Master Degree Thesis

A study on structural and electrical properties of ZnO nanorods on PES substrate by hydrothermal methods

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A study on structural and electrical properties of ZnO nanorods on flexible substrate by hydrothermal methods

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Abstract

디스플레이(Display), 솔라 셀(Solar cell), 대면적의 센서 어레이(Sensor array) 등의 잠재적 적용성에 의해, 최근 경량화, 유연성과 용이한 휴대성을 가진 플렉서블 전자 소자들에 대한 다양한 연구가 이루어지고 있다. 저온 공정, 고 투자, 우수한 전기적 특성을 갖는 플렉서블 소자들을 사용하기 위해서 TOS(Transparent Oxide Semiconductor) 물질에 대한 연구가 요구되고 있다. TOS 물질은 넓은 밴드갭과 우수한 전도성을 가지고 있으며, 또한 저 비용과 높은 이동성으로 높은 잠재력을 갖고 있다. ZnO가 많은 관심을 받고 있는데, II-VI족 산화물 반도체인 ZnO는 상온에서 우르짜이트 구조를 가지고 있으며, 저온에서 성장이 가능하다. 3.36 eV의 넓은 밴드갭을 가진 ZnO는 가시 영역에서 높은 투과율을 보여준다. 또한 LED(Light Emitting Diode)와 LD(Laser Diode)등의 광학 소자로 응용이 가능한데, 이는 60 meV의 엑시톤 결합 에너지를 갖기 때문이다. 또한 n-타입 반도체인 ZnO는 협소한 전도대역을 가지고 있으며, 도핑 물질에 의해서 전기적, 광학적 특성을 쉽게 제어할 수 있다.

저차원 나노 구조의 연구는 현대 과학의 발전에 중요한 역할을 한다. 저차원 나

노 구조들 중, 높은 투명성과 우수한 압전성, 저온 성장 및 넓은 밴드갭으로 인한 우수한 특성으로 1-D ZnO 나노 구조체가 주목받고 있다.

나노 구조물의 성장 방법은 반응에 관여하는 물질의 종류와 그 상(phase)에 따라 VLS(Vapor Liquid-Solution), SLS(solution-liquid-solution), VS(vapor-solid) 등으로 나뉜다. 그러나 위의 방법들은 고온과 고비용의 공정이 요구되므로, PES 기판에 나노 구조체를 성장시키기에 적합하지 않다. 따라서 수열합성법을 이용하여 1차원 나노 구조체를 성장시켰다.

1장에서는 본 연구에 대한 소개를 간략하게 설명하였다. 2장에서 나노 물질의 특성과 제조, ZnO의 물성과 ZnO를 이용한 1차원 나노 구조에 대해 설명하였다. 3장에서는 씨앗층의 제작, 1-D ZnO 나노 구조체 성장, 전기적 특성을 측정하기 위한 전극 형성 방법 및 1-D ZnO 나노 구조체의 특성을 측정하는 장비들을 소개하였다. 4장에서 증착 조건에 따른 씨앗층의 구조적 특성을 분석하여 ZnO nanorods를 성장하는데 최적의 조건을 설정하였다. 또한 각 수용액의 농도와 성장 온도에 따른 구조적 특성과 전기적 특성을 3장에서 언급한 장비를 이용하여 분석하였고, 5장에서 요약 및 결론을 나타내었다.

Chapter 1 Introduction

In the future, flexible display seems to lead the display industry, and flexible display has advantages such as flexibillity of device, various shape, a high productivity by the roll to roll process, and economic efficiency due to the lightweight compared to conventional devices[1]. For the flexible display device, it should be made on plastic substrate instead of glass or sapphire. It is possible to obtain excellent electrical and structural properties on the glass and sapphire substrate, because it can fabricate at high temperature. However, it is difficult to obtain good electrical and structural properties on the plastic substrate, because high temperature is impossible. In case of ITO used to TCO materials of conventional display device, it need to heat treatment of over the 300℃ for get to excellent electrical and structural properties. And a-si TFT, p-si TFT what used to drive circuit AMLCD(Active Matrix Liquid Crystal Display) had a low electron mobility and needed to heat treatment of high temperature, so it has limit for applying of flexible display devices[2-4]. Recently ZnO has attracted attention as materials that are applied to flexible electronic device, in addition, ZnO has fast electron mobility and can low temperature process below 200℃.

ZnO, as a representative oxide semiconductor of Ⅱ-Ⅵ group, has stable state of thermally and chemically, and it can be process at low temperature. It also has relativity large band gap energy of 3.36 eV and high free exciton binding energy of 60 meV. In addition, it is a direct transition type compound semiconductor, has light transmission of more than 80%, high electrical conductivity. So it has been spotlighted in the field of TCO, TTFT, solar cells [5-8]. In addition, a study is being actively conducted to the band gap engineering for expanding of the band gap energy, applied to the optical element in the UV range [9, 10].

Nanostructures are classified zero-dimensional nanoparticles such as macromolecules, quantum dots and one-dimensional nanostructures of less than 100 nm and a diameter such as nano wire, nano rod, and nano ribbon, and nano thin-film, and other nanostructure having a size of less than 100 nm. Among these nanostructures, the one-dimensional materials has been found that it can be applied such as transistors, diodes, light emitting diode, solar cell, the electronic sensor, and an optical element.

Therefore the research is begun for commercialization of nano-structure technology. However, in order to be put to practical use for this technology, there are many technical problems to be solved, such as assembly technology to implement a nano-devices, fine-turning of the crystal growth of the one-dimensional structure and establishing correlation of affecting the physical properties of synthesized one-dimensional nano material values and physical properties[11-14].

The growth methods of one-dimensional ZnO nanostructures can be way of accessed a bottom to up, various methods for controlling have been proposed, because it can be grown various shape and size according to growth condition. However these conventional methods for nano structure demand complex process such as high temperature or vacuum system in the expensive equipment such as MBE(molecular beam epitaxy), PECVD(plasma-enhanced chemical vapor deposition), and PLD(pulsed laser deposition). Whereas the hydrothermal method is one of the liquid methods to obtain a solid solution compound having a uniform crystalline. Hydrothermal method is driven simple equipment by a comparatively low cost, low temperature of under the 100℃, can be used at high pressure, and it has advantages for the large area[15-17]. However as noted above, it is required to manufacture the nanostructure of the quality structures and controlled of the size of nanostructure. In addition, Establishment of assembly technology must be established[18-20].

Therefore, in this study, the experiments for getting the conditions of ZnO nanorods grown by hydrothermal methods for growth and controlling ZnO one-dimensional nano-structures of good quality by a simple process on the PES substrate was carried out. In particular, the PES substrate, the crystal structure of the amorphous as well as the surface morphology is not good. So research of thin films growth for epitaxial growth by the use of a buffer layer on the amorphous PES substrate is essential. The growth of nanorods is very difficult because of the characteristics of PES substrate. In the growth of ZnO nanorods, the effect of the seed layer, and studied about ZnO nanorods according to the structural properties of ZnO seed layer was investigated. In addition, electrical and structural properties of growth of ZnO nanorods was analyzed, and the possibility of controlling of the size and controlling properties was suggested.

Chapter 2 Background of Theory

2.1 Nanomaterials

2.1.1 Properties of nano materials

Development of technology is changing rapidly reflecting the speed of the rate of change of life. And the nanotechnology a kind of conventional technology is being actively studied to determine and control the development of nanometer. Nano science and technology is the technology has been expected what is controlled nano size materials physical and chemical and nano science and technology are building new technology areas by fusing together the traditional material such as physics, materials, and electronics. And the nano science and technology has been expected to be implemented in the best performance while minimizing size. It is very important to analyze the properties of the nanomaterial to the development of nano-science and technology, because it starting from materials of the nano-sized. The material of the nano sized will have unique physical properties because of the very large surface area relative to volume as compared to the conventional bulk state. Nano materials have atomic energy per unit higher than the materials of bulk state. Because, in generally, the surface atoms of the solid materials are a significant contribution to the free energy as compared to the inner atoms. In addition, the bulk state consists of more than several million particles, and it has continuous energy levels. And the material consisting of several atoms and molecules, has discontinuous energy levels. But nanomaterials have both of these properties. Therefore, the electrical and optical properties have different properties with bulk, atoms, and molecules. So it can be called the quantum size effects. But this effect is appears in all cases of a metal, an insulator, molecular crystals, semiconductor. Especially, in case of semiconductor nano materials, the properties are appeared prominently. That is, when the band is formed according to the growth of crystal, the edge band is formed after the forming of

center of band. In case of metal which Fermi level is formed the center of band, the changing of energy level is very small between HOMO(Highest Occupied Molecular Orbital) and LUMO(Lowest Unoccupied Molecular Orbital) determining optical and electrical properties at the very small nanomaterial. So the band has similar properties with bulk at very low temperature. Otherwise, in case of semiconductor nano crystal, the Fermi level is formed between the band, so the edge of band exist in discontinuous energy state, and it caused the effect to optical and electrical properties. Thus, in case of semiconductor nano crystal, the properties of optical transition and electronic transition crossing the band gap is changed. It is specifically called quantum confinement effects on the semiconductor. The changing of band gap can be thought of a simple relationship between the position and momentum by the uncertainty principle of Heisenberg caused by quantum confinement effects with the equation (1) above.

