

Ammonia plasma modification towards a rapid and low temperature approach for tuning electrical conductivity of ZnO nanowires on flexible substrates

Wei Li Ong,^a Chun Zhang^{bc} and Ghim Wei Ho^{*a}

Received 25th May 2011, Accepted 27th July 2011

DOI: 10.1039/c1nr10527b

Though the fabrication of ZnO nanostructures is economical and low temperature, the lack of a facile, reliable and low temperature methodology to tune its electrical conductivity has prevented it from competing with other semiconductors. Here, we carried out surface modification of ZnO nanowires using ammonia plasma with no heat treatment, and studied their electrical properties over an extended time frame of more than a year. The fabrication of flexible devices was demonstrated *via* various methods of transferring and aligning as-synthesized ZnO nanowires onto plastic substrates. Hall measurements of the plasma modified ZnO nanowires revealed p-type conductivity. The N1s peak was present in the X-ray photoelectron spectrum of the surface modified ZnO, showing the presence of ammonia complexes. Low temperature photoluminescence showed evidence of acceptor-bound exciton emission. The resulting electrical devices, a chemical sensor and p–n homojunction, show the tunable electrical response of the surface modified ZnO nanowires.

1. Introduction

ZnO has been used as liquid-crystal displays, energy-efficient white lighting, room temperature gas sensors,¹ a transparent conductor in solar cells and transistors. The combination of a large direct band-gap of 3.37 eV and 60 meV excitonic binding energy² has promoted ZnO as the next generation of electronic and optoelectronic materials.^{3,4} Furthermore, nanoscale devices with arrays of ZnO nanowires, as compared to thin film counterparts, are expected to deliver enhanced performance and unique functions with diverse applications. Similar to ZnO thin film devices, the success of ZnO nanodevices depends on the ability to control and tune transport and electrical properties effectively and economically. However, doping remains a challenge for nanostructured materials. Non-reproducible and non-uniform doping often occurs due to limited access of dopants in the nanoscale structure. Other issues reported are unstable doping due to self-compensating doping, low dopant solubility and complex doping procedures. Recently, p-type conduction was observed in phosphorus-doped ZnO nanowire arrays,⁵ however they switched to n-type after two months storage in an ambient environment. Despite the considerable efforts that have been carried out to tune ZnO nanostructures' electrical properties, low temperature and facile tuning of the carrier density in

one dimensional ZnO nanowires is not available. Herein, we demonstrated an easy surface modification using ammonia (NH₃) plasma which results in an effective tuning of ZnO nanowires conductivity. The variation of electron concentration at the surface of the ZnO nanowires dictates the sensing and electrical properties. To the best of our knowledge, there are no reports on p-type conductivity ZnO nanowires/films by surface modification using NH₃ plasma with no heat treatment. With the synthesis and plasma treatment both conducted at low temperatures, this technique not only provides a low-cost and easy implementation of modifying electrical properties, but also a processing flow compatible with silicon technologies. In addition, it provides a feasible methodology to fabricate devices on flexible substrates with surface modified ZnO nanowires. Most importantly, the resulting functional groups on the ZnO nanowires are stable in air for more than a year.

2. Experimental section

ZnO nanowires were synthesized *via* the simple and low temperature hydrothermal method,^{6,7} consisting of a seeding step followed by the growth step. The substrate was seeded with a seed solution comprising of zinc acetate (0.01 M) dissolved in ethanol (10 ml). The seeded substrates were then placed into the precursor solution containing 25 mM of hexamethylenetetramine (HMT), 25 mM of zinc nitrate hydrate and 0.1 g of poly(ethyleneimine) solution (PEI) in de-ionized (DI) water, and heated at 90 °C for 7 h. The as-synthesized nanowires were then transferred to a flexible poly(ethylene terephthalate) (PET) substrate *via* 3 methods, namely: slide transfer, roll transfer and heat transfer. In the slide transfer method, the silicon substrate

^aDepartment of Electrical and Computer Engineering, National University of Singapore, 4 Engineering Drive 3, Singapore 117576. E-mail: elehgw@nus.edu.sg; Fax: +65-67754710; Tel: +65-65168121

^bDepartment of Physics, National University of Singapore, 2 Science Drive 3, Singapore 117542

^cDepartment of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543

with the ZnO nanowires (donor) was placed face down onto the PET surface (receiver) and slid against the receiver by applying gentle pressure as shown in Fig. 1a. For the roll transfer method, the receiver substrate was first placed firmly on a flat substrate and the donor substrate was then placed face down on top of the receiver. A cylindrical rod was then positioned onto the donor substrate and rolled from one end to the other to transfer the ZnO nanowires onto the receiver substrate (Fig. 1b). To transfer nanowires using the heat transfer method, the PET receiver substrate was first placed on a hotplate at 180 °C, just slightly higher than the glass transition temperature (T_g) of the donor. A piece of PET substrate of a size slightly smaller than the receiver substrate was then placed face down on top of the PET substrate and left there for 30 min. After 30 min, the substrates were left to cool down to room temperature and the donor substrate was peeled off gently from the receiver substrate. A schematic illustration of the steps is shown in Fig. 1c. To study the effect of NH_3 plasma treatment on the carrier characteristics of the as-synthesized ZnO nanowires, the nanowires grown on the substrate were treated with NH_3 plasma. The RF power was 250 W at a pressure of 0.4 mbar, and the samples were plasma treated for 90 s.

Several characterisations and device fabrications were carried out on the intrinsic and treated ZnO nanowires. Hall measurements were carried out on $1 \times 1 \text{ cm}^2$ samples using the Van der Pauw sample configuration at room temperature. The hydrogen gas sensors were fabricated by sputtering Pt electrodes onto the nanowires sample, with a 10 μm gap, and attaching copper wires to the electrodes with silver paste. Flexible sensors on plastic substrates can be fabricated either by direct hydrothermal growth of ZnO nanowires on PET at 90 °C or by transferring the synthesized nanowires onto the PET substrate *via* the three transfer methods described previously. The hydrogen gas sensors were tested in hydrogen ambient of various concentrations at room temperature. A p–n homojunction was formed between NH_3 plasma treated ZnO nanowires on an n-type ZnO seed layer. Metal contacts were fabricated by evaporating aluminum (Al) on the seed layer and platinum (Pt) onto the treated nanowires. A Metal-Oxide-Semiconductor (MOS) capacitor was also fabricated by spin coating PMMA onto the ZnO nanowires to fill

the gaps. A layer of SiO_2 (20 nm) was then sputtered on the nanowires followed by Cr/Au (10/100 nm) as the metal contact to form the capacitor. For the formation of ohmic contacts on the seed layer, Cr/Au was deposited on the intrinsic ZnO seed layer while Pt was deposited on the NH_3 plasma treated seed layer.

