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A Comparative Study of Single- and Multi-Walled Carbon Nanotube Incorporation to Indium Tin Oxide Electrodes for Solar Cells

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***Abstract*—**Alternative electrode materials for optoelectronic devices have been widely investigated in recent years. Since indium tin oxide (ITO) is the most preferred transparent conductive electrode, producing ITO films by simple and cost-effective solution-based techniques with enhanced optical and electrical properties has great importance. In this study, single- and multi-walled carbon nanotubes (SWCNT and MWCNT) incorporated into the ITO structure to increase electrical conductivity, mechanical strength, and chemical stability. Carbon nanotubes (CNTs) were firstly functionalized by acid treatment (HNO_3:H_2SO_4), and the thermal resistance of CNTs after functionalization was determined by thermogravimetric analysis (TGA). Thin films were then prepared by spin coating technique and characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), four-point probe measurement system and UV-Vis spectrophotometer. The effects of process parameters were compared for ITO, MWCNT-ITO, and SWCNT-ITO films. Two factors including CNT concentration and annealing temperature were considered. The UV-Vis measurements demonstrated that the transmittance of ITO films was 83.58% at 550 nm, which was decreased depending on the concentration of CNT dopant. On the other hand, both CNT dopants provided an enhancement in the crystalline structure and electrical conductivity. Due to compatible diameter and better dispersibility of SWCNTs in the ITO solution, the best result in terms of electrical conductivity was obtained by SWCNT-ITO films with the 0.1 g/L SWCNT dopant concentration and heat-treatment at 550 °C for 1 hour.

***Keywords*—**CNT incorporation, ITO electrode, spin coating, thin film.

I. Introduction

ONE of the key components of the solar cells is a transparent electrode layer since it may remarkably influence the cell performance by transmitting incoming photons to the active layer with high efficiency. ITO is a commonly used transparent conductive electrode because it shows low sheet resistance (<200Ω/sq) and high transmittance (>80%) in the visible region [1] owing to its wide bandgap more than 3.75 eV [2]. Commercial ITO films are mostly prepared by vacuum-based magnetron sputtering technique which can be very efficient to obtain low sheet resistance; however, this causes a dramatic increase in the production cost [3]. Because of that, there have been several attempts in recent years to produce ITO films by low-cost and simple techniques as well as to optimize the process for large-scale productions by solution-based techniques [4], [5] or replace with novel electrode materials [6]. It is unfortunate that the solution based techniques are applied to produce ITO films, and problems such as the brittle nature of ITO and high sheet resistance can be observed [8]. CNT is one of the featured alternatives to ITO electrode owing to flexibility, chemical stability and relatively low-cost [7]. However, different from the individual CNT, the conductivity of the CNT film is affected by the high contact resistance in the junction points of the tubes which requires post-treatment such as acid treatment [9]. As a consequence, the use of ITO or CNT as the transparent conductive electrode brings about different advantages and disadvantages. For this reason, it is possible to produce highly efficient electrode material for next-generation optoelectronics by CNT doping into ITO structure instead of using separately [10].

In this study, it was expected that, when CNTs are doped into the ITO structure, they will act as a nano-bridge which increases conductivity and stability. Because of that, it was aimed at not only improving the mechanical properties of ITO by doping with single-walled carbon nanotube (SWCNT) and multi-walled carbon nanotube (MWCNT) into ITO structure and reducing the micro-crack formation but also increasing the electrical conductivity due to the high mobility of CNTs.

II. Experimental

A. Materials

For the preparation of ITO solution, anhydrous indium(III) chloride ($InCl_3$, Alfa Asesar, 99.99%), tin(II) chloride dihydrate ($SnCl_2.2H_2O$, Merck, 98%), acetylacetone (Merck, 99%) and absolute ethanol (Merck, 99%) were used. MWCNTs (outer diameter:13 nm, >95% purity) were purchased from Baytubes, Bayer and SWCNTs (outer diameter: 1.55 nm, >90% purity) were purchased from carbon solutions. sulfuric acid (H_2SO_4, Merck, 98 %) and nitric acid (HNO_3, Merck, 65 %) were used for the functionalization of CNTs.