$$\triangle p \triangle x \geq \frac{\hbar}{2}$$

$$\hbar = \frac{h}{2\pi} \qquad \cdots\cdots \text{Equation (1)}$$

At this time, the change of crystal momentum is greater by quantum limit. The change of momentum means the change of crystal energy, and the energy transfer between the state K. And the energy transfer is increased according to increasing of quantum limit. The energy of bulk state is like equation (2).

$$E = \frac{p^2}{2\mu} = \frac{(\hbar k)^2}{2\mu} \qquad \cdots\cdots \text{Equation (2)}$$

At here, k is crystal moment quantum number; ¶ is effective mass of electrons and holes, so the transition energy between k state is like equation (3).

$$E = E_0 + \frac{(\hbar\pi)^2}{2r^2\mu} - \frac{1.8e^2}{\varepsilon_2 r} \quad \cdots\cdots \text{Equation (3)}$$

At here, r is the radius of the nanocrystals, and the ε2 is second dielectric constant. Therefore, the difference of transition energy is increased more than energy transfer of bulk state, because, in case of nano crystal, the quantum can be controlled. But, K is inversely proportional to the size of crystal, the transition energy become lager in proportion to 1/r2. From this equation, the band gap is larger according to decreasing of size of particles. And this approximation is called a simple effective mass. Based on this, when the size of the Si(silicon) nano crystal is about 1 nm. Even though the band gap of Si is 1.12 eV, the possibility has been suggested the blue emission. In case of nano materials having a linear structure, the length of short-axis is in range of the quantum size effect, and because of the length of long-axis is more than several tens of nm, if it does not appear that quantum size effect, there is the research of nanorods about polarization of absorb the light of particular direction. The quantum size effect is appeared at optical and magnetic properties of materials. There is the research about indicated a super paramagnetic or giant magneto resistance according to depending on the crystal grains of the magnetic material is smaller.

2.1.2 Manufacturing of nanomaterials

The methods of inducing the growth of the one-dimensional nano material are divided according to the type of phase and the number of type of materials. For example, VLS(vapor-liquid-solid), VS(vapor-solid), SLS(solution-liquid-solid), etc. In case of VLS methods, the reactants in the gas state are reached the droplet of a metal catalyst of nanometer size. And then, diffusion is made into the catalyst, the nucleus is generated by Supersaturated. As this time, the diameter of the nanomaterial grown by VLS method is determined by the pore diameter of the droplets, because the growth of the one-dimensional direction is induced and dominated by the metal droplets like Fig 1, and Fig 2.

VS is a method that does not require a specific catalyst, unlike the VLS method. That is, the materials what need growth, is evaporated for generating of vapor. So, one-dimensional nanostructure is grown at low temperature because of coagulation at Fig 3. VLS method and SLS method have similar principles, but SLS is not required high temperature and vacuum condition, so SLS has been used as an alternative VLS. Atoms and molecules are aggregated with each other when the concentration of the metal to be precipitated by chemical reaction is increased beyond the supersaturated limit in the SLS methods. And then, the crystal nucleus is occurred by cluster, it is grown through crystal growth or particle-to-polymer. Since the concentration of materials and growth of particle, nucleation is reduced and the particle growth proceeds only. It shows the overview of growth methods at Fig 4.

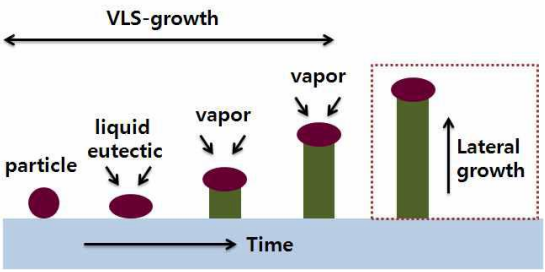


Fig 1. Schematic illustration of VLS growth mechanism with increasing time.

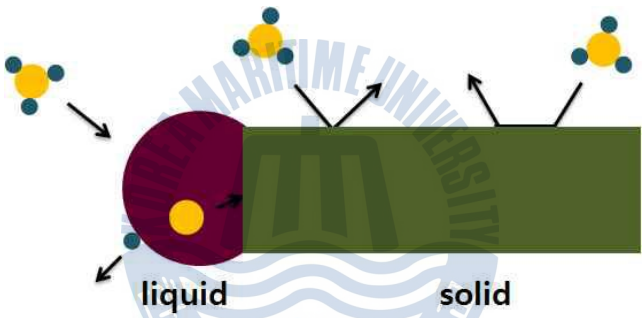


Fig 2. Schematic illustration of VLS growth at vapor step for nanowire growth.

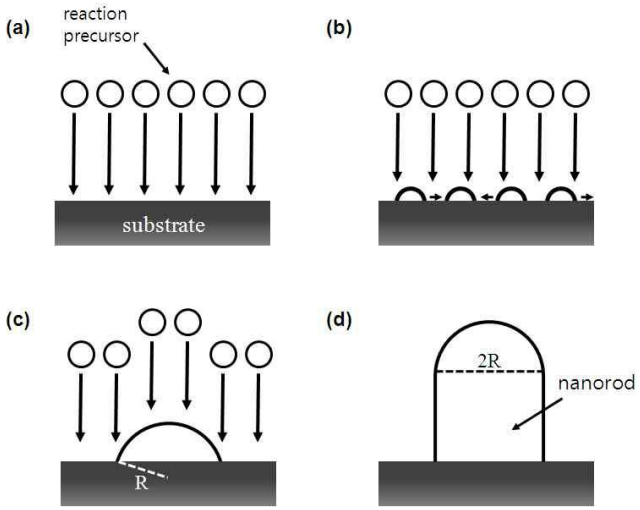


Fig 3. Schematic illustrating VS nanowire growth mechanism including four stages: (a) reaction precursor, (b) cluster migration, (c) nucleation on substrate surface, (d) anisotropic 1-D growth of nanorods.

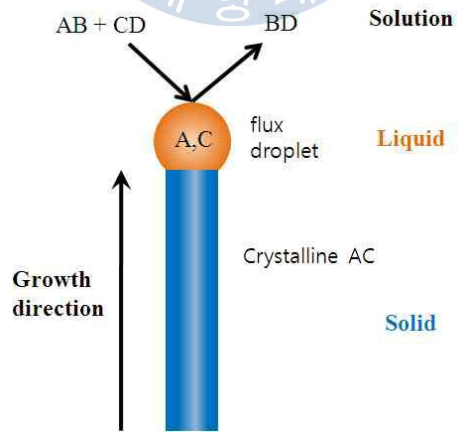
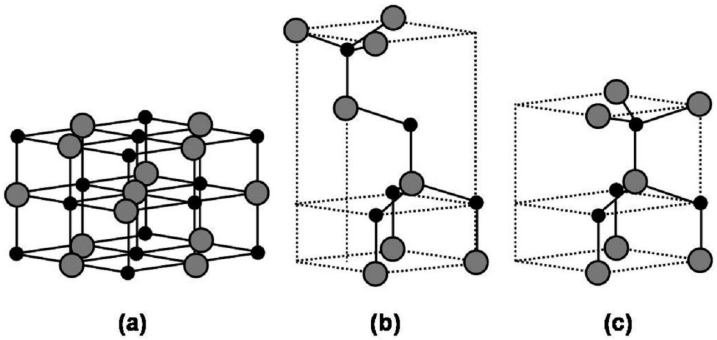


Fig 4. Schematic illustrating the SLS mechanism: A and C are elements of the nanostructure dissolved in the flux droplet.

2.2 Basic properties of ZnO

2.2.1 Properties of ZnO

ZnO is a compound semiconductor with Ⅱ-Ⅵ group, oxygen vacancies or interstitial defect itself of Zinc, so it has the properties of n-type semiconductor. And it has the 3 kind of crystal structure such as hexagonal wurtzite, cubic zinc blend, and cubic rocksait at room temperature. Hexagonal wurtzite, cubic zinc blend, and cubic rocksait are shown in Fig 5. ZnO is hexagonal wurtzite at room temperature, and ZnS is the structure when the substrate is cubic, and rocksait is stable only at a high pressure[21, 22]. There is a wurtzite structure of ZnO at Fig 6. O ions are located on hexagonal site and Zn ions are located on tetrahedral site at ZnO, so Zn layer and the O layer is can be seen that it is composed of a shift. O ions are located in hexagonal site, and Zn ions occupy the half in tetrahedral site in ZnO. And due to the difference of diameter of Zn and O, the relatively large gap of tetrahedron. So penetration-type of Zn is exist, because Zn atoms are penetrated these places. And it is not the tetrahedral isotropic, because of the short gap of c-axis direction. It has a lattice constant of a = 3.251 Å, and c = 5.206 Å, the resistivity is change to 108Ω from 10-4Ω according to the growth conditions. There are various properties of ZnO in table 1.



