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# Incorporation of carbon nanotube into direct-patternable ZnO thin film formed by photochemical solution deposition

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**Abstract**

Direct-patterning of ZnO hybrid films containing MWNT was realized without using photoresist and dry etching. Photosensitive 2-nitrobenzaldehyde was introduced into the solution precursors as a stabilizer and contributed to form a cross-linked network structure during photochemical reaction. According to the incorporation of multi-walled nanotube (MWNT) into ZnO films, the transmittance of ZnO hybrid film containing MWNT did not change but the sheet resistance was improved due to the enhancement of charge mobility due to π-bonding nature of MWNT. These results suggested a possibility that a micro-patterned system can be fabricated relatively easily and without high-cost processes, for example, by conventional etching procedure.


*Keywords:* A. Sol–gel processes; B. Composites; C. Electrical properties; C. Optical properties

## 1. Introduction

Indium tin oxide (ITO) is widely used as a transparent conducting oxide (TCO), but it shows many drawbacks such as rarity, high cost, exhaustion possibility, and instability in the hydrogen plasma [1]. Recently, zinc oxide (ZnO) has attracted much attention as a TCO of solar cell and more recently transparent thin-film device, because it is non-toxic, low cost, high abundance, and especially stable in the hydrogen plasma comparing with ITO [2]. ZnO exhibits numerous characteristics that may enable its efficient utilization in these novel devices. ZnO is an n-type semiconductor with a wide band gap of 3.37 eV [3]. It has therefore been considered a promising candidate as a TCO material for the development of light-emitting structures and solar cells. However, for applying to the electrical devices, an improvement in electrical property of ZnO film has been absolutely required. Recently, the hybridization with carbon nanotube (CNT) has been widely investigated [4–8]. Multi-wall and single-wall carbon nanotube (MWNT and SWNT, respectively) are relatively chemically inert, exhibit excellent electrical and thermal conductivity, and show nonlinear optical properties and superior mechanical strength [9].

For the fabrication of electronic circuit, a micro-patterning process is inevitably introduced but conventional dry-etching process is accompanied by physical defects generation, properties degradation, pollution due to hazardous-material usage, and so on. However, if we use photosensitive additives in thin-film deposition, we do not need either photoresist or dry etching for microscale patterning, because photosensitive additive acts as the negative type photoresist. So, we can avoid etching damage and many other problems from dry etching.

In this work, we investigated the optical and electrical properties of ZnO film by the incorporation of MWNT into ZnO film. Furthermore, direct-patterning of ZnO hybrid film containing MWNT was carried out to overcome the dry-etching damage and simplify the micro-patterning procedure by using photosensitive additive and UV exposure.

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## 2. Experimental procedure

ZnO thin films were prepared by sol–gel process. Zinc acetate dihydrate ($Zn(CH_3COO)_2\cdot 2H_2O$), 2-methoxyethanol, and monoethanolamine (MEA) were used as starting Zn precursor, solvent, and sol stabilizer, respectively. Zinc acetate dihydrate was dissolved in 2-methoxyethanol and MEA was added for stabilization at room temperature and 2-nitrobenzaldehyde (NBAL) was introduced as a photosensitive additive. MWNT (CM-95, ILJIN NANOTECH) was used for a MWNT source. The concentration of zinc acetate dihydrate was 0.5 M. 0.025, 0.05, and 0.1 wt% MWNT was incorporated into ZnO photosensitive solution. The mixed solution was stirred at room temperature for 3 h. The MWNT in mixed solution was dispersed by sonicator and then spin-coated on glass (Corning 1737) substrate at 2000 rpm for 20 s. For direct-patterning of the film, the spin-coated film was exposed to UV light with 365 nm wavelength. Then the UV exposed film was washed with 2-methoxyethanol for removing unexposed area of the film. After washing, the films were dried at 250 °C for 5 min on a hot plate to remove the solvent and organic residuals. This spin-coating and preheating procedure was repeated five times to obtain the desired thickness. After final deposition of the layer, the film was annealed in a tube furnace under air-atmosphere at 400, 500, and 600 °C for 1 h. The crystallinity was analyzed by using X-ray diffractometer (XRD, D/MAX-2000, Rigaku) with Cu Kα radiation. The sheet resistance of film was measured by using four-point probe. Optical transmittance measurements were carried out by using a UV–vis–NIR spectrophotometer. For surface chemical bonding state of film, X-ray photoelectron spectroscopy (XPS, ESCALAB 220i-XL, VG Scientific) was used with an Al Kα monochromatic source.

