Nanoscale

PAPER

Cite this: Nanoscale, 2014, 6, 1680

Tuning of multifunctional Cu-doped ZnO films and nanowires for enhanced piezo/ferroelectric-like and gas/photoresponse properties[†]

Wei Li Ong,^a Hejin Huang,^b Juanxiu Xiao,^c Kaiyang Zeng^c and Ghim Wei Ho^{*a}

The prospect of tuning and enhancing multiple properties of ZnO from optical, electrical, piezo to ferroelectricity/magnetism with Cu dopants will certainly spur the pursuit of facile doping methodology to immensely advance this field of research. Here, a one-step aqueous synthesis of Cu-doped ZnO nanostructured materials with effective controllability over the morphology (film to nanowire) and doping concentrations both on rigid and flexible substrates has been developed. High structural integrity Cu-doped ZnO films and nanowires were achieved without multiple/harsh post-processing which tends to degrade their functional properties. Comprehensive investigations of varying doping concentrations on the enhancement and tunability of room temperature piezo/ferroelectricity to gas/photosensing multifunctional properties were systematically reported for the first time.

Received 20th September 2013 Accepted 13th November 2013

DOI: 10.1039/c3nr05034c

www.rsc.org/nanoscale

Introduction

Zinc oxide (ZnO) is garnering an increasing level of interest in the area of spintronics and microelectronics due to its wide bandgap of 3.37 eV.¹ Defect engineering and the introduction of transition-metal ions have also tailored certain properties of ZnO towards various functional applications.^{2,3} One particular dopant that can induce several interesting properties in ZnO nanostructures is copper (Cu). It is known that group Ib metals are fast diffusers in compound semiconductors.⁴ During the diffusion of Cu into ZnO, the Cu atoms can replace either substitutional or interstitial Zn atoms in the ZnO lattice creating structural deformations.⁵ This can significantly affect the electrical, chemical, structural and optical properties of ZnO.^{4,6,7}

There is extensive work on the synthesis, doping and study of Cu-doped ZnO properties. Several synthesis methods for Cu-doped ZnO that have been reported include spray pyrolysis, molecular beam epitaxy, sputtering, filtered cathodic vacuum arc, pulsed laser deposition and thermal evaporation.^{5,7–9} As for

the study on the Cu-doped ZnO properties, it has been demonstrated that the incorporation of Cu into ZnO modifies electrical conductivity due to the introduction of deep acceptor levels which trap electrons.⁷ It was also reported that Cu-doped ZnO possesses ferromagnetic and multi-ferroic-like properties8-11 and exhibits a bipolar charging phenomenon,12 suggesting that Cu-doped ZnO can be used for data and charge storage applications. The presence of Cu dopants has also been observed to enhance the piezoelectric and ferroelectric-like properties of ZnO.13 Besides these properties, Cu impurities are also known to alter the gas and light sensing properties of ZnO, however, there are limited reports in this area of research.14-18 All these reported studies bring about the prospect of an emerging class of multifunctional Cu-doped ZnO devices that possess enhanced optical, electrical, ferro/piezo, etc. properties. However, independent investigations of selective properties based on various syntheses and doping methodologies have been reported thus far.

View Article Online

View Journal | View Issue

Furthermore, for practical applications several issues have to be resolved, such as the ease of synthesis and doping as well as effective control of the doping concentration, which tunes the chemical and physical properties. However, there is no work reported to date on the controlled synthesis of Cu-doped ZnO nanostructured materials (nanowires to films) for tuning of the doping level *via* an *in situ* aqueous method. The ability to carry out *in situ* tuning of variable nanostructured materials from nanowires to films *via* an aqueous method is important since this ensures that the process is economical and attractive in terms of structural controllability, scalability and low synthesis temperature for microelectronic and plastic electronic process compatibility. Moreover, the ease of tuning dopant solubility *via* an *in situ* aqueous method establishes reproducible and

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

^bEngineering Science Programme, National University of Singapore, Singapore 117576, Singapore

^cDepartment of Mechanical Engineering, National University of Singapore, Singapore 117576, Singapore

[†] Electronic supplementary information (ESI) available: Survey XPS spectra of 5% and 10% Cu–ZnO films; I–V plot, hydrogen gas, UV and white light sensing of pristine and Cu-doped ZnO films; SEM images of bent sample; I–V plot and UV sensing of 10% Cu–ZnO nanowires after repeated bending. See DOI: 10.1039/c3nr05034c

homogeneous doping of nanostructured materials to attain reliable device performances. Such work has yet to be demonstrated since it poses a technological challenge to synthesize highly crystalline doped ZnO films and nanowires of superior structural integrity on rigid and flexible substrates without multiple/harsh post-processing which tends to degrade the functional properties of the added dopant.

In this work, we demonstrate a practical one-step aqueous synthesis of Cu-doped ZnO nanostructured materials with effective controllability over the morphology (film to nanowire) and doping concentrations. Cu-doped ZnO films and nanowires of high structural quality were achieved without any high temperature or multiple processing. To fulfill the long-sought understanding of the myriad of exciting properties of Cu-doped ZnO, comprehensive investigations of varying doping concentrations on the optical, piezoelectric, ferroelectric-like and charge storage properties based on a dedicated doped material system were systematically reported for the first time. The enhancement and tunability of room temperature piezo/ferroelectricity to gas/photosensing *via* Cu-doping are demonstrated. Finally, the feasibility of fabricating a Cu-doped ZnO device on a flexible substrate together with its robustness and stability is also shown.

