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Visibly transparent metal oxide diodes prepared by solution processing

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Visibly transparent metal oxide diodes were fabricated using p-type doped zinc oxide on tin doped indium oxide coated substrates by sol-gel solution processing. The influence of various nitrogen doping concentration on the hole carrier concentration and the device operation of the diodes was investigated. The diodes exhibit high optical transmission in the visible spectra and high on/off ratios at low operating voltages. The operation is limited by the low hole carrier concentration, which affects the ideality factor and the series resistance of the diode. The influence of the carrier concentration on electronic properties of the diode will be discussed.

1. Introduction

Zinc oxide (ZnO) belongs to the group of II-VI compound semiconductors with a wide bandgap of 3.2 eV and its growth is characterized as hexagonal wurtzite structure. Wide bandgap metal oxide semiconductors like ZnO have gained substantial attention due to its potential in optoelectronic applications as short wavelengths light emitting diodes (LEDs), photodiodes, photodetectors, and laser diodes [1]. Furthermore, ZnO holds potential as active layer and transparent conductive oxide for various applications such as gas sensors, thin film transistors in active matrix addressed displays, piezoelectric devices, surface acoustic wave devices, and photovoltaics [2–7]. The fabrication of pn-diodes and complementary metal-oxide-semiconductor based digital circuitry requires both p- and n-type ZnO semiconductors. The difficulty to realize p-type ZnO has encouraged many researchers to focus on heterojunction devices based on n-type ZnO with different p-type materials. P-type gallium nitride (GaN) and p-type silicon (Si) are commonly coupled with n-type ZnO as ultraviolet (UV) LEDs and photodiodes, respectively [8,9]. GaN exhibits similar crystal structure and lattice constant with ZnO, which are essential in achieving high quality heterostructure epitaxial layers. Meanwhile, the maturity of Si in microelectronics makes it feasible to integrate ZnO based photodiodes in existing circuit technology.

The challenges to produce p-type ZnO are mainly caused by self-compensating effect, deep acceptor level, and solubility of acceptor dopants [10,11]. Furthermore, with strong electronegative oxygen compound, ZnO exhibits a lower valence band maximum, which directly affects its symmetrical tendency to be n-type or p-type, also known as 'unipolarity' [12–14]. However, in recent years, the fabrication of p-type ZnO has been progressively improved by single doping group V elements (N, P, As, and Sb) and co-doping III–V elements via different methods such as sputtering, molecular-beam epitaxy (MBE), metal-organic chemical vapor deposition (MOCVD), and sol-gel technique [15–18]. The similarity of electronegativity and ionic radius between nitrogen and oxygen has prompted the developments in p-type nitrogen doped ZnO (ZnO:N) films [19–22]. These developments have also extended to homojunction and heterojunction device fabrication based on p-type ZnO. In the work by Dhara et al., p-type ZnO:N layer and n-type ZnO layer were deposited using sputtering technique to form pn-homojunction, which has demonstrated a typical rectification behavior of the junction diode with a threshold voltage 2.0 V [23]. Huang et al. has presented a heterojunction photodiode based on ZnO:N and n-type GaN in their work by using chemical vapor deposition (CVD) method [24]. The I–V characteristic shows the formation of a typical p–n junction as well as distinct light

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emission in 20 or 30 mA pumping current.

While there have been studies on ZnO:N based devices, the fabrication of thin film transition-metal oxide based devices usually required high power vacuum technologies that are generally more costly in order to achieve a high quality junction interface. The desire to reduce the cost of fabrication leads to strong interests in fabricating oxide thin films using wet chemical process such as spray pyrolysis and sol-gel methods as shown in many recent works. The sol-gel method offers an alternative way to conventional physical vapor deposition methods to fabricate high quality thin films at lower cost. Recent reports have confirmed the presence of p-type carriers in ZnO semiconductor with proper doping mechanism using sol-gel method [19,20]. In this work, a sol-gel spin coating method was utilized to obtain p-type ZnO:N films on glass substrates. ZnO:N thin films with nitrogen doping concentration of 5, 10, 15, 20, 25, 30 at.% were integrated into metal oxide diodes with n-type tin doped indium oxide (ITO) coated glass.

2. Experimental

The ZnO solution contains zinc acetate dihydrate, isopropanol (IPA), and monoethanolamine as precursor, solvent, and stabilizer, respectively. As the nitrogen doping source, ammonium acetate was added into the solution at concentration of 5, 10, 15, 20, 25, 30 at.% to obtain ZnO:N solutions with different doping concentration. The solutions were then spin-coated at 3000 RPM on cleaned glass substrates. Next, the samples were annealed at 450 °C in ambient environment to obtain polycrystalline ZnO:N thin films. The final film exhibits thickness ranging from 180 nm to 200 nm. The sol-gel spin-coated ZnO:N thin films were also integrated with commercially available sputtered ITO coated glasses with sheet resistance of 10 Ω/sq and thickness of 185 nm to form metal oxide diodes (Fig. 1(a)). The surface morphology of ZnO:N thin film was scanned by atomic force microscope (AFM), followed by ultraviolet–visible (UV–Vis) spectroscopy for the measurement of optical transmittance. Lastly, the characterization of electronic properties was achieved by Hall Effect system. The diode characteristic and optical properties of ZnO:N based metal oxide diodes were characterized by current-voltage (I-V) measurement system and UV–Vis spectroscopy, respectively. A standard fabrication and characterization setup based on our previous work were adopted to ensure consistent and repeatable results [25,26].

