

ELECTRICAL AND OPTICAL PROPERTIES OF COMPOSITE TRANSPARENT CONDUCTING OXIDE THIN FILMS

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Abstract

A single layer composite transparent conducting oxide films (NiO:AZO) was successfully synthesized by a simple and low cost sol-gel solution method. The results indicated that the enhancement of conductivity could be achieved by annealing the NiO:AZO films in N₂/H₂ forming gas. P-type conductivity of NiO:AZO film with resistivity of 1.24×10^{-3} Ωcm, p-type carrier concentration of 4.09×10^{20} cm⁻³, and a Hall mobility of 12.7 cm²/Vs were obtained when molar ratio of NiO is 1.5%. This study opens the possibility of developing high conductive p-type composite transparent conducting oxide for optoelectronics devices.

1 Introduction

Among the transparent conducting oxide (TCO) materials, indium tin oxide (ITO) is the most typical and extensively used. It has a conductivity of 3000–5000 S/cm and transparency of 85–90 % in the visible range. However, the rising cost of indium [1] as well as unsatisfied ITO electrical conductivity raises the significant question of whether this material will be continuously used in future optoelectronic devices. Other alternative TCO candidates, such as aluminum doped ZnO (AZO), and gallium doped ZnO (GZO), suffer from high contact resistivity with p-GaN layer, low carrier concentration and mobility, and low optical transmittance compared with ITO materials. In particular, parasitic resistance in the form of contact resistance is one of the main problems that substantially reduce the overall performance of LEDs. For example, non-ohmic contact with a rectifying property results when AZO is deposited directly onto p-GaN [2, 3]. Other studies have shown that a very low specific contact resistance of 3.4×10^{-4} Ω cm² can be

achieved by using indium doped ZnO (IZO) directly on p-GaN [4]. However, the operation voltage of the LED with an IZO TCE is still high. These studies conclude that serious drawbacks of the current TCO thin films for GaN LEDs with high luminous efficacy remain; these limitations include high contact resistance to p-GaN and low carrier concentration and mobility. Research on developing high performance TCO thin films for GaN LEDs with high luminous efficacy is still limited.

To reduce the interface resistance between TCO and p-GaN, a layer of p-type NiO thin film (possessing nickel vacancies and oxygen interstitials properties) was added between the TCO and p-GaN [5]. This NiO layer was created through thermal annealing of Ni/Au (5 nm/5 nm) metal in an air ambient on p-GaN. In general, GaN LEDs incorporated with TCO thin films as TCEs are fabricated using two separate processes (e-beam evaporation of Ni metal and magnetron sputtering of TCO thin films). To simplify the fabrication process and resolve the unsatisfied electrical performance of current planar AZO thin films in GaN LEDs, it is important to develop a desirable single layer composite TCO (cTCO) thin film which acts as TCE to p-GaN for GaN LEDs with high luminous efficacy. This paper investigates the structural, electrical and optical properties of a single layer cTCO thin film (NiO:AZO) with different molar ratios of NiO doped into AZO by sol-gel solution method.

2 Experimental

2.1 Materials

Zinc acetate dihydrate, aluminum nitrate nonahydrate, nickel chloride hexahydrate, propylene glycol monoethyl ether (PGME) and diethanolamine

(DEA) were obtained from Sigma Aldrich. All chemicals were analytic grade reagents and used without further purification.

2.2 Synthesis of AZO and NiO doped AZO thin films

Undoped AZO and NiO doped AZO (NiO:AZO) thin films were prepared by sol-gel method. First, 0.75 M of zinc acetate dihydrate was dissolved in PGME. To extract a sufficient quantity of zinc acetate dihydrate, equal moles of DEA were dripped and mixed with PGME. AZO precursor solution was prepared by adding the required amount of aluminum nitrate nonahydrate to the above solution such that Al/Zn at an atomic ratio of 1.5%. The mixture was then stirred for 1 h at room temperature, until a clear, transparent AZO solution was formed. The addition of different molar ratios (0.5 %, 1.0%, 1.5%, and 2%) of NiO was added by dissolving nickel (II) chloride hexahydrate into the AZO solution. The prepared solution was then stirred overnight.

To form the thin film, prepared solution was dripped onto a clean glass substrate (Corning glass E2000). The substrates were spin-coated at 3000 rpm for 30 s and placed onto a hotplate at a temperature of 160 °C for 10 min in order to dry the films. After this step, the substrates were put into a 400 °C furnace for 10 min to evaporate the solvent and remove organic residues. The spin coating and drying procedures were repeated 10 times. Finally, the thin film was placed into a tube furnace in Ar at 550 °C for 2 hr to yield the thin film. The sintered samples were finally annealed in tube furnace in N₂/H₂ (95/5) forming gas at 550 °C for 1 hr to reduce NiO to Ni nanoparticle to improve the NiO:AZO film electrical conductivity. The overall process is summarized in a flow diagram in Fig. 1.

