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ZnO nanotips and nanorods on carbon nanotube/Si substrates: anomalous p-type like optical properties of undoped ZnO nanotips

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Abstract

ZnO nanotips and nanorods were grown on screen-printed multi-walled carbon nanotube (MWCNT) films via thermal chemical vapor deposition at relative low growth temperatures of 400 and 500 °C. Uniform formation of ZnO nanotips and nanorods occurred on MWCNT-printed Si substrates, but were rarely observed on bare Si substrates at the same growth temperatures. In photoluminescence (PL) measurements, it was found that ZnO nanorods exhibit typical intrinsic optical properties, while ZnO nanotips revealed p-type like luminescence behavior. Acceptor-related emission bands originating from neutral acceptor–bound exciton, free-to-acceptor and donor–acceptor pair transitions are clearly observed in temperature-dependent PL spectra of ZnO nanotips.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

One-dimensional (1D) ZnO nanostructures such as nanotubes, nanowires, nanotips, nanorods and nanobelts have been regarded as a promising candidate for realizing high-quality light-emitting diodes, sensors for chemical and biological species and solar cells [1–5]. In this regard, a large number of research groups have reported on the fabrication of 1D ZnO nanostructures via a vapor–liquid–solid (VLS) mechanism typically needing a high-temperature process over 800 °C for their uniform formation. However, high-temperature growth processes limit the applicable substrate materials and also lead to the formation of a large number of point defects in nanostructures causing deep-level emission and charged carrier trapping [6]. Very recently, Yu et al have showed dramatically enhanced field-emission properties of screen-printed carbon nanotube (CNT) films by coating ZnO nanostructures of nanoparticles and nanomultipods [7]. In addition, Jo et al have also reported an extremely low threshold field value for field emission in the hybrid system of ZnO nanowires and carbon clothes [8]. The above-mentioned ZnO nanostructures were grown via a typical vapor-phase transport process at relatively high growth temperatures over 600 °C. However, as mentioned above, the high-temperature growth of ZnO nanostructures can
thermally attack the CNT layer, resulting in the degradation of field-emission properties.

Low-temperature and catalyst-free synthesis of ZnO nanorods by metal-organic chemical vapor deposition (MOCVD) has been intensively investigated [4, 9]. However, mass production and large-area synthesis of 1D ZnO nanostructures by the MOCVD system are currently not economical or even available, indicating that a large quantity of ZnO nanostructures should be achieved by thermal chemical vapor deposition (CVD) with simple equipment set up in a low-temperature growth process. Catalyst-free synthesis of 1D ZnO nanostructures on CNTs in a thermal CVD process at low temperature is still not common and little is known about their optical properties. Herein we describe a large-scale catalyst-free synthesis of ZnO nanotips and nanorods on screen-printed multi-walled carbon nanotube (MWCNT) films via thermal CVD at low temperatures of 400 and 500 °C. In addition, optical properties of the ZnO–CNT heterostructures were investigated.

2. Experimental details

MWCNT paste for the screen printing was formulated with commercially available MWCNTs, additives (glass frits and ITO powders), and organic binder mixtures consisting of ethyl cellulose with terpineol. The MWCNT paste was prepared by mixing 2 wt% of MWCNTs and 6 wt% of additives in organic binders. The pre-mixed MWCNT paste was better dispersed by a three-roll milling process. The MWCNT films with a thickness of 4 μm were transferred on p-type Si(100) substrates via a screen-printing technique. Then the thermal treatment of the screen-printed MWN films was carried out at 400 °C for 60 min in an air ambient to eliminate the organic materials and other impurities. High-yield synthesis of the ZnO nanowalls was achieved by evaporating a mixture of ZnO (99.999% purity) and graphite (99.999% purity) powder (1:1) in an Ar atmosphere. The MWCNT film-printed Si substrates were placed 10 cm downstream from the center of the alumina tube. Once the Ar gas flow had stabilized at 1000 sccm (standard cubic centimeters per minute), the mixed powder positioned at the center of the alumina tube was evaporated at 1000 °C. The MWNT/Si substrates were kept at 400 and 500 °C for 30 min. The morphology of as-grown samples was examined by field-emission scanning electron microscopy (FE-SEM). Optical and structural properties of the samples were investigated by temperature-dependent photoluminescence (PL) and grazing-incidence wide-angle x-ray scattering (GIWAXS) (beamline 5A at Pohang Light Source (PLS)) measurements.

