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Enhancing the thermoelectric performance of ZnO film by sputter-deposition of Ag nanoparticles

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Abstract

Owing to the surface plasmon resonance (SPR), noble metal nanoparticles (NPs) have been intensively employed to improve the optical properties of semiconductors. In this work, Ag NPs are deposited on fully c-axis oriented ZnO film with high-crystallinity prepared by radiofrequency magnetron sputtering on glass substrates. After Ag sputtering of 15 s, the ultraviolet light emission intensity of ZnO film significantly is increased by 50% due to the SPR of Ag NPs. Moreover, the conductive behavior changes from n-type semiconductor to metal-like with room-temperature conductivity sharply increasing by nearly three orders of magnitude from 4.8 × 10⁻¹⁹ cm² V⁻¹ s⁻¹ for pure ZnO film to 3400 S cm⁻¹ for Ag-deposited ZnO film. The change of conductive behavior and the remarkable increase of the conductivity can be ascribed to isolated Ag NPs with high-density electrons which are distributed on the ZnO film, leading to an increase of carrier concentration that exceeds Mott’s critical density (>10¹⁹ cm⁻³). Hall measurements show that after Ag sputtering of 15 s, the mobility increases from about 8 to 40 cm² V⁻¹ s⁻¹ and that the carrier concentration increases from 4 × 10¹⁸ to 5 × 10²⁰ cm⁻³. Owing to the remarkable improvement of the conductivity, the power-factor value at room temperature is enhanced from 11.5 to 49.2 μWm⁻¹K⁻².

1. Introduction

Nowadays, seeking for renewable energy is of strong interest to mankind. Among the various energy-conversion processes, thermoelectric technology has drawn growing attention because it comprises a green energy-conversion system in which a voltage gradient can be generated from materials with a temperature gradient [1, 2]. ZnO possesses a wide direct band gap of 3.37 eV and a large exciton binding energy of 60 mV, making it a promising material for optoelectronic applications such as ultraviolet (UV) blue lasing media and nanoelectronic devices [3]. In addition, ZnO has shown great potential for thermoelectric applications due to its low cost, not being toxic and, especially, because of its superior stability compared to heavy-metal-based compounds, such as Bi₂Te₃ and PbTe [4]. The power factor (PF) of thermoelectric materials, defined as σS², where σ is the conductivity and S the Seebeck coefficient, reflects the ability of a material to convert energy. Among the transitional-metal oxides, ZnO film possesses the highest thermoelectric PF with a value of about 1 mWm⁻¹K⁻² [5]. A thermal conductivity value which is almost an order of magnitude lower than the bulk value for Al-doped ZnO has been reported [6], which illustrates the potential of thin films in improving the thermoelectric properties of ZnO. Doping the Zn sites with Al, Ga may enhance σ and change the conductive behavior from insulator through n-type semiconductor to metal by controlling the doping level [7–9]. Ga-doped ZnO (GZO) film deposited on an Al₂O₃ single crystal by pulsed laser deposition (PLD) technology shows an enhanced PF of about 57 μWm⁻¹K⁻² at room temperature compared to the PF value of about 10 μWm⁻¹K⁻² for pure ZnO film [9]. Mele et al systematically explored the effect of different substrates on the

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thermoelectric properties of Al-doped ZnO (AZO) film and the results show that fully c-axis oriented AZO film grown on SrTiO$_3$ exhibits the highest PF of 130 $\mu$Wm$^{-1}$K$^{-2}$ at room temperature due to its lowest epitaxial strain and dislocation density [10].

Nanostructuring is the logical next step in improving ZnO thermoelectric thin films and various fabrication methods have been employed to optimize the morphology and size to fabricate superlattice structures [11]. Liu et al. optimized the thermoelectric properties of ZnO film by controlling the content of the nanowire [5]. The conductivity of Al-doped mesoporous film was increased by a factor of five upon incorporation of Au nanoparticles (NPs) [12]. ZnO thin films with a sandwiched Ag layer were prepared on polymer substrates with remarkably improved conductivity [13]. Owing to the surface plasmon resonance (SPR), noble metal (Au, Ag) NPs have been intensively employed to improve the optical properties of ZnO [14–16]. Also, the Raman scattering from molecules near the surface of noble metal NPs is enhanced by 5–8 orders of magnitude due to localized SPR [17]. In the present work, high-quality fully c-axis oriented ZnO film with particle size of 6 nm was prepared by a radiofrequency (RF) magnetron sputtering technique on glass substrate, after which Ag NPs with an average particle size of 3 nm were deposited on the film surface by sputtering. The conductivity was increased by about three orders of magnitude and, accordingly, the PF was enhanced by nearly a factor of five at room temperature.

