Invited Paper

Controlling the properties of electrodeposited ZnO nanowire arrays for light emitting diode, photodetector and gas sensor applications.

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ABSTRACT

Electrochemical deposition (ECD) is a versatile technique for the preparation of ZnO nanowires (NWs) and nanorods (NRs) with high structural and optical quality. The bandgap of the ZnO NWs can be engineered by doping. Depending on the doping cation and concentration, the bandgap is increased or decreased in a controlled manner. The NW arrays have been grown on various substrates. The epitaxial growth on single-crystal conducting substrates has been demonstrated. By using p-type GaN layers, heterostructures have been fabricated with a high rectifying electrical behavior. They have been integrated in low-voltage LEDs emitting in the UV or in the visible region depending on the NW composition. For visible-blind UV-photodetector application, ZnO NW ensembles, electrochemically grown on F:SnO$_2$, have been contacted on their top with a transparent graphene sheet. The photodetector had a responsivity larger than 10^4 A/W at 1V in the near-UV range. ECD ZnO NWs have also been isolated and electrically connected on their both ends by Al contacts. The obtained nanodevice, made of an individual NW, was shown to be a H$_2$ gas sensor with a high selectivity and sensitivity. Moreover, it was shown that Cd-doping of ZnO NWs significantly improved the performance of the sensor.

Keywords: ZnO Nanowires, Electrodeposition, Doping, Light emitting diodes, Visible-blind UV-Photodetector, Nanosensor.

I. INTRODUCTION

ZnO is a II–VI group compound semiconductor with a hexagonal wurtzite crystal structure [1]. It has a wide and direct band gap of 3.37 eV at 300 K and a large free exciton binding energy of 60 meV [1]. Zinc oxide nanowires are the most promising one-dimensional (1D) nanostructures emerging as building blocks for active elements in various nanophotonics systems [2,3]. Moreover, by doping zinc oxide with new elements, it is possible to achieve desirable optical, electrical, magnetic or sensing properties which are important for multifunctional device applications.

Low dimensional ZnO structures have been reported for use in short wavelength optoelectronic devices [3–7]. They have unique physical and chemical properties, small footprint, high aspect ratio, enhanced light-matter interaction, cost-effectiveness and can be synthesized by various chemical and physical methods [3–8]. Among

various synthesis techniques, electrochemical deposition (ECD) [6-8] is a low temperature process compatible with different types of conducting substrates [6-8] which produces highly crystalline nanowires (NWs)/nanorods (NRs) of excellent electronic quality.

In this context many device structures, such as heterojunction, homojunction, metal-semiconductor-metal or metal–insulator–semiconductor structures have been explored for a broad range of applications. The field of nanoelectronics is emerging and has attracted great attention of researchers with promising new optoelectronic devices with multi-functionality capabilities, such as nano-LED, nanowire-based solar cells, nanophotodetectors, nanosensors, and so on.

As ECD can be easily scaled-up for optoelectronic device fabrication, it is of great interest to develop the integration of ECD ZnO NRs/NWs in various advanced optoelectronic devices. In the present paper, we describe the integration of ZnO nanowire ensembles and individual nanowires prepared by ECD in efficient low-voltage functioning LEDs, in a visible-blind UV-photodetector and in nanosensors.

II. LIGHT EMITTING DIODES

Arrays of ZnO NRs/NWs with tailored dimensions can be prepared by electrodeposition on various substrates. The zinc precursor concentration in the electrodeposition bath is the key parameter to grow nanowire arrays instead of 2D thin films. It has been shown that the ZnO crystallite diameter [9] and the rod density can be finely controlled by adjusting the Zn(II) concentration: the lower the precursor concentration the smaller the rod diameter [10]. The physico-chemical growth conditions are important to control the quality of the material. It has been shown that increasing the bath temperature increases markedly the NW structural and optical quality.[11] The quality of the nanostructure can also be improved by using a post-deposition conventional annealing treatment in air at about 400°C. Alternatively, hydrothermal treatment of the ZnO NWs at a lower temperature of 150°C by hot steam is also highly efficient to boost the UV photoluminescence[12]. Interestingly, this treatment is compatible with fragile substrates such as the plastic lightweight ones[12].

The epitaxial growth of ZnO on single crystal substrates such as GaN[3,7], GaAs[13] or Au[14] has been demonstrated by several authors. Using these substrates permits the growth of ZnO with high structural quality (higher than on polycrystalline substrates) due to the structural continuity between the single-crystalline substrate and the deposited ZnO NWs. Heteroepitaxy is a means to obtain ZnO NWs with low interfacial and low bulk defect density and high photoluminescence emission in the near-UV.

