공학석사학위논문

Electrical and thermal transport properties of atomic layer deposited Al-doped ZnO films

2015년 2월

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지도 교수 김 기 범

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Electrical and thermal transport properties of atomic layer deposited Al-doped ZnO films

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Abstract

Electrical and thermal transport properties of atomic layer deposited Al-doped ZnO films

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As the demand of energy is growing with the industrial development in the world, thermoelectrics has gathered significant interest due to its availability to convert energy from wasted heat to electric energy. The efficiency of thermoelectric materials is determined by their figure of merit, $ZT=S^2\sigma T/k$, which points to the need to increase the seebeck coefficient S and electrical conductivity σ while depressing the thermal conductivity. In order to achieve high ZT values(~1.5), tellurium-, antimony- and germanium- based compounds have been widely investigated as thermoelectric materials while their toxicity and stability to oxidation at ambient conditions have been pointed out as critical issues. Recently, as an alternative to the conventional materials, ZnO- and In_2O_3- based transparent conducting oxides (TCOs) have been considered as thermoelectric

materials due to its thermal stability and additional merit from the transparency to the visible rays. In order to integrate the TCO materials into the thermoelectrics, it is important to control both electrical and thermal transport properties of those. In this regard, atomic layer deposition (ALD) can give a great benefit to elucidate the purpose of thermoelectrics since this novel method guarantees excellent reproducibility and adjustability of film composition.

In this work, ALD is utilized as a means for preparing Al-doped ZnO (AZO) films with controllability on its thermal and electrical transport properties. Contrary to the conventional homogeneous AZO composite, ALD-AZO films exhibit a unique heterolayer structure consisting of a ZnO matrix and AlOx dopant layers embedded within the matrix. These AlOx layers not just provide additional free electrons to the system but also additional interfaces that impede the thermal transport. We show that, by widely controlling the linear density of these dopant layers, the electrical conductivity can be enhanced by more than three-fold while the thermal conductivity can be suppressed to about 22% compared to that of the undoped ZnO film. This tunable feature of ALD-AZO films suggests the feasibility of using ALD-TCOs for thermoelectric purposes, which is a significant expansion to its range of applications.

Keywords : Thermoelectrics, Atomic layer deposition, hetrolayer structure, Al-doped ZnO, Thermal properties, Thermal boundary resistance

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CHAPTER 1.

Introduction

1.1. Thermoelectrics

1.1.1. General overview of thermoelectrics

According to the report written by US department of energy in 2006, wasted-heat energy from every industrial facilities was way more than an energy that was produced from all renewable sources such as solar photovoltaic, wind power and geo-thermal power, etc.[1] Following this situation, it has been thought that it would be very efficient if wasted heat energy could be converted into electric energy. This is why thermoelectrics started being studied considering its availability to convert energy from wasted-heat to electric energy.[2,3] It is very interesting filed of study as the demand of energy is growing with the industrial development in the world, in addition, due to the fact that it would be an one of answers of energy diversification policy.

Seebeck effect and peltier effect generally represent to explain thermoelectric effect. Below in Figure 1-2., two different kind of metals that are labeled P and N are connected in a closed circuit. If temperature difference is maintained in a joint area, there would be a current flow in the circuit. This phenomenon is called seebeck effect, And seebeck coefficient value, S, means a ratio of temperature difference to occurred power of the current. On the contrary to this phenomenon, if a certain amount of current is applied to the closed circuit there would be absorption or emission of heat in the junction. This phenomenon is considered as peltier effect, And the ratio of heat energy to current is called peltier coefficient, Π.[4] Since temperature and voltage are relatively easy to be measured, seebeck coefficient is

normally considered to estimate thermoelectric properties of materials.

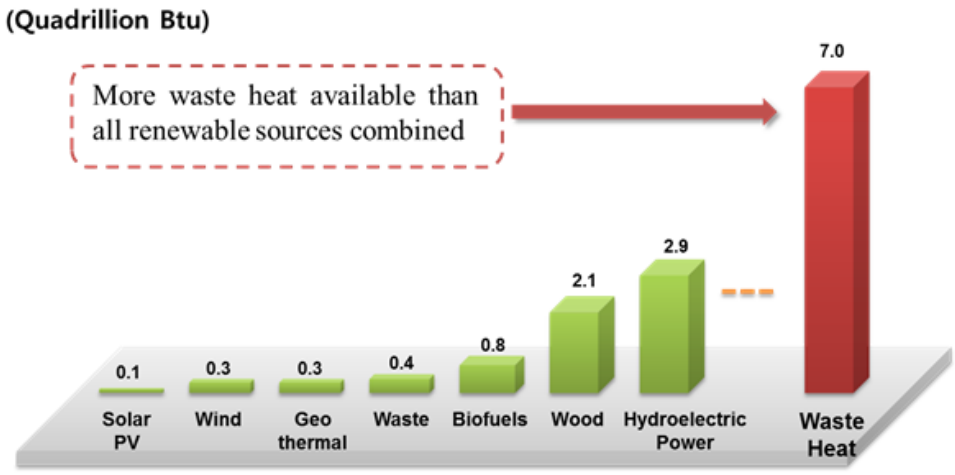
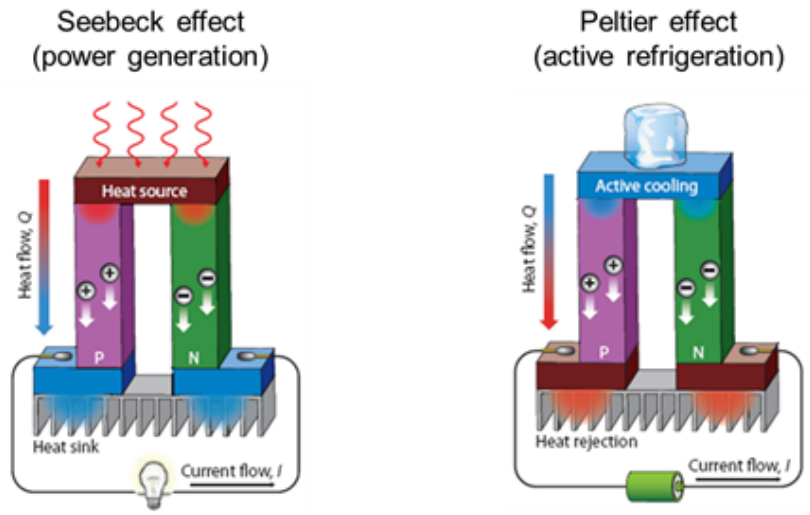


Figure 1-1. Renewable energy consumption by sources[1]



$$\Delta V = S\,\Delta T$$

V = Voltage
S = Seebeck coefficient
T = Temperature

$$Q = \Pi \times I$$

Q = Heat absorbed or emitted
Π = Peltier coefficient
I = applied current

Figure 1-2. Typical structure of power generation and active refrigeration using seebeck and peltier effect[4]

1.1.2. Theoretical background of thermoelectric property

Thermoelectrics, a field of study that research one of abnormal effects so-called seebeck effect, started with experimental discovery of relation between electricity and heat by Thomas J. Seebeck in 1820.[5] Seebeck made an instrument consisted of two different metals joined in a closed loop. Then, he found that a needle placed in the middle of instrument was moved when he heated one of the junctions of two metals as shown in Figure 1-3.. He called this phenomenon seebeck effect, which occurred by electric current circulated by the metal loop.

The seebeck effect is basically related to the fact that electrons are both carriers of electricity and heat. If a temperature gradient exists over a piece of electrically conductive wire like in Figure 1-4.. There is a net diffusion of electrons from the hot end toward the cold end. Therefore, hot region tends to be positive biased while cold region exhibits negative bias, creating an opposing potential field so-called thermo-electro-motive force.[6]

Seebeck coefficient explaining a magnitude of Seebeck effect of materials is defined as :

$$S = \frac{\Delta V}{\Delta T} \qquad \cdots (1\text{-}1)$$

where ΔV is a thermoelectric voltage induced by a temperature difference ΔT across materials. Based on the asymmetry in the density of states near the Fermi level, the sign of Seebeck coefficient would be determined as N-type and P-type. Simply, electrons and

holes work as major carriers in N-type material and P-type materials, respectively.[7]

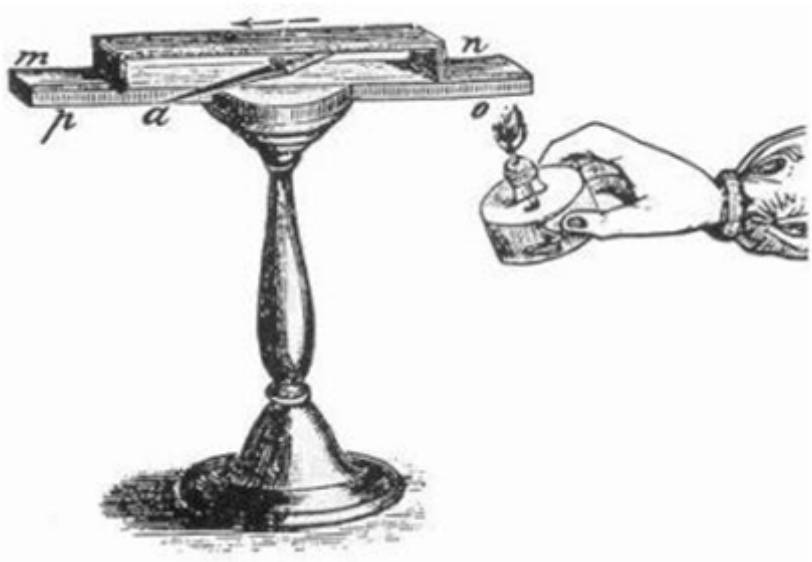


Figure 1-3. Seebeck's instrument observing deflection of a needle[5]

