

Ultrasonic-assisted mist chemical vapor deposition of II-oxide and related oxide compounds

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Received 8 October 2013, revised 20 November 2013, accepted 30 December 2013

Published online 7 April 2014

Keywords oxide thin films, solution-based deposition, non-vacuum process, environmental friendly

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Basic concepts of ultrasonic-assisted mist chemical vapor deposition (CVD), and its applications to the fabrication of II-oxide and related oxide films are described. Fairly good thin film properties and device performance, compared to those achieved by conventional vacuum-based

processes, encourage the mist CVD as a simple, inexpensive, energy-saving and non-vacuum process, opening new and wide application of oxide materials for novel devices supporting the future environment.

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1 Introduction A variety of oxide compounds are considered to be *green materials*, which are safe and can achieve *green applications* such as low power-consumption devices and solar cells. Evolution of oxide "semiconductors" began with II-VI compound oxides (II-oxides) such as ZnO [1–4] and MgZnO [5–9], and the basic policy is now extending to related oxides such as III-oxides (Ga₂O₃ [10–13], In₂O₃ [14, 15], etc.) and IV-oxides (SnO₂ [16, 17], etc.).

It is also another demand from the semiconductor industry that careful considerations should be paid for cost and energy necessary in thin film fabrication processes, towards the future sustainable society. Different from arsenides or nitrides, oxides are suitable to be fabricated by *green chemistry* (or *green processes*), that is, by non-vacuum and solution-based fabrication methods, because one does not need to be so nervous on oxygen contamination which is a fatal problem for non-oxide materials. Nevertheless, the evolutionary development of oxide semiconductors has mainly indebted to vacuum-based deposition technologies such as molecular beam epitaxy (MBE) [1, 3, 4, 6, 9–13, 15–17], pulsed laser deposition (PLD) [2, 5, 7, 8], and metalorganic chemical vapor deposition (MOCVD) [14].

In order to explore *green materials* for *green applications* by *green chemistry*, we have developed a novel technology of ultrasonic-assisted mist chemical vapor deposition (CVD) for the fabrication of oxide compounds. In this paper we show and discuss the potentials and advantages of this technology from the recent achievements of a variety of oxide thin films.

2 Basic concept of mist CVD

2.1 Sources and reaction system Suppose the fabrication of an M_xO_y film, where M denotes a chemical element. We need a gaseous source containing M, which is supplied to a heated reaction area, and one of the ideas to meet this demand is to use organic compounds of M such as M(CH₃)_z or M(C₂H₅)_z which has high vapor pressure. This is the basic concept of MOCVD. However, metalorganic compounds are generally flammable and expensive, and a leak-tight vacuum-based system is indispensable.

On the other hand, there are a variety of chemicals containing M, soluble to water and/or alcohol, safe and inexpensive. M(CH₃COO)_z (acetates) and M(acac)_z (acetylacetonates) are typical examples. These chemicals are desirable to be used as sources of M from the viewpoints of

safety and cost, but the vapor pressures of the chemical solutions are too low so that the chemical element M to be transported by bubbling with a carrier gas. The basic concept of mist CVD is to utilize ultrasonically-atomized mist particles formed from the solution of safe and inexpensive chemicals. The mist particles are transferred by a carrier gas, and in this manner the chemical element M is supplied to the reaction area. An example of mist generators is given in Fig. 1, which may be equivalent to a metalorganic source in MOCVD but enhances safety by using water or alcohol solution of safe materials. In the reaction area, we found that sufficient suppression of source gases onto a substrate is a key for the film fabrication. We have developed a fine-channel system [18] for small (<100 mm) substrates, a linear-source system [19] for large (>100 mm) substrates, and a high-temperature system [20] for the growth of single-crystals.

