

STRUCTURE AND PHOTOLUMINESCENCE PROPERTIES OF TeO₂-CORE/TiO₂-SHELL NANOWIRES

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1 Introduction

Tellurium dioxide (TeO₂) is an attractive semiconductor oxide material owing to its unique physical and chemical properties suitable for various technological applications such as deflectors [1], modulators [2], dosimeters [3, 4], optical storage material [5], laser devices [6], and gas sensors [7, 8]. TeO₂ thin films have been prepared by various techniques such as reactive sputtering [9], dip-coating [10], and vapor deposition [3]. However, there have been few reports on the synthesis of TeO₂ nanostructures. TeO₂ nanowires have been synthesized by thermal evaporation of Te powders [11], laser ablation of Te [7], direct thermal oxidation of Te at ambient pressure in a flow of O₂ without the presence of any catalyst [12], and hydrolysis of tellurium isopropoxide in the presence of tetra alkyl ammonium bromide solution [13]. In particular, there have been very few reports on the luminescence properties of the TeO₂ nanostructures in spite of the wide applications of TeO₂ nanostructures in optical and optoelectronic fields.

A common technique to control and enhance the properties of nanostructures is to create core-shell coaxial heterostructures [14,15]. For example, the intensity of the light emitted from core-shell nanostructures can be increased significantly or the wavelength of the emission can be controlled by selecting a proper coating material and a proper coating layer thickness [16-18]. This paper reports synthesis, structure, and photoluminescence (PL) properties of TeO₂-core/TiO₂-shell nanowires. In particular, the origin of the enhancement of the PL properties of TeO₂ nanowires by their encapsulation with a TiO₂ thin film and thermal annealing is discussed in detail.

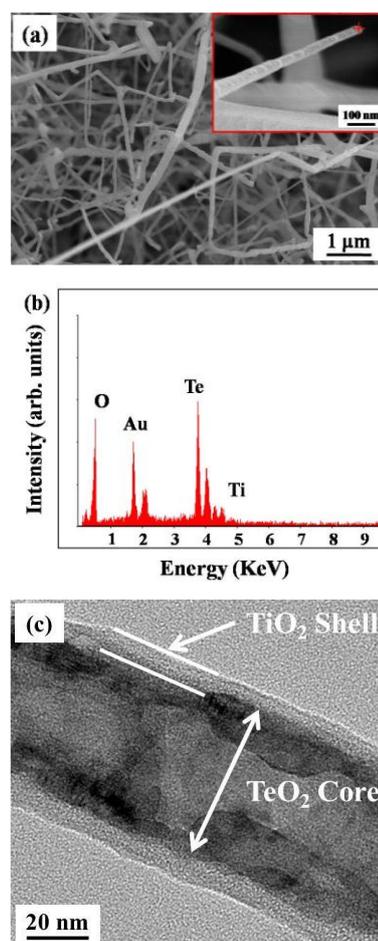


Fig. 1. (a) SEM image and (b) EDX spectrum of TeO₂-core/TiO₂-shell nanowires synthesized by a two-step process: thermal evaporation of TeO₂ powders and MOCVD of TiO₂. (c) Low-magnification TEM image of a typical TeO₂-core/TiO₂-shell nanowire.

2 Experimental

TeO₂-core/TiO₂-shell one-dimensional (1D) nanostructures were prepared by using a two-step process: thermal evaporation of Te powders and metal organic chemical vapor deposition (MOCVD) of TiO₂. The 1D nanostructures will be simply called nanowires hereafter because most of the individual 1D nanostructures have a wire-like morphology as can be seen in SEM images later. First, TeO₂ nanowires were synthesized on a p-type Si (100) substrate in a quartz tube furnace by thermal evaporation of Te powders at 400 °C in the air without using any metal catalyst and supplying any other gas. The thermal evaporation process was conducted for 1 h and then the furnace was cooled down to room temperature. Next, the prepared TeO₂ nanowires were transferred to an MOCVD chamber. The TiO₂ was deposited on the nanowires using the following method: The chamber was evacuated to a base pressure of 135 mTorr. Titanium isopropoxide (TTIP) was used as a precursor for TiO₂. N₂ at a flow rate of 30 sccm was employed as the carrier gas for TTIP during the coating process. At the beginning of the process, O₂ was flushed into the chamber at a flow rate of 4 sccm for approximately 2 s to help dissociate the TTIP. The substrate temperature, canister temperature, and mixture temperature were maintained at 350, 60, and 70 °C, respectively, and the chamber pressure was kept at 800 mTorr throughout the process. Subsequently, the prepared TeO₂-core/TiO₂-shell nanowires were optionally annealed at 650 °C for 1 h in an Ar atmosphere.

