國立交通大學

電子工程學系　　電子研究所碩士班

碩士論文

正型氧化鋅薄膜之製備及電學性質之研究

The preparation of P-type ZnO thin films and the research for the electrical characteristics

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摘要

隨著光電產業的蓬勃發展，氧化鋅也廣泛地應用在光電材料方面。氧化鋅具有獨特的性質，例如：具有寬及直接能隙的半導體、激發光的波長為短波長(藍光)。本實驗專注於成長 P 型氧化鋅薄膜之製備及氧化鋅薄膜之電學性質討論，在簡介中，可以了解一般氧化鋅薄膜之應用及目前用來參雜 P 型氧化新的參雜元素還有成長 P 型氧化鋅困難的原因。在結果與討論中,由氧化鋅薄膜的電學性質分析，吾人發現用純的氮氣成長的氧化鋅薄膜特性並不好，雖有 P 型氧化鋅薄膜的產生，但只有在特定條件下才會發生；而用純的笑氣成長的氧化鋅薄膜則呈現出 P 型，且參雜濃度相當高，而在如此高的參雜濃度之下，飄移率則會下降。在氧化鋅薄膜的物理性質中，吾人發現當溫度越來越高，氧化鋅的晶粒大小會越來越小，且表面平整度會越來越差。
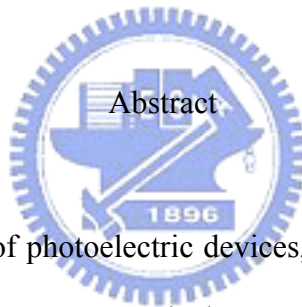
The preparation of P-type ZnO thin films and the research for the electrical characteristics

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Abstract

In the growing industry of photoelectric devices, ZnO is extensively used as the photoelectric material. There are some typical properties for ZnO, for example: it is the semiconductor with wide and direct band gap, and it emits light with the short wavelength (blue light range). We focus our attention on growing p-type zinc oxide thin films and study their electrical properties. In the introduction, we illustrate the general applications of zinc oxide thin films, and further explain what is the element used for doping p-type zinc oxide and the difficulties of growing p-type zinc oxide thin films. Furthermore, in the chapter of result and discussion, from the analysis of electric properties of ZnO thin films, we find the properties of the ZnO thin films prepared with pure nitrogen are not good. Although we obtain p-type ZnO thin films, it take place only at a specific growth condition. The ZnO thin films prepared with pure nitrous oxide reveal the characteristic of p-type, and the doping concentration is

very high. At such a high doping concentration, the mobility is reduced. Regarding to its Physics properties, we find the grain sizes decreases and the surface roughness gets worse with increasing the substrate temperature.

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Chapter 1

Introduction

1-1 A summarized account of zinc oxide

Zinc oxide (ZnO) is a - compound semiconductor (Table) with a wide

and direct band gap (3.2eV). The thin films of ZnO are used as transparent

electrodes in electronic devices like indium tin oxide because of their transparency

in the visible light region. So it can be utilized as transparent electrode films [1] or

an active channel layer of transparent thin film transistors (Fig.1-1)[2]. It has a

hexagonal wurtzite structure (Fig.1-2)[3]. ZnO is the direct transition type with high

exciton binding energy (60meV)[4] as compared with other - compound

semiconductors, like ZnSe (19meV), and has the possibility of using as a

UV-light-emitting materials[5]. In wide-band-gap optoelectronics, zinc oxide is

conventionally used as a substrate for GaN [6]. As a result of many unusual

electrical and optical properties, it not only attracts much attention but also is

largely used in our daily utilities. It has been used as a varistor due to highly

nonlinear current-voltage quality [7], a novel material for short wavelength

optoelectronic devices because of its direct band gap (3.4eV) and large exciton

binding energy (60meV). Furthermore, due to its individual properties such as

optical transmittance[8], electron conductivity [9], piezoelectricity[10], etc, a very

wide applications can be realized like UV resistive coatings, solar cell, piezoelectric

transducers, optical waveguide, surface acoustic wave device, gas sensors, and

pyroelectric devices. Since zinc oxide has a lot of unique characteristics, recently

many laboratories and research workers have investigated and researched the

electrical and optical properties of zinc oxide. At the same time, there are various

kinds of fabrication technologies and special shapes of zinc oxide that have been realized. Generally, there are three methods to fabricate nanometer scales of zinc oxide:

1   **Vapor-liquid-solid (VLS) mechanism**

First, the zinc oxide ZnO powder or target is made, which is then evaporated to vapor phase. And by letting the vapor phase of zinc oxide to transport to lower temperature area, ZnO condenses on the substrate surface. VLS crystal growth mechanism has been widely used for the preparation of nanosize zinc oxide:

(1)   Vapor-phase transport process[11];

(2)   Chemical vapor deposition[12];

(3)   Arc discharge[13]; and

(4)   Laser ablation[14].

2   **Catalytic growth assisted by a small amount of transition metal**

Use of a transition metal as the catalytic agent to help zinc oxide crystallize on a restricted zone where we want.

3   **Template-induced growth**[15][16]

In general, the method involves three-steps:

(1)   Generating an alumina template with highly ordered hexagonal array of nano-channels;

(2)   Using electro-deposition method to deposition pure metal zinc in the nano-channels of alumina template; and

(3)   Oxidation of zinc nanowire array in air.

Template-induced growth often operates in coordination with sol-gel and electro-deposition method. As the devices are scaled down, catalytic growth assisted by a small amount of transition metal method is unacceptable.

2

Because during growth, the metal might be incorporated into nanowires and generate unintentional defect levels; (e.g: Au used as a typical catalyst in V-L-S growth is well known to be a trap center.)

Zinc oxide thin film is widely under research and development. High quality ZnO thin film has been successfully fabricated on silicon or sapphire substrate by sol-gel[17], sputtering[18], molecular beam epitaxy[19], metal organic CVD[20], pulsed laser deposition[21] etc [Table.   ]. The growth conditions of thin films can influence obviously the electrical and optical characteristics of zinc oxide[18][22]. It has been reported that correlation was found between the grain size and the bound exciton states. For example, photoluminescence intensity and photoluminescence decay rate increased with increasing the grain boundary of zinc oxide. With increasing O_2 and Ar ratio in the growing ambient, the visible emission was drastically suppressed without sacrificing the band-edge emission intensity in ultraviolet region[22].

1-2　The characteristics of p-type ZnO

Another most important property of zinc oxide is its ability to be doped as n-type or p-type by the incorporation of appropriate impurities [Table   ]. Many papers show that n-type zinc oxide is easily available even without any dopant[23][24]; while the p-type ZnO thin films had a high resistance of 100Ω-cm and a low carrier concentration of 1 x10^{16} cm^{-3}, suggesting that hole injection was very difficult. If one can make a p-type ZnO film, it will lead to the fabrication of a unique pn junction, a key structure in the semiconductor technology. Ever since the first report[25] (in 1959) on the enhancement of n-type activity in ZnO by doping In was published, considerable efforts were made to produce p-type ZnO [26][27][28]. The problems of p-type doping in ZnO arise for various reasons such as, the donor level may be

sufficiently deep that there is low thermal excitations into the valence band, low solubility of the dopant or inducing self-compensating processes on doping.

1-3 Problems of fabrication the p-type ZnO

Several mechanisms depict doping difficulty of zinc oxide thin films[29][30][31]. These are (1) Low solubility the suitable dopants (shallow acceptors) may be less soluble than the lowest achievable concentration of donors, (2) The dopants that are shallow acceptors on one site may act as donors by occupying wrong site. For example substitutional group impurities are acceptors, but group impurities are electron donors at the interstitial site. (3) Compensation by low formation energy of native defects oxygen vacancy V_o and zinc interstitial Zn_i in zinc oxide. The formation energy is calculated by using first-principles pseudopotential method. It has been calculated that the formation energy of donor-type defects is quite low under p-type condition (Fermi energy is the same as the valence band maximum), and the formation energy of oxygen vacancy is the lowest among the donor-type defects under n-type condition (Fermi energy is the same as conduction band minimum). Because the V_o and Zn_i can govern the formation of p-type or n-type zinc oxide. Successful control of p-type and n-type conductivity in sputter deposited undoped zinc oxide has been reported by changing oxygen fraction in the O_2/Ar feed gas at constant total pressure of 30mTorr[32]. The paper shows that under the stated conditions of O_2 fraction 55 the n-type zinc oxide can be obtained, and under the stated condition of O_2 fraction 55 the p-type zinc oxide can be obtained. (4) The AX and DX complex centers the dopants (acceptor-type) have a great tendency to pair with native defects (Zn_i and V_o) and become the stable complex centers. Such as, P and As.

1-4   The reasons of using N element in the experiment

Generally speaking, the group-   elements Li, Na, and K and group-   elements N, P, and As can be made use for the doping p-type zinc oxide. Why do we use N element as the dopant to grow p-type zinc oxide thin film? The reasons are[29]-[34] (1) Between group-   elements and group-   elements, we can find that group-   elements have shallower acceptor level than group-   elements. But it has been reported that group-   elements are favored to occupy interstitial site in zinc oxide thin films under Fermi energy that is close to valence band maximum (p-type condition occur). So group-   elements are more suitable as the dopants for zinc oxide thin film than group-   elements under this mechanism. (2) Among group-   elements, N has the shallowest acceptor energy level. The acceptor energy level of N is 0.4eV, P is 0.93eV and As is 1.15eV. The calculation of acceptor energy level is carried out using the first-principle pseudopotential method based on the local density approximation. (3) N does not easily form stable AX complex center with native defect (A   a dopant atom on a lattice site, X   may be vacancy, interstitial or interstitialcy)because it has smaller lattice strain. (The ideal Zn-O bond length is 1.93 Å, and the bond lengths between group-   elements and the nearest neighbor of negative charged atoms are   N is 1.88 Å, P is 2.18 Å and As is 2.23Å). The large lattice strain will result in the formation of other compensation defects around the dopant easier. Therefore, P and As easily form AX complex centers. The mechanism of forming the AX centers is explained by double broken bond mechanism [Fig.1-3]. When the complex centers form, two oxygen bonds (O-O), or one group-   elements bond (group-   elements-O) and one oxygen bond (O-O) are broken (here, if the substitutional impurities are group-   elements, the oxygen will be substituted by group-   elements. If the substitutional impurities are group-   elements, then the zinc will be substituted by group-   elements), then releasing four electrons. At the

same time two electrons will be recaptured to form anion-anion bond for the stability of the double broken bond lattice distortion. The result of the whole process is the loss of two electrons. So, the formation of AX complex centers are donor-like defects and can lead to dope p-type zinc oxide thin film with difficulty.

Even though it is difficult to dope p-type zinc oxide thin film, it has been grown successfully by using novel methods[35][36][37]. These are   (1) Use of nitric oxide gas to dope zinc oxide p-type films, fabricated utilizing metalorganic chemical deposition reaction of a zinc metalorganic precursor and NO gas. (2) P-type zinc oxide thin film was realized by the codoping method and using a conventional radio frequency diode sputtering system. (3) P-type zinc oxide thin film is obtained by pulsed laser deposition method with an electron cyclotron resonance plasma source.

1-5   Motivation

Although it was recently reported that p-type zinc oxide can be doped with novel techniques, the publications about using radio frequency sputtering system and with utilizing pure zinc oxide target, nitrogen and nitrous oxide gases are very rare. Moreover, the properties of zinc oxide thin films are greatly influenced by the substrate temperature, the pressure of sputtering gases, growth rate. Therefore, the main goals of the experiment are to build up the data of sputter deposited zinc oxide thin films under different substrate temperature, different reaction gases and the different source of N element.

1-6   The first-principle pseudopotential method

Electronic band structures play an important role in explaining about the properties of materials and in the interpretation of experimental data. Many different approaches and techniques have been studied and developed. It ranges from semi-empirical methods for modeling optical properties to first-principles calculations of the structural and dynamical properties of order or disorder systems. Each method

has its own set of advantages and disadvantages. The use of pseudopotentials in first-principles electronic structure calculations of solids has been by now extensive. The first-principles pseudopotential method is also called the Norm-conserving pseudopotential method. The first-principles pseudopotential method is based in large part on the compatibility between pseudopotentials and the use of plane waves as a convenient basis set for expanding the electronic states (Notice The method will be divided into two parts, G space method and Real space method, under choosing different Basis wavefunctions at that time. The Basis wavefunctions of the G space method is based on Plane waves and the Basis wavefunctions of the Real space method is based on spherical wavefunctions of pseudopotential pseudoatom); the elimination of the core electrons and the short wavelength structure in the valence wave functions allow Fourier expansions to converge reasonably rapidly. For first-principles calculations, pseudopotentials and a plane-wave basis are computationally simpler than the more accurate all-electron approaches, and can be extended more easily to make use of modern techniques such as iterative diagonalization to treat large systems. It is important to keep in mind that pseudopotentials are approximations to the underlying all-electron results. The quality of the first-principles pseudopotential should be judged by comparing the calculated results with all electrons.

1-7 Hexagonal wurtzite structure

The crystal structure is composed of Bravais lattice and basis. The Bravais lattices of hexagonal wurtzite structure (Fig.1-1-1) are $t_1 = a/2\ (1,3^{1/2},0)$, $t_2 = a/2\ (-1,3^{1/2},0)$, $t_3 = c\ (0,0,1)$. The basis of hexagonal wurtzite structure are $d_1 = (0,0,0)$, $d_2 = (0,0,uc)$, $d_3 = (0,a/3^{1/2},c/2)$, $d_4 = (0,a/3^{1/2},uc+c/2)$, where a and c are the lattice constants,(The lattice constants of ZnO are: a = 3.25 Å, c = 5.21 Å) and u is a dimensionless parameter (u = 0.345 for ZnO). The hexagonal wurtzite structure is a

composite crystal structure because there are four atoms in the primitive unit cell (primitive unit cell contains one lattice point)

1-8 Thesis organization

This dissertation is divided into four chapters

➢ Chapter 1 is composed of a summarized account of zinc oxide, explaining the difficulty of doping p-type zinc oxide thin films by using N element to dope zinc oxide, the motivation of the experiment, and an introduction of first-principle pseudopotential method.

