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Carbon nanotube/indium tin oxide hybrid transparent conductive film: Effect of nanotube diameter



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ABSTRACT

Hybrid transparent conductive films (TCFs) based on indium tin oxide (ITO) and carbon nanotubes (CNTs) are prepared through a sol–gel dip coating method. The effect of CNT diameter on optoelectrical properties of TCF is investigated. The surface roughness and grain size are decreased and the optical transmittance is increased with CNT diameter. The existence of bundles in smaller CNTs is the main reason for lower transmittance in these samples. In terms of electrical resistivity, the large diameter CNT incorporated ITO film shows lower sheet resistance than bare ITO film at high enough film thicknesses. It seems that the large diameter CNT incorporation in ITO matrix can remarkably reduce the microcrack formation, especially at higher thicknesses, and act as nanobridges when microcracks are formed. Furthermore, the sensitivity of ITO film to thermal cycling is dramatically enhanced with these CNTs. In addition, the figure of merit of ITO film is considerably improved with large diameter CNT incorporation.

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1. Introduction

Transparent conductive films (TCFs) are widely used in various optoelectronic devices such as liquid crystal displays, thin film solar cells, touch panels, e-papers, and flexible displays [1–4]. So far different types of TCFs have been introduced, including binary oxides (indium tin oxide (ITO), fluorine tin oxide (FTO), aluminum zinc oxide (AZO)) [5], ternary oxides (Cd_2SnO_4 , $\text{Zn}_2\text{In}_2\text{O}_5$, and Zn_2SnO_4) [6], conducting polymers (poly(3,4-ethylene dioxythiophene/polystyrene sulfonate (PEDOT/PSS) and polyaniline (PANI)) [7], and new generation materials (carbon nanotubes (CNTs), graphene, and metal grids) [8]. Among them, tin doped indium oxide (ITO) is widely used due to its high transparency, low electrical resistivity, and proper chemical stability. However, the expensiveness and brittleness of ITO films strongly limit their application [9–11].

The expensiveness of these films results from very high price of indium raw material as well as high production cost of ultrahigh vacuum deposition systems [12,13]. The production cost can be reduced by using chemical deposition methods such as spray pyrolysis and sol–gel. The sol–gel method with the advantages of inexpensiveness, high yield, ability to form composite structure,

and non-vacuum apparatus seems to be a promising candidate for ITO preparation with high performance per cost [14,15]. The brittleness of ITO films causes microcrack formation during film deposition, which strongly affects the charge transport properties and optical transmittance [16]. The microcrack formation can be entirely neutralized by incorporating second conductive tough phase in ITO matrix such as CNTs, graphene, conductive polymers, or metal grids. Although graphene sheets have very low resistivity and very high mobility (μ), they should be fully reduced from graphene oxide to show their appropriate electrical properties [17]. Also, the suitable dispersion of graphene in ITO sol and defect spreading in graphene structure after high temperature calcination still remain as challenges in this composite [18]. The problems for conductive polymers are their high electrical sensitivity to humidity, UV, and thermal exposure [19]. The major bottlenecks for metal grids are their surface sensitivity to oxidation and high photon scattering [20]. Outstanding chemical, optical, electrical, and mechanical properties of CNTs represent them as a promising substitute for TCFs [21]. However, the relatively low visible transparency of CNT films, low density of CNT films, and charge transport barrier at the CNT/CNT junctions limit their application as TCF [22].

Although CNTs have much lower carrier concentration than ITO films ($\sim 10^{17}/\text{cm}^3$ for CNT and $10^{20}/\text{cm}^3$ for ITO), they show substantially higher μ [23]. Since the conductivity (σ) of a film is directly related to the number of charge carriers and μ , the σ can

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be tuned by either doping or using high mobility charge transport channels. The figure of merit for TCF film, which can be described by σ/α ratio (α is absorption coefficient), is dramatically reduced by increasing the number of charge carriers as a result of scattering [24]. Therefore, enhancing the charge mobility would be a more efficient strategy for improving the σ of ITO film without affecting the figure of merit. CNTs with high mobility may act as transport channels in ITO matrix without affecting the film transparency in visible region. Furthermore, they may reduce the microcrack formation in ITO matrix and lead to higher σ .

Most composite TCFs are based on conductive polymers such as PEDOT:PSS with CNTs [25–27]. Making a composite based on ITO and CNT is rarely reported, (for example, ITO was deposited on CNT layer to make multilayer ITO/CNT film) [28]. However, incorporation of CNTs in ITO thin film has never been reported. Since the CNT diameter can entirely affect its chemical, thermal, and electrical properties [29–31], in this research, CNTs with different diameters are incorporated in sol–gel synthesized ITO thin films and the effects of CNT diameter on optical and electrical properties of ITO/CNT hybrid electrodes are investigated.

2. Experimental

2.1. Materials

Anhydrous indium chloride (InCl_3 , Alfa Aesar, 99.99%), tin chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, Merck, 98%), acetylacetone (AcAc, Merck, 99%), absolute ethanol (EtOH, Merck, 99%), sulfuric acid (H_2SO_4 , Merck, 98%), and nitric acid (HNO_3 , Merck, 68%) were used as received without further purification. SWCNT (outer diameter < 2 nm, 95% purity, 60% single-wall, 350–400 m^2/g), MWCNT-10 (outer diameter < 10 nm, 97% purity, 250–300 m^2/g), and MWCNT-60 (outer diameter 40–60 nm, 97% purity, 130–160 m^2/g) were purchased from Shenzhen Nanotech port. Deionized water (DIW, 18.2 $\text{M}\Omega$) was used in all experiments.

