Intense ultraviolet emission from needle-like WO₃ nanostructures synthesized by noncatalytic thermal evaporation

Sunghoon Park, Hyunsu Kim, Changhyun Jin and Chongmu Lee*

Abstract
Photoluminescence measurements showed that needle-like tungsten oxide nanostructures synthesized at 590°C to 750°C by the thermal evaporation of WO₃ nanopowders without the use of a catalyst had an intense near-ultraviolet (NUV) emission band that was different from that of the tungsten oxide nanostructures obtained in other temperature ranges. The intense NUV emission might be due to the localized states associated with oxygen vacancies and surface states.

Background
Tungsten oxide is of particular interest owing to its outstanding electrochromic, optochromic, and gas chromic properties [1-3], which make it a promising candidate for applications in smart windows, wide-angle high-contrast displays, gas, and temperature sensors [4-6]. Tungsten oxide in bulk form has been studied extensively over the past few decades. Nevertheless, there are relatively few reports on tungsten oxide nanostructures. In particular, little is known about the luminescence properties of tungsten oxide nanostructures possibly because tungsten oxide is an indirect band gap semiconductor with low-emission efficiency. Two strong emissions from tungsten oxide nanostructures, near-ultraviolet (NUV) emission and blue emission, have been reported [7-12]. Nevertheless, there is still some controversy regarding the origins of the two emissions. Niederberger et al. [7] suggested that the blue emission from WO₃ nanoparticles in an ethanol solution was due to a band-to-band transition. Luo et al. [8] also reported that the NUV and blue emissions from the WO₃-x nanowire network were due to the state of oxygen vacancies and a band-to-band transition, respectively. On the other hand, several reports have suggested the opposite. Lee et al. [9] and Feng et al. [10] reported that the NUV emission was attributed to a band-to-band transition; whereas, the blue emission was due to the localized states of oxygen vacancies or defects. Chang et al. [11] also suggested that the blue emission from nitrogen-doped tungsten oxide nanowires was due to oxygen vacancies.

In recent years, one-dimensional (1D) nanostructures have been investigated extensively owing to their interesting properties and potential applications in electronics and optoelectronics. A range of methods have been used to synthesize tungsten oxide 1D nanostructures, such as thermal oxidation, thermal evaporation, chemical vapor deposition, hydrothermal reaction, electrochemical techniques, aid of intercalated polyaniline, solution-based colloidal approach, and a combination of electrospinning and sol-gel techniques [13]. Of these, thermal evaporation might be the most attractive technique with the advantage of synthesizing a range of tungsten oxide nanostructures depending on the substrate temperature at lower temperatures than other techniques. This paper reports a simple novel thermal evaporation technique to obtain tungsten oxide nanostructures with a range of morphologies and sizes using a single apparatus and a single process and an intense ultraviolet emission from the needle-like tungsten oxide nanostructures grown in the temperature zone from 590 to 750°C by thermal evaporation.

Experimental
Tungsten oxide nanostructures were synthesized by a thermal evaporation technique without a catalyst. The
thermal evaporation process was carried out in a conventional horizontal tube furnace, as shown in Figure 1. An alumina boat with a length of 4 cm and a diameter of 1.5 cm containing a mixture of WO₃ and graphite powders (1:1) were placed at the center of the quartz tube, and five pieces of P-type Si(100) wafer used as substrates were placed in five different temperature zones approximately 12 cm away from the alumina boat in the downstream direction: zone 1 (450°C to 590°C), zone 2 (590°C to 750°C), zone 3 (750°C to 860°C), zone 4 (860°C to 920°C), and zone 5 (920°C to 1000°C). Figure 1 shows the schematic diagram of the thermal evaporation system used to synthesize the tungsten oxide nanostructures and the temperature versus substrate position showing five different substrate temperature zones.
4 (860°C to 920°C), and zone 5 (920°C to 930°C). After arranging the substrates, the tube was pumped down to 10⁻³ Torr using a rotary pump. High-purity nitrogen, and oxygen gases were introduced into the tube at flow rates of 200 and 5 sccm, respectively, throughout the entire synthesis process. The furnace temperature was increased to 1,050°C at a heating rate of 30°C/min. After being maintained at 1,050°C for 1 h, the furnace was cooled to room temperature, and the products were removed. During synthesis, the temperature in each of the five different zones was monitored using a thermocouple.