## 3. Results and discussion

The possibility of direct-patterning of ZnO hybrid film containing MWNT by removing the area unexposed to UV using a solvent was examined. The direct-patterned film was dried at 250 °C for 5 min and the result is given in Fig. 1. In the optical micrograph, the relatively bright area (whitish area) corresponds to ZnO hybrid film containing MWNT and the relatively dark area (bluish area) corresponds to glass substrate. The reaction stage of photolysis of photosensitive additive is explained as follows. Metal ion in metal–alkoxide is acid and aldehyde is base then they are strongly attracted to each other. From this attraction, hydrolysis and condensation reactions are limited. After exposure to UV, intermolecular proton transfer and hydrogen abstraction are happened then 2-nitrosobenzoic anion is produced. Metal ion in metal–alkoxide formed by condensation reaction attracts to nitryl ligand and a cross-linked structure would be formed. This cross-linked structure is no more fluid state and it will not be removed by dissolving at the next solvent-rinsing step. From the result of Fig. 1, a direct-patterning process was proved to enable to fabricate a micro-patterned system without using either photoresist or dry-etching process.

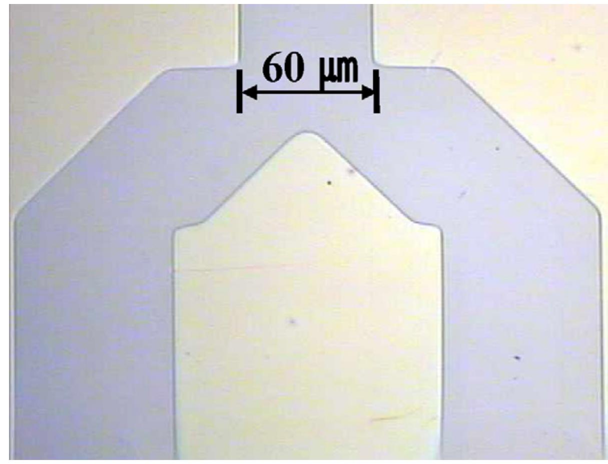


Fig. 1. Optical micrograph of ZnO hybrid film containing MWNT dried at 250 °C for 5 min.

Fig. 2 presents XRD patterns of ZnO film annealed at from 400 to 600 °C with an interval of 100 °C and ZnO hybrid films containing various amount of MWNT annealed at 400 °C. All the films were crystallized with a random orientation growth of hexagonal wurtzite structure [10]. Generally, the nucleation and growth of film is strongly affected by the orientation of