This property has been exploited for the preparation of near UV-LEDs with high brightness and low emission voltage. Vertically aligned free-standing arrays of n-type ZnO NWs have been grown on p-type GaN layers deposited on sapphire. The heterojunction has been integrated in a LED device by contacting the n and p-type structures. The devices were highly electroluminescent with a single emission peak centered at 397 nm and no visible emission due to defects. The emission was detected at low applied forward bias [10,15]. We note that similar results have been achieved in the case of ZnO NW arrays hydrothermally grown on p-GaN with an emission threshold as low as 4V [16].

The emission wavelength can be tuned by bandgap engineering. The bandgap of ZnO is increased or decreased by doping with metal cations. The dopant is integrated in the crystal lattice of ZnO by adding a low concentration of dopant ions in the electrodeposition bath. The dopant atomic concentration in the material is adjusted by changing the initial ion concentration in the bath. Many dopants have been investigated such as: Er, Eu, Cu, Cd, Ag, Mg and Al [17-23]. In the $ZnCl_2$/KCl/O_2 system, copper doping was done with $CuCl_2$ [18,19], cadmium doping was obtained by using $CdCl_2$ [20,21], and silver doping with $Ag(NO_3)$ [22]. A reduction of the ZnO bandgap was measured experimentally for ZnO NWs doped by these elements.

The bandgap of doped-ZnO has been calculated by density functional theory (DFT) for various molar concentrations of dopants. In the case of copper, the computed data showed that the dopant gives rise to an additional acceptor level due to Cu 3d-O 2p orbitals and a donor level due to Cu 3d orbital [18]. Their width increases with the dopant concentration and consequently the bandgap is reduced. In the case of Cd:ZnO it was shown that the bandgap reduction is due to an enlargement of the oxide lattice parameters. These parameters increase continuously with Cd content [20]. On the contrary, a bandgap enlargement was reported for Mg doping [23]. It is also possible to increase the conductivity of electrodeposited ZnO NWs by Al-doping.

Arrays of doped-ZnO NWs have been grown by ECD on p-type GaN single-crystal substrates and the heterostructures have been integrated in LED devices. A red-shifted emission in the violet-blue range was found at low applied voltage in the case of Cu, Cd and Ag [22]. The wavelength shift increased with increasing the dopant concentration in the oxide nanostructure. On the other hand, the electroluminescence of the LEDs was blue-shifted at lower wavelength in the case of Mg doping. In this way, the emission wavelength could be adjusted to the maximum of the absorbance of red phosphors to get LEDs with a mixed color emission [23]. These experiments on doping have proved that, for these devices, the emission is due to exciton recombination in the ZnO NWs. Figure 1 shows relationship between the RT-EL of ECD ZnO/p-GaN LED structure and the dopant(Mg, Cu) in zinc oxide nanowires at forward bias voltage of 6.8 V.
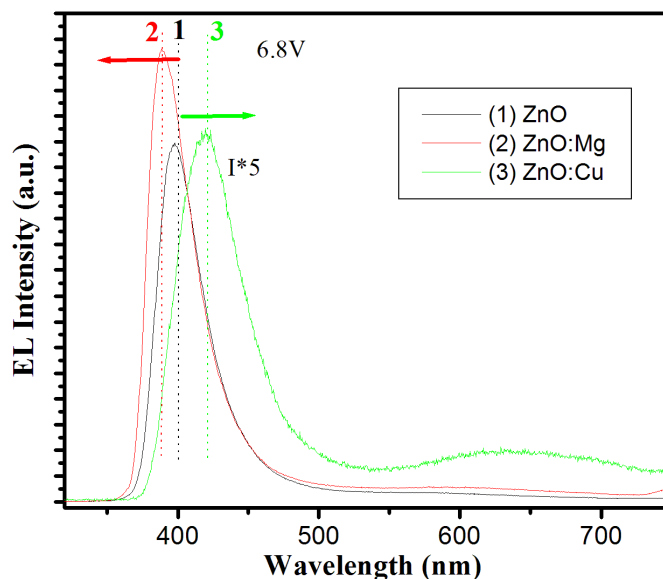

Figure 1. Relationship between the RT-EL and the dopant(Mg, Cu) in ZnO at forward bias voltage of 6.8 V.