Scanning electron microscopy (SEM, JEOL FEG JSM 6700 F) and transmission electron microscopy (TEM, Phillips FEG CM300) characterized the morphology of the synthesized products. X-ray photoelectron spectroscopy (XPS) was employed to study the elemental composition of the intrinsic and NH_3 plasma treated ZnO nanowires. X-ray diffraction (XRD, Philips X-ray diffractometer equipped with graphite-monochromated Cu-K α radiation at $\lambda = 1.541 \text{ \AA}$) characterized the crystal structures of the ZnO nanowires. The room temperature photoluminescence (PL) of the nanowires was measured by micro-PL with a He-Cd laser at 325 nm. Low-temperature PL measurements were performed at 5 K in a helium closed cycle cryostat using the 325 nm line of a He-Cd laser. The Hall effect was measured at room temperature by a Bio-Rad Hall system. The current–voltage (I – V) and capacitance–voltage (C – V) measurements were carried out using Keithley 4200-SCS semiconductor characterisation system.

3. Results and discussion

The density of ZnO nanowires on the substrate is quite dense and they have an average length of 2.5 μm and diameter of 70 to 90 nm (Fig. 2a). The cross-sectional view in Fig. 2b shows the vertical alignment of the nanowires. Structural characterization of the hydrothermally grown nanowires was carried out *via* TEM. Fig. 2c shows that the nanowires have a uniform diameter with a smooth surface. The lattice fringes in the HRTEM image (Fig. 2d) have an interplanar spacing of about 0.52 nm, confirming that the pristine ZnO nanowires are single crystalline and have a preferential growth in the [0001] direction.⁶ No morphological changes of the nanowires were observed after plasma treatment and the surfaces of the nanowires remained smooth.

Fig. 3a shows an SEM image of the ZnO nanowires slide transferred onto a PET substrate. When the donor is rubbed against the receiver, the shear force of the rubbing and sliding motion causes the nanowires on the donor substrate to break and

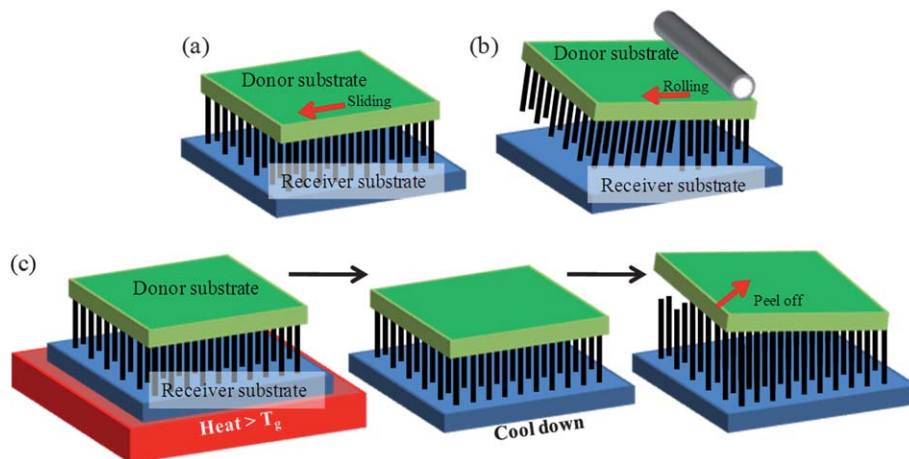


Fig. 1 Schematic diagrams of (a) the slide transfer method, (b) the roll transfer method, and (c) the heat transfer method.

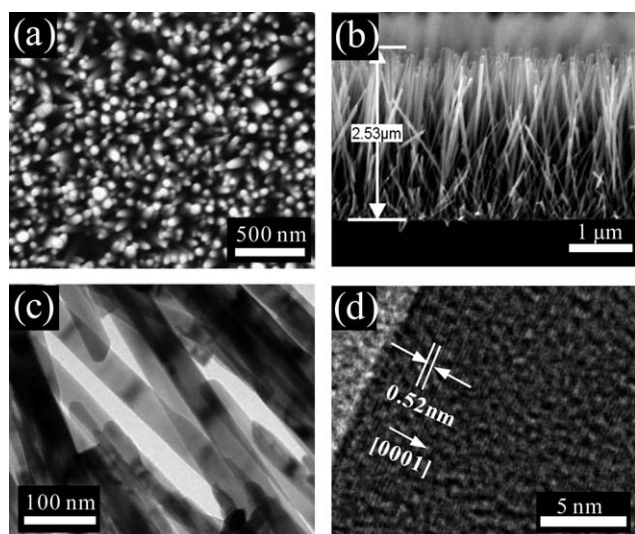


Fig. 2 (a) Top view and (b) cross-sectional SEM images of hydrothermally synthesized ZnO nanowires, (c) a TEM image of synthesized ZnO nanowires, and (d) a HRTEM image of the nanorod showing the [0001] growth direction and lattice spacing.

align along the sliding axis on the receiver substrate. This transfer method is also applicable for other substrates such as silicon (Fig. 3b and c). Platinum (Pt) electrodes can easily be sputtered onto the PET sample for device fabrication. Fig. 3d and e show an optical micrograph and an SEM image, respectively, of the PET sample with sputtered Pt electrodes and an electrode spacing of 10 μm . In the roll transfer process, the shear forces experienced by the nanowires caused them to break and get transferred onto the receiving substrate. However, the lack of a directional force causes the nanowires on the receiver to be less aligned than those obtained from the slide transfer method (Fig. 3f). An optical micrograph of the PET substrate after the heat transfer process is shown in Fig. 3g, and some patches can be seen in the image. The patches are the transferred ZnO nanowires (inset of Fig. 3g). It can be observed that not all of the ZnO nanowires were successfully transferred onto the PET. During the peeling of the donor substrate from the PET, some of the ZnO nanowires remained on the donor substrate. It was also observed that some of the transferred patches of ZnO nanowires did not adhere strongly to the PET substrate. From the study of these three transfer methods, it can be seen that the slide transfer method gave the best alignment with a high density of transferred nanowires.