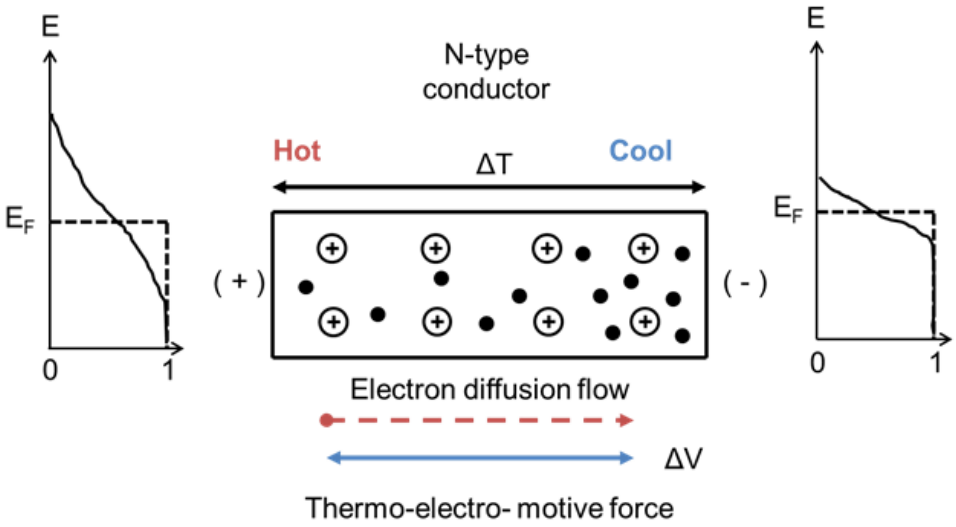


Figure 1-4. Schematic image explaining physical origin of seebeck effect[8]

Typical structure for thermoelectric generators (TEG) using N-type and P-type semiconductor is described in Figure 1-5.. Then, an output power of the generators, P, is described as:

$$P = \left[\frac{S_{N-P} \times \Delta T}{R + R_L} \right]^2 \times R_L \qquad \cdots (1\text{-}2)$$

Where $S_{N\text{-}P}$ is Seebeck coefficient difference of N-type and P-type materials, ΔT is temperature difference between hot and cold junctions, R and R_L are sum of resistance of N-type and P-type materials and resistance of load, respectively.

Therefore, to enlarge an output power of the generator, three conditions have to be satisfied. First, materials should have low thermal conductivity so that large temperature difference between two junctions needs to be maintained. Second, there should be as less as of electrical energy loss from the circuits. Materials consisted of generators require to have high electrical conductivity. Lastly, materials with high Seebeck coefficient would induce high potential difference in a response of temperature difference.

Combining three conditions mentioned above, Figure of merit Z value is defined below meaning energy conversion efficiency from thermal energy to electrical energy.

$$Z = \frac{S^2}{\rho \times k} \qquad \cdots (1\text{-}3)$$

where S is seebeck coefficient, ρ resistivity, k thermal conductivity of materials.

Sometimes temperature parameter is multiplied to Z value. Then, ZT also means the energy conversion efficiency.

According to reports, certain ZT values are required for thermoelectric generators to be utilized industrial-wise. Therefore, most of thermoelectrics researches have been focused on finding materials exhibiting high ZT values. Possible applications with required ZT values are listed in Table 1-1.[9]

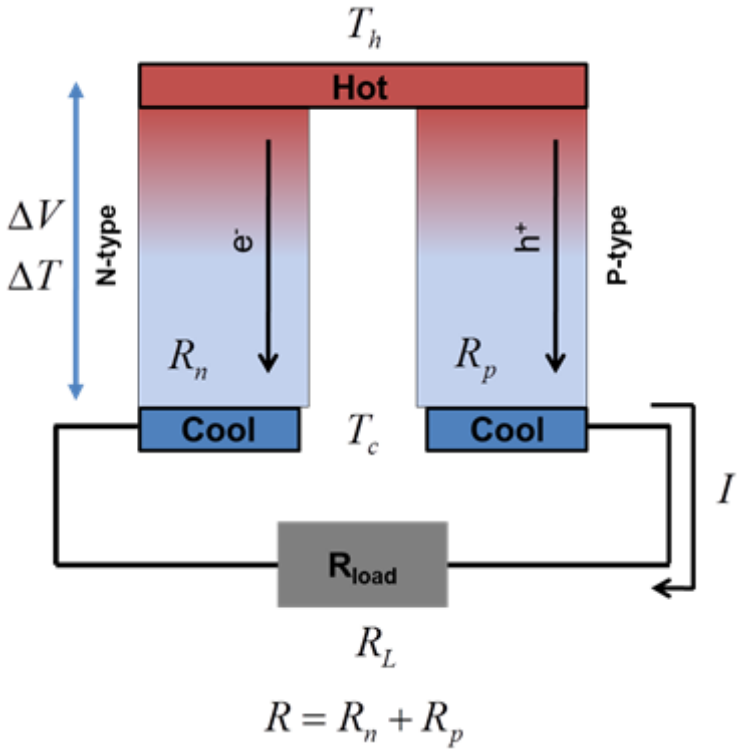


Figure 1-5. Typical structure of Thermoelectric generator (TEG)

Table 1-1. Required ZT value with possible applications[9]

Power scale (kW_e)	Examples	Required ZT
>1,000s	Solar Thermal'engine'replacement	**>8-20**
>10s	Cooler/heater in car seats, industrial waste heat	**>4**
0.5-several	Vehicle waste heat, home co-generation	**>1.5-2**
<0.5	Remote power, 'personal' micro power	**>0.5-1**

1.1.3. Material Challenge

Achieving high efficiency of Thermoelectric geometry means to gain high value of ZT. It is well known that high Z value would not be gained easily due to the correlation-ship of three parameters composing Z value, which are seebeck coefficient, thermal conductivity and electrical conductivity.

According to Wiedemann-franz law, in metal, the ratio of electrical portion of thermal conductivity, k_e, is linear to and electrical conductivity, σ, and to Lorentz number, L, and absolute temperature, T. Therefore, thermal conductivity of metal could be defined as in equation (1-4) below.

$$\begin{aligned} k &= k_e + k_{ph} \\ &= \sigma L T + \frac{1}{3} c_v l_{ph} v_{ph} \end{aligned} \qquad \cdots \text{ (1-4)}$$

Where k is thermal conductivity of material, k_e is electrical portion of thermal conductivity, k_{ph} is phonon portion of thermal conductivity, σ is electrical conductivity, L is Lorentz number, T is absolute temperature, c_v is specific heat capacity, l_{ph} is mean free path of phonon, v_{ph} is velocity of phonon.

In case of metal and degenerate semiconductor, seebeck coefficient could be generally defined as below equation (1-5) based on Mott-Jones relationship.[10]

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{\frac{2}{3}} \qquad \cdots \text{ (1-5)}$$

Where h is Plank constant, k_B is Boltzmann constant, m^* is effective mass of carrier, n is carrier concentration.

Then, it could be found that all of the three parameters, S, k and σ, are function of carrier concentration. This means that to earn high ZT value with fixed carrier concentration, phonon portion of thermal conductivity should decrease.[6]

There has been two approaches to have low value of phonon portion of thermal conductivity, in material and structural aspects. In early 1950s, bulk material compound using heavy elements such as Bi, Te, Pb were researched to decrease thermal conductivity by lowering phonon velocity.[11] As ZT values of those materials researched in those days could not reach above 1, it seemed that the study of thermoelectrics lost its shining. However, along with advancement of technology, materials having 2-dimensional and 1-dimensional structure jumped in the thermoelectrics field. With low dimensional structure of materials like thin films, nano-wires and nano-dots, materials having sharp and nearly dispersionless band structure could be fabricated. This means that if appropriate size of nano structure is tuned to place those bands near the Fermi level, possibility to gain high thermopower would increase.[12] To be specific, in nano structure, it could be expected to get low thermal conductivity without reducing electrical conductivity if the size of nano structures is smaller than the mean free path of the phonons and yet larger than that of electrons.[13]

