The Influence of Al Content on the Thermoelectric Property of Al-Doped ZnO Thin Films

Ying-Zhen Li, Zhuang-Hao Zheng, Jing-Ting Luo, Fu Li, Guang-Xing Liang and Ping Fan

Abstract Direct current magnetron reactive sputtering was used to deposit Al-doped ZnO (AZO) thin films on BK7 glass substrates by using Zn–Al alloy target at room-temperature. Al contents of Zn–Al alloy target were changed and all AZO thin films were annealed at 773 K for 1 h. It can be found that all the AZO thin films were n-type semiconductor material, and have preferred orientation with the c-axis normal. The thermoelectric properties results show that the Seebeck coefficient of the AZO thin films with Al content of 4 wt% has higher Seebeck value of 64 μV/K in comparison with others. The electric conductivity and power factor of AZO thin films with Al content of 2 wt% have maximum values of that 5.30×10^4 S/m and 0.74×10^{-4} W/mK^2, respectively.

Keywords AZO thin film · Oxygen argon ratio · Thermoelectric properties Zn–Al alloy target

Introduction

Nowadays, there is a lot of waste heat in the social life and production. One of the ways which heat to electrical energy directly is using thermoelectric materials [1]. Thermoelectric device is a kind of the applications about renewable energy resource alternatives to fossil fuels [2]. The efficiency of thermoelectric device is decided by the merit (defined as $S^2T\sigma\kappa^{-1}$) of thermoelectric material [3]. ZnO has outstanding thermoelectric property and chemical stability, so it is considered to be one of the

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best materials about thermoelectric application [4]. The large exciton binding energy of ZnO is 60 meV at room temperature and the wide band gap material with an energy gap is 3.3 eV [5]. ZnO film is one of n-type semiconductor material. Because there are oxygen vacancies and interstitial Zn in the ZnO film, electrical conductivity of ZnO thin film improves and the Seebeck on high temperatures keeps high [6]. ZnO thin film can be deposited by different of techniques, for example sputtering, chemical vapor deposition and so on [7]. In the paper, the deposition technique is direct current magnetron reactive sputtering using Zn–Al alloy target. And the thermoelectric properties of AZO films were investigated as the function of Al contents.

Experimental

AZO films were deposited on BK7 glass substrates with the size of 30 × 30 × 2 mm using direct current reactive magnetron sputtering by Zn–Al alloy target at room-temperature. Prior to thin film deposition, the BK7 substrates were ultrasonically cleaned in alcohol for 5 min and then in deionized water for 5 min. The background pressure reached 6.0×10^{-4} Pa. The work pressure was set to 0.5 Pa with 6 sccm of O_2 as the reactive gas and 40 sccm of Ar as the working gas. The sputtering power of Zn–Al remained 100 W. In order to remove contaminants and native oxides on the surfaces of the Zn–Al alloy target, a 10-min sputter cleaning process was performed. The deposition time was 30 min. After the films were deposited, the films were annealed at 773 K for one hour in the chamber pressure of 8.0×10^{-4} Pa. In order to study the influence of Al content on the thermoelectric properties of AZO films, Zn–Al alloy targets with Al content of 1, 2, 3 and 4 wt% were used for depositing the thin films.

The electric conductivity [defined as $\sigma = (R_s d)^{-1}$] of the thin films were tested by using the of four-probe technique to obtain the sheet resistance R_s and DEKTAK3 ST (RIGAKU ULTIMA4) surface-profile measurement system to obtain the thickness d. The Seebeck coefficient was obtained at by a Seebeck coefficient measurement system with the temperature from 313 to 553 K under air atmosphere. The microstructure was characterized by X-ray diffractometer technique (BRUKER DEKTAKXT). The surface morphology was obtained by using scanning electron microscope.

Results and Analysis

The electrical conductivities of the AZO films on different measuring temperature were changed, and the result is showed in Fig. 1a. The electrical conductivities of the films decrease with the increasing temperature, manifesting the behavior of metallic conduction. The thin film with 1 wt% Al content has low electrical

