

Growth mechanism of Zinc Oxide thin film by mist-CVD via the modulation of $[\text{H}_2\text{O}]/[\text{Zn}]$ ratios

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Abstract

In this work, the mechanism of ZnO film fabrication via mist-CVD was proposed by analyzing the experimental data of growth rates, crystallinities, surface morphologies, and chemical states of the films which were grown under the conditions of fixed precursor material supply amount and changed H_2O concentrations. When the conditions are appropriate, e.g. $[\text{H}_2\text{O}]/[\text{Zn}] \approx 60\text{-}70$ at the precursor concentration of 0.02 M, high quality ZnO thin film with high growth rate, (001) dominant orientation, smooth surface below 5 nm RMS roughness, and low oxygen deficiency was achieved, because it enables to maintain the sufficient diffusion length of precursor materials on the surface and the appropriate collision probability of precursor and oxygen sources.

1. Introduction

ZnO crystal orientations are typically affected by several parameters such as growth temperatures, gas flow rates, material concentrations, oxygen partial pressures, and chemical reactions that happen during the film growth. The influence of these parameters on the film crystal orientation was previously investigated in vacuum-based processes. [1,2] The control of ZnO crystal orientation in those studies was explained by a surface adatom diffusion growth model [3] and the control of zinc and oxygen atom diffusion during film growth is one of the keys to controlling ZnO film crystal structures.

The control of atom diffusion in solution-based processes is problematic because zinc and oxygen precursors are mixed in the solvent, which produces complex reactions and precipitations that could form in the solution prior to deposition. This may affect the control of atom diffusion. ZnO film structures and morphologies were already controlled by varying the concentrations of cationic surfactants in those processes [4], but the film growth mechanism was not elucidated and the understanding of specific growth mechanisms of ZnO films prepared by solution-based processes is rather limited.

In this work, ZnO film crystal orientations were simply controlled by adjustment of $[\text{H}_2\text{O}]/[\text{Zn}]$ ratios via the third generation (3rd G) mist chemical vapor deposition. [5] We investigated the influence of $[\text{H}_2\text{O}]/[\text{Zn}]$ ratios on ZnO film growth rates, crystal orientations, surface morphologies, and chemical states in the films. Finally, the ZnO film growth mechanism was proposed based on the systematic investigation of the relationship between these experimental results.

2. Experiment section

In the 3rd G mist CVD system, single or multiple kinds of precursor solutions are set into separate solution chambers to avoid the mixing of the precursors. In this current experiment, Zn and O solutions were set into separate solution chamber. Zinc acetylacetonate hydrate ($\text{Zn}(\text{acac})_2 \cdot \text{H}_2\text{O}$) was used as the Zn source with various concentrations of 8, 20, and 50 mM. The mixture of methanol and ethylenediamine (EDA) with a mixing ratio of 97:3 was used as the solvent to dissolve Zn precursor. The oxygen source (H_2O supporting-solution) was prepared from the mixture solvent of methanol and H_2O with mixing ratios from 100:0 to 0:100. N_2 gas was used for carrier and dilution gases. The gas flow rate of carrier and dilution gases in Zn-solution chamber was set at 2.5 L/min, while in O-solution chamber were varied from 0-5 and 5-0 L/min for carrier and dilution gases, respectively. All the films were grown on quartz at growth temperature of 400 °C. The $[\text{H}_2\text{O}]/[\text{Zn}]$ ratios were controlled in the range from 0 to 1600, where the H_2O and Zn concentrations ($[\text{H}_2\text{O}]$ and $[\text{Zn}]$) were calculated from the solution used in the O and Zn solution-chambers after 10 min growth, respectively.

3. Results and Discussion

The trend of the film growth rate in Fig. 1(a) can be explained by the thermal decomposition reaction of $\text{Zn}(\text{acac})_2$ with H_2O as follow: $\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2 + \text{H}_2\text{O} \rightleftharpoons \text{ZnO} + 2\text{C}_5\text{H}_8\text{O}_2$ where $\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2$ decomposed to form ZnO by directly reacting with H_2O . In the film grown without H_2O support, the H_2O molecules present in the zinc acetylacetonate hydrate and/or the O atoms next to the Zn atoms were used as the oxygen source for ZnO film formation. However, the low H_2O content could not promote thermal decomposition reaction of $\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2$, resulting in low ZnO film growth rate. On the other hand, as $[\text{H}_2\text{O}]/[\text{Zn}]$ increased, the equilibrium of the thermal decomposition of $\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2$ moves to the right due to an increase in the probability of the collision of these materials on the surface, resulting in an increased ZnO film growth rate. However, when the $[\text{H}_2\text{O}]/[\text{Zn}]$ ratios were too high ($[\text{H}_2\text{O}]/[\text{Zn}] = 500, 350, 300$ for $[\text{Zn}] = 8, 20, 50$ mM, respectively), the film growth rates started to decrease. This could be explained by the following reasons (i) the equilibrium constant ($K = [\text{ZnO}] \cdot [\text{C}_5\text{H}_8\text{O}_2]^2 / [\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2] \cdot [\text{H}_2\text{O}]$) of the reaction was less than 1 ($K < 1$) and the equilibrium of the reaction shifted to the left, (ii) higher H_2O and $\text{C}_5\text{H}_8\text{O}_2$ forms acetylacetonate acid

($\text{H}_2\text{O} + \text{C}_5\text{H}_8\text{O}_2 \rightleftharpoons \text{H}_3\text{O}^+ + \text{C}_5\text{H}_7\text{O}_2^-$), (iii) the dissociation of the different bonds (Zn-O or C-O) of zinc acetylacetonate generates various types of Zn-reactive species (e.g., Zn^{2+} , ZnO_x , and Zn-O-R) to form ZnO and (iv) the decrease in the probability of meeting next Zn or O atoms.

