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Mist CVD Growth of ZnO-Based Thin Films and Nanostructures

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As a safe, simple, environmental-friendly, and cost-effective growth technique of oxide materials, we have developed the mist chemical vapor deposition method. To grow ZnO, a water and/or alcohol solution of zinc-compounds (for example, zinc acetate) is used as the source, and micron-sized aerosol or mist particles formed by ultrasonic atomization are supplied to the reaction area with a carrier gas. The ZnO thin films grown on glass substrates exhibited c-axis orientation under the selected growth conditions. The transparency in the visible region was higher than 90 %, the room temperature photoluminescence showed near band edge emission without noticeable deep level emissions, and the surface root-mean-square roughness was 7.5 nm despite the polycrystalline structure. These results are satisfactory for optical applications. The minimum resistivity, however, by gallium doping was $1.1 \times 10^{-3} \Omega$ cm, which needs further progress by enlarging the grain size. The growth of other oxide thin films, for example, MgO and CdO, as well as ZnO nanorods was reported, suggesting potential of wide applications of this growth technique to various oxide thin films and nanostructures with the friendliness to environment.

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I. INTRODUCTION

A variety of growth or deposition techniques have been developed to elicit promising potentials of zinc oxide (ZnO) and related oxide materials. Vacuum-based processes such as sputtering, pulsed laser deposition (PLD), and molecular beam epitaxy (MBE) have successfully demonstrated low resistive transparent conducting films [1–4], ultraviolet (UV) light emitters [5], heterojunction transistors [6,7], and thin film transistors [8–10]. Vaporbased processes, on the other hand, such as chemical vapor deposition (CVD) have advantages in growth on large area substrates and mass production with a continuous system. However, necessity of utilizing toxic, flammable, and hazardous sources such as metalorganics in order to supply metal precursors in gas phase requires a complicated, expensive, and vacuum-based system for the growth. Evolution of more safe and economical growth technologies keeping the advantages of CVD process, therefore, is significant so that ZnO-based materials, which are supported by abundant resources, can really help and promote the environmental-friendly economical development.

We have developed, for the above purpose, the mist CVD method for the deposition of ZnO-based materials and other oxide thin films [11,12]. In this paper, we show the fundamental properties of ZnO thin films on glass substrates grown by the mist CVD. Further, we recently found the growth of nanorods with this technique using gold catalyst. This achievement, due to its safe and economical features, is quite useful for wide application of nanostructured materials, and the results are briefly described in this paper.

II. EXPERIMENTS

In the mist CVD method, we use a liquid solution of constituent elements as a metal source. It is ultrasonically atomized, and the aerosol or mist particles hence

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Fig. 1. Schematic illustration of an atomizer.

formed are transferred by a carrier gas to the reaction area for the growth of thin films. An atomizer is schematically illustrated in Figure 1. We can apply a variety of chemicals as the sources, including innocuous and nonpoisonous ones, as far as they can be solved in water or alcohol and the solution can be ultrasonically atomized. The growth is made under atmospheric conditions and no vacuum system is necessary. This growth method, therefore, possesses advantages of safety, cost-effective, innocuousness to men and environment, and applicability to many materials.

The mist CVD technique is sometimes categorized as one of the spray pyrolysis techniques [13–19], but aerosols formed by ultrasonic atomization are as small as a few μ m in diameter and 1 pl in volume [20], which are almost 1/10 and 1/1000 in diameter and volume, respectively, compared to those in the spray pyrolysis. We can transfer the aerosols with a carrier gas, that is, the source precursors can be supplied like gas sources in CVD. This unique feature in the mist CVD allows precise growth control. Furthermore, the water or alcohol solvent is vaporized near the substrate area and offers sufficiently high vapor pressure of oxygen. This is advantageous to suppress oxygen vacancies, which have been recognized as degrading quality of oxide films.

