Reduction the Electrical Resistivity of ZnO Thermoelectric Thin-Films by Ag, WO_3 and Al_2O_3 Doping

Eka Wahyu Cahyaningsih[a], Retno Kurniya[a], Elysa Nensy Irawan[a], Somporn Thaowankeaw[b], Watcahra Chao-Moo[b], Melania Suweni Muntini[a,]*

[a]*Department of Physics, Faculty of Science, Sepuluh Nopember Institute of Technology (ITS)*
Jalan Arief Rahman Hakim, Surabaya, 60111 Indonesia
[b] *Thin Film Research Laboratory, Center of Excellence on Alternative Energy, Research and Development Institute and Program of Physics, Faculty of Science and Technology, Sakon Nakhon Rajabhat University, Sakon Nakhon, 47000 Thailand*

Received 25 October 2019; Revised 22 December 2019; Accepted 24 December 2019

Abstract

The electrical resistivity of ZnO thermoelectric material has been successfully reduced by doping Ag, WO_3 and Al_2O_3. This thin-film was made using the DC Magnetron Sputtering method. Research on thin-film thermoelectric material was carried out in stages. First, the target material is synthesized, then the sputtering process is carried out to grow a thin-film of thermoelectric. Thin-film thickness was measured using the Tolansky Apparatus method. XRD test performed to analyze the structure of crystals that form in thin-film. The ZEM-3 test was carried out to measure the thermoelectric properties of thin-film. Based on the results of the ZEM-3 test, it was found that the electrical resistivity of ZnO thin-film was reduced to 0.18 Ωm by doping Ag. The thickness of ZnO thin-film doped by Ag, WO_3, and Al_2O_3 were 100.50 nm, 380.70 nm, and 74.72 nm.

KEYWORDS: DC Magnetron Sputtering; Thermoelectric Properties; Thermoelectric Thin-Film; ZnO Material

*Corresponding authors ; E-mail: melania.muntini@gmail.com

Introduction

Based on Syafruddin's research, it is estimated that electricity demand in 2030 will reach almost double the demand in 2014. Factors affecting the increase in electricity demand are population growth, industrial sector growth, and ranking of public facility requirements [1]. The increase in electricity demand needs to be balanced with the availability of adequate electrical energy sources. This has aroused interest in research to develop alternative energy sources, one of which is the conversion of heat energy into electricity. Utilization of heat energy into electrical energy still has a low level of efficiency. One reason is the ability of the material used to convert this energy is limited. Some technologies that utilize heat energy are solar cells, thermoelectric, thermionic, and other technologies [2].

Thermoelectric is an alternative energy way to overcome energy problems. The principle of thermoelectric work is to convert heat energy into electrical energy. Thermoelectric relatively more environmentally friendly, efficient, durable, also capable of producing energy on large and small scale. There are two types of thermoelectric, namely bulk thermoelectric and thin-film thermoelectric. In this study, thin-film was chosen because of its simple, lightweight and flexible form. Thin-film is material that coats the surface of a substrate with thickness ranging from nanometers to micrometers. The thin-film covers the surface of the media evenly with a fairly high degree of uniformity. Besides thin-films also have a stable surface temperature, intermolecular adhesion force, and crystal structure [3].

Thin-film manufacturing can use several methods, one of which is the DC-Magnetron Sputtering method. In the sputtering process, high-energy argon ions move to the cathode and shoot into the target, producing splashes of atoms from the target material (Fig. 1). The vaporized target atom will move to the anode, forming a thin-film that covers the surface of the substrate. There are several advantages possessed by this sputtering method, including the film formed has a composition similar to the target material, the quality, structure, and uniformity of the layer is controlled by the degree of homogeneity of the target, has a large current density so as to allow high levels of precipitation, and the formed film has a high adhesive strength on the surface of the substrate [3]. In addition, in this sputtering method, DC resources are used because they are easy to control and are inexpensive to use in the coating process [4].

