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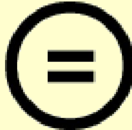
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工學碩士 學位論文

AZO 박막의 미소구조 성장에 따른 광학적/전기적 특성에 관한 연구

Research on the optical and electrical properties of Al doped ZnO films as growth of micro-structure

指導教授 金 允 海

2012年 8月

韓國海洋大學校 大學院

材 料 工 學 科

安 勝 濬

本 論文을 安 勝 濬의 工學碩士 學位 論文으로 認准함.

委員長 : 文 慶 萬 工學博士 ㊞

委　員 : 金 俊 榮 工學博士 ㊞

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2012 年 8 月

韓國海洋大學校 大學院

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Abstract

TCO (transparent conducting oxide) films are widely used as photoelectric devices in flat panel displays and solar cells. Until now, ITO (indium-tin oxide) films have been used as TCO films. However, with the increase in the cost of ITO films, researchers have been searching for new materials to use as TCO films. And in this study, the application and improvement of the optical and physical properties of optical thin film by manipulating the micro-structure was studied. Transparent and conductive aluminum-doped zinc oxide films were prepared by RF reactive magnetron sputtering at different substrate temperatures. The electric and optical properties of these films were studied by Hall measurement and optical spectroscopy, respectively. All of the films that were deposited at temperatures higher than 200 ℃ substrate temperature demonstrated over 80% transmittance in the range of the visible spectrum. Since the surface mobility of a particle is limited at a low temperature, the growth rate of AZO thin films would be higher than that at a high temperature. And the films showed minimum resistivity of 6.77×10^{-3} Ω•cm at substrate temperature of 200 ℃.

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1. Introduction

Recently zinc oxide (ZnO) films have been widely studied because of their potential practical applications as transparent electrodes, window materials in displays, solar cells, and various optoelectronic devices. [1-3] At present, indium tin oxide (ITO) films are generally used as transparent electrodes in practical applicationsbecause of their low resistivity, on the order of 10^{-4} Ω•cm, and stable electrical, optical and mechanical properties. However, ITO is a relatively expensive material because indium is not abundant. On the other hand, ZnO could be useful as a less expensive coating material than ITO if a thin film deposition technique can extract highly conductivity and high physical properties from ZnO at low cost. Al-doped ZnO (AZO) is a particularly attractive material because of its excellent properties, such as higher thermal stability, lower resistance against damage by hydrogen plasma and lower cost of fabrication, compared to ITO. [4] Additionally, ZnO maintains stable chemical and thermal properties during the hydrogen plasma sputtering process. The electrical and optical properties of TCO films have been enhanced by using ZnO films [5,6]. And transmittance is significantly influenced by the Index of Refraction. The American physicists first made optical thin film with the reflactive index which is close to air. This optical film consists of arrangement of nanorods which were diagonally deposited about 45 degrees. They generally have the reflactive index of about 1.05. This reflactive index is the lowest value which has been reported until now. These physicists also argue that optical coating which actually remove reflection in all the wavelengths can be made into film of several layers. The reflactive index is the most basic property in

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optics because it explains the speed change when light enters materials. As the result, the more the difference of the reflactive index in two materials is, the more light which passed through the first material will be reflected in the second one. This relationship was quantized by Augustin Jean Fresnel about 200 years ago and is called fresnel reflection. If a material is surrounded by air, the reflactive index of the material surface should be closed to the reflactive index of air, 1.0 to minimize the quantity of reflected light. But solids don't usually have the reflactive index of 1.0 to 1.4. Synthetic porous materials hae these reflactive index but they cannot be made as thin as they can be used as practical optical coating. Graded-index coatings with several reflactive index profile have been studied to accomplish the broadband antireflective characteristics. But the broadband antireflective coatings have not been realized until now because the optical materials with the very low reflactive index which matches the reflactive index of air cannot be obtained. On the other hand, multi-layer thin film has been traditionally and widely used to accomplish the proper reflection and penetration characteristics. The multi-layer thin film is done accumulating the material layers of the high and low reflactive index. And it was generally accumulated in order which is alternately repeated. The more difference of the reflactive index between layers is, the easier high performance coating can be designed and the more performance can be improved. The larger difference of this reflactive index can be obtained by controling the growth of thin films and making gradients of each layer different.[7] The growth of the thin films should be first checked to make the gradients different. The studies on the growth of the thin films have not been properly done in the direct current

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magnetron sputtering system yet. Therefore, this paper tries to observe the growth of the thin films according to temperature and the AI contents and study the electrical and optical properties of the AZO films about it.

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2. Background

2.1 The characteristics of transparent conductive oxide

Transparent conductive oxide means thin films with the two properties of (1) high transmittance of visible rays (Transmittance is more than about 80% when wavelength of visible light is 380 to 780 ㎚) and (2) high electric conductivity (specific resistance is less than about $1\times10^{-3}\Omega$. cm).

Historically, metal such as Au, Ag, Pt, Cu, Rh, Pd, Al, and Cr has been used as transparent electrode with the certain transmittance of visible light by making them thin films of 3 to 15nm. These thin films had been used by laminating transparent conductive oxide thin film between metal films and the metal thin films have the essential problems that optical absorption is great, hardness is low, and stability is not good. So how to form transparent thin films with good conductivity by using oxide, nitride, and borides and their properties of matter have been studied to solve these problems. The typical materials of the electro-conductive thin films are shown in Table 2.1.

Table 2.1 Typical Transparent Conductive Materials

Type	Film Materials
Metal Film	Au, Ag, Pt, Cu, Rh, Pd, Al, Cr
Oxide-semiconductor film	In_2O_3, SnO_2, ZnO, CdO, TiO2, $CdIn_2O_4$, Cd_2SnO_2, Zn_2SnO_4, In_2O_3, ZnO, In_2O_3, SnO_2
Compound of Spinel-type	$MgInO_4$, $CaGaO_4$,

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Conductive nitride film	TiN, ZrN, HfN
Compound of Conductive Boron	LaB_6
Etc.	Conductive Macromolecule

The typical electroconductive oxide thin films with certain conductivity are shown to be In_2O_3, SnO_2, ZnO, CdO, $CdIn_2O_4$, Zn_2SnO_4 and ZnO. Optical absorption by succession between electromagnetic bands is just generated in the infrared area of more than 350 to 400nm because these oxide semiconductors have the band gap of more than 3eV. And this gets to be transparent in the visible region because its optical energy is not sufficient to make electrons of the valence band be abandoned to the conduction band of more than the band gap. And the conduction electrons density(the carrier density) is risen to about 1018～1019cm^{-3} because intrinsic defects including oxygen vacancy form the donor level by nonstoichiometric creation. As for the band structure of these conductive oxides, the valence band is usually atomic oxygen 2p wall map and the conduction band consists of metallic valence s wall map. If the carrier density is higher than 1018cm^{-3}, the Fermi level is located in the conduction band and that is, it's so-called degeneracy (is piled up back). It can be called the state which is closed to metal because there are conduction electrons in the conduction band. The conduction electrons can comparatively have large mobility because this s wall map is spatially, cubicly, and largely widened if there are electrons in the conduction band. And it is possible to lower low resistance to about 10^{-3}～10^{-4}Ω. cm by increasing the conduction electron density to 1020～1021cm^{-3} as Sn(ITO) is added in In_2O_3,

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Sb and F are done in SnO_2, and In, Ga(GZO), and Al(AZO) are done in ZnO. As for these dopants, for example, in case of ITO(indiumtin oxide), Sn of tetravalence was employed by the substitution type in In site of trivalence and in case of GZO and AZO, Ga and Al of trivalence were done by the substitution type in Zn site of divalence so that 1 ea of the carrier per atom can be released. But, because the entire dopants are not actually employed by the substitution type and there the cases that they exist as interstitial atoms in crystal grains, form oxidation or are segregated on the grain boundary and the surface, the study on improvement of doping efficiency by employing dopants by the substitution type is the very important parameter to manufacture lower specific resistant transparent conductive films. In_2O_3 (ITO) thin film which added Sn of the electroconductive oxide thin films that dopants are added is most widely used now as the transparent electrode for display of several visible light by the reasons that it is most excellent in the two aspects of the high penetration ratio and high electrical conductivity when compared with other materials and it is easy to form the transparent electrode fine pattern by wet etching by acid solution. As for the transparent electrode except these oxides, that is, metal films, nitride thin films, and boron films, for example, Ag is used by laminating it by the three layer structure with the oxide thin film of ZnO/Ag/ZnO, nitride thin films are done by laminating it by the three layer structure with the oxide thin film of $TiO_2/TiN/TiO_2$ and $ZrO_2/ZrN/ZrO_2$. Until then, the transparent electrode using these multi-layer laminated films had been limited to be used in glass with good thermal efficiency, heat reflective glass, and electromagnetic shield glass.

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But laminating the very thin metal films such as Ag, Au, and Cu between ITO thin films is designed in the simple matrix liquid crystal device using the STN(Super twistednematic) method by the necessity of the transparent electrode with the very low sheet resistance according to the recent enhanced industry (e.g. 3～5Ω/□ is necessary in case of 800pixels × 600pixels of SVGA) because the transparent electrode has the electrode for scanning signal and the pixel electrode together. It's because improvement of the penetration ratio by low sheet resistance and the optical interference effect of the oxide layers can be attempted by inserting metal thin films. For example, If ITO/Ag/ITO is laminated by cold films with the film thickness of 450/180/450 Å, manufacturing of transparent electrodes with the very low sheet resistance that it's 2.6Ω/□ and 200℃ before plasticity and it's 2.1Ω/□ after air-firing and the penetration ratio of visible light is about 75%. Like this, the development of transparent electrodes which mixed oxide transparent conductive materials with non-oxide ones is expected to be more accelerated.

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2.2 The Method to Manufacture Transparent conductive oxide

The methods to manufacture ITO thin films includes the physical manufacturing process using the physical phenomena of vacuums which are represented as sputtering and vapor deposition and the chemical manufacturing process using chemical reaction including the spray method and CVD. They are classified like Table2.2.