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B. Functionalization of CNTs

SWCNTs and MWCNTs were functionalized with the 0.6 M HNO_3 and H_2SO_4 solutions in the volumetric ratio of 3:1, respectively. CNTs were refluxed with the acidic solution for 1 hour at 120 °C. After cooling down to room temperature, the solution was filtered and washed several times with the DI water, and the functionalized CNTs were allowed to dry. Finally, the thermal resistance of CNTs was measured by TGA.

C. Preparation of ITO and CNT-ITO Solutions

To prepare the ITO solution, firstly 0.5 M $InCl_3$ was dissolved in acetylacetone and refluxed at 85 °C for 1 hour. Simultaneously, 0.5 M $SnCl_2.2H_2O$/ethanol solution was stirred at room temperature for 40 minutes. After cooling, the indium solution was combined with the tin solution in 9:1 (In:Sn) ratio by mass and refluxed again at 85 °C for 1 hour. The ITO solution was obtained after aging for 1 day.

Two different CNT concentrations of 0.05 g/L and 0.1 g/L were used for the preparation of CNT-doped ITO solution. The CNT-ITO solution was mixed with the ultrasonic homogenizer for 40 minutes, and the resultant solution for coating was obtained.

D. Preparation of Thin Films

Bare glass substrates were cleaned by ethanol, boiled DI water, isopropyl alcohol and DI water in the ultrasonic bath, respectively. After drying, the substrates were subjected to UV Ozone Cleaner. Subsequently, ITO and CNT-ITO solutions were coated onto cleaned bare glass substrates by the three-step solution-based spin coating method. These steps consisted of spreading the solution at 500 rpm for 5 s, coating at 3000 rpm for 30 s and lastly drying the film at 4000 rpm for 30 s. The substrate was coated for 7 times, and each step the film was dried at 200 °C. Effects of process parameters such as CNT concentration (high:0.1 g/L, low:0.05 g/L) and annealing temperature (high:550 °C, low: 500 °C) were investigated for ITO, MWCNT-ITO, and SWCNT-ITO films. Thin films were characterized by scanning SEM, XRD, four-point probe measurement system (5 measurements), and UV-Vis spectrophotometer.

III. Results and Discussion

A. Characterization of CNTs

Since the thermal resistance of CNTs is important for the determination of annealing temperature, the functionalized CNTs were investigated by TGA. Derivative thermogravimetric curves of the MWCNT and SWCNT, which are given in Fig. 1, indicate that the maximum temperatures that CNTs resist are 600 and 560 °C, respectively. Also, both CNT samples did not show amorphous carbon degradation in the range of 200-400 °C. The peak at 650-700 °C in the DTG curve of the SWCNT sample observed due to the functionalization because the expansion of the peaks, constriction, increase in intensity or multiple peak formation can be observed depending on the functional groups [11].

B. Surface Properties of Thin Films

Fig. 2 shows the SEM images in the 100,000x magnification of ITO (Fig. 2 (a)), MWCNT-ITO (Fig. 2 (b)) and SWCNT-ITO (Fig. 2 (c)) thin films which were doped with 0.1 g/L concentration CNT and heat treated at 500 °C for 1 hour to observe properly CNTs. It was observed that the MWCNTs were not homogeneously distributed during the measurements and caused the aggregation of the ITO particles in the region where they were found.