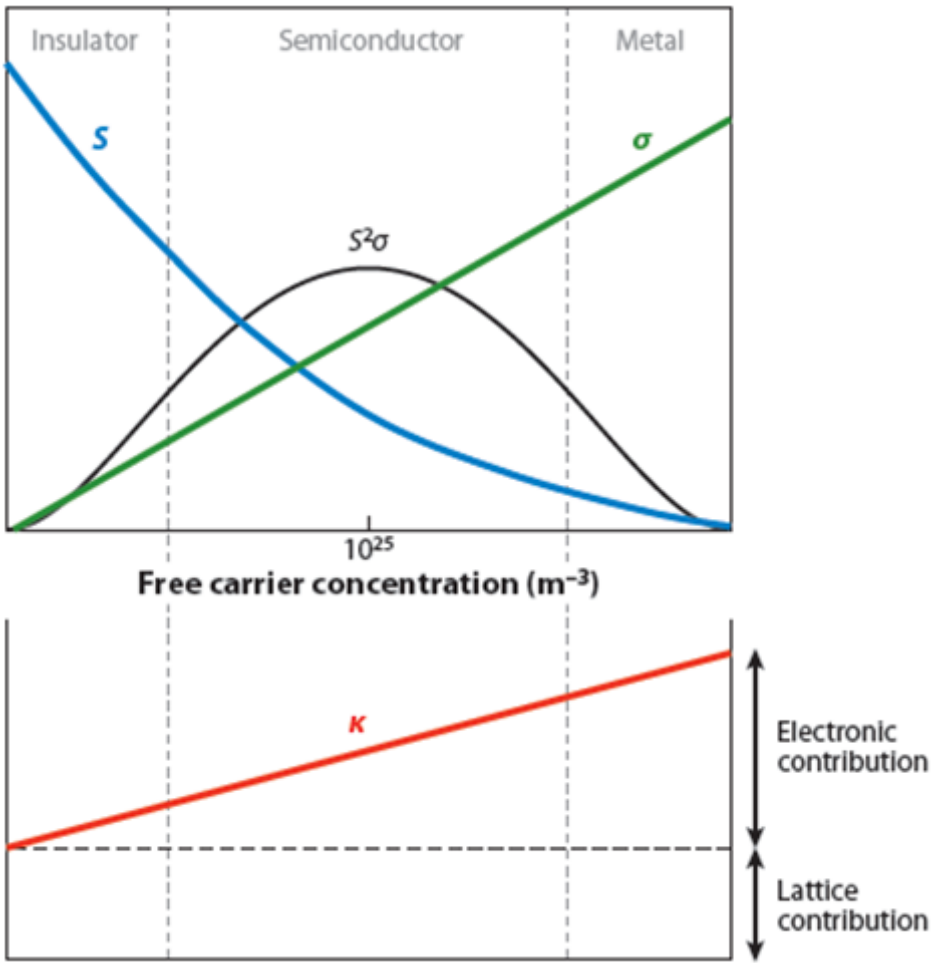


Figure 1-6. Change of thermoelectric parameters as a function of carrier concentration[6]

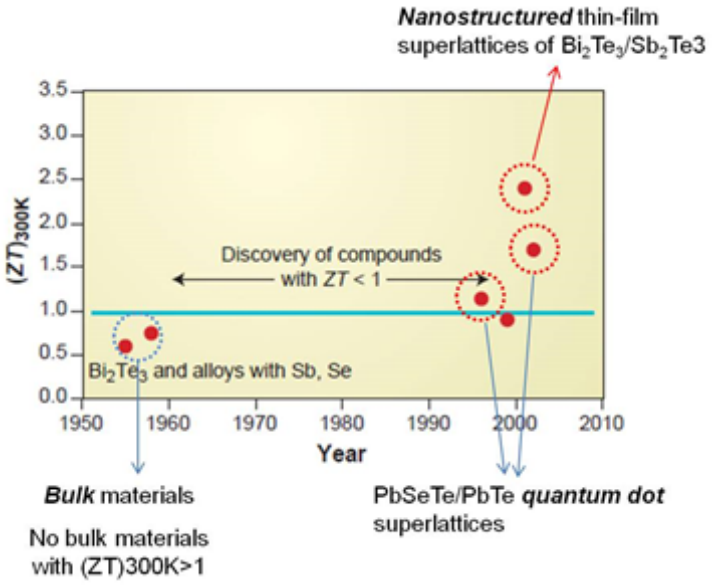


Figure 1-7. Experimental trend with historical change of ZT value of thermoelectrics[11]

1.2. Structural and electrical properties of ALD-AZO and ZnO films

Contrary to conventional homogeneous Al-doped ZnO (AZO) composites fabricated by Pulsed laser deposition method (PLD) or Sputter, AZO films utilized atomic layer deposition method (ALD) exhibit a unique hetero layer structure consisting of a ZnO matrix and a AlOx dopant layer embedded within the matrix. In Figure 1-8., typical deposition process of Atomic layer deposition system is explained which consists of alternate injection and purging of precursors delivery like shown in Figure 1-9 below. In addition, this novel method, ALD, guarantees excellent reproducibility and adjustability of film composition.

One of major strengths of utilizing ALD to deposit AZO films is that electrical properties of AZO films could be easily controlled. it is well known that Al (Group Ⅲ) works as a dopant material to generate electron carriers in ZnO by forming charged donors such as Al ion substituted by Zn, Al_{Zn}^{+}, Oxygen vacancy, V_o^{1+}, Zn interstitial, Zn_i^{2+}.[14,15,16] Then, this means that through differenciation of relative injection ratio of two precursor Trimethylaluminium(TMA) and Diethylzinc(DEZ) that are precursors depositing Al_2O_3 and ZnO films respectively, linear density of AlOx layer in AZO films could be managed, which results in varying electrical properties.[17] For example, DJ Lee *et al.*. already reported that the electrical property of ALD-AZO films is controllable by varying injection ratio of TMA to DEZ on a substrate shown in Figure 1-10..[18]

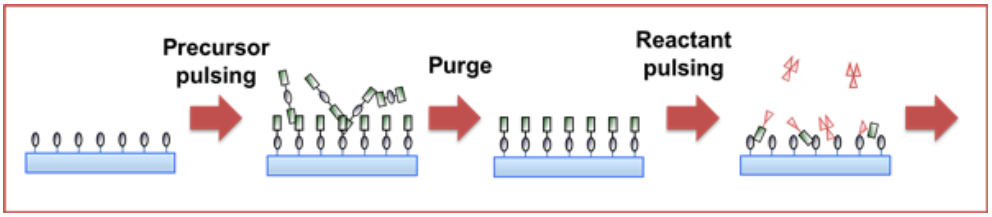


Figure 1-8. Schematic image of typical ALD process

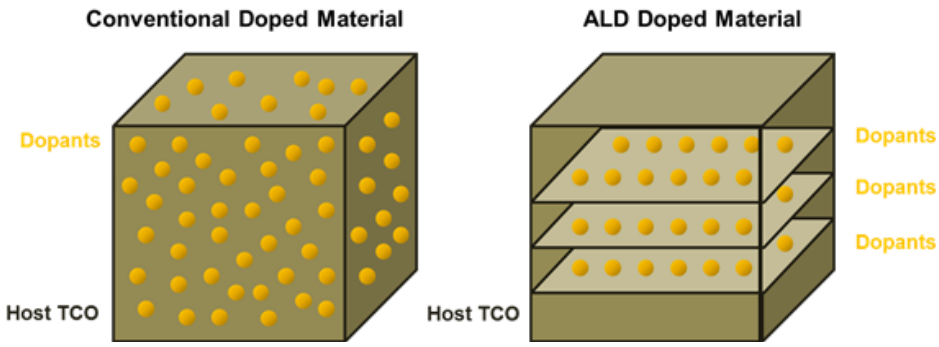


Figure 1-9. (Left) Structure of homogeneously doped TCO materials deposited in conventional ways such as PLD, Sputter. (Right) Structure of heterogeneously doped TCO material deposited by ALD

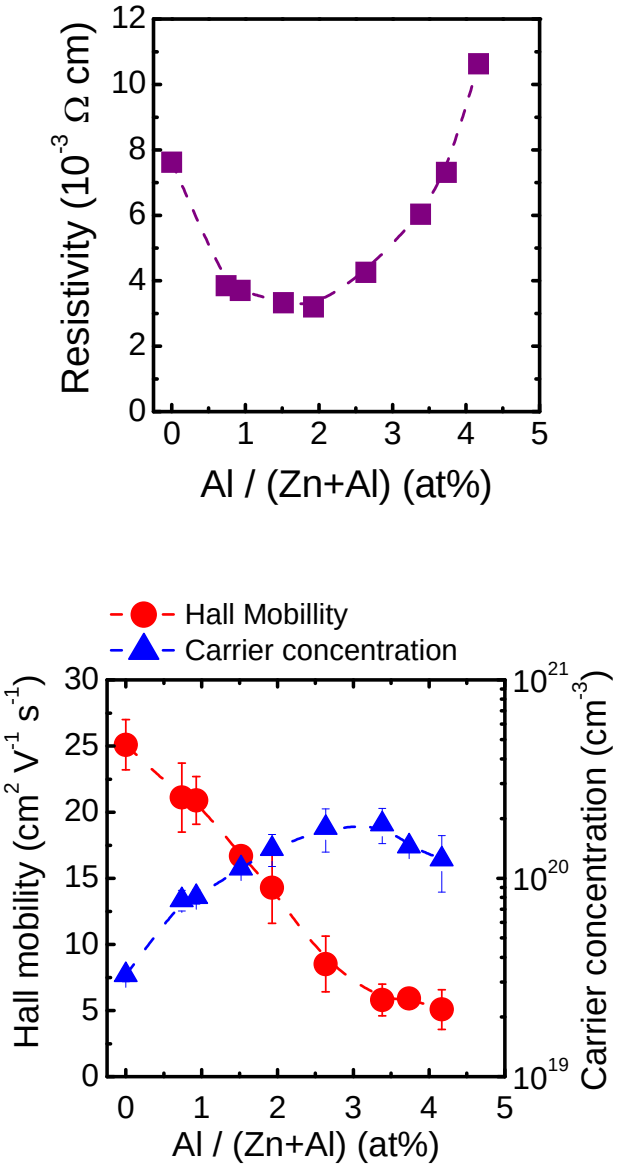


Figure 1-10. Electrical properties of ALD-AZO films with different Al doping concentration[19]

1.3. Objectives of Experiment

In thermoelectric filed of study, conventional materials such as Bi, Te, Pb, Sb have been widely investigated in order to achieve high ZT values as they are heavy material for lowering thermal conductivity. However, their toxicity and stability to oxidation at ambient conditions have been pointed out as critical issues. Recently, as an alternative to the conventional materials, ZnO- and In_2O_3-based transparent conducting oxides (TCOs) have been considered as thermoelectric materials due to its thermal stability and additional merit from the transparency to the visible rays.