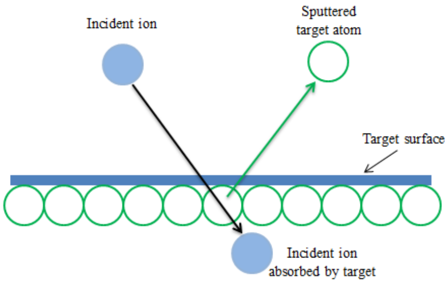

Fig. 1 Illustration of the physical process of sputtering on the target surface [3]

Fig. 2 shows the sputtering process in the vacuum chamber, where the target material is placed parallel to the substrate to be coated in the vacuum chamber. The target material is mounted on the cathode as negative bias, while the substrate is attached to the anode as positive bias. The vacuum is set at a basic pressure, around 0.5 – 100 mTorr, this aims to remove H_2O and H_2 then replace it with argon gas. Argon gas is classified as an inert gas with high purity which has a large kinetic energy to hit the target. In addition, argon gas has a relatively high atomic weight (Mr = 40), including an inert noble gas (difficult to bond with other elements), and is easily ionized [7].

After the basic pressure is set, the next step is between the cathode and the anode given a high DC voltage to produce a large electric field and form a plasma in a vacuum. A large electric field will cause electrons at the cathode to detach and move at high speed to the anode. Electron energy that collides with argon gas will be absorbed and will produce argon ions. The scattering of electrons from the cathode to the anode is controlled using a DC magnetron located behind the cathode. The thin-film deposition rate can be increased by increasing the electric current at low pressure. If the pressure is lower than the optimal limit, it will cause the ion distribution to be uneven. Thin-film thickness can be controlled by sputtering time [4].

Semiconductor material is a material that has electrical properties between resistors and conductors. Semiconductor material has an energy band gap value of $0\ \text{eV} < E_g < 6\ \text{eV}$ with electrical conductivity between $10^{-8} - 10^{6}$ S m^{-1} at room temperature. Semiconductor materials have resistivity values between $10^{-2} - 10^{7}\ \Omega$ m [8]. The value of semiconductor conductivity is quite good, not too low or too high. Semiconductors have a good Seebeck coefficient as a thermoelectric material. Semiconductor materials meet the criteria to be used as thermoelectric materials. A good

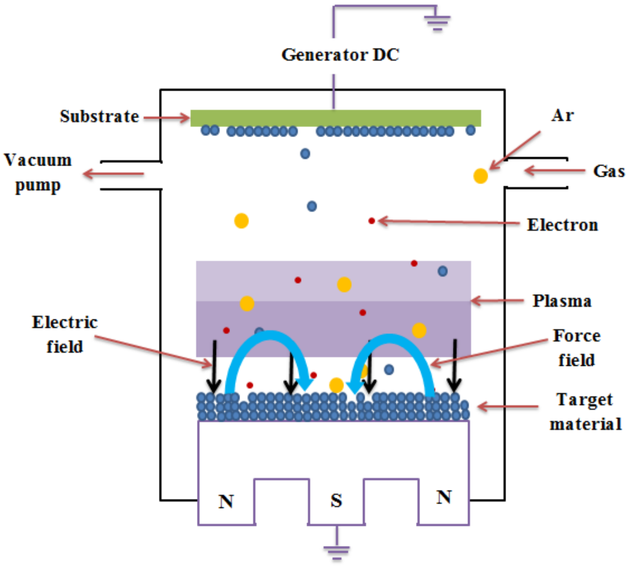

Fig. 2 Illustration of sputtering Process in a Vacuum Chamber [7]

thermoelectric material has a value of the figure of merit close to one ($ZT \sim 1$). The value of ZT can be determined by equation (1) [9].

$$ZT = \frac{S^2 \sigma T}{\kappa} \qquad (1)$$

Equation (1) shows that ZT is influenced by the square of the Seebeck coefficient (S^2), electrical conductivity (σ), and thermal conductivity (κ).