III. ULTRAVIOLET PHOTODETECTOR

Near-UV light detection is important for many applications such as environmental monitoring, flame detection, military applications, industrial quality control, etc. [24]. Contrary to Si-based devices, which are widely used for these applications, detectors based on wide bandgap materials have the advantage to be insensitive to the visible light allowing for visible-blind detection without any additional filters. The interest in using GaN or ZnO nanowires for UV detection has emerged in the early 2000's with the demonstration of highly sensitive photodetectors based on individual nanowires [25]. A giant photoconductive gain up to 10^8 leading to very high

detector responsivity has been reported in single nanowire ZnO photodetectors [26] and attributed to surface-related phenomena.

The ZnO nanowire arrayed ensembles were grown by ECD [7]. The deposition bath contained 0.2 mM $ZnCl_2$ as cation precursor and 0.1 M of potassium chloride (KCl) employed to ensure a good electrical conductivity in the aqueous solution (Milli-Q quality water). The bath was thermoregulated at 85°C. The ZnO nanowires were grown on a conductive FTO layer deposited on a glass substrate with a sheet resistance of 10 Ohm/square. The ZnO nanowires were encapsulated in SiO_x and the electrical contact on the top of the wires was ensured by a transparent graphene sheet containing up to 4 monolayers. Ti/Au Metal contacts were finally added to produce the photodetector [27]. Figure 2a shows a SEM image of the metal contact on top of the grapheme sheet.
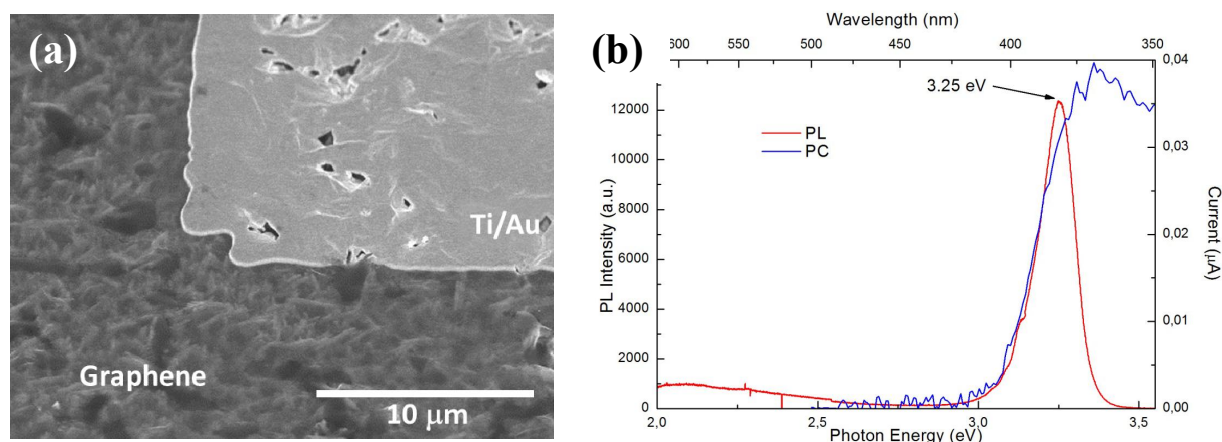

Figure 2. (a) SEM Image of the graphene sheet and metal contact on top of the ZnO NW array; (b) PL spectrum of ZnO NWs and room temperature photoconductivity (PC) spectrum of the photodetector with graphene transparent contact. The PC spectrum was measured under 20 mV bias.

Optical and electrical properties of photodetectors were characterized by current-voltage (I-V) measurements and by photocurrent (PC) spectroscopy [27]. The graphene/ZnO detectors exhibited linear I-V behavior in the dark, which showed that the graphene/ZnO contact had ohmic properties. This was indeed expected due to the similar work function of ZnO and of graphene and the high doping level of the ZnO nanowires. Under illumination, the conductivity increased. Figure 2b shows the PC spectrum superimposed with the photoluminescence (PL) spectrum of the detector. The PC spectrum showed a signal starting from approx. 3 eV in good agreement with the photoluminescence energy. The response was maximal at 3.365 eV. The responsivity was larger than 10^4 A/W at 1V bias in the near-UV range thanks to a high photoconductive gain in ZnO NWs. The photocurrent dependence on the incident power is shown to be linear at low excitation, it becomes sub-linear for power densities above 10^{-4} W/cm² and it almost saturates above 10^{-2} W/cm². A comprehensive model of the photoconductive mechanism has been proposed in Ref.[27] showing that the main process responsible for the photoconductive gain is the modulation of the conducting surface due to the variation of the surface depletion layer.