➢ Chapter 2 is the description of experiment details, including introduction of sputter system, the fabrication of target, the experiment process and Measurements with X – Ray Diffraction Analysis, Scanning Electron Microscopy and Hall Effect Analysis.

➢ Chapter 3 is the results and discussion. It is divided into two sections, one is doping p-type using nitrogen, and the other is using nitrous oxide.

➢ Chapter 4 is the conclusion.

Table   Important properties of   -   compound semiconductors

material property	ZnO	ZnS	ZnSe	ZnTe
Wurzite Lattice Parameters at 300K	$a_0 = 0.32495$ nm $c_0 = 0.52069$ nm	$a_0 = 0.3811$ nm $c_0 = 0.6234$ nm	$a_0 = 0.398$ nm $c_0 = 0.653$ nm	$a_0 = 0.427$ nm $c_0 = 0.699$ nm
Phase Stable at 300K	wurzite	blende & wurzite	blende	blende
Melting Point	1975 ^{o}C	1850 ^{o}C	1100 ^{o}C	1240 ^{o}C
Refractive Index	2.008	2.368(zinc-blende structure) 2.356(wurzite structure)	2.5	2.5
Energy Gap E_g at 300 K	3.4 eV Direct	3.68eV, Direct(zinc -blende) 3.91 eV, Direct（wurzite)	2.82 eV, Direct	2.4 eV, Direct
Dielectric Constant	10.8-11.0	8.9(zinc -blende) 9.6(wurzite)	9.1	7.4

Table   Methods of growing Zinc oxide thin film with growth conditions and properties.

Method	growing ambient	properties
metal organic CVD	carrier gas argon and nitrogen precursors diethyl zinc and oxyhen substrate sapphire	optical and surface acoustic wave properties is close to single-crystal ZnO
pulse laser deposition	substrate sapphire	electrical and optical properties of the films were improved with increasing the film thickness
molecular beam epitaxy	gas zinc and oxygen substrate sapphire	Carrier mobility $42cm^2V^{-1}S^{-1}$
sputtering	gas argon and oxygen substrate p-type silicon	increasing O_2 and Ar ratio, visible emission was drastically suppressed without sacrificing the band-edge emission intensity
sol-gel	solution zinc acetate and aluminum nitrate substrate glass	low resistivity 1.5×10^{-4} Ωcm max transmission about 91%

Table　　　　Doping p and n-type zinc oxide with the impurities.

dopant type	Group	group
P	N, As	------
N	------	Al, Ga, In
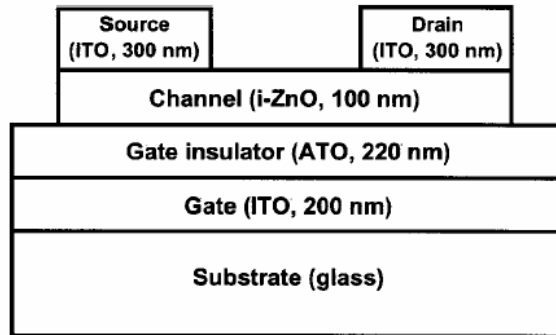
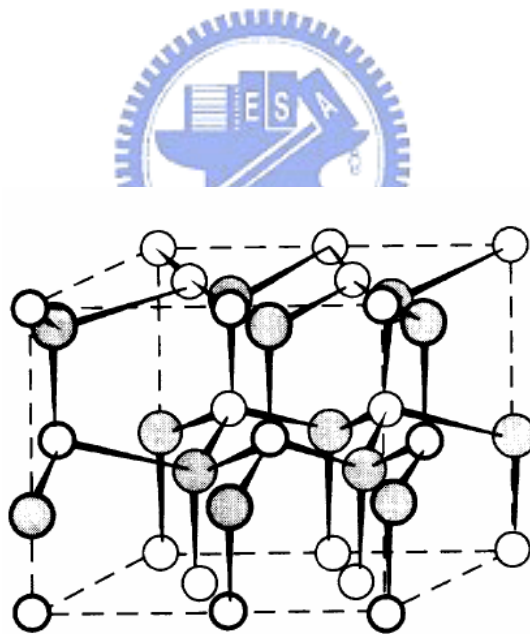Fig.1-1   ZnO-based transparent thin-film transistor

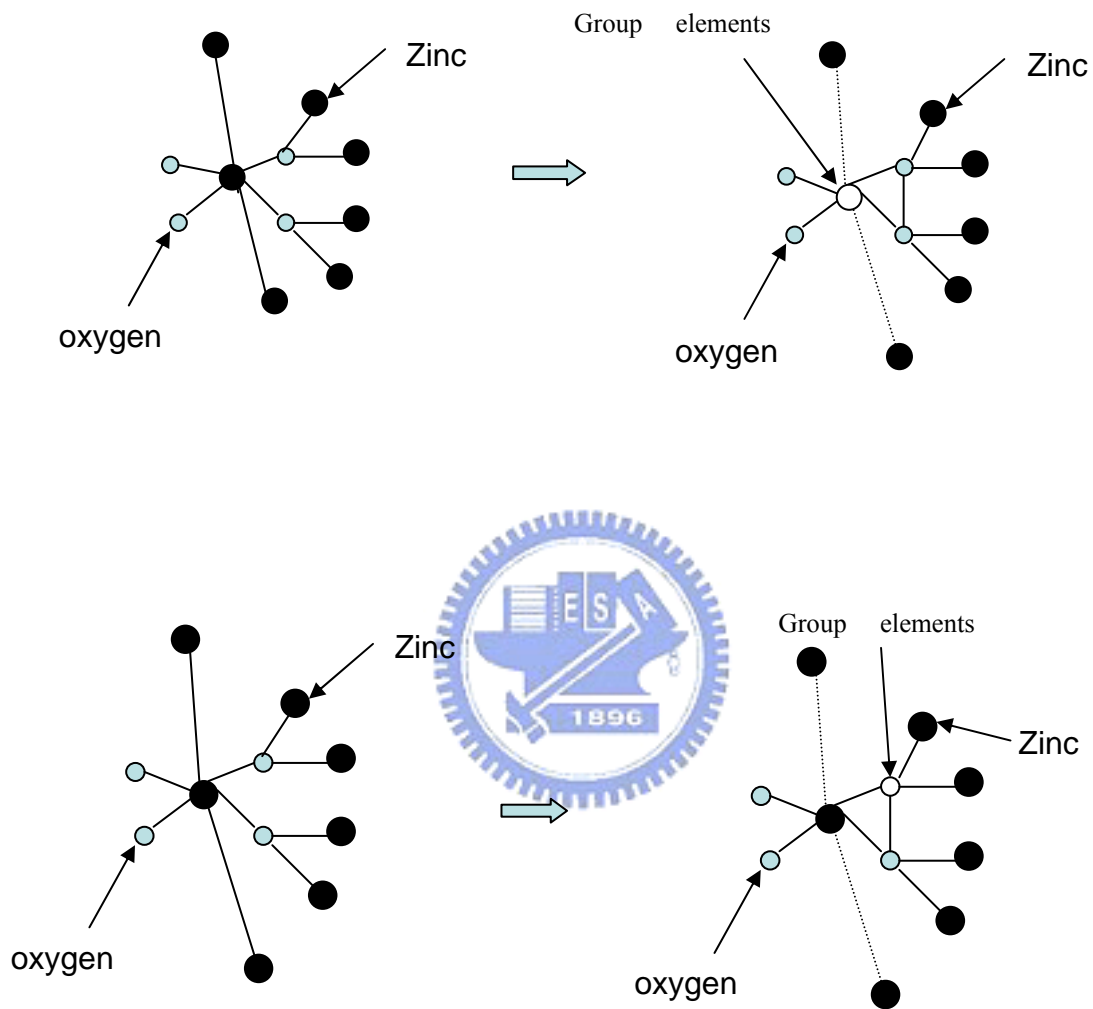Fig.1-2   Hexagonal wurtzite structure of zinc oxide

Fig.1-3   The double broken bond mechanism for (a) group   elements: two Zn-O bonds are broken and form a new O-O bond; (b) group   element: two Zn-O bonds are broken and form a new group   -O bond.

Chapter 2

Experiment details

2-1　Introduction

There are several processes for depositing thin films　vapor phase ,liquid phase and solid phase deposition. The vapor phase deposition is commonly used to deposit thin films because the qualities and properties of the thin films prepared by vapor phase deposition are better than those prepared by liquid phase deposition and solid phase deposition. And the step coverage of vapor phase deposition is much more efficient than others. In our experiment , the ZnO thin films are prepared by radio frequency magnetron sputtering system, which is a kind of physical vapor deposition process.

The reasons we use sputtering system to deposit ZnO thin films are as follow:

(1) Properties of thin film, like film thickness, step coverage, deposition rate, grain size, stress and adhesion can be controlled by altering the negative bias, heat applied to the substrate, power and pressure.

(2) The alloy composition of thin films by sputtering can be easily controlled.

(3) Sputtering can deposit large-area thin films by utilizing large-area targets.

(4) There is sufficient material in a sputter target to allow many deposition runs.

Basically, the process of sputtering composed of five steps

(1) Create a glow discharge as a plasma source.

(2) Ions are generated and directed at a target.

(3) The ions will sputter the atoms out of the target.

(4) The sputtered atoms are diffused to the surface of substrate.

(5) The atoms condense and form a thin film upon reaching the surface of substrate.

2-2 Sputtering system

The sputtering can be divided into two systems according to the source used for generation of plasma; these are DC sputtering and RF sputtering. The DC sputtering has a serious drawback; the target must be a conductive material. For the RF sputtering system, it is not restricted, because the positive ions are oscillating between two electrodes instead of accumulating on the target. Therefore, the target of RF sputtering system can be a conductive or insulating material. Recently, the magnetron sputtering system has become more popular for depositing thin films.

In this experiment, a radio frequency magnetron sputtering system is used and the sputtering system includes:

(1) the sputter chamber,

(2) vacuum pumps of rotary and diffusion,

(3) power supplies of DC and AC,

(4) sputtering gas supply and flow controller,

(5) monitoring equipments of pressure gauges, voltage meters, and residual-gas
   analyzers.

(6) the wafer holders,

(7) the lamp heater,

(8) the sputter gun and

(9) cooling system.
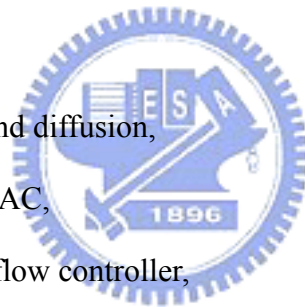
2-3 Fabrication of target

The target consists only zinc oxide powder(purity 99.99%). First, put the zinc oxide powder is placed in an earthen bowl and then ground the powder for thirty minutes. Second, the ground powder is poured to a mold of three inch. Third, ramming the zinc oxide powder down until the applied pressure is attained, the target

is accomplished.

2-4 Experiment process

Before depositing zinc oxide on (100) p-type silicon substrate, the 4-inch silicon wafer was cleaned with standard initial cleaning process. The initial clean processes are:

(1) silicon wafers were put in the glassware and rinsed with deionized water for five minutes.

(2) After washing with deionized water washed, silicon wafers were laid in chemical solution which consists of sulfuric acid (600 mL) and hydrogen peroxide (200 mL) for fifteen minutes. The objective of this step is to remove organic matter and particles.

(3) Then, rinse the silicon wafers with deionized water for five minutes again. Rinse all the chemical solution out of silicon wafers in this step.

(4) This step removes the native oxides from the surface of silicon wafers by using chemical solution which composed of hydrofluoric acid (12 mL) and deoxidizing ionic water (1200 mL).

(5) After fourth step, dip the silicon wafers into deoxidizing ionic water for twenty seconds. Next the silicon wafers were moved to spinner with nitrogen purge.

After initial cleaning, the clean silicon wafers are placed in chamber for sputtering right away. The zinc oxide thin films were prepared using radio frequency magnetron sputtering system. The substrate can be heated by the quartz heating tube. The chamber of sputter is evacuated to a low pressure of 8×10^{-6} Torr. High purity (1) nitrogen, and (2) nitrous oxide were used as the reaction gases. In order to study the relation between the nitrogen, nitrous oxide and electrical, optical properties of zinc oxide, the total pressure was kept at 20 mTorr . The relation between substrate temperature and electrical,

optical properties of zinc oxide thin films is also the important point in this experiment. The processes are listed in Table

2-5　Measurements

The following measuring instruments are indispensable to the experiment. These measuring instruments help me to accomplish the analysis of the data.

X – Ray Diffraction Analysis

The information of crystalline phase, lattice orientation and grain size calculated from Scherrer equation were obtained by a Rigaku Dmmax-B diffractometer with 0.02 degree beam divergence. And it is operated at 30KV 20mA with copper $K\alpha_1$ radiation.

Scanning Electron Microscopy

We acquired the information of planar view and cross-section of thin film by using the High-Resolution Scanning Electron Microscope & Energy Dispersive Spectrometer (Hitachi, S-4700I, with the resolution 15A° (at 15kV) or 25A° (at 1kV)) in the Semiconductor Research Center.