Experimental section

Synthesis of ZnO and Cu-ZnO films

The Si substrates were first cleaned by sonicating in isopropyl alcohol (IPA) and ethanol for 5 min each, and then sputtered with 100 nm of platinum (Pt) using a Jeol JFC-1600 Auto Fine Coater. This conductive layer is used as a bottom electrode and necessary for piezoresponse force microscopy (PFM) and Kelvin probe force microscopy (KPFM) measurements. A seed solution containing zinc acetate and polyvinylpyrrolidone (PVP) in IPA was then spincoated onto the substrate followed by annealing at 540 °C for 10 min. The seeded substrates were placed into a 50 ml growth solution containing 25 mM zinc nitrate and trisodium citrate. Ammonium hydroxide was then added until the pH value of the solution reached 10.9. The growth solution was then heated at 90 °C for 1 h. To prepare Cu-doped ZnO films, an amount of copper (π) nitrate solution with a Cu content corresponding to 5 and 10 at.% of Zn content in the solution was added.

Synthesis of ZnO and Cu-ZnO nanowires

The polyethylene terephthalate (PET) substrates were cleaned by sonicating in IPA and ethanol for 5 min each. The substrates were then seeded by sputtering a 6 nm layer of ZnO. Nanowires were grown on the substrate by placing it into a 50 ml growth solution containing 25 mM zinc nitrate and hexamethyltetramine (HMT) with 0.1 g polyethylenimine (PEI) at 90 °C for 6 h. The Cu dopants were incorporated into the growth solution by adding a corresponding amount of copper(n) nitrate solution equivalent to 5 and 10 at.% of Zn content in the growth solution.

Materials characterization

Various characterization techniques were carried out on the pristine and Cu-doped ZnO. The morphology of the synthesized

products was characterized by scanning electron microscopy (SEM, JEOL FEG JSM 7001F) while the crystalline structure was analyzed using transmission electron microscopy (TEM, Philips FEG CM300) operated at 200 kV and X-ray diffraction (XRD, Philips X-ray diffractometer equipped with graphite-monochromated Cu K α radiation at $\lambda = 1.541$ Å). Room temperature optical properties were measured with a UV-Vis-NIR spectrophotometer (UV-Vis, Shimadzu UV-3600) and micro-photoluminescence (PL) with a He-Cd laser at 325 nm. X-ray photoelectron spectroscopy (XPS) was employed to study the elemental composition of the pristine and Cu-doped ZnO. A commercial Scanning Probe Microscope (SPM) (MFP-3D, Asylum Research, USA) was used as the primary tool for PFM imaging and analysis. The electrical and sensing properties of the samples were studied by current-voltage (I-V) measurements carried out using a Keithley 4200-SCS semiconductor characterization system.

Measurement of piezoelectric properties

PFM is a variation of the SPM technique, which allows nondestructive high resolution ferroelectric domain imaging.¹⁹ PFM works according to the reverse piezoelectricity principle, i.e. a piezoelectric material will deform in accordance with the applied biases. To magnify the signal and improve the signal-tonoise ratio, samples were preferably scanned at their contact resonance frequency, which depends greatly on the tip-sample interaction. To track the resonance frequency, the dual frequency resonance tracking (DART) technique was used throughout the PFM observation. The DART technique scans the sample surface continuously at two frequencies, one slightly below and the other slightly above the contact resonance frequency. In this way, the contact resonance shift can be closely tracked by amplitude detection.20 During the PFM experiments, an ac voltage was applied between the cantilever with a conductive tip (Electri-Lever, Olympus, Japan, Si tip with Al coating at the cantilever and Pt coating at the tip, spring constant = 2 N m^{-1} , and tip radius < 15 nm) and the Pt bottom electrode of the sample. Topography (height image), strength of piezoelectric response (PR) (amplitude image) and domain polarization directions (phase image) could be obtained simultaneously during the PFM scanning. An area of 2 μ m \times 2 µm on the ZnO film was scanned with the AFM tip driven by several ac voltages (V_0) and the corresponding surface deflection (ΔZ) was recorded. The slope of V_0 against ΔZ will give the local piezoelectric constant (d_{zz}) of the film.

Polarization switching analysis

For characterization of polarization switching behavior, the phase angle within an area of 10 μ m \times 10 μ m was first characterized by applying an ac voltage to the scanning AFM tip. To induce polarization switching, a +9 V dc poling voltage was applied to the conductive tip which scans through a 6 μ m \times 6 μ m area with 1 Hz line frequency within the previously characterized 10 μ m \times 10 μ m area (in contact mode). During this dc poling process, if the intrinsic polarization is upward, under a positive dc bias polling process, it will be rotated downwards

and the memory is "written" into the material. The phase angle of polarization in the area under study (10 μ m \times 10 μ m) was then characterized again using PFM by applying an ac bias to the tip. After this scan, the phase difference between the poled and unpoled regions could be compared.

Surface potential measurement

To study the charging characteristics, SPM was used for dc bias writing in contact mode followed by surface potential measurement in KPFM (noncontact mode). The KPFM technique is another variation of the SPM technique and is based on the measurement of the electrostatic forces between the conductive tip and the sample surface. It reveals the surface charge distribution and polarization, and also measures the relative work function of the material.21 All the KPFM measurements were performed at 3 V ac voltage with a lift height of 40 nm. To investigate the charge storage characteristics, an 8 μ m \times 8 μ m area was first scanned with a conductive tip using 1 Hz line scan frequency. This was followed by applying a positive (+9 V) dc bias in a 4 μ m \times 4 μ m area within the first scanned area, and subsequently, a negative (-9 V) dc bias was applied to a smaller area of 2 μ m imes 2 μ m within the second scanned area. After these biasing operations, KPFM was then used to measure the surface potential of the sample. As the surface potential values are affected by the charges during the tip-surface interaction and absorption layer under ambient conditions,²¹ the contact potential value of the unbiased region is reset to 0 V for all the samples in order to compare the different results quantitatively.

Sensing measurement

The hydrogen sensing measurement was carried out by applying a 10 V bias to the sample and measuring the resistance of the sample when it was exposed to alternating intervals of air and hydrogen ambient. The concentration of hydrogen was varied from 100 to 500 ppm by adjusting the flow rates of air and hydrogen. To determine the photoresponse of the ZnO nanowires, a voltage bias of 10 V was applied to the sample and the current was measured both in the dark and under illuminated conditions. Besides the ultraviolet (UV) light source, a white light emitting diode (LED) was also used to determine the response of the nanowires to the visible spectrum. The flexibility and robustness of the samples were also tested by carrying out hydrogen and light sensing measurements on bent samples.