IV. HIGHLY SENSITIVE GAS NANOSENSORS

Hydrogen sensors are widely used in combustion systems of automobiles to monitor pollution, certain types of bacterial infections, as well as in the petroleum, chemical, or semiconductor industries [28,29]. ECD ZnO NWs and Cd-doped ZnO NWs have been investigated for the preparation of gas nanosensors. The NWs with uniform diameter were grown on a conducting glass substrate used as the working electrode. They were subsequently annealed at 300°C for 11h and then detached by ultrasonication in ethanol. After their transfer to a SiO$_2$ coated Si substrate, they were connected at both ends by Al contacts by using the metal deposition function of a focused ion beam apparatus. Figure 3a shows that each nanosensor was made of an individual NW [30].
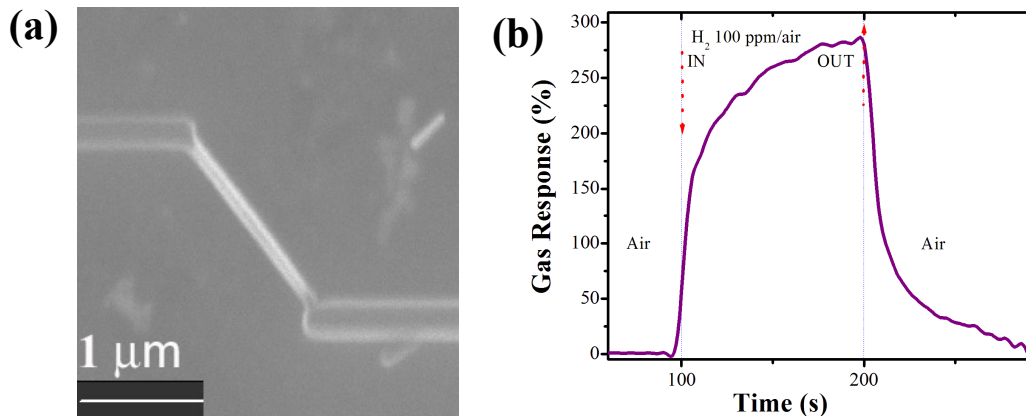

Figure 3. (a) The SEM image of a single ZnO-Cd(6 µM) NW connected in a nanosensor configuration. (b) Room temperature gas responses of nanosensors based on a single ZnO-Cd(6 µM) NW versus time, and

The nanoscale devices were tested for gas detection. The sensitivity to H$_2$ was higher (down to 100 ppm) and the response time was shorter in the case of Cd-doped ZnO NWs compared to pure ZnO NWs (Figure 3b). Moreover, the sensors had an excellent selectivity with a poor recorded response to CH$_4$, C$_2$H$_5$OH, O$_2$, LPG (liquefied petroleum gas) and ammonia. The response was significantly improved in comparison with previous results on pure ZnO NWs [30].

The dependency of the gas response of individual Cd–ZnO NWs on their diameter was observed. In particular, NWs with a diameter of 90 nm showed a higher gas response due to an optimized conduction channel width. Additionally this parameter was found to depend on the Cd-doping with a significant improvement over previously related reports for undoped ZnO. Adding 6 µM CdCl$_2$ in the electrolyte during ECD (about 1 at.% in the NW oxide material) permitted the growth of NWs with improved hydrogen response. It has been explained by an increase in the carrier concentration due to higher native defects. Furthermore, the low nanodevice power consumption (<5 nW at 2 mV) make them suitable for use in portable devices without the need of external microheaters. The fact that the described devices require extremely low power to operate represents an important advance in power efficiency and nano-miniaturization. This is an important step forward toward low power and fast zinc oxide gas sensing nano-devices [30].

V. CONCLUSIONS

The deposition of ZnO NRs and NWs by the electrochemical method has many advantages compared to other techniques, which include: (i) well-suited for scaling-up; (ii) low temperature operation; (iii) each NR/NW is a single crystal of high structural and optical quality even without annealing; (iv) homogeneous deposition on arbitrary substrate shapes, (v) tuning of the morphology and size by manipulating the deposition parameters; (vi)

precise control of deposition positions by selective patterning of the substrate; (vii) excellent electrical contact between structures and substrate; (viii) minimum inter-reaction or inter-diffusion between deposit and substrate due to the low temperature processes and (ix) facile doping by metal cations.

We have illustrated that the ECD ZnO NWs can be integrated in various advanced optoelectronic devices with promising performances. The examples include LEDs with tunable emission wavelength, a visible-blind UV photodetector with a transparent top contact made of a grapheme sheet and miniaturized H_2 nanosensors. It has notably been shown that cadmium doping in single-crystal zinc oxide nanowires is an efficient means to enhance the sensor response to gases without the requirement of external heaters for instance.

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