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Chemical, vibrational and optical signatures of nitrogen in ZnO nanowires

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ABSTRACT

ZnO nanowires with various concentrations of nitrogen molecules have been fabricated by remote plasma annealing. X-ray absorption near-edge spectroscopy (XANES) reveals that nitrogen exists mainly in two chemical states: atomic nitrogen substituting oxygen (N_O) and molecular nitrogen (N_2) weakly bound to the ZnO lattice; the latter state increases substantially with prolonged plasma time. Cathodoluminescence microanalysis of individual nanowires reveals a broad emission band at 3.24 eV at 10 K, attributable to the recombination of a shallow donor and a N_2 acceptor state. The Raman modes at 547 and 580 cm^{-1} from the N-doped nanowires are found to rise in proportion to the N_2 concentration, indicating they are related to N_2 molecules or defects caused by the incorporation of N_2 in the nanowires.

1. Introduction

One-dimensional ZnO nanowires are a promising material system for various applications in nano-optoelectronic devices, such as short-wavelength light emitting diodes, field emission transistors and ultraviolet lasers [1]. Utilization of nanowires requires a good understanding and control of their properties that are largely affected by intrinsic defects and impurities. The lack of reliable *p*-type material poses a major challenge to the realization of ZnO nanowire-based nanodevices. Group V elements, especially nitrogen which has a similar radius to oxygen, are believed to be the natural choice for achieving *p*-type conductivity in ZnO [2,3]. ZnO nanowires possess a large surface-to-volume ratio, which enables facile incorporation of nitrogen at a high concentration, making gas phase ion doping an effective doping method for ZnO nanostructures [4]. Furthermore, the use of nanowires allows control over the type of native surface defects prior to nitrogen incorporation, which can enhance its doping level [5].

Understanding the chemical states of nitrogen dopants and their signatures in ZnO is pivotal in investigating the physics and chemistry of *p*-type doping in this semiconductor. Previous studies have shown that atomic nitrogen substituting oxygen (N_O) is a deep acceptor in ZnO, whereas N_2 on an oxygen site $(N_2)_O$ is regarded as a shallow donor which compensates the *p*-type doping [6–8]. However, the nature of the N-related acceptor state is complex and to date remains controversial. Recently, it has been proposed that N_2 molecule could be accommodated at a Zn site $[(N_2)_{Zn}]$, which is predicted to be a double shallow acceptor responsible for the experimentally observed donor-acceptor-pair (DAP) transition in N-doped ZnO [9]. Our previous study of N-doped nanowires using the X-ray absorption spectroscopy established that nitrogen molecules are formed prevalently during nitrogen plasma doping [10]. Nitrogen-related vibrational modes, in particular those appearing at 275, 510, 582, and 643 cm^{-1}, have been ascribed to nitrogen doping [11–13]. These anomalous modes, on the other hand, were also observed in bulk ZnO doped with other elements such as Fe, Sb and Al [14], which further adds ambiguity to the assignment of nitrogen vibrational modes. The aim of this work is to investigate the relationships between the chemical states of nitrogen and their optical and Raman signatures in ZnO nanowires. It is clear that precise chemical characterization of nitrogen dopants is a prerequisite to the evaluation of ZnO Raman data.

2. Experimental details

ZnO nanowires were grown on the *a*-sapphire substrate via the vapor phase transport method as described in detail previously [15]. Admixture of ZnO and graphite powder was used as the source material. To enhance nitrogen incorporation by vacancy doping [7], nanowires were grown under oxygen-deficient conditions, which lead to an intense defect emission band peaking at 2.47 eV, attributable to V_O [16]. Nitrogen doping was conducted by annealing nanowires at 300 °C in radio-frequency (RF) nitrogen plasma with 230 V cathode bias. The combination of abundant nitrogen radicals and the low-temperature annealing enabled the nanowires to be efficiently doped with nitrogen without significant damage to their crystal structure and homogeneous distribution of the dopants. The nanowires were characterized using an FEI Quanta 200 Scanning Electron Microscope

