Growth of High Mg Content Wurtzite MgZnO Epitaxial Films via Pulsed Metal Organic Chemical Vapor Deposition

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Abstract

We report on the growth of high Mg content, high quality, wurtzite $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ (MgZnO) epitaxial films using pulsed metal organic chemical vapor deposition (PMOCVD) method. Series of MgZnO films with variable Mg concentration were deposited on bare and AlN coated sapphire substrates. The band gap of the films estimated using UV-visible transmission spectra ranges from 3.24 eV to 4.49 eV, corresponding to fraction of Mg between $x=0.0$ to $x=0.51$, as determined by Rutherford backscattering spectroscopy. The cathodoluminescence (CL) measurement has shown a blue shift in the peak position of MgZnO with an increasing Mg content. No multi-absorption edges and CL band splitting were observed, suggesting the absence of phase segregation in the as grown films. The crystal structure and phase purity of the films were also confirmed by XRD analysis. Hall effect measurement in van der Pauw configuration was employed to evaluate the electrical properties of the films. With a rise in Mg incorporation into the ZnO lattice, the films became very resistive, consistent with the widening of the band gap. The AFM measurement on the films has shown a decreasing surface roughness with an Mg content. To the best of our knowledge, the current result shows the highest Mg content ($x=0.51$), high quality, wurtzite MgZnO epitaxial film ever grown by MOCVD. The high Mg incorporation without phase separation is believed to be due to the non-equilibrium behavior of the PMOCVD in which the kinetic processes dominate the thermodynamic one.

Keywords: B2: MgZnO films, A3: Pulsed metal organic chemical vapor deposition, A1: X-ray diffraction, A1: RBS, A1: UV/Visible transmission, A1: Cathodoluminescence (CL)

1. Introduction

Zinc oxide (ZnO) is a direct wide bandgap ($E_g \sim 3.24$ eV at 300 K) semiconductor that has attracted broad interest for its use in optical and electronic devices such as ultraviolet (UV) detectors and emitters, thin film transistors (TFT), transparent electrodes, and solar cells [1-3]. Particularly, the large exciton binding energy (~ 60 meV) along with its direct band gap makes it an efficient UV optoelectronic material that can be used at room temperature and above [4]. However, given the broad spectral window of the UV light (10 nm - 400 nm), the use of pure ZnO for various practical applications demanding wider band gap is limited, requiring the need for band gap engineering technique to tailor the band gap of ZnO.

$\text{Mg}_x\text{Zn}_{1-x}\text{O}$ ($0 < x < 1$) is a solid solution of ZnO and MgO used to tune the band gap of ZnO between 3.24 eV ($x=0$, ZnO) and 7.8 eV ($x=1$, MgO) [5,6]. However, though in principle the band gap of MgZnO alloy can be continuously tuned between the two boundaries, the limited solubility of MgO into ZnO or vice versa impedes the growth of single phase material with high Mg or low Zn content [7]. According to the phase diagram of binary ZnO-MgO system, the thermodynamic solubility of the former into the latter is ~ 4 mol % [8] implying the formation of stable wurtzite $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloy with maximum x of 0.04. Additionally, it is essential to note that although the ionic radii of Mg^{2+} (0.57 Å) and Zn^{2+} (0.61 Å) are comparable [9] (i.e. MgZnO is considered a lattice-matched system), the structural dissimilarity between ZnO (wurtzite, $a=3.25$ Å, $c=5.21$ Å) and MgO (cubic, $a=4.22$ Å) leads to a major phase segregation problem.

Despite the challenge in phase separation, a continuous improvement in the epitaxial MgZnO deposition techniques has led to the growth of wurtzite MgZnO crystal with an Mg content up to 37 % [5,6], and cubic MgZnO when an Mg concentration exceeds 62 % [7,10]. The maximum achievable band gap for the highest Mg composition ($x=0.37$) in the wurtzite MgZnO

is 4.28 eV. Whereas, for the cubic MgZnO the band gap of the material can be tuned from 5.40 eV ($x=0.62$) to 7.8 eV depending on the concentration of Mg [7,10]. For the Mg composition between 37 % and 62 % (identified as transition range), the alloy is observed to have a mixed wurtzite and cubic phases MgZnO structure with no defined band gaps [7,11]. This introduced discontinuity in band gap tailoring between 4.28 eV-5.40 eV limits the development and application of MgZnO alloys for photodetectors and emitters in the solar blind spectral window (220 nm -290 nm).

