論 文 内 容 の 要 旨

In recent years, the rapid development in the fields of energy, electronics and medicine has resulted in the increasing demand of the semiconductor devices. With the development of semiconductor manufacturing processes, the functional thin films for devices gradually showing an enormous application potential and broad market prospects, particularly the optical, electrical and insulating thin films, which are promoted in the fields of optoelectronic and microelectronic devices. However, the defects of the thin films become the primary factors which have effects on devices performances.

The film fabrication methods can be classified into either a non-equilibrium reaction systems, such as vacuum evaporation and sputtering, or an equilibrium reaction systems, such as chemical vapor deposition and sol gel technique. For the nonequilibrium reaction systems, the uniform and high-quality thin films usually are obtained with high environmental load, and the films are easy to damage. For the equilibrium reaction systems, the uniform and high-quality thin films cannot be attained without careful control of the complicated chemical reactions and the atmosphere interactor. However, the stress-free and damage less thin films can be easily obtained using the equilibrium reaction systems. So, an equilibrium reaction system with superior controllability is necessary for fabricating high quality functional thin films. Based on this standpoint, Prof. Kawaharamura have developed a method of mist chemical vapor deposition (CVD), which is a novel non-vacuum fabrication method utilizing mist sources for film formation, it can easily prepare the uniform and high qualities thin films without complex system.

The mist CVD technique was used to fabricate the function thin films in my research. However, the study of mist CVD is still in the primary period, the detailed reaction processes and how to apply the special characteristics during the film fabrication are not yet well understood, they all limit the obtaining of the high quality functional thin films. In order to solve above problems, I focused on a challenging study of fabricating several functional thin films with high qualities under low growth temperature and atmospheric-pressure using mist CVD technique in this research. Through the studying of mist CVD system, the continuous optimization of experimental conditions, and the search of various reaction mechanisms, the magnetic thin films (YIG), insulating thin films (YO_x), and the conductive thin films (ATO) were successfully fabricated by mist CVD. Moreover, the study on the key reaction mechanisms of fabricating functional thin films using mist CVD system is conducive to optimizing the properties of functional thin films according to the requirements of devices in the future.

This dissertation mainly includes the following parts:

1. Fabrication of YIG thin films by mist CVD system and studying the reaction paths of fabricating multi-component films;
2. Fabrication of YO_x thin films with high dielectric constant by mist CVD system and studying the effects of oxidation assistants on the properties of YO_x thin films;
3. Fabrication of SnO_x:Sb thin film with low resistivity by novel mist CVD system, studying the effects of supporting materials on the fabrication processes and the reaction behaviors of supporting components.

Chapter 1 Introduction

In the Introduction, the history background and current researches of the functional thin films, especially the yttrium iron garnet (YIG) thin films, yttrium oxide (YO_x) thin films and antimony doped tin oxide (SnO_x:Sb, ATO) thin films, were investigated in details. According to the previous researches, the above three films, which are ferromagnetic, insulating and transparent conducting materials, are

the attractive and potential candidates for the application in preparing the spintronic and optoelectronic devices. In addition to the introduction of materials, the characteristics of traditional film fabrication methods and the commonly used ways to improve the qualities of thin films were also summarized. However, the performance of materials and the fabrication conditions with high energy consumption all limit the commercial application of these functional thin films. In order to solve these remained issues in the film fabrication process, the objectives of this thesis were proposed and the outline of the thesis was built.

Chapter 2 Mist chemical vapor deposition system and characterization techniques

Chemical vapor deposition (CVD) technique is a chemical process widely used to produce the high quality and high performance solid materials in various forms. In the typical CVD methods, the substrate is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposit. The CVD can be classified three type by operating conditions: atmospheric pressure CVD (APCVD), low-pressure CVD (LPCVD), and ultrahigh vacuum CVD (UHVCVD).

The mist CVD technique, which will be used and studied in my work, is defined as one kind of APCVD techniques. However, mist CVD is not a simplex vapor phase deposition, it has both characteristics of vapor phase and liquid phase during the fabrication process. The second generation mist CVD system was designed and built by Prof. Toshiyuki Kawaharamura. Through more than ten years development, this method has made a big leap to further improve the film quality. Currently, the 3rd generation mist CVD (novel mist CVD system), which has a special supply unit with two solution chambers and one mixing chamber, is in the applying and disseminating. The detail information about development of mist CVD and the special features of it were introduced in Chapter 2.

Moreover, in order to evaluate the performance of thin films, various characterization techniques were carried out, and the working principles, apparatus structures, operation processes and commonly parameters of the instruments were also introduced in this part.

Chapter 3 Fabrication of yttrium iron garnet (YIG) thin films

Chapter 3 introduces the successful fabrication of yttrium iron garnet (YIG) thin films under low growth temperature using mist CVD system and the study on the reaction paths in the fabrication process.

According to previous researches, the fabrication of YIG thin films always used high growth temperature and/or vacuum conditions. However, the YIG thin films under atmospheric pressure was deposited by mist CVD technique via the rationally designed reaction conditions. Spectroscopic ellipsometry, transmittance, SEM-DEX and XRD were measured to study the thicknesses, optical properties, composition and crystal structures of the thin films. The thickness results indicated that there were several reaction paths at the same time under different growth temperatures. The optical properties and composition of the thin films grown at low temperatures (250-350 °C) significantly differed from those grown at high temperatures (400-450 °C). The abrupt changes in the film properties were observed at temperatures of 350-400 °C. The films grown at temperatures of 400-450 °C showed the [Y]/[Fe] ratio of ~0.6, which was in good agreement with stoichiometric YIG, when that ratio in the solution was set at 1.5.