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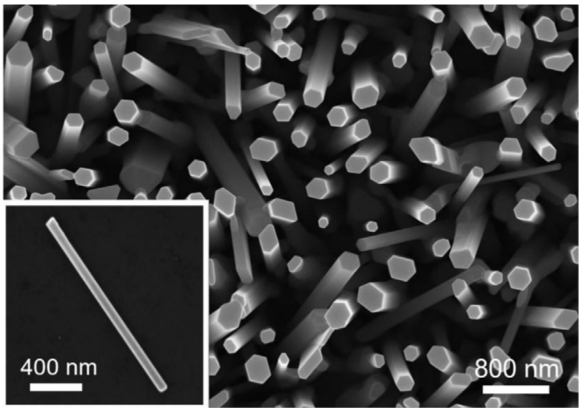

Fig. 1. SEM image of N-doped ZnO nanowires on an *a*-plane sapphire substrate. The nanowires exhibit a regular hexagonal cross section and a smooth *c*-plane tip surface. No changes in the nanowire morphology were observed after remote plasma annealing. Inset displays the SEM image of one nanowire with a diameter of ~100 nm.

(SEM) with attached cathodoluminescence (CL) spectrometer. X-ray Absorption Near Edge Spectroscopy (XANES), implemented in the Total Fluorescence Yield (TFY) mode, was performed on the Soft X-ray Spectroscopy beamline at the Australian Synchrotron. The incident X-ray beam was parallel to the *c*-axis of the nanowires. The photon energy scale was calibrated against the Au $4f_{7/2}$ peak at 84 eV from a clean gold film in electrical contact with the sample. Raman spectroscopy was conducted in backscattering geometry using a LabRAM HR800 spectrometer (Horiba Jobin Yvon) with the 457.48 nm laser excitation line. The laser power on the sample was set at 1 mW.

3. Results and discussion

Fig. 1 shows the N-doped ZnO nanowires grown on *a*-sapphire substrate. The single-crystal ZnO nanowires are preferentially grown along the crystallographic [0001] direction of the wurtzite crystal and possess hexagonal tip facets. The nanowires have a diameter in the range of 120–250 nm and the typical length varies from 1 to 1.5 µm. The inset of Fig. 1 is the close-up view of a truncated nanowire removed from the substrate. There were no observable changes in the nanowire morphology after the nitrogen doping. Fig. 2 shows the N *K*-edge XANES spectra of the undoped and N-doped ZnO nanowires, which represent resonant electron transitions from the N 1 *s* core state to the final unoccupied N-related states of *p*-symmetry [8]. The spectra can be decomposed into Lorentzian components corresponding to three chemical states of nitrogen: P_1 at 400.1 eV, P_2 at 400.7 eV and P_3 at 404.5 eV. The solid lines represent the fitted results of the XANES data points. The main component P_1, associated with atomic nitrogen substituting oxygen (N_O) in the lattice, is the transition of a 1*s* electron to $2p\pi^*$ state in the hybridized N-Zn orbital [17,18]. The P_2 component arises from the $1s\rightarrow\pi^*$ transition in the N-N bond [19], which is identified as the signature of N_2 molecules. This N_2-related resonance at 400.7 eV has previously been observed in N-doped ZnO [18], GaN [20] and InN [21]. XANES is highly sensitive to the bonding arrangement of dopants; the similar XANES characteristics of N_2 in various compounds strongly suggest that this molecular species is bound weakly to the host material. The P_3 energy is identical to the signature absorption peak of N_2O gas and has been assigned as the N 1*s* to $2p\sigma^*$ transition in N-O species [17], hence the P_3 peak is attributable to atomic N at Zn sites (N_{Zn}). The N_2 concentration grows substantially with plasma time, indicating more nitrogen present as molecular species, whereas N_O and N_{Zn} concentrations are virtually unchanged (inset of Fig. 2). N_2 has a lower formation energy than N_O [9], and given the high-temperature ballistic transport of atoms in nanowires, the highly mobile N atoms are anticipated to form pairs with increasing doping concentration.