Results and discussion

The synthesized ZnO films and nanowires are shown in Fig. 1. The synthesized films show fully coalesced ZnO grains and there is no observable morphological difference between the undoped and doped ZnO films (Fig. 1a–c). The morphology of the pristine ZnO nanowires grown on the PET substrate is shown in Fig. 1d. The nanowires have an average diameter of 70 nm and a length of 2 μ m. The 5 and 10 at.% Cu-doped ZnO nanowires are shown in Fig. 1e and f respectively. There are no observable differences between the morphologies of the

Paper



Fig. 1 SEM images of (a) pristine, (b) 5%, (c) 10% Cu–ZnO films and (d) pristine, (e) 5%, and (f) 10% Cu–ZnO nanowires.

undoped and doped ZnO nanowires. Cross-sectional SEM images of the ZnO film and nanowires are shown in Fig. 2a and c respectively. The ZnO grains are vertically aligned and fully coalesced throughout the film, while the nanowires exhibit good vertical alignment. The structural quality of the ZnO films and nanowires was also characterized by TEM and XRD. The grains of the ZnO film were of single crystalline structure with clearly defined lattice fringes in the HRTEM image (Fig. 2b) and are highly *c*-oriented in the out-of-plane direction. The lattice



Fig. 2 (a) Cross-section SEM image and (b) HRTEM image of the ZnO film. (c) Cross-section SEM image and (d) HRTEM image of ZnO nanowires. (e) XRD pattern of the pristine and Cu-doped ZnO films. The inset shows the small range XRD pattern to illustrate the shift in the (002) peak.

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. The XRD spectra in Fig. 2e also indicate that the ZnO films are single crystalline. The pristine ZnO film exhibited a prominent ZnO (002) peak which can be well indexed to the hexagonal phase of ZnO with lattice constants a = 0.3242 nm and c = 0.5194 nm (JCPDS card no. 79-0205). The (002) peak indicates preferential growth in the [0001] direction, and also the good crystal structure and phase purity of the product. The peak located at 32.85° is due to the (200) peak of the Si substrate. These results show that high quality ZnO films and nanowires can be produced by hydrothermal synthesis despite it being a low temperature synthesis method. Moreover, the morphology can be controlled just by tuning the synthesis parameters. The XRD spectra of the Cu-ZnO films also show the (002) peak, however, careful observation of the peak reveals a shift towards higher angles with increasing amount of doping (inset of Fig. 2e). The (002) peak of undoped ZnO is located at 34.19° and it shifts to 34.21° and 34.23° for dopant concentrations of 5% and 10% Cu respectively. The shift in the (002) peak could be due to the substitution of Zn by Cu in the hexagonal lattice.²² The Zn²⁺ and Cu²⁺ cations have ionic radii of 0.06 nm and 0.057 nm respectively.²² Upon substitution of Zn²⁺ by the smaller Cu²⁺ ions, the formation of the shorter Cu_{2n}-O bonds and smaller [Cu_{Zn}-O₄] units results in a shrinkage of lattice constants and a slight deformation in the lattice.23 This shrinkage in the lattice spacing results in a shift of the (002) peak towards higher values.

The optical transmittance of a plain PET substrate and PET substrates grown with ZnO nanowires is measured over the wavelength range of 300 to 700 nm (Fig. 3a). The transmittance of the plain PET substrate is 81-86% in the visible range (400 to 700 nm) with ultraviolet (UV) light of wavelength less than 306 nm being absorbed by the PET. The PET substrate with undoped ZnO nanowires showed a decrease in transmittance to 56-83% in the visible range of 400 to 700 nm. The transmittance of UV light was also red-shifted to 370 nm due to absorption by the ZnO nanowires. The transmittance of the PET substrates with Cu-doped ZnO nanowires was similar to that of the undoped ZnO nanowires, indicating that Cu-doping does not affect the transmittance of the ZnO nanowires. Optical properties of the pristine and Cu-ZnO nanowires were also analyzed by room temperature PL measurements. As shown in Fig. 3b, all the samples exhibited two distinct emission peaks. The UV peak at 380 nm (inset of Fig. 3b) is attributed to near band-edge emission while the visible peak at 600 nm is due to the defects in the ZnO nanowires.²⁴ The intensity of the visible peak can be used as an indicator of the defect concentration in ZnO. It is observed that the intensity of the defect peak increases with increasing amount of Cu-doping, suggesting that Cu-doping strongly increases the concentration of defects in ZnO. The enhancement effect of the increased defect concentration on the various properties of ZnO will be elaborated later. To determine the presence of Cu in the doped samples, XPS measurements were carried out on the undoped, 5% and 10% Cu-ZnO films. No Cu was found in the undoped ZnO film but Cu was detected in the 5% and 10% Cu–ZnO films (Fig. S1†). This shows that *in situ* Cu-doping during hydrothermal synthesis is possible and the dopant concentration can be tuned by controlling the amount of Cu precursor added to the growth solution. The Cu 2p XPS binding region for 5% and 10% Cu–ZnO films is shown in Fig. 3c and d respectively. The peak corresponding to the Cu $2p_{3/2}$ core level of Cu was observed at 932.7 eV in both spectra, indicating that Cu dopants were successfully incorporated into the ZnO films. However, the Cu $2p_{3/2}$ peak is asymmetric, suggesting the presence of more than one Cu species. The peak could be deconvoluted into two peaks centered at 932.5 eV and 933.5 eV, corresponding to Cu⁺ and Cu²⁺ respectively.²⁵

