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Composition control of ZnMgO thin-films by Mist Chemical Vapor Deposition

Phimolphan Rutthongjan[1], Li Liu[1], Misaki Nishi[2], Masahito Sakamoto[2], Shota Sato[1], Ellawala K. C. Pradeep[3], Giang T. Dang[3], and Toshiyuki Kawaharamura[1,2,3]

[1]Graduate School of Engineering, [2]Intelligent Mechr.Sys. Eng. Course
[3]Center for Nanotechnology, Research Institute
Kochi University of technology,
185, Miyanokuchi, Tosayamada, 782-8502 Kochi, Japan.
Phone: +81-887-57-2316, E-mail: 208007q@gs.kochi-tech.ac.jp, kawaharamura.toshiyuki@kochi-tech.ac.jp

Abstract

The precise control of growth rate and composition ratio of multi-component thin-films in equilibrium reaction processes is problematic due to the complex reaction of various precursors involved in the processes. In Mist CVD, the various precursors can be separately included into two units to prevent the occurrence complex reactions among those components. In this research, ZnMgO films were grown by Mist CVD using precursors mixed in one solution chamber or using precursors separated into two solution chambers. The results show that ZnMgO growth rate and Mg composition ratio of thin-films grown up by using separated two precursors solutions were more controllable than those obtained using one solution. This suggests that the growth rate and composition ratio of multi-components thin films can be more reliably controlled by Mist CVD using separated units.

1. Introduction

Currently, multi-component thin films (binary, ternary alloys, etc.) are used for several applications. For examples, AlGaN film is suitable material for application in electronic devices, IGZO film is a promising material for thin-film transistors, YIG film is a suitable material for application in magnetic devices [1,3].

Thin-film growth rate and composition ratio are two important parameters in thin film fabrication process, which affects to design structure with corresponding devices. In the cases of equilibrium reaction based typical thin film fabrication techniques such as CVD, spray, to grown alloy thin film, the film growth rate and composition ratio cannot be easily controlled due to the difference in reaction rates of each component and the complex reactions occurring when various precursors are mixed together. This issue can also be found in conventional Mist CVD that precursor solutions were mixed in one chamber. To solve this problem, the two chamber Mist CVD system is developed. In the two chamber system, two different of precursor are separately added into each mist generation chamber. Mists generated from each chamber are transferred to an additional mixing chamber placed prior to the growth unit. It is supposed that the complex reactions can be avoided due to phase boundaries between mist droplets and insufficient time for collisions [4].

In this paper, we verify whether the two chamber Mist CVD system could prevent occurrence of complex reactions by using the system to grow ZnMgO films on quartz and ZnO buffer layers at various growth temperatures, characterizing the film properties, and comparing them with those grown by the one chamber system.

2. Experiment section

In this work, all thin films were grown by Mist CVD under atmospheric pressure. The schematics of the Mist CVD systems are depicted in Fig. 1. First, ZnO and MgO films were grown on quartz substrate, then ZnMgO on quartz and ZnO buffer layers. The growth conditions of ZnMgO by one chamber and two chamber systems are shown in Table I and referred hereafter as C1 and C2, respectively.

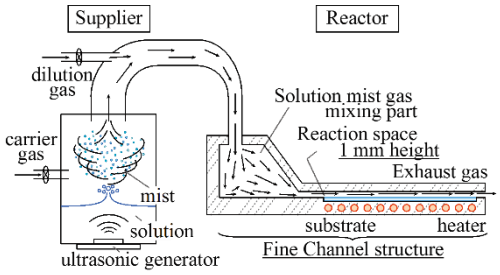

Fig 1. The schematics of the Mist CVD systems

Table I Experimental condition

Zn precursor	$Zn(acac)_2.H_2O$ (0.01 mol/l)
Mg precursor	$Mg(acac)_2.2H_2O$ (0.01 mol/l)
Solvent (Mixing ratio)	Methanol, D.I. water, NH_3 (90:7:3)
Growth temperature	200-400 °C (Intervals : 50 °C)
Growth time	15 min
Substrate	Quartz, ZnO buffer on quartz
Gas	N_2
Ultrasonic transducers	2.4 MHz, 24 V, 0.6 A, ×3

N_2 gas was used as carrier and dilution gas. In the case of one chamber system (C1), carrier and dilution gas were set at 4.5 L/min and 2.5 L/min, while carrier and dilution gas were set at 1.5 L/min and 2 L/min in two chamber system (C2). ZnO buffer layer was grown at 250 °C for 10 min with Zn precursor at the concentration of 0.02 mol/L. ZnO and MgO film were grown by using Zn precursor and Mg precursor with concentration 0.02 mol/L and 0.01 mol/L, respectively.

Thin film thickness was estimated from the spectroscopic ellipsometry (J.A. Woollam WVASE). The chemical

composition of the samples was measured by scanning electron microscopy (SEM) system equipped with an energy-dispersive X-ray (EDX) analysis device (Hitachi SU8020). The decomposition temperature of the precursor materials was evaluated using TG-DTA (Hitachi STA7200RV) under air flow of 50 ml/min with heating rate 5 °C/min.

