

Origin of low-temperature photoluminescence from SnO₂ nanowires fabricated by thermal evaporation and annealed in different ambients

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Rutile (110) tin dioxide nanowires synthesized by thermal oxidation of tin powders and having a band gap of 4.2 eV were annealed in vacuum and O₂ at 600 °C for 1 h. The photoluminescence (PL) properties of the as-grown and annealed samples were measured from 10 to 300 K. The nanowires annealed in O₂ showed weak luminescence at 393 nm at temperatures below 100 K, and no luminescence could be detected at temperatures higher than 100 K. In contrast, the nanowires annealed in vacuum exhibited strong luminescence at 480 nm at temperatures lower than 100 K and at 600 nm when the temperature was higher than 100 K. Our PL results show that the emissions originate from the defect electronic states in the band gap formed by surface oxygen vacancies and solve the long-time controversy over the origin of the luminescence. © 2006 American Institute of Physics. [DOI: 10.1063/1.2201617]

As an *n*-type wide band gap semiconductor ($E_g = 3.6$ eV at 300 K for bulk SnO₂), one-dimensional (1D) tin oxide nanostructures have attracted great interest in recent years. The nanostructures are particularly useful in gas sensors and optical devices due to their high surface to volume ratio, remarkable resistivity variation in a gaseous environment, and high exciton binding energy of 130 meV. Much progress has been made on the synthesis and structural characterization of 1D SnO₂ nanostructures.^{1–5} In addition, owing to their unique electrical and sensing properties, the use of these nanostructures in real devices is progressing rapidly.^{6–10} However, some fundamental issues pertaining to the optical properties of 1D SnO₂ nanostructures are still unclear.¹¹ Optical measurements are very useful to the determination of the structure, defects, and impurities in these nanostructures. Studies on the luminescence of 1D SnO₂ nanostructures at room temperature^{11–16} have revealed emission in the range of 400 to 600 nm. It has been generally believed that the luminescence originates from defects such as tin interstitials, dangling bonds, or oxygen vacancies, but direct experimental proof of the luminescence center has not been shown.

Surface oxygen vacancies play an important role in the semiconducting behavior of tin oxide, and they are also crucial to their optical properties. In this study, we conducted high-pressure and high-temperature oxidation that yielded a nearly ideal surface allowing the experimental investigation of the properties of surface defects on the SnO₂ nanowires. Direct comparison among the various surfaces formed by oxidation and heating in vacuum reveals the chemical, struc-

tural, and electronic nature of the oxygen vacancies on the SnO₂ nanowires.

Single-crystalline SnO₂ nanowires of transverse size of about 50–500 nm were synthesized by thermal evaporation of metal tin powders (99.99%) in a quartz tube.¹⁷ The nanowires were annealed in vacuum (about 1×10^{-6} Torr) or under flowing oxygen at 100 SCCM (standard cubic centimeter per minute). X-ray diffraction (XRD) reveals that the as-grown SnO₂ nanowires have the typical rutile phase and high-resolution transmission electron microscopy (HRTEM) images (not shown here) indicate that the surface is a (110) plane, which is terminated with bridging oxygen atoms.¹⁸

A shift of the absorption edge towards a higher energy is generally expected from nanocrystalline materials. For confirmation, UV/visible absorption spectra were acquired from the as-grown SnO₂ nanowires and the results are depicted in Fig. 1 (curve A). The optical transition of SnO₂ crystals is known to be direct.¹⁹ In this case, the absorption coefficient α is expressed as $\alpha(h\nu) \propto (h\nu - E_g)^{1/2} / h\nu$.²⁰ Plots of $[\alpha(h\nu)]^2$ vs $h\nu$ can be derived from the absorption data. The intercept of the tangent gives a good approximation of the band gap

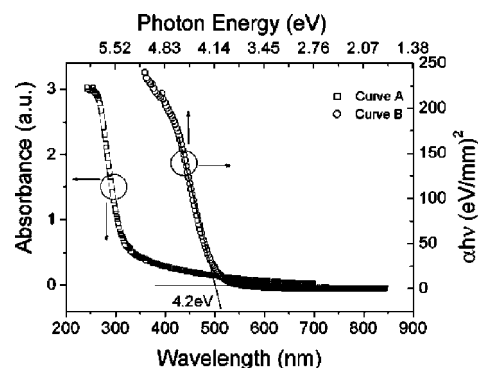


FIG. 1. UV/visible absorption spectra (curve A) acquired from the SnO₂ nanowires together with the $[\alpha(h\nu)]^2$ vs photon energy curve (curve B).