The effect of Cu-doping (0, 5, 7.5, and 10%) on the piezoelectric properties of the ZnO films was investigated by PFM. The PFM amplitude signals (Fig. 4, insets) provide information on the magnitude of the vertical displacement of each ferroelectric domain when an ac signal is introduced. The insets of Fig. 4 were obtained at the same ac bias of 2.5 V. From the amplitude signals of undoped ZnO (inset (a)), only a few grains displayed brighter contrast suggesting greater piezoresponse, while majority of the grains in the scan area have a darker contrast indicating weaker piezoresponse. In comparison, the amount of grains with bright contrast has increased in the 5% Cu-ZnO film (inset (b)), but the amount of bright contrast grains is the highest in the 10% Cu-ZnO film (inset (d)). This means that the presence of Cu dopants in ZnO films improved the piezoresponse amplitude and the amount of improvement increased with the amount of Cu dopants. This improvement in piezoresponse could be better appreciated by studying the piezoelectric constant, d_{zz} , which measures the deformation of the ZnO film in the z-axis per unit of voltage applied in the same direction. The x- and y-directions are quantum confined, thus only the d_{zz} value is considered for the piezoelectric properties. In order to obtain the d_{zz} value of the ZnO film, the vertical displacement at various applied ac biases was measured from the amplitude images. The vertical displacements were then plotted against the ac biases for the undoped and Cu-ZnO films. The slope of the best fit line in these plots gave the d_{zz} values of 23.2 pm $V^{-1}\!,$ 39.0 pm $V^{-1}\!,$ 46.5 pm V^{-1} and 79.8 pm V⁻¹ for undoped, 5%, 7.5%, and 10% Cu–ZnO films respectively (Fig. 4). It was observed that the d_{zz} value increased with increasing amount of Cu-doping. This phenomenon is consistent with results reported by Wang et al.13 The dominant effect of the electric field in wurtzite semiconductors is to rotate the bonds that are non-collinear with the polar *c*-axis toward the direction of the applied field, thus producing strain.²⁶ When Cu ions substitute Zn in the ZnO lattice, the smaller ionic radius results in the Cu-O1 bonds being able to rotate more easily in the direction of the applied field, thus producing larger piezoelectric displacement and enhancing the corresponding electromechanical responses.27 The smaller ionic radius of Cu can also result in smaller repulsive force between the ions, which in turn produces a larger displacement of Cu under stress. Therefore, when the same amount of stress is applied, the dipole moment induced in Cu-ZnO films would be larger and a higher piezoelectric constant would be obtained.



Fig. 3 (a) UV-Vis transmission spectra and (b) room temperature PL spectra of the pristine and Cu-doped ZnO nanowires. The inset of (b) shows the PL peak in the UV region. XPS spectra corresponding to the Cu 2p core level of (c) 5% and (d) 10% Cu–ZnO films.



Fig. 4 Relationship between the doping concentration and the d_{zz} constant. The inset shows PFM amplitude images obtained from (a) 0%, (b) 5%, (c) 7.5% and (d) 10% Cu-doped ZnO films.

Polarization switching in ZnO films was also investigated for possible applications in nonvolatile memory. "Switching" in this context refers to reversal of the dipole moment in the film by an applied dc bias and the subsequent retention of the polarization after removing the electric field.²⁸ The ferroelectriclike domains in the noncentrosymmetric ZnO crystal could be polarized upwards or downwards depending on the direction of the electric field. The polarization switching behavior of undoped, 5% and 10% Cu–ZnO films was investigated and the corresponding phase images (10 μ m × 10 μ m scan area) after poling are shown in Fig. 5a–c. A remarkable contrast between the unpoled and the poled (6 μ m × 6 μ m) region was observed. Most of the domains had spontaneous upward polarization (yellow color) in their as-grown state. After applying a positive voltage (+9 V), the domains flipped by 180° as shown in the phase histogram (Fig. 5d), indicating that downward polarization has been written in the ZnO film. The histogram shows the domain counts for various phase angles of the polarized domains in the 10% Cu–ZnO film over a scan area of 10 μ m × 10 μ m before (red) and after (green) poling. The phase angles of dipoles within the characterized area of 10 μ m × 10 μ m have been rotated by approximately 180° for a large number of dipoles. However, small amounts of white dots corresponding to defect pinning could be observed on the ZnO films, especially



Fig. 5 PFM phase images within the 10 μ m \times 10 μ m area of (a) undoped, (b) 5% and (c) 10% Cu–ZnO films after dc writing. (d) Phase histogram of 10% Cu–ZnO films.

for the undoped ZnO film. The presence of defects, which act as pinning centers, affects poling of the local ferroelectric domains in the desired direction.29 The undoped ZnO film has relatively poor ferroelectric-like properties as shown by the poorly defined boundaries between the poled and unpoled regions in Fig. 5a. The low resistance of the undoped ZnO film also results in current leakage which affects the effectiveness of poling. Moreover, a significant amount of defect pinning exists on the undoped ZnO film, which affects the poling of the local domains by dc voltage. Therefore, the undoped ZnO film does not seem to possess good ferroelectric-like properties. On the other hand, the 10% Cu-ZnO film has a clearly defined boundary between the poled and unpoled regions and can be regarded as a good ferroelectric material. The ferroelectric-like behavior of the Cu-ZnO films can be attributed to the substitution of the smaller Cu^{2+} and Cu^{+} ions into Zn^{2+} sites in the crystal lattice.30 The smaller dopant ions cause a permanent electric polarization to be induced when the dopant ions occupy off-center positions. Therefore, the local induced electric dipole will lead to ferroelectric-like behavior in the Cu-ZnO films. It can be concluded that Cu-doping significantly improves the ferroelectric-like properties of the ZnO thin film. With no leakage of poling and less defect pinning, these Cu-ZnO films are potential candidates for memory storage materials.