The majority of the work on growth of MgZnO alloys have been conducted using pulsed laser deposition (PLD) [1,6,7,12,13] and molecular beam epitaxy (MBE) [3,14-16] methods. However, despite the epitaxial growth of quality ZnO and its alloys the use of these techniques for mass production is limited owing to their high cost and low throughput. An alternative to these methods for growing epitaxial MgZnO films is using metal organic chemical vapor deposition (MOCVD). It has great advantages for growing materials on large-area substrates, controlling atomic composition as well as excellent technique for epitaxial growth [10,17,18]. Nevertheless, there are few reports showing the use of MOCVD for the growth of MgZnO, particularly wurtzite MgZnO, epitaxial films [17,18]. In this work, we use pulsed metal organic chemical vapor deposition (PMOCVD) method to grow single phase wurtzite $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloy with high Mg composition so that the band gap, $E_g > 4.28$ eV ($\lambda_g < 290$ nm) to realize a material that can be used in the solar blind spectral window.

2. Experimental Procedures

MgZnO films were grown on sapphire substrates with and without AlN (~25 nm) layer via pulsed metal organic chemical vapor deposition (PMOCVD) in a vertical-geometry rotating disc reactor. The reactor was kept at a constant pressure of 10 Torr while the substrate rotates at

1000 rpm for the entire growth period. For the films growth, bis-cyclopentadienyl magnesium (Cp_2Mg), diethyl zinc (DEZn) and oxygen (99.999 %) were used as precursors. Argon gas (99.9999 %) was passed through the Cp_2Mg and DEZn bubblers to introduce the source materials into the reactor. In addition, we have used point of use gas purifiers both for Ar and O_2 gasses to reduce the impurity level below ppb. During the MgZnO growth via PMOCVD, the Zn and Mg metalorganic (MO) sources as well as oxygen gas are introduced to the reactor for 12 seconds to grow $\sim 5.5\text{\AA}$ thick MgZnO layer, a layer with a thickness comparable to the c-parameter of ZnO ($\sim 5.2\text{\AA}$). Then, the Zn and Mg source valves are closed for 6 seconds leaving the oxygen gas to oxidize the grown layer. This periodic process cycles as many times as needed—similar to the traditional atomic layer deposition (ALD) method—to grow the intended film thickness. The fraction (x) of Mg in the alloy is varied by changing the mass flow rates, bubbler temperature and pressure of the two MO precursors. The value of x was estimated as:

$$x = Q_{Mg} / (Q_{Mg} + Q_{Zn}), \quad (1)$$

where, Q_{Mg} and Q_{Zn} are the molar flow rates ($\mu\text{mol}/\text{min}$) of Cp_2Mg and DEZn, respectively [19]. Table I presents MgZnO samples grown with variable x via PMOCVD method. To improve the crystal quality of the films, thin ($\sim 30\text{ nm}$) ZnO nucleation layer were grown on the substrates at $450\text{ }^\circ\text{C}$, before raising the temperature to the actual set point, $500\text{-}630\text{ }^\circ\text{C}$, to grow the main body of the film.

Table I. Variable Mg composition (x) MgZnO films. The molar flow rate (Q_{MO}) was estimated from the flow rate, bubbler temperature (T_B) and pressure (P_B) of the MOs

Samples	Flow rate (sccm)		T_B ($^\circ\text{C}$)		P_B (Torr)		Q_{MO} ($\mu\text{mol}/\text{min.}$)		x
	DEZn	Cp_2Mg	DEZn	Cp_2Mg	DEZn	Cp_2Mg	DEZn	Cp_2Mg	
A	60	-	15	-	450	-	55.04	-	0
B	30	200	15	40	450	450	27.52	3.14	0.10
C	30	300	15	40	450	380	27.52	5.58	0.17

D	25	300	15	44	450	350	22.93	8.41	0.27
E	22	310	15	45	450	350	20.18	9.42	0.32

The thickness of the MgZnO films was measured by Filmetrics (F-40) thin film analyzer and ranges between 0.45-0.89 μm . The transmission spectrum of the films was recorded using Perkin Elmer Lambda 25 UV/VIS spectrometer. Rutherford backscattering spectroscopy (RBS) was employed to measure the composition of the films (MAS 1700 pelletron tandem ion accelerator (5SDH) with a 165° fixed ion detector) using 2.3 MeV He^+ ions beam. The crystal structure and phase purity of the films were investigated by XRD using Bruker D8 Discover X-ray diffractometer with Co Ka radiation equipped with X-ray collimator of 0.8 mm. The surface roughness and morphology of the films were assessed by atomic force microscopy (AFM, Veeco Dimension 3100). Cathodoluminescence (CL) spectroscopy was measured using Perkin-Elmer (15-110A) Auger electron gun (accelerating voltage of 3 kV and emission current of ~ 2 mA) as an electron source. The emitted light is collected by an optical lens and then directed into 1/8m monochromator. The light is then detected by photomultiplier tube (PMT) whose output is further amplified by Keithley (427) current amplifier. The electrical properties of the films were evaluated by Hall measurement (Ecopia HMS-3000) using van der Pauw configuration at room temperature.

