Na-Doped *p*-Type ZnO Microwires

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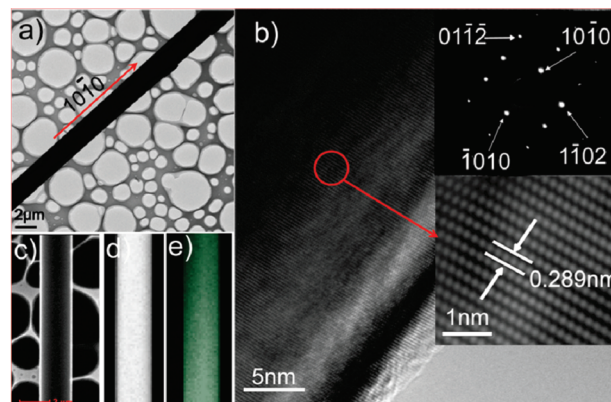
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With a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature, ZnO has received considerable attention as a promising material for optoelectronic devices such as light-emitting diodes, photodetectors, and short-wavelength laser diodes with low thresholds in the UV region.[1] To realize highly efficient optoelectronic devices, it is imperative to have high-quality single-crystalline *p*-type ZnO. To date, enormous efforts have been dedicated to fabricating *p*-type ZnO thin films using group I and group V elements as *p*-type dopants.[2] In contrast, there have been only a few reports on *p*-type ZnO nanowires (doping with N and P).[3] It is well-known that the ZnO nanostructures are ideal material candidates for many novel applications, such as nanoscale multiplexing biosensors, ultraviolet detectors, and electrically driven nanolasers. The synthesis of genuine *p*-type ZnO nanostructures with good stability would be the key to open up substantial opportunities for nanoelectronic and optoelectronic applications.

Among several *p*-type dopants of ZnO, the group I element Na was theoretically predicted to have a shallow acceptor level of 170 meV, assuming that Na substitutes for Zn.[4] In a physical picture, the valence-band maximum consists mainly of the anion p orbitals with some mixing of the cation p and d orbitals, which gives only small perturbations when Zn is replaced with Na.[4] In other words, the strain around the dopant atoms is small, and the coupling between the anion and cation orbitals is weak. Therefore, the acceptor levels are relatively shallow. Indeed, Ye et al.[5] experimentally demonstrated reliable fabrication of *p*-type ZnO thin films doped with Na on quartz and glass with hole concentrations up to 3×10^{18} cm^{-3}, but to date there has been no report on one-dimensional *p*-type ZnO structures doped with Na.

Here we report the first demonstration of the synthesis of single-crystalline Na-doped *p*-type ZnO microwires using chemical vapor deposition (CVD). *p*-Type ZnO microwires were grown by a vapor−liquid−solid process from a mixture of zinc powder, graphite powder, and NaCl. The experimental details are provided in the Supporting Information. The incorporation of Na was confirmed by our extensive transmission electron microscopy (TEM) experiments and temperature-dependent photoluminescence (PL) studies. Single-wire field-effect transistors (FETs) were subsequently fabricated and shown to have hole conduction channels, confirming the *p*-type conductivity of the Na-doped ZnO microwires.

ZnO wires were grown directly on iron screens serving as substrates. The typical length of these microwires was found to be

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Figure 1. (a) TEM image of a single ZnO microwire. (b) HRTEM image of the microwire. Inset images are (top) the SAED pattern and (bottom) a Fourier-filtered HRTEM image. (c) Typical TEM image of a ZnO microwire. (d, e) Distribution maps of (d) Zn and (e) Na obtained using EDX.

several hundred micrometers, as shown by scanning electron microscopy (SEM) (Figure S1 in the Supporting Information). The diameters of most of the microwires were in the range 2−6 μm.

The TEM image in Figure 1a shows a ZnO wire with a diameter of ~2 μm. We obtained high-resolution TEM (HRTEM) images to further reveal atomically resolved wurtzite ZnO single crystals (Figure 1b). The growth axis was along the [10$\bar{1}$0] direction, as confirmed by the selected-area electron diffraction (SAED) analysis (Figure 1b inset). The interspacing between ZnO and Na planes was determined to be 0.289 nm, which is slightly larger than that in intrinsic ZnO thin films (0.281 nm).[6] This indicates the lattice expansion due to the substitution of Na for Zn, as has been observed recently.[7] The X-ray diffraction (XRD) pattern (Figure S4) shows an intense [10$\bar{1}$0] peak, verifying the single-crystallinity of the Na-doped ZnO wires. In order to determine the internal structure and composition of the wires, we performed elemental mapping using energy-dispersive X-ray spectroscopy (EDX). Figure 1c shows a regular TEM image of an individual wire, and Figure 1d,e presents its EDX elemental mappings of Zn and Na, respectively. Within the spatial resolution of EDX, the distribution of Na dopants was uniform throughout the microwires. The Na concentration was estimated to be ~1%, corresponding to ~10^{20} cm^{-3}.