The charge storage characteristics of the ZnO films were investigated by studying the charge or surface potential behaviors of the films in response to an applied bias. Positive (+9 V) and negative (-9 V) dc biases were applied on selected regions to transfer positive and negative charges respectively onto the sample surface. The measured surface potential of the films after dc bias writing is shown in Fig. 6a-c. The brighter and darker regions (relative to that of the unbiased region) in the surface potential images indicate an increase and decrease in the surface potential value respectively due to charge/hole injection from the bias application. The surface potential changes against the poling position are plotted in Fig. 6d for quantitative comparison. For the undoped ZnO film, a change of ~210 mV in the surface potential was observed in the positive-biased region while no significant change (\sim 30 mV) was observed in the negative-biased region. For the 5% Cu-ZnO film, the change in the positive-biased region was $\sim 180 \text{ mV}$ whereas the change in the negative biased region was \sim 75 mV. The 10% Cu-ZnO film exhibited ~120 mV and ~60 mV changes in the positive- and negative-biased regions respectively. In KPFM measurements, the surface potential measured includes contributions from (1) surface charge, (2) injection charge, and (3) polarization charge.³¹ The polarization charge is attributed to the rotation of the electric dipoles under the applied electric field. The changes in the surface potential of the Cu-ZnO films after the samples were scanned by a grounded tip are most likely due to the polarization and injection charges. The schematic diagram in Fig. 6e illustrates the interaction between the polarization and injection charges after dc bias writing, assuming that both polarization states have the same amount of polarization charges. When a dc bias is applied to the films, the injected charges will screen the polarization charges of the oriented dipoles. The rest of the injection charges that did not partake in this compensation process will contribute to the measured surface potential. $^{\rm 32}$

For the negative-biased region, the changes in surface potential are the highest for the 5% Cu-ZnO film and the lowest for the undoped film.¹² This is because Cu²⁺ is able to trap free electrons in its 3d orbital.³³ For the undoped ZnO film where no copper dopants exist, electrons could hardly be injected into the ZnO film, whereas electrons are easily injected and trapped in Cu²⁺ in the 5% Cu–ZnO film. For the 10% Cu–ZnO film, a large portion of the copper dopants exist as Cu⁺ instead of Cu²⁺ as previously seen in Fig. 3d. It was reported that Cu⁺ states cannot trap electrons as effectively as Cu²⁺,³³ thus, the surface potential change observed in the 10% Cu-ZnO film is smaller than the 5% Cu-ZnO film in the negative-biased region despite its higher copper doping concentration. For the positive-biased region, the change in surface potential decreases with increasing copper doping concentration. The undoped ZnO film is observed to have the largest change in the surface potential for the positive-biased region. This result is different from that reported by Wong et al.12 because of the different synthesis and doping method of the ZnO film. Most of the previously reported results were based on the n-type ZnO film, while the assynthesized ZnO film in this project is p-type. For p-type ZnO, zinc vacancies exist on the ZnO surface and they act as hole trapping centers. With more zinc vacancies, holes can be injected into the ZnO film more easily. Therefore, the largest surface potential change in the positive-biased region was observed in the undoped ZnO film. Higher copper doping concentration meant more zinc vacancies are occupied by copper ions, therefore, the surface potential change in the positive region decreased with increasing copper doping concentration. The undoped ZnO film has good charge characteristics for positive charge storage, as indicated by its increase in surface potential with application of positive bias. For the Cu–ZnO film, the incorporated Cu²⁺ is regarded as electron trapping centers. The negative charge storage capacity increases with Cu2+ concentration while the positive charge storage capacity decreases with copper doping concentration. Therefore, the charge storage characteristics of the ZnO film could be tuned by varying the copper doping concentration.

ZnO photodetectors and gas sensors that are based on films usually have performance that is severely hampered by the limited surface to volume ratio. Moreover, gas sensors usually operate at relatively high temperatures of over 300-500 °C, which after prolonged cycling result in structural instability, causing electrical drift. On the other hand, 1D ZnO nanowire arrays of high structural integrity possess a high surface to volume ratio, ideal for enhanced sensing performance.34 The dark I-V curves of the ZnO nanowires are shown in Fig. 7a. The magnitude of the dark current decreased drastically upon incorporation of Cu dopants, with the resistance increasing from 6.8×10^6 to $1 \times 10^8 \Omega$ as the doping level increased from 0% to 10%. This increase in resistance is due to the trapping of electrons at the defect sites related to Cu.33 The ZnO nanowires were then exposed to hydrogen gas and the sensitivity of the sensor is calculated using the following equation:



Fig. 6 Surface potential images after dc bias writing for (a) undoped, (b) 5% and (c) 10% Cu–ZnO films. The darker areas represent the decrease in the surface potential value and the brighter (white) areas represent the increase in the surface potential value (on the same scales). (d) The surface potential changes (caused by dc bias writing) are plotted against the poling size. (e) Schematic diagram of polarization states and charge distributions on different applied biases and the number of charges that remained after charge compensation. The square and circular charges show polarization and screen charges respectively.

Sensitivity =
$$100\% \times |(R_{hydrogen} - R_{air})/R_{air}|$$
 (1)

