Catalyst-Free Synthesis of ZnO Nanorods on Metal Substrates by Using Thermal Chemical Vapor Deposition

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We report successful synthesis of ZnO nanorods on metal (Cr)-deposited Si substrates in a thermal chemical vapor deposition (CVD) process via a self-catalytic mechanism at relatively low growth temperatures of 400 and 500 °C. The nanotips were densely grown onto the Cr layer while ZnO nanorods with low density were synthesized on the same substrates. Grazing-incidence wide-angle X-ray scattering measurements showed a uniform distribution and a random directionality of the nanotips and the nanorods grown on Cr-deposited Si substrates. Free-exciton emission from the nanorods was clearly observed from the samples at a very low temperature of 50 K in the photoluminescence measurements. In addition, strong free exciton and relatively weak deep level emission bands were detected from both samples even at room temperature, indicating the ZnO nanotips and nanorods on Cr/Si substrates in this work had a low defect density.

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I. INTRODUCTION

Recently, ZnO has attracted considerable attention as a representative II-VI compound semiconductor. Its many attractive properties, such as a wide band gap of 3.37 eV, a large exciton-binding energy of 60 meV and a biexciton-binding energy of 15 meV, can lead to realization of optoelectronic devices with high efficiency [1–4]. Recently, great attention has been paid to one-dimensional (1D) nanostructures such as nanorods, nanowires, nanobelts and nanotubes [5–7] and to zero-dimensional (0D) nanostructures, such as quantum dots (QDs) [8], due to the ability to enhance device performance through nanostructuring. Especially, 1D and 0D ZnO nanostructures, such as nanowires and QDs, can be expected to exhibit enhanced luminescence efficiency due to their large surface areas emitting photons and due to quantum confinement effects [9,10]. In addition, 1D ZnO nanostructures, such as nanorod and nanorod arrays, are attracting worldwide interest on account of their field emission properties [11,13,13]. A large number of groups have reported the fabrication of ZnO nanorods and nanowires by using a vapor-liquid-solid (VLS) process with a metal catalyst at high growth temperatures over 800 °C [14]. High-temperature processes seriously limit device applications and increase thermal strain in the grown nanostructures. Metal-organic chemical vapor deposition has been regarded as a promising method to synthesize 1D ZnO nanostructures at low temperatures below 500 °C [15]. However, this method involves complex procedures and sophisticated equipment systems, indicating difficulty in large-area fabrication of nanostructures with a simple approach.

In addition, ZnO thin films and nanostructures have been typically prepared on sapphire substrates because of the relatively low lattice mismatch between ZnO and
sapphire [16]. However, the insulating sapphire substrate might prevent the nanostructure arrays from being applied in nanomaterial-based optoelectronic devices with simple fabrication processes. In these regards, realization of 1D ZnO nanostructures on highly-conductive substrates at low temperatures has been regarded as one of the important issues in related research communities. Moreover, the optical properties of 1D ZnO nanostructures grown on metal substrates at low temperatures by using thermal chemical vapor deposition (CVD) have rarely been investigated. In this work, photoluminescence (PL) measurements, we clearly observed strong free exciton emission, as well as a relatively-weak deep-level emission, from single-crystalline ZnO nanotips and nanorods grown on Cr-deposited Si substrates at 400 and 500 °C by using thermal CVD without the introduction of a metal catalyst.

II. EXPERIMENTS

Firstly, Si substrates were cleaned in an ultrasonic bath with acetone and methanol for 20 min at room temperature (RT) and were then blown by nitrogen gas. After the substrate cleaning, a Cr thin film with a 200-nm thickness was deposited on a bare Si substrate by using a DC magnetron sputtering system. Proceeding to the main experiment, growth of ZnO nanostructures on Cr-deposited Si substrates was carried out by using a thermal CVD process without the help of a metal catalyst. High-yield synthesis of ZnO nanotips and nanorods was achieved by evaporating a mixture of ZnO (Aldrich, 99.999% purity) and graphite (Aldrich, 99.999% purity) powder (1 : 1) in an Ar atmosphere. The mixed powder in an alumina boat was loaded into the left side from the center of a quartz tube (the first heating zone). Once the Ar gas flow had stabilized at 1000 sccm (cubic centimeter per minute at STP), the Cr-deposited Si substrate placed on the second heating zone of the tube (the right side from the center of the tube) was heated and kept at 400 and 500 °C for 30 min. The morphology of as-grown samples was examined by using field-emission scanning electron microscopy (FE-SEM). The optical and the structural properties of the samples were measured by using a continuous-wave He-Cd laser with an excitation wavelength of 325 nm and grazing-incidence wide-angle X-ray scattering (GIWAXS) [beamline 5A at the Pohang Light Source (PLS)] measurements.

III. RESULT AND DISCUSSION

Figure 1 shows FE-SEM images of ZnO nanotips and nanorods grown on Cr-deposited Si substrates at 400 and 500 °C, respectively. As shown in Figure 1(a), the grown ZnO nanotips are of uniform distribution over the entire substrate area while they are randomly grown on the Cr surface. The diameters and the lengths of the nanotips are in the ranges of approximately 20 – 50 nm and 150 – 500 nm, respectively. The FE-SEM image of ZnO nanorods in Figure 1(b) shows that ZnO nanorods with lengths and diameters of about 50 – 100 nm and 500 – 800 nm, respectively, are uniformly distributed. The nanorods at 400 °C were densely grown on the Cr layer while ZnO nanorods with low density were synthesized onto the substrate at 500 °C.

