Quenching of surface-exciton emission from ZnO nanocombs by plasma immersion ion implantation

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Surface modification of ZnO nanocombs was performed through a Ti plasma immersion ion implantation (PIII) with low bias voltages ranging from 0 to 5 kV to quench surface-originated exciton emission. The ion energy dependent surface modification on ZnO was investigated using transmission electron microscopy and temperature-dependent photoluminescence (PL). The surface exciton (SX) was clearly identified for the as-grown sample at 4.5 K, and complete quenching was observed for sample treated with 5 kV PIII due to surface state passivation. The SX related surface states were located within 5 nm in depth from the surface corresponding to the implantation depth of 5 kV PIII. Room-temperature PL enhancement of these surface-modified ZnO nanocombs was observed and discussed. The results show that PIII can become a viable technique for nanostructure surface passivation. © 2007 American Institute of Physics. [DOI: 10.1063/1.2772668]

ZnO is a multifunctional semiconductor material with a wide-direct band gap (~3.37 eV at room temperature) and large exciton binding energy (60 meV), much larger than that of GaN (~25 meV). Recently, it has stirred new interest as a promising optoelectronic material in UV lasers and light-emitting diodes, solid state lighting, and transparent electronics. 1–2 For a nanometer-sized system, the photoluminescence (PL) becomes more surface related than that for bulk ZnO crystal. 3–4 It was observed recently that in a ZnO nanowire/nanowall system, a prominent near-band-edge PL peak at around 3.367 eV was clearly identified for the as-grown sample at 4.5 K, and complete quenching was observed for sample treated with 5 kV PIII due to surface state passivation. The SX related surface states were located within 5 nm in depth from the surface corresponding to the implantation depth of 5 kV PIII. Room-temperature PL enhancement of these surface-modified ZnO nanocombs was observed and discussed. The results show that PIII can become a viable technique for nanostructure surface passivation.

On the other hand, plasma immersion ion implantation (PIII) is a well developed surface modification technique. 11–13 It is a simple, non-line-of-sight process, as opposed to conventional beamline ion implantation; nonplanar samples can be implanted with good conformity and uniformity without special sample manipulation. During PIII, the substrate is immersed in plasma and negative voltage pulses can be applied to implant ions from the plasma to the surfaces. The modification depth can be well controlled by the bias voltage, which is suitable for surface modification of thin films and nanostructures with complicated morphologies. 11–14 The current research of the PIII is focused on modification of polymer and diamondlike carbon film, impurity doping, etc. 12,13,15 However, surface modification of nanostructures by PIII is much less investigated. In this letter, we shall report an effective quenching of ZnO SX by PIII modification, which provides us with a powerful tool to overcome the problem associated with increased surface area (reduced dimension).

The growth of ZnO nanocombs was carried out in a horizontal tube furnace by vapor phase transport method. The detailed fabrication process can be found elsewhere. 16 The nanocomb was chosen because of its large surface area. The as-grown products were then directly treated with Ti-PIII. Prior to the treatment, a base pressure of 3×10⁻⁶ Torr was obtained. The pressure was kept at 8×10⁻⁵ Torr with 8 SCCM (SCCM denotes cubic centimeter per minute at STP) Ar flow during PIII. Negative pulse voltage of 0 and 5 kV were applied to the substrate holder for 2 min. The ion dose was estimated to be ~1×10¹³ ions/cm² upon 5 kV bias. The substrate temperature was monitored to be below 100 °C. The morphology and lattice structure were characterized by scanning electron microscopy (SEM) (JSM-5910LV) and transmission electron microscopy (TEM) (JEM-2010), respectively. The chemical composition analysis was carried out using energy dispersive x-ray spectroscopy (EDX), and x-ray photoelectron spectroscopy (XPS) measurement on the surface of the samples was performed in a Kratos AXIS Ultra spectrometer with a monochromatized Al Ka x-ray source (1486.71 eV). Temperature-dependent PL measurements were carried out with the sample placed in a close-cycle He gas cryostat in the temperature range of 4.5–300 K, using 325 nm He–Cd laser as the excitation source.

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5 kV, the Ti signal was below the detection limit of XPS. However, as the bias voltage rises above 3.65:1:7.68, indicating significant changes in surface chemistry by quantitative analysis obtained from EDX represents the bulk characteristics of the nanocombs. From XPS surface analysis, the ZnO comb fingers after 0 kV Ti-PIII, respectively. The inset shows room-temperature PL spectra of the as-grown ZnO comb fingers in Fig. 2(c). All the comb fingers observed in TEM are growing in the [0001] direction, which is consistent with the growth model of ZnO combs.19 No visible line or planer defects can be seen from the HRTEM image of the as-grown ZnO comb fingers [Fig. 2(e)]. The d spacing of 0.52 nm corresponds to lattice spacing of (0001) planes of wurtzite ZnO. After 0 kV Ti ion treatment (without bias voltage), the surface of the nanowire is covered by a discontinuous layer less than 3 nm thick [Fig. 2(d)]. This ultrathin amorphous layer is formed by both Ti ion deposition and bombardment on the ZnO surface with a typical ion energy of 20–150 eV with no bias voltage,17 in agreement with XPS results. Careful examination of the coating [Fig. 2(d)] shows that it contains some nanocrystals with the d spacing of 0.216 nm which matches that of (111) planes of rutile TiO2. Figure 2(e) shows the HRTEM of the ZnO surface after 5 kV ion treatment. The Ti ions are completely implanted into ZnO crystals, where no Ti-related coating layer or new crystalline phases such as TiO2 could be found. From our experiments, ZnO nanostructures treated under 2–5 kV bias showed similar HRTEM images as Fig. 2(e). The contrast of inhomogeneous regions in Figs. 2(b) and 2(e) increases with negative bias voltage applied, indicating increased implantation dose of Ti (most likely at interstitial sites of ZnO) and lattice defects.20