where $R_{hydrogen}$ is the resistance of the nanowires in hydrogen gas and R_{air} is the resistance in clean dry air. The undoped ZnO nanowires were able to detect 500 ppm of hydrogen gas but with a sensitivity of only 41% as shown in Fig. 7b. The sensitivity improved with Cu-doping and the 5% Cu-ZnO nanowires had the highest sensitivity of 117% while further increment to 10% Cu-doping resulted in a drop in the sensitivity to 54%. This indicates that 5% Cu-ZnO is the optimal doping concentration for hydrogen gas sensing and the sensitivity is much better than the undoped and 10% Cu-ZnO nanowires. When ZnO nanowires are exposed to air, oxygen molecules will adsorb at the surface defect sites. These charge accepting molecules will trap electrons and deplete them from the conduction band, leading to a reduced conductivity of the ZnO nanowires. However, when the nanowires are exposed to hydrogen gas, the molecules would react with the surface adsorbed oxygen and remove it, leading to an increase in conductivity.35 In Cu-doped ZnO nanowires, the number of adsorbed oxygen species on the surface of the nanowires is governed by the doping concentration. The increased amount of defect sites induced by Cu-doping results in more adsorbed oxygen species on the surface.17 Therefore, more hydrogen molecules can react with the increased amount of adsorbed oxygen species, causing a decrease in the barrier height which leads to the reduction in electrical resistance.16 The hydrogen gas molecules adsorb preferably on the Cu sites forming Cu-H bonds. This weak Cu-H bond involves the exchange of electrons between the hydrogen molecules and the d-orbitals of Cu, and the adsorption results in an enhancement in the gas reactivity.³⁶ The adsorption of the gas molecules takes place mainly at the Cu sites instead of the Zn sites, and the hydrogen molecules subsequently migrate from the Cu sites to the Zn sites.³⁶ In this way, the Cu sites enhanced the gas adsorption and in turn the reaction of hydrogen with the oxygen species. The 5% Cu-ZnO nanowires were tested with several concentrations of hydrogen gas and the sensor exhibited different sensitivity values for each hydrogen concentration with a sensitivity of 82% at the lowest hydrogen concentration of 100 ppm (Fig. 7c). The repeatability of the sensing performance was also tested by exposing the nanowires to alternating cycles of hydrogen (500 ppm) and air ambient. The plot in Fig. 7d shows that the 5% Cu-ZnO nanowires could recover to their initial resistance level after exposure to hydrogen gas and they exhibited consistent hydrogen sensing and recovery performances over several cycles.

Besides hydrogen sensing, the ZnO nanowires were also sensitive to light. The change in the resistance of the nanowires under UV illumination (300 s) was measured with an applied voltage bias of 10 V. When the nanowires were exposed to UV illumination, there was an immediate drop in the resistance of the nanowires. The photoresponse of the samples towards UV light can be quantified by taking the ratio of the current flowing through the nanowires under illumination (I_{on}) to the current flowing through the nanowires in the dark (I_{off}). The photoresponses of the pristine and Cu–ZnO nanowires are shown in



Fig. 7 (a) I-V plot of pristine and Cu-doped ZnO nanowires under dark conditions. The inset shows a magnified view of the I-V curve. (b) Hydrogen gas sensing (500 ppm) of undoped and Cu-doped ZnO nanowires at room temperature. (c) Hydrogen gas sensing of 5% Cu–ZnO nanowires at various concentrations (100–500 ppm). (d) Repeated hydrogen gas sensing (500 ppm) of 5% Cu–ZnO nanowires. (e) UV sensing of undoped and Cu-doped ZnO nanowires. (g) White light sensing of undoped and Cu-doped ZnO nanowires. (h) Repeated white light sensing of 10% Cu–ZnO nanowires.

Fig. 7e. The undoped sample has a maximum $I_{\rm on}/I_{\rm off}$ ratio of 38, while 5% Cu–ZnO nanowires exhibited an $I_{\rm on}/I_{\rm off}$ ratio of 63 and this value improved to 79 for the 10% Cu–ZnO nanowires. The improvement in the response to UV illumination for Cu-doped ZnO nanowires is due to the increased number of defects introduced by Cu-doping. When ZnO nanowires are kept under dark atmospheric conditions, the oxygen molecules adsorbed

on the ZnO surface capture free electrons to form chemisorbed O_2^- , leading to the formation of a surface depletion region which decreases the conductance of the nanowires. When the nanowires are irradiated by UV light, the photon energy larger than the bandgap of ZnO causes the generation of electron-hole pairs. The photogenerated holes will migrate to the surface and get trapped at the negatively charged oxygen molecules, while



Fig. 8 (a) Digital photograph of the sample mounted on a glass vial and schematic diagram illustrating the degree of bending. (b) I-V plot of 10% Cu–ZnO nanowires before, during and after bending. (c) UV sensing and (d) white light sensing of bent 10% Cu–ZnO nanowires. (e) I-V plot of 5% Cu–ZnO nanowires before, during and after bending. (f) Hydrogen gas sensing (500 ppm) of bent 5% Cu–ZnO nanowires.

the photogenerated electrons contribute to an increased carrier density, increasing the conductivity of the nanowires and producing a large photocurrent.³⁷ However, when the ZnO nanowires are doped with Cu, the defect sites created by the Cu dopants trap the free carriers causing a decrease in the dark current as evidenced from the *I*-*V* curves in Fig. 7a. In this case, the enhanced photoresponse in the Cu–ZnO nanowires can be explained by the following equation:

$$\eta \approx 1 + \frac{\Delta n}{n_0} \tag{2}$$

where Δn is the photogenerated excess carrier density and n_0 is the equilibrium carrier density. Since n_0 decreases and Δn increases, the resultant η value increases.³⁸ Therefore, the enhanced photosensitivity is due to the reduced dark current which in turn increases the difference between the dark and photocurrents. The reproducibility of the sensing performance was also tested by exposing the 10% Cu–ZnO nanowires to repeated alternating UV light (300 s) and dark (600 s) conditions (Fig. 7f). The sample was able to consistently recover to its

original resistance value and the peak $I_{\rm on}/I_{\rm off}$ ratio obtained under UV illumination was also consistent for all the 3 cycles. The sample was also tested for photosensitivity to visible light by exposing the sample to illumination from a white LED. Both the undoped and 10% Cu-ZnO nanowires showed a change in the current under white light illumination but the corresponding peak $I_{\rm on}/I_{\rm off}$ ratios were much lower than those obtained from UV illumination (Fig. 7g). This is because highly energetic UV photons were able to cause near-bandgap absorption, while the photons of visible light could only be absorbed by defect states due to their lower energy. The undoped ZnO nanowires showed a response to white light with a peak $I_{\rm on}/I_{\rm off}$ ratio of 5 despite being a wide bandgap semiconductor because intrinsic defects were present in the nanowires as shown by the PL spectrum in Fig. 3b. The native defect-related deep electronic states conferred the sensitivity of the undoped ZnO nanowires towards visible light.³⁹ When the nanowires were exposed to light with energy lower than the bandgap, the electrons captured at the defect states related to oxygen adsorption are photoexcited to the conduction band,