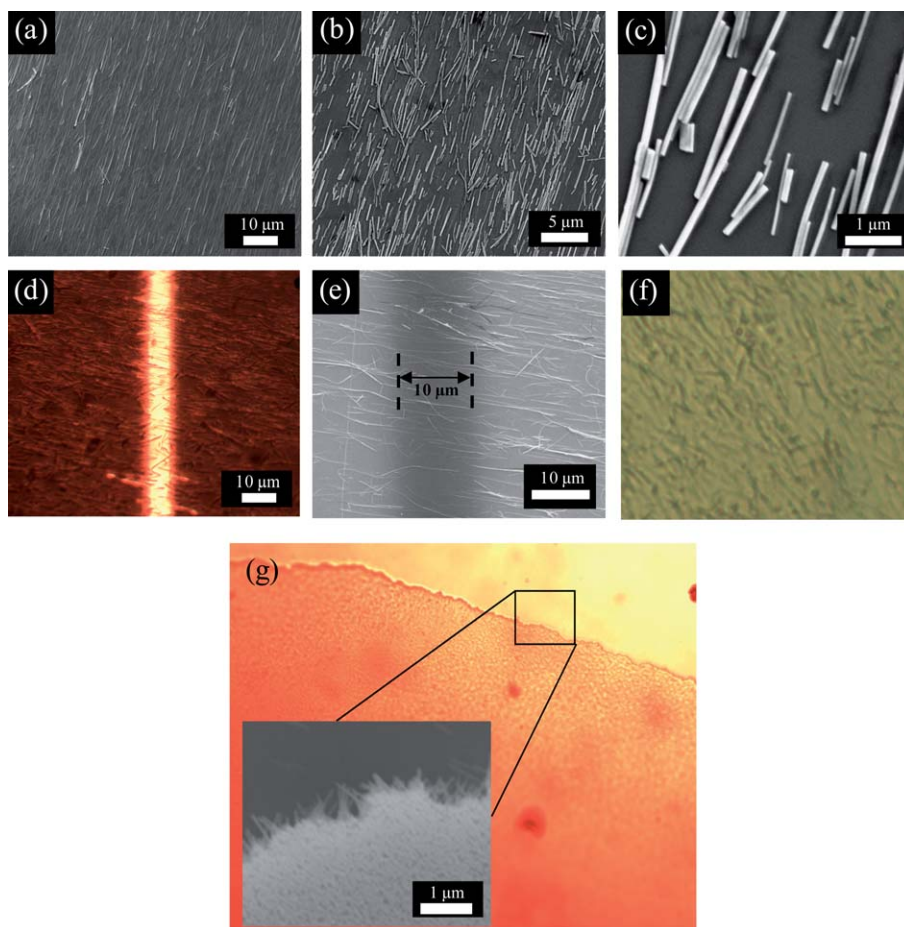


Fig. 3 SEM images of slide transferred ZnO nanowires on (a) a PET substrate, and (b) a silicon substrate at a magnification of 3000 times and (c) a magnification of 200 000 times. (d) An optical micrograph of slide transferred nanowires with Pt electrodes; (e) an SEM image of nanowires with a spacing of about 10 μm between Pt electrodes; (f) an optical micrograph of nanowires after roll transfer, and (g) an optical micrograph of a PET substrate with heat transferred ZnO nanowires (the inset shows the edge of a patch of nanowires).

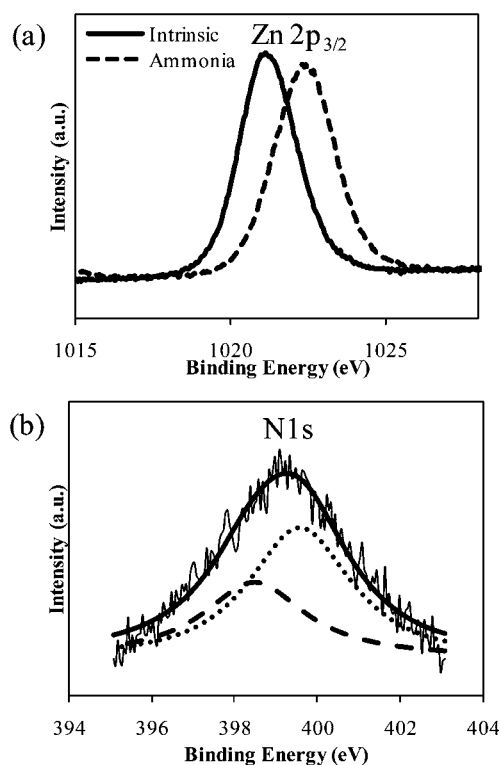


Fig. 4 High resolution XPS spectra of (a) the Zn 2p_{3/2} peak obtained from the ZnO nanowires before and after NH₃ plasma treatment, and (b) the N1s peak from ZnO nanowires after NH₃ plasma treatment.