Figure 3 shows the normalized near-band-edge (NBE) PL spectra of the as-grown, 0 and 5 kV Ti-PIII treated ZnO nanocombs obtained at 4.5 K for curves A–C, respectively. The inset shows room-temperature NBE PL spectra of the as-grown (curve A') and 5 kV Ti-PIII treated nanocombs (curve C'). The PL spectra of ZnO nanocombs before surface modification are dominated by the emission peak at 3.3576 eV originating from the radiative recombinations of donor-bound excitons (D̃X’s).9 Another strong peak at 3.3641 eV is assigned to the recombinations of SX’s,4,6,8 consistent with the large surface area of nanocombs. Two small shoulders can be observed at 3.3773 and 3.3889 eV, which are assigned to the recombinations of the A- and B-free excitons (FX’s), respectively.9 On the lower energy side of these bands, the phonon replicas of D̃X and A-FX are obv.
erved, with average spacings of 71.7 and 71.8 meV, respectively, consistent with the LO-phonon energy of ZnO. According to Teke et al., the peak at 3.3217 eV might be due to two-electron satellite (TES) transitions of the $D^0X$ recombination. In this process, the donor electron of the $D^0X$ is left in an excited state when the donor-bound exciton recombines. Comparing to the well-resolved SX, phonon replicas of $D^0X$ and FX of the as-grown ZnO at 4.5 K, the PL spectra of the 0 and 5 kV Ti-PIII treated ZnO show gradually suppressed SX and weakened FX emissions as the bias voltage increases. The suppression of SX recombination can be attributed to filling of surface states, such as dangling bonds and trapping sites, of ZnO nanocombs after Ti ion implantation. This evidently distinguishes SX and $D^0X$, where SX and $D^0X$ correspond to trapping of FX at a broad energy distribution of the near-surface states and discrete energy levels of defects and donor impurities, respectively. They can be well resolved by PIII with an implantation depth of ~5 nm (5 kV) or less. As a by-product, we can conclude that the surface states responsible for SX’s are located within 5 nm in depth from the surface. On the other hand, the $D^0X$-related and TES emissions are retained, suggesting that the donor-bound radiative recombination persists inside the bulk of the nanocombs. These SX quenched samples showed a better PL performance at room temperature, where distinct PL enhancement (300 K) can be seen in the inset of Fig. 3.

As temperature increases [Fig. 4(a)], the intensities of $D^0X$-related and SX emissions decrease much faster than that of A-FX and its first two replicas due to thermal activation of the donor-bound excitons, and finally the FX becomes dominant at room temperature. The dissociation of the $D^0X$ results in increased emission from the free excitons and other shallower donor-bound excitons. This is consistent with the observation in Fig. 4(b), in which the $D^0X$ replicas vanish and FX replicas reappear at 60–80 K. The SX emission is thermally quenched and merged with $D^0X$ around 60 K due to the dissociation of excitons trapped to SX states into FX states with increasing temperature, with a low thermal activation energy corresponding to the energy separation between the FX and SX peaks (~13 meV), which is slightly larger than the value reported by Wischmeier et al. (~9 meV), and smaller than that of $D^0X$ (10–20 meV). In comparison to donor impurities which are the origin of $D^0X$ emission, the broad-energy-distributed surface states responsible for the SX recombination, in accordance with large surface-to-volume ratio, could be less stable at high temperature. The ionization of these surface states at relatively low temperatures can create nonradiative surface traps which induce rapid decay of FX’s at room temperature, resulting in a weak PL. Our surface modification thus blocked this nonradiative recombination process of FX by passivating these surface states. This is the reason why the surface passivation layer containing Ti impurities can enhance room-temperature NBE PL. It is worth mentioning that other elements, e.g., Fe, Ni, Cu, and C, have similar modification effect through low energy PIII, indicating that the PL of ZnO is insensitive to the implanted elements used.

In conclusion, SX emission from ZnO nanocombs has been quenched by Ti-PIII treatment. TEM analysis gave a clear observation on the Ti-PIII modified surface of ZnO. The modification effects on SX and $D^0X$ emissions by PIII strongly deviated, where the near-surface located SX emissions at 4.5 K were gradually quenched by increasing the ion energy, indicating their surface related origins. The depth of SX emission was estimated according to the ion implant depth and distinct room-temperature PL enhancement was achieved.

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