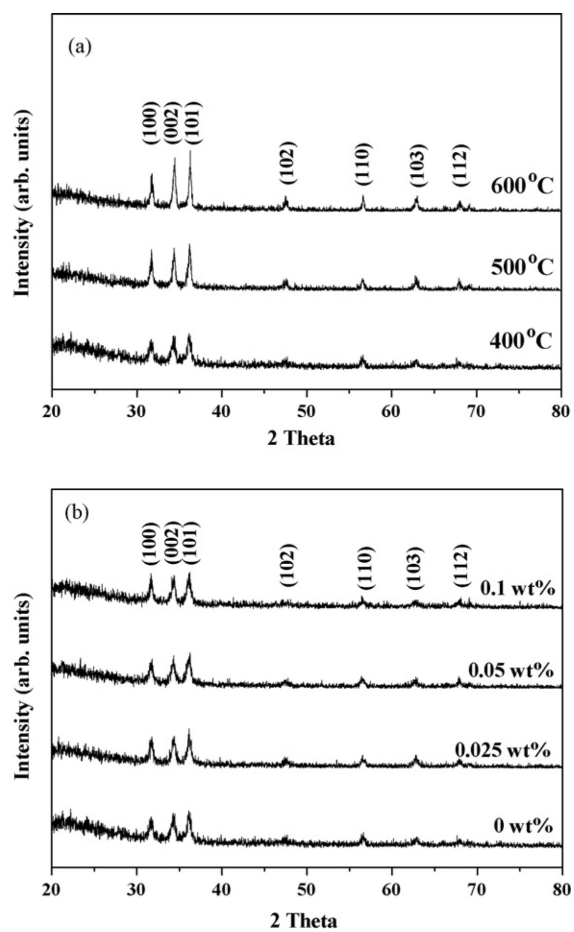


Fig. 2. XRD patterns of (a) ZnO films annealed at 400, 500, and 600 °C and (b) MWNT-incorporated ZnO films annealed at 400 °C with MWNT contents of 0, 0.025, 0.05, and 0.1 wt%.

substrate [11,12]. In our case, because ZnO and ZnO hybrid films was grown on amorphous glass substrate, all the films did not show any preferred orientation. According to increase of annealing temperature in the case of ZnO film, the crystallinity of ZnO film was not remarkably enhanced but slightly increased. It means that the temperature of phase formation is enough for ZnO film at 400 °C. In case of ZnO hybrid films containing MWNT, the presence of MWNT did not affect on the crystallization of ZnO film. Yu et al. [13] reported that MWNTs are very stable and no thermal decomposition takes place in the temperature range of 30∼1000 °C. In our experimental condition, the crystallinity and growth orientation of ZnO hybrid films containing MWNT was not changed, namely MWNT did not affect the crystallization of ZnO.

UV–vis absorption spectra of ZnO and ZnO hybrid films containing MWNT are shown in Fig. 3. As shown in Fig. 3(a), according to the increase in annealing temperature, the transmittance of ZnO films was decreased. The values of average transmittance of ZnO films annealed at 400, 500, and 600 °C in visible region were 90.52, 87.09, and 83.42%, respectively. This reduction in the transmittance might be due to the increase in the light scattering by defects at ZnO film surface. During high-temperature annealing, ZnO surface generates defect state with oxygen deficiencies [14] and this defect state generates defect level in the energy gap of ZnO at the film surface then light is absorbed at the defective surface of ZnO [15]. However, the transmittance of ZnO hybrid films containing MWNT was not changed even with the incorporation of MWNT into ZnO films. We can say that the incorporation of MWNT does not reduce the transmittance of ZnO film because the size and distribution of MWNT are quite different from the wavelength of light for scattering.

The sheet resistances of ZnO and ZnO hybrid films containing MWNT were measured by using four-point probe and the results are given in Fig. 4. The value of ZnO films annealed at 400, 500, and 600 °C were 136, 187, and 223 k Ω/square, respectively. The sheet resistance was increased with annealing temperature. This increasement of the sheet resistance might be due to decrease in charge mobility resulted from the increase in scattering probability because there was an increase in electrical scattering centers from oxygen deficiencies on ZnO film surface during high-temperature anneal such as 500 and 600 °C [14]. According to increase of MWNT contents, the tendency of reduced sheet resistance was observed [16]. The sheet resistance of ZnO and 0.1 wt% MWNT-incorporated ZnO films annealed at 400 °C were 136, 108 k Ω/square, respectively. This improved behavior of sheet resistance was due to the increase in carrier mobility by the incorporation of MWNT to ZnO film.