The XPS spectra in Fig. 4a show the Zn 2p_{3/2} peak obtained from the intrinsic ZnO nanowires before and after surface modification with NH₃ plasma. The peak for the intrinsic sample is located at 1021.7 eV, which corresponds to Zn bonded to O in ZnO. However, the peak shows a shift of 1.19 eV towards higher binding energy after plasma treatment. This shift is due to degradation of the crystal lattice symmetry, which caused the electrical cloud surrounding the Zn atom to be asymmetric. Since the position of the Zn 2p_{3/2} core level is representative of the charge and chemical environment around the Zn atom, a shift in the peak position implies that ammonia complexes have diffused into the ZnO nanowires during the plasma treatment and created an asymmetry in the lattice structure.⁸ The presence of the N1s peak in the XPS spectrum of the treated ZnO nanowires (Fig. 4b) shows that nitrogen has been successfully incorporated into the nanowires. The N1s peak is centered at 399.3 eV with a full width at half maximum (FWHM) of approximately 3 eV, suggesting the presence of more than one chemical state of N. Deconvolution of the N1s peak revealed two peaks centered at 398.5 eV and 399.6 eV, which can be attributed to the N–Zn and N–H bonds, respectively.⁹ The higher binding energy peak at 399.6 eV related to N ions corresponding to amines, N–H,⁹ may be derived from the hydrogen-passivated N acceptor or N–H radicals. It can be observed that there is a lower concentration of N–Zn bonds relative to N–H pairs in the treated ZnO nanowires, indicating low solubility of the N acceptor. There are no substitutional N₂ molecules at oxygen sites (404.2 eV)¹⁰ and also no N–O bonds (407 eV)¹¹ found in the ZnO nanowires after NH₃ plasma treatment.

This simple surface modification technique which uses NH₃ plasma to introduce a variety of atomic and molecular radicals (N, H, NH, and NH₂)¹² into ZnO lattices was successful in tuning the electrical conductivity from n to p-type. The electrical conductivity tuning of ZnO is due to a competitive process of simultaneous introduction and compensation of acceptors resulting from the NH₃ plasma. Essentially, a N radical from the NH₃ plasma can be incorporated into the ZnO lattice in at least two chemical states, either as a N₂ molecule or a N atom occupying an O site. However, from the XPS studies, the chemical state of N₂ does not exist in these ZnO nanowires since the peak at binding energy of 404 eV is absent. The presence of the peak at 398.5 eV indicates that N radicals from NH₃ are incorporated substitutionally at O sites. As for atomic radical H from the NH₃ plasma, an isolated interstitial H is exclusively a donor in ZnO. However, hydrogen and nitrogen tend to interact strongly to form a neutral N_O–H complex. This in turn leads to the overall reduction of the hole concentration due to H passivating the acceptors. As for N–H complexes, they have no effect on reducing the electron concentration since the complex is neutral/electrically inactive. However, the introduction of neutral N–H complexes can prove to be useful in achieving high p-type conductivity. In contrast to N acceptors, neutral N–H complexes do not result in the formation of compensating n-type defects. Thus, optimization of the annealing temperature (not in this present work) to dissociate N–H complexes after NH₃ plasma treatment can be used to activate a large concentration of N acceptors to achieve high p-type conductivity.¹³ The occupation of N–H complexes at the oxygen vacancy sites may also aid in reducing the oxygen vacancy related n-type defects, hence making the ZnO nanowires less n-type.

Fig. 5a shows XRD patterns of pristine and NH₃ modified ZnO nanowires which exhibit a dominant peak at 34–35°, which corresponds to the ZnO (002) diffraction. This indicates that the nanowires are crystallized in the wurzite phase and present a preferential orientation along the *c*-axis. The (002) peak position of ZnO nanowires shifted with gaseous NH₃ plasma treatment. The ionic radius of N–H is bigger than that of oxygen, thus their incorporation into the surface of the ZnO nanowires brings about asymmetry expansion of the crystal lattice. The peak position of (002) of the NH₃ modified ZnO nanowires shifts to a smaller angle, according to the Bragg diffraction law:

$$2d\sin\theta = \lambda \quad (1)$$

Room temperature PL measurements were carried out on the as-synthesized and NH₃ plasma treated ZnO nanowires, as shown in Fig. 5b. The as-synthesized nanowires have a UV peak at 3.28 eV, corresponding to the near-band-edge (NBE) emission of ZnO. A broad visible emission band centered at 2.07 eV was also observed, signifying the presence of native defects such as oxygen vacancies, V_O, and zinc interstitials, Zn_i. After NH₃ plasma modification, the ZnO nanowires displayed a significant visible emission quenching, which may be attributed to the reduction of the defect concentration due to the occupation of N–H atom pairs on the defect sites.¹⁴ N–H will most likely be incorporated into oxygen substitute sites (V_O) since the valency charge and activation energy of the N–H is similar to that of

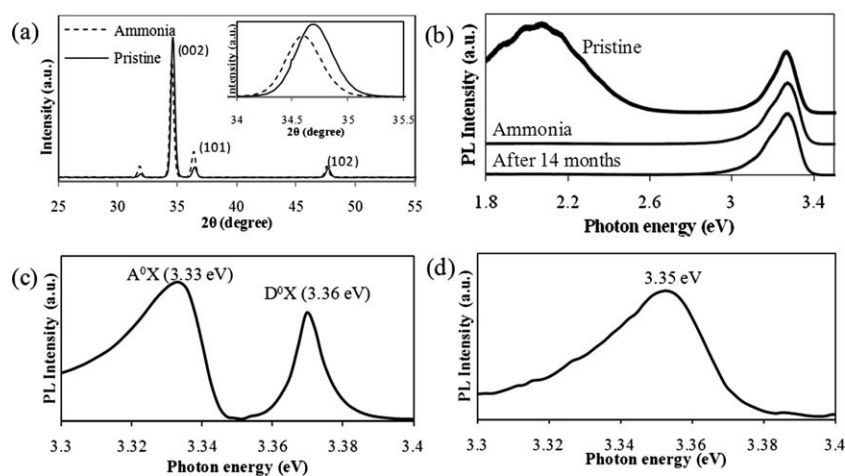


Fig. 5 (a) An XRD pattern and (b) PL spectra of as-synthesized and NH_3 plasma treated ZnO nanowires; the inset of (a) shows the corresponding shift of the (002) peak position. (c) A low temperature PL spectrum at 5 K for NH_3 plasma treated nanowires, and (d) a low temperature PL spectrum at 5 K for pristine nanowires.

oxygen.¹⁴ The NH_3 plasma treated sample was characterized by room temperature PL again after 14 months. The PL spectrum still displayed similar optical characteristics of a strong UV emission with insignificant defect peak. The optical properties of the NH_3 plasma treated ZnO nanowires were further investigated using low temperature PL measurements at 5 K (Fig. 5c). Two peaks could be observed in the PL spectrum in Fig. 5c, namely at 3.33 eV and 3.36 eV. The peak at 3.33 eV can be attributed to the excitons bound to the acceptor (A^0X) and the existence of this strong peak signifies the presence of acceptors in the nanowires after NH_3 plasma treatment. The emission at 3.36 eV is attributed to the NBE emission of excitons bound to donors (D^0X).¹⁵ Low temperature PL measurements at 5 K were also carried out for as-synthesized ZnO nanowires, as shown in Fig. 5d, and only the donor bound exciton peak at 3.35 eV was observed.¹⁶ The absence of the acceptor bound exciton peak provides additional evidence that the acceptors were derived from the NH_3 plasma treatment.