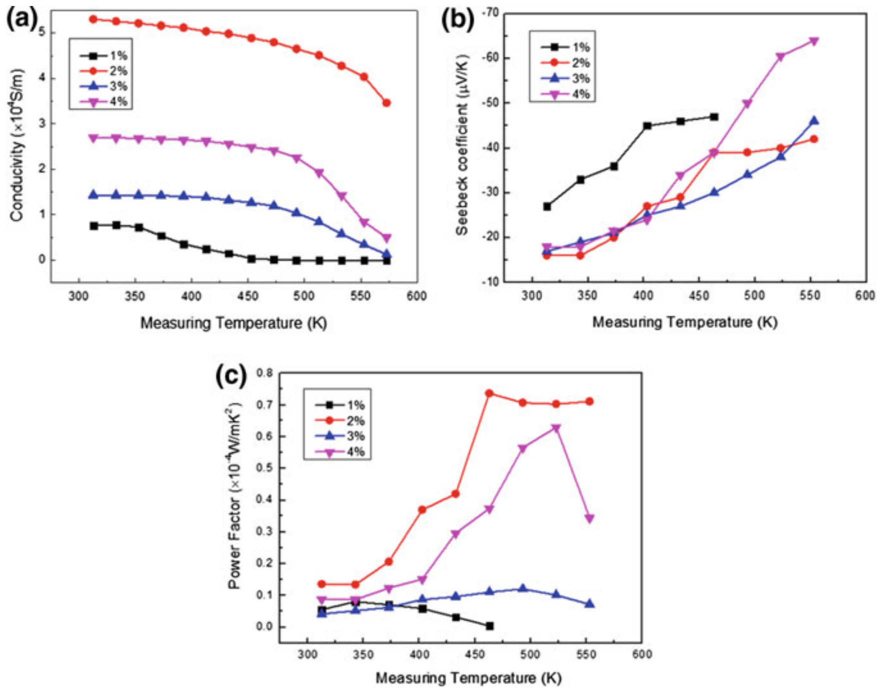

Fig. 1 Electrical conductivities, Seebeck coefficients and power factors of AZO films **a** electrical conductivities, **b** Seebeck coefficients, **c** power factors

conductivity, which is lower than 30 S/m when the measuring temperature is higher than 493 K. The electrical conductivity of the thin film with 2 wt% Al content is higher than others and the maximal value is 5.30×10^4 S/m. The electrical conductivity is defined as $\sigma = nev$. Because Al^{3+} ions replaces Zn^{2+} ions, the carrier density (n) increase when Al-doping content of AZO films increases. Meanwhile, the carrier mobility (v) decreased due to the scattering by ionized impurity [8].

The Seebeck coefficients of the AZO films on different measuring temperature are showed in Fig. 1b. All the Seebeck coefficients are negative, which illustrates that all of the films are n-type semiconductor. The Seebeck coefficient of the film with 1 wt% Al content is higher than others when the measuring temperature is lower than 463 K. However, it is unstable that the Seebeck coefficient transforms to positive and then changes to negative again when the measuring temperature is higher than 463 K, so the accurate measurement of the Seebeck coefficients can't be obtained in high temperature. That is why we did not provide the data over 463 K of this sample. The Seebeck coefficients (defined as $S = \gamma\text{-ln } n$) of the thin films increase with the increasing temperature. It explains that scattering factor (γ) increase with increasing of Al-doping content which may due to scattering process of Al^{3+} ions in high temperature. And the interaction between carrier and lattice vibration may also intensify in high temperature. The absolute values of the thin films are similar to each other in the low measuring temperature, but when the measuring temperature is higher than 463 K, the Seebeck coefficient of the thin film with 4 wt% Al content is highest. Besides, the maximal absolute value is 64 μV/K.

The power factors of the AZO films on different measuring temperature are showed in Fig. 1c. When the measuring temperature is increases, the power factors of thin films increase. But they have a little decrease when the measuring temperature continues to rise. When the Al content of the films increases, the power factors of the films trend to rise firstly and then decrease. The maximal value of power factor is 0.74×10^{-4} W/mK^2 with the Al content of 2 wt%.

X-ray diffraction patterns of AZO films are shown in Fig. 2. The thin films with 2, 3 and 4 wt% Al content have two major diffraction peaks and the peaks locate at 34.4° and 72.5°. Which are indexed as the reflection from the diffraction of the ZnO (002) and (004) planes. It indicates that the AZO films have preferred orientation with the *c*-axis normal. The intensity of the (002) plane first increases and then decreases as the Al contents of thin films increase. The thin film with 4 wt% Al content has a relatively stronger intensity. However, the thin films with 1 wt% Al content have eight major diffraction peaks located at 31.8°, 34.4°, 36.3°, 47.5°, 56.6°, 62.9°, 38.0° and 72.5°, which are indexed as the reflection from the diffraction of the ZnO (100), (002), (101), (102), (110), (103), (112) and (004) planes. It indicates that the growth orientation of this thin film is various which may cause the weak intensity of planes with 1 wt% Al content. In addition, it may also cause that the thin film with 1 wt% Al content has a low electrical conductivity and an unstable Seebeck coefficient in high temperature. On the whole, the films with suitable Al-doping content have preferable crystallinity and stronger texture. Besides, the peak of Al or aluminium oxide measured in the XRD pattern is not exist. It infers that Al atoms have been combined in the lattice. And there is no elemental or oxide of Al in the films [9].