A thermodynamic model was developed to explain the reaction paths of the YIG film fabrication process using thermogravimetric differential thermal analysis (TG-DTA) results. The model indicates that the decomposition rate of yttrium precursor was much lower than that of iron precursor. The difference decomposition rate of the precursors and the colloidal formation of yttrium precursor in the solution may explain the large difference between the composition ratio of thin films and the setting composition ratio of precursor solution. Thus, YIG thin film fabrication by fine channel mist CVD and the study of corresponding metal precursor decomposition reactions may enable us to precisely control the composition ratio of YIG thin films.

Chapter 4 Fabrication of yttrium oxide (YO_x) thin films

Fabrication of yttrium oxide (YO_x) thin film at low temperature by the mist CVD) is demonstrated in this chapter. Recently, high dielectric (high-k) materials have received much attention because of their wide application prospect in microelectronics devices. Study of high-k materials is beneficial not only to solve the problem of the thin gate-oxide (such as SiO_2) limitation in semiconductors, but also to prepare the new devices with special properties. We fabricate one of high-k materials, i.e. yttrium oxide thin film which is considered as a potential material for oxide dielectrics due to the excellent electronic properties, such as high dielectric constant (14~18), large band gap (~5.5 eV), and high refractive index (1.7 ~ 1.9).

Usually, yttrium oxide thin films are fabricated using high deposition temperature or controlling the working pressure. However, we have developed a novel reaction supporting system in mist CVD, and yttrium oxide thin films can be fabricated at low temperature (400 °C) under atmospheric pressure. In this work, yttrium (III) acetylacetonate hydrate ($Y(C_5H_7O_2)_3 \cdot nH_2O$) ($n$=2.36 as determined by TG-DTA) was selected as the precursor solute, and dissolved in methanol. In order to save the energy consumption, we tried to use oxygen gas and/or pure water to support the fabrication of YO_x thin films while keeping the high properties. For controlling the atmosphere in reaction area of mist CVD system, the precursor solution and supporting solution were set in different solution chambers. Using mist CVD system with two solution chambers, we have obtained the yttrium oxide thin films with the deposition rate of 5.0 nm/min, and the refractive index of 1.77 using assistants, while, the thin films with deposition rate of 7.0 nm/min, and the refractive index of 1.65 were obtained without using assistants. In order to improve the properties of YO_x thin films, we investigated the effect of the supporting materials ratio on fabricating YO_x thin films and studied the plausible mechanism of fabrication of YO_x using mist CVD system. It is observed that the H_2O is most effective oxidation material, and the use of H_2O improved the dielectric constant of YO_x thin films.

Chapter 5 Fabrication of the high conductivity antimony doped tin oxide (SnO_x:Sb) thin films

In this chapter, we focus on studying the fabrication of SnO_x:Sb thin films with low resistivity using the 3rd generation mist CVD system (novel mist CVD system). Different from previous research, which changed the dopant ratio or increased the growth temperature to improve the conductivity of SnO_x:Sb films, we tried to use some materials to support the reaction process of fabricating the SnO_x:Sb thin films for increasing the film conductivity due to the characteristics of 3rd generation mist CVD system, and studied the factors contributing to high conductivity of SnO_x:Sb thin films.

In the first of this work, the Sn host and Sb dopant precursor solutions were prepared separately when we fabricated the SnO_x:Sb thin films using novel mist CVD system with two solution chambers and one mixing chamber. The host and dopant precursor solutions were added to different solution chambers of novel mist CVD system. In order to find the way to improve the conductivity, we studied the effects of each additive component in dopant solution on the electrical property of SnO_x thin films. Besides checking the optical and electrical properties, the XPS, IR-vase, and PYS measurements were also used to analyze the SnO_x thin films. From the experiment results, it was found that HCl (aq) in dopant solution is important for dissolving $SbCl_3$ in H_2O, but the excess HCl (aq) may etch the ATO thin films. Both $SbCl_3$ and HNO_3 affected the electrical property of SnO_x thin films, and the resistivity of SnO_x fabricated using the dopant solution including $SbCl_3$ and HNO_3 simultaneously was much lower than that using either $SbCl_3$ or HNO_3 in dopant solution. The nitrogen originated from HNO_3 was considered to act as a dopant and/or oxidizing agent, could contribute to the electrical conductivity of SnO_x:Sb thin films, and the XPS measurement confirmed the presence of N in the thin films. The results of infrared spectroscopy analysis confirmed that the SnO_x fabricated by novel mist CVD was a mixture of SnO and SnO_2. By calculation, it was obtained that the SnO_x fabricated using the dopant solution including HNO_3 only had similar intrinsic band gap and band structure with the films fabricated using the dopant solution including both $SbCl_3$ and HNO_3.

Due to the results we obtained from first part experiment, we tried to prepare some simple materials to support the fabrication of SnO_x:Sb thin films. In the second part of this work, the Sn host and Sb dopant were dissolved in MeOH simultaneously, the main solution (Sn and Sb were dissolved in MeOH) and supporting solution were added to different solution chambers of novel mist CVD system. The effects of the supporting solutions on the electrical, optical, chemical properties, surface morphologies, and crystallinity were investigated to confirm the contribution of the supporting components to the fabrication process of high conductivity of SnO_x:Sb thin films. The experiment results verified that the components in supporting solution assisted multiple reactions of the film fabrication and the suitable supporting solution could effectively improve the electrical properties of the SnO_x:Sb thin films while remaining appropriate optical properties.

Chapter 6 conclusions

In the conclusion, the main results obtained from my research work are summarized.