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Effect of thermal annealing on the performance of WO_3–Ag–WO_3 transparent conductive film

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ABSTRACT

As a candidate for transparent electrodes, oxide–metal–oxide tri-layer films have attracted a lot of interest by virtue of their low cost and decent performance. However, their thermal stability needs to be considered before device integration. Here, we report a thermal annealing effect on the performance of WO_3–Ag–WO_3 (WAW) transparent conductive thin film prepared by thermal evaporation. We find that the sheet resistance of the as-prepared WAW film gradually increases from 6.55 to 21.4 Ω/sq when the annealing temperature reaches 400 °C. With a low annealing temperature (below 200 °C), the luminous transmittance of the WAW film slightly increases but decreases rapidly when the annealing temperature exceeds 200 °C. The maximum figure of merit ($11 \times 10^{-3}\ \Omega^{-1}$) was obtained at the annealing temperature of 100 °C. Above the annealing temperature of 300 °C, the film shows significant transmittance and conductivity degradation, which can be attributed to the decrease of intrinsic dielectric constant of WO_3 layers and the reduction of connectivity between Ag islands upon high temperature annealing, respectively. Annealing at a temperature of 500 °C leads to severe destruction of the tri-layer structure. In addition, we believe that the localized surface plasmonic absorption of annealing-generated Ag nanoparticles results in a valley centered at 410 nm on the transmittance spectrum of the 500 °C annealed WAW film.

1. Introduction

Transparent conductive electrodes are essential components for optoelectronic information (displays) and energy (solar cells) devices [1–4]. Material candidates include transparent conductive oxide (TCO) films (such as In_2O_3:Sn (ITO), SnO_2:F, and doped ZnO), micro/nanoscale metal periodic grids or random networks, carbon nanomaterials (such as carbon nanotube and graphene), and conductive polymer [5]. Although ITO film is the most commonly used transparent electrode, the exploration of alternative transparent conductive film is actively pursued considering the increasing price of indium [6]. Recent emerging graphene, metal nanowires, and their composites do show superior electrical conductivity, high transmittance, and fantastically mechanical flexibility [5]. However, incompatibility with the current mass-production of transparent electrode based on vacuum thin film deposition technique and/or material intrinsic environmental instability retards their rapid commercializing steps [5]. Before these issues are resolved, indium-free TCO thin films would be more practical candidates for transparent electrodes.

Recently, dielectric–metal–dielectric tri-layer films as transparent electrodes have attracted great attention [2,7]. These tri-layer films possess the following advantages: very low resistivity comparable to metal electrodes, high optical transparency in the visible wavelength region, relatively lower thickness, and superior flexibility [2,8–10]. Among them, WO_3–Ag–WO_3 (WAW) tri-layer film has been extensively demonstrated as transparent electrode for organic light emission diode, solar cell, and thin film transistor owing to its advantage of thermal evaporation fabrication process compatibility (avoiding sputter damage in the ITO case) [11–14]. Particularly, WAW film can act both as transparent electrode and electrochromatic coating [15], which may greatly reduce the fabrication cost of electrochromatic devices. However, the thermal stability must be evaluated before its widely practical applications [16], especially working in harsh environment including localized electrical current heating and strong external thermal irradiation. Reported thermal stability experiment on ITO/Ag/ITO transparent conductive films focused on exploring the electrical degradation mechanism from the crystal structure point of view [16]. Here, we investigate the thermal annealing effect on the performance of WAW transparent conductive film and elucidate the transmittance evolution mechanism from the light-matter inaction point of view. We find that low temperature annealing slightly increases the dielectric constant of WO_3 film, reduces the surface plasmon coupling and thereby improves the transparent conductive performance. While annealing temperature above 300 °C leads to significant transmittance and conductivity degradation. Such degradation can be attributed to the decrease of dielectric constant of WO_3 film and the reduction of connectivity between Ag islands upon high temperature annealing, respectively.

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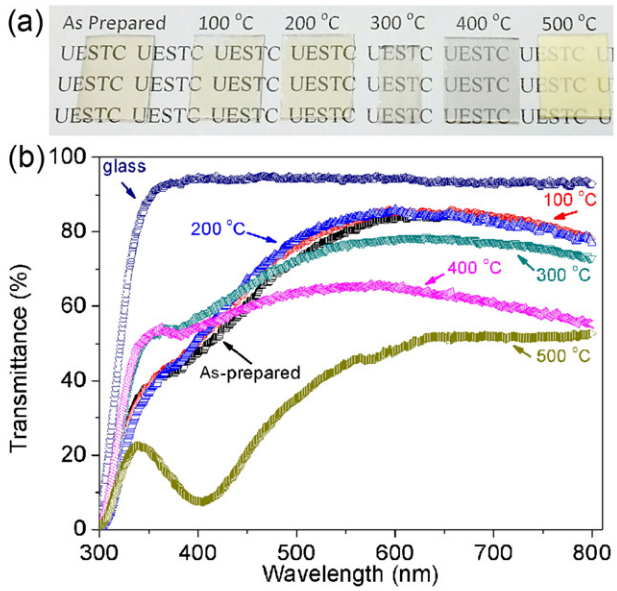

Fig. 1. (a) Optical image of the as-prepared and annealed WAW films (50 nm WO_3, 12 nm Ag, 50 nm WO_3) on glass substrates. (b) Transmittance spectra of glass, as-prepared and annealed WAW films on glass substrates.