Table 2.2 Process of Transparent Conductive Film

Physical Manufacturing Process	Sputter Deposition	DC Sputtering process
		DC Magnetron Sputtering
		RF Sputtering Process
		RF Magnetron Sputtering Process
		Opposite Target Sputtering
		ECR Sputtering Process
	Vacuum Metallizing	Resistive Heating
		Electron Beam Evaporation
	Ion Plating	Activated Reaction
		High Density Plasma
Chemical	Thermal Spraying	

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Manufacturing Process		
	CVD	Thermal CVD Process
		Plasma CVD Process

The high substrate temperature of about 350～400℃ is required. And there is the limit of speed up of the growth films because oxidation reaction is late. It can be thought to be because there is the limit in reactivity of In, Sn, and O_2 in the surface of the substrate. The test was conducted using the slope counter-target DC magnetron sputtering process in this test. The sputtering process is now most widely used as the method to manufacture transparent conductive films. Basically, the thin films are formed as plasma is generated by discharge, positive ion of this generated plasma collides with the surface by being accelerated by the target which is the negative ion. And the target materials (sputtering particles) are being scattered by that collision and form thin films by depositing them on substrates. Generally, Ar gas is used in discharge gas, direct current (DC) or high frequency (RF) power supply is used in electric power source. First, it was not good in the non-resistance and etching characteristics when compared to vapor deposition, the same physical manufacturing process with it. But now, the equivalent thin films can be obtained by improvement of the manufacturing method. Especially, the magnetron sputtering process which makes the high speed deposition process possible focusing plasma around the surface with the high density by the magnetic field that the magnet arranged in the back of the target has been widely used in the technical mass production line. The general characteristics of the technology to manufacture thin films in the sputtering process are as follow:

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1) The thin films of wide materials including metal, alloy, insulating materials can be manufactured.
2) The thin films with nearly same creation can be manufactured with targets with plural and complex creation by setting of proper conditions.
3) The thin films of mixture of the target materials with gas molecule and chemicals can be manufactured by adding activated gas including oxygen in the discharged atmosphere.
4) Control of thin film thickness is easily possible by control of the target input electric power and the sputtering time.
5) Manufacturing of thin films with the uniform thickness is very favorable on large scaled substrates.
6) There is no need to control the location relationship between the targets and the substrates because the effect of gravity on motion of the sputter particles can be ignored.
7) The sputter particles have the strong adhesion that is more than 10 times than vapor deposition under pressure which is usually used because it is injected on substrates as it has high energy. And the sputter particles become strong and dense films by making surface diffusion on the growth surface of films by the high energy. Furthermore, they easily tend to be crystal films even on the substrates of comparatively low temperature by the high energy.
8) Manufacturing of very thin continuous films of less than 10nm is possible in the initial process of thin film process because the density of nucleation is high.

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9) It is suitable for continuous operation during the long period and automation because the target lifespan is long.

2.3 The Growth of Thin Films and the Micro Structure

2.3.1 The micro structure of the thin films

Optical thin films can be manufactured by the several methods including physical vapor deposition (PVD), chemical vapor deposition (CVD), spin coating, and dip coating . The physical vapor deposition forms thin films as evaporated particles are absorbed and cohered on substrates and the thermal evaporation method, electron beam evaporation, and sputtering belong to this. Chemical vapor deposition (CVD) is the method to grow thin films by chemical reaction that electronic switching is done .[7-10] The thin films which are grown like this have different micro structures, elementary composition ratio, crystal structures, and chemical bond according to vacuum evaporation. Especially, the optical thin films have the great effect on the optical characteristics by the micro structure and crystal structure because interference of light is easy in the boundary surface of the thin films. If the thin film has the structure which consists of bulk of an ideal single crystal or the amorphous state like Figure 2.3.1(a), light which is injected by strength of I0 gets to be divided into reflection(IR) or penetration(IT) in the boundary surface. At this moment, the law of the conservation of energy about light intensity becomes ideally I0 = IT + IR. But the actually evaporated thin films have the complex microstructure like Figure 2.3.1(b) by their internal and external defects and get to show the

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different characteristics from the bulk state. Due to it, absorption (IR) or scattering (IT) which is different from ideal thin films can be created in the actually evaporated ones. In this case, the law of the conservation of energy becomes I0 = IT + IR + IA + IS [9]. Like this, the actual thin film micro structure is directly related to the optical and physical characteristics and has the great effect on the deposition process and conditions. Therefore, the study on the relationship between the micro structure and optical and physical characteristics is very important in all the application fields of thin films which use the structural and electrical characteristics as well as in the optical thin film field which use the optical characteristics. The study on the relationship between the micro structure and the optical characteristics of the thin films was begun by Hass in 1938 and many studies on the relationship between the micro structure and the optical characteristics have been done until now since Heitmann reported the great effect of the temperature of substrates on the optical characteristics in the dielectric substance thin films in 1968. The most evaporated optical thin films have the micro structure of unstable metastable state, not the stable energy state with low energy and get to be changed to the stable state when energy is enough applied. Therefore, the micro structure of the thin films can be effectively changed by applying energy to the evaporated particles from the outside when they are evaporated. [9,13]

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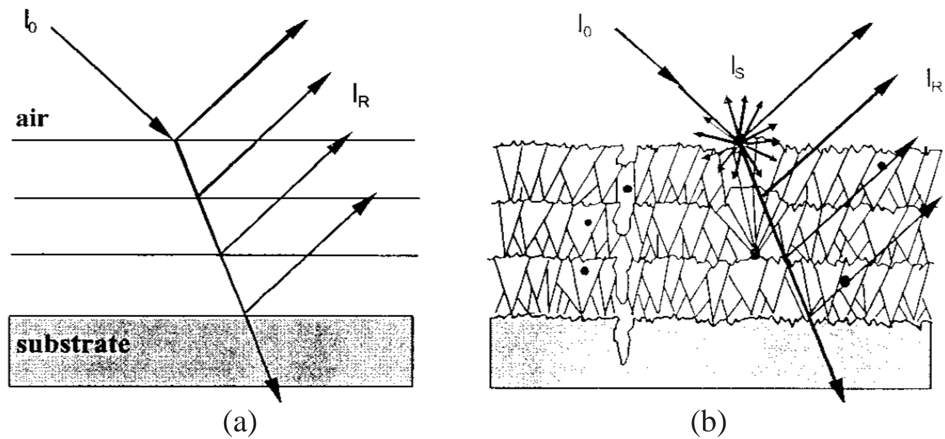

Fig. 2.3.1 The model of the thin film structure (a) The ideal thin film structure, (b) The actually evaporated thin film structure

2.3.2 The growth of the thin film

Understanding about the growth mechanism of the thin films is necessary to study the micro structure of the thin films because it is significantly influenced by the initial growth process. The phenomena which are shown on the surface when the thin films are evaporated include cohesion, adhesion, adsorption, absorption, and desorption. Like this, the complex phenomena are created on the surface of substrates and the thin films get to grow by interaction between flying particles and interaction between evaporated particles and the substrates. The growth of the thin films consists of the several stages and they generally get to grow going through the following stages like Figure 2.3.2[.14] That is,

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1) The materials which compose the thin films collide with the substrates, lose energy of the vertical component and be physically adsorbed on them.

2) The adsorbed materials create nuclear atoms as they reach the critical size by making thermal balance.

3) Nuclear atoms grow, make an island and form the islands which grow by the horizontal component.

4) As the islands grow, coalescence is done each other.

5) Continuous films are formed due to coalescence of the islands.

Like this, vacuum evaporation of the thin films by vapor deposition is the case that typical non-uniform nuclear atoms are created and is created by condensation between flying particles after being evaporated and the ones on the substrates. At this moment, creation of nuclear atoms occurs in the high degree of saturation. And the degree of saturation(S) is defined as follow:

$$S = Pv / Pe \qquad (2.3.1)$$

Where,

Pv is steam pressure of flying evaporated materials after being evaporated from the source, the temperature T and Pe is the balance steam pressure of the materials in the substrate temperature Ts. At this moment, the evaporation rate(R) has the following relationship with Pv, steam pressure of the evaporated material.

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$$R = Pv\sqrt{2\pi mkT} \qquad (2.3.2)$$

Where, k is Botzmann constant, m is the molecular weight of the evaporated materials, and t is the temperature of evaporation source. Generally, the degree of saturation S gets to be very high because the temperature of the substrates is very lower than the one of the evaporation sources, the evaporated particles lose thermal energy on their surface, get colder rapidly and are condensed. Rearrangement of particles is not done in the stable state that energy is minimized due to it and they are condensed on the substrates as they are. Therefore, the unstable amorphous islands are created as shown in Figure 2.3.3. But crystallization is rapidly shown from the moment that the islands gradually grow and get to be bigger and masses contact each other (around 14 nm of Figure 2.3.3) [10,16]. Cohesion of the thin films is largely divided into three growth mechanism as shown in Figure 2.4 and it is determined by interaction and strength between growing thin film particles and interaction between particles of the thin films and the substrates [15,16].

1) 3D nucleon formation, growth, and connection of islands (Volmer-Weber mechanism): the 3D growth mode that the thin films grow as they are separated by the island forms on the substrates if interaction between thin film atoms is greater than interaction between the thin films and the atoms which is close between the substrates.
2) The growth by layers and layers (Frank-van der Merwe mechanism): the 2D growth mode that the thin films grow from the substrates to the layers if interaction between the substrates and the thin film atoms is greater than interaction between thin film atoms and another layer

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grows above it.

3) Adsorption of the single layer and nucleon formation which is continued above it (Stranski-Krastanov mechanism) : It's the case that it grows by the layers by interaction of the substrates and thin film particles in the initial stage and does by the independent islands and layers by interaction between thin film atoms as the thin films gradually grow. The growth mode that 3D nucleon formation mechanism and mechanism by layers and layers are simultaneously shown.

In case of the optical thin film in three growth modes of these thin films, cohesion of the thin films occur by 3D nucleon formation, growth, and the Volmer-Weber mode by connecting islands to each other because interaction of the substrates and evaporated particles is greater than interaction between evaporated particles [14].