Hall measurements were also carried out to determine the conductivity type, resistivity, carrier concentration and Hall mobility of the NH_3 plasma treated ZnO samples. Two types of samples, namely ZnO nanowires and films, were treated and measured. Samples 1 and 2 refer to ZnO nanowires and samples 3 and 4 refer to ZnO films after plasma treatment, while sample 5 refers to intrinsic ZnO nanowires. The ZnO films were synthesized *via* the hydrothermal method with the addition of sodium citrate in the precursor.¹⁷ Good ohmic contacts between the electrodes and the nanowires and film were confirmed before

carrying out the measurements. Table 1 is a summary of the Hall measurement results of the nanowires and film samples and the plot is shown in Fig. 6. Error bars are included in the plot to indicate the possible error that may be inherent in the results. The NH_3 plasma treated ZnO nanowires show p-type conductivity with an average resistivity of $6.04 \pm 0.5 \Omega \text{ cm}$ with a carrier concentration of $1.42 \pm 1 \times 10^{17} \text{ cm}^{-3}$ and mobility of $7.34 \pm 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The ZnO films also exhibit p-type conductivity with an average resistivity of $1.4 \pm 0.5 \Omega \text{ cm}$ with a carrier concentration of $1.72 \pm 1 \times 10^{18} \text{ cm}^{-3}$ and mobility of $2.6 \pm 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The Hall results obtained are comparable to those of nitrogen-doped p-type ZnO reported in the literature, as

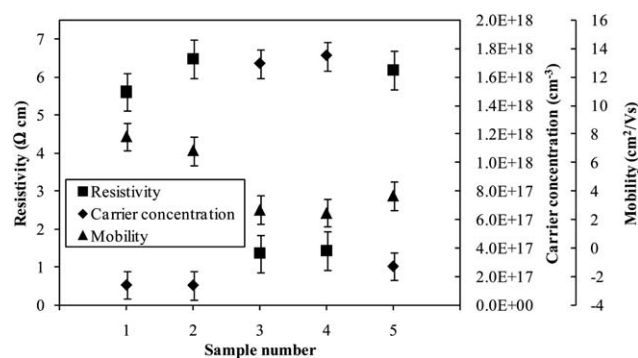


Fig. 6 A plot of the Hall results from intrinsic and NH_3 plasma treated ZnO nanowires and films with error bars.

Table 1 Resistivities, mobilities and carrier concentrations of intrinsic and NH_3 plasma treated ZnO nanowires and films

Sample no.	Resistivity ($\Omega \text{ cm}$) $\pm 0.5 \Omega \text{ cm}$	Mobility ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) $\pm 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	Carrier concentration ($\times 10^{17} \text{ cm}^{-3}$) $\pm 1 \times 10^{17} \text{ cm}^{-3}$	Carrier type
1	5.61	7.82	1.42	p
2	6.47	6.85	1.41	p
3	1.36	2.71	16.9	p
4	1.44	2.49	17.5	p
5	6.18	3.7	2.73	n

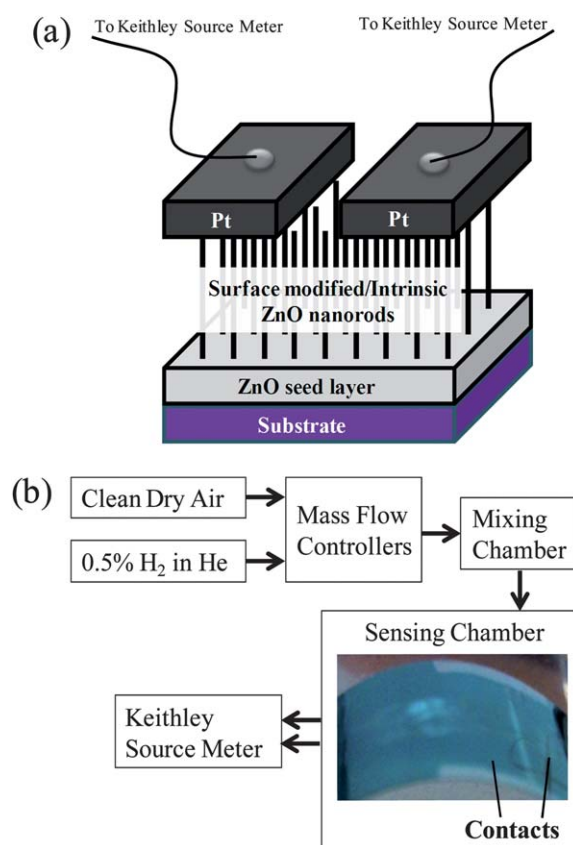
Table 2 Data on nitrogen-doped p-type ZnO samples reported in the literature

