Thesis for the Degree of Master of Science

Dielectric properties of Li-doped ZnO thin films prepared by pulsed laser deposition

by

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The graduate school

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(PLD 방법으로 증착한 Li 이 첨가된 ZnO 박막의 유전 특성 연구)

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By

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Abstract

ZnO is becoming more and more popular third-generation semiconductor for its wide band gap and large exciton binding energy. But the pure ZnO gradually can’t meet the people’s demands in nowadays, then impurity doping and the using of the defects which can improve and enlarge the properties are hot spot in nowadays. This article introduces the way of Li doped into ZnO. Thin films of Li-doped ZnO with different compositions ($Zn_{1-x}Li_xO$, x = 0.02-0.2) have been prepared on heavily doped Si substrates by a pulsed laser deposition technique, and we get the good quality transparent conducting oxides thin film with a ferroelectric nature. Through many substantial tests, theoretical studies and comparisons to the conclusions in hand, our mainly contents as following:

1. We choose the Li element doped into the ZnO and the impurities are well doped into the ZnO; the impurities affect little to the structure of the ZnO.
2. The thin films are made by the PLD method, and the structure of the crystal in the thin film grows well follow the c-axis. The ferroelectricity of the thin film

$Zn_{0.88}Li_{0.12}O$ is observed in the P-E hysteresis loop test ,and E_c is 5.53 KV/cm and P_r is 0.186 μc/cm^2

3. The permittivity of the $Zn_{1-x}Li_xO$ is involved with the temperature and the frequencies. And we also find a crest in the test around certain temperature, so we can call the change temperature T_c for short , for example, the T_c of the $Zn_{0.85}Li_{0.15}O$ is about 95℃

4. The optical transmission of the .$Zn_{1-x}Li_xO$ thin films are good, most are over 75%; through the calculation with the test dates, we can roughly get the academic thickness of the thin film, which is coincide with the actual result.

Chapter1. Basic properties and applications of ZnO

1.1 Introduction

In the recent years, people keep a high enthusiasm in studying zinc oxide. As we all know the ZnO has been widely used since 1935[1]. Why people pay much attention to the material for a so long time? And what's the aporia in this kind of "common thing"? The renewed interest in this material has been over the development of growth technologies for the fabrication of high quality single crystals and epitaxial layers but risen to the realization of ZnO-based electronic and optoelectronic devices.

Silicon is the most common semiconductor in our life and is called the first generation, and the second-generation semiconductor which is risen in 90s last century absolutely changed our life. As the third generation representative, ZnO, which is with a wide bandgap of 3.4 eV and a large exciton binding energy of 60 meV at room temperature semiconductor, what attract us?

Materials，traffic，energy sources and information is the backbones of the mordent society developing. In the new 21-st century, as the leader of the industries, semiconductor, IT industries, prominently developed. On the other hand, the IT industry largely depends on the exploitations of the semiconductor. A semiconductor is a material that has an electrical conductivity between that of a conductor and an insulator. It is the basic material in making transistor, integrated circuit, electronic components, which are supporting communication, computer, information applications and network technology.

From the 50s last century, the 1st-generation semiconductor silicon and correlative materials replace the ponderous electron tube and start a integrated circuit time. The living standard and society feathered promote while the IT industry developed. But the narrow band gap, electronic mobility and low breakdown voltage hinder the further development. Then about 20 years later, GaAs, InP, GaP, InAs, AlAs and their alloys come up to the world. They and the application of laser accelerate fiber-optical communication technology, human beings entered the information time.

Recent years, blue and green LED laser short-wave photoelectric devices show a great application and perspective, the 3rd-generation wide band gap semiconductor ($Eg > 2.3eV$), including SiC, ZnSe, silicon and GaN fighting for people's eyeballs. Compare to previous generations, the most important characteristic is owning wide band gap and can give out the shorter wave-length blue light than red light. It can meet the demand of high power, high temperature, high frequency devices.

GaN is the most successful 3rd-generation semiconductor in application till now, but the expensive production equipments, rare substrate materials, demanding condition of preparation restraint its further application. So, it is signality to try to find a "suitable" new material to overcome the defects.

As one of the 3rd-generation semiconductor—ZnO, not only in lattice structure, constant, but also band gap is similar to GaN. Besides, ZnO has other advantages: first, the excitonic binding energy is as high as 60meV, is about 3 times of GaN. This means the excitonics are more stable and can be used to made high-efficiency luminescent devices; second, ZnO is a kind of cheap, no poison and no pollution, good thermal stability, low epitaxial temperature material. And so, ZnO tends to be the hot off the press domain of international semiconductor.

1.2 Crystal structure and lattice parameters of ZnO

At ambient pressure and temperature, ZnO crystallizes in the wurtzite (B4 type) structure, as shown in figure 1.1. This is a hexagonal lattice, belonging to the space group $P6_3mc$, and is characterized by two interconnecting sub lattices of Zn^{2+} and O^{2-}, such that each Zn ion is surrounded by tetrahedra of O ions, and vice-versa.

This tetrahedral coordination gives rise to polar symmetry along the hexagonal axis. This polarity is responsible for a number of the properties of ZnO, including its piezoelectricity and spontaneous polarization, and is also a key factor in crystal growth, etching and defect generation. The four most common face terminations of wurtzite ZnO are the polar Zn terminated (0001) and O terminated $(000\bar{1})$ faces (c-axis oriented), and the non-polar $(11\bar{2}0)$ (a-axis) and $(10\bar{1}0)$ faces which both contain an equal number of Zn and O atoms. The polar faces are known to posses different chemical and physical properties, and the O-terminated face possesses a slightly different electronic structure to the other three faces[3]. Additionally, the polar surfaces and the (1010) surface are found to be stable, however the $(11\bar{2}0)$ face is less stable and generally has a higher level of surface roughness than its counterparts. The (0001) plane is also basal.

Aside from causing the inherent polarity in the ZnO crystal, the tetrahedral coordination of this compound is also a common indicator of sp3 covalent bonding. However, the Zn–O bond also possesses very strong ionic character, and thus ZnO lies on the borderline between being classed as a covalent and ionic compound, with an ionicity of $f_i = 0.616$ on the Phillips ionicity scale [4]. The lattice parameters of the hexagonal unit cell are a=3.2495Å and c=5.2069 Å, and the density is 5.605 g cm^{-3} [5].

In an ideal wurtzite crystal, the axial ratio c/a and the u parameter (which is a measure of the amount by which each atom is displaced with respect to the next along the c-axis) are correlated by the relationship uc/a=(3/8)1/2, where c/a=(8/3)1/2 and u=3/8 for an ideal crystal. ZnO crystals deviate from this ideal arrangement by changing both of these values. This deviation occurs such that the tetrahedral distances are kept roughly constant in the lattice. Experimentally, for wurtzite ZnO, the real values of u and c/a were determined in the range u=0.3817–0.3856 and c/a=1.593–1.6035 [6–8].

Additional to the wurtzite phase, ZnO is also known to crystallize in the cubic zincblende and rocksalt (NaCl) structures, which are illustrated in figure 1.2. Zincblende ZnO is stable only by growth on cubic structures [9–11], whilst the rocksalt structure is a high-pressure metastable phase forming at 10 GPa, and cannot be epitaxially stabilized [12]. Theoretical calculations indicate that a fourth phase, cubic cesium chloride, may be possible at extremely high temperatures, however, this phase has yet to be experimentally observed [13].

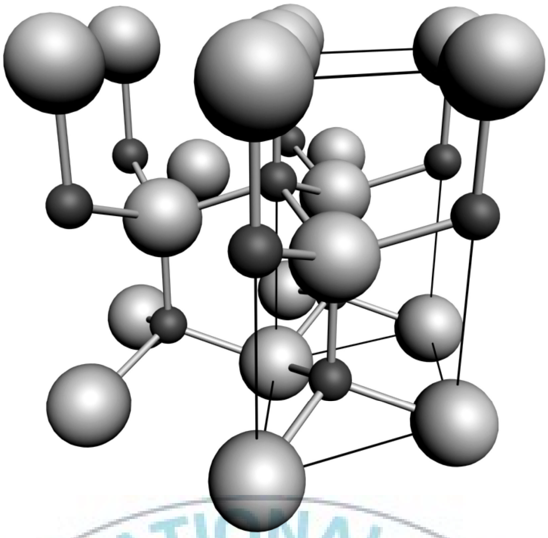


Figure 1.1: The hexagonal wurtzite structure of ZnO. O atoms are shown as large white spheres, Zn atoms as smaller black spheres. One unit cell is outlined for clarity.

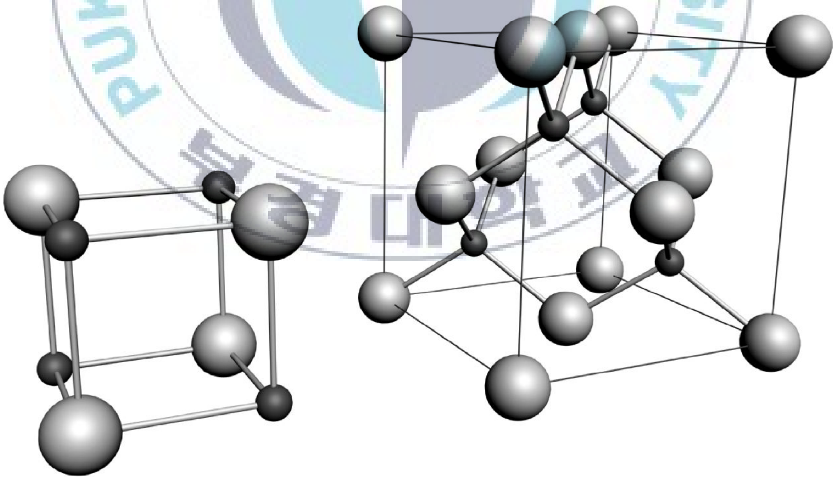


Figure 1.2: The rock salt (left) and zincblende (right) phases of ZnO. O atoms are shown as white spheres, Zn atoms as black spheres. Only one unit cell is illustrated for clarity.

1.3 Physical properties of the ZnO

In the table 1.1, the conmen properties of the ZnO are shown, it is comfortable for our reading.

Table 1.1 Some physical constants of crystal ZnO (compared to Si and GaN)[14]

physical constant	Si	ZnO	GaN
crystal structure (300K)	cubic	wurtzite	wurtzite
lattice constant a (nm)	0.5431	0.32495	0.3189
lattice constant c (nm)	--	0.52069	0.5186
Atoms number （/cm^3 ）	5.00	4.15	4.25
Molecular weight （M）	28.09	81.38	83.73
band series	Indirect	Direct	Direct
Band gap E_g (300K)	1.12	3.37	3.44
Density ρ(g/cm^3)	2.329	5.606	6.15
melting point	1412	1975	＞1700

Tm (℃)			
thermal conductivity σ_v (W/cm K)	1.31	1.2	1.5
dielectric constant ε	11.9	7.9	9.5
Exciton binding energy (meV)	--	60	28
Intrinsic carrier concentration	28.09	81.38	83.73
effective mass of electron $m_e \cdot (m_0)$	0.26	0.24	0.2
effective mass of hole $m_h \cdot (m_0)$	0.69	0.59	0.8
μ_e (300K, $cm^2V^{-1}s^{-1}$)	1450	200	900
μ_h (300K, $cm^2V^{-1}s^{-1}$)	505	5-50	10

1.4 Dielectric of the ZnO

1.4.1 Piezoelectric and thermoelectricity of ZnO

ZnO is the wurtzite crystal without symmetric center and with the polarity follow the c-axis, Zn (0001) and O (0001) are different polar planes. ZnO is a kind of piezoelectric and thermoelectricity materials for its high electromechanical coupling coefficients and low permittivity. It can be used in surface acoustic wave device, body surface wave device, pressure-sensitive device, air-sensitive device, catalyzer and battery, electronmechanical regulator.