The Hall Effect Analysis

The carrier concentration, carrier mobility, resistivity and conductivity of zinc oxide thin films are measured by Hall Effect. And the sample size is 8mmX 3mm. The concept of Hall Effect formula will be introduced[38]

Hall Effect is usually used for measurement of carrier concentration of semiconductor and gauges the semiconductor as p-type or n-type. Fig.2-1 is the typical geometric figure for measuring the Hall Effect. With a charged +Q particle moving (the velocity of particle is v_x) in the magnetic field B_z. The particle will feel a

magnetic force F_B

$$F_B = Q \, v_x \times B_z$$

Because the particle also feel an induced electrical force F_E when a bias (V) was applied on semiconductor. The induced electrical force F_E

$$F_E = Q \, E_y$$

In the meantime, the F_E is equal to F_B at the stable state

$$Q \, v_x \times B_z = Q \, E_y \text{ -----------(1)}$$

The E_y is called the Hall electrical field. The E_y will generate a voltage (V_H) which was across the semiconductor in y direction. And we can also write V_H

$$V_H = E_y \, W \text{ -------------(2)} \qquad \text{where W is the width of the}$$

semiconductor. Combining equation (1) with equation (2), we can obtain another equation

$$V_H = v_x \, B_z \, W \text{ --------(3)}$$

For a p-type semiconductor with n_p hole concentration , the drift current density can be written as

$$J_d = e \, n_p \, v_d \text{ ----------(4)} \qquad \text{where } v_d = v_x \text{ in this case}$$

Combining with equation (3) with equation (4), equation (5) can be acquired

$$V_H = J_d \, W \, B_z \, / \, e \, n_p \text{ ----------(5)}$$

Therefore we can get the carrier concentration n_p by measuring V_H, B_z and J_d. Further, we can solve out the carrier mobility, resistivity and conductivity of semiconductor by utilizing following equations

carrier mobility of hole $\qquad u_p = J_x \, L \, / \, e \, n_p \, V_x \qquad$ where L is the length of the semiconductor.

Similarly, for the n-type semiconductor

$$V_H = - \, J_d \, W \, B_z \, / \, e \, n_n$$

carrier mobility of electron $\qquad u_n = J_x \, L \, / \, e \, n_n \, V_x$

And resistivity and conductivity $\rho = 1 / (e\, u_p\, n_p + e\, u_n\, n_n) = 1 / \sigma$.

Table   Processes of the experiment

```
┌─────────────────────────────────┐
│      The fabrication of target   │
└─────────────────────────────────┘
                 │
                 ▼
┌─────────────────────────────────────────┐
│ Initial clean                            │
│ (1) DI water 5 minutes                   │
│ (2) H₂SO₄ + H₂O    15~10 minute          │
│        600   :    200                    │
│ (3) DI water 5 minutes                   │
│ (4) HF   +   H₂O      about 20 seconds   │
│         1  :   1000                       │
│ (5)DI water dip                          │
│ (6)Purge N₂ with spiner                  │
└─────────────────────────────────────────┘
                 │
                 ▼
┌──────────────────────────────────────────────────────────┐
│ Deposit zinc oxide thin films on p-type (100) silicon substrate │
└──────────────────────────────────────────────────────────┘
        │                 │                        │
        ▼                 ▼                        ▼
┌──────────────────┐  ┌─────────────────────┐  ┌────────────────────┐
│ X-Ray Diffraction│  │ Scanning Electron   │  │ Hall Effect Analysis│
│ Analysis         │  │ Microscopy          │  │                     │
└──────────────────┘  └─────────────────────┘  └────────────────────┘
```

Initial clean

(1) DI water 5 minutes

(2) $H_2SO_4 + H_2O$ 15~10 minute

      600   :   200

(3) DI water 5 minutes

(4) HF   + H_2O about 20 seconds

        1   :   1000

(5)DI water dip

(6)Purge N_2 with spiner

The fabrication of target

Deposit zinc oxide thin films on p-type (100) silicon substrate

X-Ray Diffraction Analysis

Hall Effect Analysis

Scanning Electron Microscopy

Fig.2-1 Typical geometric figure for measuring the Hall Effect

Chapter 3

Results and Discussions

3-1　ZnO thin films prepared with nitrogen under various conditions

Fig.3-1 to Fig.3-12 are the pictures of ZnO thin films grown under various conditions by Scanning Electron Microscopy. It is obvious that the thickness of the ZnO films is dependent on RF power and flow rate greatly, the higher the RF power and flow rate, the thicker the film thickness, and the thickness of the films are about 200nm~400nm. But at the same growing condition , the relation between the thickness of ZnO thin films and the temperature of substrate are not regular, especially at high temperature of 500　, the growth rate is not affected greatly by substrate temperature. The ZnO is not column-like if we use pure nitrogen gas when depositing ZnO thin films, because lateral growth rate is higher than vertical growth rate. From Fig.3-1 to Fig.3-3 and Fig.3-13, it is shown that the grain size of 300　is larger than any other temperatures, and the grain size increased with decreasing substrate temperature. The surface roughness of thin films at 400　is much better than it at 300　because the atoms at the surface obtain enough energy from high temperature and make the atoms diffuse rapidly. But at high substrate temperature of 500　, we find the roughness of thin films is much different with any other temperature, it is obviously rough, because the melting point of zinc is lower than 500　, when the substrate temperature is higher than the melting point, the zinc atoms would succeed in escaping to form the surface vacancies, so it reveal rough. It is apparently shown in Fig.3-1, Fig.3-4, and Fig.3-10.

Figs.3-13 to3-16 are the X-Ray Diffraction patterns of zinc oxide thin films, all

figures show that the orientation of zinc oxide peaks are at (002), and the FWHM of the patterns are all smaller than 1 , *so the films are high consistence*. In these figures, the intensities of XRD peaks are getting higher while the substrate temperature is low. It is showed that the X-Ray intensities of films grown at substrate temperature of 500 are the lowest and those at 300 are the highest. It had been reported[35] that high temperature (higher than 650) will damage the crystallization of ZnO thin films, so the higher temperature would reduce the crystallization of zinc oxide thin films prepared by sputtering system. Therefore, according to the results of scanning electron microscopy and the XRD patterns, it could be explained that substrate temperature of 300 is the optimum growth temperature of ZnO films by sputtering system, which have the flat surface and largest XRD peak intensities. In these figures, the grain size increases as the substrate temperature decreases, the result in XRD is corresponding with the result in scanning electron microscopy. Comparing the Fig.3-13 and Fig.3-14, at same substrate temperature, the intensities of larger flow rate are lower than those of smaller flow rate.

The electrical properties of zinc oxide thin films were carried out by Hall measurement, the Hall measurement could determine the type of the semiconductors, carrier concentration, resistivity and carrier mobility. Table shows the result of zinc oxide films measured by Hall measurement, including carrier type, carrier concentration, resistivity and carrier mobility. As the table shown, we have p-type ZnO thin films only at the growth condition 100W and 2 sccm, at this condition, we get the carrier concentration about 4×10^{16} cm^{-3}, the carrier concentration we have is fitting with the reported papers which indicated that the carrier concentrations of the N element doped ZnO thin films are about $10^{15} \sim 10^{18}$ cm^{-3}[35], the carrier concentration would increase up to 10^{19} cm^{-3} while we using codoping method by Ga and N element[36]. And we have the lower resistivity that the value is about 0.3 Ω-cm

to 0.2 Ω-cm. It is quite a low value. We lose some data because the value of the resistance is too large to measure. Except for the particular growth condition we have p-type zinc oxide thin films, we almost got n-type zinc oxide thin films, because the bonds between nitrogen are too strong to break, so the effective N element act as acceptors are few, it is reported[35] that as long as the N element concentration greater than 2 atom% in the film, the film will be p-type. Only under high RF power, the bonds would be broken, then it would make the dopant as acceptors.

Fig. 3-17 and Fig. 3-18 are carrier concentration and resistivity associate with various substrate temperature.
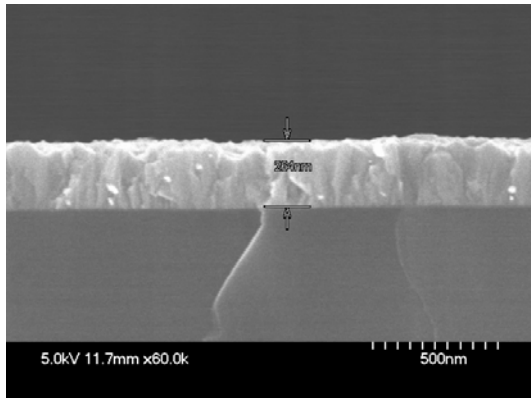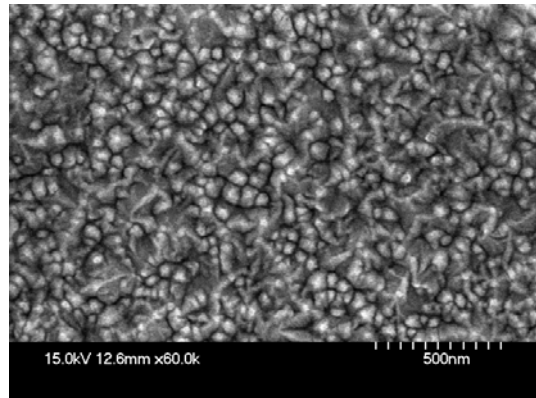
(a) cross- section

(b) plane-view

Fig.3-1   The substrate temperature is 500 , RF power is 100W and flow rate of N$_2$ is 5sccm.

(a) cross- section

(b) plane-view

Fig.3-2   The substrate temperature is 400 , RF power is 100W and flow rate of N$_2$ is 5sccm.


(a) cross- section

(b) plane-view

Fig.3-3   The substrate temperature is 300 , RF power is 100W and flow rate of N$_2$ is 5sccm.
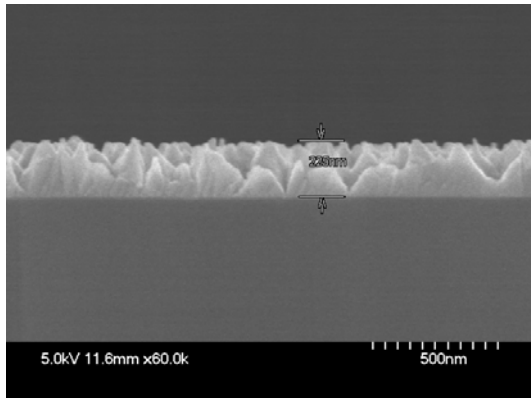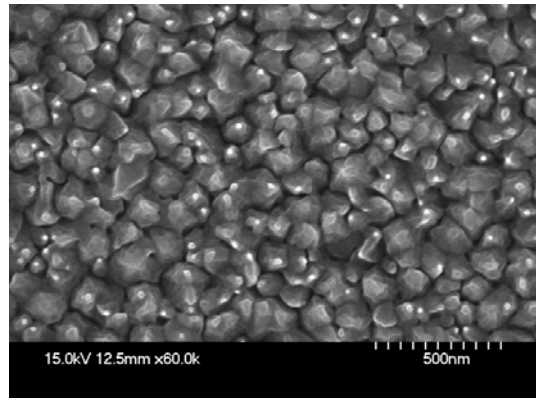
<div align="center">(a) cross- section   (b) plane-view</div>

Fig.3-4　The substrate temperature is 500　, RF power is 100W and flow rate of N_2 is 2sccm.

<div align="center">(a) cross- section   (b) plane-view</div>

Fig.3-5　The substrate temperature is 400　, RF power is 100W and flow rate of N_2 is 2sccm.

<div align="center">(a) cross- section   (b) plane-view</div>

Fig.3-6　The substrate temperature is 300　, RF power is 100W and flow rate of N_2 is 2sccm.

| | |
| (a) cross- section | (b) plane-view |

Fig.3-7   The substrate temperature is 500   , RF power is 80W and flow rate of N$_2$ is 5sccm.
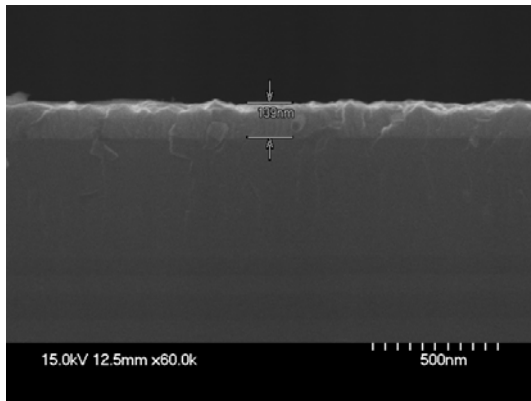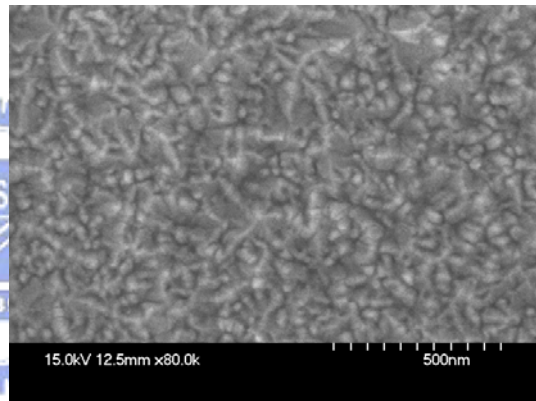
| | |
| (a) cross- section | (b) plane-view |