2. Experimental

2.1. Materials and instruments

ZnO and Ag target (Size: 50.8 × 3 mm; Purity: 99.99%) were purchased from Beijing Dream New Material Technology Co. Ltd (China). Glass substrate (Size: 50 × 10 × 0.5 mm), acetone, ethanol were purchased from Baida Chemical Reagent Distribution Co. Ltd (China). The morphology, phase structure of the samples and particle-size distribution were characterized by scanning electron microscopy (SEM, FEI Quanta 200 F, equipped with an energy-dispersed x-ray (EDX) spectrometer), x-ray diffraction (XRD, PANalytical, X’Pert Pro, with Cu-K$_\alpha$ radiation) and atomic force microscopy (AFM, Bruker). The photoluminescence (PL) measurements were performed by spectrofluorimetry (HORIBA, Fluoromax-4, 325 nm excitation). The conductivity, carrier concentration, and mobility of the pure and Ag-deposited ZnO films were determined by Hall measurements (Ecopia HMS-5000, Korea). NETZSCH’s SBA 458 Nemesis was employed for the Measurement of Seebeck Coefficient and Electrical conductivity.

2.2. Deposition of ZnO thin film and Ag nanoparticles

The preparation process of the Ag-deposited ZnO thin films is shown in figure 1(a). First, pure ZnO film was sputtered from a ZnO ceramic target and deposited on a glass substrate by the RF magnetron sputtering technique. After the vacuum chamber was pumped to a pressure below 5.0 × 10$^{-3}$ Pa, high-purity Ar (at a flow rate of 60 sccm and with a purity of 99.99%) was introduced through a mass-flow controller into the vacuum chamber. After the substrate temperature was stable at 400 $^\circ$C, a mixture gas of high-purity O$_2$ and Ar with a flow-rate ratio of 1:4 was introduced and the pressure was fixed at 1 Pa. Then, sputter deposition was performed for 30 min with a RF power of 70 W and a fixed target–substrate distance of 8 cm. Ag NPs were then deposited on ZnO thin films by sputtering the Ag target at room temperature with an Ar flow rate of 40 sccm and pressure of 0.8 Pa. The sputtering times were 5, 15 and 45 s, and the corresponding Ag/ZnO nanocomposites are named ZnO-Ag-5s, ZnO-Ag-15s and ZnO-Ag-45s, respectively. As shown in figures 1(b)–(e), after sputtering, white Ag NPs with an average particle size of about 3 nm are distributed in the ZnO NPs and the surface density of Ag NPs increases with increasing sputtering time.

3. Results and discussion

Figures 2(a)–(d) show the SEM images of pure ZnO film and Ag-deposited ZnO films with different sputtering time. As seen in the inset of figure 2(a), a layer of continuous ZnO film with a homogenous thickness of 243 nm are formed on the surface of the glass substrate. An EDX study was carried out for determining the elemental composition of the ZnO film and for the confirmation of successful deposition of Ag NPs. The EDX signals and percentage compositions of all samples are shown in figures 2(e)–(h). For the pure ZnO film, no Ag signal was observed at the surface of the ZnO film and, with increasing Ag-sputtering time, the signal of Ag is remarkably enhanced and the atomic percentages of Ag increase from 0.29% to 0.94% and 2.25%, for the Ag-5s and Ag-15s and Ag-45s samples, respectively. It means that the Ag NPs have been successfully deposited on the ZnO films. In order to characterize the roughness, the particle-size distribution and more details of the morphology of the films, AFM was performed and the results are shown in figures 3(a)–(d). It is seen that the ZnO film is composed of nearly oval-shaped particles which are closely packed and form a continuous film (figure 3(a)). The particle
size of ZnO film was quantitatively analyzed by Bruker software (NanoScope Analysis), and a histogram of the NP distributions can be obtained (shown in figure 3(b)). The ZnO particles range from 2 to 10 nm with an average particle size of about 6 nm. It is worthwhile noting that the average size is much smaller than for ZnO films prepared by PLD grown on various substrates, such as 40–80 nm for AZO films grown on LaAlO3 substrate [4], 120–150 nm for AZO films grown on SrTiO3 substrates [10] and 30–50 nm for GZO films on Al2O3 substrates [9]. Figures 3(c), (d) show the three dimensional AFM images and roughness of the ZnO film. The roughness of about 1.6 nm of the present as-prepared ZnO film is of the similar magnitude as those (0.6–2.8 nm) of the GZO film grown on Al2O3 substrate by PLD at the optimized temperature of 400 °C [9] and smaller than the roughness (3–8 nm) of AZO film prepared by direct-current reactive magnetron sputtering. Previous studies suggest that highly oriented growth and good morphology, including homogeneous size distribution, regularly shaped particles and good smoothness, indicate good conductivity of ZnO films [18].