Properties of crystal structure of ZnO. (The gray color is Zn, the black color is O)
(a) cubic rock salt , (b) cubic zinc blende , (c) wurzite hexagonal

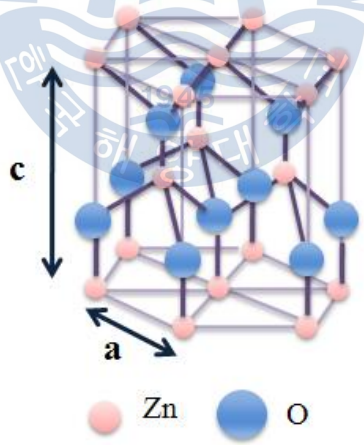


Fig 6. Properties of crystal structure of wurzite ZnO

Table 1. Properties of ZnO

Properties	Value
Lattice constants at 300 K	a = 3.251 Å b = 5.206 Å
Stable phase at 300 K	Wurtzite
Melting point	1975 ℃
Linear expansion coefficient (/℃)	a : 6.5×10^{-6}
	c : 3.0×10^{-6}
Static dielectric constant	8.656
Band gap energy	3.36 eV
Intrinsic carrier concentration	< 106 /cm^3 (max: n-type doping > 10^{20} /cm^3 electrons, max: p-type doping <10^{17} /cm^3 holes)
Exciton binding energy	60 meV
Electron effective mass	0.24
Electron mobility at 300 K for low n-type conductivity	200 $cm^2/V\cdot s$
Hole mobility at 300 K for low p-type conductivity	5 ~ 50 $cm^2/V\cdot s$
Hole effective mass	0.59
Work function	4.5 eV

2.2.2 One-dimensional nanostructures of ZnO

One-dimensional nanostructure is advantages in the application for gas sensor, chemical sensor, and vivo medical sensors. Because one-dimensional nanostructures of the nanorods and nanowire have a superior sensitivity and stable characteristic in vivo according to the adsorbed species due to the high surface area compared to the volume. The ability to control the position of nucleation can be applied to micro-laser, and remember-device array. In addition, this application is possible in a transparent flexible display device manufacturing because it can be grown on glass or polymer substrate at low temperatures. Currently there is a technical attempt being made to take advantages of ZnO nanorods and nanowire, having high charge transfer, quantum efficiency, and chemical, mechanical stability. You can see the typical applications of ZnO nanorods and nanowire in Fig 7.

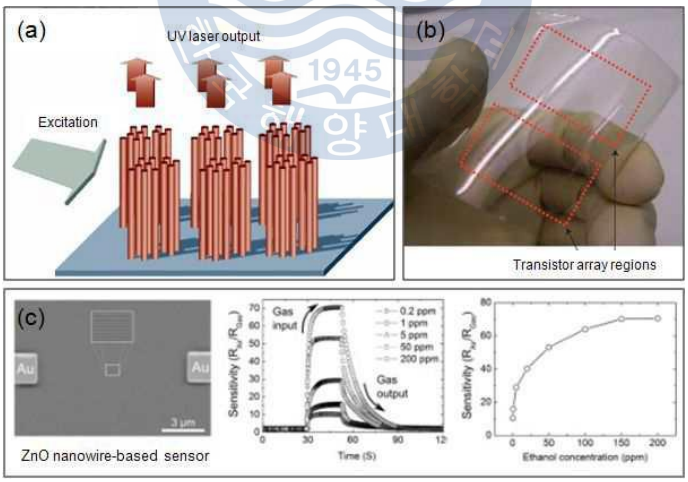


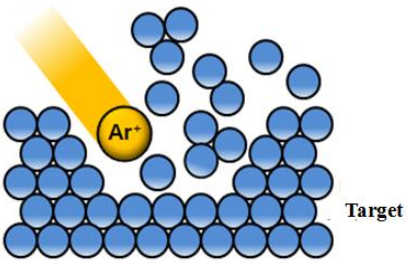
Fig 7. The application of ZnO nanorods and nanowire (a) Nano laser, (b) transparent flexible transistor, and (c) nano sensor.

2.3 Theory of equipment

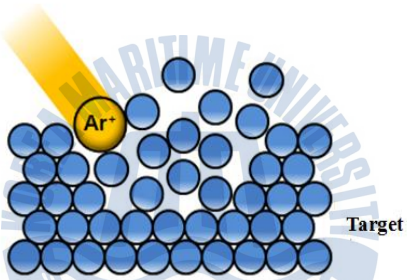
2.3.1 Sputter system

The state of materials of target, when Ar ions crash out from target, is neutral atoms. The percentage is atomic state of 90%, and particle, cluster, or molecules in 10% or less. The sputter rate is increased when the energy of Ar cationic crashing into a target is increased. If the sputter power is increased, the deposition rate increase because large cluster protruding from target. So it can be saved time and economic, but it is difficult to control the surface of thin-films. The basic principle of sputter system is shown in Fig 8.

(a)



(b)



(c)

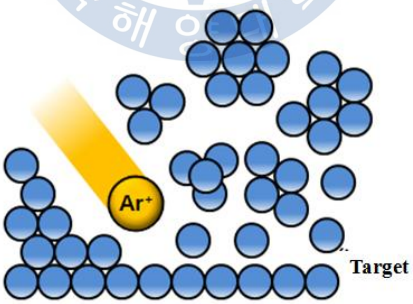


Fig 8. Movement of molecules and clusters according to crash energy (a) low values of crash energy (b) middle values of crash energy (c) high values of crash energy

The ions are most ionized in the plasma, only a small part, ions, having very higher energy then neutral particles, ions of the ionized, and other particles, are detected. The ions of very high energy, emitted from the target, are caught by the electric field. But the ions, having very high energy better than the electric field, overcome. Usually, amount of ionized particles is increased because of acid, alkali cleaning, oxidation treatment, or contamination. But there is also the material especially sputtering well with ion state. When one has a high ionization tendency, the other is composed of a material having high electron affinity in the alloy or compound. When the target is the materials of (A+B), A has a high ionization tendency, B is the higher the fraction of the electron affinity is high. So the fraction of ionized A is higher when the sputtering. And the ions incoming to the substrate are both cation and anionic. When using a ceramic target or as a reactive sputtering, it can be generated the non-metallic anions within surface of target or plasma. The accelerated anions can be entered to the substrate. The ionization of the particles due to the Plasma is shown in Fig 9.

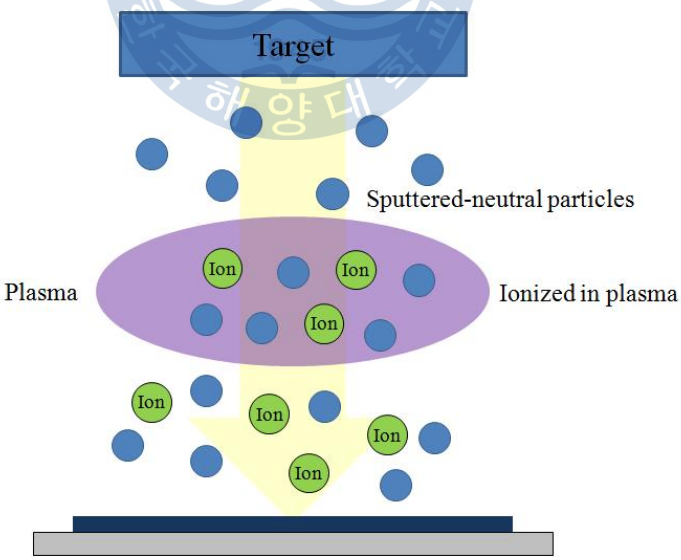


Fig 9. Ionization of the particles generated in the plasma

2.3.2 E-beam evaporator

The kinetic energy of the deposition particles reaching the substrate is same with the size of the heat rate, because, in case of vacuum deposition, source is evaporated by heating. So, it is impossible to largely kinetic energy of deposition particle. Ion plating is the methods which ionized deposition what the portion of the generated atoms or molecules, accelerated in electric field to make the state of energy of high level. And the atoms and molecules are absorbed on the substrate in the vacuum. Depositing particles is evaporated by electron beam heating method or electron beam evaporation or the like used in the vacuum vapor deposition. And the portion of depositing particles is ionized by plasma or an electron beam of inactive gas and the reactive gas between the evaporation source and the substrate. The ionized evaporation particles are accelerated with Ar cation by a negative potential on substrate. So the particles having a very large energy formed thin-films by crash with substrate. The particles having a large energy formed thin-films of dense and excellent physical properties because of easy of move within the thin-films. The non-ionized evaporation particles are deposited on surface of Substrate Lake a vacuum deposition. But, it can be activated the surface of thin-films because of collide at high speed by the Ar, and ionized particles. The principle and the method of ion plating are shown in Fig 12 and Fig 13.