Semiconductor material resistance will decrease rapidly as the temperature increases. The relationship between resistance and temperature in semiconductor materials is written in equation (2) [10]:

$$R(T) = R_0 e^{\left[-\beta\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]} \qquad (2)$$

$R(T)$ is resistance at temperature T. The value of $R(T)$ is influenced by resistance at temperature T_0 (R_0) and β is a characteristic constant of each semiconductor material. The β constant can be determined by equation (3) [10]:

$$\beta = \frac{\ln \frac{R}{R_0}}{\frac{1}{T} - \frac{1}{T_0}} \qquad (3)$$

ZnO is an N-type semiconductor material that is anisotropic in hexagonal crystal structure. ZnO has electrical resistivity of 0.78 Ω cm, and it has a band gap energy of 3.20 eV at room temperature. This makes ZnO thin film suitable for use as thermoelectric materials. The electrical resistivity of ZnO can be decreased by doping. Ag, as a dopant, has the lowest resistivity compared to other metals, which is 1.60×10^2 μΩm. The melting point of WO_3 ranges between 1743 – 1748 K and the Seebeck coefficient is ~780 $\mu V\ K^{-1}$. Al_2O_3 is used because it has an energy gap of 0.68 eV. The energy gap of Al_2O_3 shows that this material has high conductivity and low resistivity.

Materials and Methods

Sputtering targets were synthesized using ZnO powder (> 99% SAP Chemicals), Ag, WO_3, and Al_2O_3. The powdered material is crushed using mortar and alu, so that the particle size is smaller, finer, and evenly mixed. Furthermore, the powder which has been mixed is compacted using a hydraulic press machine at 21.50 MPa, 20 MPa, 0.25 MPa for Ag-doped ZnO, WO_3 doped ZnO, and Al_2O_3 doped ZnO. The compacted target is then sintered at temperatures of 1073 K, 373 K and 873 K for Ag-doped ZnO, WO_3 doped ZnO, and Al_2O_3 doped ZnO. The sintering process aims to eliminate the moisture content in the material, increase density and reduce porosity of target solids. Next, the thin film sputtering process is carried out in a vacuum chamber. A thin-film was deposited on the surface of the glass substrate for material Ag-doped ZnO and Al_2O_3 doped ZnO. WO_3 doped ZnO thin-film was deposited on the surface of the ceramic substrate. Then the thin-film will be tested with the Tolansky Apparatus test to measure the thickness, XRD test to analyze crystal structure, and ZEM-3 test to measure thermoelectric properties. The ZEM-3 test is carried out at temperatures from 323 – 573 K.

The ZEM-3 test is a test conducted with the aim of measuring the Seebeck coefficient, resistivity, and power factor. The Seebeck coefficient and electrical resistance can be measured from room temperature to 1173 K in the helium atmosphere. Electrical resistance is measured by the DC four terminal method. Constant current, I, is applied to both ends of the sample to measure and determine the dV. Measuring the resistance value R and the sample dimension (the distance between voltage leads (L) and the cross-sectional area of sample (A)), the electrical resistivity (ρ) is given by equation (4) [11]:

$$\rho = R\frac{A}{L} \qquad (4)$$

The Tolansky Apparatus method is one method for measuring the thickness of a thin layer. This method utilizes monochrome light interference on two simple glass beams. Tolansky Apparatus is capable of measuring thin film thickness in the range of 30 – 350 nm. This measuring instrument can only be used on samples with transparent media, such as glass. Disturbances that occur will form a pattern of dark light when the subject is analyzed [14]. The thickness of thin-film (t) is influenced by measurement of the thin-film calculated by using equation (5).

$$t = \frac{\Delta x}{x} \times \frac{\lambda}{2} \qquad (5)$$

λ is the wavelength of monochrome light used in the measurement process. ΔX is a shift in the pattern of dark light formed, and X is the width of the pattern of dark light formed [14].

Results and Discussion

The result of XRD test shown in Fig. 3, Fig. 4, and Fig. 5.