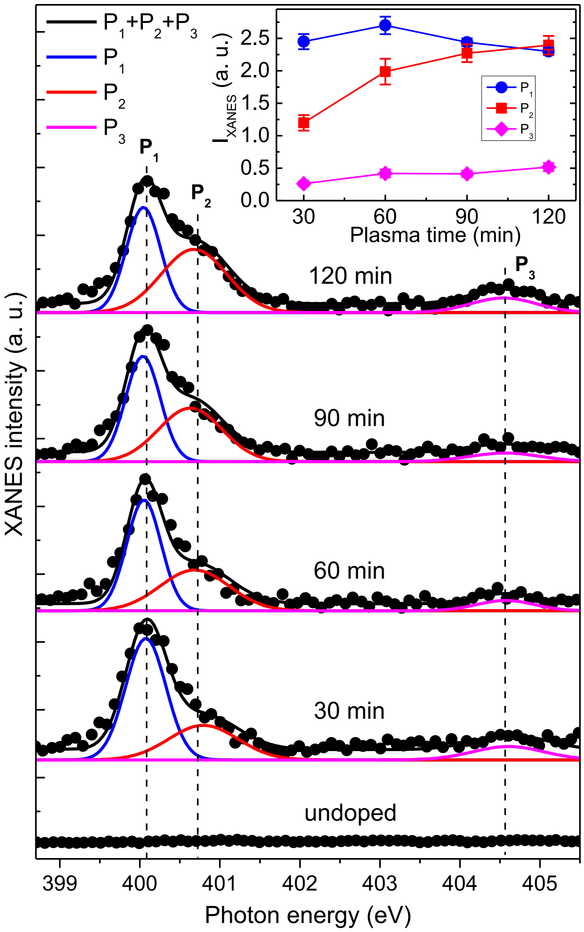

Fig. 2. N *K*-edge XANES spectra of the ZnO nanowires that were nitrogen plasma annealed for different time periods. No nitrogen was detectable in the as-grown nanowires (bottom spectrum). The spectra were fitted with three Lorentzian functions (labelled as P_1, P_2 and P_3) associated with three nitrogen chemical states. The inset shows the XANES integrated intensities of P_1, P_2 and P_3 states as a function of plasma time.

Fig. 3 displays the temperature-dependent CL spectra of N-doped ZnO nanowires at temperatures from 10 K to 300 K. The luminescence features of the as-grown (nominally undoped) nanowires are depicted in the inset with two narrow phonon replica peaks of free excitons (FX-LO and FX-2LO), separated by the longitudinal optical phonon energy (73 meV). For the N-doped nanowires (120 mins plasma), the dominant feature is a broad, asymmetrical band at 3.24 eV in addition to the D°X emission at 3.35 eV. The luminescence band at 3.24 eV bears close resemblance in peak energy and shape to those observed in Zn-face *c*-plane ZnO epilayers doped with a high concentration of nitrogen (> 5×10^{19} cm^{-3}) [22]. This band is relatively independent of temperature up to 40 K but quenched quickly as temperature is increased up to 140 K. Based on the XANES measurements in Fig. 2 and previous correlative investigations [10], this band can be ascribed to a donor-acceptor pair (DAP) emission with the shallow acceptor being loosely bound N_2. The asymmetrical shape and large half-width of the luminescence band arise from the superposition of the DAP zero phonon line and its phonon replica. This broad band, not previously reported in ZnO nanowires, has been observed in heavily compensated ZnO and ZnSe crystals and explained by fluctuating Coulomb potentials arising from high densities of ionized impurities [22,23]. The recombination energy of the DAP can be written as:

$$E_{DAP} = E_g-(E_A + E_D) - 2\gamma$$

where E_g, E_A and E_D are the band gap, acceptor and donor binding energies, respectively, and γ is the amplitude of the potential fluctuations, $\gamma \propto (N_A^- + N_D^+)^{2/3}$. With this model, it is apparent increasing