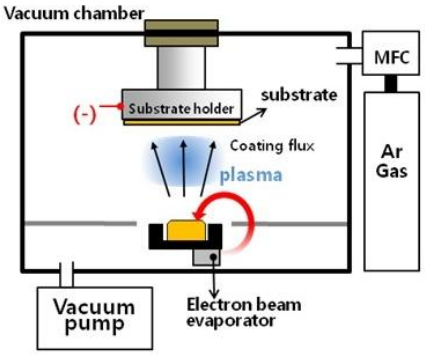


Fig 12. General methods of Ion plating system

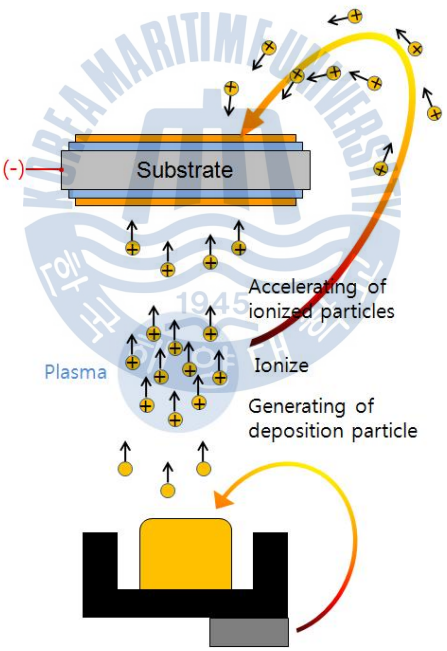


Fig 13. The role of Plasma in Ion plating

Chapter 3. Experiment and Measuring properties

3.1 Growth of Seed layer

3.1.1 Growth of Seed layer

Now days, the growth methods of ZnO could be divided into physical and chemical methods according to the synthesis of ZnO nanostructure. Physical methods refers prepare ZnO nanostructure based device using growth of thin-films and nanolithography which needs discrete and expansive system and remains many difficulties to overcome. Otherwise, the chemical growth means that from the atoms or nucleation of molecules, grow or condenses into small particles with certain size and shape. ZnO nanostructure is mainly prepared by luquid and vapor phase methods in experiment. Hydrothermal methods to prepare ZnO seed layer and ZnO nanorods was assumed.

The ZnO seed layer was grown on the PES substrate which cleaned in methanol, and deionized(DI) water for 5minutes. After that, PES substrates are located in chamber of sputter. Prior to deposition, the vacuum level of chamber is 6×10-6 Torr. Ar gas was introduced through mass flow controllers(MFC) valve at a rate of 20 sccm. ZnO(purity of 99.99%) was used as the target and the RF power was increased to 100W to create plasma. Before deposition, it was pre-sputtering for 10 minutes. During the deposition, the vacuum level of chamber was kept 5 mTorr at room temperature. And the deposition time was kept during 1 hour. After deposition, the thickness of ZnO seed layer was approximately 100nm. And the condition of deposition of ZnO seed layer is shown table 2.

Table 2. The growth conditions of ZnO thin-films

Parameter	Deposition conditions
Target	ZnO (99.99%)
Substrate	PES
Deposition time	1 hour
Deposition Temperature	Room temperature
Vacuum level	5 mTorr
Ar gas	20 sccm
Thickness	100 nm

3.2 Growth of ZnO nanorods

3.2.1 Hydrothermal methods

The ZnO nanorods were grown in the hydrothermal methods. It consists of temperature sensor, hot plate, spin bar, round bottom flask, substrate holder and Si oil as shown in Fig 10. As the Fig 10, the holder could be used for substrates with carious materials, shape, and size. The spin bar in the Si oil rotated to heat and the Si oil is applied to create a homogenous temperature surround the round bottom flask. In particular, the end of temperature sensor is positioned the same as position with substrate for minimize the range of the difference of temperature. After the stabilization of solution in the round bottom flask, attaching the sample by using a sample holder, and the sample holder is fixed so as to be located in the central part of the solution. The substrate is facing the bottom of round bottom flask, attaching at the bottom of the sample holder. Because if the substrate was facing the top of round bottom flask, it was interrupted from ZnO bulk and particles. And by the substrate is facing the bottom of round bottom flask, the ZnO nanorods grow uniformly. The growth temperature was change from 90℃ to 150℃ and the growth concentration be change from 0.05 M% to 0.5 M%.

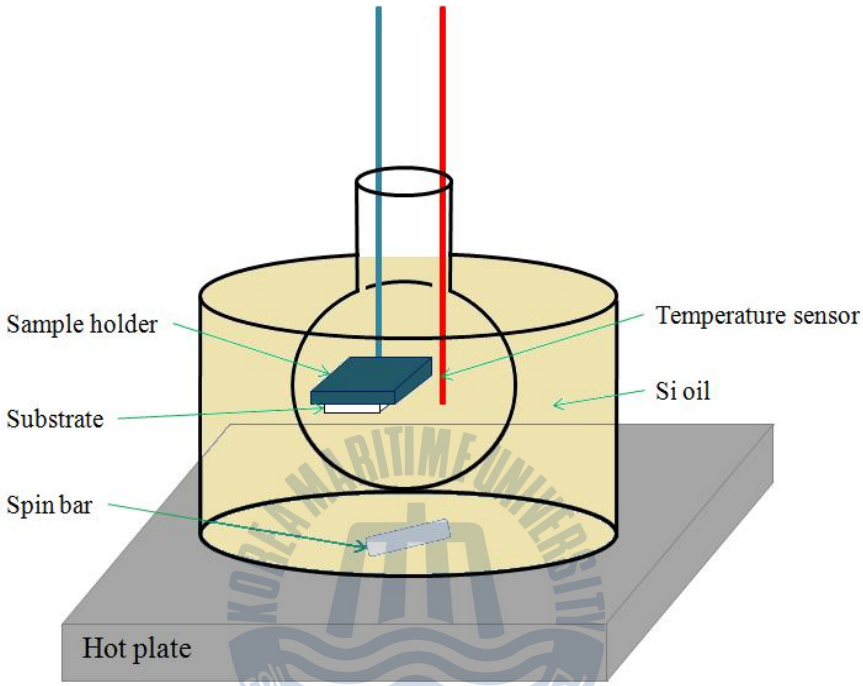


Fig 10. Schematic of the reactor system used for the growth of ZnO nanorods on various substrates.

3.2.2 Reagents and reaction

The hydrothermal methods, as aqueous solution methods, are processed by chemical reactions in a reaction solution. Each of the zinc nitrate hexahydrate(Zn(NO3)2•6H2O, purity 99.0 %) and hexamethylenediamine(HMT, (CH2)6N4, purity 99.0 %) stirred in DI water. When dissolving HMT in DI water, HMT digested with formaldehyde(HCHO) and ammonia(NH3), and NH3 digested with ammonium ion(NH4+) and hydroxide ion(OH-). Zn(NO3)2・6H2O are dissolved in DI water, decomposed to Zn2+, Zn(OH)2 is synthesized by an ionic bond Zn2+ with OH-, in obtained in HMT like a formula 5. Zn(OH)2 in the solution are obtained ZnO receives energy by hydrothermal.

Reaction equations as follows:

$$(CH_2)6N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3 \quad \cdots\cdots \text{식 (4)}$$

$$NH_3 + H_2O \longleftrightarrow NH_4^+ + OH^- \quad \cdots\cdots \text{식 (5)}$$

$$Zn(NO_3)_2 \cdot 6H_2O \rightarrow Zn^{2+} + 2(NO_3)^- + 6H_2O \quad \cdots\cdots \text{식 (6)}$$

$$Zn^{2+} + 2(OH) - \rightarrow Zn(OH)_2$$

$$(\text{heating}) \rightarrow ZnO + H_2O \quad \cdots\cdots \text{식 (7)}$$

3.2.3 Growth of ZnO nanorods

The ZnO nanorods is grown using sample depositied ZnO seed layer by hydrothermal methods. Zinc nitrate hexahydrate of X M% and hexamethylenediamine of X M% is dissolved for 15 minutes with each DI water of 100 ml. And then two solutions were stirred together in the round bottom flask. The flask loaded the two solutions is placed in a beaker filled with Si oil and bath for maintain a uniform temperature during the process time. When the temperature of solution is stable, the substrate is setted on center of beaker, and the substrate is facing downward at that time. After the growth experiment, the sample was rinsed using DI water, and dry for remove the DI water with nitrogen gas. Summary of the experimental process is showed in Fig 11 and experimental conditions were indicated in the table 3.

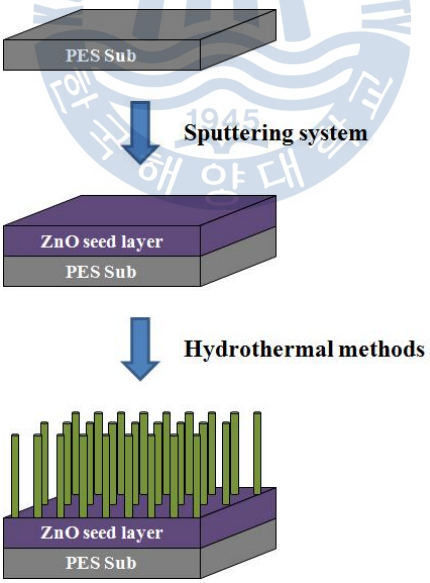


Fig 11. Schematic diagram for the growth of ZnO nanorods using hydrothermal methods on PES substrates

Table 3. The growth condition of ZnO nanorods

Variables of experiments		range	etc.
Substrate		PES substrate	
Seed layer		ZnO	
Thickness of seed layer		100 nm	
Growth of ZnO nanorods	Temperature [℃]	90, 110, 130, 150	
	Concentration [M%]	0.05, 0.1, 0.3, and 0.5	
	Growth time [h]	1 hour	

3.3 Formation of electrode

3.3.1 Formation of electrode

The electrode of Al(aluminum)/Ti(titanium) is formed by e-beam evaporator for study about electrical properties of ZnO nanorods on PES substrate. The Al electrode of 50 nm is formed on substrate, after the Ti electrode of 10 nm is formed on substrate. Because Ti electrode, having a good conductivity, used to improve the contact between the Al electrode and the ZnO nanorods. The diameter of electrode is about 1 mm. The electrode made by dot mask, and dot mask is shown Fig 14, conditions of forming of electrode are shown table 4.