3. Results and discussions

AFM measurements were carried out to determine the morphology of the polycrystalline ZnO:N thin films. The surface morphology of a ZnO:N film is shown in Fig. 1(b), which was prepared using a 20 at.% ammonium acetate concentration. The film exhibits a granular surface morphology with RMS roughness of 9 nm. The distribution of grain sizes across the measured area of ZnO:N film is plotted in Fig. 1(d). From the plot, it can be observed that the most grains are in the size ranging from 27 to 37 nm. The granular structure on the film's surface is similar to that of AZO and GZO films as reported previously [26]. The variation of nitrogen doping concentration has no significant effects on the mean grain size and RMS roughness. For comparison, the AFM image of a sputtered ITO is shown in Fig. 1(c), where the granular structure appears to be finer as compared to that of ZnO:N film. The average mean grain size of ITO film is 35 nm with RMS roughness of 5 nm.

The optical transmittance of ZnO:N (20 at.%) film is plotted in Fig. 2(a). An average transmittance of 86% across the visible region of 390 nm–700 nm is observed, which is of crucial importance in optoelectronic applications. This optical transmittance result is comparable to other ZnO:N films fabricated using MOCVD [27], sputtering [28], and spray pyrolysis [29]. This indicates that the film obtained in this work is of high quality. Using the Tauc method, as described in the previous work [30], the optical bandgap of ZnO:N film is estimated at 3.27 eV, which is smaller than the band gap of the intrinsic ZnO (3.37 eV). The incorporation of the N atoms inside the ZnO lattice may have caused the band gap narrowing [23]. The optical bandgap of ZnO film depends on several parameters such as the method of fabrication, temperature, particle size, and shape [31,32]. Also shown in Fig. 2(a) is the optical transmittance of the sputtered ITO thin films. The ITO thin film exhibits a bandgap at approximately 3.92 eV and an average transmittance of 85% across the visible region. The average optical transmittance of the metal oxide diode based on the integration of ZnO:N (20 at.%) with ITO coated glass is shown in Fig. 2(b). The average optical transmittance of the metal oxide diode is larger than 80% throughout the visible spectra, representing a diode with excellent transparency. The transparency of this device offers great benefits in transparent electronics, which is an emerging technology that is paving the way for large area invisible circuits [33].

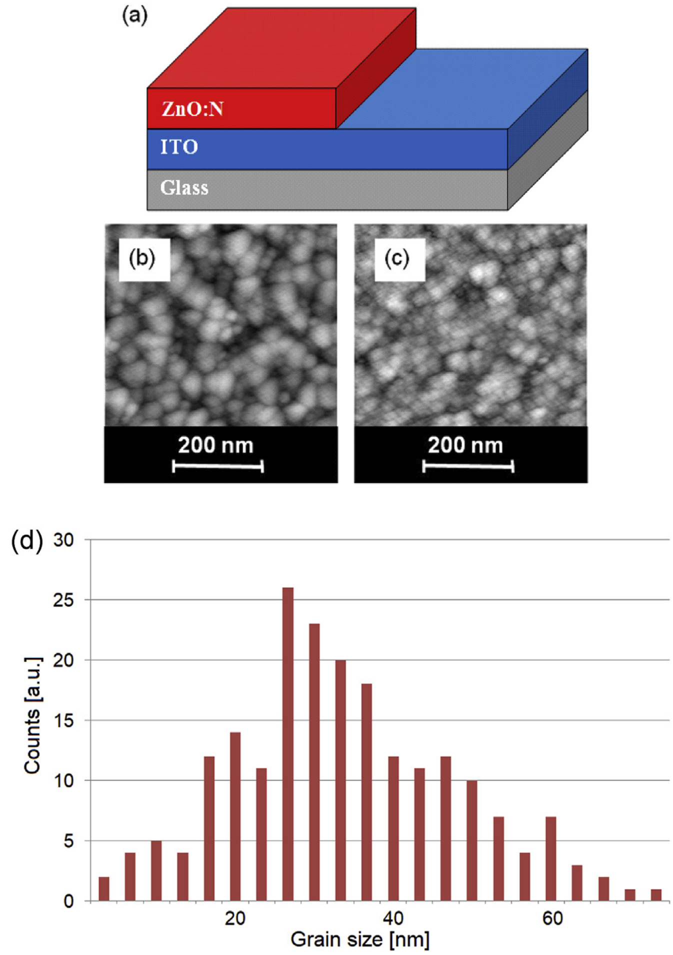

Fig. 1. (a) Cross-section of the transparent diode; surface morphology of (b) ZnO:N (20 at.%) and (c) ITO thin films; (d) grain size distribution of ZnO:N (20 at.%).

The electrical properties of the ZnO:N thin films were characterized by Hall Effect measurements. The ZnO:N film with doping concentration of 20 at %. has a resistivity of 2.92×10^2 Ω-cm, while the ITO film exhibits a significantly higher electrical conductance with resistivity as low as 7.72×10^{-5} Ω-cm. Hall Effect measurement reveals that ZnO:N features a lower carrier density at 1.08×10^{15} cm^{-3}, while ITO has a higher carrier density at