ZnTe Nanowires with Oxygen Intermediate Band Grown by Bismuth-Catalyzed Physical Vapor Transport

So Ra Moon, Jung Hyuk Kim, and Yong Kim*

Department of Physics, Dong-A University, Hadan-2-dong, Sahagu, Busan 604-714, Korea

ABSTRACT: We investigated the growth of ZnTe nanowires by a physical vapor transport method catalyzed by Bi. Straight and single-crystalline nanowires were grown at relatively low substrate temperatures (410–360 °C). Micro-PL measurements revealed an unexpected color-tuning effect from green to red as the laser excitation position was moved from the tip to the bottom of nanowire. The red photoluminescence band can be ascribed to the highly radiative intermediate band formed by nonintentional O-doping from residual O2/H2O vapor. As the growth of nanowires proceeds, O-containing species diffuse through the side walls of nanowires. In addition, with changing laser excitation intensity, a similar color-tuning effect due to the interplay between red and green photoluminescence bands was observed. The red band dominates photoluminescence at low excitation intensity due to the fast electron relaxation to intermediate band. ZnTe NWs with this intermediate band may be useful for high efficient solar cells and two-color photodetectors.

1. INTRODUCTION

Recently, II–VI nanostructures catalyzed by Au or other metals have attracted a great deal of attention because these structures offer unique properties useful for novel optoelectronics devices.1–3 ZnO,4 ZnS,5 CdS, and CdSe6 are material systems that have been extensively investigated. Because of the inherent polar nature of these materials with wurtzite crystal structure, these quasi 1-D nanostructures show morphological variations that include nanowires (NWs), nanobelts, nanosprings, nanosaws, and so on.7 In contrast, the reports on the growth of ZnTe NWs are relatively limited despite the attractive optoelectronic properties of ZnTe.8–10 ZnTe is a semiconducting material with the direct band gap of 2.26 eV at room temperature. The band gap is useful for pure-green light-emitting diodes and photodetectors.11,12 Unlike other II–VI semiconductors that usually exhibit n-type conductivity, p-type ZnTe with high hole concentration, which is useful for heterostructure P/N diodes, can be readily achieved.16 ZnTe is widely used in terahertz applications for both emission and detection of terahertz radiation.17

Recently, ZnTe with intermediate band formed by O doping has been considered as suitable material for “intermediate band solar cell” with conversion efficiency possibly exceeding Shockley–Queisser limit (∼34%) for single junction solar cells.18,19 Because of the large difference in electronegativity between O and Te, O atoms, when substituted for Te atoms in ZnTe host lattice, form an intermediate band lying ∼0.5 eV below the conduction band (CB).20 O doping in ZnTe layer has been documented.21 However, O doping in ZnTe NWs has not yet been investigated.

ZnTe NWs have been grown by research groups via molecular beam epitaxy, physical vapor transport, and chemical synthesis.5–11 Almost exclusively, ZnTe NWs grown under vapor–liquid–solid (VLS) mechanism have used Au nanoparticles as catalysts.5–10 Although Au is inert and has ideal phase diagram with host materials for NW growth, Au is known to form nonradiative recombination centers that greatly deteriorate the optical properties of NWs.22 Bi is a possible candidate for alternative catalysts because Bi has low melting temperature of 271 °C and low solubility in most semiconductors.23,24 Indeed, Bi has been widely used as a catalyst for chemical synthesis of NWs under solution–liquid–solid mechanism.25 However, to the author’s best knowledge, there have been no reports on the growth of ZnTe NWs by Bi-catalyzed physical vapor transport. Our initial motivation of the present study was the growth of ZnTe NWs with high optical quality grown in vapor phase at low temperatures by taking advantage of Bi catalysts. Unexpectedly, we observed apparent color tuning from green to red in photoluminescence (PL) as we moved the excitation laser position from the tip near the Bi catalyst toward the bottom of a single ZnTe NW during micro-PL (μ-PL) measurements. In addition, when decreasing the excitation laser power at a fixed excitation position on the NW, we observed the similar color tuning in PL from green to red. This study discusses the origin of these interesting phenomena.
2. EXPERIMENTAL METHODS