(a) (b)

Fig 14. (a) The pattern of dot mask, (b) the ZnO nanoprods and electrode

Table 4. The growth condition of pole

Variables of experiments			Range	Etc
Substrate			PES substrate	
The structure of surface			ZnO nanorods	
Thickness of seed layer			100 nm	
Formation condition of pole	Titanium	Working pressure	4.5 × 10-6 [Torr]	
		Thickness	10 nm	
	Aluminum	Working pressure	4.5 × 10-6 [Torr]	
		Thickness	50 nm	

3.4 Characterization methods

AFM(Atomic Force Microscope) and EDS(Energy Dispersive x-ray Spectrometer) was used for analyzing to surface and structural properties of PES substrate deposited ZnO seed layer. And FE-SEM(Field Effect-Scanning Electron Microscope) and HP 4145B semiconductor parameter analyzer was used for analyzing the shape, crystalline and electrical properties of ZnO nanorods grown by hydrothermal methods.

3.4.1 4145B Semiconductor Parameter Analyzer

HP 4145B semiconductor parameter analyzer is an instrument that can determine the electrical properties of the semiconductor device in conjunction with LabVIEW. HP 4145B semiconductor parameter analyzer is divided into two parts. These two parts are applying a voltage to semiconductor device, and reading the measured current for transmitting back to the LabVIEW. The basic principle of HP 4145B semiconductor parameter analyzer is shown in Fig 15.

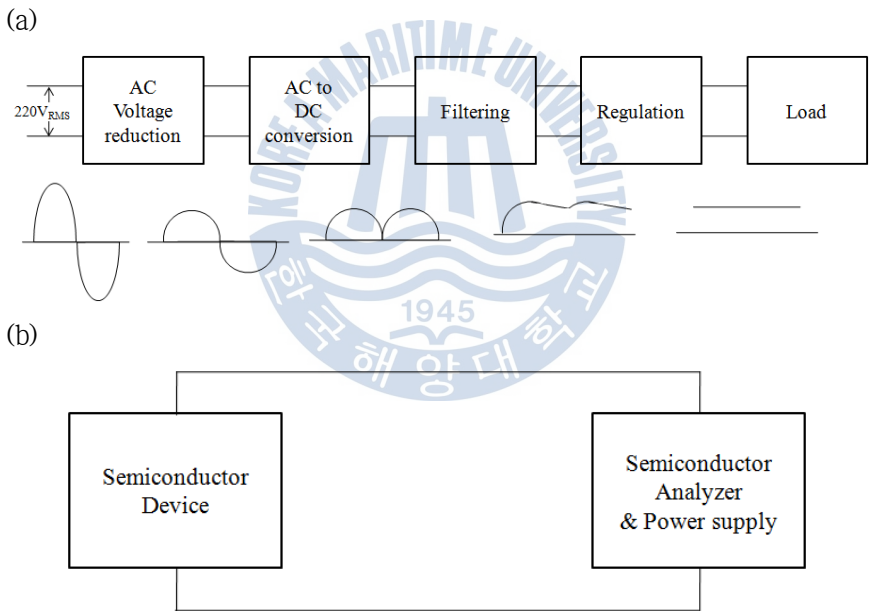


Fig 15. The principle of HP 4145 semiconductor parameter analyzer (a) Power supply unit and (b) wiring to semiconductor

3.4.2 Field Emission Scanning Electron Microscope

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image. SEM can achieve resolution better than 1 nanometer. Specimens can be observed in high vacuum, in low vacuum, in wet conditions (in environmental SEM), and at a wide range of cryogenic or elevated temperatures.

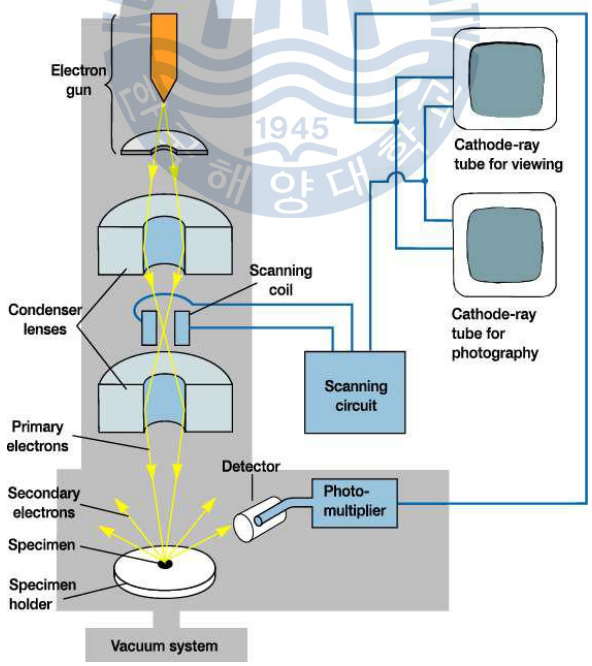


Fig 16. Schematic describing the operation of the SEM

3.4.3 Atomic Force Microscope

Atomic force microscope has measured the shape of the surface of sample using cantilever by taking a picture about surface of sample, measuring the displacement in the cortical direction of the probe with a regular interval. And it can measure insulators, also measure in a variety of environments. AFM of contact mode uses a repulsive force, and the size of force is very micro, so 1~10 nN, but the probe bent by the force, because of sensitivity. It measured using photodiode to measure that the probe is bent up or down. The movement of probe is measured using reflected angle of beam from the cantilever. In this way, it is possible to measure the end of needle the minutely moving about 0.01 nN. Movement of the needle tip can be determined the shape of the sample by feedback to the actuator. AFM of non-contact mode is suitable to measure soft sample. Because it used gravitation, and the force is very smaller than the force of contact mode. Non-contact mode, the tip is vibrated at near the resonant frequency mechanically. When the needle nears to the surface of sample, the amplitude and the phase is changed. Because natural frequencies are changed due to the gravitation interatomic. And it measures the change using lock-in amp. The interatomic force is present, regardless of the electrical properties of the sample. Therefore, it is possible to observe all of the conductor, non-conductive at a high resolution. A schematic of the atomic force microscope is shown in Fig 17.

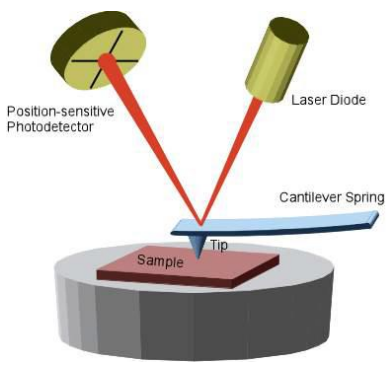
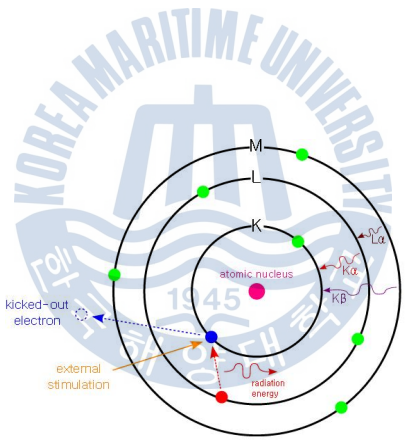


Fig 17. A schematic describing the operation of the AFM

3.4.4 EDS(Energy-Dispersive x-ray Spectroscopy)

Energy-dispersive X-ray spectroscopy(EDS, EDX, or XEDS), sometimes called energy dispersive X-ray analysis(EDXA) or energy dispersive X-ray microanalysis(EDXMA), is an analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray emission spectrum. The basic principle and example of EDS is shown in Fig 18.

(a)



(b)

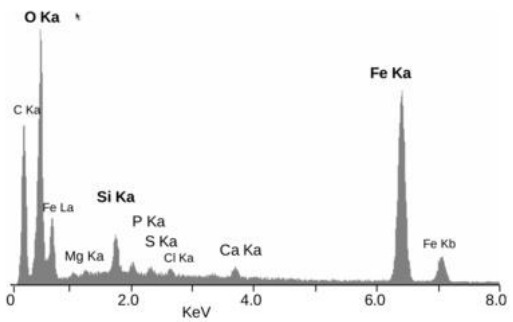


Fig 18. (a) Basic principle and (b) example about result of EDS

Chapter 4. Result and discussion

In this experiment, RF magnetron sputtering and hydrothermal methods were used to growth ZnO nanorods on PES substrate. The growth condition of ZnO seed layer is shown in table 2. The inside vacuum was maintained at 5 mTorr using N2 gas, has not the heating treatment in consideration of the maximum process temperature of 230 ℃ of the PES substrate. ZnO target(99.99%) of 4 inches was used to deposited ZnO seed layer. Before the deposition, the PES substrate was cleaned with methanol and DI water called the organic cleaned, and dried using N_2 gas of 99.99% purity. And the initial vacuum level of chamber was formed at 6×10^{-6} Torr using TMP(Turbo molecular Pump).

