Temperature dependent photoluminescence from ZnO nanowires and nanosheets on brass substrate

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The temperature-dependent optical properties of ZnO nanosheets and nanowires fabricated on conductive brass substrates with different surface-to-volume ratios and morphologies are investigated. The near band edge and deep-level emission mechanisms are studied. The blueshifted donor bound exciton \( D^0 \) peak and enhanced deep-level emission in the low-temperature photoluminescence spectrum of the nanosheets are due to the large surface-to-volume ratios. Although \( D^0 \) is the dominant emission from both the nanowires and nanosheets at low temperature, the room-temperature spectra are dominated by \( D^0 \) (nanowires) and first order longitudinal optical phonon replica of free exciton (nanosheets). The decay in the \( D^0 \) peak intensity stems from the thermal dissociation of \( D^0 \) to free exciton. © 2008 American Institute of Physics. [DOI: 10.1063/1.3033823]

One-dimensional (1D) semiconductor nanostructures such as nanowires (NWs), nanotubes, and nanobelts (NBs) are potential building blocks in nanoelectronic and nanophotonic devices.1–4 As an important metal oxide semiconductor, 1D ZnO nanostructures have received increasing attention because of their excellent properties such as wide band gap (3.37 eV), large exciton binding energy (60 meV), good piezoelectricity properties,5–7 potential applications in dye sensitized solar cells, gas sensor nanogenerators, and field emission displays.8–10 In our previous study, ZnO nanostructures including NWs, nanocombs, nanosheets, and NBs were produced directly on a brass substrate via a simple thermal oxidation method under Ar/O\(_2\) at different temperatures.5 The brass foil serves as both the substrate and Zn source and the resulting ZnO nanostructures have good electrical contact with the underlying conducting brass substrate. The conducting brass substrate provides a direct path for electron transport from the cathode to ZnO nanostructures resulting in good field emission performance.9 Since no catalyst is used, the ZnO nanostructures are of high purity9 and different types of ZnO nanostructures can be synthesized controllably by adjusting the reaction temperature. The resulting nanostructures have interesting photoluminescence (PL) properties depending on the structure and morphology. In this work, the optical properties of ZnO nanosheets and NWs produced on brass substrates with different surface-to-volume ratios and morphologies are studied. Nanosheets can be considered as a quasi-two-dimensional structure, whereas NWs constitute a typical 1D morphology. Their band edge and defect emission mechanism are investigated and discussed in order to gain a better understanding of their optical and electrical characteristics.

ZnO nanosheets and NWs were synthesized by annealing a brass foil (Cu\(_{0.66}\)Zn\(_{0.34}\) alloy) under an Ar/O\(_2\) (O\(_2\) 4% v/v) gas mixture at 700 and 900 °C. The synthesis details can be found in our previous paper.9 The PL measurements were performed on a FLS920 (Edinburgh Instruments) fluorescence spectrometer using a xenon lamp with a grating monochromator as the excitation light source. The excitation wavelength was 300 nm. A 340 nm short-\(\lambda\) cutoff filter was placed in front of the detector and the measurement temperature was varied from 15 to 290 K. The morphology, composition, and structure of the materials were characterized by scanning electron microscopy (SEM), transmission electron microscopy, x-ray diffraction (XRD), and x-ray photoelectron energy spectroscopy (XPS). XRD and XPS results (not shown here) indicate that both the NWs and nanosheets possess a single-crystal wurtzite structure and have no impurities such as Cu incorporated into the lattice even at a high reaction temperature of 900 °C.

Figure 1 shows the PL spectra of the ZnO nanosheets and NWs at 15 K and room temperature (RT) and their corresponding SEM images. It can be observed that most of the NWs have diameters of about 40–60 nm, whereas most of the nanosheets have thicknesses of about 20–30 nm and widths of 800–1500 nm. Thus, the nanosheets have larger surface-to-volume ratios than the NWs. The PL spectra suggest that two bands are observed from both samples at 15 K and RT. In the 15 K PL spectrum, the stronger and sharper peaks are located at 3.356 eV for the NWs and 3.361 eV for the nanosheets, corresponding to the near band edge (NBE) emission, indicative of the typical excitonic characteristic. There is a noticeable blueshift of about 5 meV in the NBE emission of the ZnO nanosheets compared to the NWs.11–13 The weaker and broader peak centered at around 2.5 eV results from defects related deep-level (DL) emission, that is, electron transition from the bottom of the conduction band to an antisite defect (\( O_Z \)) level or electron transition from an oxygen vacancy \( V_O \) to a \( V_O \) level (\( V_O + h \rightarrow V_O \)).
The DL emission from the ZnO nanostructures is believed to mainly come from the surface region where the defects segregate. As a result, nanosheets have a larger intensity ratio of the DL to NBE emission ($I_{DL} / I_{NBE}$) due to the larger surface-to-volume ratios. The PL spectra at RT indicate that the NBE emission from the nanosheets is redshifted for about 40 meV compared to the NWs and this phenomenon will be discussed later in this paper.