Till now, the most nature application is SAW. As the increase of digital transmission and contact information transport quantity, the requirement of the SAW is over 1GHz high frequency because the ZnO with the good high frequency property. And it is widely used in the high-frequency filter, resonator, optical waveguide and etc. fig 2.6 shows the sound wave resonant cavity made by ZnO thin film, ZnO deposits on the Si substrate and forms the optical waveguide structure. The electrode may be Al or Au/Cr, and the structure is with good High-Frequency Response ability.

1.4.2 Ferroelectric and ferromagnetic properties of ZnO

For ZnO follows the c-axis polar, and the polar plane, surface polarization of its structure make it with ferroelectric and to be a good material of t polar ferroelectric property studying. Curie temperature of the intrinsic ZnO is approximately 330K; in general, Tc will arise with the increasing of the band gap. ZnO is a kind of good Diluted magnetic semiconductors material, elements of the transition state usually well Solvent in the ZnO, and they are Mn, Ni, Fe, Co …

1.5 Application of the ZnO

The applications of zinc oxide powder are numerous, but this part in not important one, so there only a brief summaries of the daily use of the ZnO. Consequently, it is added into various materials and products, including: rubber, plastic, ceramics, pharmaceutical industry, cosmetics, adhesives, mastics, sealants, photocopying, lubricants, paints, cigarette filters, sulfur removal, foods and food-packaging materials, fire retardants, ferrites, batteries, fuel cells, photocells, thermoelements, silicate, silicate compositions, fungicides, portland cement, etc. [15]

Chapter2. Theories of the impurities doped into the ZnO

2.1 Intrinsic defect of ZnO and the doping difficulty

2.1.1 Intrinsic defect of ZnO

As the semiconductor, the electrical properties are closely related to the defects and impurities in the ZnO. Full comprehending the defects and impurities can improve our knowledge and work. The wurtzite structure of the ZnO can be seen as the O atoms hexagonal and the Zn in the a half of the tetrahedral interstices and the other is empty. This kind of structure is open and the impurities can be easily doped. The open structure can also affect the formation of the defects. In the intrinsic ZnO thin film, there are six kind of intrinsic point defects: vacant Zn (V_{Zn}), vacant O (V_O), interval Zn (Zn_i), interval O (O_i), (Zn_O), (O_{Zn}). Investigators tried many ways to study defects in the ZnO, for example: Electron paramagnetic resonance (EPR)[15,16];Cathodoluminescence (CL)[17]; Deep level transient spectroscopy (DLTS)[18,19]; E-annihilation spectra[20,21]; Perturbed angular correlation spectroscopy[22], etc. The results show that the Zn_i and V_o are main factors affecting ZnO properties. But people argue without reaching a decision on which defect takes the dominant position.

Kohan calculated the formation energies of the defects through the first-principles plane wave pseudo potential way [23]. We can see that, in the Zn-rich condition, the formation energy of V_o is the lowest, so the main defect is Vo; in the

O-rich condition, the formation energy of V_{zn} is the lowest, so the main defect is V_{zn}. It is clear the main defects are V_o and V_{zn}, but which is more will depend on the Zn amount.

Figure 2.3, Y.sun, through FP-LMTO (full potential linear muffin-tin orbital) calculated the theoretical value of perfect crystal and effect four kinds of defects to the ZnO DOS (density of states)[24]. Form the 1-5 (b) and (c) O^t_i (tetrahedral interstice O) and O^o_i (octahedral interstice O) defects sates are about 0.5eV to the band top. From the level of the Femi-energy, O^t_i defect state is full and O^o_i defect is half full. Because O^o_i change little compare to the pure ZnO DOS except it is in forbidden ban level, the interaction between the octahedral site O and adjacent atoms is weak. Zn^t_i and Zn^o_i are similar to the O^t_i and O^o_i as 1-7 shows, P.S.Xu calculate values of the defects in the wurtize ZnO[25]. V_{zn} defect state over the VBM 0.3eV, partial-filling; V_o defect state is more than V_{zn}, usually exist as follow: one is under the VBE (valence band edge) 0.15eV, one is in the middle of the forbidden band, one is in the conduction band. Forbidden band and VBE is full filled band, far from the center of conduction band, centre of forbidden band and VBE are filled band, far from the base conduction band, is deep acceptor level.

Although people go on disputing on the defects, they at least reach agreement that the V_o and Zn_i are the main defects affect the ZnO properties.

2.1.2 Impurities doping difficulty in ZnO

High carrier density, low resistance, stable electrical properties p-type ZnO are the problems in front the researchers. In the six kinds of defects, V_o is the positive electricity center, with negative coulomb attractive potential, its conduction band level moves to the low level band gap, to form the donor state. O_{zn} can attract the valence electron of adjacent atoms to form the negative charge center, value band move to the band gap to form the accepter state. From the 2.1, in six kinds of the intrinsic defects, O_i, V_{zn} are shallow accepter, Vo, Zn_i and Zn_o are donor defects. Difficulty level of formation is depending on the formation energy. V_o and Zn_i in both rich-Zn and rich-O conditions are low, may easily form in the ZnO than V_{zn} and O_i. These donors can compensate p-type shallow acceptor, this is the self-compensation effect. Another reason why it is hard to get the p-type semiconductor by purities doping is Madelung energy. In the ZnO, electronegativity of Zn is 1.65, and O is 3.44, differencing is 1.79, so the ZnO is a kind of ionic crystal. Its difficulty level of crystallization is related to its Madelung energy. When p-type doping, the Madelung energy increase with the purities doped in, while the n-type doping is just the opposite.

On the other hand, ZnO single crystal or thin film is prepared in the vacuum, so Zn is more than O. For the atomic radius of Zn is much smaller than O, so there must be interstitial Zn and oxygen vacancy, and shows the n-type electrical conductivity. At the same time, as the Ⅱ-Ⅵcompound semiconductor, there are intrinsic point defect compensation and residual impurity compensation, make the p-type ZnO preparation difficult [26].

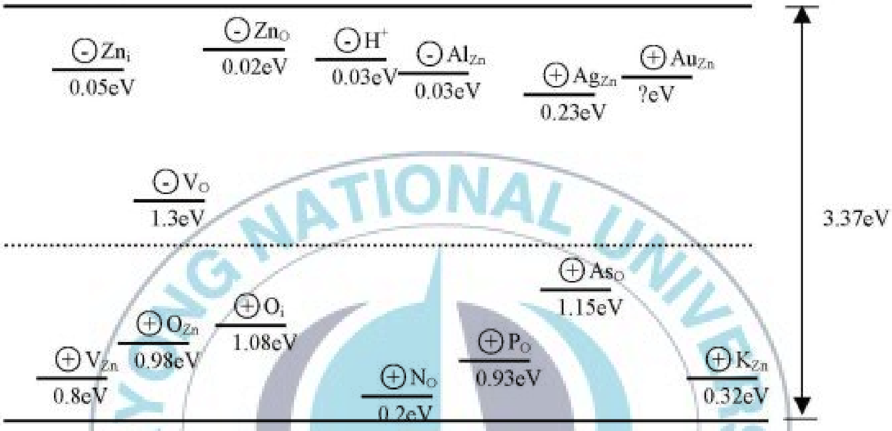


Figure 2.1 Intrinsic ZnO and the impurities energy levels

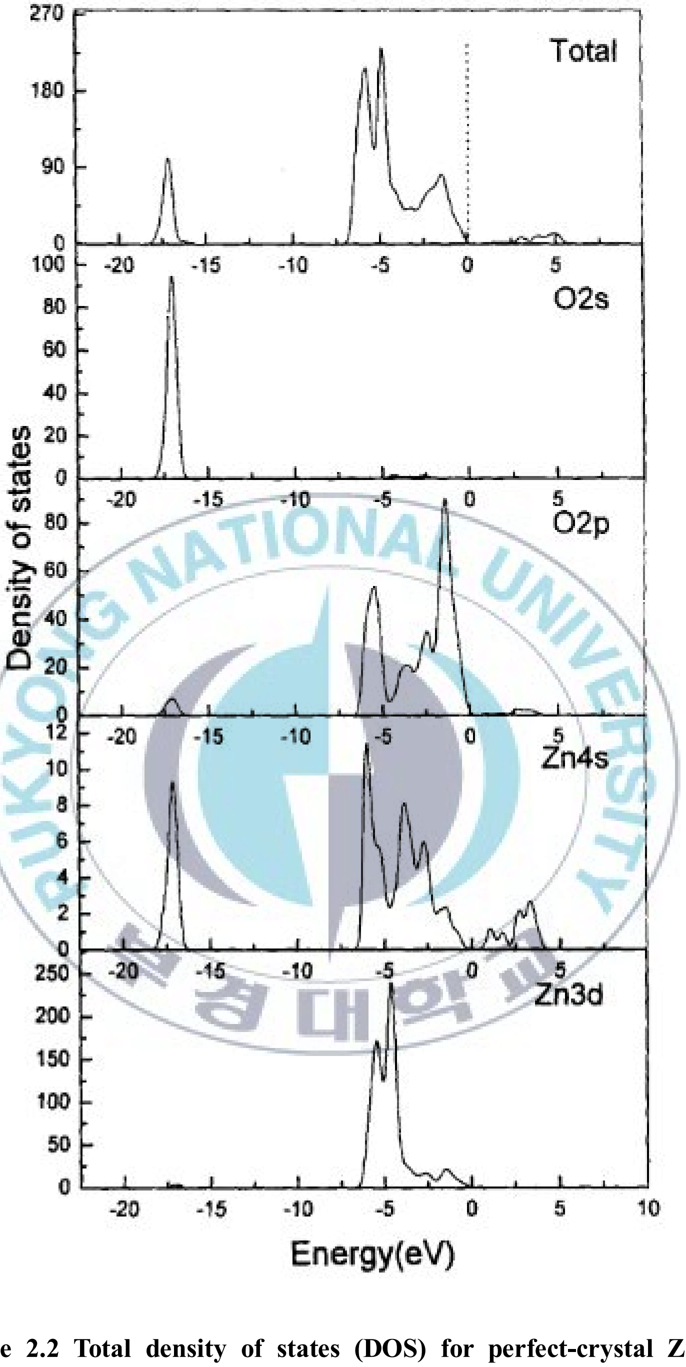


Figure 2.2 Total density of states (DOS) for perfect-crystal ZnO and partial density of states (PDOS) for O2s, O2p, Zn4s and Zn3d, respectively

2.2 Ways to get the p-type ZnO

The most common ways are group-Ⅰ elements substitution for Zn site and the other is the groupⅤelements substitution for O site donor and acceptor codoping, etc.