Fig.3-8   The substrate temperature is 400   , RF power is 80W and flow rate of N$_2$ is 5sccm.
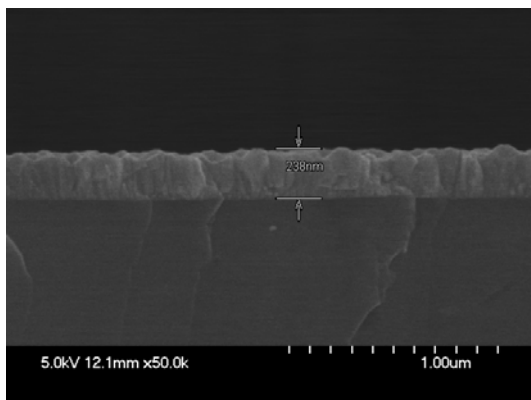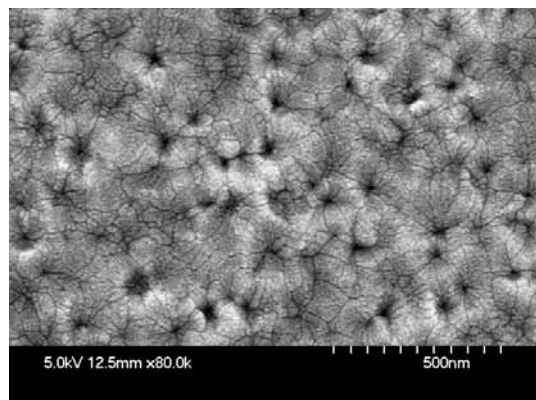
| | |
| (a) cross- section | (b) plane-view |

Fig.3-9   The substrate temperature is 300   , RF power is 80W and flow rate of N$_2$ is 5sccm.
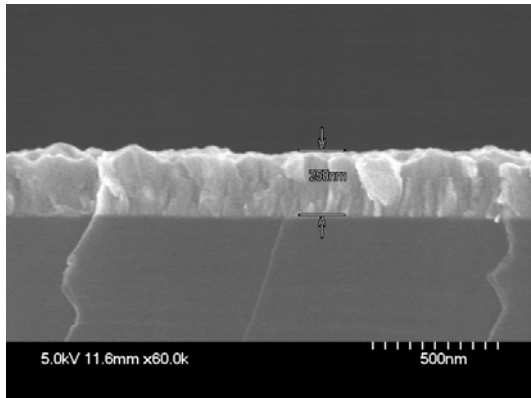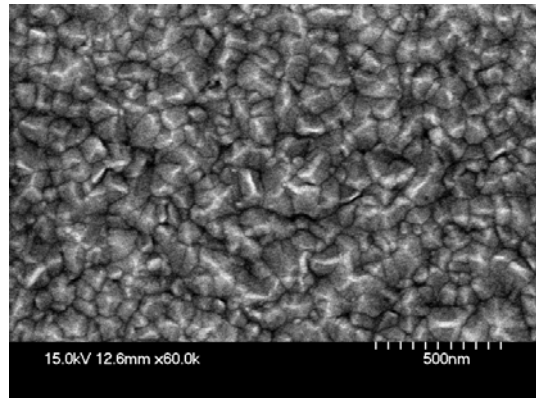
(a) cross- section   (b) plane-view

Fig.3-10   The substrate temperature is 500 , RF power is 80W and flow rate of N$_2$ is 2sccm.
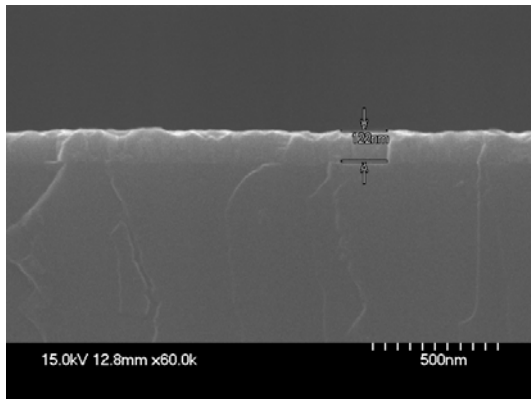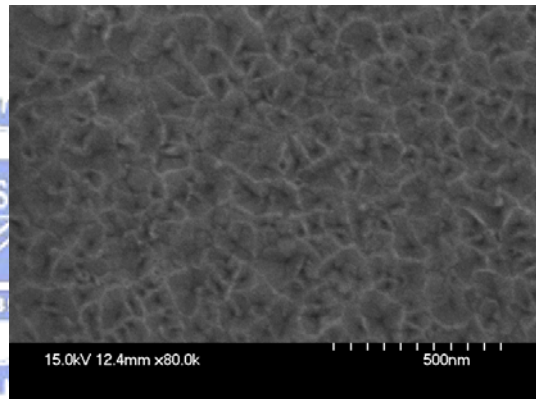
(a) cross- section   (b) plane-view

Fig.3-11   The substrate temperature is 400 , RF power is 80W and flow rate of N$_2$ is 2sccm.
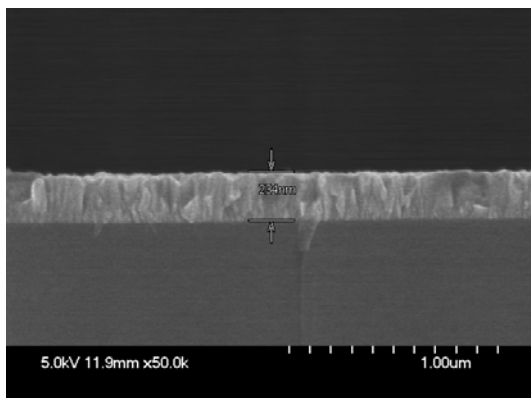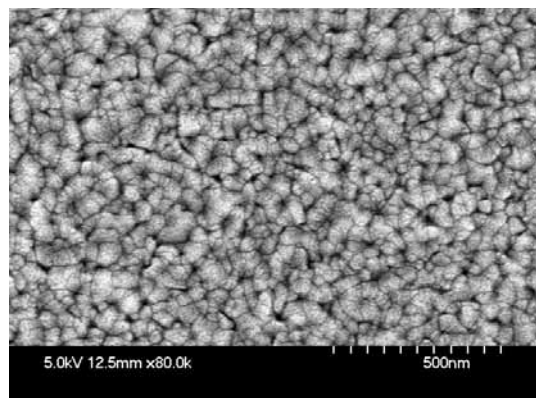
(a) cross- section   (b) plane-view

Fig.3-12   The substrate temperature is 300 , RF power is 80W and flow rate of N$_2$ is 2sccm.
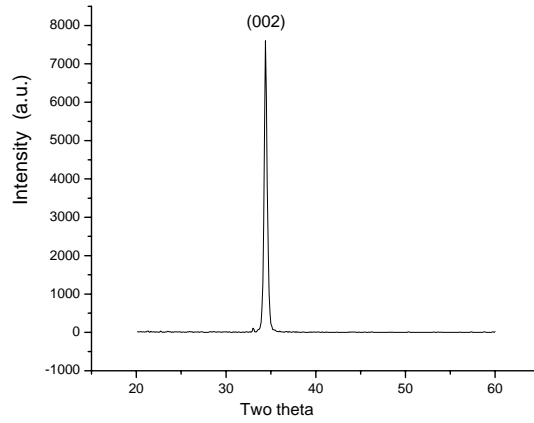
(a)The substrate temperature is 500
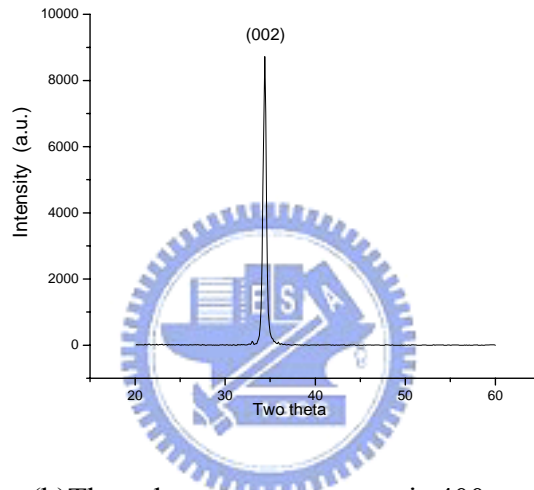
(b)The substrate temperature is 400
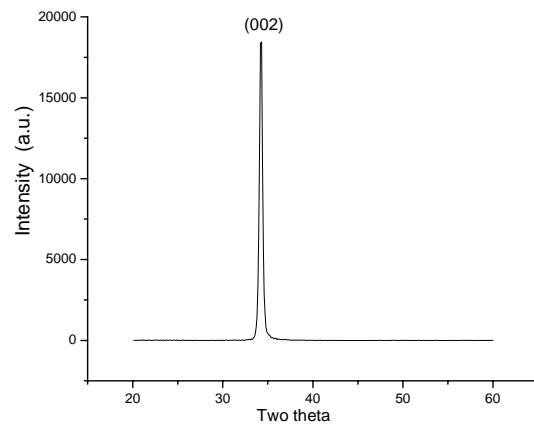
(c)The substrate temperature is 300

Fig.3-13 XRD pattern of ZnO films grown under conditions: RF power 100W, flow rate 5sccm and (a)500 , (b)400 , (c)300 as substrate temperatures.
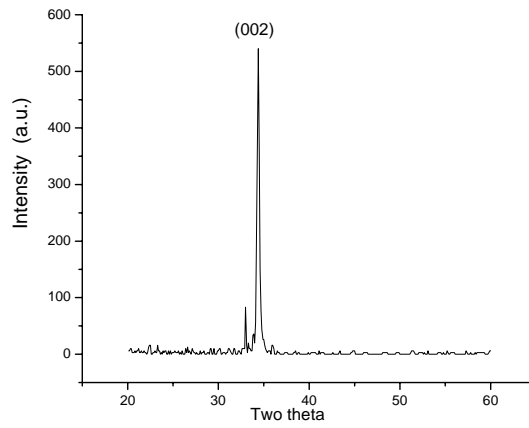
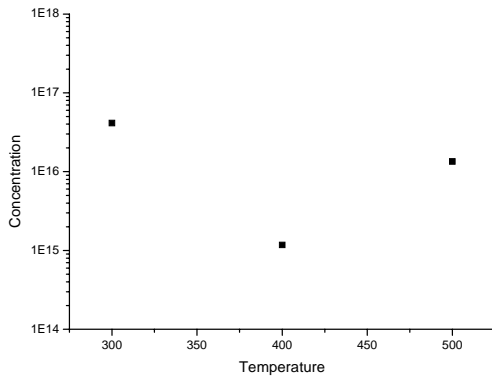(a) The substrate temperature is 500
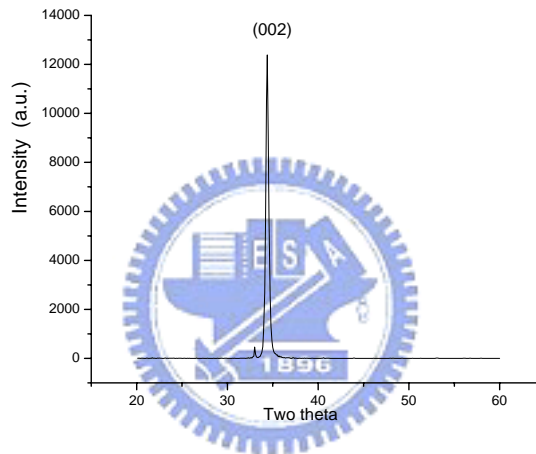
(b)The substrate temperature is 400
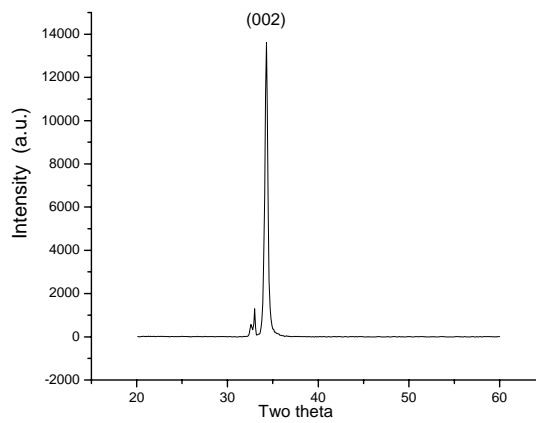
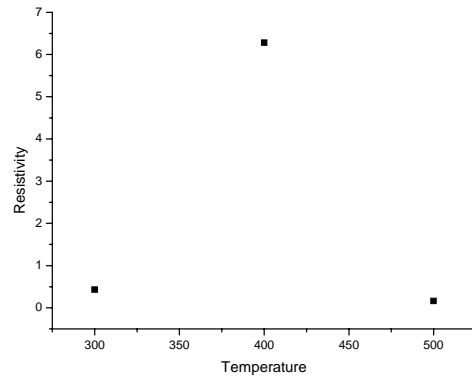

(c) The substrate temperature is 300

Fig.3-14   XRD pattern of ZnO films grown under conditions: RF power 100W, flow
rate 2sccm and (a)500   , (b)400   , (c)300   as substrate temperatures.
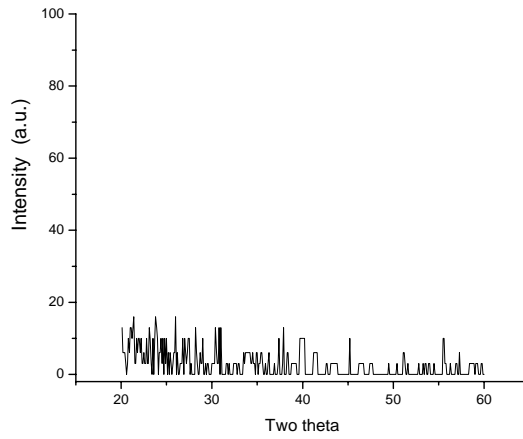
(a)The substrate temperature is 500
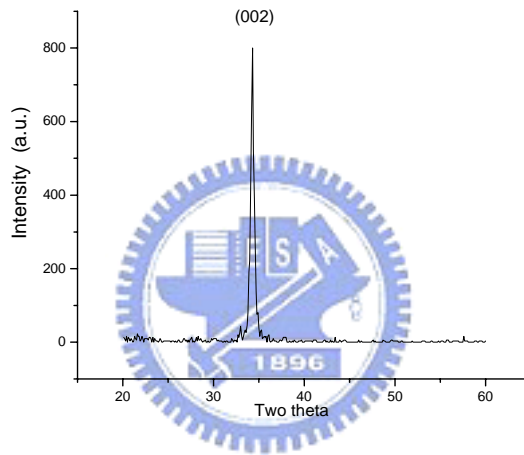
(b)The substrate temperature is 400
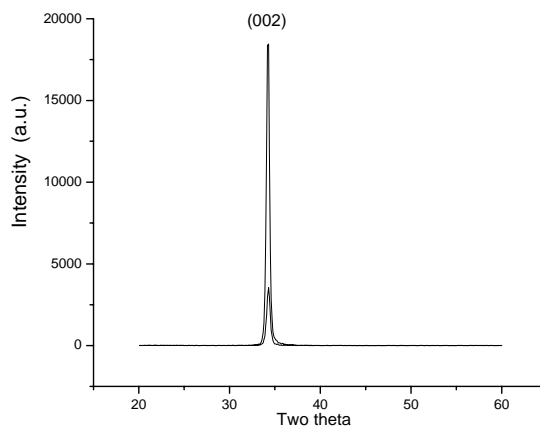
(c) The substrate temperature is 300