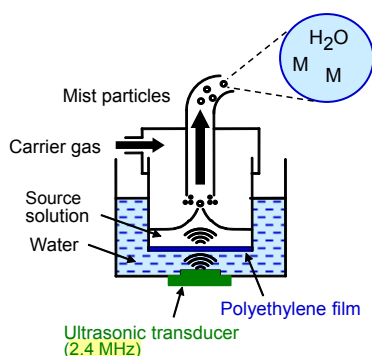


Figure 1 Schematic illustration of a mist generator.

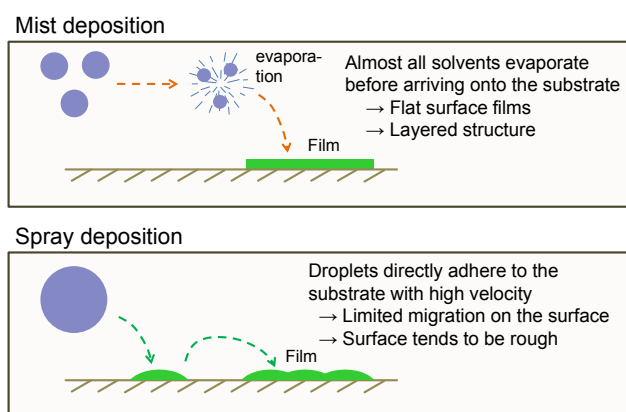


Figure 2 Plausible models for the deposition processes by the mist deposition and the spray deposition.

The diameters of mist particles are given by the Lang's formula [21] as 2–3 μm for the ultrasonic frequency of 2.4 MHz. These small mist particles are transferred with the carrier gas. On the other hand in the spray deposition [22] diameters of the particles formed are generally >10 μm with wide variation [21], and the particles are sprayed onto

the substrate at a high velocity. Figure 2 compares the plausible models for the deposition processes by the mist deposition and the spray deposition. In the mist deposition the mist particles will be thermally evaporated in the gas atmosphere and the source chemicals will react with oxygen source at the substrate surface. This is the same as the CVD processes and the sources will migrate on the surface followed by the well-controlled formation of the film.

2.2 Basic reaction kinetics

Figure 3 shows how the deposition rate depends on the substrate temperature in the deposition of ZnO with the source of $\text{Zn}(\text{CH}_3\text{COO})_2$. Since the linear-source system has been used for the experiments, we cannot define the deposition rate in the unit of nm/min because the formation of thin films has been due to repeated scanning of the linear-source nozzle. The horizontal axis is expressed by the film thickness under the same growth time. The curves exhibit the tendency similar to those in case of MOCVD or other CVD processes, that is, they are classified into three regions in terms of the substrate temperature, reaction limited, diffusion limited and evaporation limited regions. Further, the deposition rate is almost twice when the flow rate of the Zn source, $\text{Zn}(\text{CH}_3\text{COO})_2$, is doubled from 2.5×10^{-5} mol/min to 5×10^{-5} mol/min. These results well suggest the formation of the films by CVD processes.

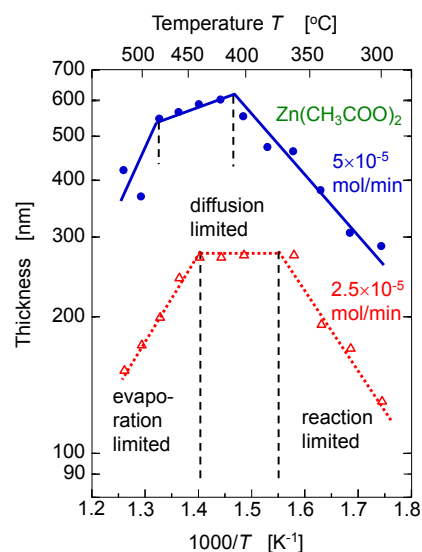


Figure 3 Thicknesses of ZnO films as a function of the substrate temperature deposited by a linear source mist CVD system at the same deposition times, that is, the horizontal axis reflects the deposition rate.