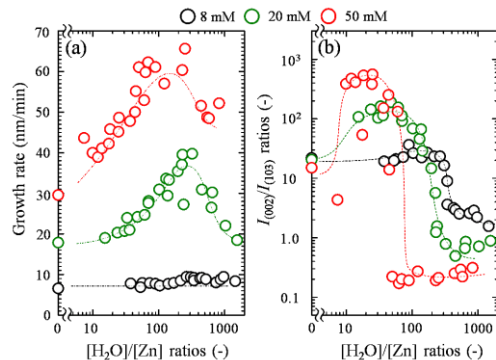


Fig. 1. The dependence of (a) ZnO film growth rates and (b) the ratios of the intensities of the (002) and (103) reflections $I_{(002)}/I_{(103)}$ on the $[\text{H}_2\text{O}]/[\text{Zn}]$ ratios for different Zn precursor concentrations.

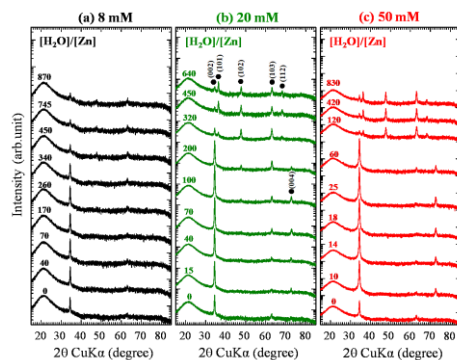


Fig. 2. $2\theta/\omega$ scans of ZnO films grown with different $[\text{H}_2\text{O}]/[\text{Zn}]$ ratios and Zn precursor concentrations of (a) 8, (b) 20, and (c) 50 mM.

The influence of H_2O on the ZnO film orientation (see Fig. 2), surface morphology [see Figs. 3(a)-(d)], and chemical states in the films [see Figs. 3(i)-(l)] can be explained by a surface atom migration growth model reported in several previous studies. [1-3] In the case of low $[\text{H}_2\text{O}]/[\text{Zn}]$ and/or without H_2O support, the diffusion length of zinc and oxygen atoms was sufficient but the probability of the atom colliding with another atom was low. Therefore, the ZnO film was obtained with a low growth rate, (001) dominant orientation, and spherical surface morphology, which induces smooth surface roughness [see Fig. 3(a)] but with high oxygen-related defects [see Fig. 3(i)]. In contrast, in the case of excessive $[\text{H}_2\text{O}]/[\text{Zn}]$, the diffusion length is limited because of the high density of atoms on the surface, including the high probability of the atom colliding with another atom. Therefore, atoms form ZnO nuclei with nearest atoms or with new coming atoms during their diffusion causing absorption of atoms one after another before ZnO stabilized in the lowest energy state. This led to the growth of the ZnO film with the rising of the (101), (102), and (103) reflections and the suppression of the (002) reflection. As a result, ZnO crystallized into the irregular

morphology [see Fig. 3(d)] with rough surface and high densities of oxygen-related defects and hydroxyl groups [see Fig. 3(l)].

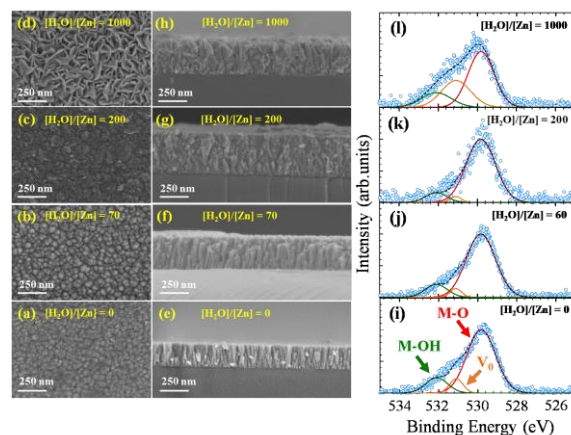


Fig. 3. Top-view [(a)-(d)] and cross-section [(e)-(h)] FE-SEM images of ZnO films grown with $[\text{Zn}] = 20$ mM and $[\text{H}_2\text{O}]/[\text{Zn}] = 0$, 70, 200, and 1000 and [(i)-(l)] the XPS spectra of the O 1s core level of ZnO films and $[\text{H}_2\text{O}]/[\text{Zn}] =$ (i) 0, (j) 60, (k) 200, and (l) 1000.

Only at suitable $[\text{Zn}]$ and $[\text{H}_2\text{O}]/[\text{Zn}]$, a high growth rate, high crystallinity with a (001) preferential orientation, high $I_{(002)}/I_{(103)}$ [see Fig. 1(b)], spherical surface morphology [see Fig. 3(b)], and low oxygen-related defects [see Fig. 3(j)] can be achieved owing to a sufficient diffusion length and appropriate collision probability of precursor and oxygen sources. All of these explanation will be exclusively discussed in the conference.

4. Conclusions

In this work, the mechanism of ZnO film growth via mist-chemical vapor deposition was proposed by analyzing the experimental data of film growth rates, crystal orientations, and surface morphologies. ZnO films were grown with various $[\text{H}_2\text{O}]/[\text{Zn}]$ ratios. The crystal orientations changed from *c*-axis dominant to random growth orientations with increasing $[\text{H}_2\text{O}]/[\text{Zn}]$ ratios. Due to the difference in those crystal orientations, film surface morphologies evolved from spherical to irregular structures. The ZnO crystal orientation could be controlled by changing the $[\text{H}_2\text{O}]/[\text{Zn}]$ ratios. We believe that these findings pave the way for optimizing the crystal growth of other metal-oxide films in other solution-based processes via the control of the metal-oxygen ratio.

References

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