The products were characterized by using field emission scanning electron microscopy (FESEM, Hitachi S-4200) equipped with an energy-dispersive X-ray spectrometer (EDXS). The high resolution TEM (HRTEM) images and the selected area electron diffraction (SAED) patterns were also taken on the same systems. Photoluminescence (PL) measurements and X-ray diffraction (XRD) analyses were performed at room temperature on the products by using a 325 nm He-Cd laser (Kimon, IK, Japan) as the excitation source and an X-ray diffractometer (Philips X'pert MRD) with Cu-K_α characteristic radiation, respectively.

3 Results and discussion

Fig. 1a shows the FE-SEM image of the TeO₂-core/TiO₂-shell 1D nanostructures synthesized by a two-step process comprising thermal evaporation and MOCVD in this study. The core-shell nanowires were 40 - 140 nm in diameter and up to a few tens of micrometers in length. No globular particle was observed at the tip of a typical nanowire (inset in Fig. 1a) and no catalyst metal was detected in the EDX spectrum (Fig. 1b) taken at the tip of a typical core-shell nanowire marked by '+' (Fig. 1a). These two facts suggest that the TeO₂ nanowires were not grown by a vapor-liquid-solid (VLS) mechanism but by a vapor-solid (VS) mechanism. The low-magnification TEM image exhibits the TeO₂ core at the center with a thickness of 60-70 nm and two TiO₂ shell layers with a thickness of 8-10 nm at both edges of the TeO₂ core clearly (Fig. 1c). The TiO₂ shell layers were not very uniform in thickness despite having been formed by MOCVD.

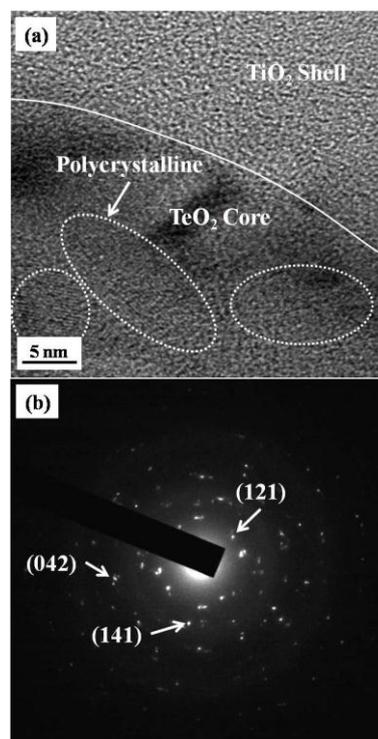


Fig. 2. (a) Local HRTEM image of a typical TeO₂-core/TiO₂-shell nanowire at the core-shell interface region. (b) corresponding SAED pattern.

Several nanocrystallites were observed in the core region on the left hand side whereas no regular

atomic arrangement was observed in the shell region on the right hand side of the HRTEM image taken from the interface region of the core-shell nanowires (Fig. 2a). All the reflection spots on several concentric circles in the corresponding SAED pattern (Fig. 2b) were identified to be (121), (141), and (042) reflections of simple tetragonal-structured TeO_2 with lattice constants $a = 0.481$ nm and $c = 0.7613$ nm (JCPDS No. 78-1713), indicating that the TeO_2 core on the lower side of the TEM image is polycrystalline. The reflections from TiO_2 shell are too weak to be observed, indicating that the as-deposited TiO_2 shell layer on the upper side of the TEM image is amorphous. The crystal structures of the core-shell nanowires was confirmed by the XRD diffraction pattern in Fig. 3. All the reflection peaks in the pattern fit to the simple tetragonal TeO_2 and no peaks from TiO_2 shells are identified in the as-synthesized nanowires. These observations confirm that the cores and shells of the as-synthesized nanostructures are crystalline and amorphous, respectively. Also, comparison of the XRD pattern of the annealed nanowires with the as-synthesized ones reveals that the transformation of the TeO_2 from the α - TeO_2 phase (simple tetragonal structure) to the β - TeO_2 phase (orthorhombic structure) and the partial crystallization of TiO_2 shells have occurred during the annealing process in the cores and shells, respectively.