Ist author	Technique	Dopant source	Resistivity (Ω cm)	Mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	Carrier concentration (cm^{-3})	Time duration (minutes)	Substrate $T/^\circ\text{C}$
Cao ⁹	Plasma	NH ₃	3.3×10^2	0.82	3.3×10^{16}	60	100
Huang ¹⁴	DC reactive magnetron sputtering	NH ₃	1.1×10^4	4.1	1.14×10^{14}	—	300–550
Minegishi ¹⁸	CVD	NH ₃	34	12	1.5×10^{16}	60–120	650–800
Lu ¹⁹	DC reactive magnetron sputtering	NH ₃	31	1.3	7.3×10^{17}	30	500
Pan ²⁰	MOCVD	NH ₃	5.7	4.6	3.0×10^{17}	—	400–600

summarized in Table 2. Carrier concentrations ranging from 1.14×10^{14} to $7.3 \times 10^{17} \text{ cm}^{-3}$ with corresponding mobilities and resistivities in the range of $0.82\text{--}12 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and $5.7\text{--}11000 \Omega \text{ cm}$, respectively, were reported.^{9,14,18–20} In particular, the Hall results are better than those reported by Cao *et al.*, who treated ZnO with NH₃ plasma at 100 °C for p-type conductivity.⁹ It was also noted that for a similar hole concentration ($\sim 10^{17} \text{ cm}^{-3}$), the NH₃ modified ZnO nanowires exhibited a higher mobility than ZnO films doped with N reported in literature.^{19,20} This suggests that surface modification of ZnO nanowires may induce fewer carrier scattering centers compared to thin films, hence making nanowires more promising for electronic applications.³ It should be noted that in the derivation of the resistivity and carrier concentration values, the length of the nanowires was used as the film thickness. Due to the uncertainty in estimating the nanowire film's thickness/porosity, the Hall measurement results should be taken as an indication of relative change in the conductivity type and electrical properties of the nanowires after plasma modification, and not absolute results. These results should be considered complementary alongside with other characterization results reported in this work. Hall measurements were carried out on numerous pristine and plasma treated samples, and the results were consistent and reproducible. In the work of Yuan *et al.*,³ the mobility values were obtained from single nanowire based field effect transistors, while the mobility values in our work were derived from Hall measurements of a nanowire film. Since the mobilities of the films reported in literature^{19,20} were also obtained *via* Hall measurements, a fair comparison of the Hall-derived mobility values of our plasma treated nanowires and the reported films can be made. The intrinsic ZnO sample shows n-type conductivity and has a resistivity of $6.18 \pm 0.5 \Omega \text{ cm}$ with a carrier concentration of $2.73 \pm 1 \times 10^{17} \text{ cm}^{-3}$ and mobility of $3.7 \pm 1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. This carrier concentration is about twice that of the plasma treated nanowires, but it results in more scattering, hence leading to lower mobility in the intrinsic nanowires. The reasons for the lower carrier concentration in the plasma treated ZnO nanowires could be due to the substitution of oxygen by a small fraction of N to become an acceptor and/or a large part of the acceptors being compensated or passivated in the form of N–H complexes. Nevertheless, from the Hall results it is evident that NH₃ plasma can be an effective method to tune the electrical conductivity of ZnO nanowires, and this method can be extended to other ZnO structures such as ZnO films. Moreover, the plasma treatment was carried out without heating, which makes it possible to fabricate devices on flexible substrates with NH₃ modified ZnO nanowires. This is an efficient method (90 s) to modify the conductivity of ZnO nanowires as compared to other

syntheses and doping methods.^{9,18,19} The functionality of these surface modified nanowires will be proven through testing of devices built upon these nanowires.

The follow-up electrical and device demonstrations of both intrinsic and surface modified ZnO nanowires are based on a p–n junction diode, capacitor and chemical sensor. The sensing and electrical properties are dictated by the variation of the electron concentration at the surface of the ZnO nanowires. Hydrogen gas sensors were fabricated from the intrinsic and NH₃ plasma treated ZnO nanowires and were tested at various concentrations of hydrogen, without any operating temperature (room temperature) (Fig. 7a). The gas sensing setup was home-made using vacuum parts and the hydrogen gas (0.5%, He balanced) and clean dry air (CDA) were supplied to the setup *via* mass flow controllers as shown in Fig. 7b. The hydrogen gas sensor was

**Fig. 7** Schematic diagrams of (a) the hydrogen gas sensor and (b) the gas sensing setup (a plastic chemical sensor is shown in the sensing chamber).

placed in the sensing chamber and electrical leads from the sample were connected to a source-meter (Keithley 4200-SCS) via an electrical feed-through. A chemical sensor fabricated on a plastic substrate is shown in the sensing chamber of Fig. 7b. Hydrogen ambient of various concentrations was created by varying the flowrates of the hydrogen gas and CDA. From Fig. 8a, the resistance of the intrinsic nanowires is observed to decrease in hydrogen ambient and increase in air ambient, indicating n-type behaviour. Fig. 8b shows the response of the device to various concentrations of hydrogen gas. The response of the device to hydrogen gas was calculated by

$$\text{Response} = \frac{R_H - R_{\text{CDA}}}{R_{\text{CDA}}} \times 100\%, \quad (2)$$

where R_H and R_{CDA} are resistance of the device in H_2 gas and CDA, respectively. At 1000 ppm, the hydrogen gas sensor showed a response of 5.0% and the response increased with the concentration of hydrogen gas, attaining a response of 26.4% at a hydrogen concentration of 5000 ppm. When ZnO is exposed to gases such as O_2 , the charge accepting molecules adsorb at the vacancy sites, and electrons are effectively depleted from the conduction band, leading to a reduced conductivity of the n-type ZnO. On the other hand, when the metal oxide is exposed to gases such as H_2 , the molecules would react with the surface adsorbed oxygen and consequently remove it, leading to an increase in conductivity.²¹ The response of surface modified ZnO nanowires is the opposite of intrinsic ZnO nanostructures. When the modified ZnO is exposed to O_2 gas, the depletion of electrons actually results in increased hole density, leading to increased

conductivity. Exposing the NH_3 modified nanowires to H_2 gas will cause the hole density to decrease, hence leading to a lower conductance.³ From the plot in Fig. 9a, the resistance of the NH_3 plasma treated nanowires is observed to increase when exposed to hydrogen and decrease in air ambient, indicating p-type behaviour in the treated nanowires. The response of this device to hydrogen ambient of various concentrations is shown in Fig. 9b. The NH_3 modified ZnO nanowires have a response of 15% at 500 ppm hydrogen ambient and it increases to 27% at a hydrogen concentration of 2500 ppm. This shows that the device is capable of showing different levels of response at different concentrations of hydrogen, hence the device could possibly be used to determine the amount of hydrogen gas present in the ambient. The NH_3 modified nanowires were tested again after 14 months and the hydrogen sensing result is shown in the inset of Fig. 9b. There is no apparent degradation in the gas sensing performance and the device exhibited the same p-type behaviour as before. It is also noted that operating the sensor at room temperature will not result in subsequent adverse structural instability which will in turn cause electrical drift due to grain coalescence, porosity modification or grain-boundary occurrence.