The growth condition of ZnO nanorods is shown in table 3. Zinc nitrate hexahydrate of X M% and hexamethylenediamine of X M% is dissolved for 15 minutes with each DI water of 100 ml. Growth time was fixed at 1 hour, structural and electrical properties of ZnO nanorods were analyzed at each of the temperature, concentration. And HP 4145B semiconductor parameter analyzer, FE-SEM, AFM, and EDS were used for analysis of structural and electrical properties.

4.1 The structural properties of ZnO seed layer

4.1.1 The structural properties of ZnO seed layer

For the selection of deposition condition, the structural properties of ZnO seed layer are analyzed by XRD. The peaks of all thin-films are located nearby 34.5°. So, the FWHM(Full Width at Half Maximum) is analyzed for the selection of conditions at the various applied power and the various vacuum level in the chamber. It is most great value at applied of 100W and vacuum level of 5 mTorr in the chamber. The result of XRD is shown in Fig 19. And the surface and the side of ZnO nanorods is shown in Fig 20. At the Fig 20, the effect of ZnO seed layer could be seen as growth of ZnO nanorods by partially growing a seed layer.

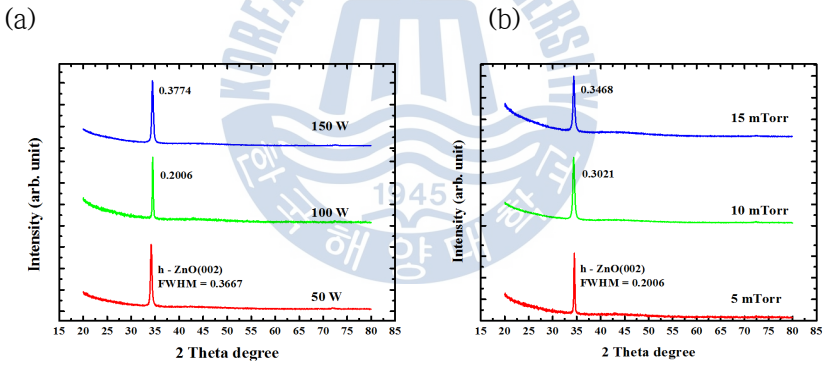


Fig 19. The result of XRD about ZnO seed layer according to (a) the applied power, (b) the vacuum level in the chamber

(a) (b)

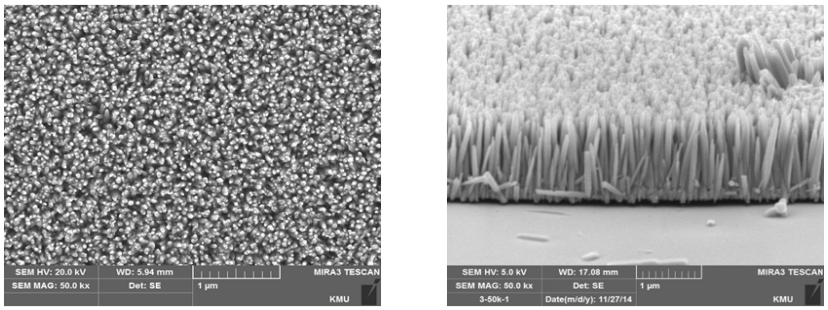


Fig 20. The effect of ZnO seed layer when grown the ZnO nanorods (a) surface of nanorods, (b) side of nanorods

4.2 The properties of ZnO nanorods according to concentration of solution

The ZnO nanorods was grown for analysis of properties according to the increasing of the growth concentration such as 0.05, 0.1, 0.3, and 0.5 M% by hydrothermal methods. At this experiment, the temperature of growth is fixed at 90℃. And HP 4145B semiconductor parameter analyzer, FE-SEM, AFM, and EDS were used for analysis of structural and electrical properties. The PES substrate was deposited a ZnO seed layer of about 100nm by using a sputter system.

4.2.1 The structural properties of ZnO nanorods

Fig 21 is a SEM image for observing the image of the fine ZnO nanorods according to the concentration of growth, the size of each nanorods are shown at graph in Fig 22. The diameter of the ZnO nanorods grown with increasing the density increases linearly until 0.5 M% of the maximum concentration and, the change of length had a relatively uniform size, regardless of the concentration of about 80 nm. Thus, ZnO nanorods are grown First of the vertical direction, after those particles of ZnO was supplied to the growth in the radial direction. So growth in the supersaturated solution shows the active shape in the radial direction. And the structural properties of ZnO nanorods can be seen that substantially vertically grown. In the EDS results of the Fig 23, C and Pt were detected in the ZnO nanorods. Because C is the effect of carbon tape and Pt is coating materials for improve the conductivity. In general, the amount of Zn and O are increased to 1.2k from 1.05k according to the increasing of the concentration. The optimum concentration of solution is 0.3 M% for the growth ZnO nanorods. Various peaks have been observed several directional as the polycrystalline structure, because of supersaturated solution at the concentration of 0.5 M%.

(a) (b)

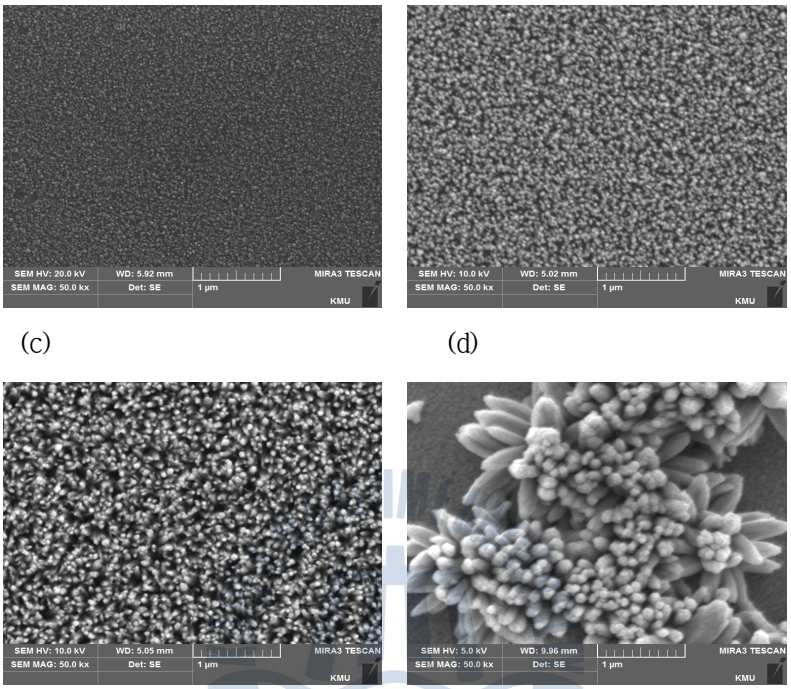


Fig 21. The result of FE-SEM about ZnO nanorods according to concentration at the growth temperature of 90℃

(a) 0.05 M%, (b) 0.1 M%, (c) 0.3 M%, and (d) 0.5 M%

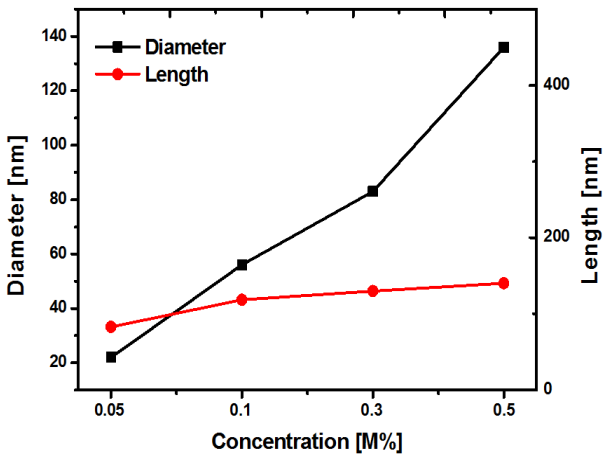


Fig 22. The length and diameter of ZnO nanorods according to concentration at 90℃