The ZnO and ZnO hybrid films containing MWNT were measured by XPS to analyze electrical bonding states of the MWNT with ZnO matrix. Both films were annealed at 400 °C for 1 h and the results are given in Fig. 5. The XPS spectra measured C 1s, O 1s, and Zn 2p core level after removing the surface contaminations of the film by ion-etching in UHV chamber. Fig. 5 shows C 1s, O 1s and Zn 2p core level spectra of ZnO and ZnO hybrid films containing 0.1 wt% MWNT films. The value of atomic percentage was calculated from core level XPS spectra of 0.1 wt% MWNT-incorporated ZnO films by using atomic sensitivity factors [17]. The values of atomic percentage of C, O, and Zn were 9.1, 38.6, and 52.3%, respectively. The value of 9.1 at% corresponds to the amount of incorporated MWNT into ZnO matrix because the surface contaminated carbon of the film was already removed by ion

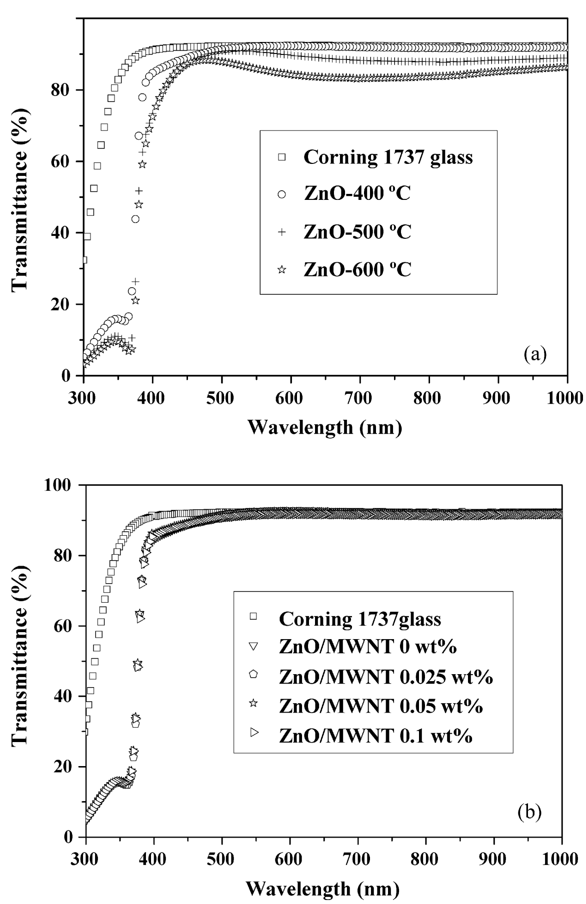


Fig. 3. Optical transmittance of (a) ZnO films annealed at various temperatures and (b) MWNT-incorporated ZnO films annealed at 400 °C with various incorporated contents.

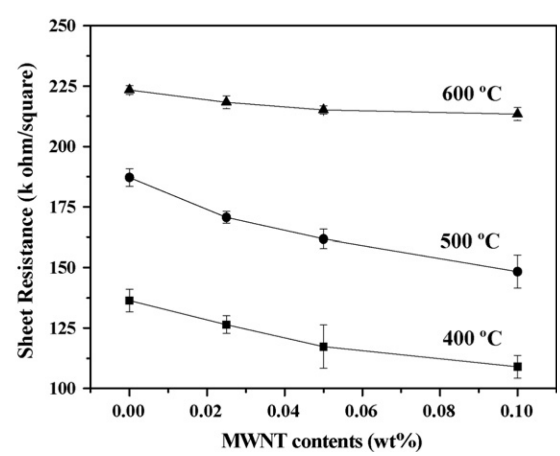


Fig. 4. Sheet resistances of ZnO and ZnO hybrid films containing various MWNT contents annealed at various temperatures.

