Preparation of ZnO thin films by MO-CVD using fibrous bis (acetylacetonato) zinc (II) and ozone

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Abstract. The fibrous bis (acetylacetonato) zinc (II) (Zn(C₅H₇O₂)₂·xH₂O) was prepared with novel apparatus involved the vaporization and the recrystallization, and was investigated by differential thermal analysis (DTA), flourier transform infrared spectroscopy (FT-IR) with attenuated total reflection (ATR), and the inductively coupled plasma optical emission spectroscopy (ICP-OES). The zinc oxide (ZnO) films were prepared by the low-pressure CVD (LP-CVD) using the fibrous Zn(C₅H₇O₂)₂·xH₂O and ozone(O₃). The DTA curve of the fibrous material with a wide-ranging endothermic peak under 100°C according to desorption of the hydrated water separated to two peaks decreasing in the evaporation temperature. The resistivity of the ZnO films has changed widely from 10⁴ to 10⁸ Ωcm by the fibrous material with a different preparation condition.

1. Introduction
Zinc oxide (ZnO) including the basis metal zinc with a wide bandgap of 3.37eV is transparent in the visible region, and are a luminescence property and a photoelectric transfer characteristic in the near-ultraviolet region. The ZnO film with these properties is applied to transparent conductive film [1], near-ultraviolet light emitting device [2], and transparent thin film transistor (TFT) [3]. A high-quality ZnO thin film is prepared by molecular beam epitaxy (MBE) [4], pulse laser deposition (PLD) [5], and metalorganic chemistry vapor deposition (MO-CVD) [6-7]. In these preparation methods, MO-CVD is advanced the industrial production because the high vacuum is not needed, and the continuous feed of the material is possible, and has been introduced into a lot of semiconductor factories. However, the crystallinity and the surface flatness of oxide films prepared with MO-CVD decrease dramatically by an intense gas phase reaction of an organometallic material and the oxygen.

Acetylacetonato zinc with the hydrated water (Zn(C₅H₇O₂)₂·xH₂O) that doesn't react intensely to the oxygen has been used as a zinc material in the present study [8]. A high-quality Zn(C₅H₇O₂)₂·xH₂O of the semiconductor grade was not sold in the market, and we had to use the material of the industrial use of the fine powder. Moreover, these materials solidified as a residue, and the evaporation of Zn(C₅H₇O₂)₂·xH₂O has not steadied. We recrystallized commercially available Zn(C₅H₇O₂)₂·xH₂O powder to vaporize in the vacuum chamber, and prepared the MO material of the fibrous shape not solidified easily. The fibrous material has the excellent carrier gas transmission characteristic that can be stably supplied without solidifying the MO material. The ZnO-TFT with the electron field-effect mobility of 5.2 cm²/V.sec is obtained by using this material [9]. Moreover, homo-epitaxially growth ZnO films with excellent flatness and the crystallinity was deposited on the ZnO single-crystal
substrate [10]. In this paper, we investigate the difference of the Zn(C$_5$H$_7$O$_2$)$_2$·xH$_2$O with the fibrous and the powder shape, and the property of the fibrous materials by using DTA, FT-IR with ATR, and ICP-OES. The resistivity of the ZnO films prepared by MO-CVD using the fibrous Zn(C$_5$H$_7$O$_2$)$_2$·xH$_2$O and ozone(O$_3$) were measured by the co-planer electrode of evaporated Al film. The structure and the composition of the ZnO films were analyzed with XRD, XPS and AFM.

2. Experimental Procedures

The fibrous Zn(C$_5$H$_7$O$_2$)$_2$·xH$_2$O produced by the unique method which has the process of vaporization and recrystallization Zn(C$_5$H$_7$O$_2$)$_2$ powder of 99.95% purity that is inexpensive, less toxic and less reactive to oxygen. The fibrous specimen was prepared by the apparatus shown in Figure 1. The preparation condition were the vaporized temperature of 160-180˚C, and pressure of 500-1000hPa. The fibrous specimen recrystallized on the wire located in the upper part of vaporized container as shown in the insertion figure.

The ZnO films were prepared by the low-pressure CVD (LP-CVD) using the fibrous Zn(C$_5$H$_7$O$_2$)$_2$·xH$_2$O and ozone (O$_3$) [9]. MO gas carried with Ar flows in the reaction chamber. The substrate temperature was maintained at 400-530˚C. O$_3$ gas was generated in the range of 0.60-2.04 g/h by adjusting both the flow rate of O$_2$ and the discharge voltage in the ozonizer.