In general, the surface diffusion of atoms adsorbed on the metal surface is more favorable at high temperatures. This fact can suggest that the surface diffusion length of a Zn adatoms for successive reactions to make ZnO is different as a function of the growth temperature. Zn adatoms have a higher surface mobility and a shorter surface lifetime at higher growth temperatures, resulting in preferred migration and desorption of the adsorbed Zn atoms from the surface area. Considering this result, it could be concluded that the density of the grown 1D ZnO nanostructures is closely related to the variations in the atomic diffusivity and the desorption rate of adsorbed atoms on the surface area with the growth temperature in this catalyst-free growth process. Zn vapor forms liquid droplets at 400 and 500 °C due to the low melting point (419 °C) of Zn [17]. The continuously supplied Zn and O vapors saturate the liquid droplets, which is followed by the precipitation of ZnO, leading to the formation of nanocrystallites. The nanotips and the nanorods were grown with no introduction of a metal catalyst. In addition, we could rule out the catalytic action of Cr atoms for the formation of ZnO nanostructures by considering the Zn-Cr binary phase diagram. Moreover, ball-shaped Zn-Cr alloys are rarely observed on the top faces of the nanotips and nanorods, unlike other reported observation for metal-catalyst-driven VLS growth methods [18]. Thus, it is suggested that the formation of ZnO nanotips and nanorods on the Cr-deposited Si substrates is attributed to a typical self-catalytic VLS process [19].

Figure 2 shows GIWAXS diffraction spectra and powder diffraction profiles along the substrate normal direction in reciprocal space measured on the ZnO nanotip
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Fig. 2. GIWAXS diffraction spectra of ZnO (a) nanotip and (b) nanorod samples. (c) Powder diffraction profiles along the substrate normal direction in reciprocal space measured on the ZnO nanotip (400 °C, solid line) and nanorod (500 °C, dashed line) samples.

Fig. 3. RT PL spectra obtained from the ZnO nanotip sample in the temperature range of 10 - 300 K.

Fig. 4. Temperature-dependent PL spectra obtained from ZnO nanotips (solid line) and ZnO nanorods (dashed line).

The measurements were done using the synchrotron X-ray source at PLS. The powder-like ring patterns from both samples in the GIWAXS measurements indicate a random directionality and a uniform distribution of the grown nanotips and nanorods on the Cr-deposited Si substrates, as shown in the FE-SEM image of Figure 1. Three peaks, corresponding to the ZnO (100), (002) and (101) planes, are clearly observed in both the nanotip and the nanorod samples in Figure 2(c). For the ZnO nanotip sample, the intensity of the ZnO (002) peak is the strongest, while for the ZnO nanorod sample that of the ZnO (101) peak is the strongest. This result indicates that the nanotips are mainly oriented to the [001] direction, showing that the nanotips are rather vertically aligned compared to the nanorods. The peak intensities from the nanotip and the nanorod samples are comparable in spite of the low density of the nanorods grown on the Cr-deposited Si substrate, suggesting that the ZnO nanorods in this work have better structural properties compared to the nanotips.

Figure 3 shows RT PL spectra from the nanotips and the nanorods. The peaks around 3.31 and 3.29 eV from the nanotips and nanorods, respectively, are due to recombination of free excitons, namely the near band-edge (NBE) emission. The broad deep-level emission bands from both samples are similarly located around 2.5 eV. The NBE emission bands from both samples are dominant while the broad deep-level emission is relatively weak. The deep-level emission in ZnO may be due to the singly ionized oxygen vacancy being from the recombination of electrons at conduction band with holes trapped in oxygen-related defects [20]. Usually, RT PL results of 1D ZnO nanostructures such as nanowires and nanorods synthesized via the thermal CVD process show a broad and strong deep-level emission band, as well as a weak NBE emission. However, as shown in the Figure 3, strong NBE and relatively weak deep-level emission bands were observed from both samples at RT, suggesting that our ZnO nanotips and nanorods on Cr/Si substrates have a small number of native point defects and impurities. The NBE emission band from the ZnO nanotips is somewhat blue-shifted compared with that of the ZnO nanorods. Considering the size of the top faces in the nanotips, the blue shift of the NBE emission band from the nanotips may be attributed to quantum size effects [21]. However, that is not clear at this present stage. Further concrete study will address the point in the near future.

Figure 4 shows temperature-dependent PL spectra from the nanotips grown at 400 °C. The emission peak located at 3.361 eV is mainly observed in the 10 K PL spectrum. The ZnO nanotip sample is undoped. Moreover, the intensity of the peak at 3.361 eV decreases
gradually with increasing temperature, indicating that the emission peak originates from neutral donor-bound exciton ($D_0X$) emission [22]. In addition, the emission bands labeled “$D_0X$-1LO, $D_0X$-2LO and $D_0X$-3LO” are clearly observed in all the PL spectra below 100 K and are due to radiative recombination of the first, second and third longitudinal optical (LO) phonon replicas of the $D_0X$ emission band, respectively, considering an energy separation of about 70 meV for each emission band.

Temperature-dependent PL spectra from the nanorod sample grown at 500°C are shown in Figure 5. The peak labeled “FX” in the PL spectrum obtained at 50 K can be attributed to free exciton emission. As the temperature is increased to above 100 K, the FX emission band becomes dominant compared to the $D_0X$ emission band due to the thermal dissociation of donor-bound-excitons. Typically, the FX emission band is not clearly observed at low temperatures due to the localization of excitons by impurities. The clear observation of the FX emission band, even at a temperature as low as 50 K indicates that low levels of impurities were incorporated in our nanorods in spite of their being formed on metallic Cr layers.

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REFERENCES