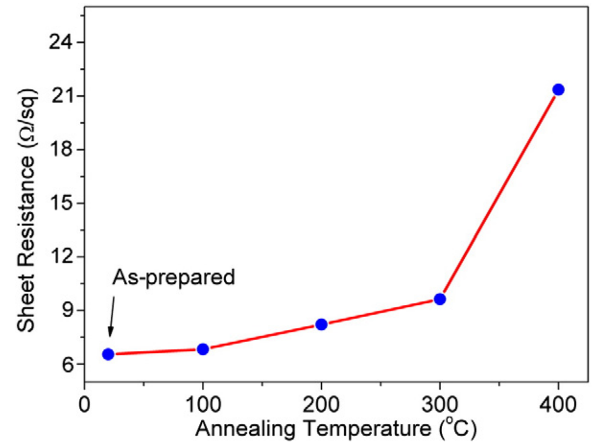

Fig. 3. Sheet resistance of the WAW films as a function of annealing temperature.

2. Experimental details

The commercial available electronic glass (BBL-001 produced by Zhuhai Kaivo Optoelectronic Technol. Co. Ltd) with a thickness of 1.1 mm was used as a transparent substrate. The WAW films were prepared by thermal evaporation under the vacuum pressure of 4×10^{-4} Pa. Films with optimized thickness (WO_3 (50 nm), Ag (12 nm), and WO_3 (50 nm)) were deposited on glass substrates sequentially without breaking the vacuum. No intentional substrate heating was applied during the deposition. The evaporation rate was controlled to be 0.1 nm/s and 0.2 nm/s for WO_3 and Ag, respectively. The as-prepared films were annealed in normal air with the heating rate of 5 °C/min. The duration was set for 2 h at each annealing temperature. No distinguishable performance variation was found for longer time thermal annealing. To measure the optical constant of WO_3 film, the 50 nm WO_3 film was deposited on glass using the same deposition condition as preparing the WAW film. The annealing condition of WO_3 film was also set the same as that of WAW film.

The transmission spectra of the films were measured by fiber spectrometer (BLK-C-SR, StellarNet Inc.). The sheet resistances of the films were examined by four probe tester (ST-2258A, Suzhou Jingge Electronic Co.). The crystal structures and surface morphologies of the films were examined by X-ray diffraction (XRD, Bruker D8, operated at 40 kV and 40 mA) with Cu Kα radiation and scanning electron microscopy (SEM, FEI Nova NanoSEM, operated at 10 kV), respectively. Optical constants of WO_3 material were obtained via the spectroscopic ellipsometer (SE850, Sentech Instruments GmbH). Characteristic matrix method was used to simulate the transmittance of the films [8].

3. Results and discussion

The optical images of the as-prepared and annealed WAW films on glass substrates are shown in Fig. 1a. The as-prepared WAW film is so transparent that the words under the film can be clearly seen. After annealing at 100 and 200 °C, no observable transparency change was found between the annealed and the as-prepared WAW film. While with a higher annealing temperature, the transparency of the films obviously declines, especially for the film annealed at 500 °C.

To quantify the film transparency, the transmittance of the glass substrate (Fig. 1b), as-prepared and annealed films on glass substrates were measured. After the WAW film deposition, the glass substrate still remains highly transparent with a maximum transmittance of 84% at the wavelength of 600 nm. With a low annealing temperature at 100 °C and 200 °C, the transmittance of the WAW film shows a slight increase, especially in the range of 350–650 nm. However, further increasing the annealing temperature leads to the rapid transmittance decreasing. The

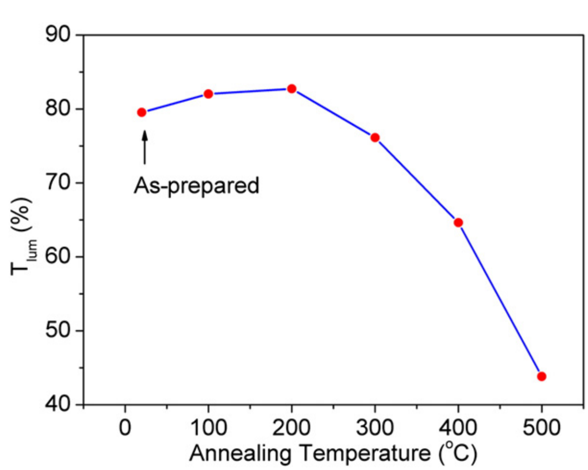

Fig. 2. Luminous transmittance of the WAW films as a function of annealing temperature.

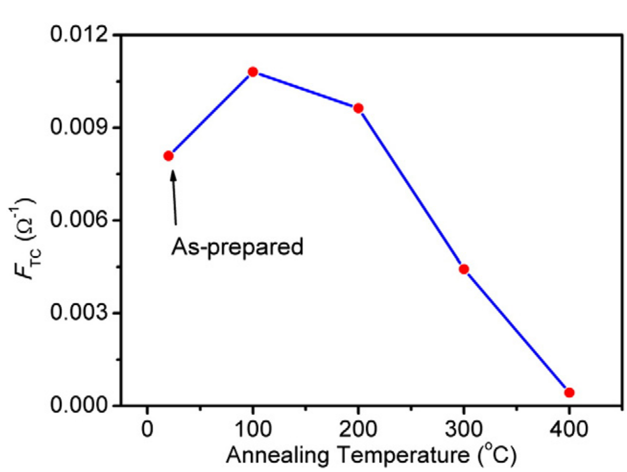

Fig. 4. Figure of merit (F_{TC}) of the WAW films.