The fibrous Zn(C$_5$H$_7$O$_2$)$_2$·xH$_2$O was analyzed by the differential thermal analysis 4(DTA), inductively coupled plasma optical emission spectroscopy (ICP-OES) and fourier transform infrared spectroscopy (FT-IR) with attenuated total reflection (ATR). The film thickness was measured by stylus instrument. Surface profile of the film was observed by atomic force microscope (AFM). The crystal structure of the film was evaluated by X-ray diffraction analysis (XRD). Chemical composition analysis was examined by X-ray photoelectron spectroscopy (XPS). The resistivity was determined by pA meter/DC voltage source (HP 4140B) with the evaporated aluminum (Al) electrodes.

3. Results and Discussion

DTA analysis for the fibrous Zn(C$_5$H$_7$O$_2$)$_2$·xH$_2$O were carried under vacuum of 500hPa similar to preparation condition of MO-CVD. The specimen was heated from room temperature to 220˚C at the heating rate of 10˚C/min. Fig. 2 shows the DTA curves of the fibrous specimen with the different preparation condition and commercially available Zn(C$_3$H$_5$O$_2$)$_2$ powder. Figure 2(a) is DTA curve of the specimen prepared by different vaporized temperature (V.T.) and pressure (V.P.). The result of the powder sample is shown as a comparison. It is thought that the endothermic peak within the range from 70 to 100˚C depends on the vaporization of the several molecules coupling hydrated water or the organic substance of low molecular weight. An endothermic peak of the temperature range of 120-150˚C depends on the melting point of the fibrous Zn(C$_5$H$_7$O$_2$)$_2$·xH$_2$O. The endothermic within the range

![Figure 1. Vaporization and recrystallization apparatus used to prepare fibrous Zn(C$_5$H$_7$O$_2$)$_2$·xH$_2$O](image-url)
from 70 to 100 °C separated to two for the sample of V.P. =500hPa, and it was not able to be identified to the powder sample. The endothermic peak by the melting point almost becomes a constant without depending on the preparation condition, and it is assumed that all specimens maintain the acetylacetonato zinc structure.

Fig. 2(b) is DTA curves of the fibrous specimen prepared by V.T.=180°C and V.P.=500-900hPa. A large endothermic peak within the range of 70-100°C moves to the low temperature side as VP increases, and a small endothermic peak move to the high temperature side and disappear. It is reported that the hydrated water contained in the Zn(C₅H₇O₂)₂·xH₂O contaminates the substrate surface, and brings a remarkable degradation of the surface quality of the ZnO film [10]. Therefore, it is very important to reveal the relation between the amount in the hydrated water included in MO-material and the physical property of the ZnO film.

![Figure 2](image)

**Table 1.** Composition ratio analyzed with ICP-OES of fibrous specimen obtained by different preparation condition

| Sample         | Zn (at.%) | C (at.%) | H (at.%) | O (at.%) |
|----------------|-----------|----------|----------|----------|
| Powder         | 22.7      | 41.1     | 6.4      | 29.9     |
| 500hPa/165°C   | 22.7      | 45.9     | 6.51     | 29.6     |
| 800hPa/180°C   | 22.5      | 46.6     | 5.95     | 29.7     |

Fig. 3 shows FT-IR spectrum with ATR of the same specimen as Fig. 2. The measurement result of the residue that remains in the vaporization container is shown in Fig. 3(a) as a comparison. All the characteristic IR vibrational frequencies have been assigned in agreement with the proposed molecular structure. In Fig. 3(a) and (b), the O-H stretching frequencies were broadly found at 3650-
2750 cm$^{-1}$, and the symmetric and antisymmetric CH$_3$ vibrations observed around 2965 cm$^{-1}$ and 2833 cm$^{-1}$. The absorption band at 1518 cm$^{-1}$ is due to the in-plane bending vibration of CH$_2$ group and bands at 1138 cm$^{-1}$ indicates the symmetric vibration of CH$_3$ group attached to carbon atom. From FT-IR spectrum of Fig. 3(a), the O-H vibration remarkably observed in the powder sample decreased in the fibrous specimen, and was hardly verified in the residue. Moreover, the symmetric vibration of CH$_3$ disappeared in the powder and the residue specimen. A remarkable difference of symmetric vibration of CH$_3$ was seen though FT-IR spectrum of almost every specimen was the same approximately in Fig. 3(b).