ZnTe NWs were grown by a physical vapor transport method employing a conventional single zone furnace with a 1 in. diameter quartz tube (Lindberg Blue M Mini-Mite). A quartz boat containing ZnTe powder (100 mg, Alpha Aesar 99.99%) was placed in the center zone. Most of nanostructures reported so far by other research groups were grown on substrates coated with 5−10 nm Au. However, in the present study, a quartz boat containing Bi powder (20 mg, Alpha Aesar 99.999%) was placed at 13.5 cm upstream from the center. The source temperature was set to 780 °C. Figure 1 shows the schematic of our physical vapor transport system and temperature profile. The temperature profile was obtained by calibration with a thermocouple. According to this profile, the Bi catalyst temperature was 660 °C. Si substrates that were cleaned and hydrogen-terminated by diluted HF were placed at 14.5−18 cm downstream from center. Long Si substrates (3.5 cm × 1.2 cm) were loaded to observe the variation of morphology depending on the substrate temperature (650−300 °C), as shown in Figure 1. First, the system is evacuated by a mechanical pump for 0.5 h (base pressure ~10⁻² Torr); then, N₂ carrier gas balanced with 10% H₂ with a flow rate of 100 standard cubic centimeters per minute was introduced. The ramp-up time to 780 °C was 15 min, and another 1 h was used as growth time while keeping the pressure at 760 Torr. The sample was cooled to room temperature with the flow of carrier gas.

An additional control experiment has been conducted with Au nanoparticles as catalysts. Oxide-free Si substrates were functionalized by dipping them in a 0.1% poly-L-lysine solution for 1 min. After rinsing with deionized (DI) water, the substrates were blown dry with N₂ gas. A commercially available Au colloidal liquid solution (Ted Pella) containing 50 ± 3 nm diameter Au nanoparticles with a density of 4.5 × 10¹⁰ particles mL⁻¹ was dispersed on the substrate surface and rinsed with DI water. Au-catalyzed ZnTe NWs were grown under the equivalent growth condition.

The morphologies of as-grown ZnTe NWs were observed by a field-emission scanning electron microscope (FESEM, JEOL JSM-6700F). Transmission electron microscope (TEM) specimens were prepared in the following manner. The samples were immersed in a container with ethanol. The sample in the container was sonicated for 20 s to remove ZnTe NWs from their substrates. These NWs were then dispersed onto a holey carbon grid. TEM and selected area electron diffraction (SAED) patterns were measured by a TEM (JEOL JEM2010). Energy-dispersive X-ray (EDX) spectra were obtained by an EDX system (INCA, Oxford Instruments) attached to the FESEM.

μ-PL of a single ZnTe NWs was carried out by employing a home-built μ-PL system. An Ar⁺ laser (488 nm) was band-pass filtered and guided into a modified commercial microscope (Olympus BX60M) with a commercial Raman filter cube (Semrock). The laser beam power was attenuated by a variable neutral density filter with optical density from 0 to 4.0 (Thorlabs). The filter cube consists of exciter filter (edge steepness <1.0 nm), emitter filter (bandwidth <1.9 nm), and dichroic beam splitter. The laser beam was focused to a spot (spot diameter ~3.2 μm) by an objective lens (Olympus ×50, N.A. = 0.75). The excitation laser power was measured directly underneath the objective lens by a hand-held laser power meter (Coherent Lasercheck). μ-PL from a single nanowire was collected by the same objective lens. By using a commercial dual-port attachment, imaging by a charge-coupled device (CCD, Imaging source DBK41AF02) and spectroscopic measurements were done simultaneously. For spectroscopic measurements, the μ-PL signal was introduced into multimode fiber using a fiber-launching module. Then, μ-PL was dispersed by 0.5 m monochromator (Dongwoo Optron DMS00) and detected by a Peltier-cooled spectroscopic CCD camera (Andor, iDus DV401A). For single NW measurements, NWs were transferred to SiO₂-coated Si substrates by casting and drying of a liquid drop containing nanowires. All measurements were done at room temperature.

Figure 1. Physical vapor transport system and temperature profile.
3. RESULTS AND DISCUSSION

The narrow temperature window for reasonable NW production is found from the side-view FESEM images obtained from the various substrate regions. For the substrate region with temperatures higher than 470 °C, short and rod-like structures without any sign of Bi catalysts were observed. The rod-like structures seem to result from the self-catalytic action of Zn. For the sample region with the temperature range 470–410 °C, tall and tangled NWs with high density are observed. The lengths of NWs (diameter 400–500 nm) exceed severals hundreds of micrometers. The temperature range 410–360 °C on which we focus in the present study produces straight NWs. The temperature range is fairly low considering the previously reported growth temperatures for Au catalysis.⁵,¹⁰ Low-temperature growth is a distinct advantage of the Bi catalyst. For the sample region lower than 360 °C, no NW growth is observed. Instead, a high density of particulates of condensed Bi was found. A similarly narrow window was observed for the growth of Bi-catalyzed Ge NWs via chemical vapor deposition.⁴,²³ In our previous investigations for Au-catalyzed CdS/CdSe nanostructures,²⁶,²⁷ nanostructures showing morphological variation from NWs to nanobelts depending on the substrate temperature were obtained over a wide range of substrate temperatures. Therefore, the comparatively narrow process window is a feature of Bi-catalyzed NW growth.