Fig.3-15   XRD pattern of ZnO films grown under conditions: RF power 80W, flow
rate 5sccm and (a)500   , (b)400   , (c)300   as substrate temperatures.
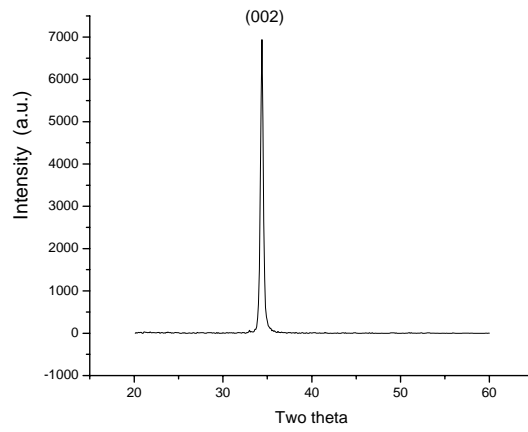
(a)The substrate temperature is 500
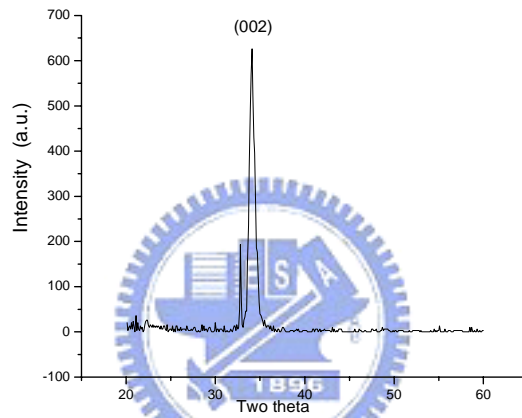
(b)The substrate temperature is 400
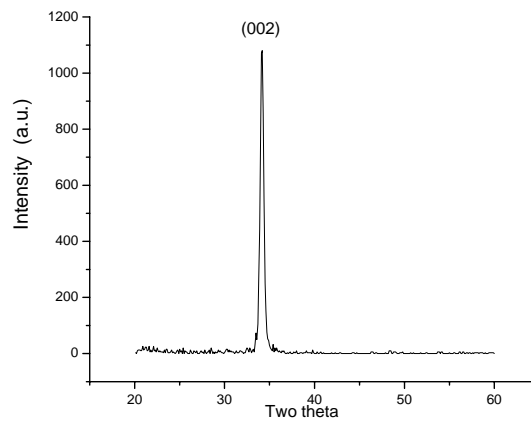
(c)The substrate temperature is 300

Fig.3-16   XRD pattern of ZnO films grown under conditions: RF power 80W, flow
    rate 2sccm and (a)500 , (b)400 , (c)300   as substrate temperatures.

Table   Electrical properties of ZnO films prepared with nitrogen under various

growth conditions

Growing ＼ Data condition	Carrier Type	Carrier Concentration (cm^{-3})	Resistivity $(\Omega\text{-cm})$
N$_2$,100W, 5sccm 500	N	3.3×10^{16}	0.159
N$_2$,100W, 5sccm 400	N	3.37×10^{16}	1.69
N$_2$,100W, 5sccm 300	---	-------	-------
N$_2$,100W, 2sccm 500	P	2.6×10^{16}	0.186
N$_2$, 100W, 2sccm 400	P	4.65×10^{16}	0.176
N$_2$, 100W, 2sccm 300	P	4.05×10^{16}	0.354
N$_2$,80W, 5sccm 500	---	-------	-------
N$_2$,80W, 5sccm 400	N	9.65×10^{15}	0.686
N$_2$,80W, 5sccm 300	P	4.25×10^{14}	13.4
N$_2$,80W, 2sccm 500	N	1.345×10^{16}	0.43
N$_2$,80W, 2sccm 400	N	1.17×10^{15}	6.28
N$_2$,80W, 2sccm 300	N	4.14×10^{16}	0.16

(a)Carrier concentration   (b)Resistivity

Fig.3-17   Carrier concentration and resistivity of n-type ZnO thin films with different substrate temperature under the growth condition of 80W, 2sccm.
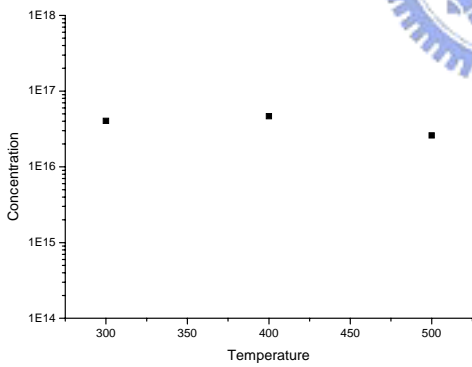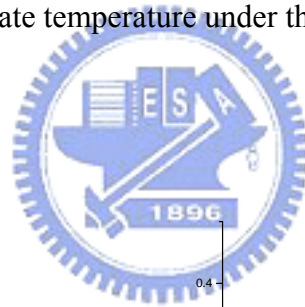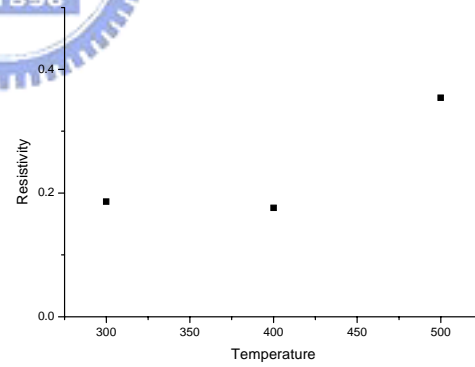
(a)Carrier concentration   (b)Resistivity

Fig.3-18   Carrier concentration and resistivity of p-type ZnO thin films with different substrate temperature under the growth condition of 100W, 2sccm.

3-2 ZnO thin films prepared with nitrous oxide under various conditions

Fig.3-19 to Fig.3-30 are the Scanning Electron Microscopy pictures of ZnO thin films grown under various conditions with pure nitrous oxide. From Fig.3-13 (b), Fig.3-14(b), Fig.3-15(b), we can find that the grain size increases as the substrate temperature decreases, the result here and the result of the film prepared with pure nitrogen are matched, but the differences of the films are that the films prepared with pure nitrous oxide gas look discrete, and the grain size of the ZnO films are much smaller. The thickness of the films are about 65nm to 200nm, it is thinner than that prepared with pure nitrogen gas under the same growth condition. The relation between the thickness of ZnO thin films and the temperature of substrate are not regular, but in principles, the lower the substrate temperature, the thicker the film thickness.

Fig.3-31 to Fig.3-34 are the X-Ray Diffraction patterns of zinc oxide thin films grown under pure nitrous oxide gas, all figures show that the orientation of zinc oxide peaks are at (002). In these figures, the intensities of XRD are getting higher while the substrate temperature is low. It is showed that the X-Ray intensities of films grown at substrate temperature 500 are the lowest and those at 300 are the highest.

Comparing the figures with Fig.3-13 to Fig.3-16, we find the peak intensities of XRD patterns are very different. The peak intensities of the films grown by nitrous oxide are much smaller than those grown by nitrogen, because the grain size of the ZnO thin films are smaller, it makes destructive interference, so the peak intensities of XRD patterns of the films are small. The bonds of nitrous oxide are not as strong as nitrogen, so it is much easier to break and dope. Therefore, we presume that it is much easier to form p-type ZnO thin films using pure nitrous oxide gas as the N element source, the doping concentration and whether the N elements were broken to act as

the acceptor or not can be determined and proved by Hall measurement.

Table   shows the results of zinc oxide films measured by Hall measurement, including carrier type, carrier concentration, resistivity and carrier mobility. As the table   shows, we have p-type ZnO thin films successfully prepared by nitrous oxide gas. Those data that we cannot obtain are because of high resistance. At table   , all the ZnO films are p-type, the result is much better than that prepared by nitrogen gas as N element source, so we can say that nitrous oxide gas is suitable to acquire p-type zinc oxide thin films because N_2O gas can supply both N element and O element to grow N-doped zinc oxide thin films and compensate the intrinsic oxygen vacancies. We obtain the carrier concentration about $10^{15}\sim10^{17}$ cm^{-3}, the value is fitting in with reported papers. And we have a lower resistivity value that is about 0.2 Ω-cm to 0.3 Ω-cm, it is also quite a low value. Lots of papers show that if the impurities can dope effectively into thin films, the electrical properties of zinc oxide, carrier concentration, carrier mobility, resistivity and conductivity will result in large improvement. And there are high densities of carriers that can be achieved with suitable dopant by novel technologies. The zinc oxide thin films grown by molecular beam epitaxy on sapphire substrates[39] had the optimum carrier mobility 42 cm^{2}V^{-1}S^{-1}, and the carrier concentration decreased with increasing the substrate temperature. The zinc oxide thin films deposited by CVD reaction with NO gas revealed p-type[35], because NO gas would decompose and supply N element to dope and O element to compensate the intrinsic defect, as long as the N element concentration is greater than 2 atom% in the film, the film will be p-type. The carrier concentration is from 10^{15} to 10^{18} cm^{-3}, and the carrier mobility is about 0.1cm^{2}V^{-1}S^{-1} and the minimum resistivity is about 20 -cm. Joseph et al.[36]prepared the p-type zinc oxide thin films by codoping with Ga (as the donor) and N (as the acceptor), when they added 0.1 Wt % Ga_2O_3 into ZnO target, the high carrier concentration(4 x 10^{19}cm^{-3}), high carrier mobility(7 x

10^{-2}cm^{2}V^{-1}S$^{-1)}$ and low resistivity (2   -cm) was obtained. However, nobody has succeeded in obtaining p-type zinc oxide thin films utilizing the pure N element. In our experiment, we deposit p-type zinc oxide thin films on p-type silicon substrate with N element successfully. We list the methods and the properties of the ZnO thin films at table   . It is shown clearly the achievements of each method.

Fig.3-35 and Fig.3-36 are the carrier concentration and resistivity associate with various substrate temperature.
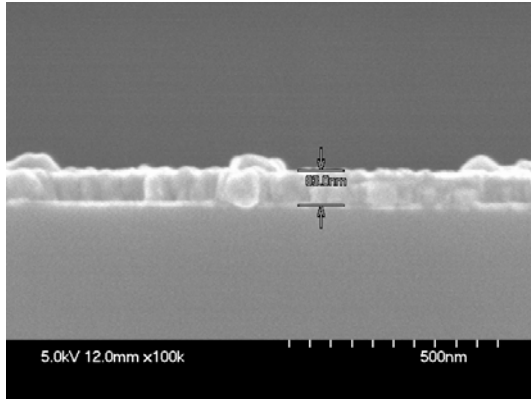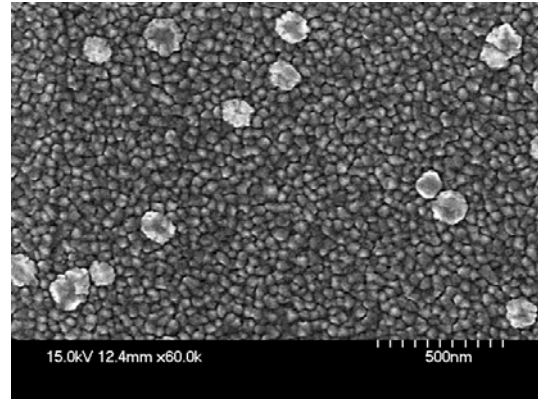
|(a) cross- section|(b) plane-view|