3. Results and Discussions

Fig. 1 shows the room temperature UV-visible transmission spectra for MgZnO films grown on AlN coated sapphire substrates with variable Mg concentration. The transmission spectrum for each film has shown a sinusoidal behavior which occurs due to an interference phenomenon between the wave fronts generated at the “air-film” and “film-substrate” interfaces. This reveals the presence of smooth reflecting surface (i.e. minimal scattering loss at the surface and bulk of the film), indicating an excellent surface quality and homogeneity of the as grown

films [20]. With increasing Mg content the absorption edge shifted from 383 nm (trace A) to 276 nm (trace E), but remains sharp. However, the drop in transmittance observed for the Mg alloyed films at ~380 nm is to the effect ZnO buffer layer. The absence of multiple absorption edges in all the spectra indicates that the grown MgZnO films are single phase materials [6,11,21].

The optical band gap (E_g) of the films was evaluated from the transmission spectra using the plot of $(\alpha h\nu)^2$ versus $h\nu$ (also known as Tauc plot, Fig. 1, inset), where α is the absorption coefficient and $h\nu$ is the photon energy. The estimated band gap ranges between 3.24 eV (pure ZnO, trace A) to 4.49 eV (trace E), with the increase in Mg incorporation (vide infra) into the ZnO lattice (Table II). The highest band gap energy obtained in this study (well within the UV-C spectral window) indicates the potential use of the as grown MgZnO films for solar blind photodetector devices [21,22].

Fig. 1. UV-Visible transmission spectra (at 300 K) for $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ samples with variable Mg content; trace A ($x=0.0$), trace B ($x=0.12$), trace C ($x=0.27$), trace D ($x=0.46$), and trace E ($x=0.51$). The inset shows the $(\alpha h\nu)^2$ versus $h\nu$ (Tauc) plot for each film out of which the band gap energy is calculated.

The concentration of Mg in the films was analyzed by RBS method. The RBS measured data (open circle) fitted with SIMNRA code [23] simulated result (solid line) to quantify the content of Mg (x in $\text{Mg}_x\text{Zn}_{1-x}\text{O}$) for samples B through E are shown in Fig. 2. The arrows indicate the channel numbers at which the backscattering from the elements start, while the abrupt edges corresponding to the Zn and Mg peaks indicate the presence of sharp interface between the film and the substrate. As one goes from sample B to E, the RBS yield for Zn decreases while that of Mg increases, demonstrating the increase of Mg content in the films. Moreover, the difference in the width of RBS spectrum is related to the variation in the thickness of the films, which is in parallel with the difference in oscillation period observed in the transmission spectra (Fig. 1). The fraction of Mg obtained for each sample by fitting the simulated result with measured RBS data is presented in Table II. The result reveals the maximum incorporation of 51 % Mg into the ZnO lattice—a record high Mg content in a single-phase wurtzite structure MgZnO ever grown by MOCVD. The inset in Fig. 2 shows the estimated band gap dependence on the measured Mg concentration (x) which is found to be linear: $E_g(x) = 3.24 + 2.35x$, eV.

Fig. 2. RBS spectra for $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys. The Fitting between measured RBS data (open circle) and simulated result (solid lines) has led to $x=0.12$ (B), $x=0.27$ (C), $x=0.46$ (D), and $x=0.51$ (E).

The inset in the figure shows the relationship between band gap (E_g) and Mg content (x).