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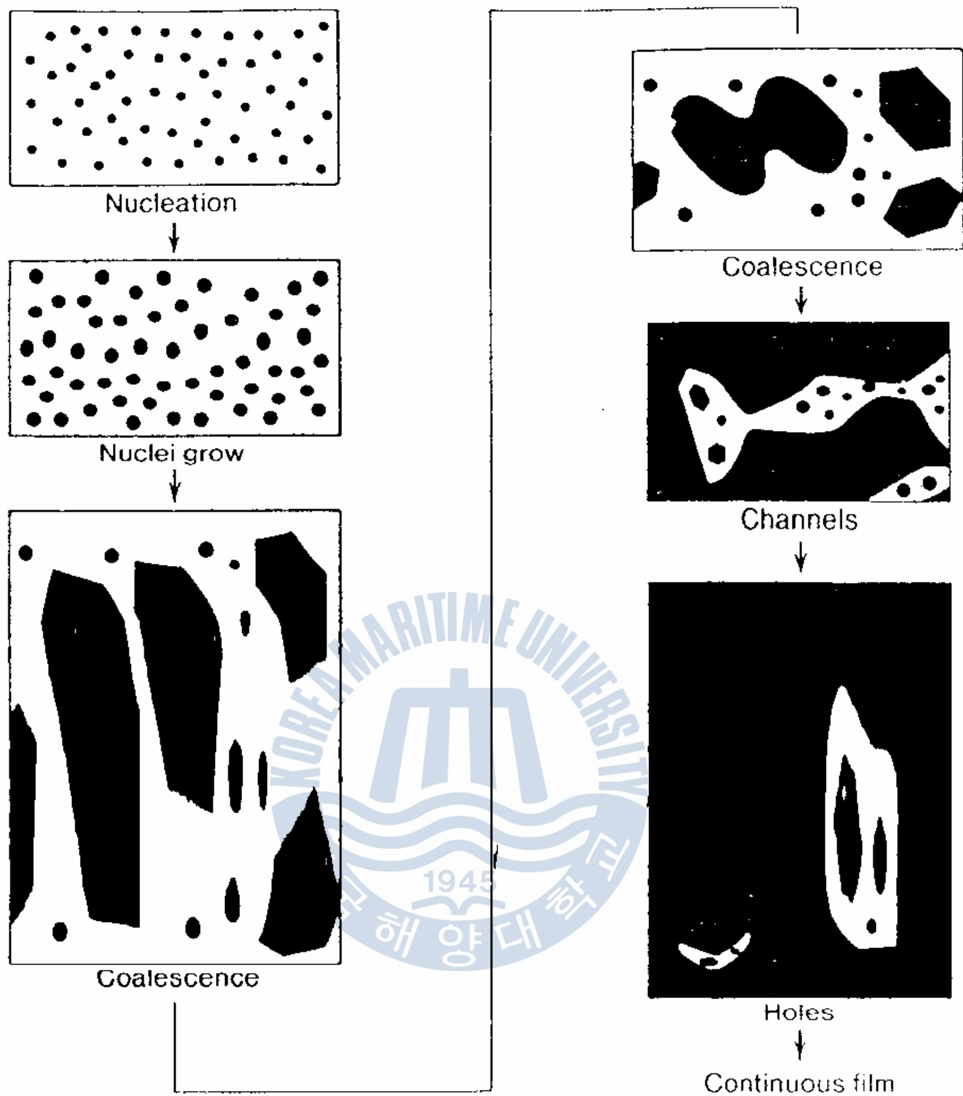

Fig. 2.3.2 The mimetic diagram of the thin film growth process.[7]

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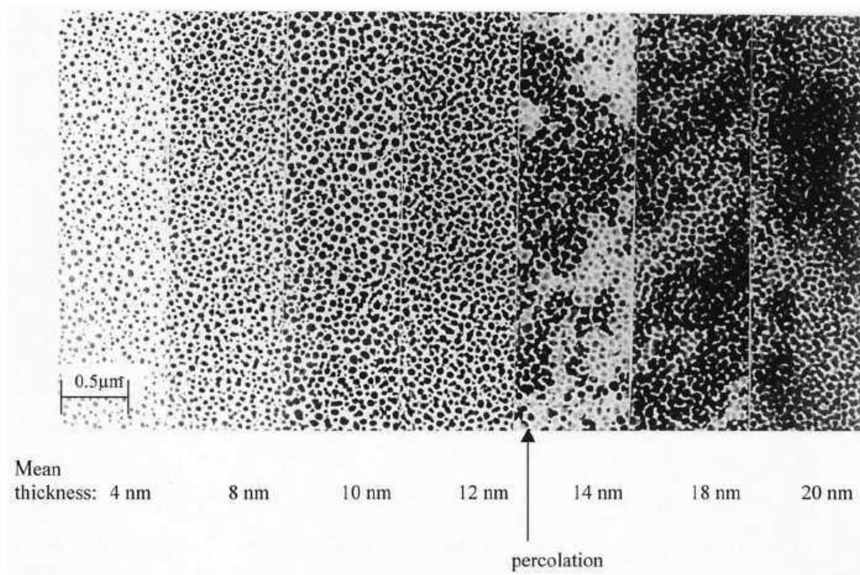

Fig. 2.3.3 TEM image according to growth of Sb thin film.[10]

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	Θ < 1ML	1 ML < Θ < 2 ML	Θ > 2ML
Volmer – Weber			
Frank - van der Merwe			
Stranski – Krastanov			

Fig. 2.3.4 The thin film growth mode of three types.

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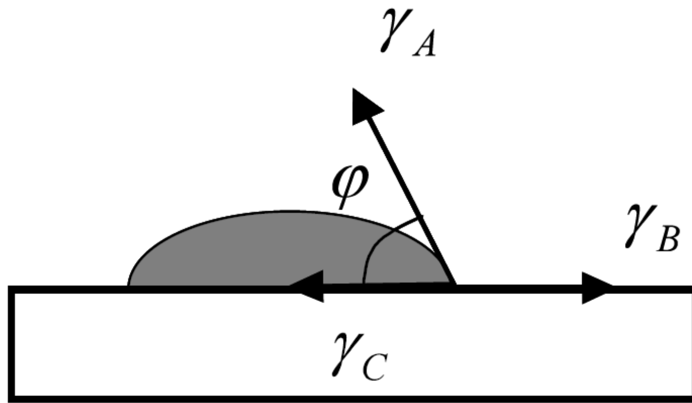

Fig. 2.3.5 The contact angle ψ of neutron on the substrate which is described as γB =γC+γA cosψ of Young (The surface energy of the substrate γB , The surface energy of the thin film material γA, Mutual energy of the thin film and the substrate γC)

The growth mode of the thin films can be more systematically classified using the surface energy equation of Young which is shown in Equation (2.3) [10,16].

$$\gamma_B = \gamma_C + \gamma_A \cos\phi \qquad \textbf{(2.3)}$$

Where, γB is the surface energy of the substrate and γA and γC are the surface energy of the thin film material and the mutual energy of the thin film and the substrate. The relationship between the contact angle of nucleon on the substrate and the surface energy is shown in Figure 2.3.5. If the contact angle of nucleon ψ is greater than 0, the thin film gets to grow. That is, the conditions of γB > γA+γC should be satisfied to make the island(ψ>0) grow in Equation (2.3) and the conditions of γB > γA+γC should be satisfied to make the layer(ψ= 0) grow. The growth of the layer and islands occur by increase of the thin film

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thickness and mutual energy and the layer on the substrate generally pulls the substrate. This growth mode is controlled by supersaturation as well as the surface energy. And the growth of the thin film generally tends to move from the islands to the layers as supersaturation increases [10,16].

The thin films grow until they have the effect on each other in the continuous net form after 3D thin films are formed and get to go through the coalescence process. This coalescence process is very important to manufacture the thin films like the metal thin films. Especially, the thickness growth is important in evaporation of the metal mirror or most of evaporation of the optical films which evaporate dielectric thin films. This thickness growth process is actually determined by the following four processes, not the simple increase of thickness [16].

1) Shadowing: it is remarkably shown in the low substrate temperature (Ts) by the geometric interaction between roughness of the surface by the surface growth and the arrived particles and because the evaporated particles have directional properties.
2) Surface diffusion: It occurs by mobility of particles in the boundary between the surface and particles and it is remarkably shown when the substrate temperature (Ts) is medium.
3) Bulk diffusion: It occurs by mobility of particles' size and in the high substrate temperature (Ts).
4) Recrystallization: It's the process that phase transition is shown like the change by decision of directional properties and depends on the high substrate temperature (Ts) and the thickness of thick films, and

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diffusion thickness.

2.3.3 The structure zone model(SZM)

The thin film get to grow through a series of process as explained before. And one of the most important factors to determine the micro structure of the thin films is the effect of the temperature. The temperature becomes the important element in diffusion, desorption, and nucleation speed in the surface of thermally activated particles. Figure 2.3.6 shows that creation of the thin films is changed by the increase of the substrate temperature due to the temperature change after thermal treatment of the surface image and the substrate by 500 ℃ for 20 minutes after evaporating Cu thin film evaporated on the SiO substrate and the effect of the temperature is great. The most metals and dielectric thin films are closely related to the point that the activated energy melts(Tm). Movchan and Demchishin first suggested the structure model to explain the characteristic behavior about formation and growth of the thin films [17]. They suggested the structure zone model (SMZ) which divides the structure of the thin films into the three zones. According to the structure zone model, it is shown that the thin films have the micro structure of porous column which consists of column and empty space if it's $Ts / Tm < 0.3$[17]. According to the characteristics of the substrate that it is difficult that the temperature of high substrate that the melting point is more than 2000 ℃ to increase by more than 550 ℃, the most dielectric optical thin films get to grow in the area I($Ts / Tm < 0.3$) and do as the column structure that empty space exists between materials,

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and get to be evaporated as the thin film with great residual stress. If the temperature of the substrate is increased and it's the area II(0.3 < Ts / Tm < 0.5), a lot of empty space which existed in the area I is filled as the mobility of particles is increased by the activated energy of about 0.1 to 0.3 eV, the thin films with the high density are evaporated due to it, the size of the crystal gets to be increased as it gradually formed if it's the area III (Ts / Tm > 0.5) because the temperature of the substrate is much more increased.

The structure zone mode that Movchan and Demchishan suggested could not explain the evaporated structure of the thin films due to the vapor deposition such as sputtering or ion plating with high density in the low temperature of the substrate as the model which considers the temperature of the substrate and the melting point only. Therefore, Thornton suggested the structure zone model with the transition zone I that the column structure disappeared and crystal is not formed as the result that they properly mixed the temperature with non-active gas between the area I and the area II like the Figure 2.3.7 to explain this phenomenon in 1974.[18] The important points in Thornton's structure zone model are that the less pressure of Ar is when sputtering is done, the less number of collision between sputtered atoms is(That is, the mean free path is increased) so that high energy can be obtained and the great surface mobility can be obtained even though the temperature of the substrate is lower. Because of it, there is the transition area (zone T). Figure 2.3.7 shows that the higher pressure of Ar is, the more TJT.. that zone transition occurs is increased.