3. Results and Discussion

Figure 2 shows TG-DTA data of $Zn(acac)_2.H_2O$ and $Mg(acac)_2.2H_2O$. It can be seen that $Zn(acac)_2.H_2O$ sublimated and decomposed to ZnO around 180 °C and $Mg(acac)_2.2H_2O$ started to decompose from 200 °C and changed to MgO around 275 °C. These results suggest that temperature higher than 200 °C (at least) is required to grow ZnMgO thin-films.

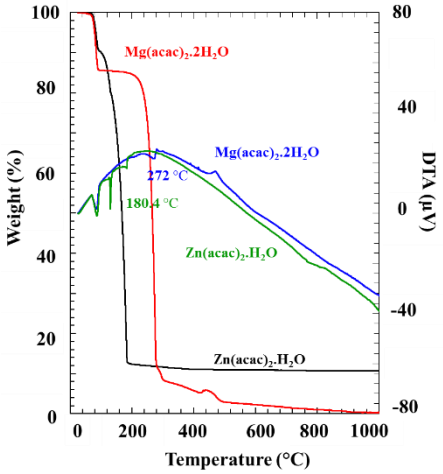

Fig 2. The TG-DTA curve of $Zn(acac)_2.H_2O$ and $Mg(acac)_2.2H_2O$

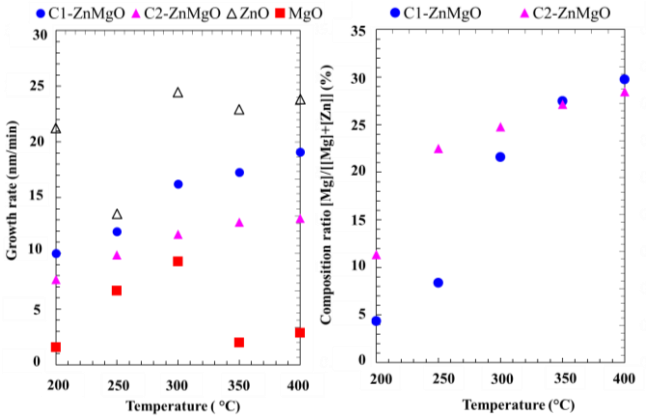

Fig 3. The relationship between ZnMgO growth rate (a) and Mg composition ratio (b) with growth temperature from 200 to 400 °C.

Fig. 3(a) shows the dependences of growth rate on growth temperatures in the range from 200 to 400 °C, it can be seen that ZnO film growth rate was almost constant with increasing of growth temperature because the Zn precursor completely decomposed at ~180 °C. Notice that the growth rate at 350 °C was lower than that at 200-300 °C, probably, because crystallinity started to improve above 350 °C [5]. In the case of MgO films, growth rate increased from 200 °C because Mg precursor started to decompose at ~200 °C. However, at high temperatures from 350 to 400 °C, MgO film growth rate sharply decreased. This might happen because H_2O in the solution changed to an oxygen source, which provided enough energy to improve the crystallinity of MgO [6].

Figure 3(b) shows the dependences of Mg composition ratio on growth temperature in the range from 200 to 400 °C, it was found that Mg composition ratio increased monotonically with growth temperature for both conditions, which is similar to the result of ZnMgO growth rate. However, at growth temperature 250 °C under condition C1, Mg composition ratio was too small when compared with condition C2, possibly, due to the fact that in the one chamber system (C1), the Zn precursor and Mg precursor were dissolved in the same solution and the ionization tendency of Mg^{2+} is higher than Zn^{2+}. Therefore, at low temperature, Mg precursor cannot obtain the enough energy to decompose to become MgO. In contrast, at low temperature under condition C2, the effect of ionization tendency of the precursors did not influence, since Zn and Mg precursors were separated into two chambers. This result was consistent with the difference of film growth rate changing under condition C1 and condition C2 from 250 to 300 °C that shown in Fig. 3(a). Therefore, these results indicate that two chamber mist CVD system produce thin films with more controllable growth rate and Mg composition ratio than those of the one chamber system.

Crystal structure and optical properties of these films on quartz and ZnO buffer on quartz grown by Mist CVD one chamber system and two chamber systems will be exclusively discussed in the conference.

4. Conclusions

ZnMgO thin films were grown by one chamber and two chamber Mist CVD systems. It was found that the growth rate and Mg composition in the thin films grown by the two chamber system were more stable than those by the one chamber system at temperature larger than the Mg decomposition temperature. The results support the hypothesis that complex reactions can be avoided with the use of the two chamber system equipped with the additional mixing chamber. Furthermore, the two chamber system clearly controls the Mg incorporation of ZnMgO thin films. Therefore, the two chamber system is the desirable method for the growth of multi-component thin films by Mist CVD.

References

[1] Kenji ltoh, JJAP 30, 9A (1991).
[2] T. Kawaharamura, Phys. Status Solidi **C 10** (2013)1565-1568.
[3] Li Liu, JJAP 56, 04CJ02 (2017).
[4] T. Kawaharamura, et al., the 64th JSAP Spring Meeting 2017, 17a-502-9
[5] M. Nishi, et al., the 64th JSAP Spring Meeting 2017, 14p-502-14
[6] T. Kawaharamura, JJAP 52, 035501 (2013)