Materials and Design 154 (2018) 41–50

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Joint improvement of conductivity and Seebeck coefficient in the ZnO:Al thermoelectric films by tuning the diffusion of Au layer

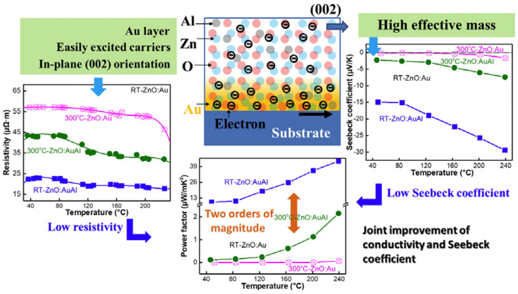
Guojian Li [a], Shiying Liu [a,b], Yongjun Piao [a,b], Baohai Jia [a,c], Yi Yuan [c], Qiang Wang [a,*]

[a] Key Laboratory of Electromagnetic Processing of Materials (Ministry of Education), Northeastern University, Shenyang 110819, China
[b] School of Materials Science and Engineering, Northeastern University, Shenyang 110819, China
[c] School of Metallurgy, Northeastern University, Shenyang 110819, China

HIGHLIGHTS

- Joint improvement of Seebeck coefficient and conductivity is achieved in ZnO films.
- Power factor is two orders of magnitude larger than film without joint improvement.
- Resistivity is at the same magnitude of transparent conducting oxide due to Au layer.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 February 2018
Received in revised form 8 May 2018
Accepted 9 May 2018
Available online 16 May 2018

Keywords:
Thin films
Thermoelectric
ZnO
Physical vapor deposition

ABSTRACT

Joint improvement of the Seebeck coefficient S and conductivity σ is a pressing issue to overcome the limit of the figure of merit (ZT) enhancement of thermoelectric materials. This study presents a joint improvement in the ZnO:Al films by tuning the diffusion of Au layer via substrate temperature, using a radio frequency-assisted molecular beam vapor deposition method. The phenomenon occurs in the ZnO:Al films at the room temperature (RT) substrate deposited on a 10 nm Au layer (RT-ZnO:AuAl). The films have a hexagonal wurtzite structure with an in-plane (002) preferred orientation and smooth surface. The resistivity values of the films are at the same magnitude of the transparent conducting oxide (~10^{-6} Ω·m). The carrier concentration reaches 2.60×10^{21} cm^{-3} for the RT-ZnO:AuAl film. The S is about 29.5 μV/K at 240 °C. Joint improvement of conductivity and Seebeck coefficient makes the PF of the RT-ZnO:AuAl film reaches 3.58×10^{-5} Wm^{-1} K^{-2}, which is two orders of magnitude larger than that of the RT-ZnO:Au film without joint improvement. The results indicate that the higher conductivity originates from the Au layer, in-plane (002) preferred orientation, and the easily excited carriers in the ZnO:Al due to the low binding energy of the Zn 2p electrons. The large S in the film is related to the high effective masses due to the impact of the diffusion of the Au layer on electronic interactions.

1. Introduction

Nearly 70% of world energy is wasted, as waste heat aggravates the energy crisis [1]. Thermoelectric (TE) materials can be used to convert waste heat to electricity directly without any moving components through the Seebeck effect [2]. This kind of material can be used as the energy-saving technology if the material converts the waste heat to electricity. On the other hand, it can be regarded as the secondary energy technology when the material is used to convert the heat to electricity. Thermoelectric materials play an important role in increasing energy utilization. The applications of the TE materials are limited in

---

* Corresponding author.
E-mail address: wangq@epm.neu.edu.cn (Q. Wang).

https://doi.org/10.1016/j.matdes.2018.05.019
0264-1275/© 2018 Elsevier Ltd. All rights reserved.