2.2.1 Group-Ⅰ elements doping

Through Ⅰ elements(Au, Ag, Cu, Li), substitute the Zn to form the substitution impurity, and offer the holes. Dr. Ye Zhizhen sue the DC-Ms (DC reactive magnetic sputtering) get the good electric properties Li-doped ZnO thin films. Its resistivity is 17.6 Ωcm, hall mobility is 3.47 $cm^2V^{-1}s^{-1}$, hole concentration is 1.01×10^{-3}[27, 28]. But the group-I elements Li, Na are apt to take the interstitial site to form donor defects.

2.2.2 Group-Ⅴ elements doping

ThroughⅤelements doping (N, P, As, etc) substitute the O to form the substitutional impurity, and offer the holes. Dr. Zhi Genyu through the radio frequency sputtering, at a certain O2 pressure, got the good electric property p-type ZnO. Its electrical parameter is: resistivity is 0.024 Ωcm, hall mobility is 6.9 $cm^2V^{-1}s^{-1}$, the hole concentration is $3.84*10^{19}cm^{-3}$. V-v through the PLD, got the p-type as doped ZnO thin film on the sapphire substrate, resistivity is 2.2-6.7, hall mobility is 0.83-11.4, hole concentration is 2.48×10^{17}-$1.18\times10^{18}cm^{-3}$.

2.2.3 Donor and acceptor codoping

Although the solid solubility N element is not very high, but it doesn't affect the minds of people holding .through the theoretical calculation, Yamamoto shows: Li, N doped into the ZnO, the Madelung will arise.

2.2.4 Rich-O_2 condition reaction

Besides doping the substitutional impurities, there is also a kind of way to get the p-type ZnO without any donors or acceptors. That's supply the oxygen-rich atmosphere. This kind of method is on account of "oxygen vacancies in ZnO". We supply the over excessive oxygen in order to eliminate the oxygen vacancies in the ZnO crystal. Ye Zhizhen of Zhejiang University used the plasma MOVD, intrinsic ZnO p-type conductivity on sapphire substrate. Its electrical characteristic: resistivity is 12.7Ωcm, hall mobility is 2.6 $cm^2V^{-1}s^{-1}$, hole density is $1.8\times10^{17}cm^{-3}$[29].

2.3 Theoretical study of the group-I elements doping in ZnO

Because the group-I elements ionic radius are small, so it is easy to get the interstitial impurities. The interstitial impurities two type: one is tetrahedral interstice defect and the other is octahedral interstice defect. By LEE research, octahedral is more stable, easily formed. Beside the Li_{zn}, Na_{zn} and K_{zn}, we also should consider the octahedral interstice defect Li^{o}_{i}, Na^{o}_{i} and K^{o}_{i}. Figure2.3 gives the DOS (Total density of states) of Li, Na and K replacement transfer ZnO: dotted line shows the value of Femi-energy. The DOS curves change little compare to the figure2.4 pure ZnO DOS curve, the Femi-energy move a little to low energy direction, it indicates group-I elements at the substitute position will form the acceptor energy level in the forbidden band. On the other hand, the DOS of VBM (value band edge) change little, it may because dispersibity of group-I elements impurity state is good, and form the shallow acceptor level. VBM of the ZnO is composed of O2p and a little Zn3d, so when the group-I elements substitute, the effect can be ignored. Fig 2.5 shows DOS octahedral state group-I elements, dotted line shows the value of Femi-energy compare to the high energy direction. Interstice purities in ZnO affect as donors will be compensation.

In the doping process, the concentration affects the result. Only at the high concentrate condition can get high-quality p-type thin film and the purity defects formation energy are related to the purity concentration. So we should calculate the formation energy of different defect states. q electric charge purity X in a supercell formation energy is[30]:

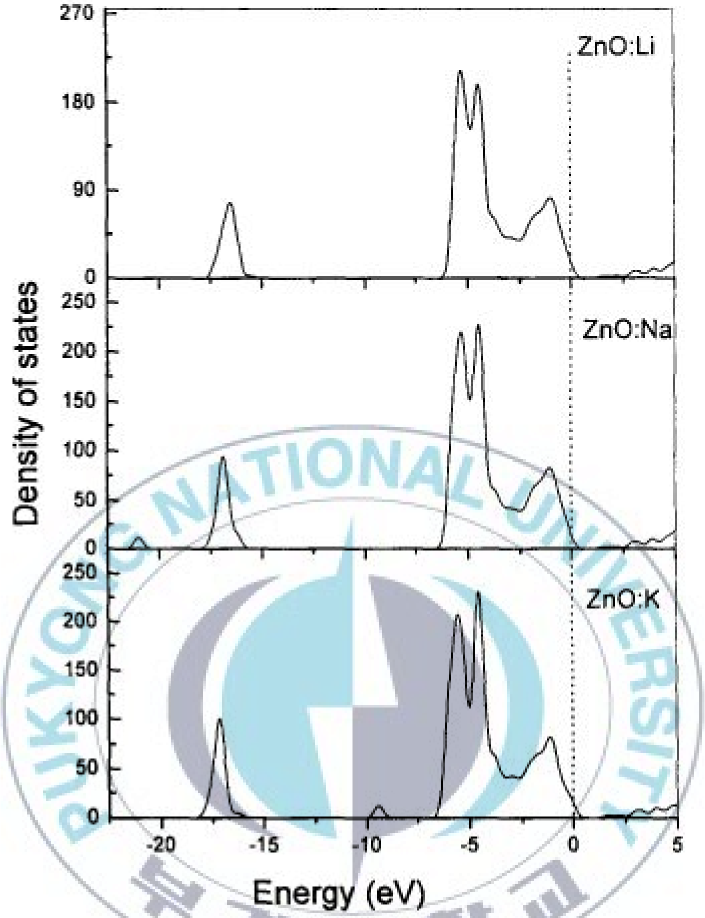


Figure 2.3 Total density of states (DOS) for ZnO doped with substitutional group-I elements

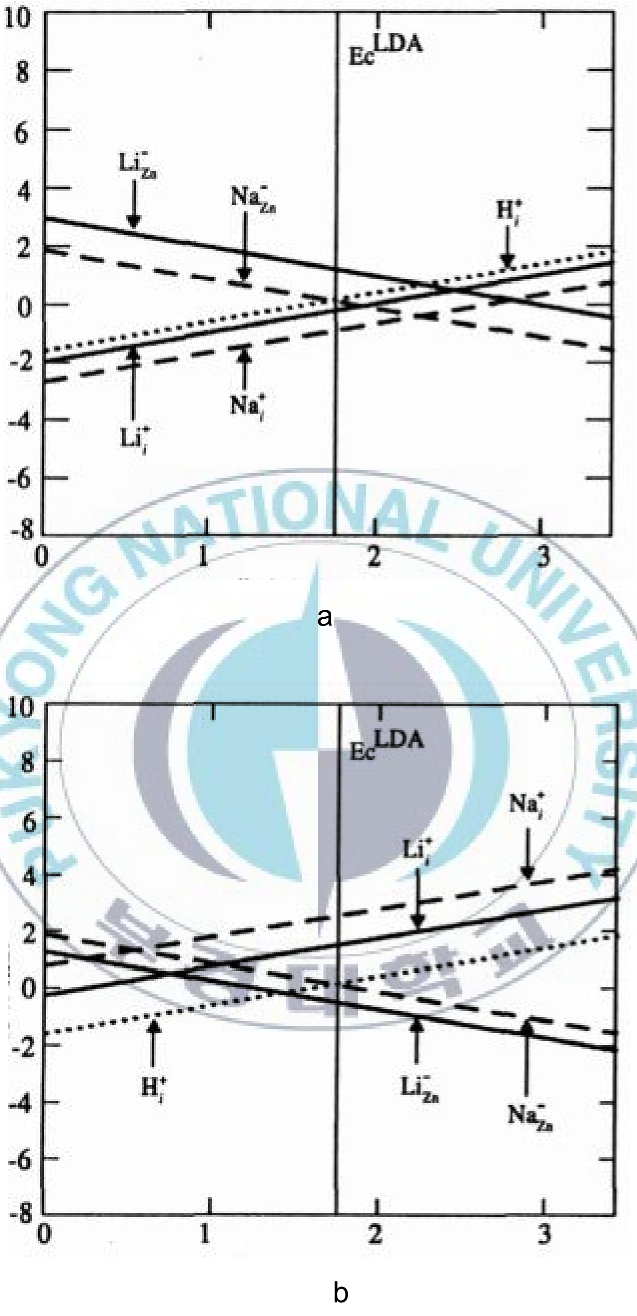


Figure 2.4 Substituted and interstitial impurities of ZnO formation energies
(a) Rich-Zn condition (b) Rich-O condition

$$E^f[X^q]=E_{tot}[X^q]-E_{tot}[bulk]-\Sigma n_i \mu_i+qE_F \tag{1}$$

$E_{tot}[X^q]$--the total energy purity filled supercell; $E_{tot}[bulk]$-- the total energy of pure supercell; n_i—the number of additional or reduce the purities in supercell; μ_i—chemical potential of the atoms; q—electric charge of the purities hold; E_F—Femi-energy.

For all the calculation processes are same, we take Li for example. Li in the ZnO has two kinds of defect state, Li_{zn} and Li_{oi}, Li_{zn} related charges are q=0 and q=+1, follow the [1]:

$$E^f[Li_{Zn}^{-1}]=E_{tot}[Li_{Zn}^{-1}]-E_{tot}[ZnO]-\mu_{Li}+\mu_{Zn}-E_F \tag{2}$$

$$E^f[Li_{Zn}^{0}]=E_{tot}[Li_{Zn}^{0}]-E_{tot}[ZnO]-\mu_{Li}+\mu_{Zn} \tag{3}$$

$$E^f[Li_{i}^{+1}]=E_{tot}[Li_{i}^{+1}]-E_{tot}[ZnO]-\mu_{Li}-E_F \tag{4}$$

$$E^f[Li_{i}^{0}]=E_{tot}[Li_{i}^{0}]-E_{tot}[ZnO]-\mu_{Li} \tag{5}$$

In group-I elements doping, it's hard to get the p-type at the rich-Zn condition, so we only consider the O-rich condition. When $\mu_{Zn}=\mu_{ZnO}-(1/2)\mu_{O_2}$ is the chemical potential of O_2, the value of μ_{Li} can be calculate by the follow way: $2\mu_{Li}=\mu_{O_2}-\mu_{Li_2O_2}$, and $\mu_{Li2O2}=2\mu_{Li(metal)}+\mu_{O_2}-\Delta H_{Li_2O_2}$, the $\Delta H_{Li_2O_2}$ is the Li_2O_2 enthalpy of formation, experimental value is 3.61eV. Na and K would follow the same way, then we get the formation energy of two defect states:

$$E^f[Li_{Zn}^{-1}]=2.51-E_F \tag{6}$$

$$E^f[\mathrm{Li}_{\mathrm{Zn}}^{0}]=2.40 \quad (7)$$

$$E^f[\mathrm{Li}_{i}^{+1}]=-0.32+E_F \quad (8)$$

$$E^f[\mathrm{Li}_{i}^{0}]=0.74 \quad (9)$$

Table2.1 Defect formation of the Li, Na and K

Defects	valence state	Formation energy
Li_{zn}	0	2.40
	-1	$2.51-E_f$
Na_{zn}	0	1.66
	-1	$1.82-E_f$
K_{zn}	0	1.47
	-1	$1.76-E_f$
Li_i	0	0.74
	+1	$-0.32+E_f$
Na_i	0	0.85
	+1	$0.13+E_f$
K_i	0	1.04

	+1	$0.08+E_f$

Table 2.2 the ionization energy of the Li, Na, K (eV)

Defect	Li	Na	K
Ionization Energy	0.11	0.16	0.29

From the table 2.1, we can get the element acceptor defect ionization energies, as shows in the table 2.2, the acceptor ionization energy is very low. Fig 2.6 shows at the rich-O condition, relationship between impurity defect formation energy and Femi-energy of group-I elements doping.

