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Use of anodes with tunable work function for improving organic light-emitting diode performance

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ABSTRACT

The effect of reactive gases—oxygen and hydrogen—on the tunable work function of Al-doped ZnO (AZO) films was studied. An increase in the work function with an increase in the oxygen flow rate was mainly interpreted as reflecting a decrease in the carrier concentration, which was attributed to the filling of oxygen vacancies. However, a decrease in the carrier concentration would result in the resistivity increasing sharply. This article presents a new concept for improving the performance of organic light-emitting diodes (OLEDs) through easy and effective hole injection from a multilayer AZO anode to the organic layer. A bilayer AZO film prepared using a tunable work function technique was used to modify the surface of AZO anodes and to ensure that the anodes had low resistivity. The AZO anode stacked with high-work-function AZO films, similar to hole transport buffer layers, had a low turn-on voltage of 2.89 V, and its luminance efficiency and power efficiency were 5.01% and 6.1% greater than those of tin-doped indium oxide anodes used in OLEDs.

1. Introduction

Transparent conductive oxide (TCO) films play a crucial role in many advanced devices such as thin-film transistors, solar cells, flat-panel displays, and organic light-emitting diodes (OLEDs) [1–5]. Doped metal oxides have high potential for use in materials science since they can be conveniently used to modify the physical, chemical, electronic, and even mechanical properties of materials. Through the use of selectively doped metal oxides, the performance of devices can be improved and new devices can be designed.

Tin-doped indium oxide (ITO) has been widely used for fabricating the anodes of OLEDs because of its high conductivity and transparency in the visible region of the spectrum and its high work function, particularly after surface treatments, which facilitates adequate hole injection [5]. However, the main component of ITO, indium, is becoming increasingly difficult to obtain because, as a rare earth element, it is expensive. Other drawbacks of ITO films have been mentioned in the literature. Studies have shown that indium can diffuse into the organic materials of OLEDs, resulting in the degradation of device performance [6]. Therefore, indium-free TCO films have been extensively researched.

Recently, because of their low resistivity, high transparency, low cost, natural abundance, and nontoxicity, Al-doped ZnO (AZO) thin films have emerged as one of the most promising alternatives for ITO films for use as an electrode in optoelectronic devices. In devices, the work functions of the electrodes must match the appropriate energy levels of the light-emitting material. AZO films can be used to inject holes in the highest occupied molecular orbitals (HOMOs) of organic materials [7,8]. As in ITO films, the efficiency of hole injection critically depends on the interface barrier height between the transparent electrode and the organic layer, and the work function of AZO films has been considered a key parameter for tailoring the interface barrier height [9]. The HOMO energy level of most organic materials is close to 5–6 eV [10,11], which is too high for directly injecting charges from AZO. The lower work function of AZO can directly influence the barrier height at the interface, resulting in inefficient carrier injection and, consequently, poor device performance.

The work function is defined as the minimum energy required for liberating an electron from the Fermi level into a vacuum [12]. Therefore, the work function should be affected by the Fermi level

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position with respect to the vacuum level. In other words, the work function can be tuned by changing the Fermi level, which is directly related to a change in the carrier concentration. In this study, the Fermi level of AZO films was controlled by introducing different reactive gases during deposition process. The maximum tunable work function was 1.44 eV. The decrease in the carrier concentration with introducing oxygen flow resulted in a positive change in the work function. By contrast, the increase in the carrier concentration with introducing hydrogen flow resulted in a negative change. Thus, the work function of AZO films can be controlled by introducing various reactive gases, and a tailor-made electrode having a work function matching the organic layer can be obtained. The purpose of this study was to show that a stacked AZO film anode with a tunable work function can have intermediate energy states that enable holes to cascade through small gaps, thereby reducing the voltage required to drive the device.

2. Experimental procedure

AZO thin films were deposited on B270 glass substrates by using a pulsed dc magnetron sputtering system. The composition of the sputtering target, which was 3 inch in diameter, was 98 wt.% zinc oxide (ZnO, 99.99% purity) and 2 wt.% aluminum oxide (Al_2O_3, 99.99% purity), and the distance between the target and the substrate was fixed at 75 mm. The sputtering chamber was evacuated using a cryopump to a base pressure lower than 8×10^{-6} Torr. To investigate the influence of oxygen and hydrogen, the flow rates of oxygen and hydrogen were varied from 0 to 12 sccm and from 0 to 27 sccm, respectively (sccm denotes cubic centimeter per minute at standard temperature, pressure, and humidity). High-purity argon flow at 120 sccm was introduced through a mass flow controller as the working gas, and the substrate temperature was fixed at a high temperature of 250 °C. The working pressure was between 2 and 3 mTorr. The dc power was 200 W, and pulsed dc excitation was provided at 13.6 kHz.