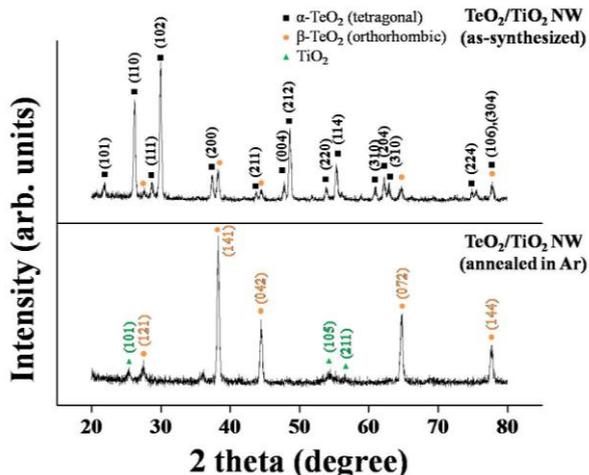


Fig. 3. XRD patterns of as-synthesized and annealed TeO_2 -core/ TiO_2 -shell nanowires.

Fig. 4 displays the PL spectra for TeO_2 -core/ TiO_2 -shell nanowires with different deposition times for TiO_2 , i.e., different TiO_2 shell layer

thicknesses. The uncoated TeO_2 nanowires (0 h) exhibit a weak broad violet emission band centered at approximately 430 nm. In contrast, the TiO_2 -coated TeO_2 nanowires (0.5-2.5 h) have an emission band at approximately 470 nm in the bluish violet region. In other words, TeO_2 nanowires were slightly red-shifted by TiO_2 coating. Also, it appears that the intensity of the bluish violet emission from the core-shell nanowires depends on the TiO_2 deposition time strongly. The bluish violet emission tends to increase very rapidly as the deposition time increases from 0 to 1.5 h and then to decrease very rapidly with further increases in the deposition time from 1.5 to 2.5 h. Consequently, the highest emission intensity was obtained for a deposition time of 1.5 h (corresponding to a TiO_2 coating layer thickness of ~ 10 nm) and its intensity was about 6 times as high as that of the violet emission from the coated TeO_2 nanowires.

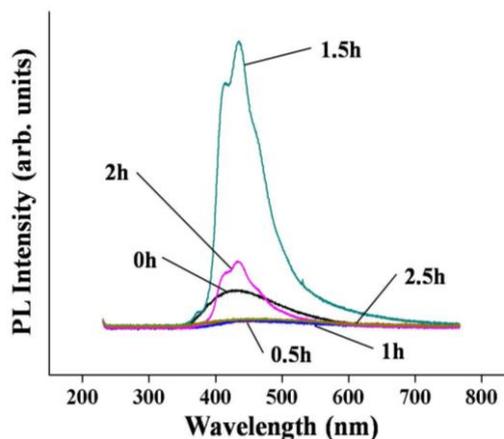


Fig. 4. Room temperature-PL spectra of the TeO_2 -core/ TiO_2 -shell nanowires with different TiO_2 deposition times, i.e., different TiO_2 layer thicknesses.