Table II. Band gap and Mg content of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ samples A through E

Samples	A	B	C	D	E
Band gap (eV)	3.24	3.52	3.87	4.23	4.49
Fraction of Mg, x	0	0.12	0.27	0.46	0.51

The emission properties of the as grown MgZnO films were characterized by cathodoluminescence (CL) spectroscopy. Fig. 3 compares the room temperature CL (solid lines) spectra of samples A through E with variable Mg content. The spectral peak position of the CL has shifted towards high energy (blue shift) with the increase of Mg content as has the UV-visible absorption edge (Fig. 3, broken lines), a sign of band gap broadening. The CL spectral peak position for each sample corresponds to the respective absorption band edge [13]. However, with Mg content over 46 %, the CL peak is shifted to lower energy (red shifted) relative to the absorption edge which is attributed to the Stoke's shift [24,25]. The observed deviation between the CL peak and absorption edge, Stokes shift, for the films with higher Mg content could be due to macroscopic compositional fluctuation of the MgZnO layers [25]. Apart from the blue shift in peak position with Mg, there is no CL band splitting observed, which is characteristics of material's phase segregation. This offers further evidence, as was the case in the transmission spectra, that the grown films are homogeneous (single phase) materials [26].

Interestingly, the absence of multi-absorption edges as well as multi-emission bands from the absorption and CL spectra, typical characteristic of phase separation, for all samples, indicates that the phase separation issue that is frequently observed in the MgZnO alloy grown via PLD and MBE [6,11] with higher Mg content does not occur in this case. Though the exact reason for the absence of phase separation is yet to be understood, the fact that MOCVD is a

non-equilibrium film growth technique may enable the kinetic process to dominate over the thermodynamic one. Particularly, in the PMOCVD method, the fast periodic transition steps between MgZnO layer growth and oxidation creates a far from equilibrium system in which radicals that are formed could not have sufficient time to reach their energy minimum. Consequently, higher Mg incorporation into the films without phase segregation is achieved. The capability of growing single phase wurtzite MgZnO without phase segregation promises high-performance solar blind photodetectors from these films.

Fig. 3. Cathodoluminescence (solid lines) and absorption (broken lines) spectra for Mg_xZn_{1-x}O samples A (x=0.0), B (x=0.12), C (x=0.27), D (x=0.46) and E (x=0.51). The spectra were measured at 300 K and the CL curves have been normalized for clarity.

The crystal structure, orientation and phase purity of the films were analyzed by measuring $2\theta - \theta$ scans of the XRD on the samples. Fig. 4 presents the XRD patterns for

$\text{Mg}_x\text{Zn}_{1-x}\text{O}$ thin films with $x=0.0$, 0.27 and 0.51 . The patterns for all the films show a single XRD peak from (0002) reflection planes which shifts from 34.50° to 35.02° (i.e. decrease of c -lattice parameter, see the inset in Fig. 4) with increasing Mg content. The observation of only MgZnO (000 l) peaks indicates that the as grown materials are single phase wurtzite MgZnO (with x up to 0.51), with no clear indication of the presence of secondary phase(s), supporting the results from the UV-visible transmission & CL spectra. The c -lattice parameter of ZnO has decreased only by $\sim 1.3\%$ compared with the $\text{Mg}_{0.51}\text{Zn}_{0.49}\text{O}$ alloy (maximum Mg composition alloy). This indicates that the total unit cell volume has barely changed, asserting the fact that the ionic radii of Mg^{2+} and Zn^{2+} are similar [6,9,13]. The decrease of the c -lattice parameter with concentration of Mg is also shown to be linear as $c(x) = 5.1985 - 0.1366x \text{ \AA}$ from the inset graph, consistent with the reported results [6].

Fig. 4. XRD patterns of MgZnO films with Mg fraction (x) of 0.0 (black), 0.27 (red) and 0.51 (blue). The inset graph shows the dependence of the c -lattice parameter on the Mg concentration of the film.

The surface roughness and morphology of the films were studied by tapping mode atomic force microscope (AFM). Fig. 5 (A)-(E) show the 2D AFM images of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ ($0 \leq x \leq 0.51$) samples grown on AlN coated sapphire substrates. The images were taken from a scan area of $5 \times 5 \mu\text{m}^2$ for each sample and exhibited a surface with no cracks, defects, or any visible pinholes. The root mean square surface roughness (rms) of each film calculated from the respective AFM image is included on the figure. With the increase of Mg content, the surface roughness of the film decreases, suggesting an improvement in the surface quality of the film.

Fig. 5. 2D atomic force microscope (AFM) images for $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ grown on sapphire substrates with AlN buffer layer, A) $x=0.0$, B) $x=0.12$, C) $x=0.27$, D) $x=0.46$, E) $x=0.51$, F) AFM image of a film with Mg of 0.51 grown on bare sapphire substrate.