Figure 2a shows the side-view FESEM images of as-grown ZnTe NWs on Si substrate in the temperature region 410–360 °C. The length of NWs (diameter 200–400 nm) ranges from ~50 to ~200 μm. The catalysts on the top of straight NWs are clearly observable. Figure 2b shows a single ZnTe NW transferred to Si substrate for close inspection. A taper-free NW with a catalyst on its top can be formed. Here tapering means the phenomenon where the diameter near the tip with catalyst surface is smaller than that near the bottom in NWs.²⁸,²⁹ Figure 2c shows a TEM image of a ZnTe NW. Periodically twinned ZnTe NWs grown by similar physical vapor transport method have been reported.⁹,¹⁰ However, as evident from SAED pattern through the [110] zone axis (Figure 2d), our ZnTe NW-catalyzed by Bi is single-crystalline with zincblende structure, and the growth direction is (111).

Figure 3a shows the FESEM image of a Bi catalyst of a ZnTe NW transferred to Si substrate. Bi catalyst appears to be faceted. However from the close inspection of many catalysts, they have irregular morphology. The diameters of Bi catalysts (~1.3 μm) are significantly larger than that of the ZnTe NW (~350 nm). This trend is general, as shown in the histograms in Figure S1 in the Supporting Information. The average diameter of ZnTe NW is 232 ± 65 nm, and the average diameter of Bi catalyst is 1031 nm ±175 nm. Despite the growth temperature variation of ~50 °C, the diameter distribution of ZnTe NWs is wide, presumably indicating the growth temperature sensitivity of Bi-catalyzed NW. However, no variation in crystal structure is observed by the inspections of SAED patterns from ZnTe NWs. The contact angle, β is ~150° on average. Larger catalyst diameters (contact angle 120–160°) have been observed for low melting point catalysts.³⁰,³¹ The relation of the contact angle to the liquid–solid surface energy (γₗₛ) and the liquid–vapor surface energy (γₗᵥ) at the triple-phase boundary in taper-free NW can be simply expressed as cos β = γₗₛ/γₗᵥ using Young’s equation.³² Noting that γₗᵥ of Au (1.13 J/m²) is larger than that of Bi (0.38 J/m²)³³, the contact angle would be larger for a Bi catalyst. Figure 3b shows EDX spectra obtained in areas 1 and 2 of Figure 3a. No sign of Bi within EDX resolution is observed in area 1. The Si peak with 75.7 atomic % comes from the Si substrate because the penetrated electron beam (beam diameter <1 nm, acceleration voltage = 15 kV) through the ZnTe NW causes X-ray emission from the Si substrate. The atomic percents of constituent elements while omitting Si peak were reevaluated. Matrix correction was made by extended Pouchou–Pichoir (XPP) correction scheme. XPP correction assumes O is involved in the matrix. However, the part of O signal could be originated from the outside of the matrix. This affects the XPP correction parameters for Zn, Te, and Bi elements. In this sense, the evaluated atomic percents of constituent elements could be tentative. However, the relative ratios between Zn, Te, and Bi are still valid. In addition, O incorporation in the matrix could be qualitatively discussed. Striking features can be observed in EDX spectra obtained from area 2. The strong Bi signal (28.6 atomic %) proves that Bi is a catalyst indeed. In addition, a large amount of O (49.8 atomic %) is present due to the oxidation of Bi. Furthermore, a significant amount of Zn (20.7 atomic %) is also detected, whereas only a minute amount of Te (0.9 atomic %) is detected. [Zn]/([Zn] + [Bi]) by EDX is ~0.42. Referring to Bi–Zn phase diagram,³⁴ a solid/liquid phase transition occurs at 440 °C for this value. The transition temperature is in agreement with the growth temperature (~410 °C) considering the possible inaccuracy in temperature calibration and EDX measurements. This suggests that Zn is preferentially dissolved in the Bi catalyst after decomposition from ZnTe vapor on the catalyst surface. Unlike the common approach for NW growth using pre-existing catalyst nanoparticles on substrate, Bi vapor is continuously supplied during our growth. The advantage of this approach is to minimize the oxidation of Bi catalysts before initial nucleation. One may raise a question why there is no trace of Bi on the side walls of the ZnTe NW. It is noteworthy that the growth temperature range (410–360 °C) is higher than the melting point of Bi (= 271 °C). During the temperature ramp-up, Bi may vaporize first and be transported to the substrate, while the temperature is not yet sufficient for ZnTe evaporation or growth. Bi vapor condenses and forms liquid droplets on the substrate. In agreement with this
explanation, growth temperatures below 360 °C only produced Bi particulates with tail-like ZnTe structures on the substrate and did not produce any ZnTe NW growth, as shown in Figure 4. Once growth temperature is reached, the evaporation of ZnTe follows and thereafter Zn dissolves into the Bi catalyst. The melting point of the Zn/Bi alloy is higher than that of pure Bi, and VLS growth initiates at a much higher temperature than the melting point of pure Bi. Supplied Bi vapor at the growth temperature (410 ∼ 360 °C) seems not to condense on the side wall of NW because of its high equilibrium vapor pressure at these temperatures.