Fig.3-19   The substrate temperature is 500   , RF power is 100W and flow rate of N$_2$O is 5sccm.
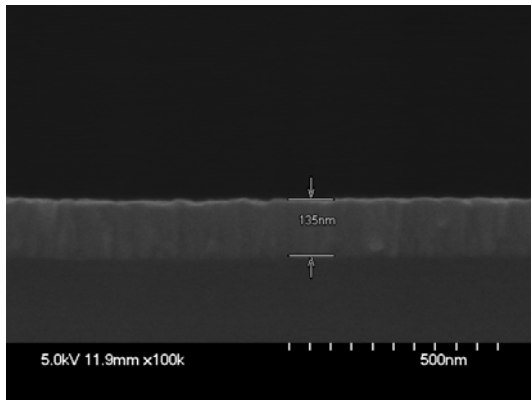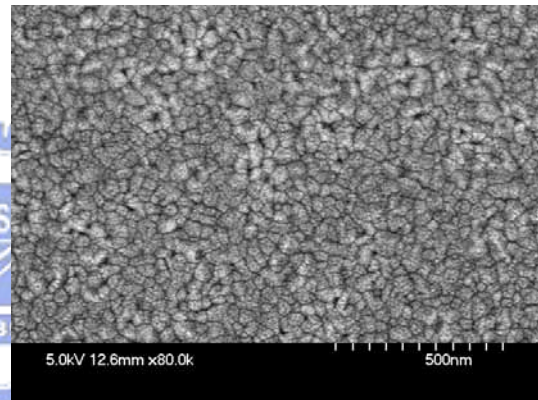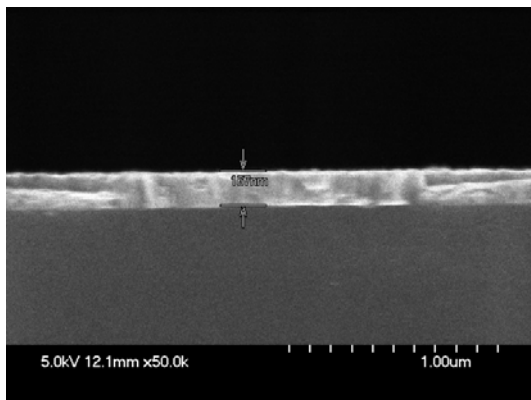

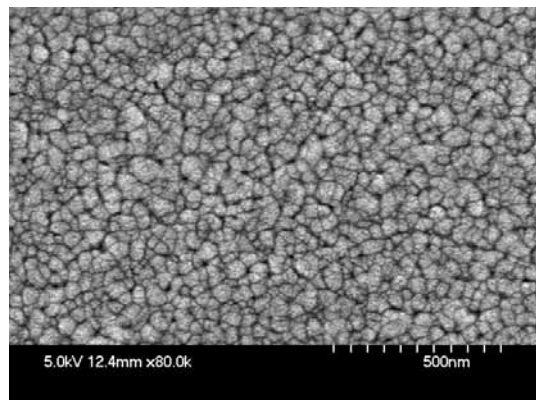|(a) cross- section|(b) plane-view|

Fig.3-20   The substrate temperature is 400   , RF power is 100W and flow rate of N$_2$O is 5sccm.
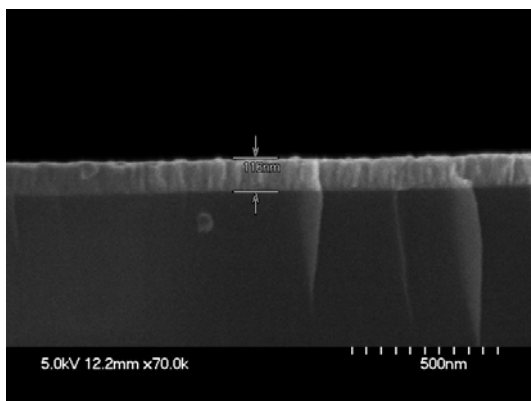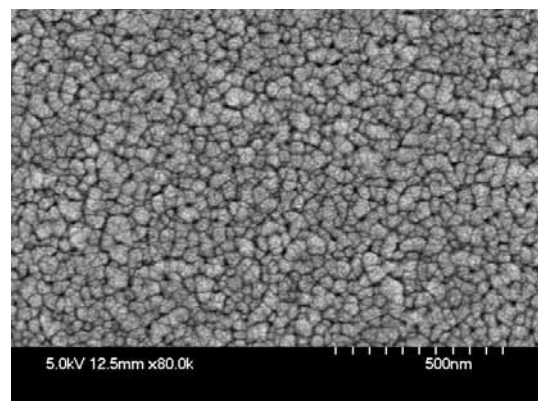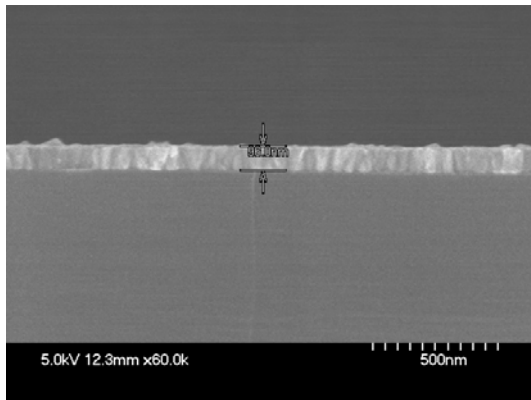

|(a) cross- section|(b) plane-view|

Fig.3-21   The substrate temperature is 300   , RF power is 100W and flow rate of N$_2$O is 5sccm.
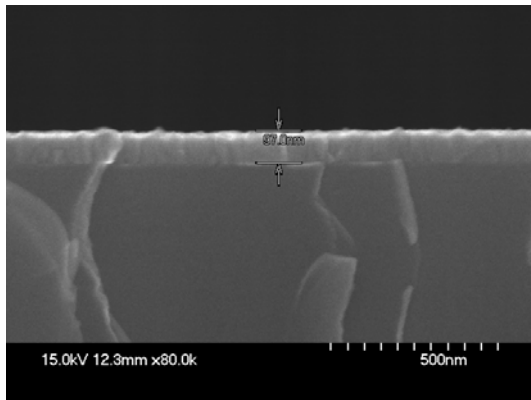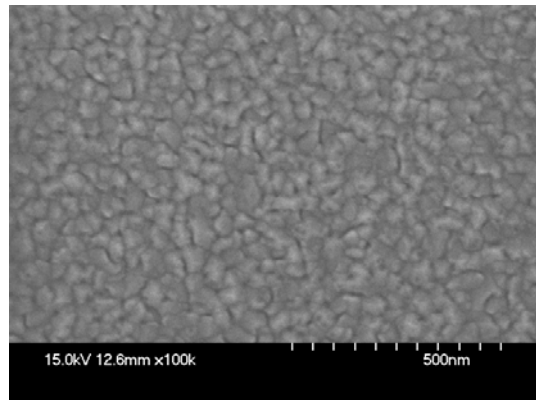
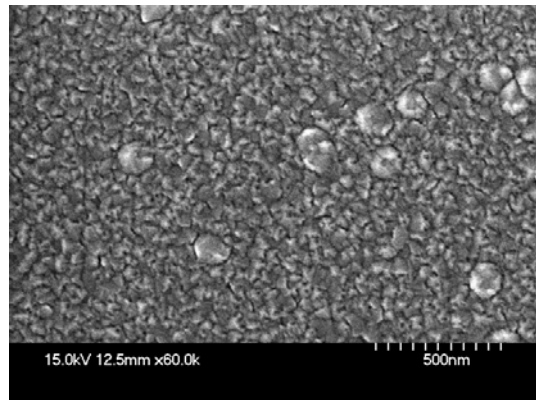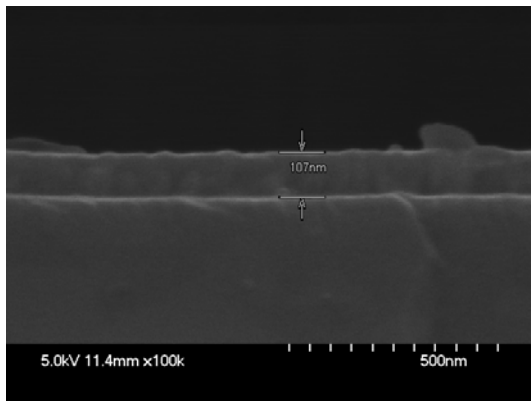(a) cross- section   (b) plane-view

Fig.3-22   The substrate temperature is 500   , RF power is 100W and flow rate of
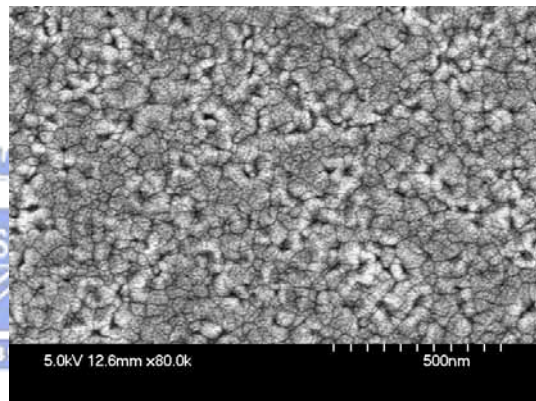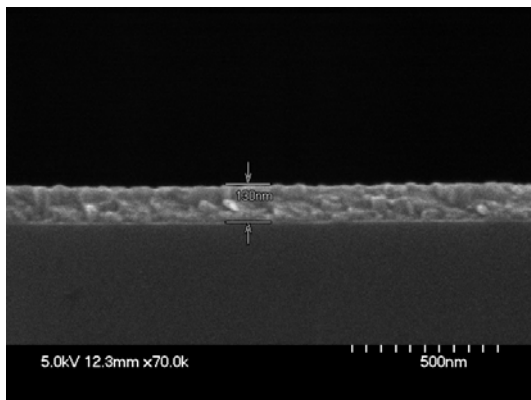N₂O is 2sccm.
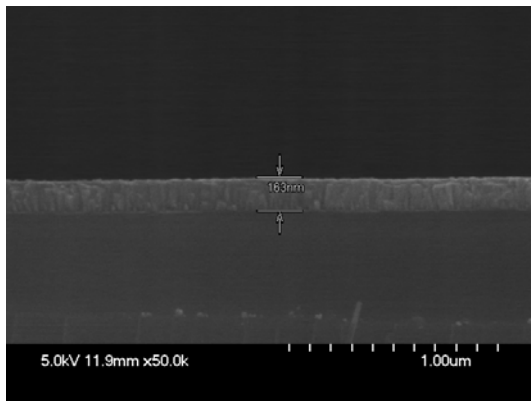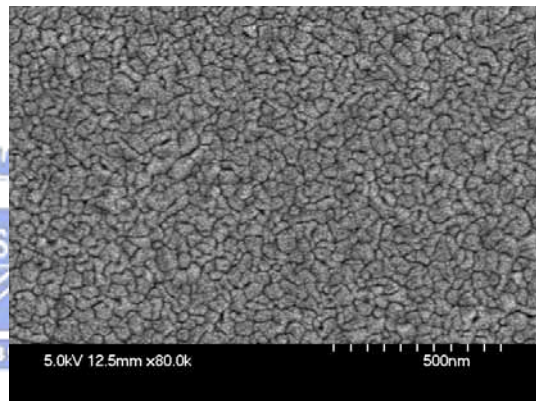
(a) cross- section   (b) plane-view
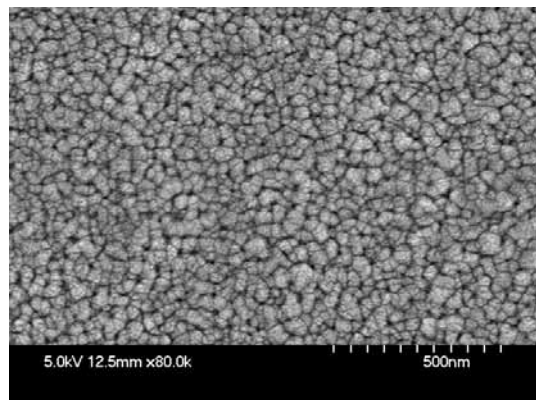
Fig.3-23   The substrate temperature is 400   , RF power is 100W and flow rate of
N₂O is 2sccm.

(a) cross- section   (b) plane-view

Fig.3-24   The substrate temperature is 300   , RF power is 100W and flow rate of
N₂O is 2sccm.

(a) cross- section	(b) plane-view

Fig.3-25 The substrate temperature is 500 , RF power is 80W and flow rate of N_2O is 5sccm.

(a) cross- section	(b) plane-view

Fig.3-26 The substrate temperature is 400 , RF power is 80W and flow rate of N_2O is 5sccm.
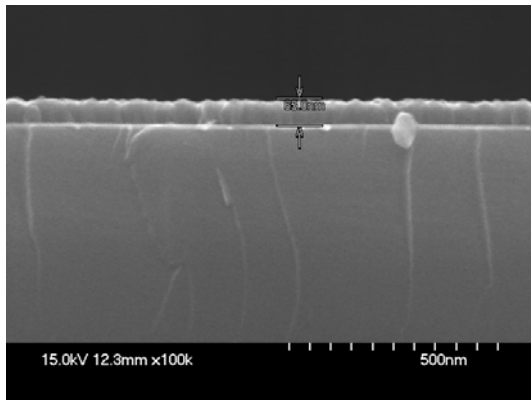

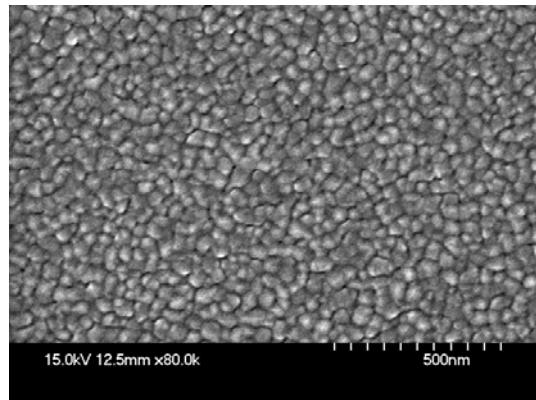|	
(a) cross- section	(b) plane-view

Fig.3-27 The substrate temperature is 300 , RF power is 80W and flow rate of N_2O is 5sccm.
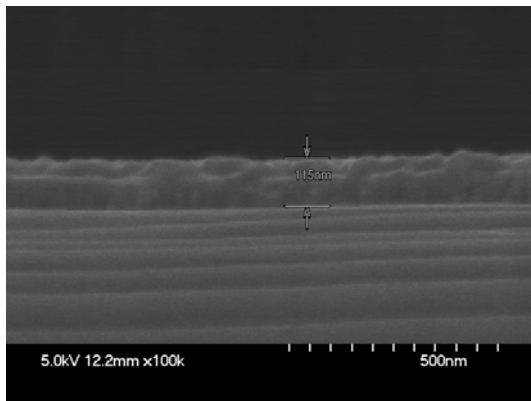
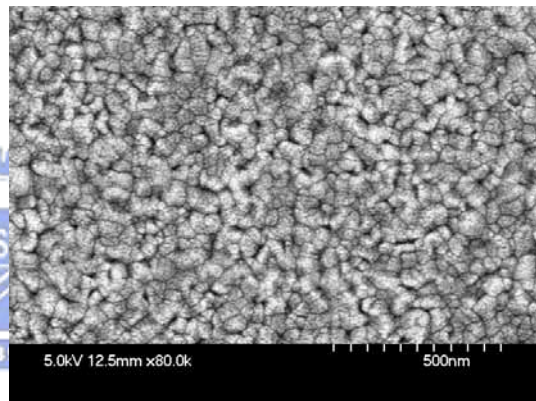(a) cross- section   (b) plane-view

