Electrical and optical properties of metal-sandwiched ZnO/Ti/Cu/Ti/ZnO transparent conductive thin film

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Metal-sandwiched zinc oxide (ZnO)/titanium (Ti)/copper (Cu)/Ti/ZnO thin film systems were fabricated using magnetron sputtering technology and then annealed using a rapid thermal annealing system at temperatures from 100 to 400°C. The influence of the Ti film thicknesses and annealing temperatures on the surface morphologies, sheet resistance and optical properties were studied. The surface morphologies change a little with the annealing temperature rises. The sheet resistances reduce with the Ti film thickness or annealing temperature increasing. Both the max transmittance and figure of merit reduce with the increase of Ti film thickness. The max transmittance increases with the temperature increasing from 100 to 300°C and then reduces. However, the figure of merit increases with the temperature increasing which indicates that the metal-sandwiched ZnO/Ti/Cu/Ti/ZnO thin film system annealed at 400°C has the optimal performance.

1. Introduction: Transparent conductive film with the advantages of low electrical resistivity, high transmittance in the visible light range and high reflectivity in the infrared range has a broad application prospect in the photovoltaic industry such as light-emitting diodes, flat panel displays, thin film transistors and solar cells [1, 2]. The most widely used transparent conductive films are transparent conductive oxide (TCO) thin films [3–7], mainly including tin oxide (SnO_2), indium oxide, indium SnO_2 (ITO), zinc oxide (ZnO) and the doped system with above oxides. There are still many shortcomings in the currently used TCO thin films such as large resistance, high radiation rate and weak reflection ability of the solar radiation in the near-infrared region. For example, when ITO thin film is used for the transparent electrode of a flat panel display [8], its higher resistance affects the resolution of the display screen. Therefore, a hot spot in the field of optoelectronic devices is to fabricate transparent conductive film with high-conductivity and high-visible light transmittance.

Dielectric/metal/dielectric (D/M/D) multilayer thin film, whose primary purpose was to fabricate selective transparent thin films, is considered to be a choice with advantages [3, 7, 9]. Various high-performance D/M/D multilayers used as transparent conductive film or electrodes have been successfully fabricated such as SnO_2/M/SnO_2[10–12], aluminum-doped zinc oxide (AZO)/M/AZO [13], ZnO/M/ZnO [14–17]. As to the advantages of high transparency in visible wavelengths and excellent room-temperature luminescence performance, ZnO thin film has great potential in liquid-crystal display, ultraviolet (UV) detector and light-emitting diode [18, 19]. Although the optical and electrical properties of ZnO thin film can be improved by adding or injecting one-dimensional nanomaterials such as nanoparticles [20], nanowires [21, 22] and nanorods [23], the complex preparation technology limits their applications. ZnO/M/ZnO multilayer thin film can effectively reduce the resistivity to improve the conductivity and performance of the film and has an important engineering application value [14–17]. Various ZnO/M/ZnO systems such as ZnO/copper(Cu)–Sn/ZnO [14], ZnO/silver (Ag)/ZnO [15], ZnO/Cu/ZnO [16, 17] have been developed and studied. As typical conductive metals, both Cu and titanium (Ti) have excellent electrical conductivity. A metal-sandwiched ultrathin bilayer film structure composed of an ultrathin and continuous Cu film inserted by an ultrathin Ti film can improve the figure of merit and stability of the thin film system [13, 24]. Cu/Ti thin film is a potential metal material that can be used as the sandwiched material of ZnO thin film.

In this Lettper, metal-sandwiched ZnO thin film systems (ZnO/Ti/Cu/Ti/ZnO) with different Ti layer thicknesses were fabricated using magnetron sputtering technology. A film system with Ti thickness of 5 nm was annealed at temperatures from 100 to 400°C. The surface morphologies, sheet resistance and optical properties of the thin films were studied.