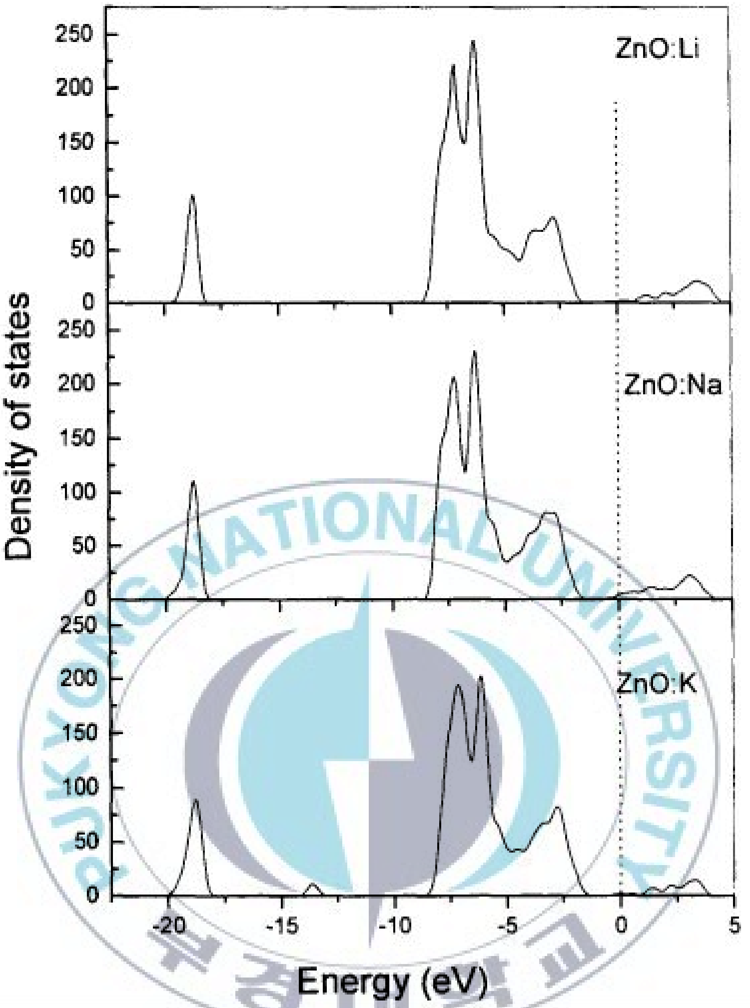


Figure 2.5 Total density of states (DOS) for ZnO doped with interstitial group-I elements.

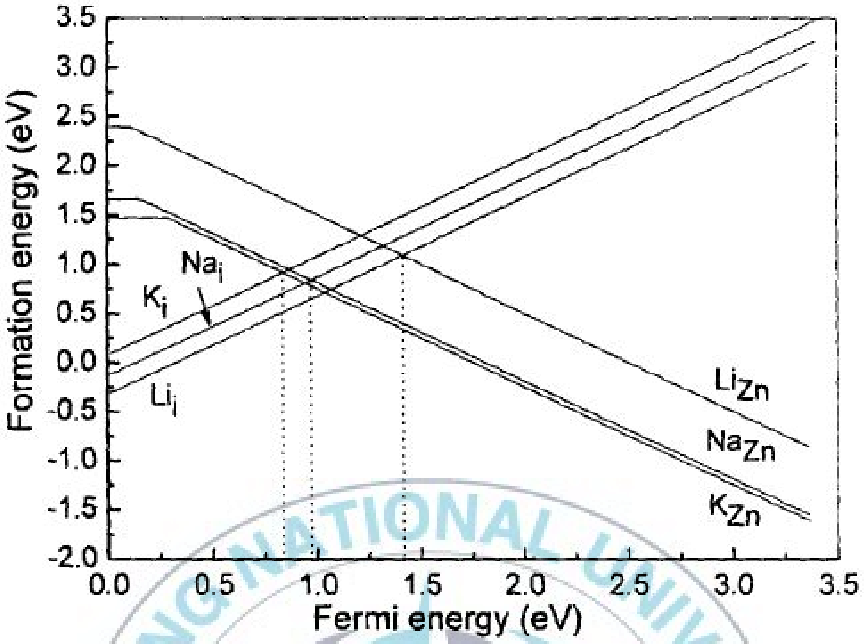


Figure 2.6 The defect formation energies of Li, Na and K as functions of Femi-energy.

Chapter3. Experiments

3.1 Main experimental principles

In this experiment, our aim is getting the Li doped ZnO thin film. So we choose pulsed laser deposition (PLD) method to produce the thin film. First step is making the ceramics by the solid-phase method; second step is making the thin film and then dong the tests.

For Li_2CO_3 decomposition temperature is 730℃, so we follow the chemical equation to get the $Zn_{1-x}Li_xO$ ceramics as it is reported:

$$Li_2CO_3 + ZnO \rightarrow Zn_{1-x}Li_xO + CO_2\uparrow \qquad (10)$$

Through the PLD method can get the p-type ferroelectric thin film.

3.2 Introduction of pulsed laser deposition

The brief think of PLD technology can date back to 60s last century, when the first ruby laser was invented. People interested in melting and vaporizing the solid material by laser and 1965, Smith firstly tried to prepare the thin films through this way. This is the sign of thin film manufacture. Then the dielectric thin films, semiconductor films and metal thin films were made by this new technology. But due to the restriction of the laser services, people only get a few kinds of poor quality films. So soon the fervor was cooled down. Every step of the PLD technology must be brought with turning up of the new laser devices and interaction between laser and materials. From 70's last century, short pulse laser devises was invested and its instantaneous power as high as 10^6W. The new machine can be used in compounding films aggradation and build the basis for PLD technology widely application.1987, Dijkkamp [31]. High quality $YBa_2Cu_3O_{7-x}$ superconductor thin films using pulsed laser evaporation. Then the PLD technology was widely used in important parts like: micro-electronic, photoelectron, carbon nitrogen, silicon compound preparation and some hard-prepared thin films [32-34]. Beside, PLD also be used in preparation of nano-sized granule and semiconductor quantum dots [35, 36].

Figure 3.2 is the typical diagram of PLD. From the figure we can see, a beam of laser, through the lens and irradiate on the target, the target materials will be ablated and the preferred orientation of ablated materials is the normal direction, then we can observe a plum like on the substrate to form a layer of thin film. Through the whole process, usually the vacuum chamber was filled with certain gas.

For example, if we prepare the oxide thin films, we usually add the O_2. A host of fact indicates: PLD technology can be widely used and compared to other thin film making methods, the PLD method advantages show below:

(1) Use the nonpolluted and easily-controlled high photo energy and high energy density pulsed ultraviolet laser as the source.

(2) The energy of the ablated materials is high, can exactly control the stoichiometric ratio and realize the same composition between thin film and target.

(3) In the preparation can add mangy kind of gases or multi-gases, this is one more way to control the component of the thin film.

(4) It's very easy to replace the different targets and prepare the multi-layer thin films and heterojuction.

(5) Can bus used in preparing many thin films and can also operate the thin film by laser.

But the PLD has some short comes:

(1) Can't operate the big square thin films.

(2)The particulate matter in and on the thin films, the films may heterogeneous from micrometer to submicron.

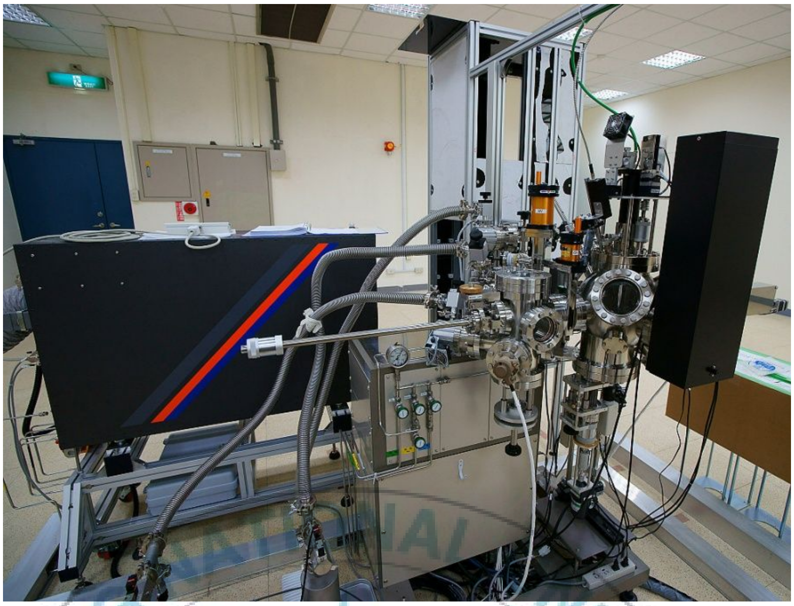


Figure 3.1 Overall view picture of the PLD machine in the lab.

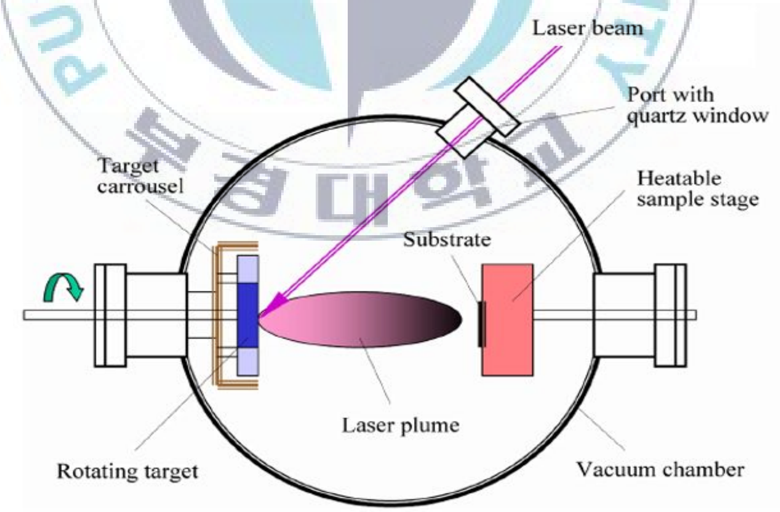


Figure 3.2 Illustration of a pulse laser deposition chamber

3.3 Operational principle of the PLD

PLD is a kind of physical vacuum deposition way, when a beam of high pulsed laser strike on the target, the surface material will be heated, melted, masticated, and change to plasma. The plasma transports from the target to the substrate and then condenses, nucleate and form the thin film. So, the whole PLD process is:

Interaction between laser and target;
Ablated materials transmission;
Ablated materials form the thin films at the substrate.