Messier et al suggested the structure zone model which considers the additional ion energy which is applied to the thin films and thickness of the thin

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films as well as the evaporated temperature like Figure 2.3.7 to explain the phenomena when the thin films that additional energy (mobility) is applied except the unique movement amount of the evaporated materials including ion assisted evaporation are evaporated. [19] This is the model that the size of column that consists of the thin films according to increase of additional ion bombardment energy is increased. They showed that the physical structure according to thickness of a-Ge thin film evaporated in the low mobility (T_s / T_m = 0.27) was investigated and the size and shape of column get to be different according to the thickness of the thin films as shown in Figure 2.3.8. [19]

Except them, Dirks and Leamy suggested the structure zone model according to increase of the thin film thickness in the existing structure zone model like Figure 2.3.9 and the thickness grows as the crystal structure of V-shape according to its increase in the structure zone model T.[20] And Bamal and Adamik suggested the model about the effect of the thin film structure according to the increase of dopants starting from the initial structure zone model without it and showed that its increase is effective to lower the temperature and has the high porous fine crystal structure even in the high temperature by its increase as shown in Figure 2.3.10. [21,22]

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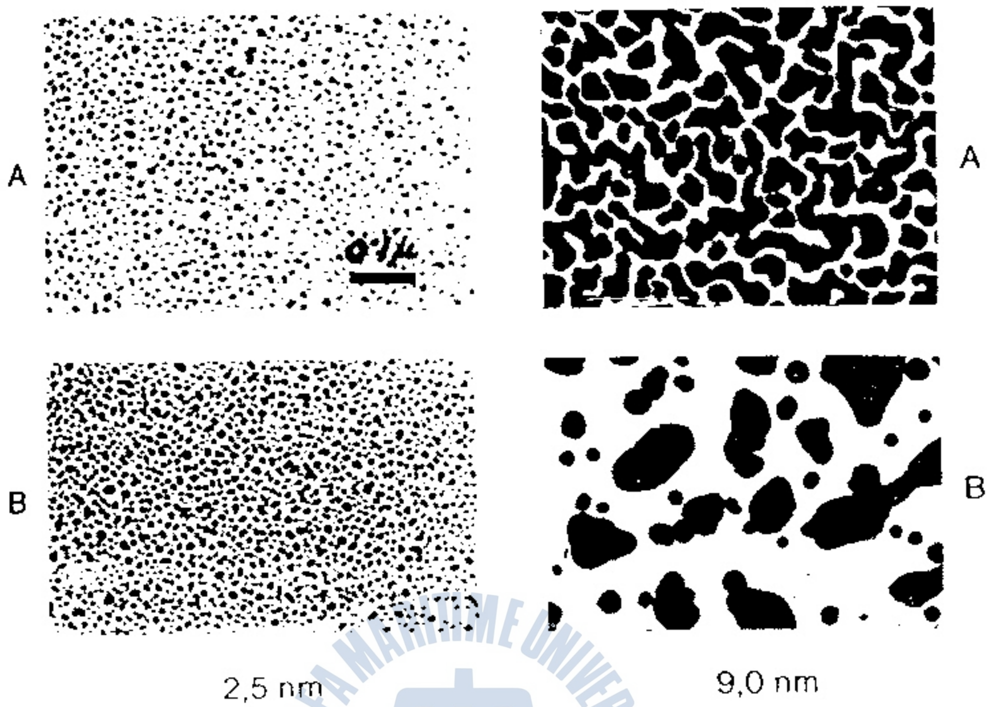

Fig. 2.3.6 The thin film surface of Cu thin film which is evaporated on SiO substrate (A) after evaporation and (B) after thermal treatment at 500 ℃ for 20 minutes.

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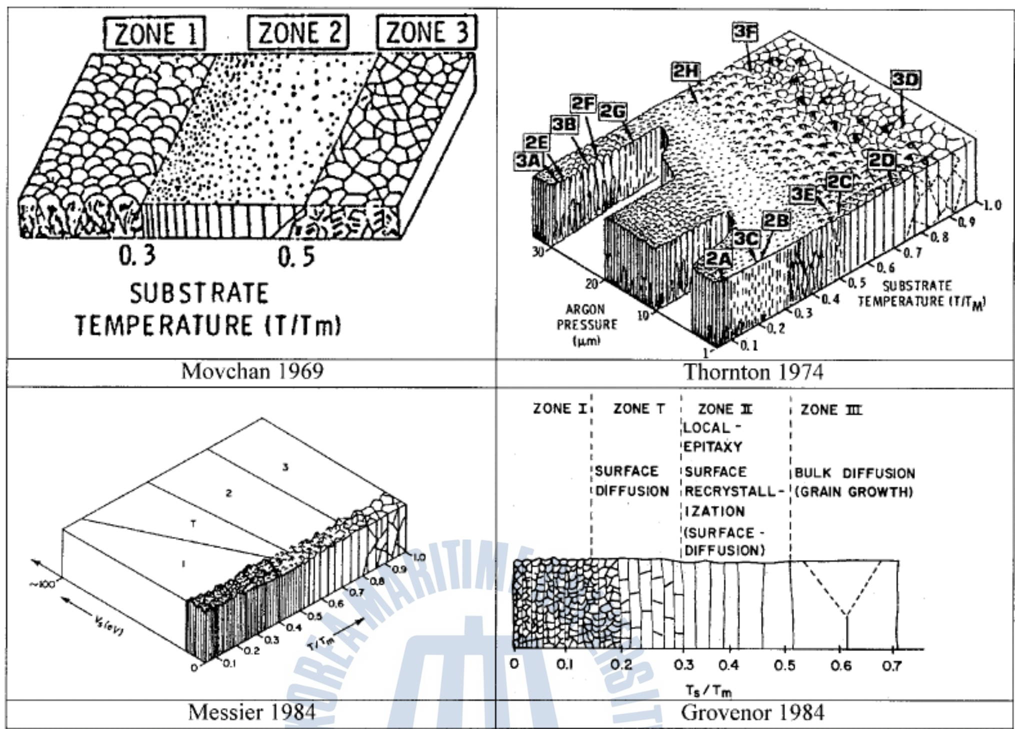

Fig. 2.3.7 The structure zone models. [16]

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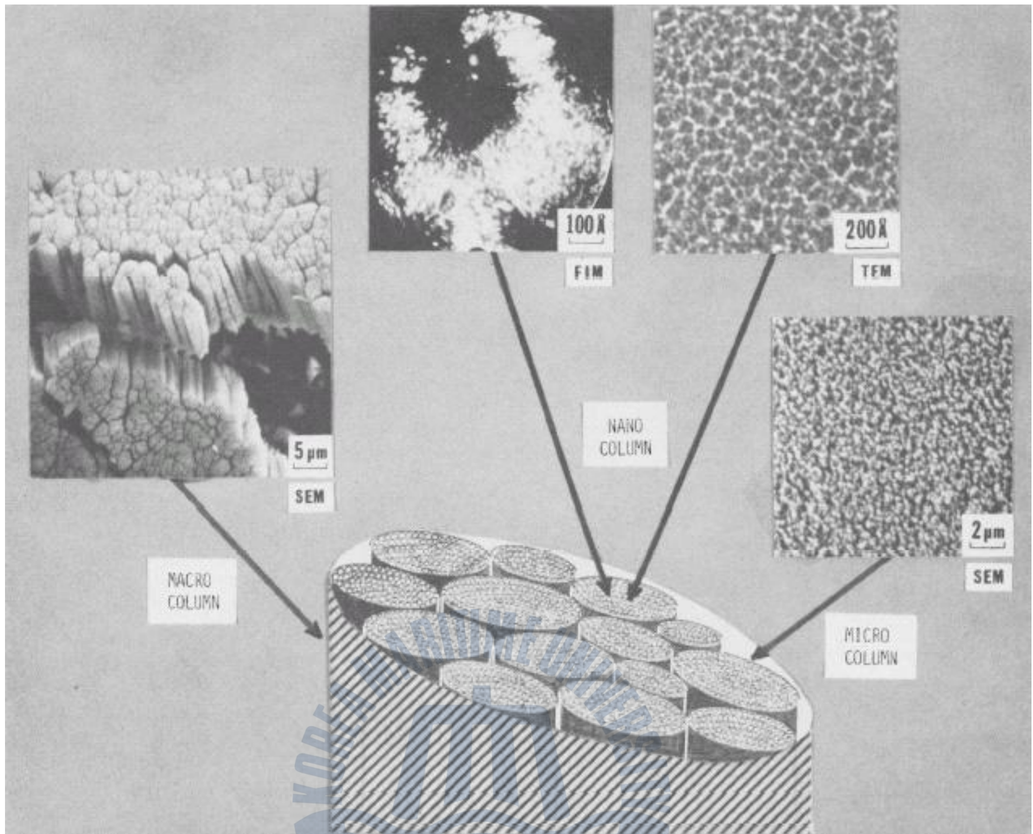

Fig. 2.3.8 The physical structure according to the thickness of a-Ge thin film which was evaporated in low mobility (Ts / Tm = 0.27). [19]

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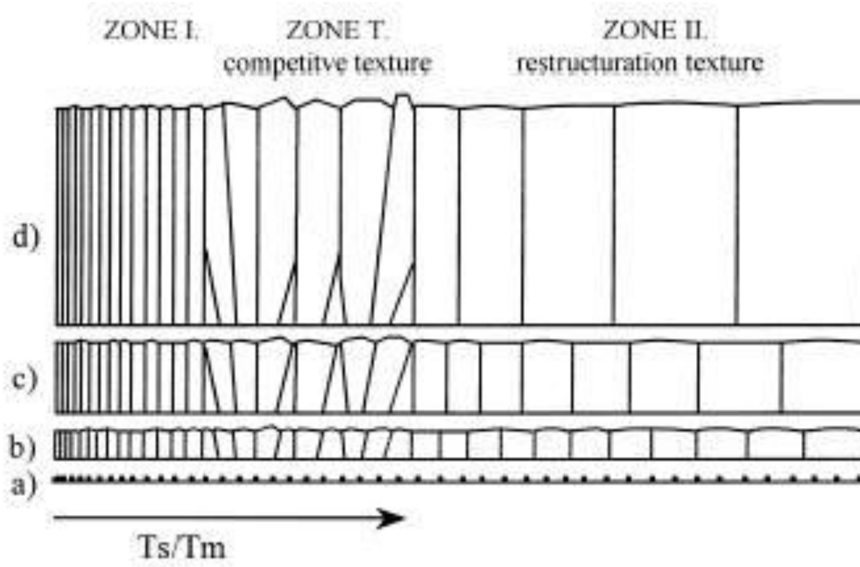
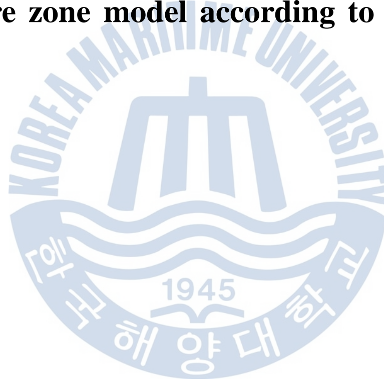


Fig. 2.3.9 The structure zone model according to the thin film thickness. [20]