As can be clearly seen in figure 3(e), the XRD pattern of the as-prepared ZnO film shows a single strong reflection corresponding to the (002) reflection of ZnO with wurtzite structure. This indicates that a high-quality ZnO film with fully c-axis preferred orientation has been successfully grown on glass substrate [19]. In order to further check the quality of the Ag-deposited ZnO films, photoluminescence (PL) spectra were studied at room temperature over a wavelength range of 345 to 550 nm (shown in figure 3(f)) and all samples exhibit a strong...
emission peak at 383 nm, which corresponds to the near band gap excitonic emission \[20\]. It is worthwhile to note that the defect-related emission band located in the range of 420–650 nm is absent for the samples, indicating a high crystallinity of the Ag-deposited ZnO films. Moreover, compared with the pure ZnO film, the band edge emission intensity is enhanced by 9%, 50% and 16% for the samples of 5 s, 15 s and 45 s Ag sputtering, respectively, due to the SPR effect of nanoscale noble metals \[14\]. In addition, the enhancement factor reaches a maximum value for the sputtering time of 15 s and then decreases, which might be ascribed to the increase of the Ag-nanoparticle size. A similar size-dependent PL enhancement has been observed for Au-capped ZnO nanorods \[15\].

Figures 4(a) and (b) show the temperature dependence of the electrical conductivity for pure and Ag-deposited ZnO films. Since the glass substrate is insulating, its contribution to \(\sigma\) of the ZnO film can be neglected. The pure ZnO film has a room-temperature conductivity of 4.8 S cm\(^{-1}\) and exhibits a semiconductive temperature dependence. With the deposition of Ag NPs, the room-temperature conductivity sharply increases by about a factor of five to 25 S cm\(^{-1}\) for Ag-5s-ZnO film and further increases by nearly three orders of magnitude to 2500 and 3400 S cm\(^{-1}\) for Ag-15s and Ag-45s samples, respectively. Metal-like conductivity was
observed for the Ag-15s and Ag-45s sputtering samples in the whole temperature range, while the Ag-5s sample shows semiconductive behavior up to 160 °C. With further increasing temperature, the conductivity decreases with temperature, indicating metallic behavior. Previous studies show that Al-doped ZnO films with Al concentration less than 4 at% exhibit metal-like conductivity and a remarkable increase of the carrier concentration upon doping, which can be ascribed to shifting of the Fermi level into the conduction band \cite{8, 21}. The carrier concentration of ZnO film is increased by about three orders of magnitude upon insertion of a Ag layer with the thickness of 8–14 nm between the ZnO layers \cite{13}. This remarkable increase of the conductivity may be ascribed to the fact that when the nanoscale Ag and ZnO are combined together, the high density of electrons of Ag, accumulated at the interface, lead to downward bending of ZnO energy band \cite{13}. In the present work, the deposited Ag NPs with size of about 3 nm are distributed on the ZnO films and the electrons of Ag lead to an increase of the carrier concentration which exceeds Mott’s critical density \((>10^{19} \text{ cm}^{-3})\) \cite{22}. Thus, metal-like conductivity is observed and, as the sputtering time increases from 5 to 45 s, the space between the isolated particles decreases, resulting in a resistivity which declines exponentially \cite{23}. 