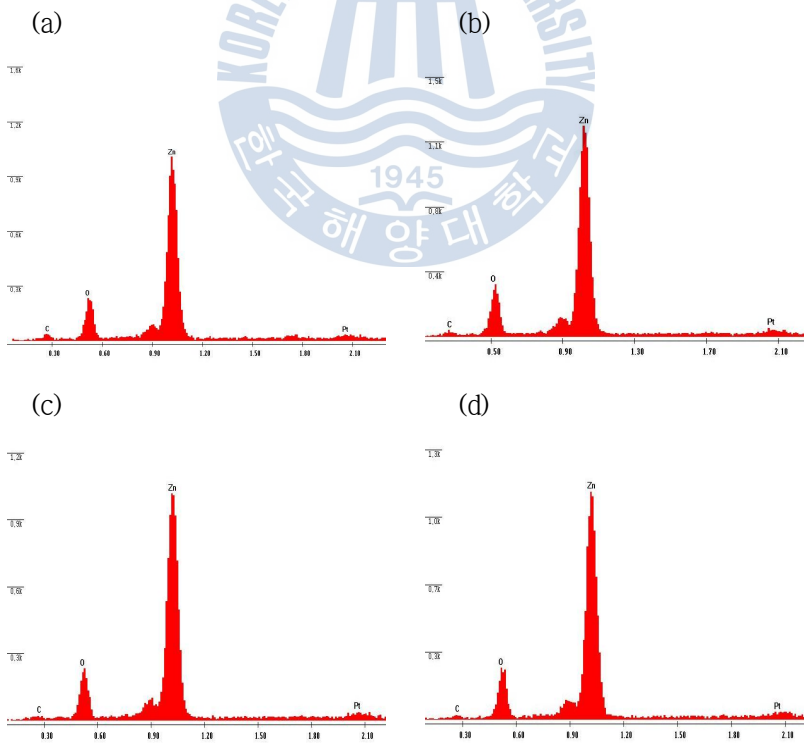


Fig 23. The result of EDS (a) 0.05 M%, (b) 0.1 M%, (c) 0.3 M%, and (d) 0.5 M%

4.2.2 The electrical properties of ZnO nanorods

The current was measured according to the applied voltage to +4V from -4V at the two electrodes formed by using dot mask for analysis of electrical properties. The current was increased flowing through the ZnO nanorods according to the increase of concentration, and current is proportional to voltage. In generally, the resistance of ZnO nanorods increased according to the linearly increase of concentration. The electrical properties of ZnO nanorods according to the concentration are shown in Fig 24. As the result of HP4145 semiconductor parameter analyzer, the resistance of ZnO nanorods is increased. So the resistance of ZnO nanorods at the concentration of 0.3 M% is representatively shown Table 5.

Table 5. The resistance of ZnO nanorods at the concentration of 0.3 M%

Growth temperature	Concentration of 0.3 M%
90℃	1.6074 MΩ
110℃	1.2972 MΩ
130℃	1.1957 MΩ
150℃	0.8442 MΩ

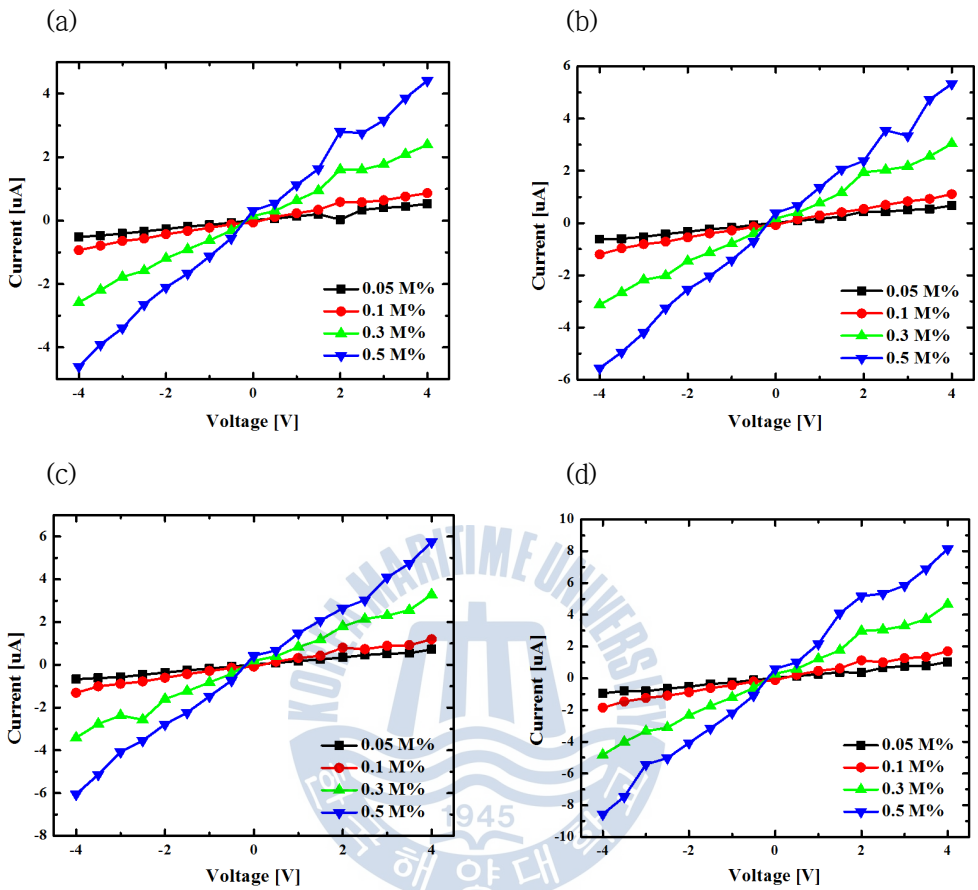


Fig 24. The result of HP 4145 semiconductor parameter analyzer at 0.3 M% of solution concentration

(a) 90℃, (b) 110℃, (c) 130℃, and (d) 150℃

4.3 The properties of ZnO nanorods according to temperature of solution

The ZnO nanorods was grown for analysis of properties according to the increasing of the growth temperature such as 90℃, 110℃, 130℃, and 150℃ by hydrothermal methods. At this experiment, the concentration of growth is fixed at 0.3 M%. And HP 4145B semiconductor parameter analyzer, FE-SEM, AFM, and EDS were used for analysis of structural and electrical properties. The PES substrate was deposited a ZnO seed layer of about 100 nm by using a sputter system.

4.3.1 The structural properties of ZnO nanorods

Fig 25 is a SEM image for observing the image of the fine ZnO nanorods according to the temperature of growth, the size of each nanorods are shown at graph in Fig 26. And the density of ZnO nanorods is higher than concentration of 0.3 M% at concentration of 0.5 M%. The diameter of the ZnO nanorods grown with increasing the density increases linearly until 150℃ of the maximum temperature and, the change of length had a relatively uniform size, regardless of the temperature of about 180 nm. Thus, ZnO nanorods are grown First of the vertical direction, after those particles of ZnO was supplied to the growth in the radial direction. So Growth in the supersaturated solution shows the active shape in the radial direction. And the structural properties of ZnO nanorods can be seen that substantially vertically grown. In the EDS results of the Fig 27, the C and Pt were detected in the ZnO nanorods. Because C is the effect of carbon tape and Pt is coating materials for improve the conductivity. As the result of EDS, the Zn and O are increased to 1.7k from 1.3k according to the growth temperature. When the increasing of thermal energy, ZnO nanorods grown more.

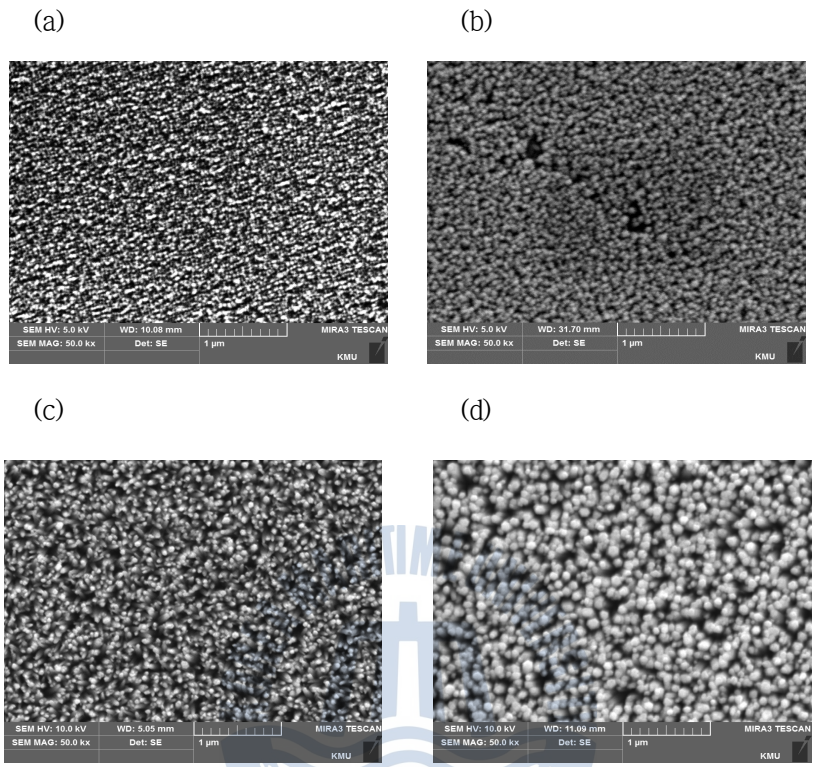


Fig 25. The result of FE-SEM about ZnO nanorods according to temperature at the growth concentration of 0.3 M%