Figure 5 shows μ-PL images of a ZnTe NW transferred to a SiO2 substrate. The tip was identified by the presence of the Bi catalyst. Figure 5a shows an image taken with additional external white light illumination to show the entire NW. The bright spot near the center is μ-PL arising from the nanowire. Panels b–j in Figure 5 show a series of μ-PL images taken at various excitation laser positions (laser power density ∼ 34.9 kW/cm2) from the tip to the bottom of the ZnTe NW. These images were taken without the external white light illumination. The color of μ-PL continuously changed from green to yellow. The close inspection reveals that yellow color resulted from the

Figure 3. (a) FESEM image of a Bi catalyst. Areas 1 and 2 indicate the probing areas for EDX spectra. (b) EDX spectra from areas 1 and 2.

Figure 4. (a) FESEM image of Bi particulates found on the substrate region with temperatures lower than 360 °C. A dashed circle represents a Bi particulate for EDX inspection. (b) FESEM image indicating the probing area of a Bi particulate and (c) its EDX spectra. (d) FESEM image indicating the probing area of a tail from a Bi particulate and (e) its EDX spectra.
color mixing of green with red. The diameter of μ-PL spot increases and then saturates. The increase in the spot diameter is not due to the increase in the NW diameter because the tapering effect of the NW is negligible, as observed in Figure 2b. In addition to the major PL spot, red μ-PL linearly extended along the NW can be observed on each side of laser excitation spot. The extension is probably due to optical guiding and is more prominent near the bottom of NW. In addition, the extended red μ-PL consists of discontinuous spots as marked in arrows in Figure 5. The reason for this discontinuous spot array is not clear at present. As will be discussed later, the red μ-PL is originated from an O intermediate band. It is possible that the O doping is not continuous due to surface irregularities or other irregularities.

Figure 6 shows selected PL spectra that correspond to the panels (b, e, g, and i) in Figure 5. The PL band centered at 548 nm (2.26 eV) is due to the band-edge transition from CB to valence band (VB). The broad PL band centered at 690 nm (1.8 eV) is due to the intermediate band formed by O doping, as previously reported for O-doped ZnTe layers. As the excitation laser position moves toward the bottom of NW, the PL intensities from the two peaks concurrently increase, and the ratio of red to green bands also changes. The inset shows the peak intensity ratio $I_{\text{red}}/I_{\text{green}}$ as a function of the position from the tip of NW. The data were well fitted to a sigmoidal curve with an aid of the commercial data analysis software. The sigmoidal curve resembles the error function curve that is commonly used for the analysis of diffusion profiles in constant source diffusion systems. This suggests that a diffusion model could explain this interesting phenomenon.