Fig.3-28   The substrate temperature is 500   , RF power is 80W and flow rate of N_2O
            is 2sccm.
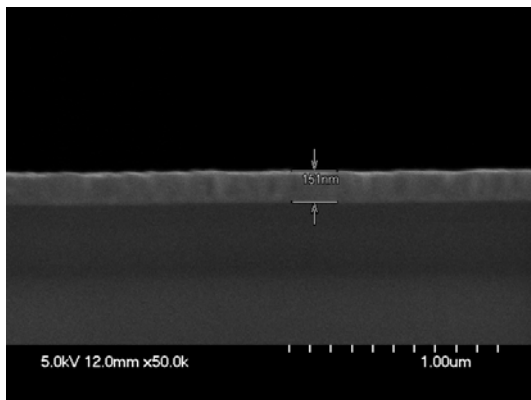

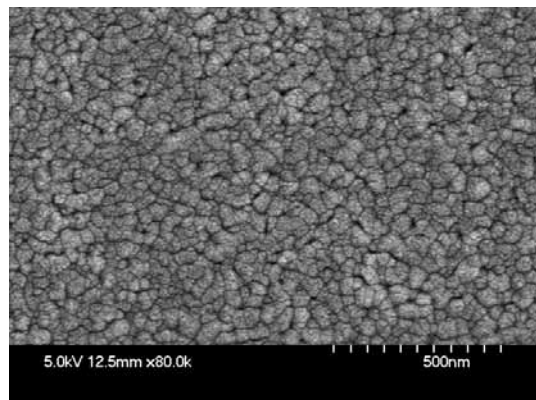(a) cross- section   (b) plane-view

Fig.3-29   The substrate temperature is 400   , RF power is 80W and flow rate of N_2O
            is 2sccm.

(a) cross- section   (b) plane-view
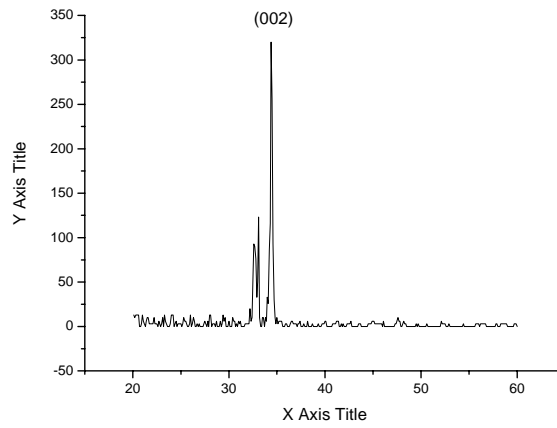
Fig.3-30   The substrate temperature is 300   , RF power is 80W and flow rate of N_2O
            is 2sccm.

(a)The substrate temperature is 500
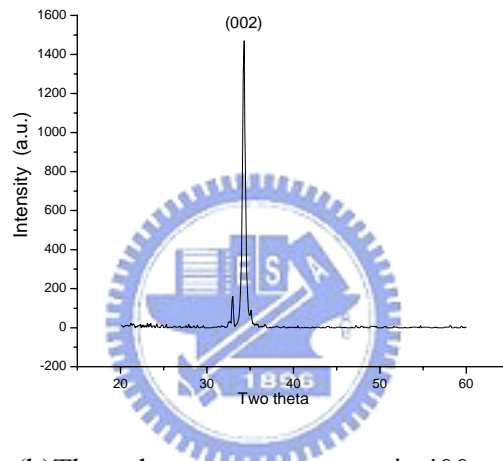
(b)The substrate temperature is 400
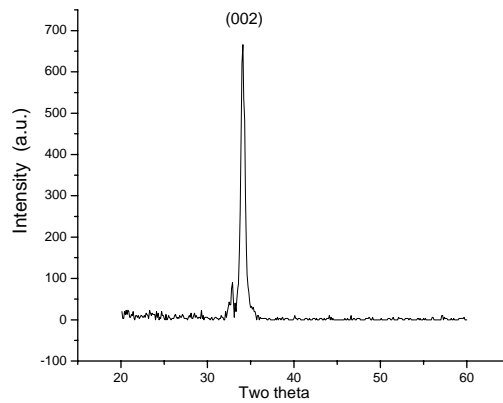
(c)The substrate temperature is 300

Fig.3-31   XRD pattern of ZnO films grown under conditions: RF power 100W, flow
rate 5sccm and (a)500 , (b)400 , (c)300   as substrate temperatures.

(a)The substrate temperature is 500

(b)The substrate temperature is 400

(c)The substrate temperature is 300

Fig.3-32　XRD pattern of ZnO films grown under conditions: RF power 100W, flow
rate 2sccm and (a)500　, (b)400　, (c)300　　as substrate temperatures.

(a)The substrate temperature is 500

(b)The substrate temperature is 400

(c)The substrate temperature is 300

Fig.3-33   XRD pattern of ZnO films grown under conditions: RF power 80W, flow
rate 5sccm and (a)500   , (b)400   , (c)300   as substrate temperatures.
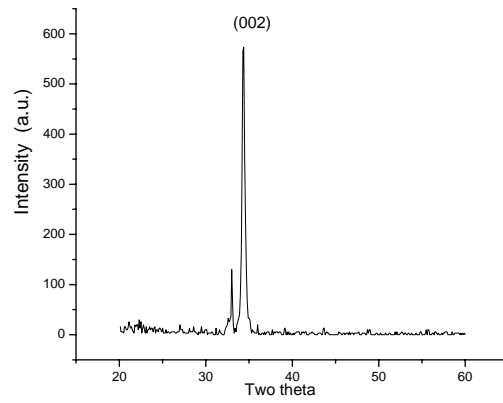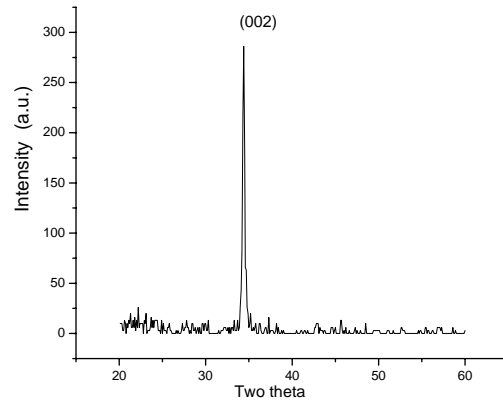
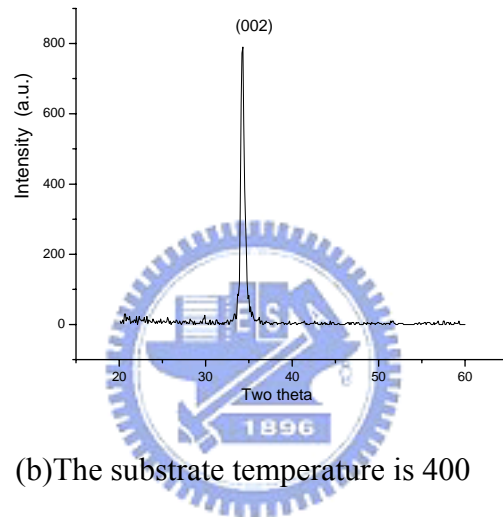(a)The substrate temperature is 500
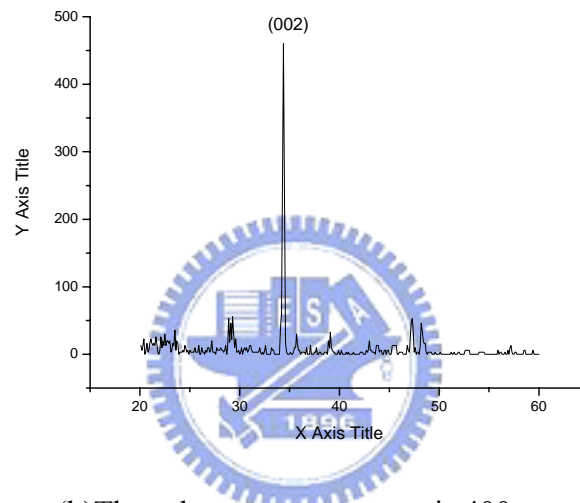
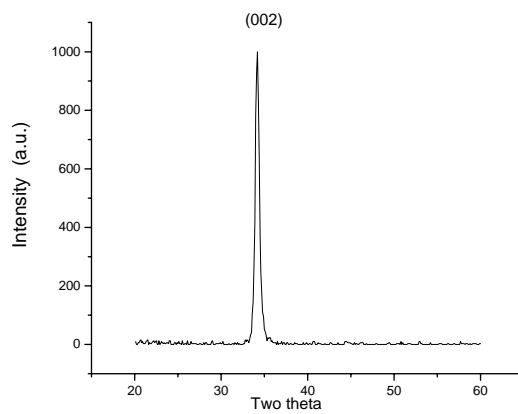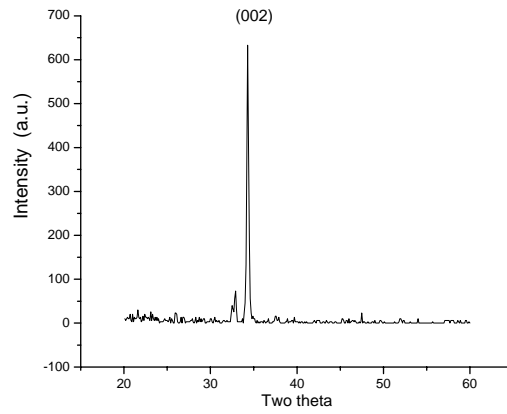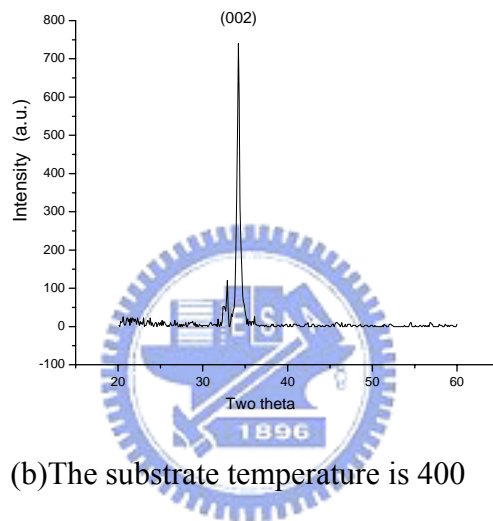(b)The substrate temperature is 400
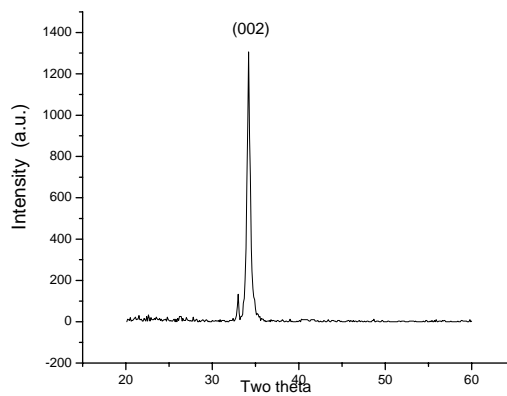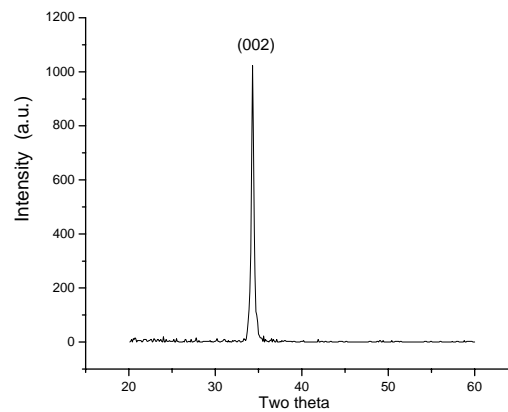

(c)The substrate temperature is 300

Fig.3-34　XRD pattern of ZnO films grown under conditions: RF power 80W, flow
rate 2sccm and (a)500 , (b)400 , (c)300 as substrate temperatures.