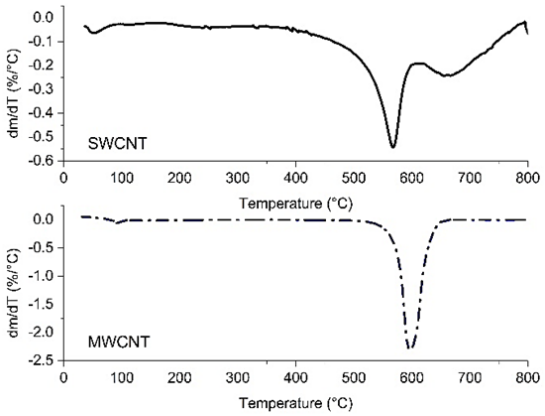

Fig. 1 DTG analysis of MWCNT and SWCNTs

This is because the MWCNT dispersion could be carried out in the desired manner both during solution preparation and film production. On the contrary, SWCNTs dispersed easily in solution in comparison with MWCNTs. Therefore, SWCNTs are homogeneously distributed on the film surface. At the same time, it was observed that ITO crystallized together with SWCNTs as cylindrical structures as a result of doping.

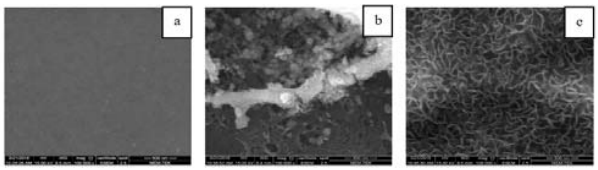

Fig. 2 SEM images of ITO, MWCNT-ITO, and SWCNT-ITO films

C. Crystal Structure of Thin Films

XRD patterns of ITO and CNT-ITO (0.1 g/L) hybrid electrodes annealed at 550 °C for 1 hour are given in Fig. 3 since the higher annealing temperature provides better crystallization for ITO. The peak intensity for the hybrid electrodes increased and the cubic bixbyite structure of the ITO remained the same which indicates that the CNT doping did not cause any defect in the lattice structure but also improved the crystallization. The clarification of the peaks in the direction of (211) and (431) at 22 and 46 ° also supports the improvement of the crystallization.

Mean crystalline size of ITO was calculated by the Debye-Scherrer equation, based on the (222) peak and was found as 30.86 nm. While MWCNT dopants increased the mean crystalline size to 34.29 nm probably because of clustering,

SWCNTs decreased this value to nearly 21.43 nm due to their small diameter.

D.Electrical Properties of Thin Films

The change of the average sheet resistance of ITO reference electrode and MWCNT-ITO hybrid electrodes due to various conditions such as dopant concentration, annealing time and temperature are given in Table I.

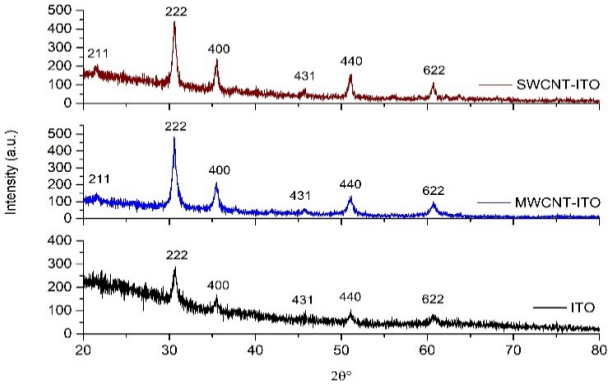

Fig. 3 XRD patterns of ITO, MWCNT-ITO, and SWCNT-ITO films

TABLE I
SHEET RESISTANCE OF ITO AND MWCNT-ITO THIN FILMS

Sample	MWCNT doping (g/L)	Annealing temperature (°C)	Annealing time (min)	Sheet resistance (kΩ/sq)
ITO	-	500	60	9.16
MWCNT-ITO	0.05	500	60	7.50
MWCNT-ITO	0.1	500	60	7.48
ITO	-	550	60	3.93
MWCNT-ITO	0.05	550	60	3.46
MWCNT-ITO	0.1	550	60	4.20

TABLE II
SHEET RESISTANCE OF ITO AND SWCNT-ITO THIN FILMS

Sample	SWCNT doping (g/L)	Annealing temperature (°C)	Annealing time (min)	Sheet resistance (kΩ/sq)
ITO	-	500	60	9,16
SWCNT-ITO	0,05	500	60	5,36
SWCNT-ITO	0,1	500	60	4,94
ITO	-	550	60	3,93
SWCNT-ITO	0,05	550	60	2,96
SWCNT-ITO	0,1	550	60	2,48

As can be seen from Table I, increasing the heat treatment temperature caused the sheet resistance to decrease. However, increasing the amount of MWCNTs led to the opposite effect.