Regarding the PL properties of TeO_2 1D nanostructures, the as-synthesized TeO_2 nanowires have a violet emission band centered at approximately 425 nm with a shoulder at approximately 540 nm from the TeO_2 crystal grown by the Czochralski method [19]. On the other hand, the room temperature PL spectrum of TiO_2 1D nanostructures is known to be typically dominated by a blue emission band centered at approximately 480 nm [20,21]. Therefore, the bluish violet emission appears to be from the TiO_2 shell layer

rather than from the TeO₂ core. The authors demonstrated recently that sheathing MgO nanorods with TiO₂ (~20 nm) resulted in ultraintense blue-green luminescence and that the origin of the ultraintense luminescence was attributed to a giant oscillator strength effect due to resonant cavity formation [22]. The particularly intense bluish violet emission from the TeO₂-core/TiO₂-shell nanowires for a specific TiO₂ layer thickness of ~ 15 nm (equivalent to 1.5 h) in this work may also be attributed to a giant oscillator strength effect due to self-contained resonant cavities known as Fabry-Perot cavities as in the previously reported TiO₂-sheathed MgO nanorods. For this core-shell nanorod system, considering quite a big difference in refractive index between TeO₂ and TiO₂ (2.25 for TeO₂, 2.609 for rutile TiO₂, and 2.488 for anatase TiO₂) [23], it is assumed that four natural optical resonant cavities form in the TiO₂ shell layer of each core-shell nanorod with a square cross-section.

The cavity length d in a Fabry-Ferot cavity can be expressed as

$$d = \frac{m_c \lambda}{2n} \quad (1)$$

where λ and n are the wavelength of the light and the refractive index of the semiconductor, respectively, and m_c is the cavity order, which is a measure of the resonant modes in the cavity [24]. Assuming that $m_c = 1$ as the cavity length is quite short, the cavity length d for optical resonance calculated by placing $\lambda = \sim 450$ nm and $n = \sim 2.55$ (the average value of the refractive indices of rutile and anatase TiO₂) into the above equation was ~ 88 nm. This calculated value for the cavity length falls well in the range of the diameter of core-shell nanorods measured from the SEM image (50-150 nm), indicating that the core-shell nanostructure system satisfies the condition for optical resonance. Formation of subwavelength resonant cavities like this has been reported recently in several other nanostructures [25-27]. It is known that the optical resonant cavities are likely to form in a box-like structure with faceted surfaces. Some of the core-shell nanowires synthesized in this work may have a rod-like morphology with a square cross-section, i.e., with faceted surfaces, but the others may not have faceted surfaces. It is assumed that subwavelength optical resonant cavities formed

favorably in the ones with faceted surfaces of these two different types of nanowires.

Figure 5 shows that the PL property of the core-shell nanowires can be enhanced significantly by annealing in an Ar atmosphere. The emission peak was shifted from ~ 470 to ~ 420 nm and the emission intensity was increased more than five times by thermal annealing. The new strong emission band at 420 nm in the spectrum of the annealed core-shell nanowires may not be from the TiO₂ shells but from the TeO₂ cores. Therefore, the blue-shift of the emission peak implies that the origin of the main emission was changed from the TiO₂ shell to the TeO₂ core by annealing. It is not clear at present why this change occurred. Further investigation is necessary to reveal the origin of this change in the emission source clearly, but we surmise that the appearance of the new intense violet emission by annealing in an Ar atmosphere may be attributed to the increase in the Ti interstitial and O vacancy concentrations in the core as a result of diffusion of Ti atoms from the shell region to the core region during the annealing process.

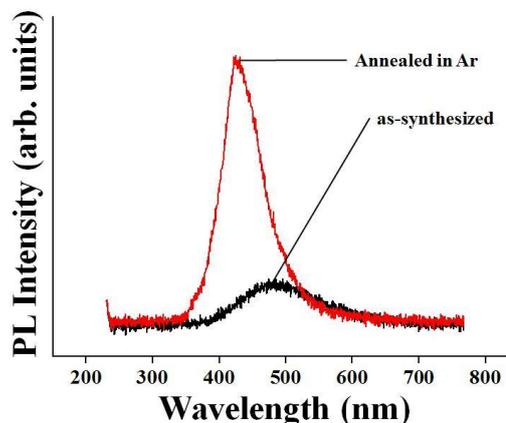


Fig. 5. Room temperature-PL spectra of the as-synthesized and annealed TeO₂-core/TiO₂-shell nanowires