2.3 Characterization

The thickness of the films was measured by using surface profiler (Dektak3, VEECO). The crystallinity of the films was estimated by X-ray diffraction (XRD, Bruker AXS D8 Discover) with Cu K α (0.154nm). The electrical and optical properties were measured by Hall effect measurement (HMS-3000, ECOPIA) and UV-Visible spectroscopy (HP 8453, Agilent).

3 Results and Discussions

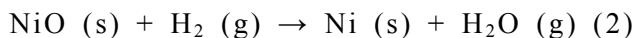
3.1 X-ray diffraction

Fig. 2. shows the XRD patterns of AZO and NiO:AZO thin films with different molar ratios of NiO. All films have mean thickness around 400 nm. The AZO film exhibited polycrystalline wurtzite hexagonal structure matched with JCPDS file no. 36-1451. In the 550 °C N₂/H₂ annealed film, the Bragg peaks corresponding to hexagonal ZnO appear at $2\theta = 32, 34.4, 35.9, 47.2, 57.5, 62$, and 66.7° from the (100), (002), (101), (102), (110), (103) and (112) reflections, respectively. It is noteworthy that the (002) peak was weaker than (100) and (101) peaks. This is because the annealing treatment at 550 °C in N₂/H₂ forming gas made H₂ combined with O atom in the AZO film, resulting in increasing the oxygen defects and lowering the crystallinity of the film. As seen, all films containing NiO doping showed polycrystalline Ni₂O₃ (202) phase at 56.7°. The formation of Ni₂O₃ crystalline phase can be explained by comparing the magnitude of bond enthalpies between Zn-O (159 kJmol⁻¹) and Ni-O (382 kJmol⁻¹) in AZO lattice. The weaker bond enthalpy of Zn-O helps to provide excess oxygen to surrounding Ni atoms in AZO matrix, resulting in the formation of Ni³⁺ ions which subsequently form the Ni₂O₃ phases. The intensity of (202) peak increased with molar ratios of NiO from 0.5 to 1.0 mol% in the films. The initial increase in the intensity of such peaks may be attributed to the increase in the degree of crystallinity by increasing the NiO solution molarity [6]. As NiO molar ratios increased from 1.5 to 2.0 mol%, the intensity of ZnO and Ni₂O₃ peaks decreased. This can be explained by the disturbance of the AZO crystal structure due to the introduction NiO which has cubic phase in the NiO:AZO films. In addition, the diffraction angles of the (002) peaks shifted toward low angle with increasing NiO molar ratios. The grain size of these films as estimated by Debye-Scherrer's formula [7],

$$D = 0.9\lambda/\beta \cos\theta \quad (1)$$

where D is diameter of the crystallites forming the film, λ is the wavelength of CuK α line (0.154 nm), β is the full width at half maximum (FWHM) of the (002) peak in radians and θ is the Bragg angle. Variation of FWHM and grain size with NiO molar ratios in NiO:AZO films were shown in Table 1. Except the NiO:AZO film with NiO molar ratio of 0.5, the grain size of NiO:AZO films is increased

with NiO molar ratio from 1.0 to 1.5 %, and then decreased by increasing NiO molar ratio at 2 mol%. This indicates the deterioration in the crystallinity of the films. The initial increase in grain size is attributed to the formation of Ni nanoparticles from the subsequent gaseous reduction of NiO with hydrogen in the N₂/H₂ annealing process. The overall reaction for gaseous reduction of nickel oxide with hydrogen can be expressed as follows:



The significant decrease in grain size at high NiO molar ratio can be explained by the fact that Ni atoms prefer to locate in grain boundary regions and prevent the grain growth because of the difference of atomic radius in Zn²⁺ (0.074 nm) and Ni²⁺ (0.069 nm). However, the Ni metal peak cannot be detected in the XRD pattern.

