# Chapter 1

## Introduction

### 1-1 Basic Properties of Zinc Oxide

Zinc oxide (ZnO) is a II–VI group compound semiconductor with a hexagonal wurtzite structure (Fig.1-1) and a wide direct band gap (about 3.37 eV at room temperature). [1] This fact, coupled with the large exciton binding energy (60 meV), makes it a candidate for optoelectronic device applications such as transparent electrodes, light emitting diodes, UV-laser-emitting devices, and laser diodes [2].

The n-type ZnO is easily available even without any doping. All experimental results have shown that the undoped ZnO is n-type. The donor is likely to be the oxygen vacancy (Vo). Although undoped ZnO films with a low resistivity were prepared by RF magnetron sputtering, they were found to be unstable in temperatures above about 150°C. The electrical resistivity of ZnO films decreases when doped with group- III elements such as Al, Ga, and In in ZnO, and their stability also can be improved as well as their electrical properties [3-5]. Transparent conducting impurity-doped ZnO films such as AZO, with a low resistivity of the order of  $10^{-4} \Omega$ -cm were stable at temperature as high as  $350^{\circ}$ C.

There are some kinds of fabrication for ZnO thin films have been used, including radio-frequency magnetron sputtering, spray pyrolysis, evaporation, chemical vapor

deposition (CVD), pulsed laser deposition (PLD), and sol-gel process. [6-10]

#### 1-2 Transparent Thin Film Transistor

Thin film transistors (TFTs) made with amorphous and poly silicon have become the key point of the electronic flat panel display industry in the last 10 years. Nevertheless these thin film transistors (especially the amorphous silicon ones) actually present some limitations like light sensitivity and light degradation, low field effect mobility, and opacity limiting the aperture ratio for active matrix arrays.

One possible way to overcome such problems is the utilization of efficient and reliable oxide based thin film transistors. Transparent oxide semiconductor based transistors have recently been proposed using as active channel intrinsic zinc oxide (ZnO) [11-13], as shown in Figure 1-2.

ZnO is one of a few oxides that can be grown as a crystalline material at relatively low deposition temperatures on various substrates such as amorphous glasses and plastics. Because it can be made at room temperature and, thus, there is good compatibility with plastic or flexible substrate materials. By using these characteristics it is possible to fabricate the ZnO-thin film transistor (ZnO-TFT) at room temperature by RF magnetron sputtering.

It is expected that the characteristics of ZnO-TFTs will not degrade on exposure to the visible light, due to the wide band gap of its active channel layer, whereas the characteristics

of amorphous Si TFTs and poly-Si TFTs do degrade. Therefore, there is no need to shield the active channel layer from visible light. This makes the TFT structurally simple and transparent to visible light, which would allow the aperture ratio of active matrix arrays to be increased.

#### 1-3 Binary Compound TCO Materials

One advantage of using binary compounds as transparent conducting oxide (TCO) materials is that their chemical composition in film depositions is relatively easier to control than that of ternary compounds and multicomponent oxides. Until now, impurity-doped ZnO, In<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, and CdO films have been developed as TCO materials consisting of binary compounds. It is well known that the transparent conducting thin films of these metal oxides also can be prepared without intentional impurity doping. These films are n-type degenerated semiconductors, with free-electron concentrations of the order of 10<sup>20</sup> cm<sup>-3</sup> provided by native donors such as oxygen vacancies and/or interstitial metal atoms. However, undoped binary compound materials are not in practical use because impurity-doped materials can use both native and impurity donors. The minimum resistivities of impurity-doped SnO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub> films have essentially remained unchanged for the past 20 years. In contrast, the obtained resistivity of impurity-doped ZnO films is still decreasing.

## 1-4 Applications of Transparent Conducting Oxide

Transparent conducting oxide (TCO) can be used as electrodes for display devices. In a basic organic and polymer LED structure, a TCO layer such as aluminum doped ZnO film, is used as anodes.

For transparent electrode applications, TCO is an essential part of technologies that require both large-area electrical contact and optical access in the visible portion of the light spectrum. High transparency (>80 %), combined with low resistivity ( $<10^{-3} \Omega$ -cm), is achieved by selecting a wide-bandgap oxide that is rendered degenerate through the introduction of native or substitutional dopants. Most of the useful oxide-based materials are n-type conductors that ideally have a wide bandgap (>3 eV), the ability to be doped to degeneracy, and a conduction-band shape (dictating electron effective mass) that ensures that the plasma-absorption edge lies in the infrared range.

At present, TCO films (such as ZnO, SnO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub>, and their doped forms) are extensively used in electronics and photonics applications, such as transparent electrodes in solar cells, flat display devices, gas sensors, waveguide devices, infrared reflective windows, etc. The most widely used TCO in optoelectronic devices is indium tin oxide (ITO). It is due to its high conductivity, work function, and transparency in the visible spectral range. Although ITO is probably the most successful TCOs, indium is a relatively scarce element in the earth's crust. The cost for ITO production is therefore high. The other drawback of ITO

films is the chemical instability in a reduced ambience. For LED applications, the indium of ITO layer can diffuse into the organic materials, leading to degradation of LED device performance. Besides, the toxic nature of indium could be hazardous to human and environment. In comparison to ITO films, AZO (ZnO:Al) films are low cost, nontoxic, and high stability. And it has comparable optical and electrical properties as those of ITO. Therefore, AZO films are going to substitute for ITO and have an extensive application prospect.

#### 1-5 Motivation

As mentioned above, ZnO thin films has the potential to become a candidate for future TCOs. We used radio frequency sputtering method to prepare the ZnO films in different deposition conditions and identify their electrical and transparent characteristics.

The content of impurity doping has influence on the physical, electrical, and optical properties of ZnO thin films. Therefore, the optimized process method could be used to get high performance films. In this study, investigations of the relationship between the properties of ZnO thin films and different deposition conditions are also carried out.

## 1-6 Thesis Organization

The thesis is divided into five chapters:

Chapter 1 introduces the basic properties of ZnO thin films and its applications.

Chapter 2 presents the material properties of ZnO thin films.

Chapter 3 presents the experimental details. The measurement methods for characterizing the films are also introduced.

Chapter 4 contains results and discussion. We present the properties of RF-sputtered ZnO films on glass substrate. The electrical and transparent properties of ZnO thin films at various process conditions are investigated.

Chapter 5 makes conclusions for this thesis.