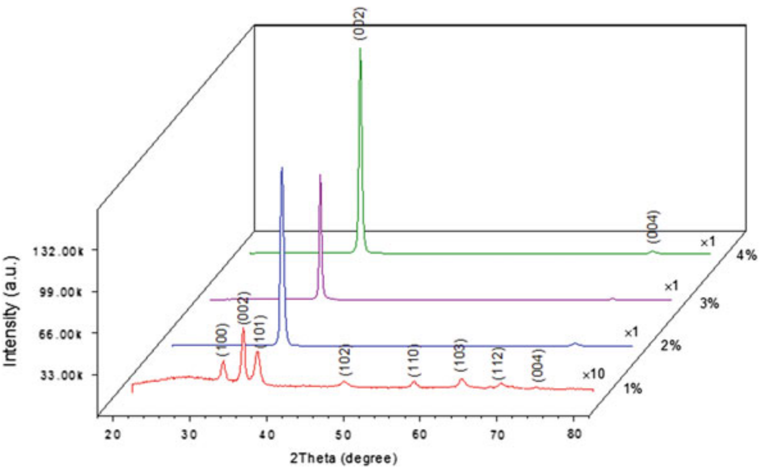

Fig. 2 XRD patterns of samples

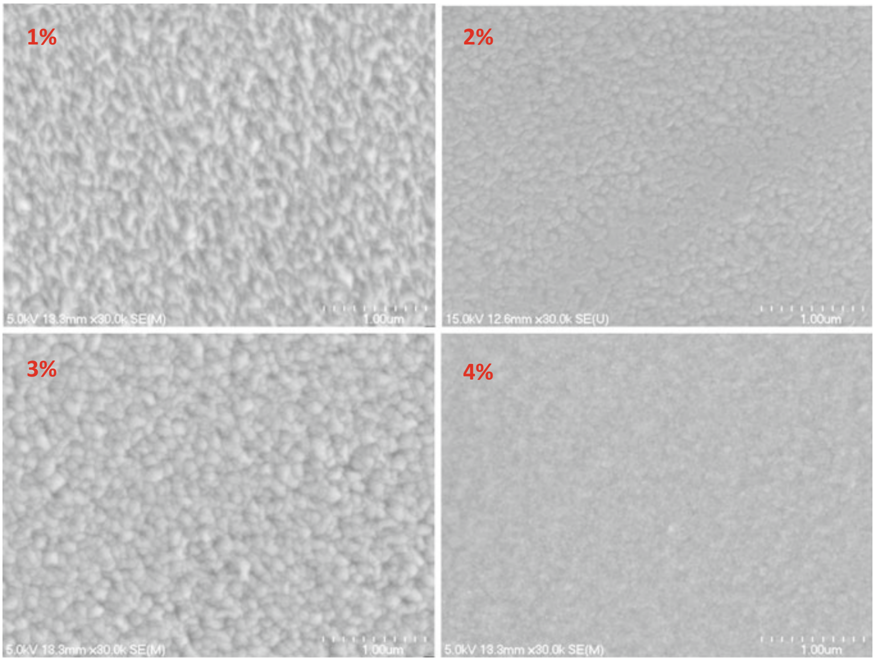

Fig. 3 The SEM of samples

The SEM of AZO films are shown in Fig. 3. It shows that the grain of AZO film with 1 wt% Al content is pointed. The electron transport of AZO films may be choked. As a results, the Seebeck coefficient become unstable and the electrical conductivity decrease [8]. The grains of films become round as the Al contents of thin films increase.

Conclusions

AZO films were obtained by using direct current reactive magnetron sputtering by Zn-Al alloy target with different Al contents at room temperature. And then thin films were annealed at 773 K for one hour. The XRD pattern illustrates that the film with Al content of 4 wt% has well crystallinity and higher Seebeck coefficient with the maximal absolute value of 64 μV/K. The electric conductivity and power factor of AZO films deposited by Zn-Al alloy targets with 2 wt% Al content are highest of all the samples, where the maximum value is 5.30×10^4 S/m and 0.74×10^{-4} W/mK^2, respectively. Therefore, appropriate Al doping-content can enhance thermoelectric properties of AZO films.

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