# Chapter 6

# Conclusions

In this research, the transparent conductive Ga-doped ZnO (GZO) thin films have been deposited on soda-lime glass substrates by RF magnetron sputtering at various $Ga_2O_3$ contents and sputtering conditions. The effects of Ga doping and sputtering conditions on the structural, electrical and optical properties were investigated. For the thin film preparation, the deposition rate is proportional to the RF power at a given Ar pressure because there are more sputtered atoms and ions resulting from the increasing of the ionization of Ar gas. For the same RF power, the deposition rate decreases slightly as the Ar pressure increases due to the decreasing of the mean free path of sputtered species in the chamber. However, the deposition rates as varied Ar pressure differ insignificantly compared to that as varied RF power because the varying of the Ar pressure in this research is limited in the narrow range ($6.0 \times 10^{-3} - 1.0 \times 10^{-2}$ mbar) due to the limitation of our sputtering system.

For all X-ray diffraction patterns of the GZO thin films, only the ZnO (002) peak was observed, revealing that the films are polycrystalline with a preferred orientation along c-axis. The crystallinity of the films depends on the deposition rate related to the RF power. The lower deposition rate yields better crystallinity because it leads to a large grain size and low density of crystal defects. On the other hand, the high deposition rate provides less formation time of the thin film growth and thus causes a decrease in the mobility of the surface atoms. Consequently the crystallinity of the deposited film decreases. For the films having poor crystallinity, they are non-stoichiometric oxide due to oxygen deficiencies and crystalline faults. These defects can be reduced by decreasing the RF power. In this research, we also found that the crystallinity can be improved by increasing the film thickness. As the thickness increases, the peak height corresponding to the plane (002) increases significantly. This is related to an increase of the preferred plane (002) which diffracts X-ray at Bragg angle of ZnO thin films.

The electrical measurement shows that the resistivity of the films decreases as increasing RF power for a given $Ga_2O_3$ content and Ar pressure. It is due to the increasing of the lattice defects (intrinsic donor) associated with oxygen vacancies and zinc interstitial atoms. Both carrier concentration and mobility increase while resistivity decreases. For the same sputtering condition, the resistivity decreases with increasing $Ga_2O_3$ content in the sputtering target. The Ga dopant (extrinsic donor) in the films plays an important role in increasing the carrier concentration. Nevertheless, it is not necessary to increase $Ga_2O_3$ content higher than 6 wt% because the resistivity is quite low and saturated. As the Ar pressure was varied, the resistivity of most deposited films also decreases with the increase of the $Ga_2O_3$ content.

There is a stress occurring in the thin films due to the deposition process. It is caused by the imperfection in the crystal structure. With the increase of the RF power related to the deposition rate, the film suffers higher stress. When the film is annealed in air atmosphere, the relaxation of the film occurs because of the rearrangement of the crystal structure. The interplanar spacing of GZO thin film becomes closer to that of the standard bulk ZnO. However, the intensity and sharpness of the XRD peak does not change after the post deposition annealing. This film annealing also enhances the chemisorption of $N_2$ or $O_2$. This reduces the donor defects and Ga dopant resulting in the high resistivity of the films. Therefore, the film annealing in air atmosphere does not improve the crystallinity and electrical properties of GZO thin films.

The optical transmission of GZO thin films decreases with increasing RF power and $Ga_2O_3$ content. At the wavelengths below 1000 nm, the optical transmission of the films slightly decreases due to the film thickness. As opposed to the wavelengths above 1000 nm that the transmission decreases strongly, mainly because of the free-carrier absorption attributed to the increase of the carrier concentration. The free carriers increase due to more donor defects and Ga dopants in the film. The absorption edge is clearly shown to shift toward shorter wavelengths (blue shift) as the increasing of $Ga_2O_3$ content. It is mainly attributed to the Burstein-Moss effect, which is the result of the shift of Fermi level into the conduction band of degenerate semiconductors, as a result of increasing free carrier concentration. It leads to the widening of the optical energy gap. In addition, the energy gap widens slightly as increasing RF power compared to increasing $Ga_2O_3$ content because the effect of Ga doping shows more influence to the increased carrier concentration. The lowest and highest energy gap values correspond to the highest and lowest resistivity of the films, respectively.

It is known that the high transparent conductive oxide thin films are necessary for making window layer in Cu(In,Ga)$Se_2$ thin film solar cells. Especially, low resistivity and high optical transmission at long wavelength (> 1000 nm) is required to improve the efficiency of the solar cells for generating high output current. In this research, the suitable sputtering conditions are at the RF power of 100 W and the Ar pressure of $8.0 \times 10^{-3}$ mbar because a low resistivity of the film can be obtained for this condition at a given $Ga_2O_3$ content. The lowest resistivity of $1.45 \times 10^{-3}$ $\Omega$·cm is achieved by using the target with $Ga_2O_3$ content of 6 wt%, however its transmission at long wavelength is less than 70% which is not sufficient for making window layer. Mostly prepared GZO thin films with low resistivity ($< 2.0 \times 10^{-3}$ $\Omega$·cm) have low transmission (< 70%) at long wavelength due to high carrier concentration ($> 2.5 \times 10^{20}$ $cm^{-3}$). The suggestion for further development of the GZO thin films in order to decrease free-carrier absorption and be a suitable window layer is to fine tune the sputtering conditions using the target with $Ga_2O_3$ content of 4wt% or 6wt%. These conditions include either position or distance between the target and the substrate. Furthermore, the substrate temperature is known as a major factor for improvement in the thin film properties. This suggests that the sputtering system should be modified to have the substrate heating during the deposition of GZO thin film.