The collected nanostructure samples were characterized by scanning electron microscopy (SEM, Hitachi S-4200, Hitachi Ltd., Tokyo, Japan), transmission electron microscopy (TEM, Philips CM-200, Koninklijke Philips Electronics N.V., Amsterdam, Netherlands) equipped with an energy-dispersive X-ray spectrometer, and X-ray diffraction (XRD, Philips X'pert MRD diffractometer, Koninklijke Philips Electronics N.V., Amsterdam, Netherlands). The samples used for characterization were dispersed in absolute ethanol and ultrasonicated before the SEM and TEM observations. Glancing angle (0.5°) XRD was performed to examine the phases of the products obtained. Photoluminescence (PL) measurements were conducted at room temperature by using a SPEC-1403 PL spectrometer (HORIBA Ltd., Tokyo, Japan) with a He-Cd laser (325 nm) as the excitation source. The power of the He-Cd laser was 55 mW, and the diameter of the focal spot was 1 mm. Thus, the power density at the surface of the sample surface was approximately 7 W/cm².

Results and discussion

Figure 2a,b,c,d,e shows SEM images of the tungsten oxide nanostructures synthesized at temperature zones 1 to 5 (Figure 1), respectively. A pad tungsten oxide layer and a very low density of tungsten oxide whiskers oriented in random directions on the pad tungsten oxide layer in zone 1 were observed (Figure 2a), which suggests that the two-dimensional (2D) nanostructures formed first on the Si substrate and subsequently 1D nanostructures formed on the pregrown 2D nanostructures. The diameters and lengths of the whiskers were in the range of a few tens of nanometers and 0.5 to 2 μm, respectively. High-density fine needle-like tungsten oxide nanowires oriented in random directions were observed in zone 2 (Figure 2b). The diameters and lengths of these nanowires were in the range of a few tens to a few hundreds of nanometers and 5 to 10 μm, respectively. The nanowires were oriented randomly, and some appeared to be connected to each other. Larva-like nanostructures were grown in random directions in zone 3 (Figure 2c). They were partially networked by the growth of secondary dendrites. The nanostructures were not uniform in diameter. The diameters of the nanostructures ranged from 0.2 to 1.5 μm, and the lengths were in the range of 3 to 6 μm. Each nanostructure had several nodes like a larva. The nanostructures grown in zone 4 had a very short rod-like morphology with a rectangular or square cross-section (Figure 2d). They were particles with an orthorhombic shape; the edge lengths of which were in the range of 1 to 3 μm. A tungsten oxide film thicker than the pad tungsten oxide grown in zone 1 was grown again in zone 5 (Figure 2e). Based on the SEM images of the nanostructures grown in the different temperature zones, the individual nanostructures appear to change from a longer, thinner needle-like wire morphology to a shorter, thicker rod-like morphology as the substrate temperature was increased.