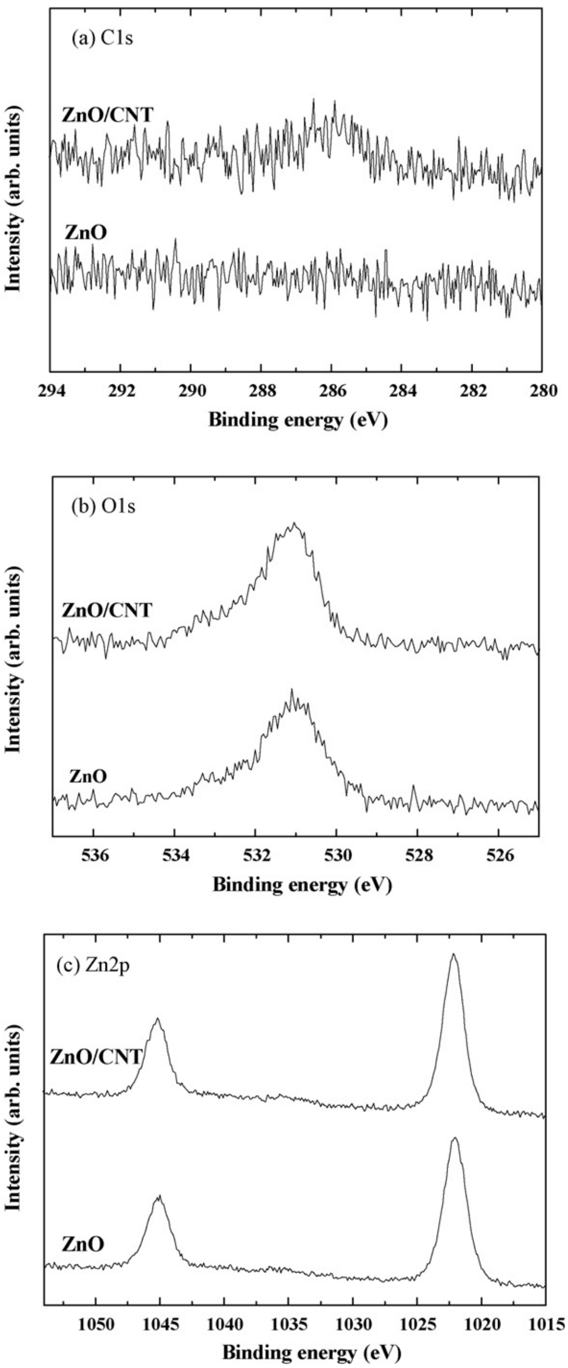


Fig. 5. XPS spectra measured at the surface of ZnO and 0.1 wt% MWNT-incorporated ZnO films annealed at 400 °C for 1 h.

etching. Namely, it means that atomic ratios of MWNT to Zn and O were 0.17 and 0.24, respectively. The changes of core level spectra in Zn 2p and O 1s should be appeared if there was a chemical bond between MWNT and ZnO matrix. However, as shown in Fig. 5(b) and (c), O 1s and Zn 2p core level spectra of ZnO hybrid film containing 0.1 wt% MWNT were identical to those of ZnO film. It means that there was no chemical bond between MWNT and ZnO matrix in our experimental condition. So, we can infer that electron transfer of MWNT in ZnO matrix or vice versa was maintained from π-bonding in the surface of MWNT without any chemical bond between MWNT and ZnO matrix [18,19]. Therefore, as shown in Fig. 4, the enhanced sheet resistance of incorporation of MWNT into ZnO film happened by enhancement of charge mobility due to π-bonding of MWNT [20].

## 4. Conclusions

Direct-patternable ZnO and ZnO hybrid films containing MWNT were successfully formed by using photosensitive additive without using either photoresist or dry etching procedure. It was shown to be easily applicable to the deposition of conventional chemical solution deposition procedure by adding photosensitive additive. ZnO and ZnO hybrid films containing MWNT were crystallized with a random orientation growth of hexagonal wurtzite structure due to the random orientation of glass substrate. In case of ZnO hybrid films containing MWNT, the presence of MWNT did not affect on the crystallization of ZnO film. According to incorporation of MWNT into ZnO films, the transmittance of ZnO hybrid films containing MWNT was not changed. O 1s and Zn 2p core level spectra of ZnO hybrid film containing 0.1 wt% were identical to those of ZnO film. We could infer that electrical bonding of MWNT in ZnO matrix was maintained from π-bonding in surface of MWNT without any chemical bond between MWNT and ZnO matrix.

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