論文内容の要旨

Chemical vapor deposition (CVD) is one of remarkable technology for fabrication various types of high quality thin films including metallic, metal oxide, alloy compounds, group II-VI, III-V compounds, and 2D materials. In the CVD processes, the gas is used as the precursor and the film deposited by the thermal decomposition and chemical reactions of the gases precursors in the vapor phase on or nearby the substrate. The properties of the films were controlled by the components of the gas phase, the solid surface, and the physical condition of the gas phase.

To date, the CVD processes have been developed into several types of CVD such as metal organic chemical vapor deposition (MOCVD), low pressure metal organic chemical vapor deposition (LP-MOCVD), plasma enhanced chemical vapor deposition (PECVD), and laser chemical vapor deposition (LCVD) in order to reduce the operation conditions from high vacuum and temperatures, to achieve the large scales fabrication, and suitable for flexible substrate (e.g. glass, polymer). However, in those conventional CVD processes, the volatile precursors are necessary for the film growth and those precursors are very high sensitive, high cost, hazard, and flammable. Therefore, the operation system is constructed with complex system in order to obtain precisely control of the precursor for high safety operation and there is a limitation for using various types of the precursors as well.

Mist-chemical vapor deposition (mist-CVD) is one of the solution-based CVD process capable of operating under the atmospheric pressure. Mist-CVD was developed to achieve the same targets as those conventional CVD processes, for reducing environmental load and to grow the high quality films under mild condition. In the mist-CVD system, the precursors were prepared by the chemical solution and the solutions were transformed to the mist-droplets by the atomization of the ultrasonic transducer. The films were deposited by the thermal decomposition and the chemical reactions of the precursor materials in the vapor phase of the droplets. Therefore, under the mist-CVD, the problem of using high volatile precursors can be prevented. This benefit for mist-CVD system to use various types of the precursors materials, the process construction and maintenance of the system become much more simplicity than conventional CVD. However, the general problems in the solution-base processes that difficult to avoid during the solution preparing are (i) the precipitation of the solution for growing metal oxide thin films. Generally, H_2O is used as the solvent for providing the oxygen source (O-source) to metal oxide films. However, the reaction between H_2O and other precursors generated the solution precipitations, which affects the stability of the solution. This may influence in the quality of the films and (ii) the complex-reactions could be formed when mixed various kinds of the precursors materials in the same solvent for growing the multi-components thin films. When various kind of the precursor materials mixed in the same solvent, the enthalpy of materials slightly changed because the difference in metal ion stabilities of the precursors. This affects the activation energy of the thermal decomposition reaction of the precursor materials. As a result, it

is difficult to estimate the reaction rates and the film composition ratio. These both issues also found in the conventional mist-CVD.

Due to the major advantage of the mist-droplets over the other solution-based processes, mist-droplets have relative velocities close to zero in the gas fluid and the behavior of the droplets follows the Maxwell-Boltzmann distribution. Base on this theory, the mean free time and mean free path of the droplets were calculated, it was found that (i) the mean free time for droplets colliding was longer than that the resident time of the droplets in the reaction system and (ii) the mean free path between droplets was very large compares with the droplet size of 10 μm. Therefore, from these data, it is possible to avoid the colliding of the droplets in order to prevent the complex-reactions from mixed various precursors and/or solution precipitation from mixing H_2O under the preparing step of the chemical solution in the solution-based processes. This became the motivation of this dissertation to conduct the research.

From the ideas of low probability of droplet collision, the conventional mist-CVD was developed with construction of the various solution chambers with an additional mixing chamber. In the developed system, various kinds of precursor are separately added into each mist generation chamber. Mists generated from each chamber are transferred to an additional mixing chamber for preparing a mist flow with all components uniformly mixed. The mist droplets were then transferred to the reactor chamber by N_2 gas.

This thesis aims to overcome the problems in the solution based processes of (i) the complex-reactions from mixed various type of the precursors materials into the same solution for growing multi-components thin films and (ii) the precipitation in the solution by using H_2O as the solvent for growing the metal oxide thin film by using the developed mist-CVD system.

To achieve these aims, this dissertation consists of three main parts. In the first part, the mist-CVD system was developed to avoid the problem of mixed precursors. The zinc magnesium oxide (ZnMgO) thin film was selected as the target material of the multi-component thin film. The ZnMgO films were grown on quartz with different growth temperatures and Zn and Mg composition ratios by the conventional and developed mist-CVD systems. When Zn and Mg precursor material mixed in the same solvent for growing the films by conventional mist-CVD, the Mg atoms are more likely to exist as ions in the solution than Zn atoms due to Mg ionization tendency is higher than that of Zn. Therefore, the enthalpy of the Mg sources slightly decreased in the solution, while the enthalpy of the Zn source slightly increased. Consequently, the activation energy of the Mg precursor decomposed to form MgO is higher than that the condition of non-mixed Zn and Mg precursors in the solution chamber (developed mist-CVD). As a result, the growth temperature to decompose the Mg incorporates into the films was supposed to be higher of films grown by the convectional mist CVD. Thus, the trend of the Mg composition in the films at different growth temperatures were used to verify the ability of the developed system. It was found that the Mg compositions in the films grown by the developed system were higher and more controllable than that of the conventional mist-CVD. Therefore, this result can prove that the problem of mixed precursors could be prevented by using the developed mist-CVD system from the low probability of droplet collision. After that the name of the developed mist-CVD was created as the 3rd generation mist chemical vapor deposition (3rd G mist CVD).