The schematic drawing of the p-n junction diode using Pt and Al as contacts is shown in Fig. 10a and the ohmic $I-V$ characteristics of the ZnO nanowires are shown in the inset of Fig. 10b. The $I-V$ curve of Fig. 10b exhibits an apparent rectifying behaviour of the p-n junction and the turn-on voltage appears at ~ 3.3 V under forward bias. The leakage current under reverse bias could be due to incomplete contact between the Pt electrode

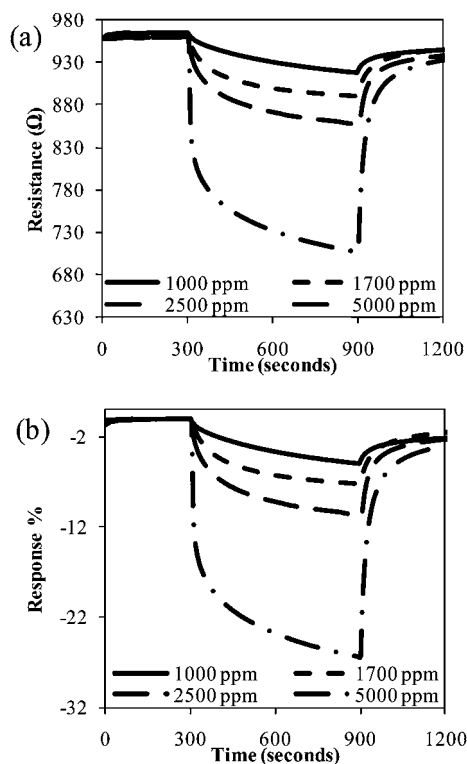


Fig. 8 The time dependence (a) resistance and (b) response change of intrinsic ZnO nanowires as the gas ambient is switched from air to various concentrations (1000–5000 ppm) of H_2 at room temperature.

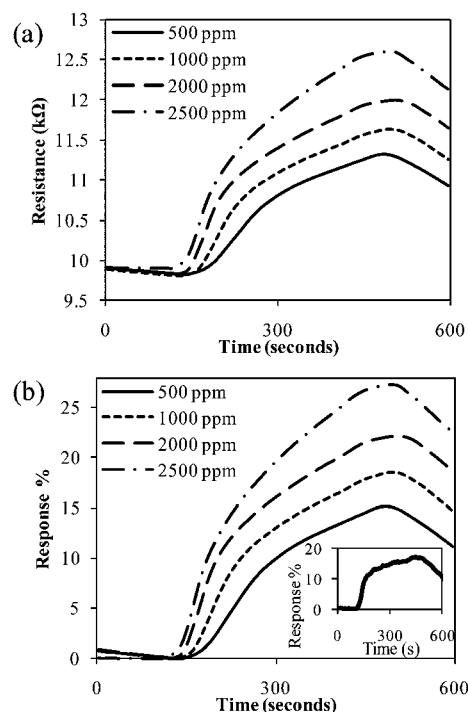


Fig. 9 The time dependence (a) resistance and (b) response change of surface modified ZnO nanowires as the gas ambient is switched from air to various concentrations (500–2500 ppm) of H_2 at room temperature. The inset of (b) shows the response of the device to 500 ppm of H_2 after 14 months.

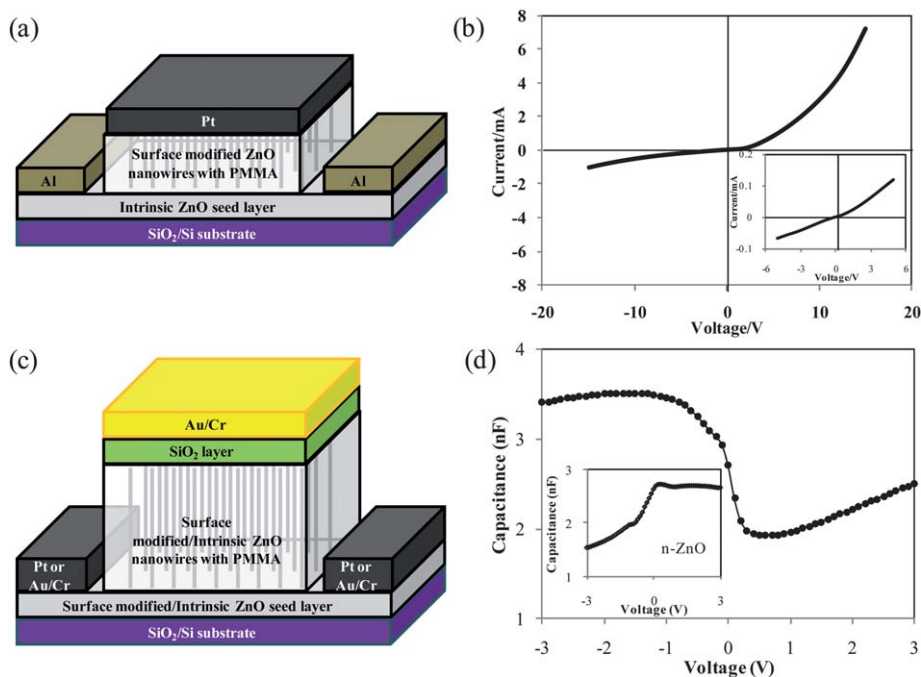


Fig. 10 (a) A schematic diagram of the p–n junction; (b) I – V characteristics of the p–n junction; the inset shows the ohmic I – V characteristics of surface modified ZnO nanowires; (c) a schematic diagram of the MOS capacitor, and (d) C – V measurements of NH_3 treated ZnO nanowires; the inset shows the C – V characteristics of intrinsic ZnO.

and some nanowires. A schematic diagram of the MOS capacitor is shown in Fig. 10c and C – V measurements were carried out on the MOS capacitor by sweeping the voltage from -3 to 3 V at 100 kHz (Fig. 10d). The C – V curve shows that NH_3 treated ZnO nanowires exhibit p-type conductivity as opposed to the C – V curve of a MOS capacitor fabricated using intrinsic (n-type) ZnO nanowires (inset of Fig. 10d). The interface traps are not able to respond to the a.c. signal and cause the C – V curve to stretch out along the voltage axis. This suggests the presence of interface traps between the oxide and the ZnO nanowires.