the field of waste-heat recovery because of the low conversion efficiency, high material cost, and low chemical stability [3–6]. To enhance the thermoelectric properties plays a key role in the field of energy conservation techniques. Improving thermoelectric efficiency is conducive to conserve energy in industry and daily life. The conversion efficiency is related to the dimensionless figure of merit (*ZT*) and temperature difference. When the temperature difference is 300 K, the *ZT* value must be higher than 3.0 in order to obtain 20% of the efficiency [7]. Thus, the central issue in the TE materials research is to increase the *ZT* value. The *ZT* value can be defined as

$$ZT = S^2\sigma T/\kappa \tag{1.1}$$

where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity and T is the absolute temperature [8]. The $S^2\sigma$ is often regarded as the power factor (PF). Generally, the *ZT* value is a non-monotonical function of carrier concentration [1]. With increasing the carrier concentration, the electrical conductivity and thermal conductivity increase, however, the Seebeck coefficient decreases. According to the relation, there exists a limitation of the maximum *ZT* with the carrier concentration. An ideal TE material with a high *S*, depends on the band gap and the carrier concentration. The carrier concentration influences both *S* and σ. The increased carrier concentration decreases the *S* and increases the σ [6]. The best way in the current research is to find an optimal carrier concentration to tune the PF. Joint improvement of the *S* and σ is the main difficulty in obtaining high thermoelectric properties, but it can be used to raise the utilization of energy. It is conducive to overcome the limitation of *ZT* value. The use of nanostructures provides a promising method to tune *S* and σ independently, such as quantum confinement, modulation doping and the increased influence of interfaces and surface effects [9]. However, it is almost impossible to find a method to increase the *S* and σ together.

The decrease of the material cost and the increase of the low chemical stability are the other important issues in order to meet the requirement of the application. Zinc oxide (ZnO) is one of the most promising candidates because of high *S*, high chemical and thermal stability, nontoxicity, and low production cost among abundant raw materials [10,11]. However, the highest *ZT* value attained in the $(Zn_{0.98}Al_{0.02})O$ bulk is 0.65 at 1000 °C [12,13], which is much lower than the value of 2.4 in the BiTe/SbTe supperlattice film [14]. The highest PF is in the magnitude of 10^{-3} Wm^{-1} K^{-2} [15–17]. Thus, it is important to increase the PF for a higher *ZT* value in the ZnO films. In fact, in the ZnO films, it is easy to achieve a higher conductivity because the ZnO films have become an outstanding candidate as a transparent conducting oxide due to its low resistivity (~10^{-6} $\Omega\cdot$m) by doping aluminum [18]. The ZnO:Al films fabricated by pulsed laser deposition in oxygen atmosphere present over 80% visible transparency and resistivity of the order of 10^{-4} $\Omega\cdot$cm. The film thickness and O stoichiometry affect the electrical and optical properties of the ZnO:Al films [19,20]. The increase of oxygen pressure leads to a reduced concentration of oxygen vacancy, which influenced the carrier mobility within the film. However, the *S* is also reduced because of a higher carrier concentration in this case. Thus, it needs to find a way to increase σ (reduce the resistivity) and to increase the *S* of the ZnO films for a higher PF. The ZnO has a relatively high *S* (−360 μV/ K at 85 °C). However, the *S* reduces to about 65 μV/ K at 600 K with doping Al [15]. This means that it is necessary to explore a new method to suppress the reduction of the *S* when doping other elements. Previous studies show that a thin Au layer of several nanometers can reduce the resistivity; meanwhile the optical transmittance has no significant decrease [21–23]. Furthermore, the Au layer can be used as a catalyst layer in the growth of the ZnO films [24,25]. This illustrates that the thermoelectric parameters of *S*, σ, and κ may be affected by introducing the Au layer. However, in the transparent conducting oxide, the Au layer without any diffusion was used as a conducting layer. The decrease of the *S* is not considered. In fact, the state of the Au atoms in the Al doped ZnO (ZnO:Al) films also affect the TE parameters. It needs to study the effect of the Au layer in the ZnO:Al films on the TE parameters and to explore a method to improve both *S* and σ.