In the second part, the 3rd G mist-CVD was used to grow metal oxide thin-film of the ZnO by using H_2O as the support solution and Zinc acetylacetonate ($Zn(acac)_2 \cdot H_2O$) was used as the Zn source. The Zn and O solution sources were set into the different solution chambers for film growth in order to avoid the problem of solution precipitation. The ZnO films were grown with various $[H_2O]/[Zn]$ ratios and Zn precursor concentrations with controlled the growth temperatures at 400 ℃. $Zn(acac)_2$ was thermally decomposed to form ZnO by directly reacting with H_2O, resulting in an increase in the film growth rate with increasing supply amounts of the precursor and oxygen source from H_2O. However, the growth rate decreased when excessive $[H_2O]/[Zn]$ ratios were introduced because the equilibrium constant was below 1 ($K<1$) and/or acids were formed. The crystal orientation of the films could be explained by a surface adatom diffusion growth model. As an appropriate range of the $[H_2O]/[Zn]$ ratios was introduced, the atom diffusion length is sufficient to enable the growth of the crystal at the lowest surface energy domain. This resulted in the growth of a columnar structure with the (001) plane parallel to substrate surface that induced a spherical surface morphology and low density of oxygen-related defects in the films, thus the crystal quality of ZnO was improved with the near-ideal (002) reflection position. In contrast, the diffusion length of atoms was limited when excessive $[H_2O]/[Zn]$ ratios were introduced, which led to (i) the growth of random orientations and the suppression of the (002) reflection, (ii) the irregular surface morphology, and (iii) the high density of oxygen-related defects in the films. In summary, the ZnO films were grown by 3rd G mist CVD, which was rationally designed to precisely control oxygen/metal supply amounts and H_2O can be used as the solvent of metal oxide thin-film growth by without the problem of solution precipitation via using the 3rd G mist-CVD.

From the results in the second part, it can be seen that (i) the 3rd G mist-CVD can be used to control oxygen-metal supply amounts precisely, (ii) the ZnO film properties were enhanced by H_2O and (iii) the ZnO film growth mechanism was supported by the surface adatom diffusion growth model. However, the temperature is one of important factor that impacts the surface adatom diffusion. Thus, to comprehensive understand surface adatom diffusion of the ZnO film growth mechanism under the 3rd G mist-CVD, it is necessary to investigate the influence of $[H_2O]/[Zn]$ and growth temperatures at the same time on the ZnO film properties. Thus, in the third part, the ZnO films were grown by various growth temperatures in the range from 200 to 400 ℃ and $[H_2O]/[Zn]$ ratios. At the low growth temperature of 200 ℃ with increasing $[H_2O]/[Zn]$ from 0 to 900, the Zn precursor was not completely decomposed to form ZnO film because the thermal decomposition temperature of the Zn precursor to form ZnO was ~ 200 ℃, which observes by TG-DTA. Therefore, the hydrocarbon from the precursor decomposed into the films. This lead to (i) films growth rates were high, (ii) the refractive index of the film was very low as 1.65, (iii) low intensity of (002) reflection peak with very large FWHM, (iv) the surface morphology of the ZnO films contained a lot of voids and large strip, indicating low film density, and (v) the optical band gap of the films were very high of 3.7 eV. However, those properties were improved with the ZnO films grown with increasing $[H_2O]/[Zn]$ over 900 because the (i) higher H_2O shift the equilibrium of the thermal decomposition reaction of the Zn precursor to the right, which generates carbon ions loosely bond of $C_5H_8O_2$ that easily to remove and (ii) the evaporation rate of the $C_5H_8O_2$ may increase with increasing $[H_2O]/[Zn]$ at the low temperatures, and (iii) the increases in density of O atoms on the surface substrate, leading to high probability of adatom collision with maintain the sufficient diffusion length of adatom. As a result, (i) film growth rate decreased, (ii) refractive index became high as 1.82, (iii) the high intensity of (002) reflection peak with narrow FWHM, (iv) no voids on the film surface but the hexagonal-likes morphology was occurred, and (v) the optical bandgap became 3.3 eV. It can be seen that at the low growth temperature (200 ℃), the properties of the ZnO films were more effectively improved by introducing large amount of H_2O for film growth. In contrast, at the high growth temperature (400 ℃), the probability of atoms collision already high because the high temperature promotes high mobility of atom diffusion and that temperature was sufficient for the thermal decomposition reaction of the Zn precursor. Therefore, only small amount of H_2O is enough to obtain good properties of the films.

Finally, the problem of volatile precursors from conventional CVD and the solution precipitation by using H_2O and complex-reactions from mixed various precursors of the solution-based processes can be successfully prevented by the 3rd G mist-CVD. The 3rd G mist CVD can be used not only for composition control of multi-component thin films but also precisely control of oxygen-metal supply amount for growing high quality metal oxide film and doping materials. These results suggested that the 3rd G mist-CVD is sustainable and environment friendly technology for growing high quality thin films.