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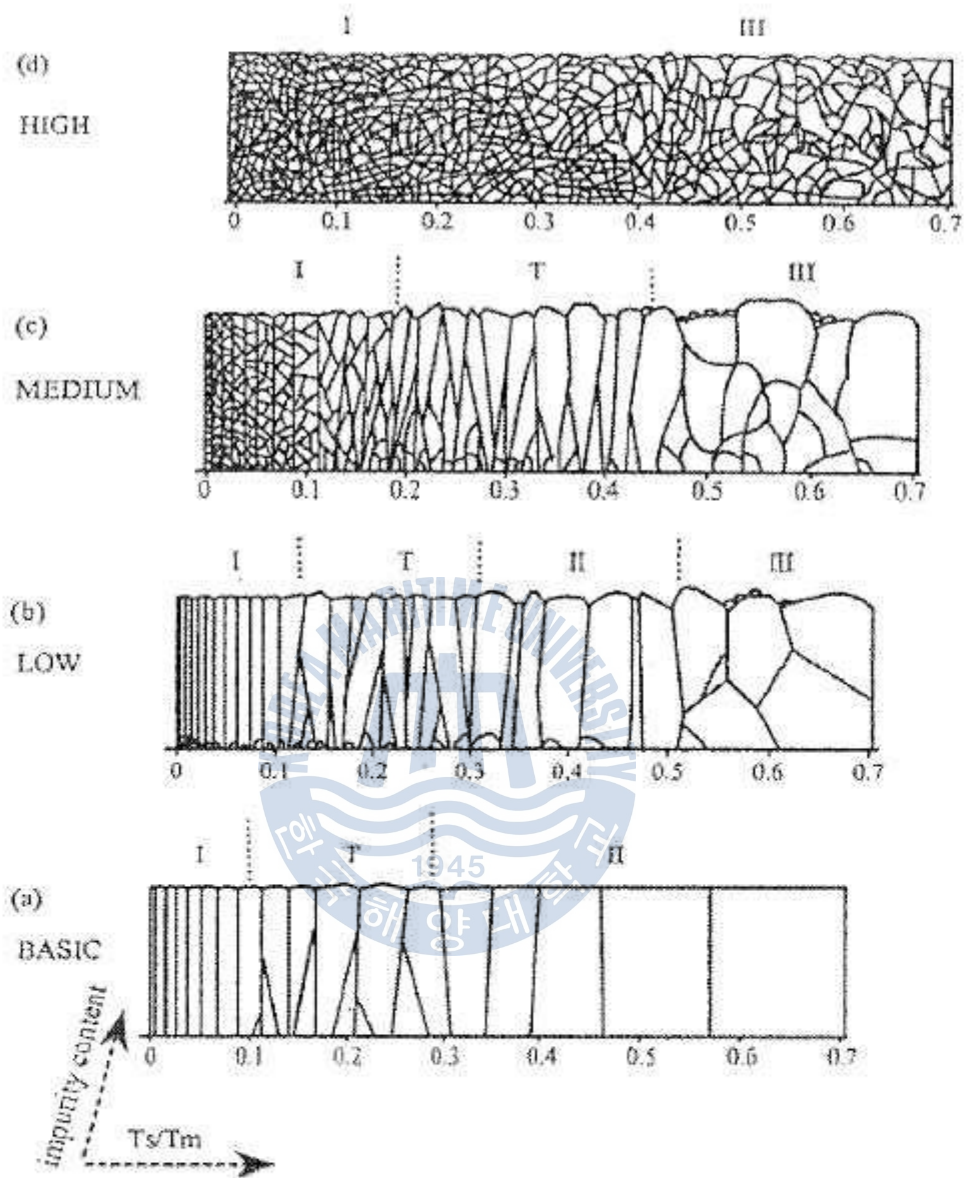

Fig. 2.3.10 The structure zone model of the thin film by addition of dopants. [22]

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3. Experiment

3.1 Manufacture of AZO films

3.1.1 Equipment of Experimental

This study used the slope counter-target DC magnetron sputtering system as shown in Fig. 3.1.1. This system is the magnetron sputtering method that membrane is possible by the high speed in the atmosphere of low gas pressure of the low temperature substrate as doping of electron is done by action of the electric field and transverse magnetic field by applying the parallel magnetic field on the target surface and focusing plasma of the high density around the target.

The DC magnetron sputtering system used in this study has the characteristics that multi element films can be evaporated by the high speed by arranging the plural slope counter-target. When compared to the previous sputtering process, films of several types can be evaporated by easy control and the applicable scope is larger. The basic specifications of the system are as follow.

Method	Unstable equilibrium magnetron sputtering
Purpose	Deposition of multiple elements thin film
Composition	Separate form of main body and control unit
Pressure condition	Exhaustion time of gas: within 5 min to 2.6×10^{-3}Pa
Control method	DC power control, vacuum control system, heater control, gas flow control, control system of valve switch, manual

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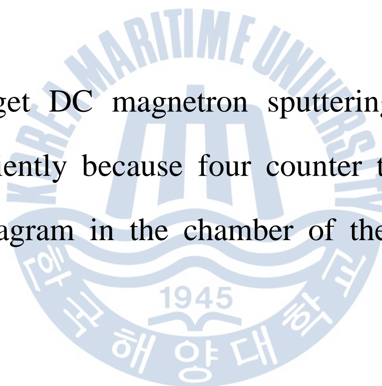
	control by panel computer
Electricity	200V 50/60Hz 3P, wring capacity: 100A
Cooling water	Above 0.1MPa and 14L/min, below 25℃ (in operation)
Air pressure	0.3 ~ 0.5 MPa
Gas	Ar 0.3 Mpa, high-purity(99.999%) O_2 0.3 Mpa, high-purity(99.999%)
Target	Zn (99.999%) : 300×48×t5 mm^3 Al (99.999%) : 300×48×t5 mm^3



The slope counter-target DC magnetron sputtering system can evaporate sputtered particles efficiently because four counter targets are attached with angles. The mimetic diagram in the chamber of the device in this study is shown in Figure. 3.1.2.

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Fig. 3.1.1 The inclination opposite target type DC magnetron sputtering equipment

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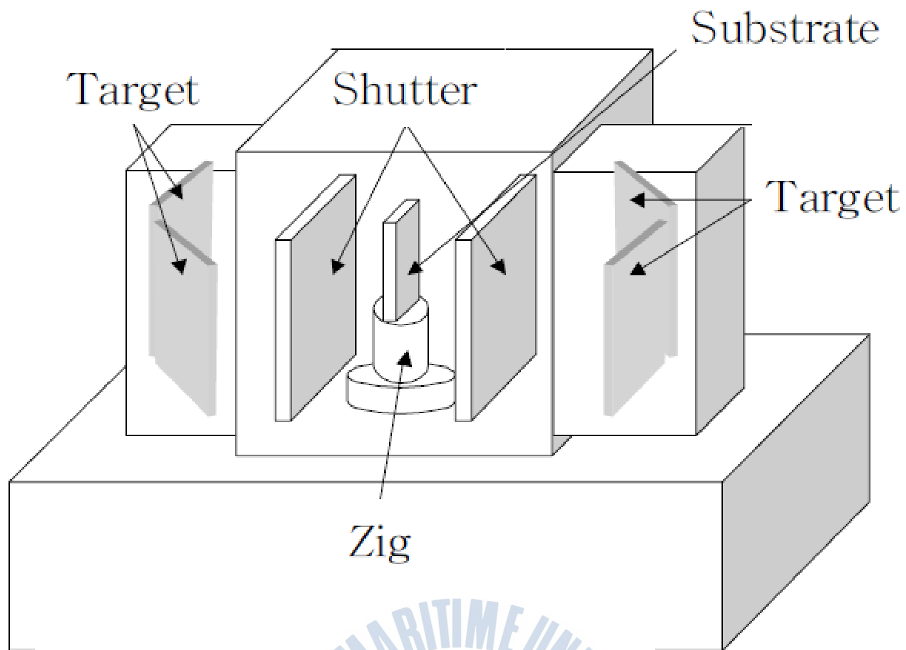

Fig. 3.1.2 Schematic diagram of inclination opposite target type DC magnetron sputtering equipment

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3.1.2 Materials of Experimental

Resistivity of transparent conductive used in display must be lower or same with metal wire, there need to be a new approach on structure or material. Therefore, in order to fulfill these purposes, transparent conductive multilayer thin film is getting its attention. Transparent conductive multilayer thin film deposits thin metal thin film layer between semiconductor oxide compound thin film layer like ITO and ZnO. Due to the metal thin film deposited in transparent conductive multilayer thin film, it produces excellent electrical conductivity and high permeability at visible range. In addition, it is possible to produce thin film with excellent durability than single layer metal thin film and thin film thickness thinner than semiconductor oxide compound thin film.[23-25]

Aluminum is widely used in aerospace, transportation, construction field since it is light and against oxidation. Aluminum is also a good conductor and resistivity is 1.6 times copper. In room temperature, electrical conductivity and thermal conductivity (4~5 times of steel) is excellent. Therefore, aluminum has been made as thin film and used as element connector during semiconductor manufacturing process or optical element such as wave guidance and reflector.

Following table shows metal's basic properties.

The experiment materials have been used to produce transparent conductive multilayer thin films by DC magnetron sputtering equipment in this study.

- Substrate: Slide glasses (L: 76mm, W: 26mm, T: 0.9 ~ 1.2)

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Table 3.1 Fundamental properties of metals for thin film materials

	Zn	Al
Elementary name	Zinc	Aluminum
Elementary number	30	13
Atomic mass (g/mol)	65.38	26.9815396
Condition	Solid	Solid
Density (g/cm3)	7.14	2.70
Melting point (K)	692.68	933.47
Boiling point (K)	1180	2792
Magnetic characteristic	Diamagnetism	Paramagnetic
Electric resistance (Ωm)	59.0×10^{-6}	26.50×10^{-6}
Thermal conductivity	$116\ Wm^{-1}K^{-1}$	$237\ Wm^{-1}K^{-1}$
Thermal expansion coefficient	25 ℃	23.1 ℃

3.1.3 Experiment procedure

To manufacture transparent Conductive multilayer thin film, experiment was conducted by the following procedure.

1) Process before Experiment

1. Use Acetone and ethanol to conduct ultrasonic cleaning for 15 minutes and remove moisture on the surface using heat dryer.
2. Remove impure substanct inside the chamber of sputtering device.
3. Install target metal inside the chamber, and install specimen at the center.

2) Deposition of Thin Film

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1. Install specimen and target metal, operate sputtering device to make the environment vacuum.
2. Inject reaction gas for 2 minute at the target metal and process sputtering for 5 minutes while the shutter of the chamber is closed. (Removing impure substance on the surface of target metal)
3. After removing impure substance on the surface of target metal, open the shutter and deposit thin film on the surface of the substrate. (ZnO: 4 hours, metal thin film: 30 min)
4. Calculate thickness of thin films which has completed deposition using Surface Profile Measuring System and divide it by deposition time to calculate deposition rate of ZnO and Metal thin film.
5. Using the deposition rate, deposit ZnO and Metal thin film on glass substrate.
6. In order to produce transparent conductive multilayer thin film, deposit ZnO thin film and stop sputtering device and then deposit Metal thin film. Then deposit ZnO thin film once again on deposited Metal thin film to complete the structure of multilayer thin film. ※ Operate preliminary sputtering for 5 minute before depositing ZnO and Metal thin film while the chamber shutter is closed. (Removing impure substance on the surface of target metal)
7. Store substrate, which deposition of transparent conductive multilayer thin film complete, by each types of metal and deposition condition.