3.3.1 Interaction between laser and target

Integration of laser and target together affect on the element of ablated material yield speed and space division. That are what most important to the quality of the thin film. Several of the important features of the thin film of PLD, for example: keep the same composition between target and film; spatial-temporal distribution of ablated material spread as $\cos^n\theta$ est. A big deal is the problem of the particulate matter also depends on the interaction of laser and target, so it’s important implication to study the interaction, especially, abatement or complete remission of the particulate matters in the thin film. When the laser radiate on the nontransparent condensed matter and is absorbed, a thin film of the target is heated, and the layer temperature will rise, and then the heat transmit to the inner of the target: But usually because of thermal conductivity is low and there is not enough heat to the deeper, so the layer temperature keep arising until begin to evaporation. At the usual PLD power density, the vapor with high temperature can excited enough atoms and product the plasma. In the end the complex layer film on the surface of substrate. At last a complicated layers as showed are formed, the layer structure will go deeper as the time goes by and at the same time, the outside layer of the plasma spills. The feature of interaction between laser and target is forming the Knudsen layer [36].

Under the laser radiation the target will evaporate, if the vapor grain density is not high enough, the collision between the particles can be neglected. But on the classic PLD condition, the laser radiation makes the particle density of the ablated material be 10^6-10^{21}cm^{-3}, the collision is considerable, the speed of the particles will be rebalanced and redistributed. The studies show the collisions usually happen in several gas mean free path near the target, this is an unbalance zone, and is called Knudsen layer. The excision of the Knudsen layer is different from evaporation, so people renamed it “ablation”. This is the basic reason why the PLD can keep the same component between film and target. In 1-10μm region from the surface to the target will form the high density and temperature plasma. The plasma can absorb the energy of the laser and the temperature rapidly rise [38]. The absorption of plasma strongly depend on its density, a little increase may consumingly absorb the energy, the phenomenon is called plasma shielding effect. [37]

The shielding effect can greatly increase the temperature and so increase the plasma radiation. And because the solid absorption efficiency of plasma radiation is higher than laser radiation, so the solid and liquid target surface temperature is very high and the target surface show the cone structure. The shielding effect also makes the plasma particles obtain high quality thin film. The relationship between target material evaporative capacity and absorbed laser energy density shows:

$$\Delta dt = (1-R)\tau(I - I_{th})/\rho\Delta H$$

Δdt: thickness of the beam spot part target; R: reflection coefficient of the material; τ: laser pulse duration; Ⅰ: energy density of the incidence laser beam; Ⅰth: laser beam evaporation threshold energy density; ρ: volume density of the target material; ΔH: enthalpy of vaporization.

It’s really a extremely complicated process interaction between target and laser, it refers to laser absorption of solid material, interaction between plasma and laser evaporant and ablated non-stationary expansion. These process usually are non-equilibrium or non-linear.

3.3.2 Ablated materials transmission

As it is said above, the transmission of the alerted materials is the process that the altered materials operate by the laser and from the surface of the target to the substrate. Usually in the chamber there are presences of background gases and so collision, scattering, exacting, gaseous phase chemical reaction. The process affect and determine the status, amount, momentum, indirectly affect and determine the mass, structure, and performance of the thin films. As we all know, everything moves in the air may produce sound waves, if the particles move faster than sound, front distance of sound between particles will be smaller and smaller, the air in them will be continually compressed and the temperature, density and pressure also increase. At one point, the gases could not be compressed anymore and will depend on the radio between moving speed and wave speed, Mach number and the character of the gas. The density and pressure increase sharply. But top of the wave, the temperature and density reduce to the normal level to form a gas discontinuity surface. It's called the shockwave. The phenomenon usually happens in the PLD. When the laser beam stopped a high speed as 10^5-10^6cm/s and density is 10^{18}-10^{21}cm^{-3}, begin to express the gases, the result is at the condition of typical condition of oxide preparation, at the position from target 1-2cm, once a strong shock wave is formed, it will independently transfer in the atmosphere. During the region forming, the temperature can reach as high as 2×10^4K. Take the O_2 for example, the condition infers the O_2 numerators can be excited dissociated, ionized to get the O atoms, O ions, Chemical active state， with shock waves goes on, they are weaker and weaker until damp to sound waves, gaseous phase, chemical reaction stop. Usually the distinct gaseous phase happens within 5 mm after the shock waves formation. When the process in the sound wave part, it nearly loose the speed of directional movement. In conclusion, there are 3 phases in the plume transmission: forming of shock wave，transport of shock wave，sound wave stage. The most important phase is the 2nd, in the stage there will be many reactions such as excitation, dissociation and ionization. These are important to the vacancy oxygen and reactive deposition in oxide thin film.

3.3.3 Ablated materials form the thin films at the substrate

The ablated particles arrive at the surface of substrate after a time of movement; the high energy particle may cause the radial injuries, such as atom sputtering. Interaction between ablated materials and the substrate mechanism: first, start to input the high energy ions to the substrate, parts of surface atoms sputtering out, because of the interaction of input ions beam impacts atoms out from the surface, form a collision zone between high temperature and high particle density. Particles hinders the ions beam directly shot at subtract when the thermalization range disperse, condense rate is faster than sputtering out particles in the film, and the thin film starts to grow. Formation and the growth of crystal thin film nucleus depend on many factors.

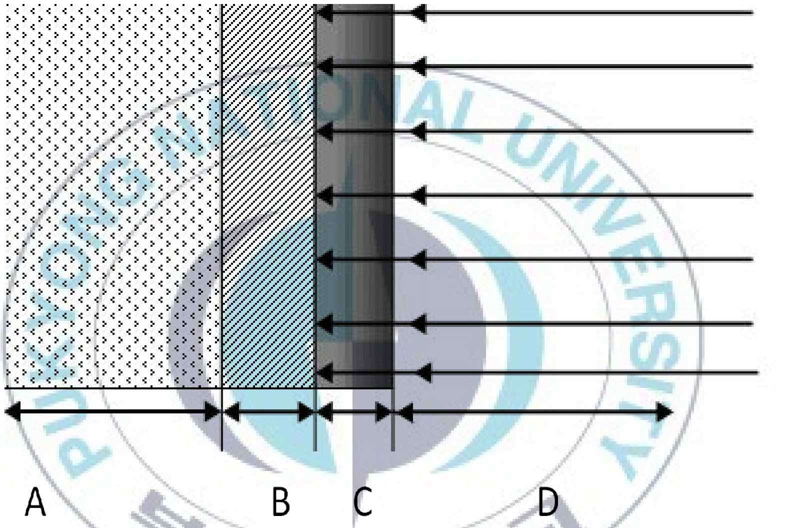
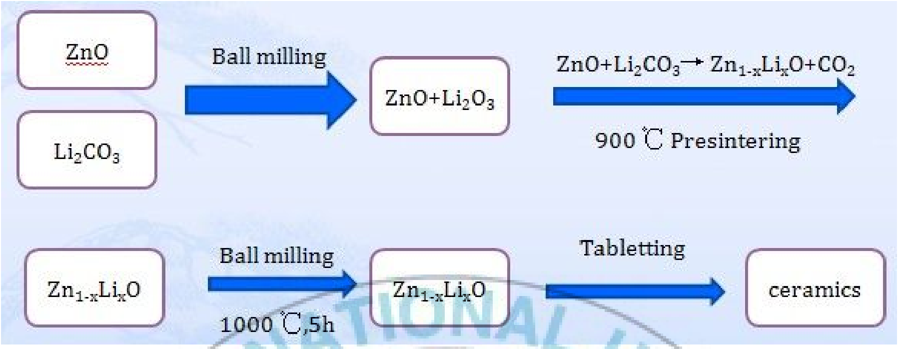


Figure 3.3 Structure of target surface during PLD. A- solid target; B-melted target; C-vapor and plasma; D-inflated plasma

3.4 Processes of the experiment



We chose the ZnO and Li_2CO_3 as the raw materials and then fully mix drugs by high-speed ball milling machine for 10 hours. And next step prestitering the powder at 800℃ and preservate for 5 hours. Then do the second time ball milling for another 10 hours to make sure the particles are small enough. Make the ceramics by table machine at 10 MPa pressure and keep for 1 minute. Fire the cramics in the furnace at 1000℃ for 5 hours. The last step is making the thin film by PLD.

3.5 Testing Techniques

XRD

The X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda=2d\sin\theta$). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material.

X-ray powder diffraction is most widely used for the identification of unknown crystalline materials; characterization of crystalline materials; identification of fine-grained minerals; determination of unit cell dimensions; measurement of sample purity.

SEM

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity.

Dielectric test

Dielectric test is the most common test for semiconductors. Usually it is including: permittivity, electrical conductivity, dielectric loss, impedance, quality factor and changes of relevant properties along with the changes of temperature and (or) frequency. It can show the basic properties of the semiconductor.

P-E loop test

Hysteresis is well known in ferromagnetic materials. When an external magnetic field is applied to a ferromagnet, the atomic dipoles align themselves with the external field. Even when the external field is removed, part of the alignment will be retained: the material has become magnetized.

A family of P-E loops for grain-oriented electrical steel (BR denotes remanence and HC is the coercivity).The relationship between magnetic field strength (E) and magnetic flux density (P) is not linear in such materials. If the relationship between the two is plotted for increasing levels of field strength, it will follow a curve up to a point where further increases in magnetic field strength will result in no further change in flux density. This condition is called magnetic saturation.

Transmission

Transmission of the thin film is usually test the wavelength from 200-800nm or longer of the light. The most important part is the UV part and visible light part. It is a common target of the transparent thin films.

Chapter4. Results and discussion

4.1 XRD results of the $Zn_{1-x}Li_xO$

XRD results is one of the most important results and we usually first need the XRD diagram when we study materials. Figure 4.1and figure 4.2 show the $Zn_{1-x}Li_xO$ ceramics when x=0-0.20, and the bottom diagram is the standard pure ZnO XRD. We can easily see that there are no hybridized peaks in each purity of Li doped ZnO ceramics. The results proved that the Li is well doped into the ZnO, some of them form substitutionary atoms and some form interstitial impurities. We take the $Zn_{0.9}Li_{0.1}O$ for example, the lattice constants are a=3.2491 Å, c=5.2054 Å; the reported values of the pure ZnO are a=3.249858 Å, c=5.206619 Å. The radio of $Zn_{0.9}Li_{0.1}O$ is a/c=0.62417 Å compare to the pure ZnO 0.62418 Å. This value is related to the positional u parameter in the wurtzite structure by

$$u=\frac{a^2}{3c^2}+0.25 \qquad (12)$$

And the Zn-O band length l is given by

$$l=\sqrt{\frac{a^2}{3}+(0.5-u)^2c^2} \qquad (13)$$

The Zn-O bond lengths are 1.9771 Å for $Zn_{0.9}Li_{0.1}O$ and 1.9778 Å for pure ZnO; other values are between 1.9756Å and 1.9769Å.