3. Results and discussion

Figure 1 reveals FE-SEM images of the ZnO nanotips and nanorods grown at 400 and 500 °C on the screen-printed MWCNT films, respectively. The grown nanotips and nanorods are quite uniform over the entire substrate area, while they are randomly nucleated on the surface of the screen-printed MWCNT films. The diameter and length of ZnO nanorods are 20–50 nm and 200–900 nm, respectively. The growth of ZnO nanotips takes place from the top surface of ZnO nanocrystallites randomly distributed on the screen-printed MWCNT surface. On the other hand, the ZnO nanorods are generated from the nanocrystalline ZnO thin film uniformly grown on the screen-printed MWCNT surface. The diameter and length of ZnO nanorods are around 50–100 nm and 0.5–1.5 μm, respectively. However, ZnO nanostructures were rarely observed on bare Si substrates with no MWCNT film in the same growth conditions, which indicates that the screen-printed surface served as the active nucleation sites for the ZnO nanotip and nanorod growth.

Zn vapor forms liquid droplets at both 400 and 500 °C due to the low melting point of Zn of 419 °C [10]. The continuously supplied Zn and O vapors saturate the liquid droplets, followed by the precipitation of ZnO leading to the formation of nanocrystallites. The nanocrystalline ZnO thin film possesses smoother surface morphology at the higher growth temperature of 500 °C compared to that grown at 400 °C. The nanotips and nanorods are grown onto the ZnO nanocrystallites formed on the MWCNT film. Thus, we suggest that the formation of ZnO nanotips and nanorods on screen-printed MWCNT films is attributed to a typical VLS mechanism via a self-catalytic process [11]. The detailed formation mechanism of the ZnO nanotips and nanorods obtained in this work is under investigation.

Figure 2 shows GIWAXS diffraction spectra and powder diffraction profiles along the substrate normal direction in reciprocal space measured on the ZnO nanotip–MWCNT (grown at 400 °C) and nanorod–MWCNT (grown at 500 °C) heterostructures, which were obtained with the synchrotron x-ray source at PLS. Powder-like ring patterns from both

![Figure 1. FE-SEM images of the ZnO nanotips (a) and nanorods (b) grown at 400 and 500 °C on screen-printed MWCNT films, respectively.](image-url)
samples in the GIWAXS measurements indicate the random directionality and uniform distribution of the grown nanotips and nanorods on the screen-printed MWCNT films. As shown in figure 2(c), three peaks of ZnO (100), (002) and (101) planes are clearly observed in both nanotip and nanorod samples. ZnO nanorods are of better crystallinity than ZnO nanotips. In addition, the CNT is better crystallized in the ZnO nanorod sample rather than in the ZnO nanotip sample, which is due to the higher growth temperature for the ZnO nanorod growth.

Figure 3 shows low-temperature PL spectra at 10 K from the nanotips and nanorods, respectively. A sharp asymmetric band centered at 3.360 eV with a very sharp full-width at half-maximum (FWHM) value of 6 meV is dominant in the nanorod sample, while emission located at 3.353 eV is a main luminescence band with large FWHM of 21 meV in the nanotip sample. The main peak at 3.360 eV observed from the nanorod sample can be assigned to neutral donor-bound exciton (D°X) emission [12]. The peak at 3.353 eV obtained from the nanotip sample possibly originates from neutral acceptor-bound exciton (A°X) emission according to the previous report [12]. However, the observation of the emission band A°X is anomalous because the nanotips on the MWCNT thin film are undoped.

To clarify the origin of the emission bands, temperature-dependent PL measurements of both samples were carried out. Figure 4 shows the temperature-dependent PL spectra obtained from the ZnO nanorods. A D°X emission band at 3.360 eV and another emission band labeled as FX at 3.376 eV attributed to free exciton emission are observed in the PL spectrum measured at 30 K. The intensity of the peak at 3.360 eV decreases gradually with increasing temperature, as shown in the temperature-dependent PL result of figure 4, confirming that the emission peak labeled as D°X originated from excitons bound to neutral donors [12, 13]. The emission bands labeled D°X-1LO, D°X-2LO and D°X-3LO in the spectrum obtained from the nanorod sample originate from the radiative recombination of the first, second and third longitudinal optical (LO) phonon replicas of the D°X emission band, respectively, considering an energy separation for each emission band of about 70 meV.