Following table shows deposition environment inside the chamber when thin film is deposited. Also, following diagram shows the image of Surface Profile

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Measuring System.

Table 3.2 Sputtering condition of multilayer thin film.

Deposition parameters	**Conditions**
Base and working pressure	3 X 10^{-3} Pa, 6 ~ 7 X 10^{-1} Pa
Ar and O_2 partial pressure	50 sccm and 2 sccm
Working time and film thickness	4 Hours, 300 ~ 500 nm
Distance from target to substrate	30 cm
Zig rotation speed	12 rpm
Working temperature	Room temperature to 300 ℃
Input power	
- ZnO cathode	DC magnetron mode
- Current	0.2 A
- Al cathode	DC magnetron mode
- Current:	1 ~ 7 mA

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3.2 Properties measurement of AZO films

3.2.1 Measurement of the thin film thickness

The thickness of thin films is the very important factor to determine the properties of transparent conductive oxide films. The methods to measure the thin film thickness include Elipsometer, Stylus, Crystal Oscilators, VAMFO, CARIS, GravimetricTechnique, SEM, TEM, Color Chart, and RBS. SEM, TEM, and RBS of them are the measurement methods to investigate other characteristics rather than the thickness and the Color Chart is the subsidiary method to guess the rough thickness of transparent thin films.

Stylus means the method to measure height of step directly as the stylus which moves along the surface after forming step in thin films as one of the typical method to measure the thickness. The diamond needle stylus of radius 10 ㎛ is used. It can be measured within the scope of 200Å～65 ㎛. And resolution is about 10Å. It has the disadvantage that it is difficult to measure the materials that it is difficult to form step, that is etching is difficult. This experiment measured it using Sloan DEKTAK 3030.

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3.2.2 The measurement of electric non-resistance of the thin film

The method to measure electric non-resistance includes two-point probe method, four-point probe method, and Van der Pauw method. But generally, four-point probe method is most used. Especially, the four-point probe method is very much used in the non-resistance measurement and surface resistance measurement because measurement is possible without any destroy of samples.

The basic properties of four-point probe method can reduce errors of the resistance value according to contact resistance, especially the measurement location by using the terminal for voltage which is separated from the current terminal. The measurement principle of the device is shown in Fig. 3.2.1

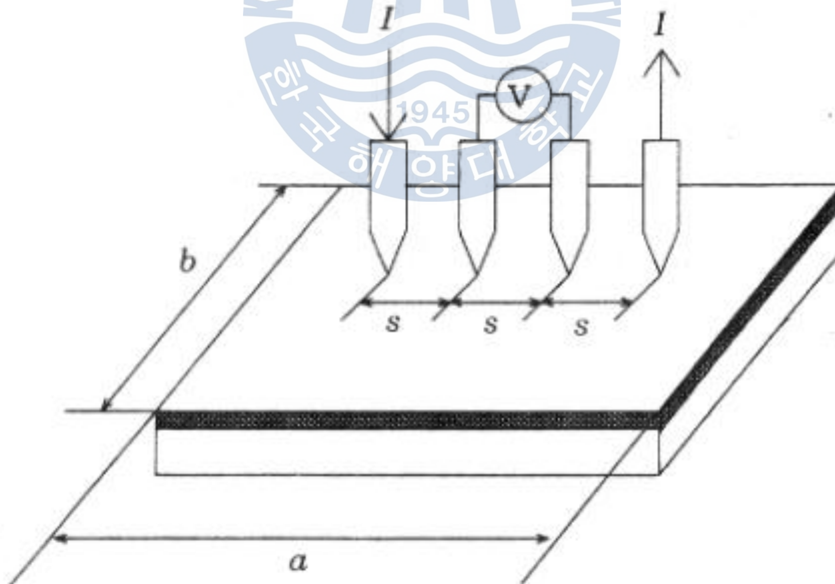

Fig. 3.2.1 Measurement of electrical resistivity by four-point probe method.

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The measurement method: The resistance value R is calculated by measuring the potential difference V which occurs between two internal terminals as the current I is flowed in the two external terminals in the four terminals installed in the straight line parallel. Electrical conduction can be divided into electronic conduction and ion conduction. And the direct current measurement is generally used in the measurement of electronic conductive ceramic.

As for ion conductor, charge ion moved by applying direct voltage causes oxidation-reduction reaction in electrode or is deposited in it. The measurement of the original conductivity is difficult because the polarizing phenomena can easily occur.

The resistance rate was calculated using the four-point probe method in this experiment. This method is to measure the voltage V of two probes which are located in the center by flowing the current I in them in the both ends after certain load is applied in four probes enumerating them in the straight line.

The sheet resistance can be calculated by the following equation.

$$R_{sheet} = \frac{\pi}{\ln 2} \bullet \frac{V}{I} \qquad (3.1)$$

And the resistance p multiplies the film thickness d by Rsheet which was calculated in the above equation.

$$\rho = R_{sheet} \bullet d \qquad (3.2)$$

The measurement of the current I was done fixing it by 1mA. There is no need to form electrode in the samples by the method of evaporation and alloy in this method and the measurement is possible without destroy of the samples

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simply. Actually, it is being sued in check of the resistance rate during the integrated circuit process.

3.2.3 Measure transmittance

In this research, UV-VIS-NIR spectrometer is used in order to measure permeability of transparent conductive multilayer thin film. Spectrometer can irradiate certain light wavelength to sample by monochromator using prism or diffraction grating. At this point, permeability can be measured by comparing the amount of light first irradiated on the sample and amount of light passed the sample. UV-VIS-NIR spectrometer, used in this research, is a device which can irradiate three different kinds of light wavelength, including ultraviolet, visible spectrum ray, near infrared ray on the sample. In this study, however, in order to observe the optical characteristic of transparent conductive multilayer thin film of general light, in the area of 200nm ~ 800nm visible wavelength light was used to measure the permeability of thin film.

Picture shows UV-VIS-NIR spectrometer used in this study.

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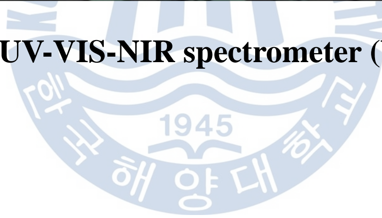
Fig. 3.2.2 The figure of UV-VIS-NIR spectrometer (V-570, Jasco)



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4. Result and discussion

4.1 Growth rates of the AZO thin films

The growth rate of the AZO thin films with respect to deposition temperature was investigated. Fig. 4.1 shows the variations of the growth rate with respect to temperature from 50 ℃ to 300 ℃ for Al current of 0.001 A. As shown in Figure 1 the growth rate decreases until the saturation temperature higher than 200 °C. The difference between the room temperature which showed the highest growth rate and 300 ℃ which is the lowest growth rate was shown to be big as about 1.7 times.

This can be thought that the growth rate is low because the dense growth is done as particles are diffused by masses when sputtering is done the high temperature of the substrates as explained above. This result can be also checked in the EMP picture. But saturation at 200 ℃ is probably due to the balance between the number of atoms arriving at the substrate surface and the number of atoms bolting out from the substrate surface by thermal desorption, and also due to lateral growth as the temperature increases. Since the surface mobility of a particle is limited at a low temperature, the growth rate would be higher than that at a high temperature.

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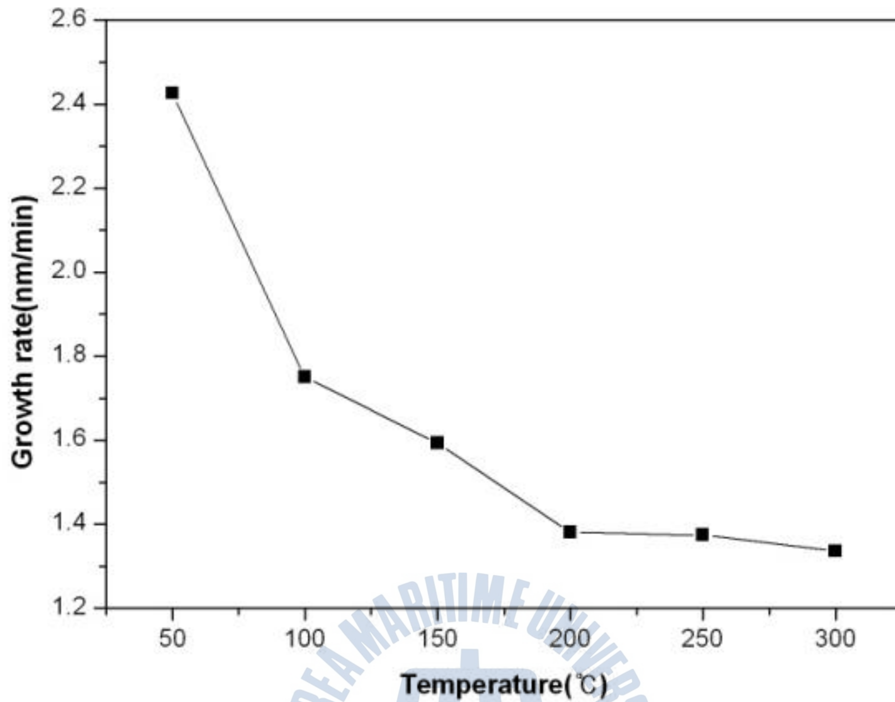

Fig. 4.1 Growth rates of the AZO thin films deposited at various substrate temperatures (IZn =0.2 A and IAl = 0.001 A).

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4.2 Check of the growth structure by SEM picture

Figure 4.2 shows the surface SEM images of the AZO thin films deposited at various substrate temperatures from RT(room temperature) to 300 ℃. The grain size increases with temperature and the surface roughness decreases. This result made the structure more clearly as the particles form a column and grow entering the stage to diffuse masses after passing the surface diffusion according to the structure zone model according to increase of the temperature of the substrate when sputtering is done. The figure 4.2 has shown that the surface gets to be soft and the mass of the structure gets to bigger up to 200 ℃ at the room temperature. This can be checked through the picture of the side view of the micro structure. It could be found that it can grow with the clearer directional properties vertically to the substrate when it's 200 ℃ and 300 ℃ rather than it's RT. It could be checked that the micro structure can be accomplished enough by adjusting the temperature of the sputtering substrate. This result is due to the big mobility of particle above. But the grain size and surface toughness is similar above substrate temperature of 200 ℃ because of the balance between the number of atoms arriving at the substrate surface and the number of atoms bolting out from the substrate surface by thermal desorption. This phenomenon is in agreement with the growth rate result.