Figure 4(c) shows the Seebeck coefficient \(S\) as a function of temperature for all ZnO films in the range of 25 °C–250 °C. All Seebeck coefficients are negative indicating that electrons are the dominating charge carriers. The magnitude of \(S\) at room temperature sharply decreases upon deposition of Ag NPs from 150 \(\mu\text{V/K}\) for pure ZnO to 137, 14, 11 \(\mu\text{V/K}\) for Ag-5s, Ag-15s and Ag-45s samples. The maximum of \(S\) corresponds to the minimum of \(\sigma\). The value of 150 \(\mu\text{V/K}\) is higher than for Al-doped or Ga-doped ZnO films, such as 20–90 \(\mu\text{V/K}\) for AZO films grown on Al\(_2\)O\(_3\) substrates \cite{10}. The low value of \(\sigma\) of only 4 S cm\(^{-1}\) can be attributed to two factors: one is the small particle size of about 6 nm for the present ZnO film and the other is that doping of Al and Ga on Zn sites may improve the conductivity by tuning the carrier concentration and the band gap. As shown in figure 4(d), the PF of the films at room temperature is increased from 11.5 for pure ZnO film and to 46.6 and 49.2 \(\mu\text{Wm}^{-1}\text{K}^{-2}\) for the Ag-5s and Ag-15s samples, respectively, and with further increase of the sputtering time to 45 s. The PF value decreases to 35.3 \(\mu\text{Wm}^{-1}\text{K}^{-2}\), which originates mainly from the significant reduction of \(S\) to 11 \(\mu\text{V/K}\) at room temperature after 45 s Ag sputtering. The value of PF of 49.2 \(\mu\text{Wm}^{-1}\text{K}^{-2}\) is comparable to the value of the temperature-optimized and In-doped GZO film (about 57 \(\mu\text{Wm}^{-1}\text{K}^{-2}\)) \cite{24} and is much

![Figure 4](image_url)

**Figure 4.** Electrical conductivity (a) and (b), Seebeck coefficient (c) and PF values (d) of pure and Ag-deposited ZnO films at 25 °C–250 °C.
higher than for GZO film (4–7 μWm⁻¹K⁻²) deposited at 300, 500 and 600 °C [9] and for AZO film (8–15 μWm⁻¹K⁻²) [8]. The largest PF value in the whole temperature range is 107.7 μWm⁻¹K⁻² at 250 °C for the Ag-15s sample, which is higher than the PF value of about ~100 μWm⁻¹K⁻² for AZO film [8] and comparable to the PF value of about 150 μWm⁻¹K⁻² for GZO film [9].

To further investigate the conductive transport properties of the films, the low-temperature conductivity, the carrier concentration and the mobility at low temperatures Hall measurements were performed from −193 to 27 °C. As shown in figure 5(a), the low-temperature conductive behavior is consistent with that above room-temperature, with metal-like behavior of the Ag-15s sample and semiconducting behavior of the pure ZnO film. After Ag sputtering for 15 s, the room-temperature carrier concentration of the ZnO film has increased from 3.8 × 10¹⁹ to 5.2 × 10²⁰ cm⁻³. A carrier concentration of 10²⁰ cm⁻³ has been reported as optimal value for thermoelectric properties [10]. The room-temperature mobility has increased from 8.2 to 38.8 cm² V⁻¹s⁻¹. These results show that the 500-fold enhancement of the conductivity after Ag deposition originates from the two orders of magnitude enhancement of the carrier concentration as well as from a significant improvement of mobility. It has been reported that several factors contribute to the PF performance of ZnO film, such as the doping efficiency on Zn sites [8], crystallinity [25, 26], stress and strain [27], the grain-boundary [28, 29] and areal concentration of dislocation [10]. The enhancement of the PF performance in the present Ag-deposited ZnO films can be mainly ascribed to the Ag NPs on the ZnO films which lead to a remarkable increase of the carrier concentration and thus to a great improvement of conductivity. It is worthwhile to note that although possessing a carrier concentration as high as 3.5 × 10²¹ cm⁻³ mainly contributed by the continuous Au layer with high-density electros, the ZnO film grown on an Au layer shows a much smaller room-temperature PF of 2–13 μWm⁻¹K⁻² [30]. This can be ascribed to the ultra low Seebeck coefficient of 1–15 μV/K.

4. Conclusions

Fully c-axis oriented ZnO film with an average particle size of about 6 nm has been prepared by RF magnetron sputtering on glass substrates. After this, Ag NPs with an average size of 3 nm were deposited on the ZnO films. PL spectra measurements of the films exhibit a strong emission peak at 383 nm from the near band gap excitonic emission. The defect-1 related emission band is absent, indicating a high crystallinity of the Ag-deposited ZnO films. Isolated Ag NPs with a high density of electrons are distributed on the ZnO films, leading to the increase of the carrier concentration that exceeds Mott’s critical density. Owing to the remarkable improvement of conductivity, the room-temperature PF value of 49.2 μWm⁻¹K⁻² and the maximal PF of 107.7 μWm⁻¹K⁻² at 250 °C for the Ag-15s-ZnO film are of similar magnitude as for AZO and GZO films and much higher than for the ZnO film with Au/Ag layer. This work opens an effective route for enhancing the thermoelectric performance of semiconducting films.

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