4 Conclusions

The core-shell nanowires fabricated by thermal evaporation of Te powders and MOCVD of TiO₂ were 50 - 150 nm in diameter and up to a few tens of micrometers in length, respectively. The cores and shells of the core-shell nanowires were polycrystalline simple tetragonal TeO₂ and amorphous TiO₂, respectively. The TeO₂ nanowires

had a weak broad violet band at approximately 430 nm. The emission band was shifted to a bluish violet region (450-460 nm) by encapsulation of the nanowires with a TiO₂ thin film. The intensity of the major emission from the TeO₂-core/TiO₂-shell nanowires showed strong dependency on the shell layer thickness. The highest emission was obtained for the MOCVD time of 1.5 h (TiO₂ coating layer thickness: ~15 nm) and its intensity was about 6 times as high as that of the violet emission from the uncapsulated TeO₂ nanowires. The origin of the enhancement in emission intensity can be accounted for by a giant oscillator strength effect due to optical resonant cavity formation in the TiO₂ shell layer. The major emission was enhanced in intensity significantly and blue-shifted by annealing, which may be due to increase in the Ti interstitial and O vacancy concentrations in the TeO₂ cores during annealing.

References

- [1] A. W. Warner, D. L. White and W. A. Bonner "Acousto-optic light deflectors using optical activity in paratellurite". *J. Appl. Phys.*, Vol. 43, No. 11, pp 4489-4495, 1972.
- [2] S. N. Antonov "Acoustooptic nonpolar light controlling devices and polarization modulators based on paratellurite crystals". *Tech. Phys.*, Vol. 49, No. 10, pp 1329-1334, 2004.
- [3] K. Arshak and O. Korostynska "Preliminary studies of properties of oxide thin/thick films for gamma radiation dosimetry". *Mater. Sci. Eng. B*, Vol. 107, pp 224-232, 2004.
- [4] K. Arshak and O. Korostynska "Gamma radiation dosimetry using tellurium dioxide thin film structures". *Sensors*, Vol. 2, No. 2, pp 347-355, 2002.
- [5] S.N.B. Hodgson and L. Weng "Sol-Gel processing of tellurium oxide and suboxide thin films with potential for optical data storage application". *J. Sol-Gel Sci. Technol.*, Vol. 18, No. 2, pp 145-158, 2000.
- [6] S.N.B. Hodgson and L. Weng "Chemical and sol-gel processing of tellurite glasses for optoelectronics". *J. Mater. Sci.: Mater. Electron.*, Vol. 17, No. 9, pp 723-733, 2006.
- [7] Z. Liu, T. Yamazaki, Y. Shen, T. Kikuta and N. Nakatani "Synthesis and characterization of TeO₂ nanowires". *Jpn. J. Appl. Phys.*, Vol. 47, pp 771-774, 2008.
- [8] Z. Liu, T. Yamazaki, Y. Shen, T. Kikuta, N. Nakatani and T. Kawabata "Room temperature gas sensing of p-type TeO₂ nanowires". *Appl. Phys. Lett.*, Vol. 90, pp 173119, 2007.
- [9] R. Nayak, V. Gupta, A.L. Dawar and K. Sreenivas "Optical waveguiding in amorphous tellurium oxide thin films". *Thin Solid Films*, Vol. 445, pp 118-126, 2003.
- [10] A. Lecomte, F. Bamière, S. Coste, P. Thomas and J.C. Champarnaud-Mesjard "Sol-Gel processing of TeO₂ thin films from citric acid stabilized tellurium isopropoxide precursor". *J. Europ. Ceram. Soc.*, Vol. 27, pp 1151-1158, 2007.
- [11] Z.-Y. Jiang, Z.-X. Xie, X.-H. Zhang, S.-Y. Xie, R.-B. Huang and L.-S. Zheng "Synthesis of α -tellurium dioxide nanorods from elemental tellurium by laser ablation". *Inorg. Chem. Commun.*, Vol. 7, pp 179-181, 2004.
- [12] T. Siciliano, A. Tepore, G. Micocci, A. Genga, M. Siciliano and E. Filippo "Transition from n- to p- type electrical conductivity induced by ethanol adsorption on α -tellurium dioxide nanowires". *Sens. Actuators. B*, Vol. 138, pp 207-213, 2009.
- [13] A. Huriet, S. Daniele and L.G. Hubert-Pfalzgraf "Effect of titanium additives on the growth of tellurium dioxide crystals in a sol-gel process". *Mater. Lett.*, Vol. 59, pp 2379-2382, 2005.
- [14] Y. Wu, J. Xiang, C. Yang, W. Lu and C. M. Lieber "Single-crystal metallic nanowires and metal/semiconductor nanowire heterostructures". *Nature*, Vol. 430, pp 61-65, 2004.
- [15] L. J. Lauhon, M. S. Gudiksen, D. Wang, C. M. Lieber "Epitaxial core-shell and core-multishell nanowire heterostructures". *Nature*, Vol. 420, pp 57-61, 2002.
- [16] Y. B. Li, Y. Bando, D. Golberg and Y. Uemura "SiO₂-sheathed InS nanowires and SiO₂