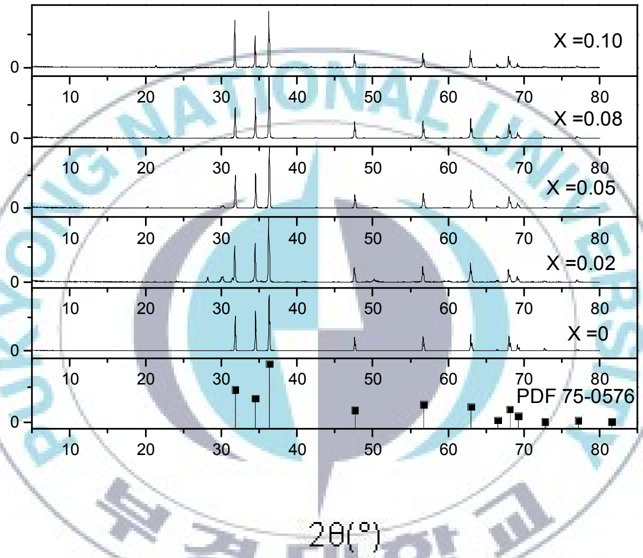


Figure 4.1 XRD results of the $Zn_{1-x}Li_xO$ ceramics, x=0-0.10

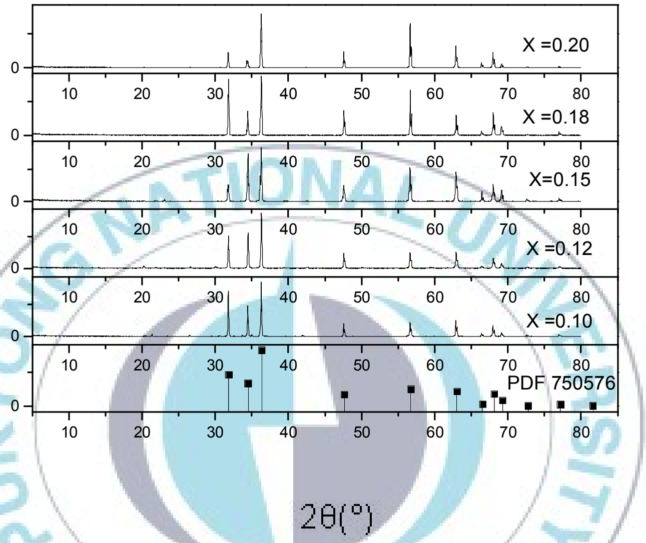


Figure 4.2 XRD results of the $Zn_{1-x}Li_xO$ ceramics,x=0.10-0.20.

4.2 FE- SEM images of $Zn_{1-x}Li_xO$ ceramics

From the figure 4.3-4.11, we can see the microcosmic structures of the $Zn_{1-x}Li_xO$, and the grain size of the $Zn_{1-x}Li_xO$ come to grow bigger and bigger, from less than 1um to nearly 10 um, until can't recognize the clear boundaries of the grains. We try to explain its reason. We have had milled the powder twice for 20 hours before we made them to ceramics and put them into the furnace. So the powder particles may as small as nano-size, the small grain will grow in the high temperature; on the other hand, some of the small Li atoms doped into the ZnO and form the interstitial impurities, this is another important reason why the grain size is big. New grains will form as the Li be the seed grain; then the small grains meet together to grow bigger or be annexed by the large grains. The grains size enlarges along with the doping amount of the Li arise.

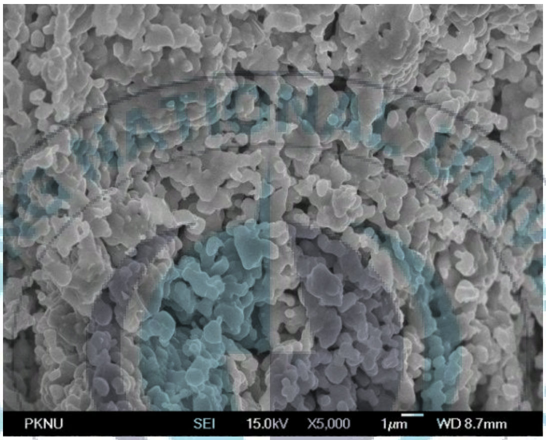


Figure 4.3 SEM of ZnO ceramics

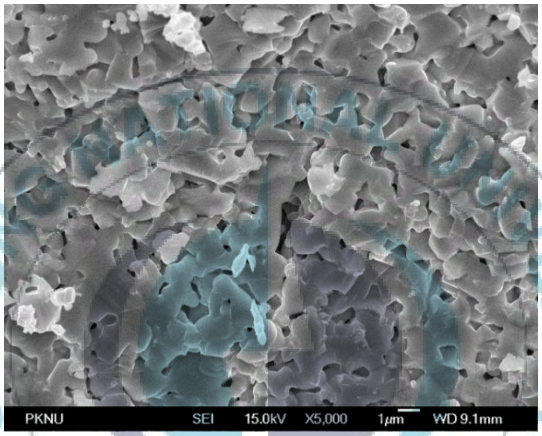


Figure 4.4 SEM of $Zn_{0.98}Li_{0.02}O$ ceramics

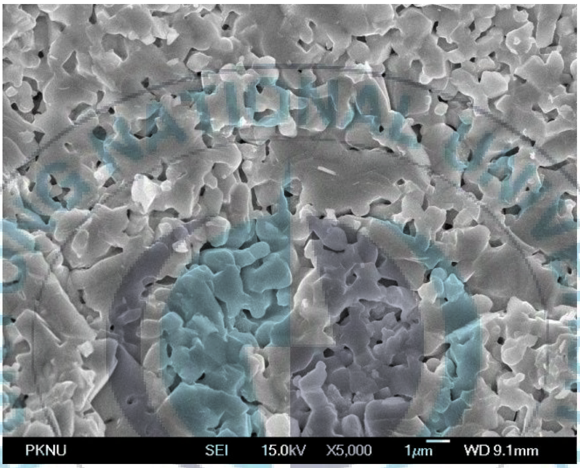


Figure 4.5 SEM of $Zn_{0.95}Li_{0.05}O$ ceramics

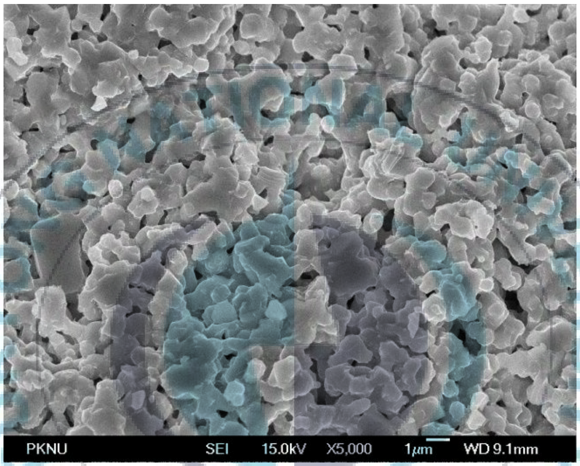


Figure 4.6 SEM of $Zn_{0.92}Li_{0.08}O$ ceramics

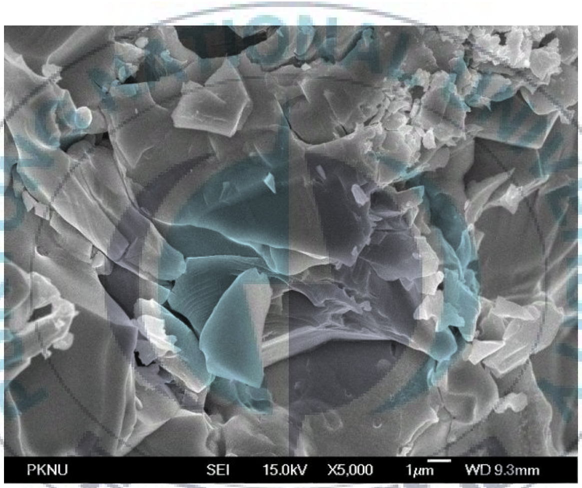


Figure 4.7 SEM of $Zn_{0.90}Li_{0.10}O$ ceramics

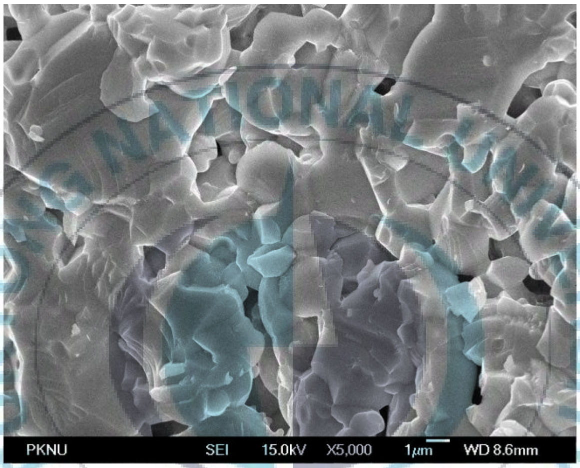


Figure 4.8 SEM of $Zn_{0.88}Li_{0.12}O$ ceramics

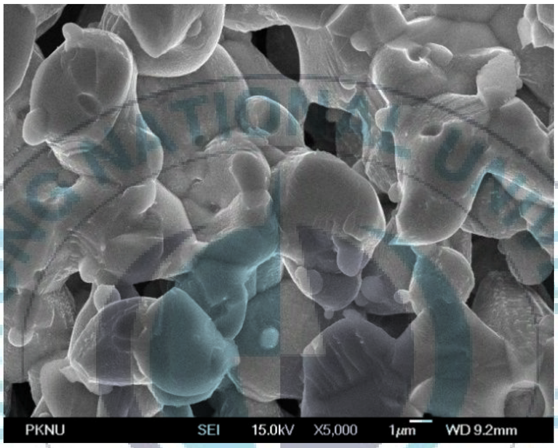


Figure 4.9 SEM of $Zn_{0.85}Li_{0.15}O$ ceramics

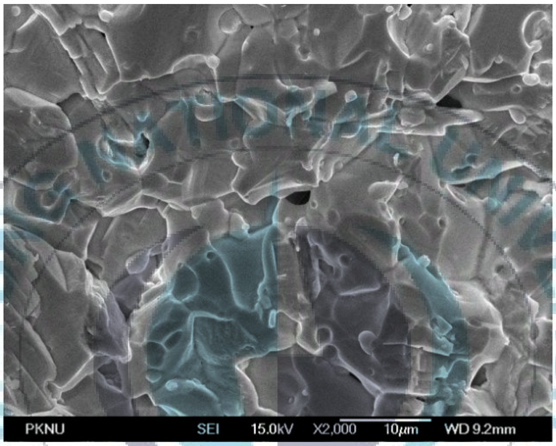


Figure 4.10 SEM of $Zn_{0.82}Li_{0.18}O$ ceramics

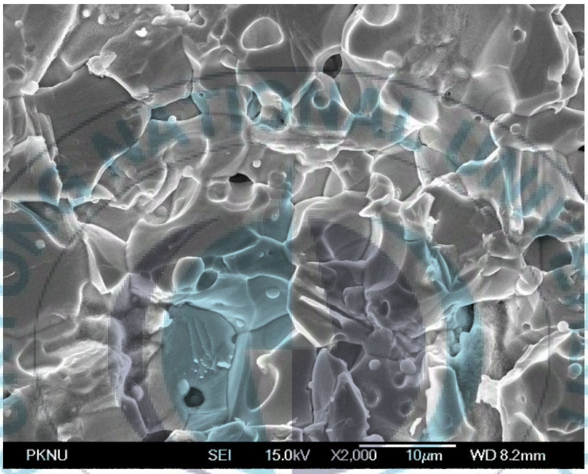


Figure 4.11 SEM of $Zn_{0.80}Li_{0.20}O$ ceramics

4.3 FE-SEM images of the $Zn_{1-x}Li_xO$ thin films

Figure 4.12-4.17 show the 25000 times FE-SEM images of the $Zn_{1-x}Li_xO$ thin films which are made by PLD method. We can see the thickness of the thin films is reducing, and some of the quality is also not as good as we expect. Through visual observation, we can know the thickness of the thin films is about between 450nm to 650nm. There is still argue about the best condition to produce the thin films by PLD method, we choose the high O_2 pressure and 500℃ substrate in the experiment, but the result is not perfect, maybe it is a long way to find the best point which should consider the machine, the air condition, the temperature and the sample types…