2. Experiment: Metal-sandwiched ZnO thin film systems (50 nm ZnO/*x*nm Ti/10 nm Cu/*x*nm Ti/50 nm ZnO, $x = 5$, 10, 15) were deposited on glass substrates at room temperature using magnetron sputtering system (explorer 14, America). The equipment has three targets with the size of 4 in, one is for radio-frequency sputtering (ZnO) and the other two are for DC magnetron sputtering (Cu and Ti). The deposited metal-sandwiched ZnO thin film systems with Ti layer thickness of 5 nm were then annealed for 30 min at temperatures from 100 to 400°C using a rapid thermal annealing system (RTP-500, China) with ramping rate at 50 °C/s and then furnace cooling to the room temperature.

The surface of the films was measured by atomic force microscope (AFM) (Innova, America) in contact mode at a small scale (<4 μm). The sheet resistance was measured using four-point probe method. Transmission spectra were obtained by UV and visible spectrophotometer (Shimadzu UV-3600, Japan).

3. Results and discussion: The surface morphologies of the ZnO/5 nm Ti/Cu/5 nm Ti/ZnO thin film systems annealed from 100 to 400°C measured by AFM were shown in Fig. 1. It can be noted that the surface morphologies change a little as the annealing temperature rising from 100 to 300°C and the distribution particles are relatively tiny. However, after being annealed at 400°C, the surface particles of the thin film are large and sparse. The roughness of the different surfaces obtained from AFM is shown in Table 1. It can be observed that the roughness does not increase significantly with the variation of the annealing temperature.

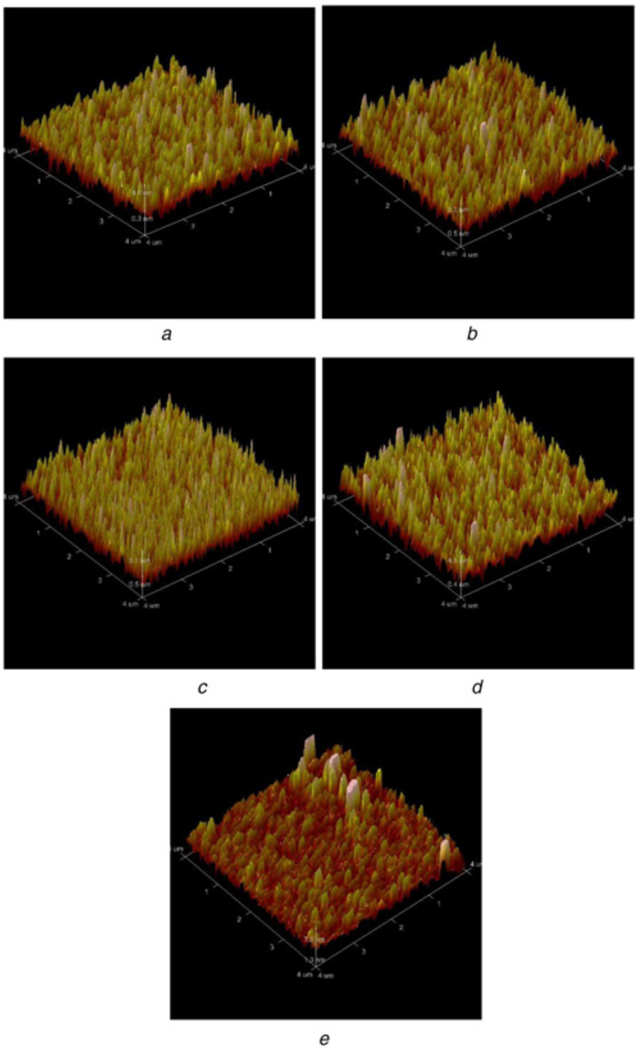

Fig. 1 *AFM images of the ZnO/5 nm Ti/Cu/5 nm Ti/ZnO thin films annealed at different temperatures*
a As-deposited
b 100°C
c 200°C
d 300°C
e 400°C

Table 1 Roughness of the thin film annealed at different temperatures

Annealing temperature	R_q, nm
as-deposited	1.190
100	1.136
200	1.137
300	1.160
400	1.110

The sheet resistances of the ZnO/Ti/Cu/Ti/ZnO transparent conductive thin films were measured by a four-point probe method. The sheet resistances of thin films with Ti thicknesses of 5, 10 and 15 nm are 6.6, 5.1 and 3.8 Ω/□, respectively. It indicates that sheet resistance reduces with the Ti film thickness increase. The sheet resistances of the ZnO/5 nm Ti/Cu/5 nm Ti/ZnO film systems annealed at different temperatures were shown in Fig. 2. It can be noted that the sheet resistances reduce with the annealing temperature increasing. It indicates that the annealing process improves the electrical properties of the films and the conductivity has been increased.