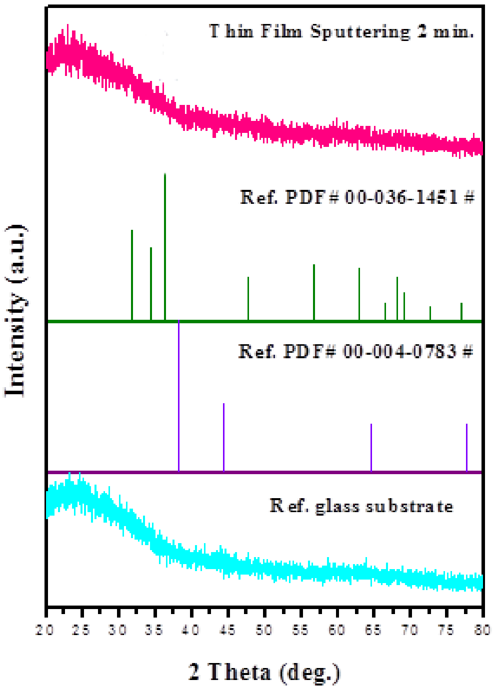

Fig. 3 Result of Ag-doped ZnO thin-film's XRD test

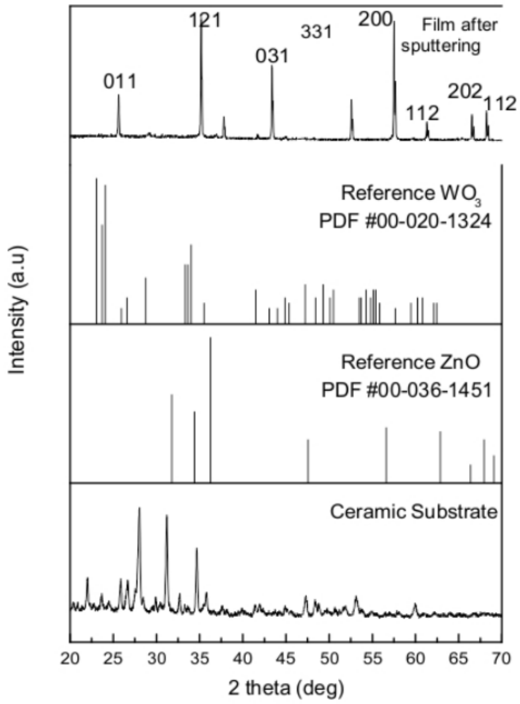

Fig. 4 Result of WO_3-doped ZnO thin-film's XRD test

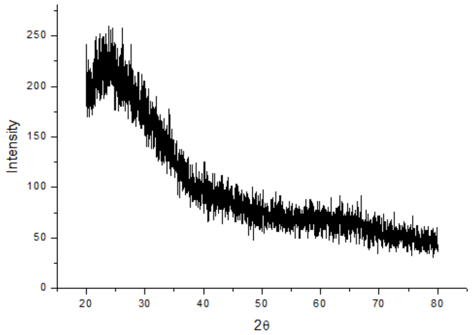

Fig. 5 Result of Al_2O_3-doped ZnO thin-film's XRD test

Fig. 3 and Fig. 5 show that the XRD test results for Ag-doped ZnO thin films and Al_2O_3 doped ZnO thin films have a high similarity with the results of XRD glass as a substrate. This shows that the thin layer formed is not thick enough, making it difficult to diffract with X-rays. Fig. 4 shows that the WO_3 doped ZnO thin-film has 8 peaks similar to ZnO and WO_3. The highest intensity was found at the peak with the orientation of the crystal plane (121) and (200). High intensity is influenced by the number of reflected fields in the arrangement of the sample atoms. The more reflection field, diffraction wave interference will strengthen each other which causes higher intensity.

The ZEM-3 test was used to measure the resistivity of thin-film made in this study. This test is performed using a 15 × 3 mm^2 thin-film sample size. The ZEM-3 test was carried out in a temperature range of 323 – 573 K. The measurement results of the resistivity values of Ag-doped ZnO, WO_3 doped ZnO, and Al_2O_3 doped ZnO shown in Fig. 6.