Table   Electrical properties of ZnO films prepared with nitrous oxide under various growing conditions

Growing \ Data condition	Carrier Type	Carrier Concentration (cm^{-3})	Resistivity (Ω-cm)
N$_2$O,100W, 5sccm 500	P	1.865 x 10^{16}	0.304
N$_2$O,100W, 5sccm 400	P	4.5 x 10^{16}	0.16
N$_2$O,100W, 5sccm 300	P	2.36 x 10^{15}	2.37
N$_2$O,100W, 2sccm 500	P	7.5 x 10^{16}	0.096
N$_2$O, 100W, 2sccm 400	P	7.7 x 10^{15}	0.97
N$_2$O, 100W, 2sccm 300	P	1.41 x 10^{17}	0.031
N$_2$O,80W, 5sccm 500	---	-------	-------
N$_2$O,80W, 5sccm 400	P	1.52 x 10^{15}	5.2
N$_2$O,80W, 5sccm 300	---	-------	-------
N$_2$O,80W, 2sccm 500	P	2.24 x 10^{17}	0.023
N$_2$O,80W, 2sccm 400	---	-------	-------
N$_2$O,80W, 2sccm 300	P	2.175 x 10^{17}	0.026

(a)Carrier concentration   (b)Resistivity
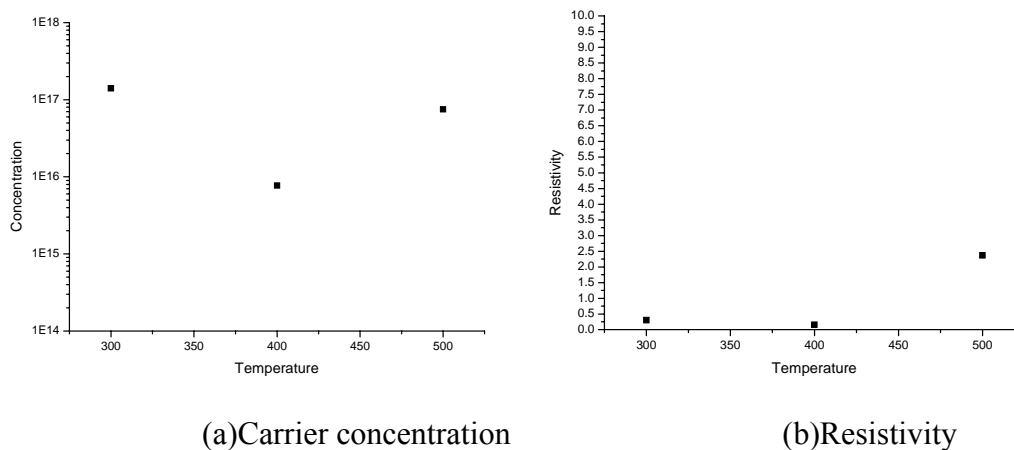
Fig.3-35　Carrier concentration and resistivity of p-type ZnO thin films with different substrate temperature under the growth condition of 100W, 5sccm

(a)Carrier concentration   (b)Resistivity

Fig.3-36　Carrier concentration and resistivity of p-type ZnO thin films with different substrate temperature under the growth condition of 100W, 2sccm

Table   Deposition methods and properties of ZnO thin films

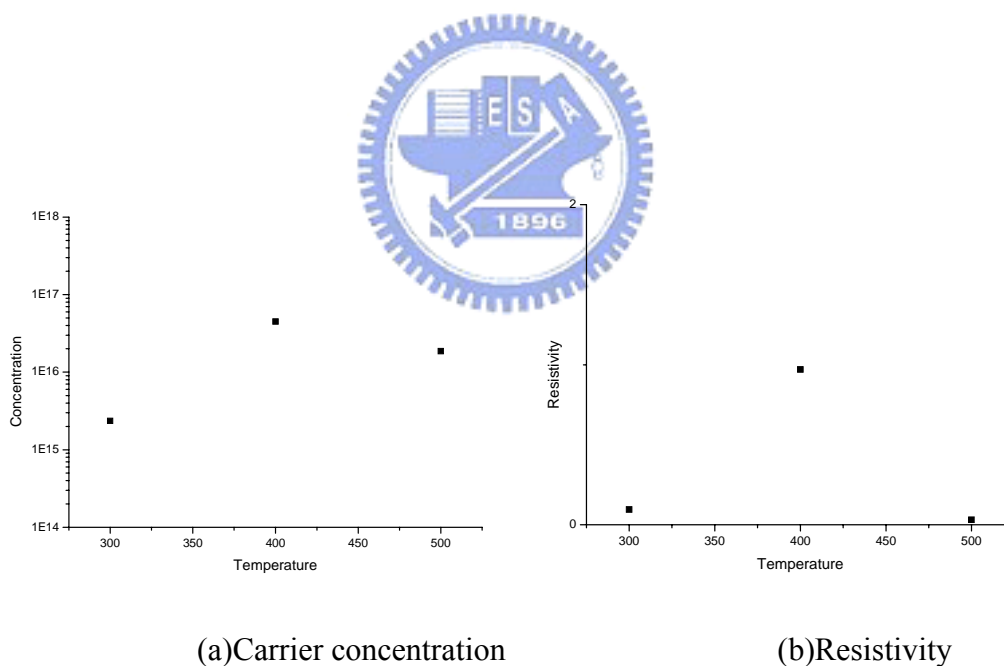| Method	growing ambient	properties
metal organic CVD[20]	carrier gas argon and nitrogen precursors diethyl zinc and oxyhen substrate sapphire	optical and surface acoustic wave properties is close to single-crystal ZnO
pulsed laser deposition[21]	substrate sapphire	electrical and optical properties of the films were improved with increasing the film thickness
Molecular beam epitaxy[39]	gas zinc and oxygen substrate sapphire	Carrier mobility $42cm^2V^{-1}S^{-1}$ Carrier concentration: $10^{19}cm^{-3}$
Sputtering[18]	gas argon and oxygen substrate p-type silicon	increasing O_2 and Ar ratio, visible emission was drastically suppressed without sacrificing the band-edge emission intensity
sol-gel[17]	solution zinc acetate and aluminum nitrate substrate glass	low resistivity 1.5×10^{-4} Ωcm max transmission about 91%
Pulsed laser dposition Ga and N codoping[36]	Substrate: Corning #7059 glass Gas: N_2 or N_2O	Hole conventration:$4\times10^{19}cm^{-3}$ Resistivity: 2 -cm
LP-MOCVD[35]	Gas: O2 and NO Zinc source: diethyl zinc Substrate : Corning #1737 glass	Carrier concentration: $10^{15}\sim10^{18}cm^{-3}$ Mobility: $10^{-1}cm^2V^{-1}S^{-1}$ Minimum resistivity: 20 -cm
Present	Gas: N2O Substrate: p-type silicon	Carrier concentration: $10^{15}\sim10^{17}$ cm^{-3} Resistivity: 0.2 -cm

Chapter 4

Conclusion

4-1 Conclusion:

In our experiment, we obtain the p-type zinc oxide thin films by using pure nitrous oxide gas successfully, but did not realize by using pure nitrogen gas. From the XRD patterns, we found the intensities of the films grown under nitrous oxide gas are smaller than those grow under nitrogen gas, so we presume that the amount of N element diffusing into the ZnO thin films from nitrous oxide is more than it comes from nitrogen, and it would damage the crystallization of zinc oxide thin films. The electrical characteristics are determined by Hall measurement, and we find the films prepared under nitrous oxide gas are all p-type. Demonstrating that there are many N element doping into the films from nitrous oxide gas. The carrier concentrations of the p-type zinc oxide thin films are $10^5 \sim 10^{17}$ cm^{-3}, and the highest carrier concentration is 2.24 x 10^{17} cm^{-3}, it is consistent with other reports, and the resistivity are of low values about 0.2~0.3 -cm, with the lowest resistivity being 0.023 -cm. And we find that the RF power of 80W, and the flow rate of N_2O 2sccm are the optimum growth conditions for zinc oxide thin films growth, yielding the highest carrier concentration and the lowest resistivity.

Reference

[1]   R. E. I. Schropp and A. Madan, J. Appl. Phys. **66**, 2027 (1989).

[2]   Satoshi Masuda, Ken Kitamura, Yoshihiro Okumura, Shigehiro Miyatake,

       Hitoshi Tabata, and Tomoji Kawai, J. Appl. Phys. **93**, 1624 (2003).

[3]   G. Grosso, G.P. Parravicini, Solid State Physics, Cambridge University
       Press,Cambridge,2000

[4]   D. G. Thomas: J. Phys. Chem. Solids **15**, 86 (1960) .

[5]   Y. Segawa, A. Ohtomo, K. Kawasaki, H. Koinuma, Z. K. Tang, P. Yu
       and K. L. Wong: Phys. Status Solidi B **202,** 669 (1997).

[6]   Shulin Gu, Rong Zhang, Jingxi Sun, Ling Zhang, and T. F. Kuech, Appl. Phys.

       Lett. **76**, 3454 (2000).

[7]   K. Negita, T. Yamaguchi, T. Tsuchie, and N. Shigematsu, Appl. Phys. Lett. **82**,
       2844 (2003).

[8]   G. A. Hirata, J. McKittrick, J. Siqueiros, O. A. Lopez, T. Cheeks, O. Contreras,

       and J. Y. Yi, J. Vac. Sci. Technol. A **14**, 791 (1996).

[9]   A. V. Singh, R. M. Mehra, Nuttawuth Buthrath, Akihiro Wakahara, and Akira

       Yoshida, J. Appl. Phys. **90**, 5661 (2001).

[10]   Yves Noel, Miquel Llunell, Roberto Orlando, Philippe D'Arco, and Roberto

       Dovesi, Phys. Rev. B **66**, 214107 (2002).

[11]   B. D. Yao, Y. F. Chan, and N. Wang, Appl. Phys. Lett. **81**, 757 (2002).

[12]   W. I. Park, D. H. Kim, S.-W. Jung, and Gyu-Chul Yi, Appl. Phys. Lett. **80**, 4232

       (2002).

[13]   Lê Thiên-Nga, Jean-Marc Bonard, Richard Gáal, László Forró, and Klara

       Hernadi, Appl. Phys. Lett. **80**, 850 (2002).

[14]   A. M. Morales, C. M. Lieber, Science **279**, 208 (1998).

[15]   G. S. Cheng, S. H. Chen, X. G. Zhu, Y. Q. Mao, L. D. Zhang, Mater. Sci. Eng.

       A **286**, 165 (2000)

[16] Y. Li, G. W. Meng, and L. D. Zhang, Appl. Phys. Lett. **76**, 2011 (2000).

[17] M. J. Alam and D. C. Cameron, J. Vac. Sci. Technol. A **19**, 1642 (2001).

[18] Sang-Hun Jeong, Bong-Soo Kim, and Byung-Teak Lee, Appl. Phys. Lett. **82**, 2625 (2003).

[19] Hee-Bog Kang, Kiyoshi Nakamura, Sung-Hwan Lim, and Daisuke Shindo, Jpn. J. Appl. Phys., Part 1 **37**, 781 (1998).

[20] C. R. Gorla, N. W. Emanetoglu, S. Liang, W. E. Mayo, Y. Lu, M. Wraback, and H. Shen, J. Appl. Phys. **85**, 2595 (1999).

[21] Jae-Min Myoung, Wook-Hi Yoon, Dong-Hi Lee, Ilgu Yun, Sang-Hyuck Bae, and Sang-Yeol Lee, Jpn. J. Appl. Phys., Part 1 **41**, 28 (2002).

[22] Takahiro Matsumoto, Hiroyuki Kato, Kazuhiro Miyamoto, Michihiro Sano, Evgeniy A. Zhukov, and Takafumi Yao, Appl. Phys. Lett. **81**, 1231 (2002).

[23] Z. Y Ning, S. H. Cheng, S. B. Ge, Y. Chao, Z. Q. Gang, Y. X. Zhang, and Z. G. Liuet, Thin Solid Films 307, 50 (1997).

[24] T. Minami, H. Sato, H. Nanto, and S. Takata, Jpn. J. Appl. Phys.,Part 2 24, L781 (1985).

[25] D. G. Thomas: J. Phys. & Chem. Solids **9,** 31 (1959).

[26] J. J. Lander: J. Phys. & Chem. Solids **15,** 34 (1960).

[27] Y. Sato and S. Sato: Thin Solid Films **281–282,** 445 (1996).

[28] K. Minegishi, Y. Koiwai, Y. Kikuchi, K. Yano, M. Kasuga and A. Shimizu: Jpn. J. Appl. Phys. **36,** L1453 (1997).

[29] G. D. Mahan, J. Appl. Phys. 54, 3825 (1983).

[30] Fumiyasu Oba, Shigeto R. Nishitani, Seiji Isotani, and Hirohiko Adachi, J. Appl. Phys. 90, 824 (2001).

[31] S. B. Zhang, S. H. Wei, and A. Zunger, J. Appl. Phys. 83, 3192 (1998).

[32] Gang Xiong, John Wilkison, Brian Mischuck, S. Tüzemen, k. B. Ucer, and R. T.

51

Williams, Appl. Phys. Lett. 80, 1195 (2002).

[33]   D. J. Chadi, Phys. Rev. B **59**, 15181 (1999).

[34]   C. H. Park and D. J. Chadi, Phys. Rev. Lett. 75, 1134 (1995).

[35]   X. Li, Y. Yan, T. A. Gessert, C. DeHart, C. L. Perkins, D. Young, and T. J. Coutts, Electrochemical and Solid-State Letters, 6 (4) C56-C58 (2003).

[36]   Mathew Joseph, Hitoshi Tabata and Tomoji Kawai, Jpn. J. Appl. Phys. Vol. 38 pp. L1205-L1207 (1999).

[37]   A. V. Singh and R. M. Mehra, A.Wakahara and A. Yoshida, J. Appl. Phys. 93, 396 (2003).

[38]   D. A. Neamen, Semiconductor Physics and Device   Basic principles, 2nd ed., McGraw-Hill Companies, USA, 1997

[39]   Takeshi Ohgaki, Naoki Ohashi, Hirofumi Kakemoto and Satoshi Wada, Yutaka Adachi and Hajime Haneda, Takaaki Tsurumi, J. Appl. Phys. 93, 1961(2003)

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（民國 91 年 9 月---民國 93 年 6 月）

論文題目：

正型氧化鋅薄膜之製備及電學性質之研究

The preparation of P-type ZnO thin films and the research for the electrical characteristics