3.2 Electrical properties

The electrical resistivity, charge mobility, and charge carrier concentrations of AZO films with various NiO molar ratios of 0%, 0.5%, 1.0%, 1.5%, and 2.0% annealed in N₂/H₂ forming gas were determined by Hall measurements, as shown in Fig. 3. In the case of AZO film annealed at 550 °C in N₂/H₂ forming gas, the main charge carriers in the film are electrons, which possess n-type conductivity and agree with the results reported in the literatures. Results indicates that the charge carriers in NiO:AZO films with NiO molar ratios between 0.5 to 1.5% are electrons whereas the film with NiO molar ratio of 2.0% are holes (Table. 2). With the addition of NiO molar ratio of 0.5 in NiO:AZO film, the further decreases in resistivity is attributed to the formation of Ni₂O₃ phases and reduction of NiO to form Ni nanoparticles from the reduction of NiO with hydrogen in the N₂/H₂ annealing process. It is also noted that NiO:AZO film with 0.5 mol% NiO exhibits the lowest resistivity (2.07×10^{-3} Ωcm) and highest carrier mobility (26.6 cm²/Vs) among NiO:AZO films. From XRD data (Fig. 2.), Ni₂O₃ (202) peaks were identified in all NiO:AZO films. NiO:AZO film with 0.5 mol% of NiO has the highest peak intensity of Ni₂O₃ (202) peak. The increase in carrier concentration is mainly caused by the generation of oxygen vacancies in ZnO matrix, and gaseous reduction of NiO during thermal

annealing in forming gas condition. Further increasing the NiO molar ratios from 0.5 to 1.5% in NiO:AZO films, an increase in carrier concentration and a decrease in carrier mobility were observed. The decrease in carrier mobility is due to the increase in lattice distortion and ionized impurity scattering centers caused by the interstitial small Ni²⁺ ions, the replacement of bigger zinc ions with smaller nickel ions, and the generation of oxygen vacancies both from removal of oxygen atoms from ZnO lattice and reduction of NiO, whereas the increases in carrier concentration is due to the generation of defects. In this study, NiO:AZO film with 1.5 mol% NiO reveals the highest carrier concentration and lowest carrier mobility. At NiO:AZO film with 2.0 mol% NiO, the carrier concentration and hole mobility is 3.15×10^{18} cm⁻³ and 12.7 cm²/Vs. The low carrier concentration is due to the compensation of electron carriers by the increases of Ni²⁺ vacancies at high NiO mol% in the NiO:AZO film. In general, the increase in resistivity with increasing the NiO mol% in NiO:AZO films is attributed to both the decreases in carrier mobility and carrier concentration. Thus, the superior electrical properties can be attributed to the generation of oxygen defects, the formation of Ni₂O₃ phases, and the formation of conductive metallic Ni nanoparticles located within the AZO lattice during the annealing process of N₂/H₂ forming gas.

3.3 Optical properties

The transmittance spectra of AZO and NiO:AZO films at different NiO molar ratios are illustrated in Fig. 4. It is obvious that the optical transmittance of these films is influenced by the molar ratio of NiO. The transmittance decreases with increasing molar ratio of NiO in the NiO:AZO thin films. The appearance of black color in NiO:AZO films indicates the presence of Ni₃O₄ phase (which is verified in the XRD pattern) and Ni nanoparticles. The average optical transmittance of the sample with 0.5 molar ratio of NiO is above 70 %. All NiO-AZO thin films except the film with 1 mol% of NiO exhibit interference fringes of the spectra with shallow valleys, indicating smooth surfaces in the films thin films [8].

4 Conclusions

NiO:AZO films on glass substrate with various NiO molar ratios have been synthesized by sol-gel

solution method. The results indicated that the enhancement of conductivity could be achieved by annealing the NiO:AZO films in N₂/H₂ forming gas. P-type conductivity of NiO:AZO films with resistivity of 1.24×10^{-3} Ωcm, p-type carrier concentration of 4.09×10^{20} cm⁻³, and a Hall mobility of 12.7 cm²/Vs were obtained when NiO molar ratio of 1.5%.

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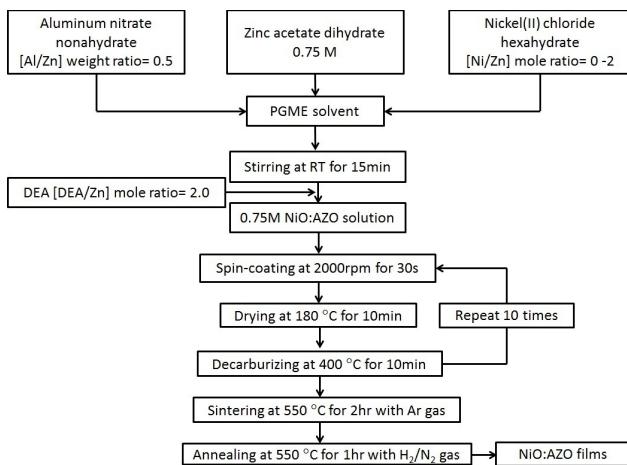


Fig. 1. Flow chart of NiO:AZO sol-gel thin films.