Fig. 6 shows that the results of Ag doped ZnO and WO_3 doped ZnO resistance tests are in accordance with the theory of the effect of temperature on the resistance of semiconductor material [11]. When the temperature gets bigger, the energy band gap is smaller. This facilitates the transfer of electrons to the conduction band, thereby increasing the conductivity of the material. Increased material conductivity shows that resistivity decreases [12]. The decrease in resistivity value due to temperature rise is caused by changes in crystal size which facilitate mobility [13]. This decrease in electrical resistivity causes an increase in the electrical conductivity of the sample. As a result, the electrical resistivity of ZnO thin films doped with Al_2O_3 increases with increasing temperature. This contradicts the theory of semiconductor properties [11]. The resistivity graph of ZnO thin films treated with

Al_2O_3 has compatibility with the electrical resistivity properties of metal materials. In metals, the electrical resistivity of materials tends to increase in proportion to the rise in temperature [9].

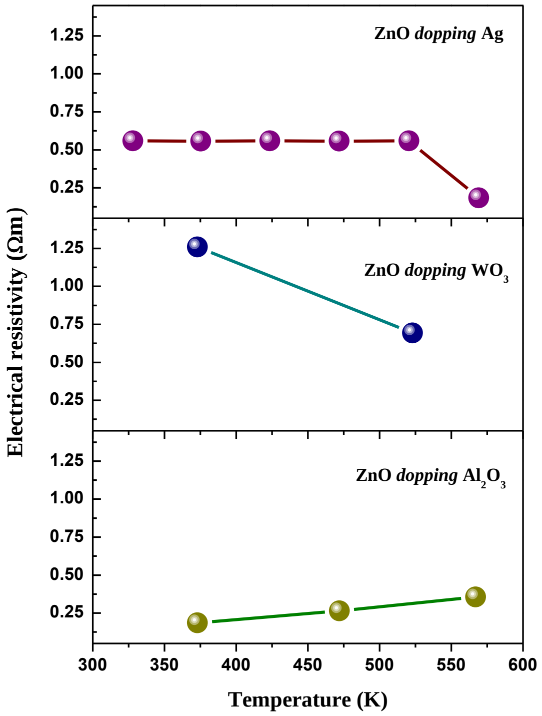

Fig. 6 Electrical resistivity of thin-film ZnO doping Ag, ZnO doping WO_3, and ZnO doping Al_2O_3

Semiconductor materials can be subject to temperatures with certain limits according to their characteristics. If the semiconductor material is subject to a temperature exceeding its limit, it will cause damage. Damage can occur in parts of the crystal structure and will eliminate the function of the material as a semiconductor [9]. This could be a factor in the results of the Al_2O_3 doped ZnO material resistance test which is incompatible with the theory of resistance in semiconductors.

Based on the graph in Fig. 6, it was found that the Ag doped ZnO thin-film had the best electrical properties at a temperature of 573 K. The electrical resistivity value at this temperature was 0.18 Ω m. The WO_3 doped ZnO thin-film is used well at a temperature of 623 K with a resistance value of 0.69 Ω m. The lowest resistivity value of the Al_2O_3 doped ZnO thin-film was obtained at 373 K with a value of 0.19 Ω m.Among the three thin-film samples that have been made, the lowest resistance value is obtained by the Ag doped ZnO sample at a temperature of 573 K. Overall, the electrical properties of ZnO doping Al_2O_3 thin-films are the best because the resistance values tend to be lowest at all temperature points. This makes the Al_2O_3 doped ZnO thin-film potentially large as a thin-film thermoelectric material. The electrical properties of Al_2O_3 doped ZnO thin-films can support the increase in work efficiency of thermoelectric modules.

In addition to testing ZEM-3, the thickness of the resulting thin-film was also measured. The light source of Tolansky Apparatus test is Na light with a wavelength of 589 nm. Na used because the light of Na has high contrast. From the calculation, the thickness of ZnO doping Ag is 100.50 nm, ZnO doping WO_3 is 380.70 nm, and ZnO doping Al_2O_3 is 74.70 nm. The thickness of the thin-film formed depends on the length of the sputtering process. The longer the sputtering time will produce a thicker film because there are many target atoms growing on the substrate.