Figure 3 shows the PL spectra of the nanostructures synthesized at five different substrate temperature zones. A relatively strong broad blue emission band centered at approximately 475 nm, and several shoulders exist in the spectrum of the nanostructures synthesized in zone 1. This blue emission might be attributed to the band-to-band emission, as suggested by Niederberger et al. [7] and Luo et al. [8], because the photon energy 2.61 eV corresponding to the wavelength of the blue emission falls in the range of the indirect energy gap of tungsten oxide corresponding to 475 nm. This is in good agreement with previous reports. Chang et al. [11] observed a strong blue emission peak at approximately 470 nm in the PL spectrum of nitrogen-doped tungsten oxide nanowires synthesized by reducing the tungsten oxide source with NH₃ gas on a Si wafer. Luo et al. [8] also reported strong blue emission band centered at 467 nm from tungsten oxide nanowire networks. In contrast, a sharp strong NUV emission band at 390 nm and a broad weak blue emission band centered approximately at 475 nm from the needle-like nanostructures grown in zone 2 were observed in this study. The strong NUV emission from our tungsten oxide nanowires synthesized in zone 2 can be explained by a combination of the following two sources:

1. Oxygen vacancies: The NUV emission is attributed to the localized states of oxygen vacancies in the conduction band of the needle-like tungsten oxide nanostructures. Luo et al. [8] reported an NUV emission band centered at 395 nm from WO₃₋ₓ nanowire networks, even if the emission band was not as sharp and strong as the one from the needle-like tungsten oxide nanostructures synthesized in this work. They attributed the NUV emission to the states of oxygen vacancies in the conduction band of WO₃₋ₓ nanowire networks. They also demonstrated using SEM and X-ray photoemission spectroscopy analyses that oxygen vacancies existed in
the WO$_3$ -$_x$ nanowire network but not in the WO$_3$ nanowire network. Needle-like tungsten oxide nanostructures were grown in zone 2 (590°C to 750°C), i.e., in quite a low-temperature range. The W/O atomic ratio (8.01/2.80) in the needle-like tungsten nanostructures is approximately 2.86 as shown in the energy-dispersive X-ray spectroscopy (EDS) line scanning profile (Figure 4), so that the nanostructures do not have a molecular formula of WO$_3$ but of WO$_3$ -$_x$. This may be due to the relatively low process temperature for the tungsten nanowire synthesis. The tungsten oxide nanostructures grown at low temperatures have been reported to commonly possess more defects such as oxygen vacancies [9]. Therefore, the NUV emission from the needle-like
tungsten nanostructures was attributed to the localized states of oxygen vacancies, as Luo et al. [8] suggested.

2. Surface states: The needle-like nanostructures obviously have a far higher surface state density than other nanostructures, such as thicker nanorods and thin films synthesized in zones 1, 3, 4, and 5. Therefore, the far stronger NUV emission from the needle-like nanostructures than that from the WO$_{3-x}$ nanowire networks in Luo et al’s report [8] may be due partially to the higher density of surface states at the surfaces of the needle-like nanostructures.

The PL spectra showed that the NUV emission intensity tends to decrease with increasing substrate temperature, but the blue emission intensity tends to increase. This tendency appears to depend on the morphology of the tungsten oxide nanostructures because the morphology of the nanostructures also changes from whiskers to nanoneedles and nanorods to thin films. In other words, the surface-to-volume ratio of the nanostructures decreases with increasing substrate temperature. In addition, the oxide nanostructures synthesized at low temperatures commonly possess more oxygen vacancies. Therefore, the blue luminescence is predominant in tungsten oxide nanostructures with a low oxygen vacancy concentration and low surface-to-volume ratios synthesized at higher temperatures. This suggests that the blue emission does not originate from deep level defects but from a band-to-band transition. The strong blue emission obtained in the lowest temperature zone (zone 1) is presumably due to the low surface-to-volume ratio of the pad tungsten oxide layer with a thin film morphology synthesized in such a low-temperature range.

| Element | Atomic% |
|---------|---------|
| C       | 64.32   |
| O       | 8.01    |
| Cu      | 24.87   |
| W       | 2.80    |
| Totals  | 100.00  |

Figure 3 PL spectra of the nanostructures. PL spectra of the tungsten oxide nanostructures grown in the different substrate temperature zones.