Figure 2 displays the temperature-dependent fine NBE emission spectra of the ZnO nanosheets and NWs in the temperature range from 15 to 200 K. The 15 K NBE emission spectrum of the nanosheets consists of four luminescence peaks at 3.369, 3.361, 3.311, and 3.236 eV, corresponding to the surface exciton (SX) emission, neutral...
donor bound exciton (D^0X) emission, as well as first order and second longitudinal optical phonon replica of free exciton (FX-1LO and FX-2LO), respectively. The emission SX at 3.369 eV results from recombination of the excitons localized at the surface states, showing lower localization energy (about 6 meV) than that of D^0X. At 70 K, the SX peak disappears and totally converts to FX.\(^{18}\) When the temperature is increased gradually, the intensity of D^0X becomes weaker and the peak shifts toward a lower energy. At above 130 K, the D^0X peak is too weak to be identified and the FX-1LO peak becomes dominant in the spectrum. Since D^0X partially thermally dissociates into FX,\(^{19}\) the attenuation of FX as well as its LO photon replicas with increasing temperature is much slower in comparison with D^0X. Consequently, when the temperature is higher than 130 K, FX-1LO and FX become the dominant emissions and the peak intensities are higher than that of the D^0X peak. A similar behavior is observed from the NBE emission of the NWs. In comparison with the NBE emission from the nanosheets, the D^0X peak of the NWs dominates the spectra over the entire temperature range of 15–200 K. In addition, the SX peak is not observed. Our results and analysis suggest that the D^0X peak is the main NBE emission peak from the NWs, while FX-1LO is the dominant one from the nanosheets at RT. Hence, the NBE emission at RT from the nanosheets is redshifted for about 40 meV compared to the NWs, as shown in Fig. 1.

Figure 3 plots the integrated intensities of D^0X as a function of reciprocal temperature. The intensity of the D^0X peak from the nanosheets decreases significantly with increasing temperature. When the temperature is higher than 130 K, the D^0X peak is masked by other peaks. Thus, we only show the data acquired from the nanosheets in the temperature range of 15–130 K. The relationship between the intensity of D^0X and reciprocal temperature can be fitted by the following expression:\(^{10}\)

\[
I = I_0/[1 + a \exp(-E_a/k_BT)],
\]

where \(E_a\) is the activation energy for thermal quenching and \(k_B\) is the Boltzmann constant. The fitted \(E_a\) value is 13 meV for the NWs and 7.5 meV for the nanosheets. It is generally accepted that a nonradiative recombination channel is responsible for thermal quenching of the D^0X intensity. The \(E_a\) values derived for the nanosheets and NWs are almost equal to the energy separation values between D^0X and FX as suggested in Fig. 2, implying that the quenching channel is from the thermal dissociation of D^0X to FX.\(^{19}\) The smaller \(E_a\) value calculated from the nanosheets means more rapid decay of D^0X due to the larger surface-to-volume ratios of the nanosheets in comparison with NWs.\(^{21}\)

In recapitulation, the optical properties of ZnO nanosheets and NWs produced on conducting brass substrates are investigated from 15 K to RT. The NBE and DL emission mechanisms are investigated and discussed. The PL spectra acquired from both the NWs and nanosheets are dominated by D^0X at low temperature. Compared to the NWs, a blueshifted D^0X peak and enhanced DL emission are observed from the low-temperature spectrum of the nanosheets. It is believed to be related to the larger surface-to-volume ratio. The RT PL spectra of the NWs are dominated by D^0X but those of the nanosheets are dominated by FX-1LO. The reduction in the D^0X peak intensity with temperature is attributed to thermal dissociation of D^0X to FX. Our results provide insight to better understand the optical and electrical characteristics of ZnO nanostructures.

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