Figure 5 shows the temperature-dependent PL spectra from the ZnO nanotip sample. The 10 K PL spectrum of the nanotip sample clearly shows the peaks at 3.353 and
3.376 eV originating from $A'$X and FX, respectively, and two other peaks at around 3.310 and 3.240 eV, which might be related to acceptors regarding previous work [13, 14]. As the temperature is increased, the FX emission band becomes dominant compared to the $A'$X band due to the thermal dissociation of neutral acceptors and excitons. In typical ZnO thin films or bulk crystals, the FX emission band is not clearly observed at low temperatures due to the localization of excitons by impurities. At high temperatures, usually over 70 K, the FX emission band is predominant because of the ionization of impurities that are used to bind excitons at low temperatures. The clear observation of the FX emission band in the emission spectrum even at a temperature as low as 10 K also suggests that low levels of impurities binding excitons were incorporated in the ZnO nanotip sample grown on the screen-printed MWCNT film although the emission is broader compared to that of the ZnO nanorod sample.

Peaks at 3.310 and 3.240 eV are not observed on the PL spectra obtained from the nanorod sample at 10 K as shown in figures 3 and 4. We further investigated the origin of the PL emission bands at 3.310 and 3.240 eV by examining the laser powder density dependence of PL behavior at 10 K. When the excitation intensity is increased, the emission band at 3.240 eV is shifted to higher energy. However, the peak at 3.310 eV is independent of the laser power density. This fact suggests that the emission bands at 3.310 and 3.240 eV originate from free-to-acceptor and donor–acceptor pair transitions (FA and DAP), respectively. For the FA emission band, the acceptor energy level located at 90 meV above the valence band maximum is achieved from [15, 16]

$$E_A = E_g - E_{eA} + k_B T/2$$

where $E_g$ and $E_{eA}$ are the band gap and acceptor energy level, respectively. The thermal energy can be neglected at 10 K. Assuming that the $E_g$ value of ZnO at 10 K is 3.4 eV, the $E_{eA}$ value of 90 meV is obtained using the above relation.

Zn vacancies and O antisites generally act as acceptors in ZnO [17]. The Zn vacancy has lower formation energy, which can lead to p-type like behavior of undoped ZnO [18]. A recent report suggested that the $\varepsilon(1/-0)$ transition level of the Zn vacancy is located at 90 meV above the valence band maximum although the Zn vacancy acts as a double acceptor [19]. Analogous PL characteristics from phosphorus-doped ZnO thin films and nanowires have been reported [20, 21]. Thus, we suggest that the origin of intrinsic p-type optical behavior from the ZnO nanotip sample grown on the screen-printed MWCNT film may be due to the formation of a Zn vacancy and some complex acceptor center.

In addition, recently, Tan et al have reported the observation of p-type conduction in unintentional carbon-doped ZnO thin films [22]. They suggested that the unintentional p-type conductivity is attributed to carbon–oxygen cluster defects (acting as shallow acceptors) formed in MOCVD-grown ZnO after post-growth annealing in N$_2$ ambient. In their PL results obtained at 4.8 K, the $A'$X emission peak positioning at 3.3564 eV is clearly observed. Carbon is an amphoteric impurity in II–VI compound semiconductors [23]. Considering atomic diffusion of carbon into the ZnO nanotips from the MWCNT film, we cannot rule out the possibility of unintentional carbon doping to the ZnO nanotips leading to p-type PL properties. On the other hand, carbon atoms incorporated into the ZnO nanorods from the MWCNT film during the ramping and/or growth can in part evaporate and escape from the ZnO nanorods at the higher growth temperature of 500 °C, which may explain why D$^+$X emission in the PL spectrum at 10 K as shown in figures 3 and 4 is dominant in the ZnO nanorod sample.

4. Conclusion

In summary, large-scale synthesis of ZnO nanotips and nanorods on MWCNT-printed Si substrates and their optical properties have been discussed. ZnO nanotips and nanorods were formed on the screen-printed MWCNT films via a self-catalytic process, indicating that MWCNTs act as effective nucleation sites for ZnO growth. In PL measurements, ZnO nanorods grown at 500 °C showed typical intrinsic PL properties of ZnO, while ZnO nanotips grown at 400 °C revealed anomalous p-type like PL characteristics.

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