As the ALD-AZO films have an unique hetero structure consisting of a ZnO matrix and AlOx dopant layers embedded within the matrix already shown in Figure 1-9., it was expected that decoupling of ZT parameters to gain high energy conversion efficiency would be possible. To be specific, addition of AlOx layers would enable ZnO films to be electrically conductive by providing free electrons. And it would be also thermally insulating by generating resistive thermal boundaries.

In addition, electrical and thermal transport behaviors in thin film structure could be understood by conducting this experiment. More specifically, it would be meaningful to discuss thermal properties in respect to carrier transport at AlOx interface layers. In order to integrate the TCO materials into the thermoelectrics, it is important to control both electrical and thermal transport properties of those. In this regard, ALD can give a great benefit to elucidate the purpose of thermoelectrics since this system exhibit excellent reproducibility and adjustability of thilm composition. Understanding the thermal resistance at the interface between two materials is of

primary significance in the study of its thermal properties. This is even more critical for nanoscale systems where interfaces could significantly affect the properties relative to bulk materials.

1.4. References

[1] US DOE - EIA Annual Energy Survey., (2006)

[2] J. W. Fergus et al., Journal of the European Ceramic Society 32, 525-540, (2012)

[3] J. R. Sootsman et al., Angew. Chem. Int. Ed., 48, 8616-8639, (2009)

[4] J. F. Li et al., NPG Asis Mater., 2(4), 152, (2010)

[5] Th. J. Seebeck "Magnetische Polarisation der Metalle und Erze Durch Temperatur-Differenz"1822-23 in Ostwald's Klassiker der Exakten Wissenshaften Nr. 70 (1895). Seebeck Biography 1. Seebeck Biography 2.

[6] A. Shakouri., Annu. Rev. Mater. Res. 41, 17.1-17.33, (2011)

[7] A. Shakouri et al., Thermal Nanosystems and Nanomaterials, ed. by S. Volz, Springer, pp.225-299, (2009)

[8] Safa Kasap., Thermoelectric Effects in Metals: Thermocouples. S. O. Kasap (1997-2001)

[9] Cronin B. Vining, Nature Mat., 8, 83, (2009)

[10] G. J. Snyder et al., Nat. Mater., 7, 105, (2008)

[11] A. Majumdar, Science, 303, 777, (2004)

[12] M. S. Dresselhaus et al., Adv. Mater., 29, 19, (2007)

[13] A. I. Boukai et al., Nature., 451, 168, (2008)

[14] S. Lany et al., Phys. Rev. Lett., 98, 045501, (2007)

[15] C. G. Van de Walle et al., Nature 423, 626, (2003)

[16] A. Janotti et al., Nat. Mater. 6, 44, (2007)

[17] M. Otto et al., Adv. Mater. 22, 5035, (2010)

[18] D. J. Lee, K. B. Kim et al., Adv. Funct. Mater., 21, 3, (2011)

CHAPTER 2.

Thermoelectric properties of ALD-AZO and -ZnO films

2.1 Sample preparation

ALD was utilized in order to fabricate hetero-structured AZO films and undoped ZnO film . AZO and ZnO films were deposited on SiO_2 (300nm) / Si wafer via ALD using Lucida D-100 at a deposition temperature of 200 °C. Diethylzinc (DEZ) and Trimethylaluminum (TMA) were used as precursors for the deposition of ZnO and AlOx layer, respectively, And water vapor was used as a reactant. Film thickness was measured by ellipsometry with wavelength 632.8 nm. ALD-AZO films were deposited with N cycles(N = 49, 24, 19) of ZnO per each cycle of an AlOx layer. Schematic image explaining a way of ALD-AZO films deposition was shown in Figure 2-1 and Figure 2-2.. Thereby, the thickness of ZnO layer in between AlOx layers was varied.

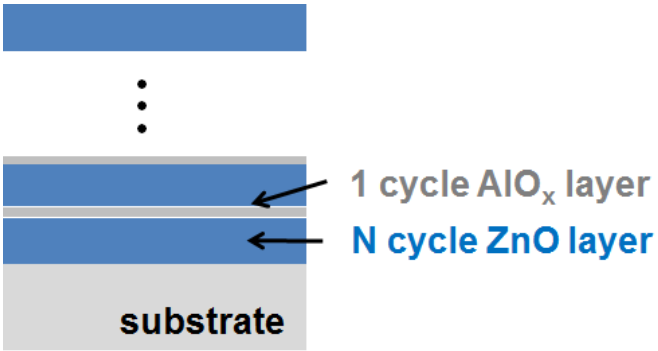


Figure 2-1. Schematic image showing a way of deposition process of ALD-AZO films

2.2. Electrical properties of ALD-AZO and ZnO films

2.2.1 Experimental details

Electrical properties including Hall mobility, carrier concentration, resistivity were measured by a Hall measurement system. Film composition was measured to figure Al doping concentration with inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The atomic ratio, Al/(Al+Zn) (at%), was 0.8, 1.86, 2.51 for AZO films deposited with N = 49, 24, 19, respectively, which is shown in Figure 2-2.

Electrical properties of the ALD-AZO and ZnO films were investigated by the Hall measurement. Figure 2-3. shows resistivity, Hall mobility, and carrier concentration of the ALD-AZO and ZnO films as a function of the atomic ratio of Al/(Al+Zn) (at%). In addition, electrical conductivity of all films were measured in temperature ranging from room temperature to 493K.

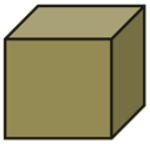
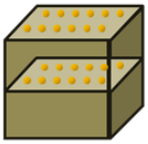
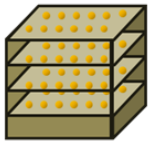
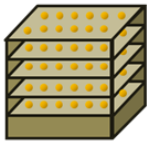
				
n cycles of ZnO : 1 cycle of AlO_x	Undoped	49 cycles	24 cycles	19 cycles
Al / (Al + Zn) (at.%)	0	0.8	1.86	2.51

Figure 2-2. Atomic layer deposited ZnO and AZO films prepared with atomic concentration of Al over total cation concentration

2.2.2 Result and discussion

As described in Figure 2-3., electrical conductivity increases with increase of atomic ratio of Al to total cations, Al/(Al+Zn) (at%). Electrical conductivity of undoped ZnO film was 346.69 $\Omega^{-1}cm^{-1}$. This value is clearly lower than those of ALD-AZO films. Especially, electrical conductivity of AZO films with 2.51 at % was 1165.09 $\Omega^{-1}cm^{-1}$ that is almost 3.3 times higher than that of undoped ZnO. This increase could be explained with variation of carrier concentration and mobility value based on a equation (2-1) below.

$$\sigma = ne\mu \qquad \cdots (2\text{-}1)$$

Where σ is electrical conductivity, n is carrier concentration, μ is mobility.

As shown in Figure 2-3, Electrical conductivity increased with a funtion of Al doping concentration. This is because increase of electron concentration is dominant over decrease of carrier mobility. Al , one of Group Ⅲ materials, incorporates with ZnO. it works as dopants and produces an electron carrier.[1,2,3] Therefore, it was obvious that the increase of electron concentration results from the increase of Al doping concentration.

It is well known that there are several mechanisms influencing on mobility of charge carrier in thin films such as grain boundary scattering, ionized scattering, lattice vibration scattering, etc.[4,5,6,7] And those mechanisms have a specific relation shown in below equation (2-2).[8]

$$\frac{1}{\mu} = \frac{1}{\mu_i} + \frac{1}{\mu_l} + \frac{1}{\mu_g} \qquad \cdots (2\text{-}2)$$

where μ is mobility, μ_i is ionized impurity scattering mobility, μ_l is lattice vibration scattering mobility, μ_g is grain boundary scattering mobility.

Especially, in TCO films with carrier concentration ranging from $10^{20} \sim 10^{21}$ cm^{-3},[9,10] it is known that ionized impurities meaning oxygen vacancies, excess metallic atoms, external dopant material have the most influence on the mobility of the films.[11,12] As a result, it was thought that the decrease of mobility with increase of Al doping concentration is due to the increase of scattering sites coming from ionized impurities.

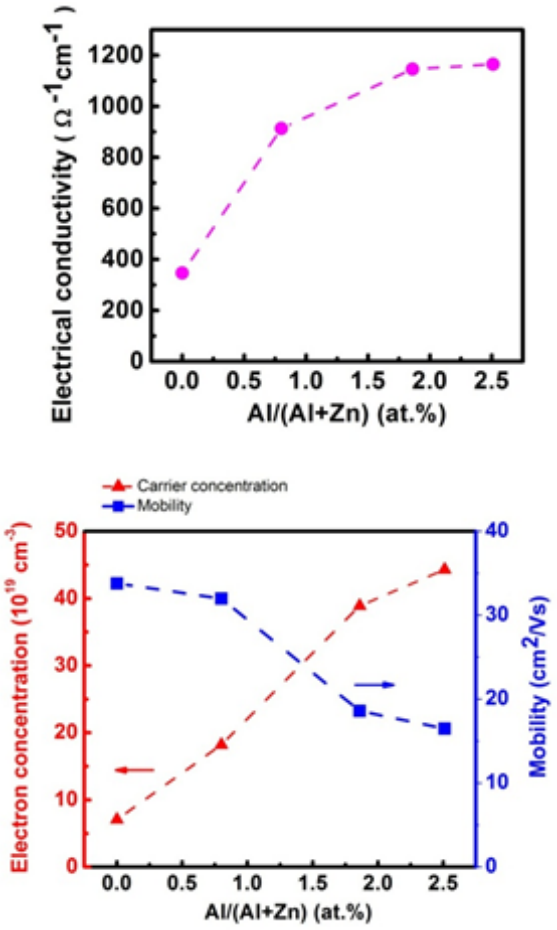


Figure 2-3. Electrical properties of ALD-ZnO and -AZO films

Figure 2-4. shows electrical conductivity of ZnO and AZO films as a function of temperature ranging from room temperature to 495 K. All films clearly exhibit metallic property that electrical conductivity slightly decreased with increase of temperature. It is well known that for degenerate semiconductor carrier concentration is independent to temperature.[13] As all the AZO films worked as a degenerate semiconductor, carrier concentration of those films would not be changed with increase of temperature.[9,10] Therefore, it was clear that decrease of electrical conductivity with a function of temperature was mainly due to the decrease of mobility.