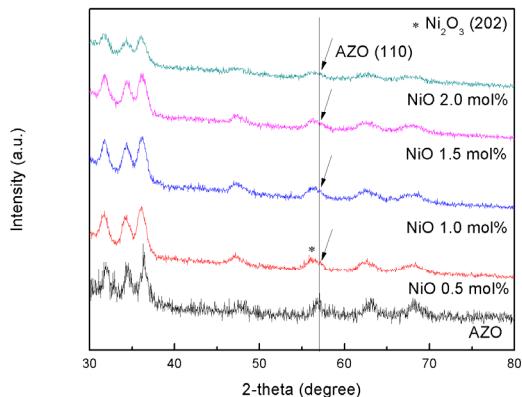


Fig. 2. XRD patterns of the NiO:AZO films with molar ratios of 0%, 0.5%, 1.5%, and 2.0%.

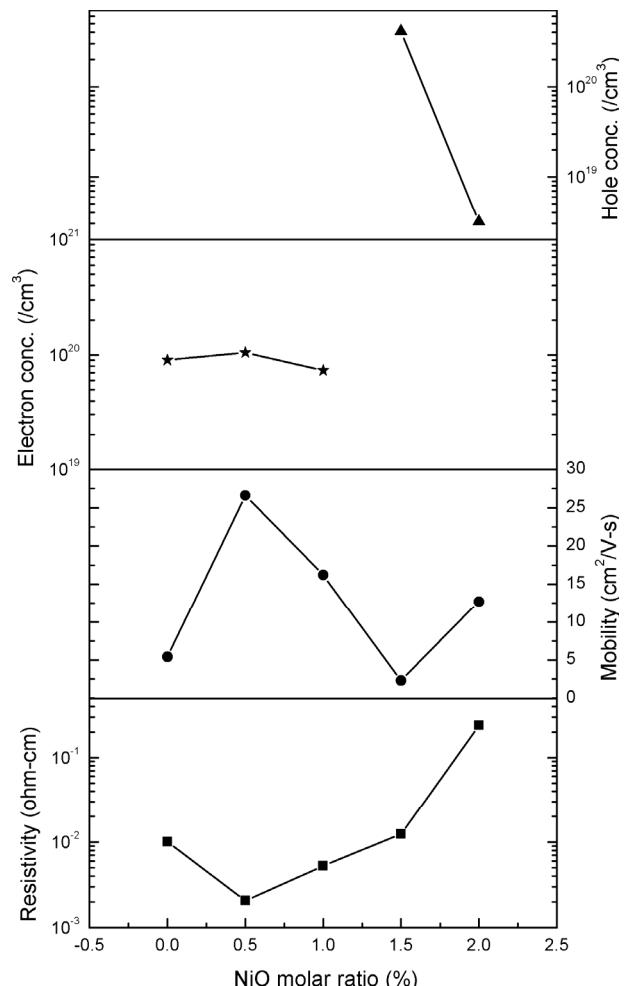


Fig. 3. Electrical properties of NiO:AZO films with various molar ratios of NiO.

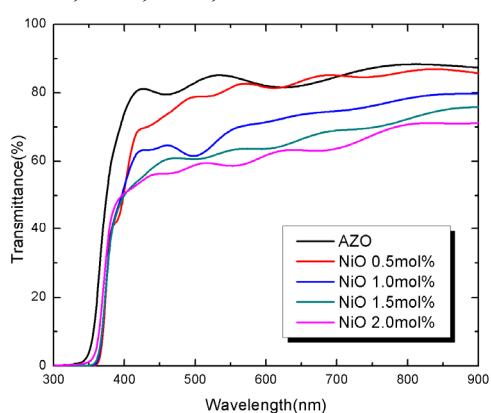


Fig. 4. Optical transmittance spectra of AZO and NiO:AZO with various molar ratios of NiO.

Table 1. Comparison of structural parameters of AZO and NiO:AZO thin films

NiO molar ratio (%)	(002) 2θ	FWHM	Grain size (nm)
0	34.46	0.63	23
0.5	34.24	0.71	20
1.0	34.33	0.63	23
1.5	34.34	0.39	36
2.0	34.27	0.79	18

Table 2. Electrical properties of AZO and NiO:AZO with different NiO molar ratios

NiO molar ratio (%)	ρ ($\Omega \text{ cm}$)	μ (cm^2/Vs)	n ($/\text{cm}^3$)	Type
0	1.01×10^{-2}	5.42	9.05×10^{19}	n
0.5	2.07×10^{-3}	26.6	1.05×10^{20}	n
1.0	5.25×10^{-3}	16.2	2.13×10^{20}	n
1.5	1.24×10^{-2}	2.33	4.09×10^{20}	p
2.0	2.39×10^{-1}	12.7	3.15×10^{18}	p