O-containing species are most likely supplied from $\text{O}_2/\text{H}_2\text{O}$ vapors in the reactor. We suspect that O-containing species enter the NWs by adsorbing onto and diffusing through the side walls of NWs. The bottom of NW will be exposed longer to O-containing species as compared with the tip of NW because the bottom part grows faster. Therefore, a gradient of O concentration naturally occurs along NW. Noting that $I_{\text{red}}/I_{\text{green}}$ saturates at $\sim25$ μm from the tip, we can infer that O diffuses completely from the side-wall surface to the center of NW for the parts of NW located more than $\sim25$ μm from the tip. The diffusion time ($\tau = 1800\sim4500$ s) can be roughly estimated considering the average NW length (50−200 μm) and the growth time (1 h). Then, estimated diffusion coefficient ($=d^2/4\tau$) will be in the range $(2\sim7) \times 10^{-13}$ cm$^2$/s for the growth temperature range ($410\sim360$ °C), where $d$ is the NW diameter ($\sim350$ nm). One may point out the possibility of O incorporation via the Bi catalyst because a large amount of O is found in Bi catalyst. However, if O-containing species in the Bi catalyst incorporate in the ZnTe matrix during the VLS growth of NWs, the O concentration should be uniform along the NW length. Figure S2 in the Supporting Information shows side-view FESEM images of Au-catalyzed ZnTe NWs. In panel b in Figure S2, the existence of Au catalyst atop ZnTe NW can be observed. Figure S3 in the Supporting Information show μ-PL spectrum obtained from Au-catalyzed ZnTe NWs. Despite the reduced PL intensity due to their smaller diameters, the general feature with O-related PL band shows no difference compared with that from Bi-catalyzed NWs. This implies that the intermediate band is not originated from O-containing species found in Bi catalyst. It is known that Bi could be an active dopant for p-type doping of II–VI nanosystems, such as ZnSe NWs. Therefore, it is possible that the red emission comes from the band formed due to Bi doping. This possibility could be ruled out again because the same PL feature can be observed from Au-catalyzed ZnTe NWs. However, the photoconductivity properties of the color-tuned ZnTe NWs will clarify the doping effect. In addition, there is the possibility of surface oxidation (i.e., the formation of ZnO) on the surface. However, SAED patterns by inspecting ZnTe NWs indicate no sign of ZnO phase. The surface oxidation on ZnTe NW may be not the principal cause of O-related PL band.

Other interesting effects can be observed in μ-PL by varying excitation laser power while fixing the excitation position on the NW. Figure 7a shows the μ-PL images taken with increasing excitation laser power density from 1.6 to 34.9 kW/cm$^2$. We again observe the apparent color change from red to green. This results from the interplay between two PL bands. With increasing excitation laser power, red PL saturates, whereas
green PL continuously increases. Figure 7b shows μ-PL spectra with five different excitation powers. The 548 and 690 nm peaks do not shift with changing excitation power, indicating that the temperature increase in the NW due to laser excitation can be neglected. To gain more insight into the interplay between these two bands, we investigate the integrated PLs from two bands in Figure 7c. The crossover point where the green PL band surpasses the red PL band occurs at the laser excitation power density of ∼26.5 kW/cm². As reported by Wang et al., the carrier lifetime for the transition from oxygen intermediate band to VB is longer (1 > μs), whereas that from the band-edge transition is shorter (<1 ps). At low excitation, red PL from the transition from the oxygen intermediate band to VB dominates because electrons quickly relax from CB to intermediate states. However, with increasing excitation laser power, the transition saturates due to limited state density of the intermediate band, whereas green PL from the transition from CB to VB continuously increases.

4. CONCLUSIONS

Bi-catalyzed ZnTe NWs grown by physical vapor transport have been investigated. Straight and single-crystalline NWs with the lengths 100~200 μm and diameters ∼350 nm were produced at low substrate temperatures (410~360 °C). The diameters of Bi catalysts were larger than those of the NW diameters reflecting the characteristics of low-melting-point catalysts. Preferential dissolution of Zn in Bi catalysts compared with Te was observed. An unexpected apparent color-tuning effect from green to red was observed as the laser excitation position was moved from the tip to the bottom of NW during μ-PL measurements. The red PL band can be ascribed to the transition from the CB to the highly radiative intermediate band formed by nonintentional O-doping from residual O₂/H₂O vapor. O-containing species diffuse through the side walls of NWs. This was inferred from the analysis of the ratio of red to green PL intensities as a function of the distance from the NW tip. In addition, with changing excitation intensity, interplay between red and green PL bands due to the fast electron relaxation from the CB to the intermediate band was observed. ZnTe NWs with highly radiative intermediate band may be useful for high-efficiency solar cells and two-color photodetectors.

ASSOCIATED CONTENT

Supporting Information

Histograms of the diameters of Bi catalysts and ZnTe nanowires; side view FESEM image of as-grown ZnTe NWs catalyzed by 50 nm diameter Au nanoparticles and magnified FESEM image of as-grown ZnTe NWs near 50 nm diameter Au catalyst; and ensemble-averaged photoluminescence spectrum of ZnTe nanowires grown with 50 nm diameter Au catalysts. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: yongkim@dau.ac.kr.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Dong-A University research fund. We thank Dr. Hannah J. Joyce in Oxford University for fruitful discussion.

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