The resistivity of the multilayers is proportional to its sheet resistance. According to the parallel circuit model, the multilayer thin film can be considered as a parallel circuit of five resistors. Therefore, the total resistance of the film system is equivalent to the individual resistance of the five single film coupled in parallel. In this condition, the total resistance (R_T) of the film system can be given as [25]

$$\frac{1}{R_{\rm T}} = \frac{2}{R_{\rm ZnO}} + \frac{2}{R_{\rm Ti}} + \frac{1}{R_{\rm Cu}}$$

where $R_{\rm ZnO}$, $R_{\rm Cu}$ and $R_{\rm Ti}$ are the sheet resistances of ZnO layer, Cu layer and Ti layer, respectively. In metal-sandwiched transparent conductive film, the conductivity of the film system is mainly supplied by the metal layer. This phenomenon can also be found in ZnO/Ag/ZnO film systems [26], in which the Ag thickness had the largest influence on the sheet resistance. Generally speaking, annealing process can improve the film quality. In this case, the crystallisation degree of the thin film increases continuously with the increase of annealing temperature, which makes the migration rate of the carrier increase and the sheet resistance of the film reduce gradually.

The optical properties of the ZnO/Ti/Cu/Ti/ZnO film systems were studied and the transmission spectra were measured using a UV and visible spectrophotometer. The transmission spectra of the films with different Ti thicknesses without annealing were shown in Fig. 3. In the wavelength range from 300 to 1000 nm, there are two peaks in the spectra: one is at the wavelength of about 670 nm with maximum transmittance and the other is at 400 nm. The optical transmittance of the as-deposited ZnO/Ti/Cu/Ti/ZnO thin film is higher than ZnO/Cu/ZnO reported by Sahu when they have the same thicknesses of the Cu and ZnO layers [27]. With the increase of Ti film thickness, the transmittance reduces and the central wavelength of the extreme peak in the long wavelength region shows a blue shift and gets closer to the central wavelength region of visible light (about 570 nm).

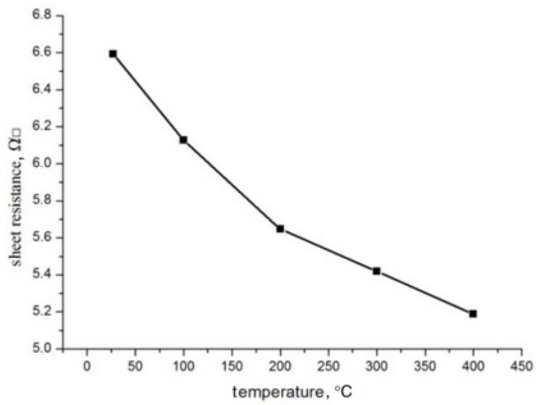

Fig. 2 *Sheet resistance of ZnO/Ti/Cu/Ti/ZnO thin films annealed at different temperatures*

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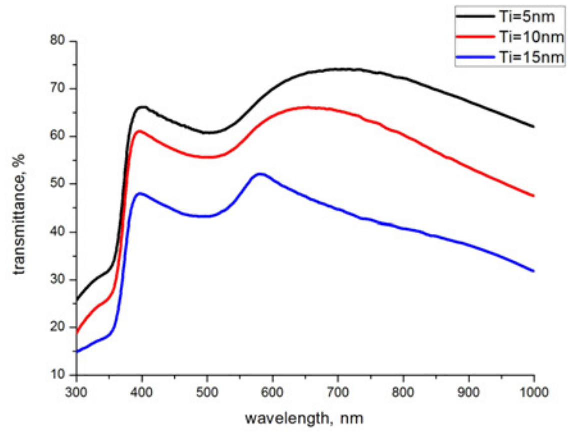