Fig. 3. FT-IR spectrum of the fibrous Zn(C$_5$H$_7$O$_2$)$_2$·xH$_2$O prepared by different preparation condition

Fig. 4 shows the effect of various CVD pressure and substrate temperature on the resistivity of the ZnO films. The fibrous Zn(C$_5$H$_7$O$_2$)$_2$·xH$_2$O were prepared with V.T.=175$^\circ$C and V.P.=500hPa. The ZnO films were prepared on the condition of deposition pressure 600-800hPa and the substrate temperature 500-530$^\circ$C. As for the ZnO film deposited by the pressure of 600-800hPa, the resistivity has increased according to an increase of the substrate temperature. The results in Fig. 4 are different from the electric characteristics of the ZnO film deposited by the powder material. Generally, the crystallinity of the ZnO film improves according to the rise of the substrate temperature, and the resistivity of the ZnO film decreases with increasing the crystallinity of the film. The improvement of the crystallinity increases the grain size of the polycrystalline ZnO film, and increases the mobility of the film that brings a decrease in the resistivity. Fig. 4 shows a result quite opposite to the paper reported before [8]. As for a decrease of the resistivity of the ZnO film, the following reasons are supposed. The first reason is a bilayer theory that the ZnO film becomes a layer structure due to the decrease in the crystallinity of the ZnO film in the substrate interface. The following reason is a mobility improved model that the resistivity decreases because of an increase in the mobility of the ZnO film. However, the result of Fig. 4 doesn't coincide to both of the above-mentioned model. It is thought that an increase in the resistivity of the ZnO film according to the rise of the substrate temperature was obtained by the synergistic effect of the optimization of the stoichiometry by the introduction of active ozone and the improvement of the crystallinity.

Fig. 5 shows the relation between resistivity of the ZnO film and vaporized pressure (V.P.) of the powder material. Vaporized Temperature (V.T.) in the vessel including the powder material was set to 180$^\circ$C, and the preparation condition of the ZnO films were the substrate temperature of 530$^\circ$C and the deposition pressure of 650hPa, respectively. The resistivity of the ZnO film indicates the highest
value at VP=800hPa in figure. It is very difficult to explain the reason why the resistivity of the ZnO film changes remarkably by different V.P. and V.T. value by using present data. The further analysis is needed to clarify these phenomena though it is considered that the structure of the material and the existence of the hydrated water greatly influence the electric characteristics of the ZnO film.

Fig. 6 shows ozone (O₃) density (g/h) dependence of the X-ray diffraction (XRD) spectrum for the ZnO films prepared on the Pyrex glass substrate at the substrate temperature of 500°C by using the O₂-O₃ mixed gas as an oxygen material. The fibrous Zn(C₅H₇O₂)₂·xH₂O materials prepared in V.T.=175°C, V.P.=500hPa were used for deposition of the ZnO film. As for all samples, the diffraction peak of the ZnO (0002) plane indicating the c-axis orientation was observed near 34.2 degrees. An increase in the diffraction peak intensity corresponding to the crystallinity of the ZnO film was observed according to an increase in the O₃ density. An increase in the O₃ density is assumed to improve activation energy to promote the ZnO crystal growth.

Surface composition of these films were analysed by X-ray photoelectron spectroscopy (XPS). The Mg-Kα excitation was used for this study. The film was etched by Ar⁺ ion beam in order to remove impurity on the surface. Zn-2p₃/₂, Zn-2p₁/₂ and O-1s can be observed easily. O-1s peak are observed at about 530.8 eV as normal shown in same binding energy, and Zn-2p₃/₂, Zn-2p₁/₂ in 1022 eV and 1045 eV.
eV, respectively. The C-1s peak that decided the amount of the carbon contained in the ZnO films was negligibly small.

Fig. 7 is an atomic force microscope (AFM) image to the same samples measured by XRD. The ZnO films in (a) - (c) are polycrystalline, and the crystal shape of (a) and (b) can identify a diameter as a sphere of around 0.05 µm from an AFM image. As for the AFM image of sample (c), the grain size increased to about 0.1 µm, and a dense, flat surface morphology was observed. The results of XRD spectrum and the AFM image show a similar tendency, and it is concluded that the increase of the ozone density contributes to expansion of the grain size and the planarization of the film surface.

![Figure 7](image)

Figure 7. The AFM images for the surface morphology of the ZnO films on Pyrex glass substrate. The ozone density is (a) 0.87 (g/h), (b) 1.98 (g/h), (c) 2.12 (g/h).

4. Conclusion
The fibrous Zn(C_5H_7O_2)_2·xH_2O was obtained by the unique method which has the process of vaporization and recrystallization the commercially available acetylacetonato zinc powder. Fibrous MO material to which the vaporization of the material gradually progressed from the interstice of the fiber was able to supply the material of Zn stably until the growth of the ZnO film finished. As for the DTA curve of the acetylacetonato zinc material, the temperature of an endothermic peak by the vaporization of the hydrated water in the fiber shape specimen is lower than that of the commercially available powder sample, and a small endothermic peak appears in a further low temperature regime according to the preparation condition of the fiber specimen. The resistivity of the ZnO film prepared by using the fibrous Zn(C_5H_7O_2)_2·xH_2O was a very high value of 1.92×10^8 Ω cm at V.T.=175°C.

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