which enhanced the electron density and lowered the potential barriers, resulting in the photoresponse observed in Fig. 7g. The physisorbed oxygen can then leave the surface of the nanowires via thermal activation at room temperature. When the light was turned off, the oxygen molecules in the ambient air will be physisorbed on the nanowire surface again, and go on to become chemisorbed oxygen after capturing electrons from the conduction band, resulting in a decrease in the photocurrent. The 10% Cu-ZnO nanowires showed an improved response to white light with a peak $I_{\rm on}/I_{\rm off}$ ratio of 11. This enhancement in visible light photoresponse can be explained by the presence of defect states at sub-bandgap energy levels (E_d) . The Cu-related defect states are located below the conduction band in the bandgap such that $E_{\rm c} - E_{\rm d} \gg k_{\rm B}T_{\rm RT}$, with $k_{\rm B}$ being the Boltzmann constant and $T_{\rm RT}$ the room temperature.⁴⁰ Electron-hole pairs can thus be generated by sub-bandgap excitation (white light), resulting in sub-bandgap response of the Cu-ZnO nanowires. The 10% Cu-ZnO nanowires also displayed consistent results for repeated cycles of alternating white light and dark conditions as shown in Fig. 7h. The sample was able to recover to its original resistance value after each exposure to visible illumination and the peak $I_{\rm on}/I_{\rm off}$ ratio obtained was also consistent for all the 3 cycles. To prove that ZnO nanowires do indeed perform better than ZnO films in terms of sensing, ZnO films were also tested for hydrogen gas, UV and white light sensing (Fig. S2[†]). The ZnO films were able to sense at room temperature and the sensing performances were observed to improve in the presence of Cu dopants (similar to that of nanowires). However, all the sensitivities were relatively lower than those of the ZnO nanowires.

One of the purposes of synthesizing ZnO nanowires on PET substrates was to fabricate flexible photodetectors and gas sensors. To test the robustness and flexibility of the nanowire sensors, the samples were subjected to repeated bending. No cracking or delamination of ZnO nanowires from the PET substrate was observed as shown by the SEM images in Fig. S3,† proving the mechanical robustness of the ZnO nanowires on the PET substrate. To further prove the robustness and functionality of the sensor in the bent state, electrical and sensing measurements were carried out on a sample mounted on a curved surface of radius 1 cm as shown in Fig. 8a. Mounting the sample on the curved surface will subject it to a bending of 40° relative to the vertical axis. The electrical integrity of the nanowires was tested by conducting I-V measurements on the sensor before, during and after bending it. The corresponding I-V curves for 10% and 5% Cu-ZnO nanowires are plotted in Fig. 8b and e respectively. No significant changes were observed in the currents measured before, during and after bending of the samples. This shows that the electrical conductivity of the nanowires was maintained and not degraded by physical manipulation. The sample was then tested for hydrogen gas (500 ppm), UV and white light sensing. When the sensing performances were compared to the flat sample, the results obtained were almost the same with no significant deterioration as shown in Fig. 8c, d and f. The 10% Cu-ZnO nanowires were tested further by bending the sample for 1000 times and studying the I-V characteristics and UV sensing performance

(Fig. S4[†]). The results show that repeated bending did not have any adverse effect on the performance of the sample.

Conclusions

We have successfully demonstrated the one-step aqueous synthesis of ZnO films and nanowires with in situ Cu-doping of various concentrations. The Cu-doped ZnO films exhibited enhanced piezoelectric properties with increasing Cu-doping concentration and a d_{zz} constant of 79.8 pm V⁻¹ was obtained for the 10% Cu-ZnO film. Besides piezoelectric properties, improved polarization switching and charge storage properties were also observed in the Cu-ZnO films, with the 10% Cu-ZnO film exhibiting a clearly defined boundary between the poled and unpoled regions. The Cu-ZnO nanowires synthesized on PET substrates also showed enhancements in hydrogen gas, UV and visible light sensing performances. The sensitivity towards hydrogen gas improved to 117% for a hydrogen gas concentration of 500 ppm. An $I_{\rm on}/I_{\rm off}$ ratio of 79 was obtained from the 10% Cu-ZnO nanowires in the presence of UV light and an $I_{\rm on}/I_{\rm off}$ ratio of 11 was obtained under white light illumination. The sensors were stable and displayed consistent and reproducible results for several cycles of exposure to light or hydrogen gas. The flexible sensors were also robust under bending with no observable deterioration in the performance.

Acknowledgements

This work is supported by R-263-000-A27-281.

Notes and references

- 1 U. Özgür, Y. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Doğan, V. Avrutin, S. J. Cho and H. Morkoç, *J. Appl. Phys.*, 2005, **98**, 041301.
- 2 Y. C. Yang, C. Song, F. Zeng, F. Pan, Y. N. Xie and T. Liu, *Appl. Phys. Lett.*, 2007, **90**, 242903.
- 3 J. W. Lo, W. C. Lien, C. A. Lin and J. H. He, *ACS Appl. Mater. Interfaces*, 2011, 3, 1009–1014.
- 4 C. West, D. J. Robbins, P. J. Dean and W. Hays, *Physica B+C*, 1983, **116**, 492–499.
- 5 J. B. Kim, D. Byun, S. Y. Ie, D. H. Park, W. K. Choi, C. Ji-Won and A. Basavaraj, *Semicond. Sci. Technol.*, 2008, **9**, 095004.
- 6 K. S. Ahn, T. Deutsch, Y. Yan, C. S. Jiang, C. L. Perkins, J. Turner and M. Al-Jassim, *J. Appl. Phys.*, 2007, **102**, 023517.
- 7 T. S. Herng, S. P. Lau, S. F. Yu, H. Y. Yang, K. S. Teng and J. S. Chen, *J. Phys.: Condens. Matter*, 2007, **19**, 236214.
- 8 D. B. Buchholz, R. P. H. Chang, J. H. Song and J. B. Ketterson, *Appl. Phys. Lett.*, 2005, **87**, 082504.
- 9 C. Xu, K. Yang, L. Huang and H. Wang, *J. Chem. Phys.*, 2009, **130**, 124711.
- 10 D. Gao, Y. Xu, Z. Zhang, H. Gao and D. Xue, *J. Appl. Phys.*, 2009, **105**, 063903.
- 11 T. S. Herng, M. F. Wong, D. C. Qi, J. B. Yi, A. Kumar, A. Huang, F. C. Kartawidjaja, S. Smadici, P. Abbamonte, C. Sánchez-Hanke, S. Shannigrahi, J. M. Xue, J. Wang,