3 Thin film fabrications by mist CVD

3.1 Transparent conducting films The mist CVD has originally been developed for the deposition of transparent conducting oxide (TCO) thin films. Figure 4 shows the resistivity of ITO films on glass substrates deposited

from $\text{In}(\text{acac})_3$ and $\text{Sn}(\text{CH}_3\text{COO})_2$ in a $\text{CH}_3\text{OH}-\text{H}_2\text{O}-\text{HCl}$ (90:9:1) solution. Marked decrease in resistivity at higher substrate temperature may be associated with increase of Sn composition in the film due to more enhanced decomposition of the Sn source. The minimum resistivity of $1.4 \times 10^{-4} \Omega\text{cm}$ is reasonably low to be applied as a TCO.

Low cost and low temperature growth of ZnO TCO films is one of the most up-to-date demands from solar cell industries. The mist CVD realized the resistivity of $1 \times 10^{-3} \Omega\text{cm}$ at the deposition temperature of 200 °C, attained the sheet resistance of $10 \Omega/\square$ [23].

The resistivity values shown above are still higher compared to those of sputtering-deposited ITOs (the order of $10^{-5} \Omega\text{cm}$). However, soft deposition by the mist CVD gives no severe damage to underlying layers, and this is desirable to transparent electrodes in emerging devices.

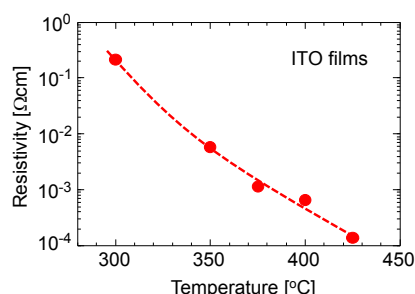


Figure 4 Resistivity of ITO films deposited on glass substrates.

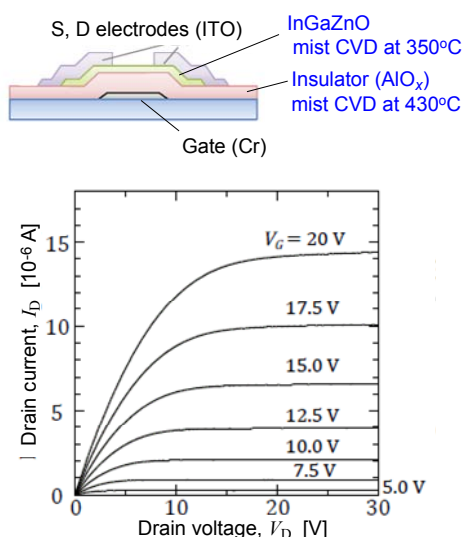


Figure 5 Device structure and drain characteristics of an $\text{AlO}_x/\text{InGaZnO}$ TFT.

3.2 Amorphous oxide thin films and TFTs A variety of amorphous and polycrystalline oxide films, such as insulators (AlO_x and SiO_x [24]) and semiconductors (InGaO , GaAlO , and InGaZnO) have been fabricated by the mist CVD. InGaZnO thin film transistors [25], as

shown in Fig. 5, where the active and insulating layers were fabricated by the mist CVD, exhibited the fairly good device performance such as on/off ratio of $>10^8$, field-effect mobility of $4.2 \text{ cm}^2/\text{Vs}$, and low leakage current of $<1 \text{ pA}$, compared to conventional devices fabricated by sputtering-deposited films,

3.3 Single crystalline oxide thin films For single-crystalline oxide semiconductors, layer-by-layer growth of ZnO, which had been difficult by MOCVD, was successfully achieved. The electron mobility was close to $100 \text{ cm}^2/\text{Vs}$ [20]. Recent reports showing potential of Ga_2O_3 for power devices [11–13] encourage the growth of Ga_2O_3 by the mist CVD for more effective saving of energy.