The improvement in the surface quality of the films with an increase in Mg content can be explained in terms of the observed reduction in the growth rate of films that drops from ~ 5.49 nm/min for pure ZnO to 3.10 nm/min - 2.76 nm/min for the MgZnO films with Mg content between $x=0.12$ and $x=0.51$. When pure ZnO film grows on hexagonal structured substrates, such as sapphire, the growth along the c -axis or $[0001]$ crystal orientation is preferred [27]. This

promotes a rapid vertical growth rate with a limited lateral growth, leading to the rough surface of ZnO thin film. However, when alloyed with MgO, the substitution of Zn ions with Mg ions suppresses the vertical growth along the [0001] crystal orientation and promotes the lateral one, as indicated by the decrease of the c-lattice parameter (Fig. 4, inset), resulting in an improved surface MgZnO films with increasing Mg content. Similar reduction in surface roughness has been reported for MgZnO films grown by co-sputtering [28].

Fig. 6. Room temperature UV-visible transmission spectra of $\text{Mg}_{0.51}\text{Zn}_{0.49}\text{O}$ films grown on sapphire substrates with (blue) and without (red) AlN buffer layer. The substrate stack layers are also shown in the figure.

The comparison of the AFM images of the films grown on bare sapphire and AlN coated substrates has shown no substantial difference in surface quality. As an illustration, the AFM image of a film with maximum Mg content (51 %) grown on bare sapphire substrate is shown in Fig. 5F for comparison with similar film grown on AlN buffer layer (Fig. 5E). The root mean square surface roughness (rms) values for the film grown without AlN buffer layer was 9.8 nm while the one grown on AlN buffer layer was 9.1 nm, indicating that the surface quality of the

two films is essentially the same. However, the use of AlN buffer layer for the growth the film has shown substantial improvement on the sharpness of the absorption edges of the films which will have impact on the response of a photodetectors. Fig. 6 shows the UV-visible transmission spectra of $\text{Mg}_{0.51}\text{Zn}_{0.49}\text{O}$ films grown on sapphire substrates with (blue line) and without (red line) an AlN buffer layer. As clearly seen from the figure, the absorption band edge for the film grown with an AlN buffer layer is sharper than the film grown on bare sapphire substrate. This is attributed to the comparable lattice parameter between AlN and ZnO (lattice misfit of only 4.0 %) that reduces strain related inhomogeneity [29].

Finally, Hall effect measurement was employed to analyze the electrical properties of the films using van der Pauw configuration. The sheet resistance of the films has risen from 1.95 $\text{k}\Omega/\text{sq}$ for $x=0.0$, to 660 $\text{k}\Omega/\text{sq}$ for $x=0.51$, consistent with the widening of the band gap due to an increase in an Mg content. However, the background concentration and mobility obtained from the Hall measurement of these films were unreliable mainly due to the challenge in separating the contributions from a relatively conductive ZnO buffer layer and an insulating $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ layer as well as carrier scattering at the ZnO/MgZnO interface [30,31]. On the other hand, the Hall measurement conducted on pure ZnO film grown on thin GaN coated sapphire substrate has shown a background concentration of $4 \times 10^{16} \text{ cm}^{-3}$ with a mobility of $\sim 61 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, indirectly proving that our MgZnO films have good electrical properties making them a potential candidate for solar blind photodetectors. Further investigation is underway to explore the detailed electrical properties of the films and will be reported elsewhere.

4. Conclusions

In conclusion, we employed pulsed metal organic chemical vapor deposition (PMOCVD) method to deposit high Mg content, high quality wurtzite $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ epitaxial films with an

optical band gap up to 4.49 eV (>4.28 eV, lower bound of the solar blind spectral window). The XRD pattern, UV/Vis absorption and CL spectra confirmed the absence of phase segregation in the as grown MgZnO films with an Mg content as high as 51 %. The decrease in c-lattice parameter and conductivity, blue shift in the absorption edge as well as CL spectral position indicated the incorporation of more Mg into the ZnO lattice. The fast periodic transition steps between MgZnO layer growth and oxidation during the growth of the film via PMOCVD method is believed to be the origin for the incorporation of high Mg into the ZnO host without phase separation. The use of AlN buffer layer in the growth of the MgZnO film has shown no significant difference on the surface quality but the absorption edge was sharper. The capability of growing high Mg content single phase MgZnO without phase segregation promises the development of high-performance solar blind photodetectors.

Acknowledgements

This work was supported by the US Department of Defense Army Research Office (ARO) contract No. W911NF-14-C-00157; monitored by W. Clark and M. Gerhold.

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