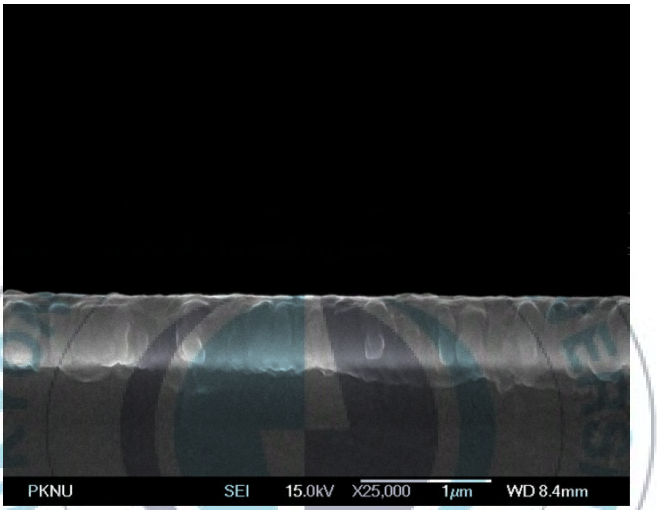


Figure 4.12 FE-SEM of ZnO thin films prepared by PLD

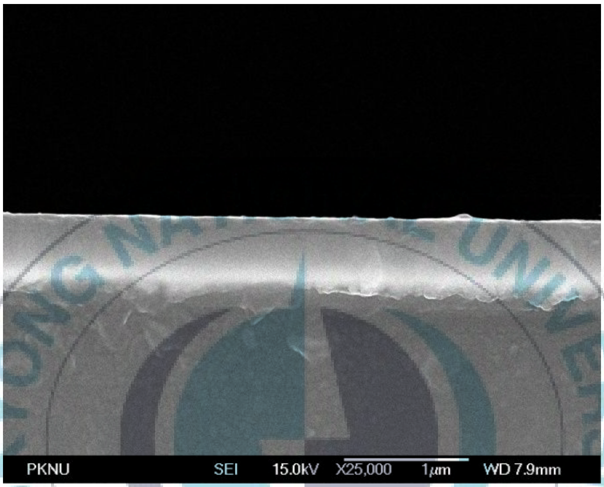


Figure 4.13 FE-SEM of $Zn_{0.98}Li_{0.02}O$ thin films prepared by PLD

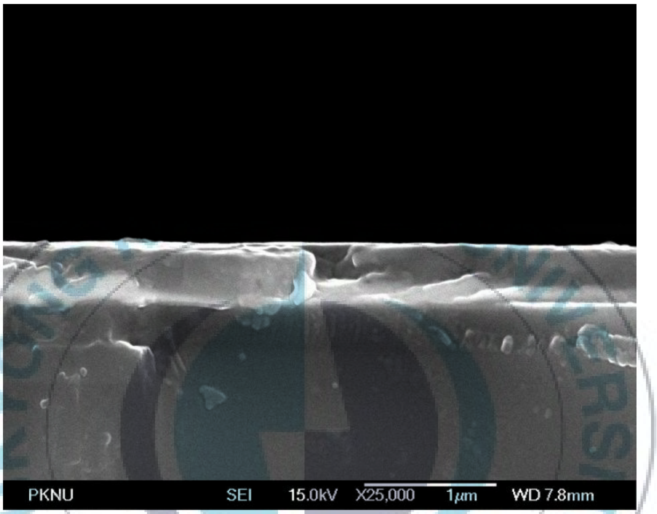


Figure 4.14 FE-SEM of $Zn_{0.95}Li_{0.05}O$ thin films prepared by PLD

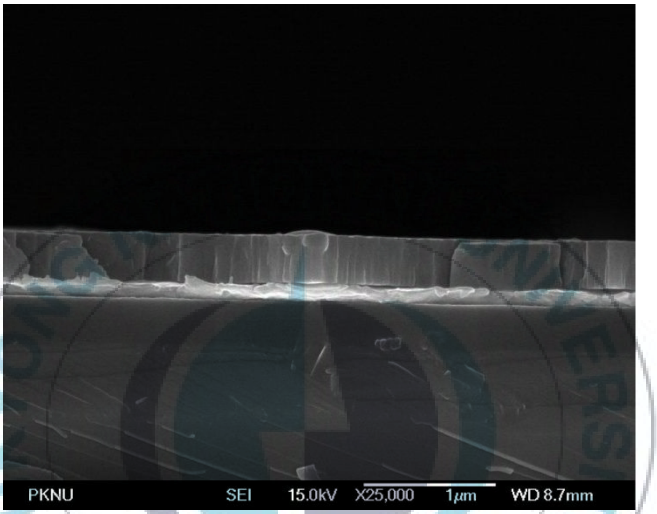


Figure 4.15 FE-SEM of $Zn_{0.92}Li_{0.08}O$ thin films prepared by PLD

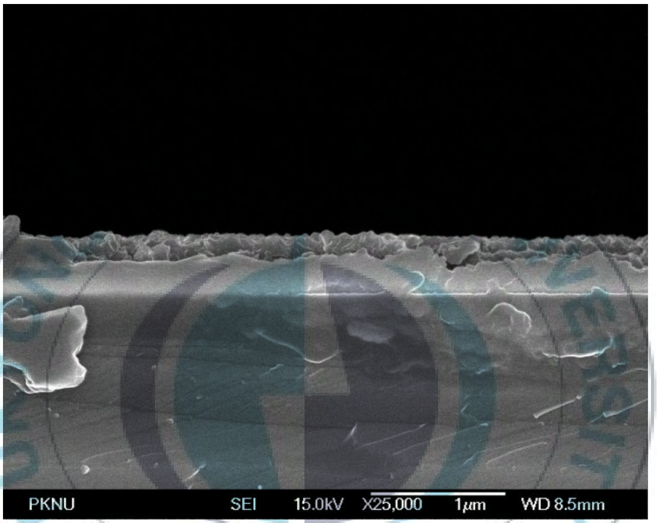


Figure 4.16 FE-SEM of $Zn_{0.90}Li_{0.10}O$ thin films prepared by PLD

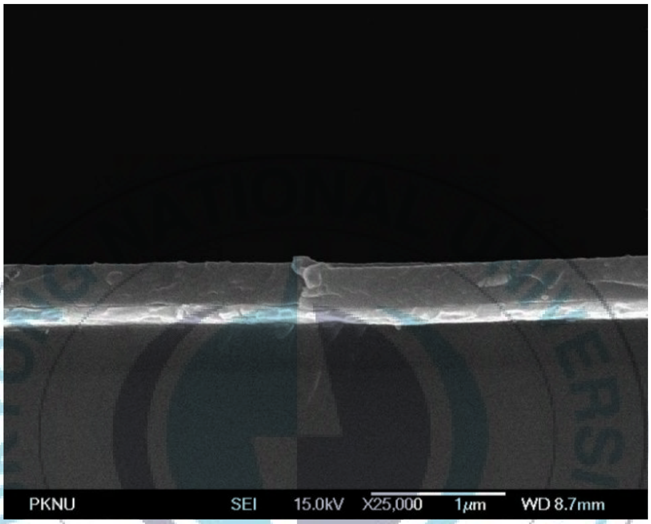


Figure 4.17 FE-SEM of $Zn_{0.88}Li_{0.12}O$ thin films prepared by PLD

4.4 Dielectric constant of the $Zn_{1-x}Li_xO$

Dielectric constant is an important nature for semiconductor. Absolute value or Relative values both mean the insulating capacity of the materials. From figure 4.18, we can see at the room temperature, ceramics at low frequency will hold a high permittivity; follow to the frequency goes high, the constant lines tend to concentrate. At the low frequency, for the lines are disperse，we can clearly recognize the permittivity of $Zn_{1-x}Li_xO$ ceramics: when $x<0.05$, the permittivity will arise, maybe it is because the impurities Li doped into the ZnO, for the doping amount is low, Li may first form the interstitial atom, the small atoms in the crystal, may enlarge the permittivity; then $0.05<x<0.12$,the Li doping amount is increase, more and more substitutional impurity formed in the ZnO, so the permittivity fall back; when $x>0.12$, large amount of the Li in the wurtize structure, and the variations are Complexity, which led to the unstable permittivity.

Figure 4.19 shows the peculiar dielectric behavior at variable temperature condition. Because x=0.15 the lines dispersity at 3 kinds of the frequency is good, so we choose it as the representation. First, we observe the three lines, there are obvious arise while the temperature goes up and form wave crests between 90 ℃ and 100℃, and then the waves fall down, the phenomenon appears because the phase change happens in the $Zn_{1-x}Li_xO$ when the wave crest temperature point, and the point is called Curie-point, and people usually write T_c for short. It is a very important characteristic value for semiconductors. The T_c of the $Zn_{0.85}Li_{0.15}O$ is about 95℃ as shows in the figure; then we can see the values of the permittivity of each lines at different frequencies, the general trend is going down with the temperature rises, this means before the phase change expansion area, the permittivity of the $Zn_{1-x}Li_xO$ goes down a little while the temperature goes high.

Figure 4.20, this is a comparison of $Zn_{1-x}Li_xO$ with different x values at the same frequency of 1KHz. Firstly, the trend of the $Zn_{1-x}Li_xO$ dielectric constants conform to the figure 4.18, it is hard to grasp the relations of the samples as the x value is rising; secondly, the T_c of each $Zn_{1-x}Li_xO$ is different, when x=0.10, the T_c is about 95℃, when x=0.18, the T_c arises to around 103 ℃, when x=0.20, the T_c is as high as 108℃. So we can say, the T_c value will be rising when we dope more impurities into the ZnO. Maybe it is not difficult to explain the phenomenon: for more and more Li element doped into the ZnO, they form the substitutional impurities and interstitial impurities; on the other hand, the appearance of the curie point means there are phase change in the ceramics. The more impurities exist the more difficult the phase changes in the ZnO.