(a) 90℃, (b) 110℃, (c) 130℃, and (d) 150℃

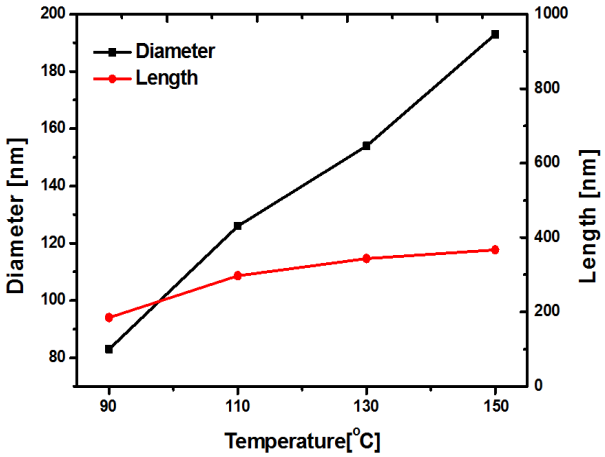


Fig 26. The length and diameter of ZnO nanorods according to temperature at 0.3 M%

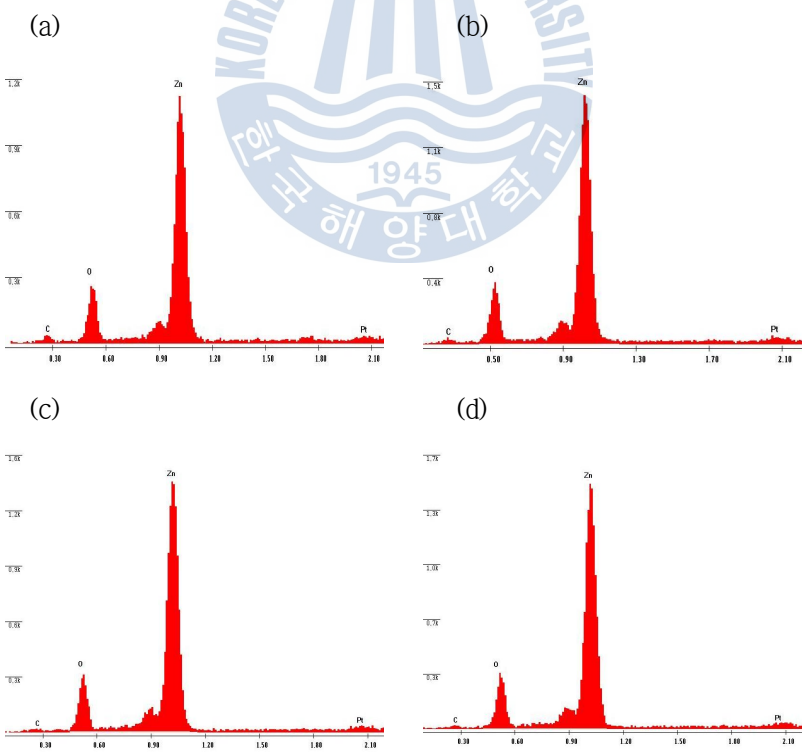


Fig 27. The result of EDS (a) 90℃, (b) 110℃, (c) 130℃, and (d) 150℃

4.3.2 The electrical properties of ZnO nanorods

The current was measured according to the applied voltage to +4V from -4V at the two electrodes formed by using dot mask for analysis of electrical properties. The current was increased flowing through the ZnO nanorods according to the increase of concentration, and current is proportional to voltage. In generally, the resistance of ZnO nanorods increased according to the linearly increase of temperature. The electrical properties of ZnO nanorods according to the temperature are shown in Fig 28. As the result of HP4145 semiconductor parameter analyzer, the resistance of ZnO nanorods is decreased. So the resistance of ZnO nanorods at the growth temperature of 90℃ is representatively shown Table 6.

Table 6. The resistance of ZnO nanorods at the growth temperature of 90℃

Concentration	Growth temperature of 90 ℃
0.05 M%	7.6146 MΩ
0.1 M%	4.8871 MΩ
0.3 M%	1.6075 MΩ
0.5 M%	0.8869 MΩ

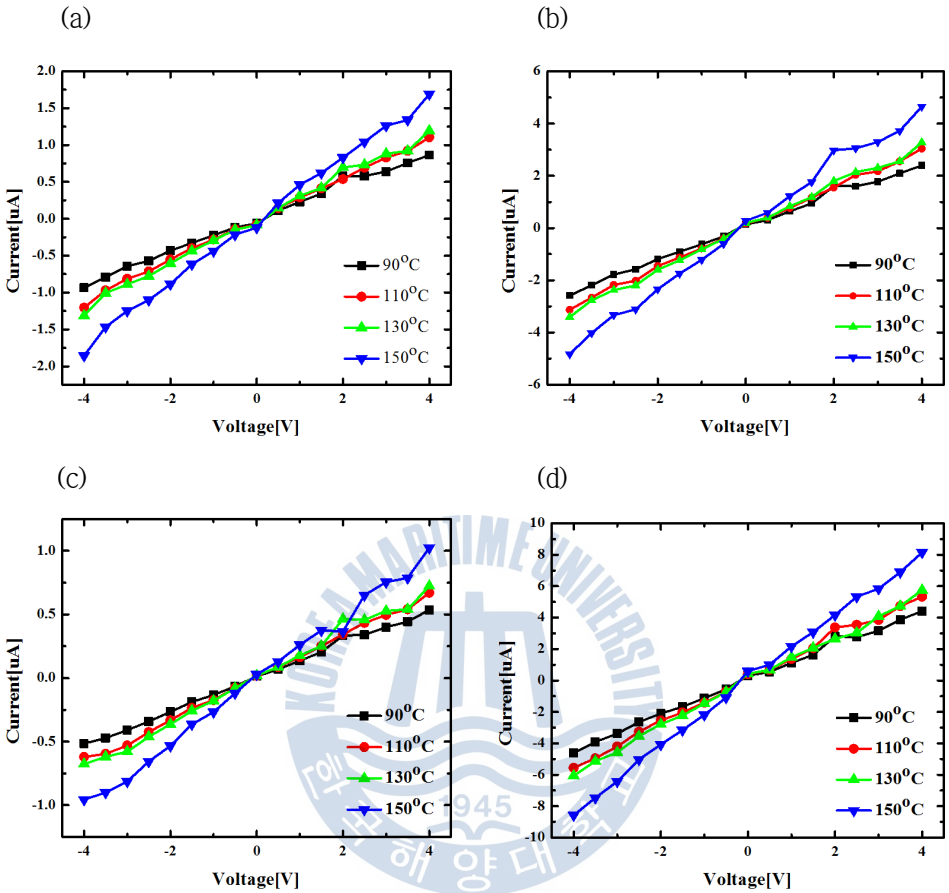


Fig 28. The result of HP4145B semiconductor parameter analyzer at 90℃ of growth temperature

(a) 0.05 M%, (b) 0.1 M%, (c) 0.3 M%, and (d) 0.5 M%

Chapter 5. Conclusion

In this study, the electrical and structural properties of ZnO nanorods based on the flexible substrate was studied. ZnO seed layer was produced using a RF magnetron sputter, condition of the thin film is kept constant. The ZnO nanorods was grown according to the temperature and concentration of solutions. As the result of the properties of the grown nanostructure were obtained as shown below.

1. As the result of electrical properties of ZnO nanorods, the diameter and the length is changed according to the growth temperature and concentration. According to the increasing of temperature, the current is increased in proportion to the voltage. And the maximum current of ZnO nanorods is about 10 uA at the voltage of +4 V. In case of the ZnO nanorods which was grown at concentration of 0.05 M% and temperature of 90℃, the maximum current is about 0.5 uA. The resistance of ZnO nanorods is increased linear at each of temperature and concentration.

2. As the result of the structural properties of ZnO nanorods, the nanostructure with the direction grown at concentration of less than 0.3 M% and the growth temperature below 110℃. ZnO nanorods was grown excessively at concentrations above 0.5 M% and more than temperature of 130℃. And, ZnO nanorods are grown first of the vertical direction, after those particles of ZnO was supplied to the growth in the radial direction. This shape is convergent to limits like a function of $y=t^{1/2}$.

3. As the result of the component of ZnO nanorods using EDS, Zn, O, and C was detected from the sample. The C was determined under the influence of a carbon tape attached to the EDS measurements. In addition, the content of O was confirmed to decrease, because of oxide vacancy.

4. In generally, the diameter and the length of ZnO nanorods showed increased as

the increasing of concentration and growth temperature. ZnO nanorods was not to grow over the threshold into the disappearance of Zn source at the concentration of 0.05 M%. In addition, the maximum diameter of ZnO nanorods is about 200 nm, and the maximum length of ZnO nanorods is about 400 nm, when applied a sufficient thermal energy and Zn source.

In this study, ZnO nanorods was grown according to the concentration and growth temperature by the hydrothermal methods. So an efficient way to grow ZnO nanorods on PES substrate was suggested. The results show that the diameter and the length of ZnO nanorods are controlled by adjustment of the variables.

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