2.2. CNT functionalization

CNTs were subjected to ultrasonication in concentrated HNO_3 : H_2SO_4 (3:1 vol%) for 10 min. Then, the mixture was refluxed at 80 °C for 1 h. Next, the mixture was diluted and washed with DIW by using centrifugation several times to ensure removal of anions. The product was dried at 60 °C and kept dry until use.

2.3. ITO/CNT sol preparation and film deposition

ITO sol preparation was previously reported [32]. Briefly, 0.2 mol InCl_3 was dissolved in AcAc and the resultant solution was refluxed at 85 °C for 1 h. Then, the required amount of SnCl_2 was dissolved in EtOH. The Sn/(In+Sn) ratio was 6% in atomic ratio. The InCl_3 solution was added to the SnCl_2 solution and refluxed at 85 °C for another 1 h. For ITO/CNT sol, 0.02 g/L SWCNT was added to SnCl_2 solution and sonicated for 30 min. The other steps were similar to those of ITO sol preparation. All the sols were aged for 24 h before deposition. Various amounts of SWCNT, 0.01, 0.02, and 0.04 g/L, were considered to investigate the effect of CNT content on optoelectrical properties of the composites. The same amounts of MWCNT-10 and MWCNT-60 were also considered.

Before film deposition, the glass substrates were thoroughly cleaned ultrasonically in DIW and EtOH. Then, the prepared sols were deposited on substrates by means of the dip coating method. The withdrawal speed was 120 mm/min. Then, the films were dried at 350 °C for 10 min. The dip coating and drying processes were repeated several times to reach the desired thickness. Finally, the films were annealed at 600 °C for 1 h.

2.4. Characterization

The surface functional groups of CNTs were investigated by a Fourier-transformed infrared (FTIR) spectrophotometer, Bruker TENSOR27, in transmittance mode at 400–4000 cm^{-1} with KBr as blank. Raman spectra were recorded using a BRUKER (SETERRA, spectral resolution < 3 cm^{-1}) micro-Raman spectrometer equipped with a confocal microscope. The excitation wavelength was the 785 nm line of an argon laser operating at the power of 25 mW. The CNTs debundling and interfaces were studied by means of a high resolution transmission electron microscope (HRTEM), Philips CM30, 300 kV. The morphology and thickness of the films were investigated by field emission scanning electron microscopy (FESEM), Hitachi S4160. The transmission spectra and optical band gap in the UV–vis–NIR range were determined on a UV–vis spectrophotometer PG instrument, model T80+. The resistivity of the films was measured by a four-point probe method Keithly model 196 Sys-DMM2 at room temperature.

3. Results and discussion

CNTs should be fully debundled before incorporation in ITO matrix. For this purpose, all three types of CNTs were subjected to acid treatment. This process not only breaks down the nodes in CNT bundles, but also develops the carboxylic functional groups on the sidewalls of CNTs [33]. These groups make CNTs hydrophilic and prevent rebundling of CNTs when placed in aqueous media. The FTIR spectra of functionalized SWCNT, MWCNT-10, and MWCNT-60 are shown in Fig. 1. The bands around 3580, 3512, 3450, and 1640 cm^{-1} are assigned to hydroxyl groups of free O–H, O–H band in carboxylic groups (–COOH), O–H stretching, and O–H bending of adsorbed water, respectively. The bands around 3265 and 1417 cm^{-1} are assigned to alkane groups (–CH₃ and –CH₂–, respectively). Also, the bands around 648 and 505 cm^{-1} are linked to NO_3^- and HSO_4^- , respectively. The bands at around 1787, 1571, and 1207 cm^{-1} correspond to the C=O, C=C, and C–O groups, respectively [34]. The FTIR spectra confirm the presence of hydroxyl and carboxylic groups on the sidewalls of CNTs after acid treatment. The C–O stretching band in MWCNT-60 is higher than that of SWCNT and MWCNT-10. The defected outer walls of MWCNT-60 cause the formation of higher amount of carboxylic groups on the surface of these nanotubes.

The dispersibility of different types of CNTs was investigated in AcAc based acidic ITO sol by comparing the extractability parameter of CNTs. The extractability parameter of CNT suspension is the CNT concentration in suspension after 7 days per CNT concentration in as prepared suspension, which can be determined from the characteristic 253 nm wavelength peak in UV–vis spectra of suspension [35]. The extractability parameter of SWCNT,

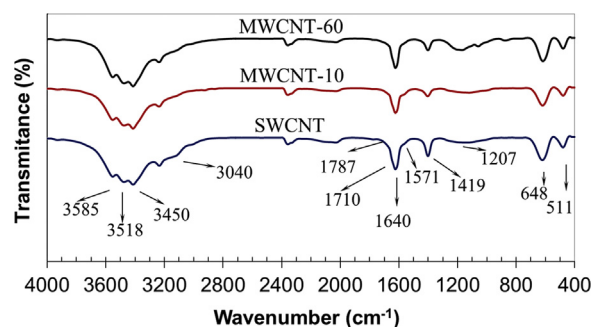


Fig. 1. FTIR spectra of functionalized SWCNT, MWCNT-10, and MWCNT-60.

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