Figure 4 EDS line scanning profile. TEM-EDX line concentration profiles of W and O along the line drawn across the diameter of a typical tungsten oxide nanowire synthesized by a catalyst-free thermal evaporation method. Cu and C in the inset table are due to TEM grid.
Conclusions

In summary, intense NUV emission was obtained from the needle-like WO₃ nanostructures synthesized in the temperature range of 590°C to 750°C by the thermal evaporation of WO₃ powders. The NUV emission might be due to localized states associated with oxygen vacancies and surface states.

Acknowledgements

This study was supported by the Korea Science and Engineering Foundation through "the 2010 Core Research Program."

Authors’ contributions

SP carried out the SEM and XRD analyses. HK SP carried out the TEM analysis. CJ performed the PL analysis. CL conceived of the study, and participated in its design, coordination, and drafting the manuscript. All authors read and approved the final manuscript.

Competing interests

The authors declare that they have no competing interests.

Received: 17 May 2011 Accepted: 13 July 2011 Published: 13 July 2011

References

1. Granqvist CG: Electrochromic tungsten oxide films: review of progress 1993-1998. Sol Energy Mater Sol Cells 2000, 60:201-262.
2. Hao J, Studenikin SA, Cocivera M: Transient photoconductivity properties of tungsten oxide thin films prepared by spray pyrolysis. J Appl Phys 2001, 90:6064-6069.
3. Salje EH: Polarons and bipolarons in tungsten oxide, WO₃⁺. Eur J Solid State Inorg Chem 1994, 31:805-821.
4. Santato C, Odziemkowski M, Ulmann M, Augustynski J: Crystallographically oriented mesoporous WO₃ films: synthesis, characterization, and applications. J Am Chem Soc 2001, 123:10639-10649.
5. Baek SH, Choi KS, Jaramillo JT, Stucky GD, McFarland EW: Enhancement of photocatalytic and electrochromic properties of electrochemically fabricated mesoporous WO₃ thin films. Adv Mater 2003, 15:1269-1273.
6. Ponzoni A, Comini E, Sberveglieri G, Zhou J, Deng SZ, Xu NS, Ding Y, Wang ZL: Ultraviolet and highly selective gas sensors using three-dimensional tungsten oxide nanowire networks. Appl Phys Lett 2006, 88:203101.
7. Niederberger M, Bartl MH, Stucky GD: Benzyl alcohol and transition metal chlorides as a versatile reaction system for the nonaqueous and low-temperature synthesis of crystalline nano-objects with controlled dimensionality. J Am Chem Soc 2002, 124:13642-13643.
8. Luo JY, Zhao FL, Gong L, Chen HJ, Zhou J, Li ZL, Deng SZ, Xu NS: Ultraviolet-visible emission from three-dimensional WO₃+ nanowire networks. Appl Phys Lett 2007, 91:093124.
9. Lee K, Seo WS, Park JT: Synthesis and optical properties of colloidal tungsten oxide nanorods. J Am Chem Soc 2005, 127:3408-3409.
10. Feng M, Pan AL, Zhang HR, Li ZA, Liu F, Liu HW, Shi DX, Zou BS, Gao HJ: Strong photoluminescence of nanostuctured crystalline tungsten oxide thin films. Appl Phys Lett 2005, 86:141901.
11. Chang MT, Chou LJ, Chuah YL, Lee YC, Hsieh CH, Chen CD, Lan YW, Chen LJ: Nitrogen-doped tungsten oxide nanowires: low-temperature synthesis on Si, and electrical, optical, and field-emission properties. Small 2007, 3:658-664.
12. Rajagopal S, Nataraj D, Mangalaraj D, Djoudi Y, Robichaud J, Khyzhun OY: Controlled growth of WO₃ nanowires with three different morphologies and their structural, optical, and photodecomposition studies. Nanoscale Res Lett 2009, 4:1355-1362.
13. Hong K, Xie M, Hu R, Wu H: Synthesizing tungsten oxide nanowires by a thermal evaporation method. Appl Phys Lett 2007, 90:173121.