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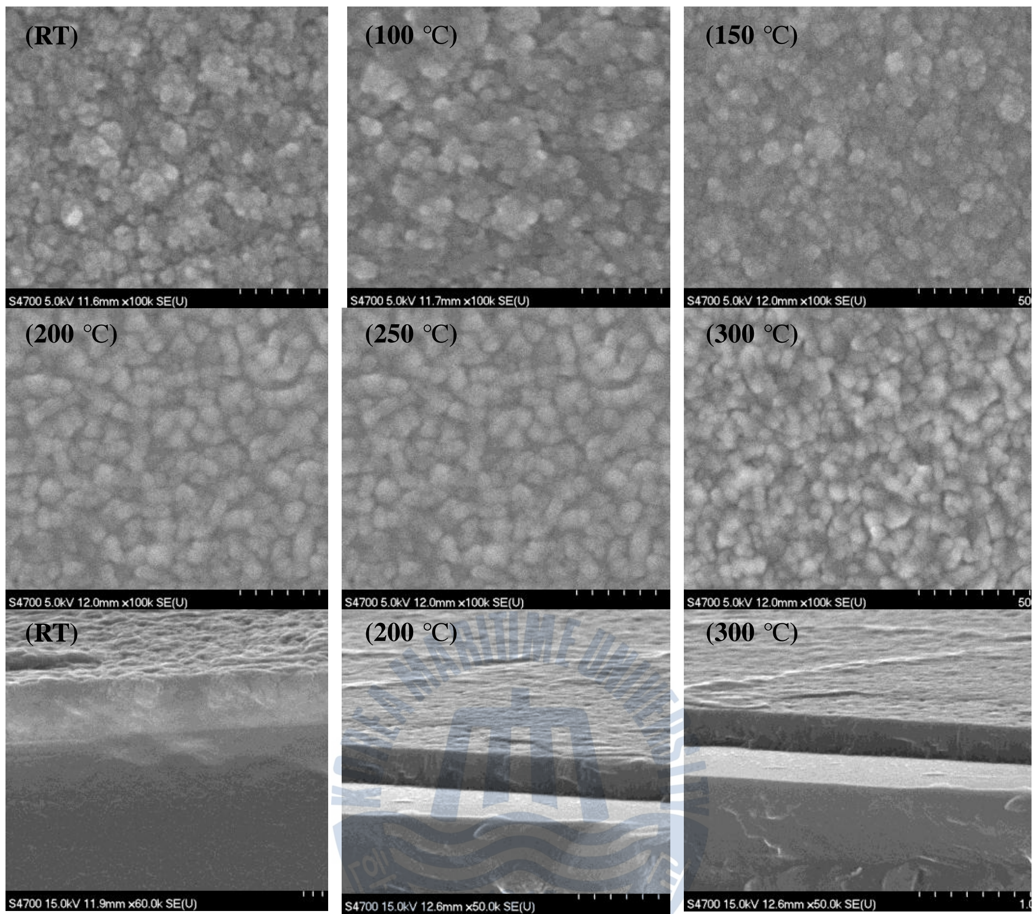

Fig. 4.2 Surface SEM images of the AZO thin films deposited at various substrate temperatures from RT to 300 ℃.

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4.3 Optical transmittances and resistivity as various temperatures

Figure 3 shows the transmittance spectra of AZO thin films deposited at various substrate temperatures. All of the films deposited above the surface temperature of 200 ℃ demonstrate over 80% transmittance in the range of the visible spectrum, but the films deposited below the substrate temperature of 200 ℃ demonstrate low transmittance. This result is due to the low mobility of a particle during film deposition at a low substrate temperature, which leads the film morphology consisting of tapered crystallites separated by voids as a result of inter-grain shadowing. Consequently, poor transmittance was obtained. This result can be found that the growth of thin films has the significant effect on transmittance. It can be found that transmittance falls as the reflected light gets to be increased when light is penetrated as the particles cannot melt and grow by shadowing with the different directional properties as they collide with the substrates when sputtering is arranged in the room temperature, the temperature that the temperature of the substrate is low. On the other hand, transmittance gets higher as the reflected light gets to be smaller by reducing the number of the micro structure and crack of the surface as particles melt on the substrate, are mixed with each other, and the masses get to be larger when sputtering is done in the state that the temperature of the substrate is higher. Figure 4 shows the electric properties of AZO thin films deposited at substrate temperatures from RT to 300 ℃. The films show minimum resistivity of 6.77×10^{-3} Ω • cm at substrate temperature of 200 °C. The resistivity decreases rapidly from

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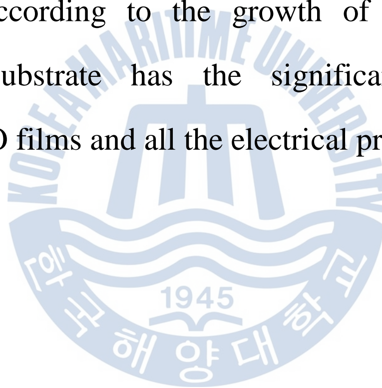
RT to 200 °C and then increases slowly from 200 °C to 300 °C. It can be found that carrier concentration and mobility get higher together. It’s because the particles grow making masses with the high density as the temperature of the substrate gets higher and they are mixed. A large amount of electron can be accepted because the density of the micro structure of AZO which plays the role of an passage is high. And mobility of electron receiving resistance less to make electron move by reducing crack as the size of the micro structure gets larger. This result shows the higher electrical characteristics at the higher temperature by reducing resistance.

The micro structure according to the growth of the particles about the temperature of the substrate has the significant correlation between transmittance of the AZO films and all the electrical properties.



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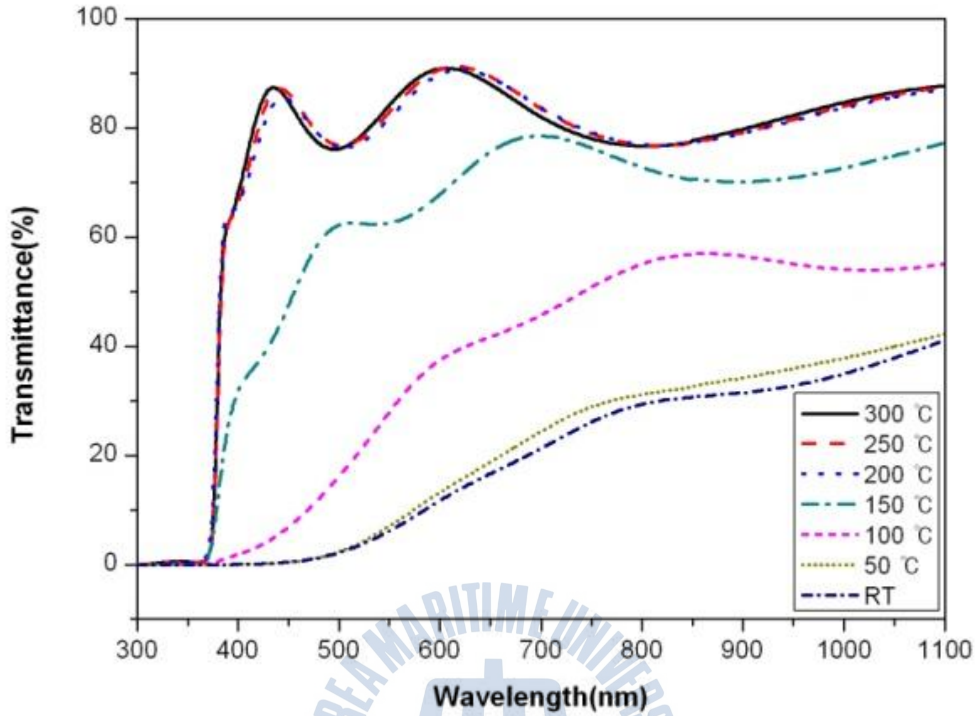

Fig. 4.3 Optical transmittances of the AZO thin films prepared at various temperatures

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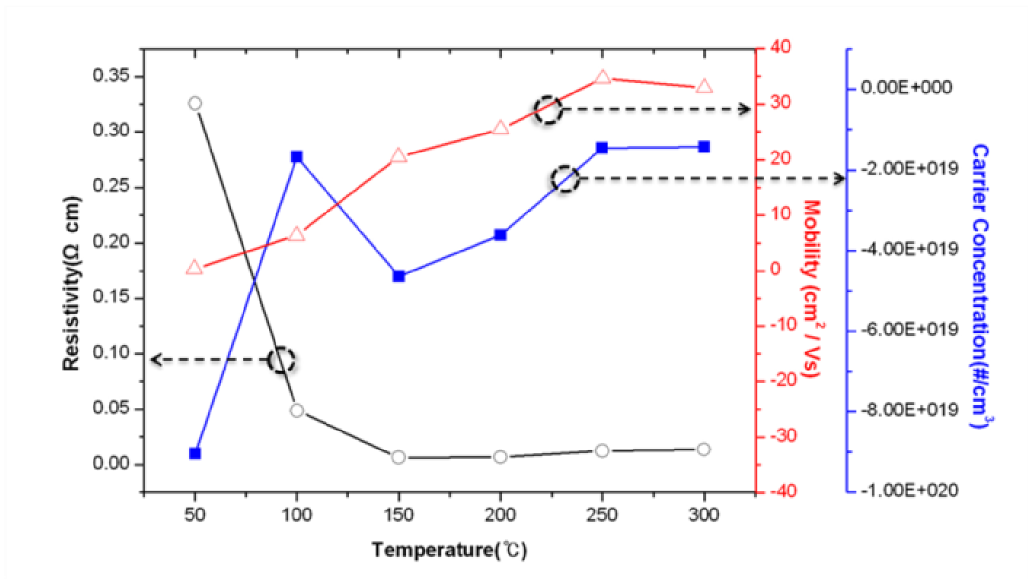
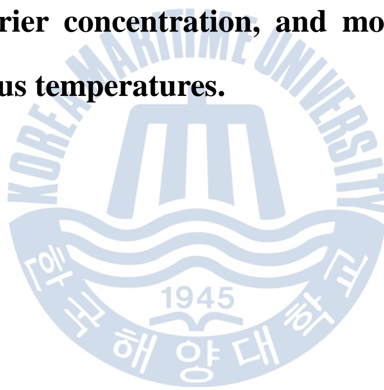


Fig.4.4 Resistivity, carrier concentration, and mobility of the AZO thin films prepared at various temperatures.



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4.4 Optical trancemittances and resistivity as various Al contents

The experiment was done by changing the current of Al target to examine the most ideal Al contents of the AZO films. Figure 4.5 shows the transmittance spectra of AZO thin films deposited at various Al currents from 0.002 A to 0.007 A. The films show transmittance spectrum of above 80 % in the range of the visible spectrum when Al current is 0.002 A. The films show transmittance spectra of below 80 % when Al current is higher than 0.002 A. Figure 4.6 shows the electric properties of AZO thin films for variations of Al content for variations of Al target current. The minimum resistivity of $3.77 \times 10^{-3}\ \Omega \cdot cm$ is shown when the Al current is 0.002 A.