We have used two different growth systems, which are illustrated in Figures 2(a) and (b). The system shown in Figure 2(a) is composed of a fine channel structure (1mm in height, for example) above the substrate, while that in Figure 2(b) possesses a linear nozzle for the source and gas supply. Both systems have been designed for the sources to firmly and effectively be insufflated onto the substrate, enhancing the partial pressure of the source precursors so that the reaction for the film formation can firmly occur against thermal convection. This concept is similar to that basically believed to be essential in the growth of gallium nitride (GaN) [21]. We named the techniques as "fine channel mist CVD (FCM-CVD)"



Fig. 2. Deposition systems of mist CVD. (a) FCM-CVD and (b) LS-CVD.

and "linear source spray CVD (LS-CVD)" methods for Figures 2(a) and (b), respectively.

The growth of ZnO films was done on soda-glass substrates. The source chemical was zinc acetate, $Zn(CH_3COO)_2 \cdot 2H_2O$, and this was diluted in deionized water with the concentrations of 0.01 - 0.1 mol/l. The carrier gas for the aerosol particles was N_2 or O_2 , whose flow rates were 3 - 12 l/min. The substrate temperatures were set at 270 - 500 °C.

III. RESULTS AND DISCUSSIONS

ZnO thin films grown by the mist CVD exhibited various different crystallographic orientations depending on the growth conditions. A general trend is that at lower temperatures or higher growth rates a ZnO film tended to have random orientation rather than c-axis orientation. This is because a certain amount of thermal energy should be given to the growing species so that they can finally fix along the preferred direction (c-axis orientation) apart from the interaction with the substrate. Figure 3 shows an example of X-ray $\theta - 2\theta$ diffraction curve, suggesting dominant c-axis orientation. ZnO films with dominant c-axis orientation have been obtained under various growth parameters with the growth rates of 1 - 500 nm/min.

Figure 4 shows the thickness variation of a ZnO thin film grown by the LS-CVD along the nozzle outlet (perpendicular to the substrate moving direction). The result indicates the uniform growth, that is, the thickness deviation was only ± 3 % over the substrate area, owing to the curtain-like uniform laminar flow of sources



Fig. 3. An example of x-ray $\theta - 2\theta$ diffraction curve from a ZnO thin film on a glass substrate, suggesting dominant c-axis orientation.



Fig. 4. Thickness variation of a ZnO thin film grown by the LS-CVD along the nozzle outlet (perpendicular to the substrate moving direction).

intentionally achieved by collision-mixing in the nozzle [22]. The similar uniformity was confirmed also for the FCM-CVD system. We consider, however, that for the evolution of mist CVD for larger substrates, the LS-CVD can be a basic concept. The surface root-mean-square (RMS) roughness was, for example, 7.5 nm for the film thickness of 300 nm, derived from an atomic-force microscope (AFM) image.

An optical transmittance spectrum of a ZnO thin film on a glass substrate is shown in Figure 5. In the measurement, a glass substrate was used as a reference sample in order to elucidate the properties of ZnO. Here the ZnO film was grown at 300 °C and its thickness was 300 nm. The transmittances in the visible range were higher than 90 % and clear fringes due to interference in the sample was observed in the spectrum, suggesting good transparency and flatness. Sharp cut-off was seen near 370 nm, at the band gap energy.

Figure 6 represents a room temperature photolumines-



Fig. 5. Typical transmission characteristics of a ZnO thin film on a glass substrate.



Fig. 6. Room temperature PL spectrum of a ZnO thin film on a glass substrate.

cence (PL) spectrum excited by a He-Cd laser (325 nm). A nearly band-edge peak was seen at around 3.28 eV (378 nm) and no distinct deep level emission was recognized. It is worth noticing that for many of the samples the deep level emissions have been very weak. Since deep level emissions are associated with oxygen vacancies, the result indicates the formation of well stoichiometric ZnO films without severe inclusion of oxygen vacancies. This is because of high vapor pressure of oxygen near the substrate, which is, as we pointed out above, one of the important and advantageous features of the mist CVD method. The band-edge peak appeared at lower energy by about 20 meV compared to the free exciton emissions in high quality ZnO single crystals, where the peak was seen at 3.30 eV [23,24]. This may be associated with high donor concentration, which was supposed from electron concentrations in undoped films of $10^{18} - 10^{19} \text{ cm}^{-3}$ and/or band tailing due to polycrystalline structure.