- nanotubes". *Appl. Phys. Lett.*, Vol. 83, No. 19, pp 3999-4001, 2003.
- [17] S. Sun, G. Meng, G. Zhang and L. Zhang "Controlled growth and optical properties of one-dimensional ZnO nanostructures on SnO₂ nanobelts". *Crystal Growth & Design*, Vol. 7, No. 10, pp 1988-1991, 2007.
- [18] J. Jun, C. Jin, H. Kim, J. Kang and C. Lee "The structure and photoluminescence properties of TiO₂-coated ZnS nanowires". *Appl. Phys. A*, Vol. 96, No. 4, pp 813-818, 2009.
- [19] I. Dafinei, C. Dujardin, E. Longo and M. Vignati "Low temperature photoluminescence of pure and doped paratellurite (TeO₂) crystals". *Phys. Stat. Sol. (a)*, Vol. 204, No. 4, pp 1567-1570, 2007.
- [20] J. Liu, J. Li, A. Sedhain, J. Lin and H. Jiang "Structure and photoluminescence study of TiO₂ nanoneedle texture along vertically aligned carbon nanofiber arrays". *J. Phys. Chem. C*, Vol. 112, No. 44, pp 17127-17132, 2008.
- [21] Y. X. Zhang, G.H. Li, Y.X. Jin, Y. Zhang, J. Zhang and L.D. Zhang "Hydrothermal synthesis and photoluminescence of TiO₂ nanowires". *Chem. Phys. Lett.*, Vol. 365, pp 300-304, 2002.
- [22] C. Jin, H. Kim, W. I. Lee and C. Lee "Ultraintense luminescence in semiconducting-material-sheathed MgO nanorods". *Adv. Mater.*, Vol. 23, pp 1982-1987, 2011.
- [23] D. R. Lide "CRC Handbook of Chemistry and Physics". CRC Press, Boca Raton, FL, 1999.
- [24] D. Delbeke, R. Bockstaele, P. Bienestman, R. Baets and H. Benisty "High-efficiency semiconductor resonant-cavity light-emitting diodes: a review". *IEEE J. Sel. Top. Quantum Electron.*, Vol. 8, No. 2, pp 189-206, 2002.
- [25] M. T. Hill, Y.-S. Oei, B. Smalbrugge, Y. Zhu, T. D. Vries, P. J. V. Veldhoven, P. J. V. Veldhoven, F. W. Otten, T. J. Eijkemans, J. P. Turkiewicz, H. D. Waardt, E. J. Geluk, S.-H. Kwon, Y.-H. Lee, R. Notzel and M. K. Smit "Lasing in metallic-coated nanocavities". *Nat. Photonics*, Vol. 1, pp 589-594, 2007.
- [26] M.-K.Seo, S.-H. Kwon, H.-S. Ee and H.-G. Park "Full three-dimensional subwavelength high-Q surface-plasmon-polariton cavity". *Nano Lett.*, Vol. 9, No. 12, pp 4078-4082, 2009.
- [27] S.-H. Kwon, J.-H. Kang, C. Seassal, S.-K. Kim, P. Regreny, Y.- H Lee, C. M. Lieber and H.-G. Park "Subwavelength plasmonic lasing from a semiconductor nanodisk with silver nanopan cavity". *Nano Lett.*, Vol. 10, pp 3679-3683, 2010.