4. Conclusions

We demonstrated that the electrical conductivity of hydrothermally synthesized ZnO nanowires can be effectively tuned by surface modification using NH_3 plasma without heat treatment. Hall measurements of the modified ZnO nanowires revealed p-type conductivity with an average resistivity of $6.04 \pm 0.5 \Omega \text{ cm}$ with a carrier concentration of $1.42 \pm 1 \times 10^{17} \text{ cm}^{-3}$ and mobility of $7.34 \pm 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The plasma treated ZnO films also exhibited p-type Hall results, showing evidence that this treatment method can be extended to other ZnO nanostructures. Low temperature photoluminescence also showed evidence of acceptor bound exciton emission. The presence of an N1s peak in the XPS spectrum of the surface modified ZnO nanowires indicates the successful incorporation of ammonia complexes into the nanowires. The fabrication of flexible devices was demonstrated *via* various methods of transferring and aligning as-synthesized ZnO nanowires onto plastic substrates. Typical rectification characteristics of a p–n junction were observed from the I – V curve of the p–n homojunction fabricated using the surface modified ZnO nanowires. The results obtained from the

electrical devices and chemical sensor show that ammonia plasma treatment is a feasible way to tune the electrical conductivity of ZnO nanowires.

Acknowledgements

This work is supported by the National University of Singapore (NUS) grant R-263-000-532-112. The authors would like to thank Dr Zhi Han Lim for his advice and assistance in this work.

References

- H. T. Wang, B. S. Kang, F. Ren, L. C. Tien, P. W. Sadik, D. P. Norton, S. J. Pearton and J. Lin, *Appl. Phys. A: Mater. Sci. Process.*, 2005, **81**, 1117.
- H. J. Fan, Y. Yang and M. Zacharias, *J. Mater. Chem.*, 2009, **19**, 885.
- G. D. Yuan, W. J. Zhang, J. S. Jie, X. Fan, J. A. Zapien, Y. H. Leung, L. B. Luo, P. F. Wang, C. S. Lee and S. T. Lee, *Nano Lett.*, 2008, **8**, 2591.
- G. D. Yuan, W. J. Zhang, J. S. Jie, X. Fan, J. X. Tang, I. Shafiq, Z. Z. Ye, C. S. Lee and S. T. Lee, *Adv. Mater.*, 2008, **20**, 168.
- B. Xiang, P. Wang, X. Zhang, S. A. Dayeh, D. P. R. Aplin, C. Soci, D. Yu and D. Wang, *Nano Lett.*, 2007, **7**, 323.
- C. H. Wang, A. S. W. Wong and G. W. Ho, *Langmuir*, 2007, **23**, 11960.
- G. W. Ho and A. S. W. Wong, *Appl. Phys. A: Mater. Sci. Process.*, 2006, **86**, 457.
- Z. Y. Xiao, Y. C. Liu, J. Y. Zhang, D. X. Zhao, Y. M. Lu, D. Z. Shen and X. W. Fan, *Semicond. Sci. Technol.*, 2005, **20**, 796.
- P. Cao, D. X. Zhao, J. Y. Zhang, D. Z. Shen, Y. M. Lu, B. Yao, B. H. Li, Y. Bai and X. W. Fan, *Appl. Surf. Sci.*, 2008, **254**, 2900.
- K. S. Ahn, Y. F. Yan, S. H. Lee, T. Deutsch, J. Turner, C. E. Tracy, C. L. Perkins and M. A. Jassim, *J. Electrochem. Soc.*, 2007, **154**, B956.
- J. M. Bian, X. M. Li, X. D. Gao, W. D. Yu and L. D. Chen, *Appl. Phys. Lett.*, 2004, **84**, 541.
- S. J. Kang and V. M. Donnelly, *Plasma Sources Sci. Technol.*, 2007, **16**, 265.

- 13 S. J. Jokela and M. D. McCluskey, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2007, **76**, 193201.
- 14 J. Y. Huang, Z. Z. Ye, H. H. Chen, B. H. Zhao and L. Wang, *J. Mater. Sci. Lett.*, 2003, **22**, 249.
- 15 H. P. Tang, Z. Z. Ye and H. P. He, *Opt. Mater.*, 2008, **30**, 1422.
- 16 B. K. Meyer, H. Alves, D. M. Hofmann, W. Kriegseis, D. Forster, F. Bertram, J. Christen, A. Hoffmann, M. Straßburg, M. Dworzak, U. Habocek and A. V. Rodina, *Phys. Status Solidi B*, 2004, **241**, 231.
- 17 Z. R. Tian, J. A. Voight, J. Liu, B. McKenzie, M. J. McDermott, M. A. Rodriguez, H. Konishi and H. F. Xu, *Nat. Mater.*, 2003, **2**, 821.
- 18 K. Minegishi, Y. Koiwai, Y. Kikuchi, K. Yano, M. Kasuga and A. Shimizu, *Jpn. J. Appl. Phys.*, 1997, **36**, L1453.
- 19 J. G. Lu, Y. Z. Zhang, Z. Z. Ye, L. Wang, B. H. Zhao and J. Y. Huang, *Mater. Lett.*, 2003, **57**, 3311.
- 20 M. Pan, J. Nause, V. Rengarajan, R. Rondon, E. H. Park and I. T. Ferguson, *J. Electron. Mater.*, 2007, **36**, 457.
- 21 J. X. Wang, X. W. Sun, Y. Yang, H. Huang, Y. C. Lee, O. K. Tan and L. Vayssieres, *Nanotechnology*, 2006, **17**, 4995.