As explained already, three scattering components such as grain boundary, ionized impurity and lattice vibration are main components influencing mobility of TCO films.[4,5,6,7] It is well known that ionized impurity scattering, which has a biggest influence on TCO films scattering, is independent of temperature if materials would be a degenerate semiconductor.14'[15,16] In addition, mobility influenced by lattice vibration scattering is inversely proportional to temperature.[8,16] That is because magnitude of lattice vibration got bigger with increase of temperature, blocking transport of carriers. Therefore, decrease of total mobility with a function of temperature would be due to effect of lattice vibration scattering.

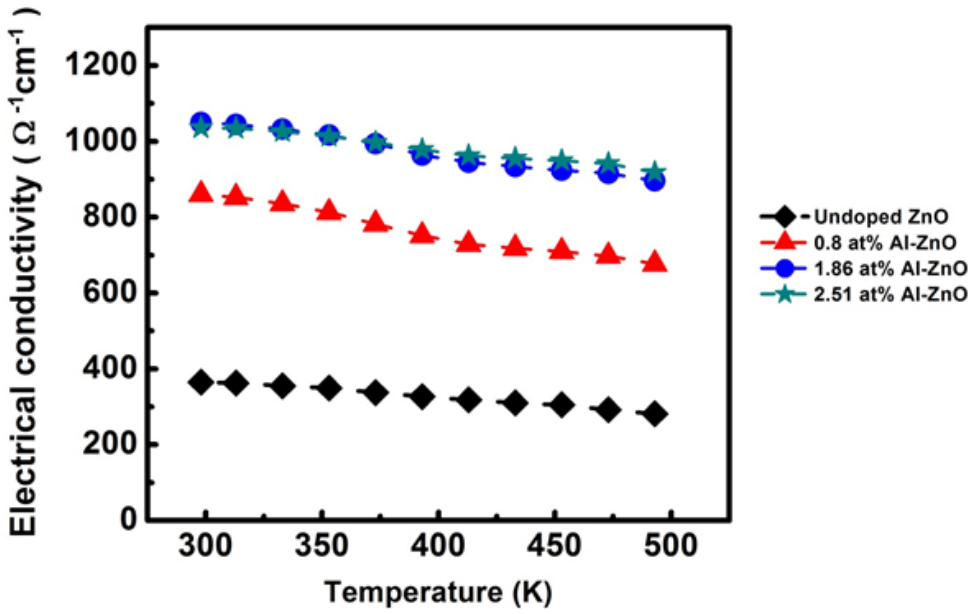


Figure 2-4. Electrical properties of Atomic layer deposited ZnO and AZO films at temperature ranging from room temperature to 493K

2.3. Thermal properties of ALD-AZO films

2.3.1 Experimental details

Thermal properties of ALD-AZO films and undoped ZnO was measured by Time-domain thermoreflectance measurement system (TDTR), which is known as quantitative analysis on thermal properties.[17] TDTR is an optical method to measure thermal property of thin films utilizing that reflectance of materials would be changed with temperature of the materials.[18] Procedure of thermal conductivity measurement of ALD-AZO and -ZnO films was shown in Figure 2-5. as following; First, Al layer was deposited using ALD on top of the films. As pump beam is absorbed in a Al layer, the layer was locally heated up. Then the heat dissipated into ALD-AZO and ZnO films and flow away. This means the velocity of heat dispersion was related to the thermal properties of the ALD-AZO films. The change in temperature of Al layer gave a change in the optical reflection coefficient of Al layer which can be approximately considered to be propotional to temperature. Then this reflectivity is measured with respect to time by probe beam. And the received data was matched to model function to export thermal conductivity of the ALD-AZO and -ZnO films.

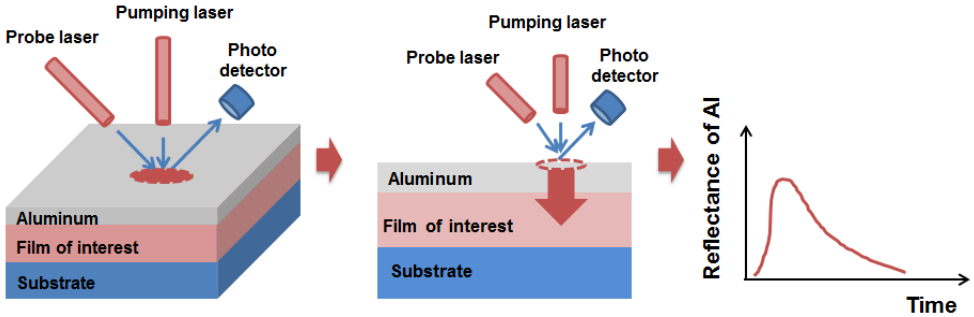


Figure 2-5. Schematic image explaining TDTR measurement system

2.3.2. Thermal conductivity of ALD-AZO and ZnO films

Figure 2-6. shows thermal conductivity of ZnO and AZO films measured by TDTR system at room temperature. Measured thermal conductivity of ZnO films was 15 W/mK, and that of AZO films decreased with increase of Al doping concentration; 5.5 W/mK, 3.8 W/mK, 3.35 W/mK. This decrease was due to the thermal boundary resistance provided by the AlOx layers in between ZnO matrix.[19] To be specific, this decrease of thermal conductivity could be explained by considering AlOx interface layer density defined below.

$$\text{Layer density of } AlO_x \text{ interface [\#/cm]} = \frac{\text{\# of } AlO_x \text{ interface}}{\text{Unit hickness of films}}$$

Layer density of AlOx interface means how many of the AlOx interface exists in unit thickness of films. Interestingly, thermal conductivity of AZO films decreased with addition of the AlOx interface layer. It means that higher layer density of AlOx interface, lower thermal conductivity of the films. This trend could be explained by thermal boundary resistance.[19,20,21] Thermal boundary resistance, also known as Kapitza resistance, is that heat energy decreases as it passes through interfaces.[20] Acoustic mismatch model (AMM) is one of models explaining heat transfer at interfaces.[22] This model is similar to Snell's law. And it assumes a geometrically perfect interface and phonon transport across the interface is entirely elastic, treating phonons as waves in continuum. Therefore, shown in Figure 2-7., phonon waves coming from ZnO layer would not pass the AlOx interface layer perfectly. And only small portion of heat energy is

able to transmit to next level of ZnO layer. This leads to an explanation that, for AZO films, decrease of thermal conductivity came from increase of AlOx interface layer density.