This is due to the fact that the nanotubes were not able to incorporate into the micro-cracks, which was also observed by the SEM image in Fig. 2 (b).

The results of average sheet resistance measurements are given in Table II depending on the dopant concentration and heat treatment temperature applied to the ITO reference electrode and SWCNT-ITO hybrid electrodes. The data given in Table II indicate that when each of the main parameters increased, the sheet resistance decreased owing to the high electrical conductivity of well-incorporated SWCNTs in the ITO lattice and better crystallization at the higher annealing temperature.

E. Optical Properties of Thin Films

The optical transmittance of the thin films annealed at 500 °C for 1 hour is given in Fig. 4. ITO thin films showed the highest optical transmittance with a value of 83.58% at 550 nm with respect to the UV-Vis results. After doping with CNT, the optical transmittance was reduced depending on the amount of doping. For MWCNT-ITO and SWCNT-ITO hybrid films with a concentration of 0.05 g/L CNT, the optical transmittance at 550 nm was determined as 78.28% and 72.10%, respectively. Also, optical transmittance was measured as 68.04% (MWCNT-ITO) and 65.35% (SWCNT-ITO) for the samples with a concentration of 0.1 g/L CNT in the visible region at 550 nm. MWCNT-ITO thin films showed higher optical transmittance compared to other doped films which can be attributed to the nonhomogeneous distribution of MWCNTs at each part of the film due to the difficulties encountered during solution preparation. On the other hand, the uniform distribution of SWCNTs on the surface caused a decrease in the optical transmittance of the film.

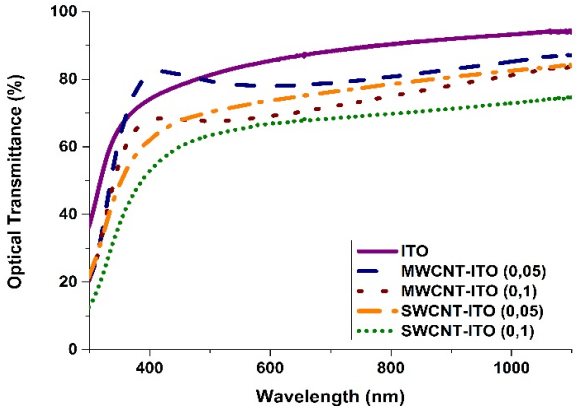

Fig. 4 UV-Vis Spectra of ITO, MWCNT-ITO and SWCNT-ITO films with different CNT concentration

IV. CONCLUSION

In this study, ITO and CNT doped ITO thin films prepared by the spin coating technique. Effects of different parameters such as dopant concentration and annealing temperature were investigated. MWCNT and SWCNT dopants improved the crystallization of ITO structure. Considering the SEM images, whereas the dispersion of acid-functionalized MWCNTs was difficult in ITO solution, acid-functionalized SWCNTs were dispersed homogeneously and reduced the sheet resistance by serving as a nanobridge which conducts electrons in the lattice. Since the maximum temperature was measured by TGA as 560 °C that SWCNTs could resist and the crystallization of solution-based prepared ITO requires high temperature, the optimum annealing temperature was determined as 550 °C. In addition, the lowest sheet resistance was obtained with the ITO doped by 0.1 g/L SWCNT sample

at 550 °C for 1 h annealing. At these conditions, the sheet resistance of ITO reduced to 2.48 kΩ/sq from 3.93 kΩ/sq.

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