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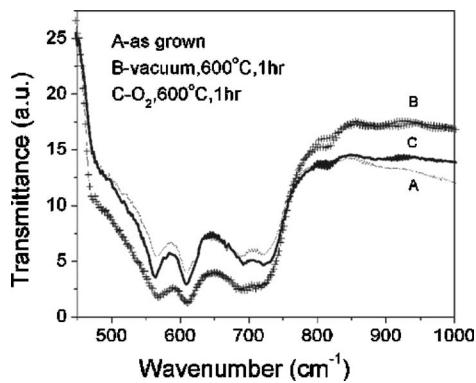


FIG. 2. FTIR spectra of the SnO₂ nanowires: (A) as grown, (B) annealed in vacuum, and (C) annealed in O₂.

energy of the direct band gap materials. As shown in curve B in Fig. 1, the band gap of the nanowires is ~ 4.2 eV which is larger than the value of 3.62 eV for bulk SnO₂ due to the quantum size effect.^{21,22}

The chemical bonding states at the nanowire surface were characterized by Fourier transform infrared (FTIR) to obtain information about the surface defects after annealing. As shown in Fig. 2, the main variable peaks appear in the range of 400 to 800 cm⁻¹. All the samples exhibit two well-defined peaks at ~ 560 and ~ 610 cm⁻¹. Two relatively weak peaks centered at 678 and 720 cm⁻¹ can be observed from the as-grown and oxidized SnO₂ nanowires and become two shoulders in the vacuum-annealed sample. The peaks at 610 and 678 cm⁻¹ can be assigned to the transverse and longitudinal E_u modes, respectively. The two absorption peaks at 560 and 720 cm⁻¹ arise from the bending vibrations of O–Sn–O, which correspond to the A_{2u} modes.²³ It can be observed that the sample annealed in vacuum shows the strongest absorption band from 470 to 800 cm⁻¹ but the weakest absorption peaks out of the three samples. The 678 and 720 cm⁻¹ absorption peaks transform into two shoulders while the 560 cm⁻¹ absorption peak broadens and extends to 470 cm⁻¹. Previous investigations²⁴ have shown that heating a SnO₂ surface in vacuum removes surface oxygen. This suggests that annealing in vacuum destroys the surface stoichiometric structure and increases the structure disorder, thereby resulting in the broadened and strong absorption bands. The sample annealed in O₂ shows the sharpest absorption peaks in the three samples, suggesting that oxidation removes partial surface oxygen deficiencies and leads to a more stoichiometric surface. This oxidized surface is believed to closely approximate an ideal, stoichiometric (110) surface.

Figure 3 shows the temperature dependence of the photoluminescence (PL) spectra measured from 340 to 640 nm using a 325 nm He–Cd laser. The as-grown SnO₂ nanowires exhibit different luminescence bands at different temperatures, with 100 K being the transitional temperature. At temperatures below 100 K, the nanowires show an asymmetric, smooth, and broad luminescence band centered at around 480 nm (2.58 eV) with a right shoulder at 600 nm (2.06 eV), whereas at higher temperatures, the asymmetric broad luminescence band centered at about 600 nm with a left shoulder at 480 nm is observed. Therefore, there appears to be two types of emission centers in the as-grown nanowires. The intensity of the emission peak centered at 480 nm decreases rapidly by about four times as the temperature rises from

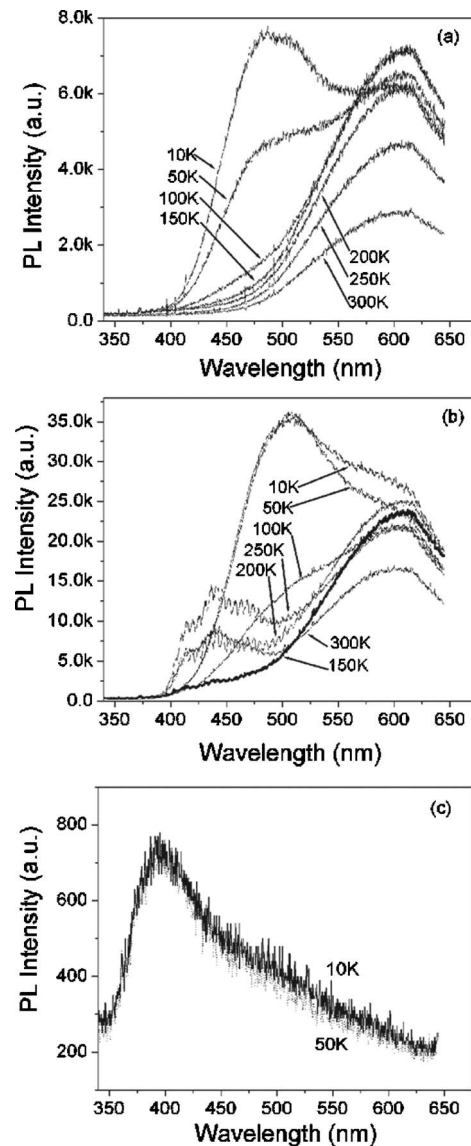


FIG. 3. PL spectra of the SnO₂ nanowires obtained between 10 and 300 K: (a) as grown, (b) annealed in vacuum, and (c) annealed in O₂.