Fig. 3 *Transmission spectra of the ZnO/Ti/Cu/Ti/ZnO multilayers with different Ti layer thicknesses*

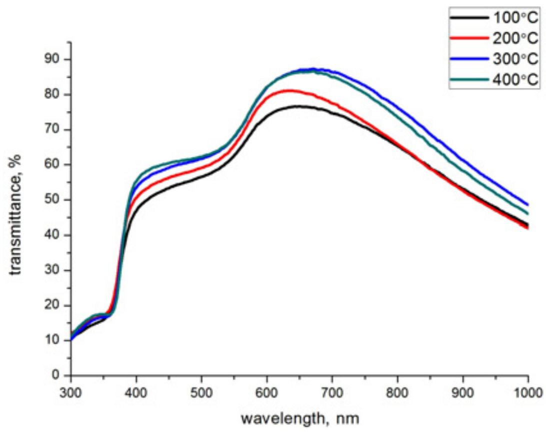

Fig. 4 *Transmission spectra of the ZnO/5 nm Ti/Cu/5 nm Ti/ZnO multilayers annealed at various temperatures*

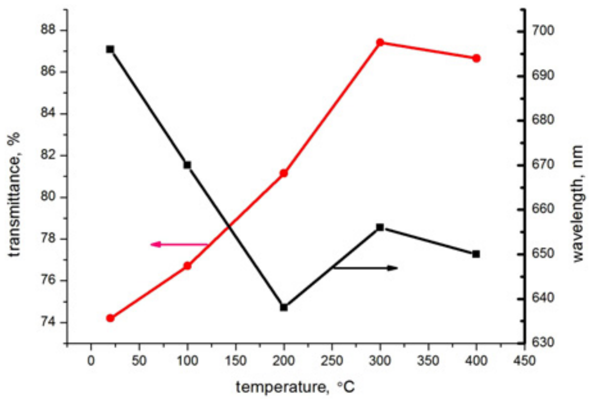

Fig. 5 *Max transmittance and its central wavelength of the ZnO/5 nm Ti/Cu/5 nm Ti/ZnO thin films annealed at various temperatures*

The transmission spectra of the ZnO/5 nm Ti/Cu/5 nm Ti/ZnO films annealed at temperatures from 100 to 400°C are shown in Fig. 4. The maximum transmittance of each thin film at different annealing temperatures is also plotted in Fig. 5 for clarity. It is observed that the optical transmittances in the visible region are all higher than 74%. The transmittance increases with the annealing temperature rising and reaches the maximum at 300°C and then reduces. The maximum transmittance at 300°C is about 87%, which is 24% larger than the as-deposited thin film. The central wavelength of the max transmittance is also shown in Fig. 5. It can be obtained that the central wavelength shifts blue at low temperatures (<200°C) and then fluctuates around 650 nm.

In general sense, transmission is primarily affected by absorption of light due to interband electronic transitions, in particular, due to the excitation of electrons from the d-band to the Fermi surface [28]. As the excitation of electrons has to jump over specific energy gap, there are few bound electrons available for excitation when the annealing temperature is below 300°C. Under this condition, the improvement of film forming quality will increase the transmittance. As shown in Fig. 2, the film forming quality was improved to a certain extent with the increase of annealing temperature below 300°C leading the increasing of transmittance. However, at annealing temperature of 400°C, there are bound electrons available for excitation leading to a drop in transmittance.