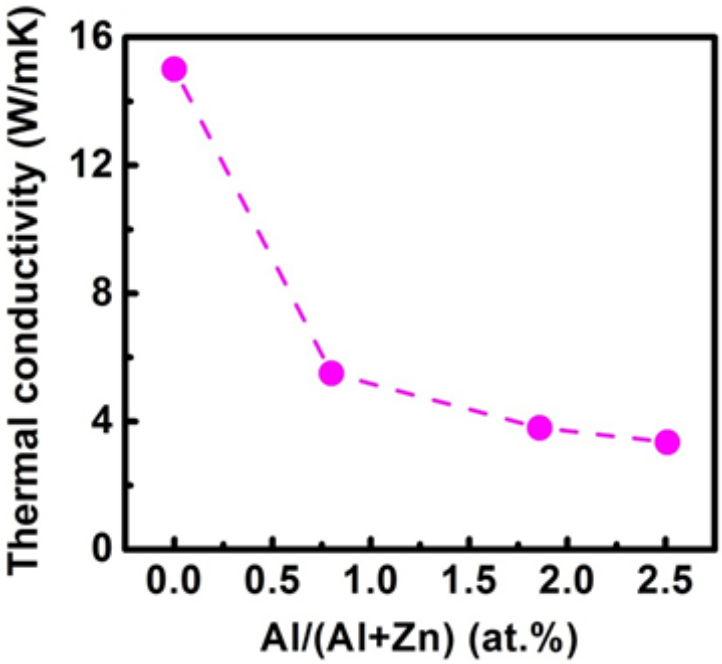


Figure 2-6. Thermal conductivity of ALD-ZnO and -AZO films

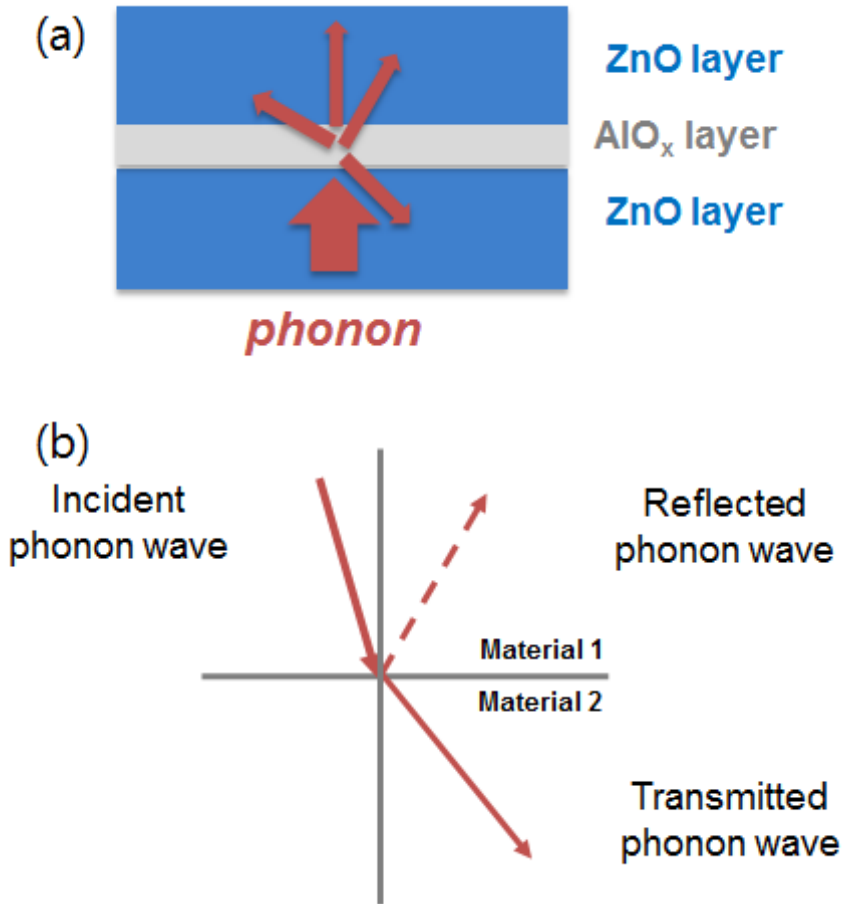


Figure 2-7. (a) Schematic image explaining thermal boundary resistance effect at AlOx layer. (b) Schematic image explaining phonon energy transferring based on acoustic mismatch model similar to Snell's law

2.2.3 Interfacial thermal conductance of AlO_x layer

Comparing with Sputtered-AZO films, one of major advantages of ALD-AZO films is that similar type of AlOx layer could be heterogeneously deposited. In addition, a density of the layer could be easily controlled. Therefore, interfacial thermal conductance of AlOx layer was calculated to figure out the influence of one AlOx interfacial layer on the thermal conductivity of AZO films.

If a material consists of matrix A and B has hetero-layered structure, thermal conductivity of the material has a relation below.

$$\frac{1}{k_{tot}} = \frac{f_A}{k_A} + \frac{f_B}{k_B} + \frac{n_d}{G_{A-B}} \qquad \cdots (2\text{-}3)$$

where k_{tot} is conductivity of a material, f_A and f_B are the fraction of matrix A and B over thickness of total film, k_A and k_B are thermal conductivity of A and B material, G_{A-B} is interfacial thermal conductance between matrix A and B with an unit of W/m^2K, n_d is Linear density of A-B interface that is equal to two times of layer density of A-B interface with an unit of #/nm.

Above relation (2-3) was applied to ALD-AZO films. As AlOx interface layer was deposited by ALD system using TMA precursor source, it could be thought that thickness of AlOx layer would be in angstrom scale. And it means that fraction of ZnO in AZO films, f_{ZnO}, would be equal to 1 and the fraction of AlOx layer in AZO films, $f_{ZnO\text{-}AlOx}$, would be close to 0. Then, thermal conductivity of hetero layered ALD-AZO films would have a relation (2-4) below.

$$\frac{1}{k_{AZO}} = \frac{1}{k_{ZnO}} + \frac{n_d}{G_{ZnO-AlO_x}} \qquad \cdots (2\text{-}4)$$

where k_{AZO} and k_{ZnO} are thermal conductivity of AZO and ZnO films, $G_{ZnO-AlO_x}$ is interfacial thermal conductance of AlOx layer, n_d is Linear density of AlOx layer that is equal to two times of layer density of AlOx layer interface.

Based on the relation (2-4) above, interfacial thermal conductance of AlOx was calculated. Interestingly, the value increased from 1389.5 MW/m^2K to 1725.3 MW/m^2K with increase of Al doping concentration. Therefore, it would be judged that the relation (2-4) was inappropriate as same type of AlOx layer have different interfacial thermal conductance.

Total thermal conductivity of AZO and ZnO films was not considered. Instead, only phonon portion of thermal conductivity was considered to get proper interfacial thermal conductance value.

According to Wiedemann-franz law, in metal, a ratio of electronic contribution of thermal conductivity to electrical conductivity is linear to an absolute temperature with a constant of Lorentz number, 2.45 x 10^{-8} V^2/K^2. Electrical conductivity of ZnO and AZO films in room temperature were applied to Wiedemann-franz law to earn phonon portion of thermal conductivity of those films.[23]

$$\frac{\lambda_e}{\sigma} = LT \qquad \cdots (2\text{-}5)$$

Where λ_e is electron portion of thermal conductivity of material, σ is electrical conductivity, L is Lorenz number, T is absolute temperature.

Then, as explained in equation (2-6), $G_{true,ZnO-AlOx}$ was calculated again by subtracting electrical portion of thermal conductivity from total thermal conductivity of the films

$$\frac{1}{k_{ph,AZO}} = \frac{1}{k_{ph,ZnO}} + \frac{n_d}{G_{true,ZnO-AlO_x}} \qquad \cdots (2\text{-}6)$$

where $k_{ph,AZO}$ and $k_{ph,ZnO}$ are phonon portion of thermal conductivity of AZO and ZnO films, $G_{true,ZnO-AlO_x}$ is calculated interfacial thermal conductance of AlOx layer, n_d is Linear density of AlOx layer that is equal to two times of layer density of AlOx layer interface.

Interfacial thermal conductance of AlOx layer calculated by two equations (2-4) and (2-6) were displayed in Figure 2-9. Interfacial thermal conductance calculated using total thermal conductivity in traditional way was set as apparent thermal conductance value and colored with red triangle. On the other hand, interfacial thermal conductance calculated using phonon portion of thermal conductivity was set as true thermal conductance value and colored with blue square. As shown in Figure 2-9., it is obvious that true interfacial thermal conductance were consistent around 1130 MW/m^2K regardless of Al doping concentration. Therefore, it was confirmed that interfacial conductance could be calculated more correctly by using only phonon portion of thermal conductivity of materials.

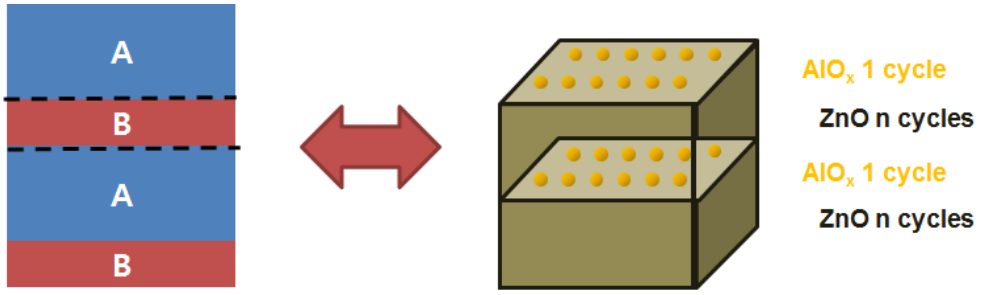


Figure 2-8. Schematic image of hetero-layered material that consist of matrix A, B and A-B interface comparing that of ALD-AZO films

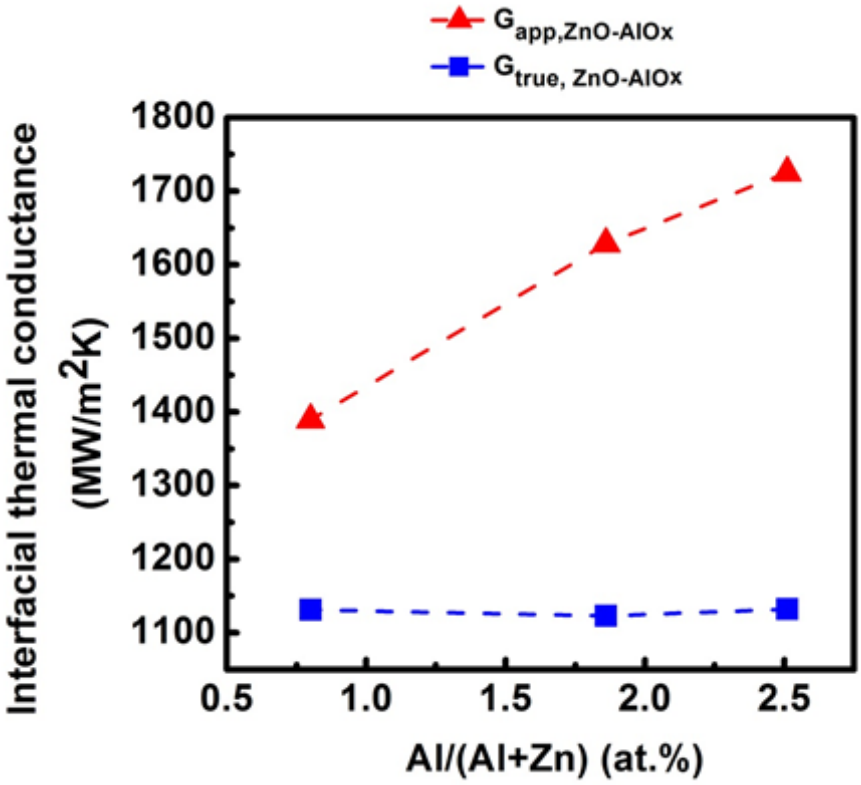


Figure 2-9. Interfacial thermal conductance of AlOx layer calculated in two different ways. G_{app} were derived from total conductivity. G_{true} were derived from only phonon portion of thermal conductivity

2.4. Seebeck coefficient of ALD-AZO films

2.4.1 Experimental details

Since it would be not easy to correctly measure small change of temperature and voltage to figure seebeck coefficient of materials, seebeck coefficient was measured by MMR tech's SB-100 Seebeck measurement system. This system uses a reference material, constantan, that seebeck coefficient value at wide temperature is well known. seebeck coefficient of ALD-AZO and -ZnO films were measured in temperature ranging from room temperature to 400 K. Procedure of seebeck measurement of the films was as following, shown in Figure 2-10.; First, the AZO and ZnO films were placed in the chamber with the pressure of 5 mtorr. Then measure the V_1 and V_2 at certain temperature with heater off. V_1 and V_2 are the seebeck voltage of the film and the reference material at that heater-off temperature, respectively. If the heater is on, it leads to have temperature gradient through the films and the reference material. And after sometime to stabilize, measure V_1 and V_2 at accelerated heater on temperature. As the seebeck coefficient of reference material is well known, the temperature difference ΔT_2 would be figured out. By placing the heat capacity of the film and the reference material same, it could be assumed that temperature difference ΔT_2 is same as ΔT_1. then with known value of the ΔV_1 and ΔT_1, seebeck coefficient value at that temperature could be figured out.