Y. P. Feng, A. Rusydi, K. Y. Zeng and J. Ding, *Adv. Mater.*, 2011, 23, 1635–1640.

- 12 M. F. Wong, T. S. Herng, Z. K. Zhang, K. Y. Zeng and J. Ding, *Appl. Phys. Lett.*, 2010, **97**, 232103.
- 13 X. Wang, C. Song, D. Li, K. Geng, F. Zeng and F. Pan, *Appl. Surf. Sci.*, 2006, **253**, 1639–1643.
- 14 Y. S. Sonawane, K. G. Kanade, B. B. Kale and R. C. Aiyer, *Mater. Res. Bull.*, 2008, **43**, 2719–2726.
- 15 H. Gong, J. Q. Hu, J. H. Wang, C. H. Ong and F. R. Zhu, *Sens. Actuators, B*, 2006, **115**, 247–251.
- 16 M. Zhao, X. Wang, L. Ning, J. Jia, X. Li and L. Cao, Sens. Actuators, B, 2011, 156, 588-592.
- 17 L. Chow, O. Lupan, G. Chai, H. Khallaf, L. K. Ono, B. Roldan Cuenya, I. M. Tiginyanu, V. V. Ursaki, V. Sontea and A. Schulte, *Sens. Actuators*, A, 2013, **189**, 399–408.
- 18 P. Schreiber, T. Dang, G. Smith, T. Pickenpaugh, P. Gehred and C. Litton, *Proc. SPIE*, 1999, **3629**, 230–248.
- 19 S. Elisabeth, J. Phys. D: Appl. Phys., 2011, 44, 464003.
- 20 B. J. Rodriguez, C. Callahan, S. Kalinin and R. Proksch, *Nanotechnology*, 2007, **18**, 475504.
- 21 Y. Kim, C. Bae, K. Ryu, H. Ko, Y. K. Kim, S. Hong and H. Shin, *Appl. Phys. Lett.*, 2009, **94**, 032907.
- 22 Z. Zhang, J. B. Yi, J. Ding, L. M. Wong, H. L. Seng, S. J. Wang, J. G. Tao, G. P. Li, G. Z. Xing, T. C. Sum, C. H. A. Huan and T. Wu, *J. Phys. Chem. C*, 2008, **112**, 9579–9585.
- 23 Q. Ma, D. B. Buchholz and R. P. H. Chang, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **78**, 214429.
- 24 M. H. Huang, Y. Y. Wu, H. Feick, N. Tran, E. Weber and P. D. Yang, *Adv. Mater.*, 2001, 13, 113–116.
- 25 B. E. Goodby and J. E. Pemberton, *Appl. Spectrosc.*, 1988, **42**, 754–760.

- 26 D. Karanth and H. X. Fu, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2005, **72**, 064116.
- 27 F. Pan, J. T. Luo, Y. C. Yang, X. B. Wang and F. Zeng, *Sci. China: Technol. Sci.*, 2012, 55, 421–436.
- 28 T. S. Herng, A. Kumar, C. S. Ong, Y. P. Feng, Y. H. Lu, K. Y. Zeng and J. Ding, *Sci. Rep.*, 2012, 2, 587.
- 29 S. V. Kalinin, A. N. Morozovska, L. Q. Chen and B. J. Rodriguez, *Rep. Prog. Phys.*, 2010, 73, 056502.
- 30 R. D. Shannon, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr., 1976, 32, 751–767.
- 31 A. Kumar, T. S. Herng, K. Y. Zeng and J. Ding, ACS Appl. Mater. Interfaces, 2012, 4, 5276–5280.
- 32 Y. Kim, C. Bae, K. Ryu, H. Ko, Y. K. Kim, S. Hong and H. Shin, *Appl. Phys. Lett.*, 2009, **94**, 032907.
- 33 X. B. Wang, D. M. Li, F. Zeng and F. Pan, J. Phys. D: Appl. Phys., 2005, 38, 4104–4108.
- 34 A. Kolmakov and M. Moskovits, *Annu. Rev. Mater. Res.*, 2004, 34, 151–180.
- 35 X. J. Wang, X. W. Sun, Y. Yang, H. Huang, Y. C. Lee, O. K. Tan and L. Vayssieres, *Nanotechnology*, 2006, 17, 4995– 4998.
- 36 H. Y. Chen, S. P. Lau, L. Chen, J. Lin, C. H. A. Huan, K. L. Tan and J. S. Pan, *Appl. Surf. Sci.*, 1999, **152**, 193–199.
- 37 Y. Chen, M. W. Chen, C. Y. Hsu, D. H. Lien, M. J. Chen and J. H. He, *IEEE J. Sel. Top. Quantum Electron.*, 2012, 18, 1807– 1811.
- 38 N. Kouklin, Adv. Mater., 2008, 20, 2190-2194.
- 39 Q. H. Li, T. Gao, Y. G. Wang and T. H. Wang, *Appl. Phys. Lett.*, 2005, 86, 123117.
- 40 D. D. Lin, H. Wu and W. Pan, *Adv. Mater.*, 2007, **19**, 3968–3972.

Nanoscale