From Figs. 2 and 4, it can be noted that the increase of annealing temperature will improve the conductivity and transmittance of the film systems. However in most cases, there is a mutual restriction between the optical properties and the electrical properties of the transparent conductive film. In other words, the increase in conductivity is more likely to lead to a decrease in transmittance. Therefore, except the sheet resistance and transmittance, the figure of merit proposed by Haacke was also used to predict the properties of transparent conductive film in order to further evaluate its performance. The expression has been defined as [29–31]

$$\Phi_{\text{TC}} = \frac{T_{\text{av}}^{10}}{R_{\text{S}}}$$

where T_{av} is the average transmittance and R_{S} is the sheet resistance. Considering the application of the transparent conductive films, the equation chosen to determine the average transmittance is given as

$$T_{\text{av}} = \frac{\int V(\lambda)T(\lambda)\,\text{d}\lambda}{\int V(\lambda)\,\text{d}\lambda}$$

where $T(\lambda)$ is the transmittance, $V(\lambda)$ is the photopic luminous efficiency function which defines the standard observer for photometry.

The figure of merit of the thin films with different Ti film thicknesses is shown in Fig. 6. It can be observed that the figure of merit reduces with the increasing of Ti film thickness, which indicates that the increase of Ti film thickness is unfavourable to the overall performance of the transparent conductive film. This figure of merit of the ZnO/5 nm Ti/Cu/5 nm Ti/ZnO thin films at different temperatures is shown in Fig. 7. It is shown that the figure of merit increases with the temperature increasing.

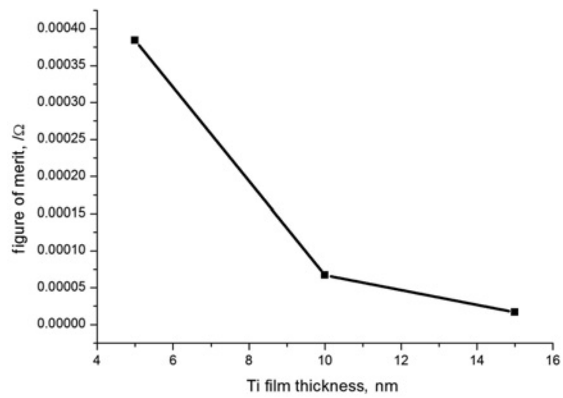

Fig. 6 *Figure of merit of the ZnO/Ti/Cu/Ti/ZnO multilayers with different Ti film thicknesses*

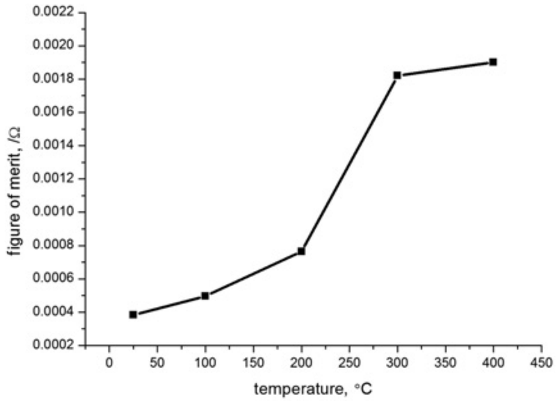

Fig. 7 *Figure of merit of the ZnO/5 nm Ti/Cu/5 nm Ti/ZnO multilayers annealed at various temperatures*

Although the film system annealed at 300°C has the largest value of the max transmittance, it does not have the optimal performance. This indicates that the rising of temperature is beneficial to the improvement of performance.

4. Conclusion: Metal-sandwiched (50 nm ZnO/$x$nm Ti/10 nm Cu/$x$nm Ti/50 nm ZnO, $x = 5$, 10, 15) thin film systems were deposited using magnetron sputtering technology and then were annealed at temperatures from 100 to 400°C. The surface morphologies of the thin film systems annealed at different temperatures change a little and the roughness does not increase significantly. The conductivity of the film system is mainly supplied by the Ti/Cu/Ti metal layers and the sheet resistances reduce with Ti film thickness and the annealing temperature increasing. The transmission spectra were measured using a UV and visible spectrophotometer and the thin film annealed at 300°C has the maximum transmittance. The figure of merit was used to predict the properties of transparent conductive film and its relation curve with annealing temperature indicates that the metal-sandwiched ZnO/Ti/Cu/Ti/ZnO thin film system annealed at 400°C has the optimal performance.

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