In this study, the ZnO:Al TE films were fabricated on an Au layer by using RF-assisted molecular beam vapor deposition method. The diffused states of the Au layer in the ZnO:Al films were tuned by changing the substrate temperature during the film growth because the diffusion of the Au atoms occurs by increasing the substrate temperature. Then, the structure evolutions and the TE parameters were measured and their relationship was discussed. Finally, a method to joint improvement of *S* and σ was presented in this study.

2. Experimental details

The ZnO:Al films were deposited on a thin Au layer which was formed on the sapphire (0001) slices using the RF-assisted molecular beam vapor deposition method. The RF source was used to produce neutral oxygen atoms, which carry non-negligible kinetic energy. The energy will increase the reactivity. In order to clarify the effects of the Al dopant and the states of the Au atoms on the TE parameters, four kinds of films were fabricated. For all the films, the Au layer of about 10 nm was first deposited at source temperature of 1350 °C using thermal evaporation when the substrate temperature is ambient. The ZnO:Al films were fabricated by the coevaporation of Zn, Al and O on the Au layer at room temperature (RT-ZnO:AuAl) and 300 °C (300 °C-ZnO:AuAl). The Au-doped ZnO (ZnO:Au) films which were also fabricated by only using the coevaporation of Zn and O, which are called RT-ZnO:Au and 300 °C-ZnO:Au. The source temperatures of the Zn and Al are respectively 350 and 980 °C. The power and flux of the RF source are 380 W and 1.8 SCCM, respectively. The growth time is about 60 min and the thickness is about 190 nm measured by surface profiler (Dektak150, Decco, USA).

Surface morphology was examined by field emission scanning electron microscopy (FESEM; SUPRA 35, Carl Zeiss Inc., Oberkochen, Germany). Phase formation was examined by X-ray diffraction (XRD; DMAX 2400, Rigaku, Shibuya-ku, Japan) with a grazing incidence of 1° in 2θ mode with monochromatic Cu Kα1 radiation (λ = 0.154056 nm). Film structure and Au layer are observed by transmission electron microscopy (TEM; Tecnai G^2 F20, USA). Resistivity and *S* were measured by using Seebeck coefficient/electrical resistance measuring system (ZEM-3; Ulvac-riko Inc., Japan). The output power is calculated from the simple relation $P = I * V$ to evaluate the ability of trapping waste heat, and the film area is about 6.4×10^{-5} m^2. Carrier concentration and mobility were measured by Hall effect measurement system (ACCENT HL5500PC, Accent Optical., British). The thermal conductivity was characterized and contrasted by infrared cameras (Fluke, Tix580). The temperature of constant 100 °C in hot side is provided by a temperature controlled heater (Etool, ET-150G). The doped ZnO films are perpendicular to the heating table, and the initial temperature at the film bottom is 100 °C. Raman measurements with the accuracy of ~0.5 cm^{-1} were performed using the Labram HR800 (HORIBA Jobin Yvon, France). The radiation of 532 nm from a coherent Ar^+ laser was focused to ~2 μm in diameter on the samples. Optical transmittance was recorded with a UV–vis spectrophotometer (Lambda 750S, PerkinElmer, Waltham, MA, USA). Elemental chemical states were measured by using X-ray photoemission spectroscopy (XPS; ESCALAB 250Xi, Thermo Fisher Scientific, Waltham, MA, USA). Roughness was examined by atomic force microscopy (AFM; Nanosurf, Flex-Axiom C3000, Switzerland). Content of elements was determined by energy-dispersive X-ray spectroscopy (EDS; Inca, Oxford Instruments, Abingdon, UK).

3. Results and discussion

The EDS mapping was used to confirm the atomic contents of Au and Al in the ZnO films. Results show that the Au contents are respectively