Figure 7 compares the photographs of glass and ZnO/glass samples taken under illumination by a white



Fig. 7. Photographs of glass and ZnO/glass samples taken under illumination by a white light and a UV (300 - 400 nm) light.



Fig. 8. X-ray $\theta - 2\theta$ diffraction curves from MgO and CdO thin films grown by the mist CVD method on glass substrates.

light and a UV (300 - 400 nm) light. Under the white lighting the both samples exhibit good transparency. On the other hand uniform darkening of the ZnO/glass sample due to absorption of UV light was evident under the UV lighting, suggesting a homogeneous ZnO film. Note that a little irregularity seen in the photograph is due to irregular UV absorption in the paper set in the back.

Conductivity control with donor doping has been made by adding chemicals containing donor elements such as gallium acetate, gallium acetylacetonato, and aluminum acetate into the source solution. The resistivity of ZnO films hence obtained so far was 1.1×10^{-3} Ω cm, which is still very high compared to the best result of the order of 10^{-5} Ω cm [2]. An existing problem may be small grain size speculated from the low mobility of about 6 cm²/Vs, for example. We should recognize the clue to overcome this problem so that this growth technique can be developed for the growth of transparent conducting films on large area substrates.

The mist CVD method can be applied to the growth of other oxide thin films, by preparing appropriate source solutions containing the desirable elements. Figure 8

Au Nanoparticle



Fig. 9. A SEM photograph of ZnO nanorods grown at 900 $^{\circ}$ C on a sapphire substrate with gold catalyst.

shows the x-ray diffraction spectra of MgO and CdO, suggesting the formation of polycrystalline films. Further optimization of the growth conditions will improve the crystallinity of these films. We have also succeeded in the growth of Al_2O_3 , Ga_2O_3 [25], TiO_2 , Cu_2O and so on with this technique. The wide application of the mist CVD for various oxide films is very promising.

A recent achievement is the growth of ZnO nanostructures by the mist CVD. Figure 9 is a scanning electron microscope (SEM) photograph of nanorods grown at 900 °C on a sapphire substrate with gold catalyst. For the growth at high temperatures, we used a furnace-heated quartz reactor. The growth has followed the vaporliquid-solid (VLS) growth mode. Since the mist CVD method offers the composition and doping controllability similar to those by metalorganic CVD (MOCVD), we can expect the formation of various nanostructures with the safe and cost-effective technique. The details of the growth of nanorods will be reported elsewhere.

IV. CONCLUSIONS

The mist CVD method has been developed as a safe and economical growth technique of ZnO-based thin films. This technique utilized aqueous or alcohol solution of zinc acetate, which is a safe material, as a zinc source, and the micro-sized aerosol or mist particles formed by applying ultrasonic-power were supplied with the carrier gas to the reaction area. The c-axis oriented ZnO films have been obtained under appropriate growth conditions, and the ZnO thin film was transparent with the naked eyes, that is, the optical transmission was higher than 90 % in the visible light region. PL spectra exhibited near-band edge emission around 3.28 eV (378 nm) at room temperature, without noticeable deep level emissions. High vapor pressure of oxygen near the substrate has been considered as effective to reduce oxygen vacancies. On the other hand, the near-band edge peak was slightly (20 meV) red-shifted compared to high quality ZnO single crystals, suggesting affects by donors and/or

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polycrystalline structures. The RMS roughness was as small as 7.5 nm despite the polycrystalline structure. Though the doping experiments need further progress, since the mimimum resistivity obtained by Ga doping so far was still $1.1 \times 10^{-3} \Omega$ cm, the overall properties of ZnO thin films grown here suggested the potential of this novel growth technique being developed to fabricate ZnO thin films with safe, simple, and cost-effective way towards various applications. We also demonstrated the further potential of this growth technique with the formation of other oxide films and ZnO nanorods.

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