We have developed corundum-structured Ga_2O_3 ($\alpha\text{-Ga}_2\text{O}_3$) [26, 27] on sapphire by using the mist CVD. It is worth noticing that orthorhombic Ga_2O_3 ($\beta\text{-Ga}_2\text{O}_3$) was grown on sapphire by MBE [10], so the soft growth by a CVD mode is desirable for an epilayer to follow crystal structure of the underlying substrate. The successful growth of high-quality $\alpha\text{-Ga}_2\text{O}_3$ is extended to the band gap engineering with $\alpha\text{-(Al}_x\text{Ga}_{1-x})_2\text{O}_3$ and $\alpha\text{-(In}_x\text{Ga}_{1-x})_2\text{O}_3$ alloys. Unintentionally doped $\alpha\text{-Ga}_2\text{O}_3$ is highly insulating while Sn doping results in n-type conduction [28, 29]. $\alpha\text{-In}_2\text{O}_3$ shows higher mobility than $\alpha\text{-Ga}_2\text{O}_3$ [30]. A variety of band gap as well as of conductivity is desirable for novel device structures utilizing the wide band gap properties.

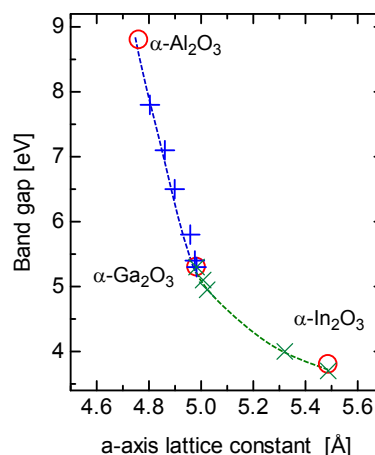


Figure 6 Relationship between a-axis lattice constant and band gap for corundum-structured oxide semiconductor films.

Figure 6 shows a-axis lattice constants and band gap energies of $\alpha\text{-(Al}_x\text{Ga}_{1-x})_2\text{O}_3$ and $\alpha\text{-(In}_x\text{Ga}_{1-x})_2\text{O}_3$ alloys grown on c-plane sapphire substrates. Acetylacetonate compounds were used as the sources of Al, Ga, and In. The growth temperature was 500 °C. Here the a-axis lattice constants and band gap energies have been determined by X-ray $2\theta/\omega$ -scan diffraction and optical absorption, respectively. For binary compounds we used 4.7617 Å [31], 4.9825 Å [32] and 5.4870 Å [33] as a-axis lattice constants

and 8.8 eV [34], 5.3 eV [26] and 3.8 eV [35] as band gap energies for α -Al₂O₃, α -Ga₂O₃ and α -In₂O₃, respectively.

For α -(Al_xGa_{1-x})₂O₃ the composition x , hence a-axis lattice constant and band gap, was fairly well-controlled by the source composition; the relationship of them was almost linear. On the other hand α -(In_xGa_{1-x})₂O₃ films tend to show phase separation for the middle-range of x . This is, interestingly, similar to InGaN alloys. The relationship between a-axis lattice constants and band gap exhibits marked bowing, which may be due to less miscibility of α -(In_xGa_{1-x})₂O₃ than α -(Al_xGa_{1-x})₂O₃, as has been evidenced by the phase separation of α -(In_xGa_{1-x})₂O₃.

Presently the sources used in the mist CVD are not always of high purity because they have not been developed for semiconductor growth, resulting in negligible contamination in the grown films. This is an important subject for future evolution of the mist CVD.

4 Conclusions This paper reports the basic concepts and fundamental system issues of ultrasonic-assisted mist CVD, followed by examples of its successful applications to deposition of oxide thin films. The results encourage the device quality of thin films in spite of the simple, inexpensive, energy-saving and non-vacuum process. It is strongly expected that the mist CVD will open new and wide application of oxide materials for novel devices supporting the future environment.

Acknowledgements The authors acknowledge Messrs. Norihiro Suzuki and Takayuki Uchida of Kyoto University for technical support in the experiments. This work was partly supported by “The research and development project for innovation technique of energy conservation” of the New Energy and Industrial Technology Development Organization (NEDO) and a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (JSPS).

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