It's when the current of Al target when sputtering is done 2 mA in the experiment by raising the Al contents to find the most suitable Al contents of the AZO films. This case showed the highest transmittance and the best electrical characteristics.

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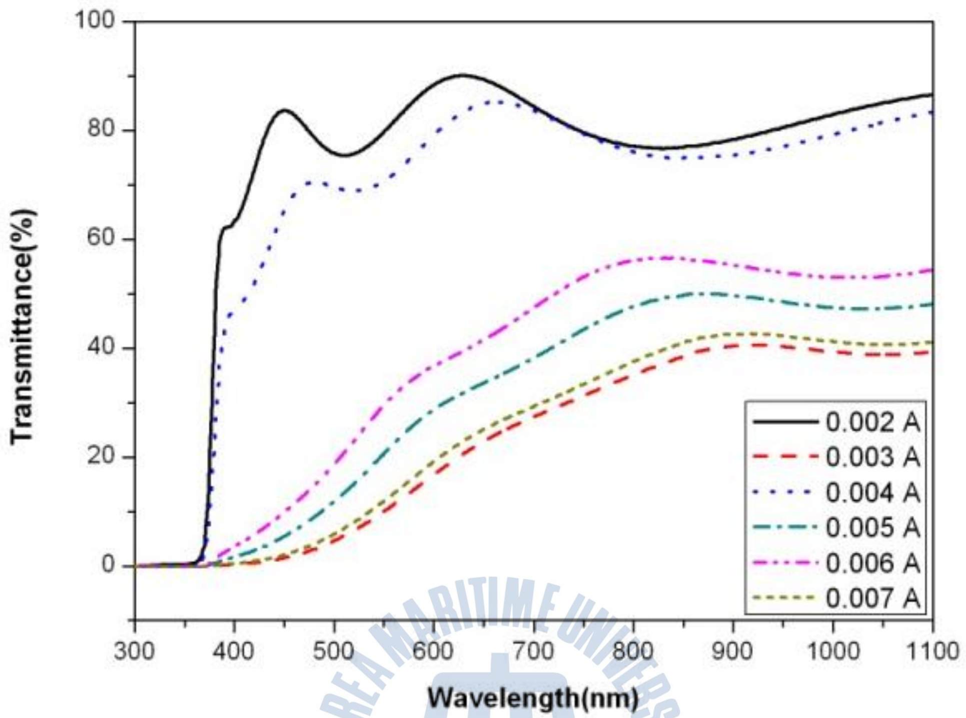

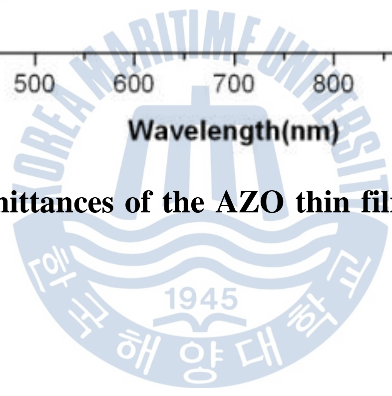

Fig. 4.5 Optical transmittances of the AZO thin films prepared at various Al contents.

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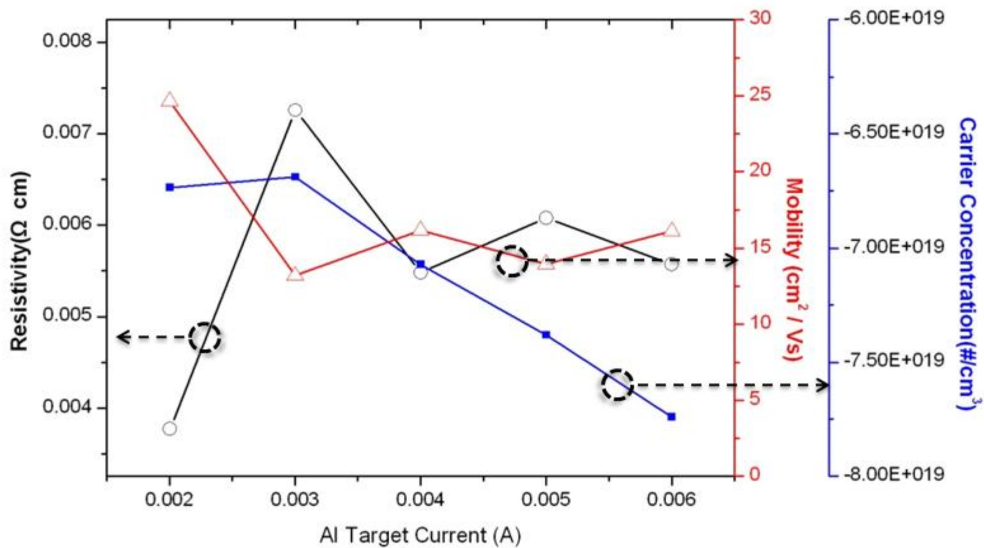
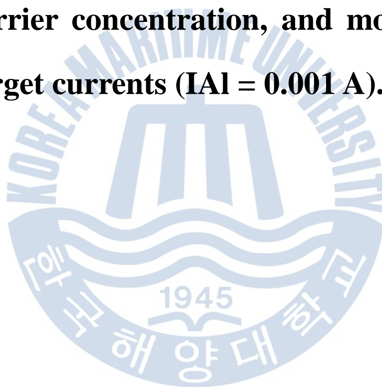


Fig. 4.6 Resistivity, carrier concentration, and mobility of the AZO thin films prepared at Al target currents (IAl = 0.001 A).



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5. Conclusion

This paper is the study to check the growth of the micro structure when sputtering of Al doped ZnO is done at the different temperatures and the effect of it on the optical and electrical properties. The temperature of the substrate was measured in the DC magnetron sputtering system and the optical and electrical properites by section from the room temperature to 300 ℃ were done in the room temperature to check this. Check of the growth of the micro structure was checked through the growth rate and SEM picture.

(1) The growth rate decreased until the saturation temperature of 200 ℃.

(2) All of the films deposited above substrate temperature of 200 ℃.

(3) The minimum resistivity was 6.77×10^{-3} Ω• cm at substrate temperature of 200 ° C.

(4) The highest optical and electrical properties were shown when the current of Al target is 2 mA.

(5) The growth result of the micro structure according to the structure zone model showed the correlationship with the optical and electrical properties.

The optical and electrical properties of the AZO films showed the result which is enought to use them for industry. And the growth of the micro structure can be also induced according to the structure zone model by controling the temperature of the substrate in the DC magnetron sputtering system.

Collection

Reference

[1] K. Vanheusden, W.L. Warren, C.H. Seager, D.R. Tallant, J.A. Voigt, B.E. Gnade, J. Appl. Phys. 79 (1996) 7983.

[2] K.L. Chopra, S. Major, D.K. Pandya, Thin Solid Films 102 (1983)

[3] K.H. Kim, T.S. Park, J. Kor. Phys. Soc. 18 (1985) 124.

[4] C.G. Granqvist, Thin Solid Films (1990) 730, pp.193-194

[5] B.S Kim, S.K Kim and Y.S Kim, submitted to Journal of the Korean Ceramic Society, Vol. 43, No. 9 (2006), pp. 532-536

[6] D.H Kim, R.I. Murakami and Y.H. Kim, Advanced Materials Research Vols. 97-101 (2010) pp 1768-1771

[7] S. k. Lee, S. J. Kwak, M. H. Lee, D. H. Seo, S. H. Shin, K. H. Choi, " The Optical Technology of Polymeric Films for the Next Generation Display", Polymer Science and Technology Vol. 19, No. 6, (2008)

[8] H. K. Pulker, Coating on Glass (Elsevier, Amsterdam, 1984), chap. 6.

[9] C. K. Hwangbo, Thin Film Deposition (Dasan Publisher, Seoul, 2001), PP. 152.

[10] M. Ohring, The materials science of thin films (Academic Press, San Diego, 1992), chap. 3

Collection

[11] N. Kaiser, and H. K. Pulker, ed., Optical Interference Coatings(Springer-Verlag Berlin Heidelberg New York, 2003), PP. 64-68

[12] D. E. Aspnes, "Optical properties of thin films," Thin Solid Films 89,249-262 (1982).

[13] K. H. Gienther, D. J. Smith, and L. Bangjun, "Structure and related properties of thin film optical coatings,: in Optical Thin Films II-. New Developments, R. T. Seddon, ed., Proc. SPIE 678, 2-11 (1986).

[14] H. A. Macleod, "Microstructure of optical thin films," in Optical Thin Films, R. T. Seddon, ed., Proc. SPIE 325, 21-29 (1982)

[15] S. Y. Choi, J. S. Kim, D. Y. Ma, W. D. Park, K. M. Choi, K. W. Kim, Basig of Thin Film Deposition (Iljin Corporation, Seoul, 2006), PP.106-110.

[16] G. Attard, and C. Barnes, Surfaces (Oxford University Press, New York,1998), PP 1-36.

[17] N. Kaiser, "Review of the fundamentals of thin-film growth," Appl. Opt.41(16), 3053-3060 (2002).

[18] B. A, Movchan and A. V. Demchishin, "Rosti struktura tonkich tverdotelnych plenok," Phys. Met. Metallogr. 28, 83-91 (1969).

[19] J. A. Thornton, "Influence of apparatus geometry and deposition

Collection

conditions on the structure and topography of thick sputtered coatings," J. Vac. Sci. Technol. 11, 666-672 (1974).

[20] R. Messier, A. P. Giri, and R. A. Roy, "Reveised structure zone model for thin film physical structure," J. Vac, Sci. Technol. A 2, 500-503 (1984).

[21] A. G. Dirks, and H. J. Leamy, "Columnar microstructure in vapor-deposited thin film," Thin Solid Films 47, 219-233 (1997).

[22] P. B. Bama, and M. A. Adanik, "Growth mechanism of polycrystalline thin films," in Science and Technology of Thin Films, in F. C. Matacotta andG. Ottaviani, eds.(World Scientific, Singapore, 1995), PP. 1-28.

[23] D.R. Sahu, S.Y. Lin and J.L. Huang, “ZnO/Ag/ZnO multilayer films for the application of a very low resistance transparent electrode”, Applied Surface Science, Vol. 252, (2006), pp.7509~7514

[24] D.R. Sahu and J.L. Huang, “The properties of ZnO/Cu/ZnO multilayer films before and after annealing in the different atmosphere”, Thin Solid Films, Vol.516, (2007), pp.208~211

[25] D.R. Sahu and J.L. Huang, “High quality transparent conductive ZnO/Ag/ZnO multilayer films deposited at room temperature”, Thin Solid Films, Vol. 515, (2006), pp.876~879

Collection

[26] F.C.M. Van de Pol, F.R. Blom, Th.J.A. Popma, Thin Solid Films 204 (1985) 349.

Collection