10 to 100 K and almost disappears at room temperature. The intensity of the peak centered at 600 nm increases slightly from 10 to 150 K and then decreases with increasing temperature. It is the dominant luminescence at room temperature, and hence, the temperature has a much larger influence on the intensity of the emission band at 480 nm.

Figure 3(b) displays the low-temperature PL result of the sample annealed in vacuum. At temperature lower than 150 K, this sample shows a PL spectrum that is similar to that obtained from the as-grown sample. There are two luminescence bands centered at 500 nm (redshifted by 20 nm after annealing in vacuum compared to the as-grown one) and 600 nm, but the intensity of the sample annealed in vacuum is higher by more than three times. When the temperature is higher than 150 K, another luminescence band centered at 435 nm with two shoulders at 415 and 465 nm on each side appears. As shown in Fig. 3(c), only a UV luminescence band centered at 393 nm can be detected from the sample annealed in oxygen at 10 and 50 K. When the temperature rises to 100 K, no obvious luminescence can be detected.

Since the band gap of the present SnO₂ nanowires is 4.2 eV (295 nm) as determined by UV/visible absorption, all

the observed luminescence bands cannot be ascribed to the direct recombination of a conduction electron in the Sn $4d$ band with a hole in the O $2p$ valence band. With regard to the strong and broadened absorption band in the FTIR result of the sample annealed in vacuum and the sharper absorption band in the sample annealed in O_2 , it is reasonable to believe that the variations in the luminescence in the SnO_2 nanowires originate from the surface state change. Together with the disappearance of the luminescence bands at 480, 600, and 435 nm with two shoulders in the sample annealed O_2 , it can be inferred that these luminescence bands are all caused by surface oxygen deficiencies. The near band edge of the UV luminescence band centered at 393 nm from the oxidized SnO_2 nanowires can only be observed at very low temperature, and the emission intensity decreases rapidly with increasing temperature due to the thermal quenching effect. Dai *et al.*²⁵ have observed near band edge emission from T-ZnO nanorods and they ascribe it to the high quality and quantum confinement effect. It should be noted that the spectrum acquired from the oxidized surface in Fig. 3(c) suggests only a very small density of states in the band gap, which is consistent with the result of FTIR. In other words, the lack of defect electronic states in the band gap indicates that the oxidized surface is stoichiometric.

Low-temperature PL at 480 and 590 nm has been reported from tin oxide powder and assigned to a single defect center.²⁶ In contrast, our SnO_2 nanowires show two distinct emission peaks and different temperature dependences due to the two different luminescence defect centers in the as-grown SnO_2 nanowires. Moreover, the 480 nm peak may originate from a shallower energy level located in the band gap compared to the 600 nm luminescence. The different variations in the two emission peaks with increasing temperature may be explained as follows. The 480 nm peak is more sensitive to temperature, as indicated by a fourfold decrease as the temperature increases from 10 to 100 K. This suggests that the 480 nm peak is related to a shallow energy level which is not thermally stable for electrons at this level. At temperatures lower than 100 K, most of the excited electrons return to the shallow level via a nonradiative transition leading to the 480 nm PL enhancement. However, as the temperature increases to higher than 100 K, most of the excited electrons are thermally ionized by a transition to the conduction band and may recombine via nonradiative transitions, resulting in the rapid reduction in the luminescence intensity at 480 nm. In comparison, the emission peak at 600 nm exhibits a smaller dependence on the temperature, suggesting that most of the electrons are excited to the deeper defect energy level and thermally stable and will return to the ground state via radiative transitions. The intensity reduction with increasing temperature may thus be mainly induced by enhanced non-radiative recombination.

The luminescence band at 435 nm observed from the sample annealed in vacuum originates from the surface of the SnO_2 nanowires as well. This emission shows the different luminescence band shape and unusual temperature dependence, suggesting that it is a different type of surface oxygen deficiency. According to previous work,¹⁸ two kinds of surface oxygen vacancies can be produced on the SnO_2 (110) surface after vacuum annealing. They are bridging oxygen vacancies at temperatures below 800 K that constitute the main oxygen deficiency in SnO_2 nanowires and in-plane oxygen vacancies at temperatures of 800 K and above.

The in-plane oxygen vacancies have different electronic configurations, neutral, singly and doubly charged, which may be the reason for the two shoulders around 435 nm. More work is being conducted to further investigate the effects of the two types of defects on the electrical and optical properties of the SnO_2 nanostructures.

In summary, the low-temperature PL characteristics of SnO_2 nanowires synthesized by thermal evaporation of tin powders in the presence of oxygen and annealed in different ambients have been studied. Our experimental results show that the ubiquitous emission peaks at 480 and 600 nm originate from defect electronic states formed by surface oxygen vacancies. The 435 nm luminescence peak from the SnO_2 nanowires annealed in vacuum shows a monotonic temperature dependence that can be attributed to the defect electronic state in band gap resulting from in-plane oxygen vacancies.

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