To characterize the optical properties of the Na-doped ZnO microwires, temperature-dependent PL measurements were carried out using a He−Cd laser with an excitation wavelength of 325 nm. The resulting PL spectra exhibited two dominant peaks centered at 3.35 and ~2.50 eV at 9 K (Figure 2). Definitive identification of donor- and acceptor-bound excitons is rather difficult because of nearly identical ionization energies, especially for shallow acceptors.[8]
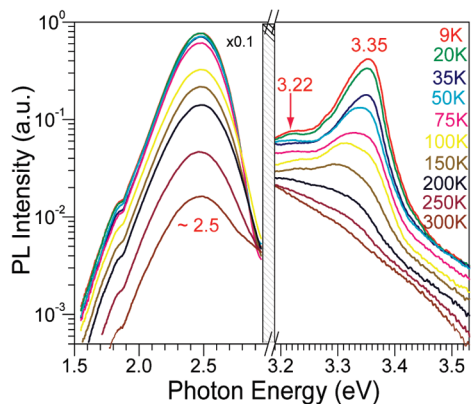
Figure 2. Temperature-dependent PL spectra for the Na-doped ZnO microwires. Three peaks were identified at 3.35, 3.22, and ~2.5 eV.

Ye and co-workers[8b] and Tomzig et al.[9] suggested that the peak at 3.35 eV is associated with the Na doping in ZnO. It could be attributed to the acceptor-bound exciton (A^0X) in view of the exclusively positive Hall coefficients for Na-doped ZnO films.[8b] As will be discussed later, the Na-doped ZnO microwires in this case were confirmed to be *p*-type by characterization of the FET devices. Therefore, we can tentatively assign the peaks at 3.35 and 3.22 eV to the acceptor-bound exciton and donor−acceptor pairs (DAPs), respectively.[2c,8b] The binding energy of an acceptor, E_A, can be approximately calculated using the following equation[2c] (with the van der Pauw polarization interaction term neglected because of the relatively large value of r):

$$E_A = E_{gap} - E_D - E_{DAP} + \frac{e^2}{4\pi\varepsilon r} \tag{1}$$

in which ϵ is the dielectric constant. The donor binding energy, E_D, is reported to be 60 meV, and the intrinsic band gap is $E_{gap} = 3.437$ eV.[1] The pair separation, r, can be estimated as $(3/4\pi N_A)^{1/3}$, where N_A is the number density of acceptors. With $N_A \approx 10^{20}$ cm^{-3}, the last term of eq 1 is ~140 meV. Therefore, the value of E_A is estimated to be ~280 meV. Besides the A^0X and DAP emissions, another broad-band emission was found at ~2.5 eV, which is customarily termed the green band emission. While several different hypotheses on the origin of the green band emission have been proposed,[10] an unambiguous identification still remains elusive at this stage. The possible origin, however, could be native defects such as ionized oxygen vacancies; there was also evidence showing that the defects were located at surfaces of ZnO nanostructures.[10c]

The electrical measurements on ZnO microwire back-gated FETs were carried out in vacuum to confirm the conductivity type of the as-synthesized Na-doped ZnO microwires at room temperature. A silicon substrate covered by a SiO$_2$ layer (thickness 300 nm) served as the global back-gate and dielectric gate oxide, respectively. The Na-doped ZnO microwires were first dispersed in alcohol and then dropped onto a substrate, and this was followed by Ti/Au deposition using photolithography and e-beam evaporation. The physical channel length measured between the source and drain electrodes was 20 μm. Figure 3 shows the output characteristics at various back-gate voltages (V_{GS}); the inset of Figure 3 demonstrates the gate-sweep characteristics of a typical Na-doped ZnO microwire at a drain bias voltage (V_{DS}) of 20 V. The monotonic increase of the drain current I_{DS} with increasingly negative gate bias clearly indicates *p*-type conduction. The carrier mobility (μ_{FE}) was estimated to be ~2.1 cm^2 V^{-1} S^{-1}, which is reasonably close to the reported results for *p*-type ZnO nanowires doped with
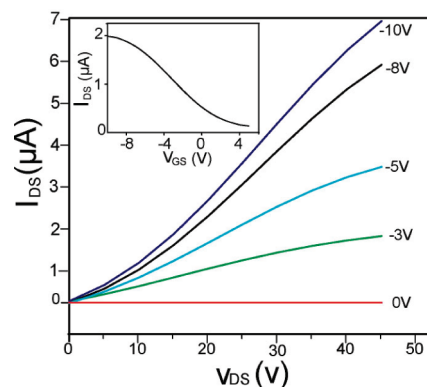
Figure 3. Output characteristics of ZnO microwire FETs at various back-gate voltages. The inset shows the $I_{DS}-V_{GS}$ plot for the Na-doped ZnO microwire transistor at $V_{DS} = 20$ V.

phosphorus.[3a,b] The hole concentration was estimated to be ~1.3 × 10^{16} cm^{-3}.

In conclusion, Na-doped ZnO microwires were successfully produced via a CVD process. The PL spectra of the Na-doped microwires show a Na-related peak at 3.35 eV, which we attribute to A^0X acceptor-bound excitons. The electrical measurements confirmed that the conductivity of Na-doped ZnO is *p*-type, and the carrier mobility was estimated to be 2.1 cm^2 V^{-1} S^{-1}.

Supporting Information Available: Experimental details, SEM and TEM images of microwires, EDX line scans and spectra, an XRD curve, characterizations of the undoped ZnO wire, complete ref 1d, and additional notes on Na acceptors. This material is available free of charge via the Internet at http://pubs.acs.org.

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