Conclusion

From the research that has been done, the following conclusions can be obtained. Ag doped ZnO, WO_3 doped ZnO, and Al_2O_3 doped ZnO thin film were successfully made using the DC Magnetron Sputtering method in the vacuum chamber. ZnO thin films treated with Ag at 573 K have the best electrical properties compared to other materials. at that temperature, Ag doped ZnO has the lowest electrical resistivity and highest electrical conductivity. Electrical conductivity is directly proportional to *ZT*. This shows an increase in the quality of the thermoelectric material.

Acknowledgement

This research was supported by Thin Film Research Laboratory, Center of Excellence on Alternative Energy, Research and Development, Institute and Program of Physics, Faculty of Science and Technology, Sakon Nakhon Rajabhat University, and the Department of Physics, Sepuluh Nopember Institute of Technology, Surabaya. We thank Dr. Athorn Vora-Ud for help in this research and Assoc. Prof. Dr. Tosawat Seetawan for comments that greatly improved the manuscript.

References

[1] M. Syafruddin, L. Hakim, and D. Despa, Metode Regresi Linier Untuk Prediksi Kebutuhan Energi Listrik Jangka Panjang (Studi Kasus Provinsi Lampung), J. Inform. Dan Tek. Elektro Terap.Vol. 2 (2014).

[2] J. T. Jarman, E. E. Khalil, and E. Khalaf, Energy analyses of thermoelectric renewable energy sources, open J. Energy Effic. Vol. 2 (2013) 143.

[3] Sudjatmoko, Aplikasi Teknologi Sputtering untuk Pembuatan Sel Surya Lapisan Tipis. Workshop: Sputtering untuk Rekayasa Permukaan Bahan, Puslitbang Teknologi Maju Batan, Yogyakarta, 2003.

[4] W. Kiyotaka, S. Hayakawa, Handbook of Sputter Deposition Technology, Noyes Publications, New Jersey, 1992.

[5] S.J. Kang, H.J. Yang, Influence of substrate temperature on the optical and piezoelectric properties of ZnO thin-films deposited by RF magnetron sputtering, Appl Surf Sci. 253 (2007) 7330 – 7335.

[6] L. Tan, R.A. dodd, W.C. Crone, Corrosion and Wear-Corosion Behavior of Ni Ti Modified by PlasmaSource Ion Implantation, Biomaterials 24 (2003) 3931 – 3939.

[7] S. Swann, Magnetron Sputtering, Physics of Technology, IOP Science, 1988.

[8] P.S. Kireev, Semiconductor physics, Mir, 1978.

[9] Y. Yin, B. Tudu, A. Tiwari, Recent advances in oxide thermoelectric materials and modules, Vacuum. Vol. 146 (2017) 356 – 374.

[10] Temperature dependence of the resistance of metals and semiconductors, http://remote-lab.fyzika.net/experiment/01/experiment-1-teorie.php?lng=en, 15 July 2019.

[11] Z. Zhou, C. Uher, Apparatus for Seebeck coefficient and electrical resistivity measurements of bulk thermoelectric materials at high temperature, Rev. Sci. Instrum. Vol. 76 (2005) 023901.

[12] Temperature Dependence of Resistivity, https://www.askiitians.com/iit-jee-electric-current/temperature-dependence-of-resistivity/, 4 Mei 2019.

[13] S. Sugianto, R. Zannah, S.N. Mahmudah, B. Astuti, N M. D.P, A.A. Wibowo, P. Marwoto, D. Ariyanto, E. Wibowo, Pengaruh Temperatur Annealing Pada Sifat Listrik Film Tipis Zinc Oksida Doping Aluminium Oksida, Jurnal MIPA. Vol 39 (2016) 115 – 122.

[14] E. N. Irawan, M.S. Muntini, A. M. Putra, T. Seetawan, K. Singsoog, S. Thawankaew, W. Caho-Moo, A. Vora-Ud, Penggunaan Metode DC Magnetron Sputtering dalam Pembuatan Lapisan Tipis Tipe N (AZO) Sebagai Modul Termoelektrik, Jurnal Sains dan Seni ITS. 8(1) (2019) 1 – 6.