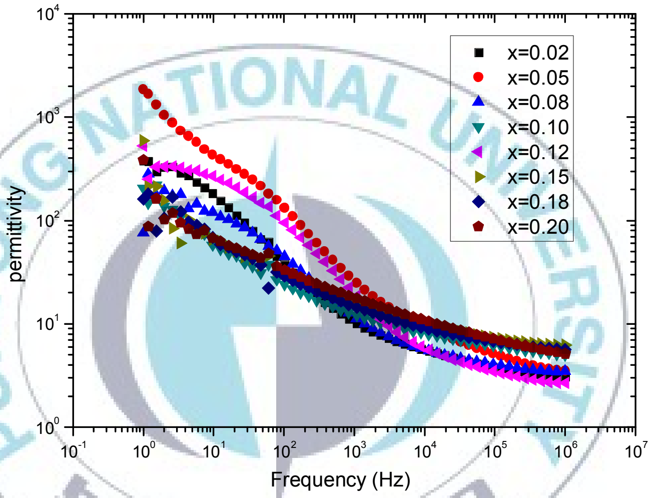


Figure 4.18 All the doping quantities of the $Zn_{1-x}Li_xO$ ceramics dielectric contents in the room temperature

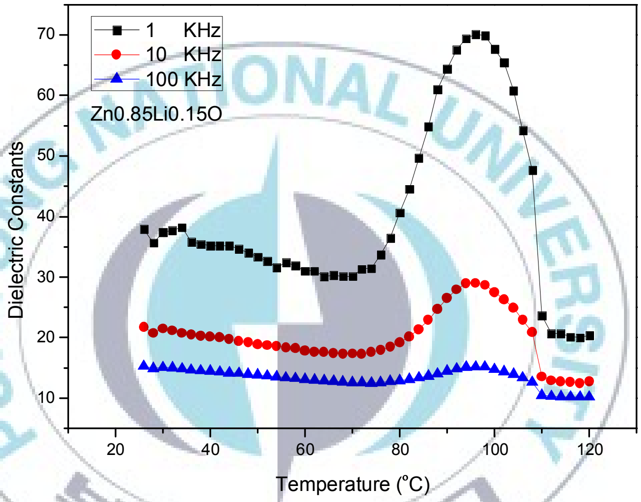


Figure 4.19 Peculiar dielectric behavior at variable temperature condition (take x=0.15 for example)

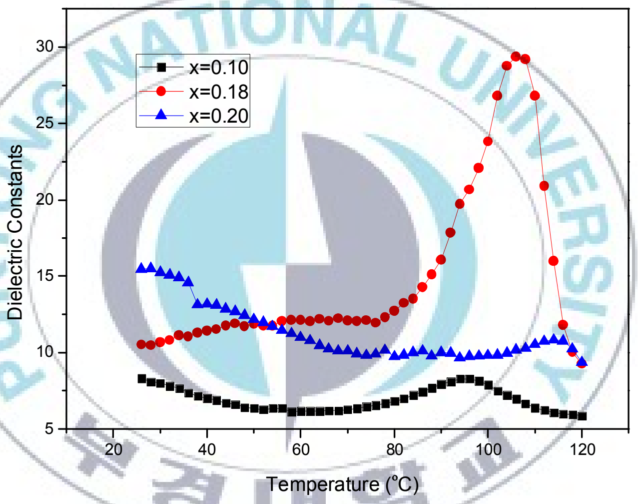


Figure 4.20 Peculiar dielectric behaviors of $Zn_{1-x}Li_xO$ with different x concentration at 1KHz condition

4.5 Ferroelectric of the $Zn_{1-x}Li_xO$ thin film

From the figure 4.21 we can see the hysteresis loop of $Zn_{1-x}Li_xO$ films with x=0.12, respectively. A positive remanent polarization ($+P_r$) of 0.186 μc/cm^2 and a positive coercive field ($+E_c$) of 5.53 KV/cm are recorded for the $Zn_{0.88}Li_{0.12}O$ thin film. We also test the P-E loop of other $Zn_{1-x}Li_xO$ thin film with other value, and the Li-doped ZnO ceramics. But no obvious hysteresis phenomenon appears. Those maybe the ceramic samples which are prepared by solid phase method can't grow follow the c-axis and the impurities also give some effect on the results. Combine the FE-SEM of the thin films, the Li concentrations are different and the O pressure and laser temperature may affect the thin film quality, so we can't get the better results regretfully.

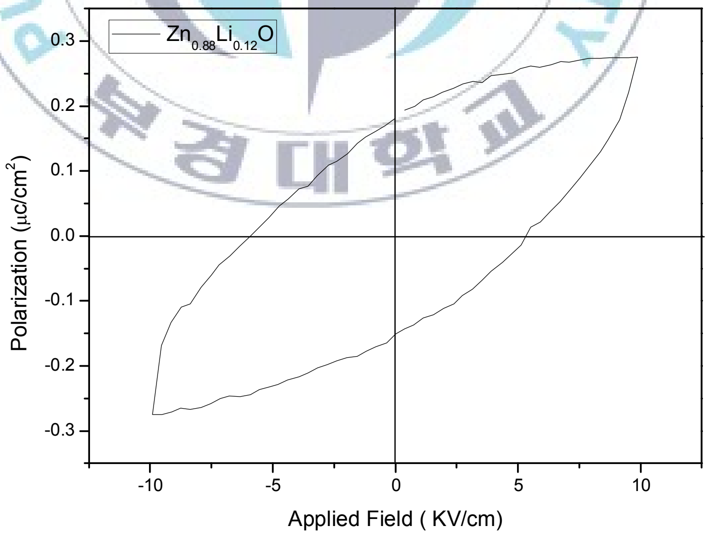


Figure 4.21 P-E hysteresis loop of the ferroelectric $Zn_{0.88}Li_{0.12}O$ thin film by PLD

4.6 Optical transmittance spectrum of the $Zn_{1-x}Li_xO$ thin films

Figure 4.22 shows the optical transmittance spectrum of the $Zn_{0.98}Li_{0.02}O$ and $Zn_{0.95}Li_{0.05}O$ thin films in the wavelength range 400-800nm; the transmittance curve is smooth and clearly oscillating. It shows that the surface of the films is very smooth and the thickness is uniform. And the figure 4.3 can give the speaking witness.

On the other hand, it is well known that the refractive index. n is given by:

$$n = \frac{c}{v} = \sqrt{\frac{\varepsilon\mu}{\varepsilon_0\mu_0}} \qquad (14)$$

In term of the relative permittivity Ke and the relative permeability K_m of the medium, n becomes:

$$n = \sqrt{K_e K_m} \qquad (15)$$

The great majority of substances, with the exception of ferromagnetic materials, are only weakly magnetic; none is actually nonmagnetic. Setting K_m=1 in the formula for n results in an expression known as Maxwell's relation [39]:

$$n = \sqrt{K_e} = \sqrt{\frac{\varepsilon}{\varepsilon_0}} \qquad (16)$$

The thickness of the film can also be calculated from the equation [40]:

$$d = \frac{M\lambda_1\lambda_2}{2[n(\lambda_1)\lambda_2 - n(\lambda_2)\lambda_1]} \tag{17}$$

Where λ_1 is the wavelength of any one of crests in fig 4.6 and λ_2 is the wavelength of any one of the troughs (as long as the trough and peak chosen are not adjacent), n (λ_1) and n (λ_2) are the corresponding refractive indices, M is the number of the maxima and minima between λ_1 and λ_2. Then through the calculation we can get the thickness of the $Zn_{0.98}Li_{0.02}O$ is about 550nm, it is coincide with the figure 4.12.

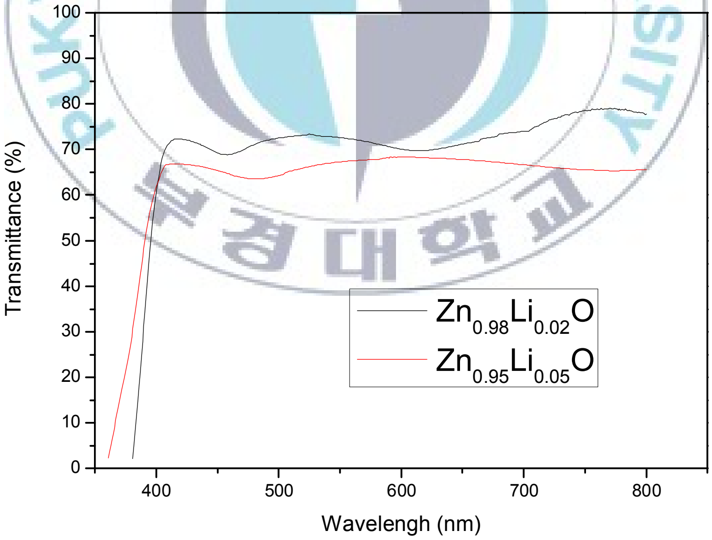


Figure 4.22 Optical transmittance spectrum of the $Zn_{1-x}Li_xO$ thin films with x=0.02, 0.05 in the wavelength of 400-800 nm

Conclusion

This article presents the preparation of Li doped ZnO thin films by pulsed laser deposition which grows on the silicon substrate and the main properties of the thin film, now summarize as follow:

1. The most important part of the experiment is preparation of the high quality Li doped ZnO thin films. From the XRD of the $Zn_{1-x}Li_xO$ ceramics, we can see the Li elements are well doped into the ZnO and hybridized peak appears. Through the calculation, we can also know some of the inner crystal condition, The Zn-O bond length are 1.9771 Å for $Zn_{0.9}Li_{0.1}O$ and 1.9778 Å for pure ZnO; other values are between 1.9756Å and 1.9769Å.
2. From the FE-SEM pictures of the $Zn_{1-x}Li_xO$ ceramics, we can know along with the impurity Li amount increase, the grain size will be affected by the impurity and grow larger and larger; and from the FE-SEM of the $Zn_{1-x}Li_xO$ thin films, it is clearly to observe the thin film thickness, feature and the relationship with the substrate.
3. The $Zn_{1-x}Li_xO$ will emerge phase change at certain temperature, we called the point is Curie point. Near this temperature, the permittivity line of the $Zn_{1-x}Li_xO$ will emerge a wave crest, and the Curie point is the peak. The Tc of the $Zn_{0.85}Li_{0.15}O$ is around 95℃. And the T_c will arise with the doping Li concentration increases; at the relative low temperature, the permittivity of the $Zn_{1-x}Li_xO$ will go down while the temperature and frequency increase, but the changing magnitudes are different, it is dependent on the host materials and the impurity concentration.

4. For the PLD method can well keep same composition between target and film, and the crystal in the film grows follow the c-axis, shows the ferroelectric property. The results of the thin film are: E_c of the $Zn_{0.88}Li_{0.12}O$ is 5.53 KV/cm and the P_r of the $Zn_{0.88}Li_{0.12}O$ is 0.186 μc/cm^2 and there are no obvious ferroelectric in other Li concentration thin films and ceramics.
5. The optical transmutation transmission is about over 75% of $Zn_{0.98}Li_{0.02}O$ thin film, the transmission of the thin films are easily affected by quality of itself. Trough the calculation by optical transmittance spectrum of the $Zn_{0.98}Li_{0.02}O$, we get the theoretical value about 550nm, which is coinciding with the FE-SEM image of the $Zn_{0.98}Li_{0.02}O$ thin film.

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