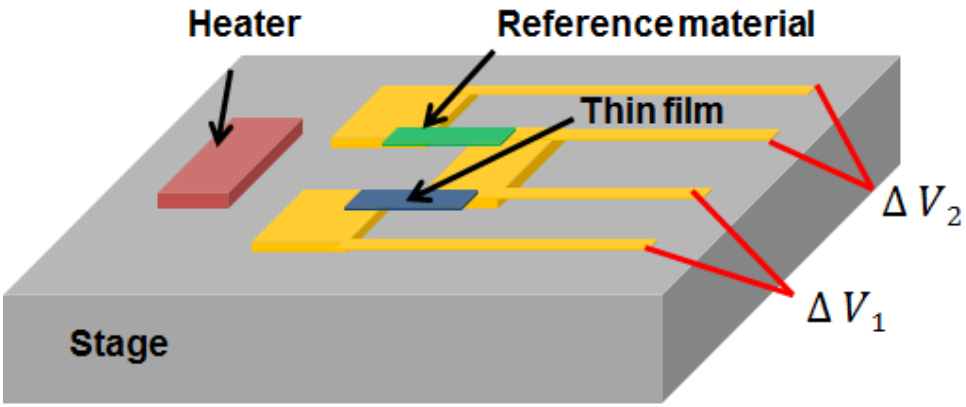


Figure 2-10. Schematic image explaining procedure of measuring seebeck coefficient using MMR tech's Seebeck measurement system

2.4.2 Result and discussion

Below Figure 2-11. exhibits seebeck coefficient of ZnO and AZO films with temperature ranging from room temperature to 400K. All four films have negative sign of seebeck coefficient meaning n-type thermoelectric material with electron as a major carrier. And it is well correspond to the sign of other AZO films reported.[24,25,26] At room temperature, AZO film with 0.8 at% of Al doping concentration has the highest seebeck coefficient value as -21.5 uV/K. And undoped ZnO film followed with -20.3 uv/K of seebeck coefficient. In addition the other two AZO films with 1.86 and 2.51 at% of Al doping concentration have same seebeck concentration value of -7.45 uV/K at room temperature.

Mott-Jones relation was considered to understand these results. Mott-Jones relationship is well known that seebeck coefficient of metal and degenerate semiconductor have general relationship like below equation (2-7) with three components, that are effective mass, carrier concentration and temperature.

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{\frac{2}{3}} \quad \cdots \text{(2-7)}$$

Where h is Plank constant, k_B is Boltzmann constant, m^* is effective mass of carrier, n is carrier concentration.

According to the relation, seebeck coefficient is linear to an absolute temperature and an effective mass.[27,28] And large number of carrier leads to have low seebeck coefficient value. A result shown in Figure 2-11. is well correspond to the relationship as seebeck coefficient of AZO and ZnO films increase with increase of temperature.

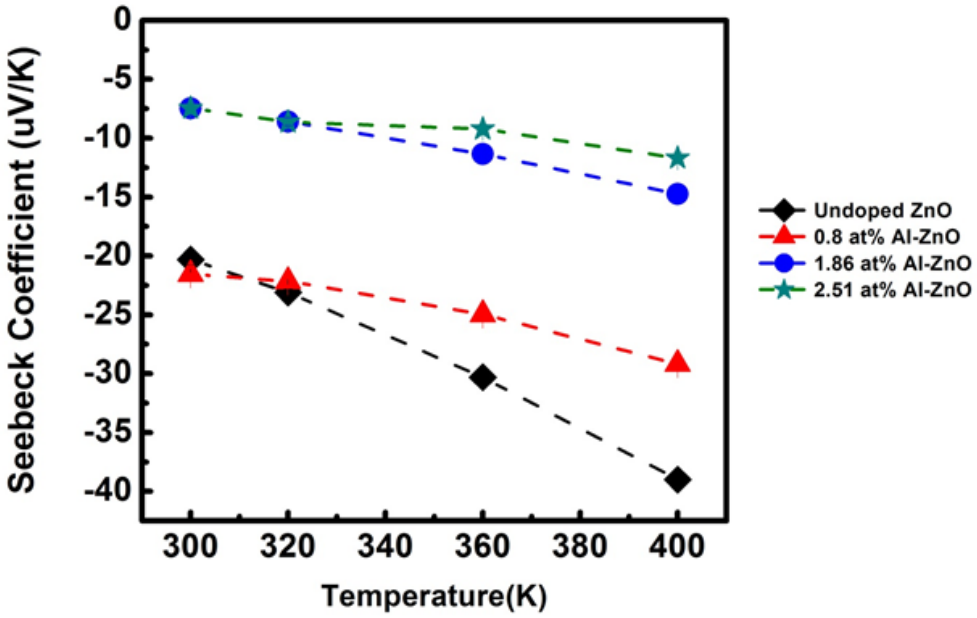


Figure 2-11. Seebeck coefficient of ALD-AZO and -ZnO films as a function of temperature

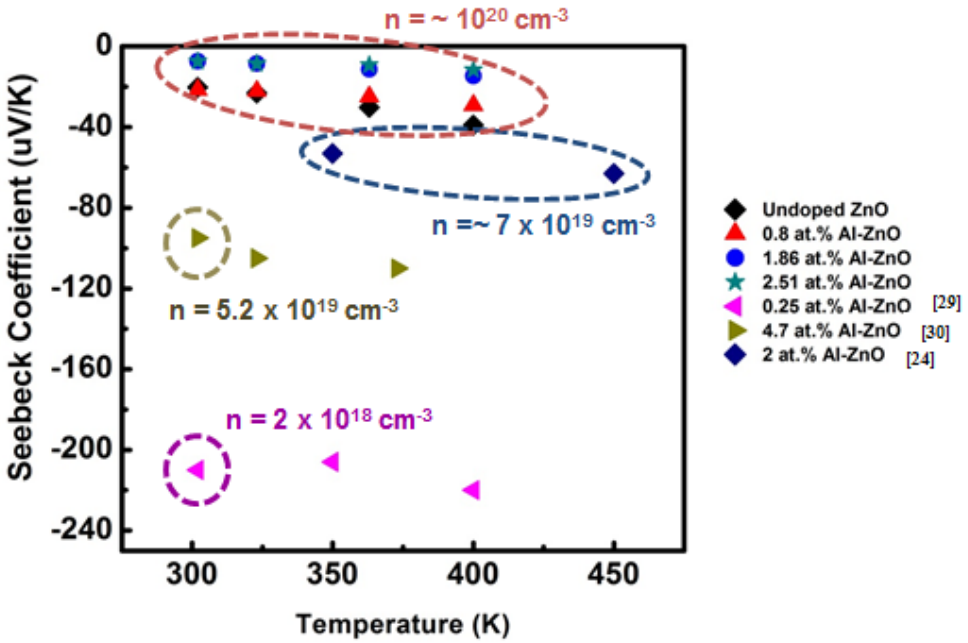


Figure 2-12. Seebeck coefficient of ALD-AZO and -ZnO films and other AZO based materials reported comparing with carrier concentration[24,29,30]

2.5. References

[1] S. Lany et al., Phys. Rev. Lett. 98, 045501, (2007)

[2] C. G. Van de Walle et al., Nature 423, 626, (2003)

[3] A. Janotti et al., Nat. Mater. 6, 44, (2007)

[4] V. A. Johnson, and K. Lark-Horovitz, Phys. Rev. 71, 374, (1974)

[5] K. Ellmer, R. Mientus, Thin Solid Films 516, 4620, (2008)

[6] Seto, J. Appl. Phys. 46, 5247, (1975)

[7] T. Makino, Y. Segawa, A. Tsukawaki, A. Ohtomo, and M. Kawasaki, Appl. Phys. Lett. 87, 022101, (2005)

[8] D. H. Zhang et al., Appl. Phys. A. 62, 487, (1996)

[9] P. P. Edwards, A. Porch, M. O. Jones, D. V. Morgan, R. M. Perks, Daltom Trans. 2995, (2004)

[10] N. F. Mott, Metal-Insulator-Transition, Talyer and Francis, London, (1990)

[11] K. Ellmer, J. Phys. D:Appl. Phys. 34, 3097, (2001)

[12] T. Pisarkiewicz, Z. Zakrzewska, and E. Leja, Thin Solid Films 174, 217, (1989)

