the presence of DEZn. This observation is based on the fact that $(MeCp)_2Mg$ and TBOH does not produce any MgO deposition on the substrate for the entire range of growth parameters studied. Due to the lower flow rate of DEZn at low growth rates Mg is significantly decreased at the growing site.

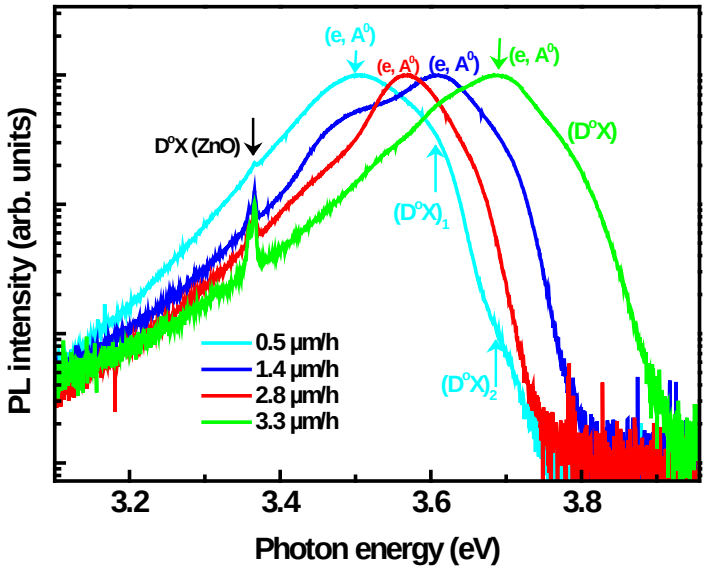

Figure 8. Normalized low temperature PL spectra (4.2 K) of $Mg_xZn_{1-x}O$ grown on c-Al_2O_3 at different growth rate (3.3 µm/h, 2.8 µm/h, 1.4 µm/h and 0.5 µm/h) with VI/II ratio of 60 and at substrate temperature of 420 ˚C

4. Conclusion

High VI/II ratios decrease Mg incorporation, possibly due to a stronger premature reaction between $(MeCp)_2Mg$ and the oxidant, or a preferential heterogeneous interaction between the Mg and oxygen species on the growth front. Also, the stacking fault density is deduced to increase. The surface morphology is independent on the VI/II ratio. A Site blocking mechanism is suspected to result in reduced growth rates of $Mg_xZn_{1-x}O$ grown at high VI/II ratios (≥240). For VI/II ratios between 15 and 120, no major effect has been observed on the incorporation of magnesium.

For all growth rates, the films reveal columnar growth with cone shape ends. The size of the columns varies depending of the growth rate. For low growth rate (0.5 µm/h), the film appears denser compare to high growth rate (3.3 µm/h). The sample grown at a growth rate of 0.5 µm/h seems to have two D^oX bands. Lower growth rate reveals existence of two bang gaps in the films. Mg incorporation is enhanced at higher growth rate.

Acknowledgements

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