Ultraviolet photoelectron spectroscopy measurements of AZO films were conducted at a base pressure lower than 7.5×10^{-7} Torr. The work function was estimated using the secondary electron cutoff method, and the absolute work function values were calibrated against the work function of pure gold. Sheet resistances were measured using a four-point probe. The optical transmittance and reflectance were measured using a UV–vis spectrometer in the wavelength range 350–800 nm.

OLED devices were fabricated using TCO substrates with multiple organic layers, sandwiched between the transparent bottom TCO anode and the top metal cathode. The organic and metal layers were deposited by thermal evaporation in a vacuum chamber with a base pressure of $<10^{-4}$ Pa without breaking the vacuum. The deposition rate of the organic layers was kept at around 0.1 nm/s. The active area of the device was 2 mm × 2 mm, as defined by the shadow mask used for cathode deposition. Current–voltage–luminance (J–V–L) characterization was performed using an Agilent 4156C semiconductor parameter analyzer equipped with a calibrated Si-photodiode. Electroluminescence spectra of the devices were recorded by using an Ocean Optics spectrometer.

3. Results and discussion

The work function changed with the Fermi level, which is often directly related to the doping concentration. Over the past few decades, a considerable number of studies have examined the effect of the oxygen content on the Fermi levels of AZO during deposition process. Generally, the carrier concentration of AZO films is influenced by the Al dopant or oxygen vacancies. An oxygen-rich AZO thin film can be obtained by introducing oxygen gas, which fills the oxygen vacancies, leading to a decrease in the carrier concentration of the thin film. In other words, stronger oxidizing conditions generally lead to a lower Fermi level, as expected. Accordingly, the work function of AZO can be increased by using oxygen with a higher partial pressure; this result is shown in Fig. 1. For a low number of oxygen vacancies, the AZO films showed a lower carrier concentration and higher work function, demonstrating that the free carrier concentration plays a vital role in tuning the work function of AZO films by changing the Fermi level position. This result is consistent with previous findings [13,14].

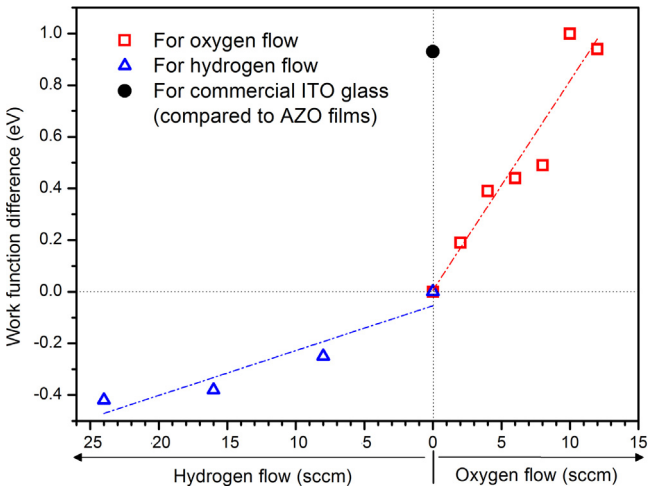

Fig. 1. Variation of the work function of AZO films as a function of the oxygen (red open squares) and hydrogen (blue open triangles) flow rates. The filled circle represents the work function of commercial ITO films, and it is provided for making a comparison with AZO films. The lines are trend lines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

An increase in the carrier concentration of AZO films can lead to a higher Fermi level, thereby reducing the work function. In our previous studies, the carrier concentration was found to increase with introducing hydrogen because the incorporated hydrogen acted as a shallow donor. Previous studies have shown that hydrogen can play a crucial role in determining the electrical properties of ZnO-based TCO films [15–18]. The work function of AZO films was measured at different oxygen and hydrogen flow rates, as shown in Fig. 1. The results indicated that a simple method for tuning the work function of AZO films is to control the Fermi level position by introducing different reactive gases. Introducing oxygen gas as the reactive gas in deposition process can increase the work function of AZO film; an appreciable increase of +1.02 eV can be achieved in the work function by increasing the oxygen flow rate. Introducing hydrogen gas can reduce the work function; a change of −0.42 eV in the work function was observed with an increase in the hydrogen flow rate. Regardless of whether oxygen or hydrogen was used as the reactive gas, the average transmittance of AZO films in the visible region exceeded 85%.

AZO films are one of the most promising alternatives for ITO films in optoelectronic devices. However, for use as anodes in OLEDs, AZO films must have a high work function and a low resistivity, which are necessary for the high efficiency of the films. Our experiments showed that a high work function and low resistivity cannot be simultaneously achieved. The results show that the lowest sheet resistance of an AZO film is 16.3 Ω/sq at a non-oxygen flow rate. The maximum work function of an AZO film, which is 100.7 Ω/sq, is 4.66 eV at an oxygen flow rate of 10 sccm; this value is slightly higher than that of commercial ITO films. More complete oxidation of AZO films resulted in a lower binding energy. Although