[13] J. G. Lu et al., J. Appl. Phys. 100, 073714, (2006)

[14] E. Shanthi, A. Banerjee, V. Dutta, K. L. Chopra: J. Appl. Phys. 53, 1615, (1982)

[15] J.J. PH Elich, E. C. Boslooper, H. Haitjema: Thin Solid Films 177, 17, (1989)

[16] K. F. Huang, T. M. Uen, Y. S. Gou, C. R. Hiang, L. C. Yang: Thin Solid Films 148, 7, (1987)

[17] D.G. Cahill, Rev. Sci. Instrum., 75, 5119, (2004)

[18] H.-K. Lyeo and D. G. Cahill, Phys. Rev. B, 73, 144301, (2006)

[19] Y. Jin, et al., Appl. Phys. Lett. 98, 093305, (2011)

[20] E. T. Swartz and R. O. Pohl. Rev. Mod. Phys., Vol. 61, No.3,

(1989)
[21] E.-K. Kim, S, -I. Kwun, S.-M. Lee, H. Seo, and J.-G. Yoon, Appl. PHys. Lett. 76, 3864, (2000)
[22] B. V. Budaev and D.B. Bogy J. Phys. A:Math. Theor. 43, 425201, (2010)
[23] G. Wiedemann and R. Franz, Ann. Phys. (Leipzig) 89, 497, (1853)
[24] W. H. Nam et al., J. Mater. Chem., 22, 14633, (2012)
[25] Y. Kinemuchi and C. Ito et al., J. Mater. Res., Vol. 22, No. 7, (2007)
[26] S. Fujita and A. Suzuki. Quantum Theory of Thermoelectric Power (Seebeck Coefficient), Electromotive Force and Measurement in Several Systems, Prof. Sadik Kara (Ed.), (2011)
[27] G. Zeng et al., J. Appl. Phys. 101, 034502, (2007)
[28] A. Shakouri., Annu. Rev. Mater. Res. 41, 17.1-17.33., (2011).
[29] P. Jood et al., Nano. Lett, 11, 4337, (2011)
[30] T. Tsubota et al., J. Mater. Chem., 7, 85, (1997)

CHAPTER 3.

Conclusion and summary

3.1. Possibility for thermoelectric application

Figure 3-1 shows thermal conductivity of ALD-ZnO and ALD-AZO films with 1.86 at% of Al concentration compared with other AZO materials reported in wide range of temperature.[1,2,3,4] Thermal conductivity of ALD-AZO film was relatively lower than other reported AZO materials.

However, calculated ZT values of AZO and ZnO films were much lower than other AZO materials. It was because seebeck coefficient was too low and dominantly influenced on ZT value even though thermal conductivity of the material was lower enough to get high ZT value.

Therefore, in order to utilize ALD-AZO films in thermoelectric industry, it would be suggested that hetero layered structure needs to be sustained to have low thermal conductivity while controlling carrier concentration to optimize seebeck coefficient and electrical conductivity in anyways such as annealing.

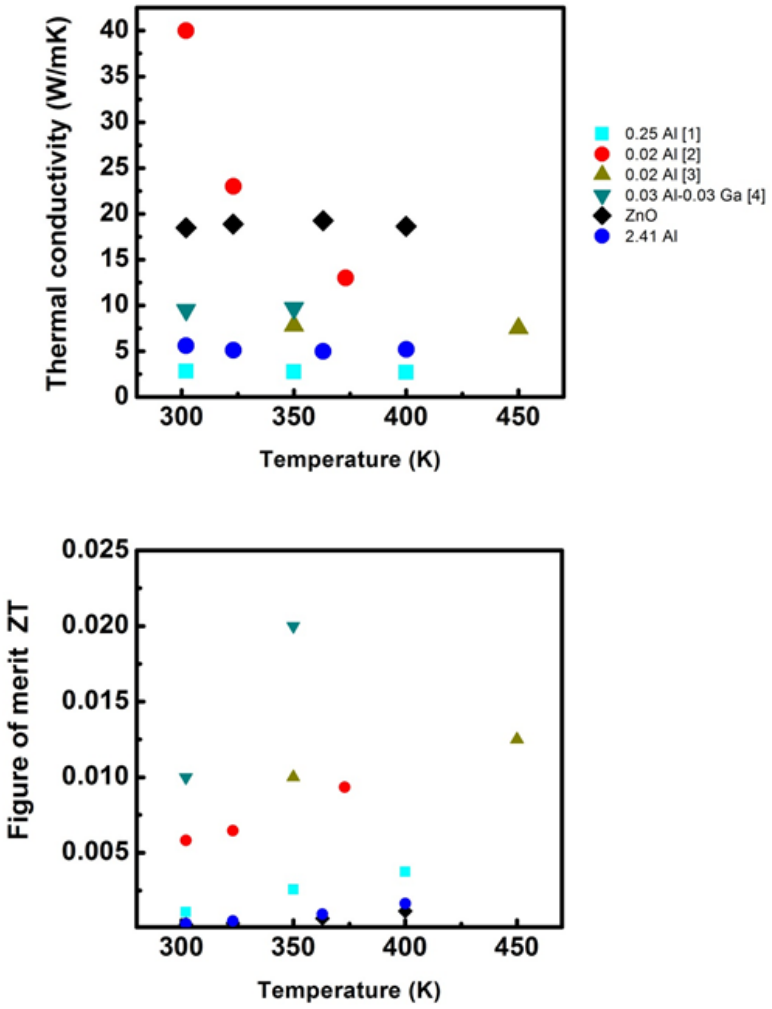


Figure 3-1. Thermal conductivity and ZT value of ALD-ZnO (black-diamond) and -AZO (blue-circle) films and other AZO based materials reported[1,2,3,4]

3.2. Summary and conclusion

It was studied that the electrical and thermal transport in atomic layer deposited Al-doped ZnO films.

The addition of AlO_x layers enable ZnO films to be electrically conductive, by providing free electrons, and thermally insulating, by generating resistive thermal boundaries.

To consider only the lattice conduction portion (phonons) of thermal conductivity, the electronic conduction portion (electrons) is subtracted from the total thermal conductivity. This procedure yields an interfacial thermal conductance value of ~1130 $MW/m^2 \cdot K$ for the ZnO-AlO_x interfaces, which was consistent for all film compositions.

Seebeck coefficient of ALD-AZO films were too low compared with that of AZO materials reported, which result from too much carrier concentration according to Mott-Jones relation.

While keeping the hetero-layered structure of ALD-AZO, annealing of the films will possibly increase thermopower ($S^2\sigma$) by engineering carrier concentration. Therefore, figure of merit ZT would increase as well.

3.3. References

[1] P. Jood et al., Nano. Lett, 11, 4337, (2011)
[2] T. Tsubota et al., J. Mater. Chem., 7, 85, (1997)
[3] W. H. Nam et al., J. Mater. Chem., 22, 14633, (2012)
[4] M. Ohtaki et al., J. Electron. Mater. 38, 1234, (2009)

Abstract (in Korean)

산업의 발전에 따라 세계적으로 에너지 수요가 증가하는 가운데, 버려지는 열에너지를 전기에너지로 바꿔 주는 열전소자 (Thermoelectrics)에 대한 연구가 조명을 받고 있습니다. 제백 계수와 전기 전도도가 높고, 열 전도도는 낮을 수록 에너지 변환 효율이 높은 열전소자로 활용 될 수 있는데, 기존에 연구되던 Te, Sb 기반의 화합물들은 독성을 띄거나 대기 중 산화 안정도가 취약하였습니다. 최근에는 가시광선영역에서 투명하고 열 안정적인 특성을 갖는 산화아연이나 산화인 기반의 Transparent Conducting Oxides (TCO)가 대체 물질로 부상했습니다. 이때 TCO가 열전 소자로 사용되기 위해서는 열적, 전기적 전달 성질을 조절 가능케 하는 것이 중요한데, 저는 완벽에 가까운 재현성과 조절 기능을 갖는 원자 단위 증착법 (Atomic Layer Deposition)으로 알루미늄이 도핑 된 산화 아연 필름을 증착하여 열전소자로의 가능성과 성질에 대해 연구해 보았습니다.

원자 단위 증착법으로 증착한 알루미늄이 도핑 된 산화 아연 필름은 기존의 균일한 구조를 갖는 산화아연 화합물과는 달리 산화아연 매트릭스 사이에 AlOx 도펀트 층이 끼어 들어간 이질적이고 독특한 구조를 가지고 있습니다. 이 연구에서는 이러한 AlOx 층이 자유 전자를 추가적으로 제공 할 뿐만 아니라 새롭게 형성된 계면을 통해 재료의 열적 전달에도 영향을 줄거라 예상을 하여 동일한 산화아연 필름의 두께 대비 AlOx 도펀트 층의 선밀도에 변화를 주며 필름을 증착해 보았습니다. 필름의 열적, 전기적 전도도를 측정해본 결과, 1.34 at%로 알루미늄이 도핑된 산화 아연 필름은 아무것도 도핑되지 않은 산화 아연 필름보다 전기 전도도는 약 세 배 증가하고, 열 전도도는 22 % 정도 감소 한 것을 볼 수 있었습니다. 이 논문에서는 이질적인 구조를 갖는 원자 단위 층착법으로 증착된 알루미늄이 도핑된 산화아연 필름의 열적 전기적 특성 변화에 대해 알아보았고, 나아가 TCO 물질의 열전 소자로의 적용 가능성에 대해 연구해 보았습니다.

주요어 : 열전체, 원자 단위 증착법, 헤테로 구조, 알루미늄 도핑된 산화 아연, 열 특성, 열 경계 저항
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