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# Transition Metal-Doped ZnO Nanowires: En Route Towards Multi-colour Light Sensing and Emission Applications

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## 1. Introduction

Opto-electronics is one of the largest and fastest evolving market segments, with revenues expected to surpass \$1.2 trillion by 2017 (Optoelectronics Industry, 2007). Continuous improvements in the size, detection limit, reliability and spectral sensitivity of existing solid-state light sensors and image detectors, which remain a key component of almost every opto-electronic system and circuit, drive the field to new heights every year. Compared with other components, light sources and detectors recently have shown the most significant revenue gains, whereas highly-miniaturized and low-power solid-state photodetectors operating in extended, UV-visible spectral ranges will continue to have an important role, as they are expected to be ubiquitously used in many electronic systems ranging from high-capacity information storage to biochemical sensing, chemical and biological analysis, and astronomy.

Compound	Crystal structure; lattice constants, $nm$ ; symmetry group	$E_g$ , eV	$\mu_n, \mu_p$ $cm^2/Vs$	$m_n / m_p$
Cu <sub>2</sub> O	Cubic; $a = 0.42$ ; $O^4_h$	2.17	$\sim 0.1, \sim 100$	$\sim 1.7$
ZnO	Hex.; $a = 0.32, c = 0.59$ ; $C^4_{6v}$	3.35	$\sim 180-1000, -$	$\sim 0.45$
In <sub>2</sub> O <sub>3</sub>	Cubic; $a = 1.01$	2.8	-	$\sim 0.36$
SnO <sub>2</sub>	Cubic; $a = 0.47$ ; $O^5_h$	3.54	$\sim 260, \sim 300$	-
TiO <sub>2</sub>	Tetr.; $a = 0.45, c = 0.29$ ; $D^{14}_{4h}$	3.0	$\sim 0.16-0.57, -$	-

Table 1. Structural and electronic characteristics of several key metal-oxide semiconductors;  $E_g$  is band gap energy,  $\mu_n, \mu_p$  are electron and hole mobilities,  $m_n / m_p$  is electron-hole effective mass ratio.

While many commercial UV-visible detectors have been realized based on the matured Si p-n junction technology, there are several limitations related to the use of Si materials for UV sensing, among which are aging effects and cooling requirements to subdue dark current. Metal oxides can easily help overcome both limitations as their band gap ( $E_g$ ) is significantly larger compared with that of cSi ( $\sim 1.1$  eV), Table 1. Given the great thermal conductivity

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and strength of the chemical bonds of wide-band gap semiconductors, photodetectors engineered based on most of metal-oxides can withstand highly elevated  $T$  and hostile environments. Despite the fact that carrier mobilities are much smaller in cases of metal oxides compared with those of many conventional semiconductors, owing to the drastically increased dielectric strength of metal oxides, much larger carrier velocities can be readily achieved by applying much higher electric fields/device biases. The property remains critical for reducing the photogenerated carrier transit time and thus improving gain characteristics of the photodetectors.

Advances in nanofabrication methodologies now allow growing many metal-oxide nanowires, including in ZnO as dislocation-free, highly faceted single crystals, which according to the above-made discussion show significant promise for diverse nano-photodetector device as well as light-emission applications. At the same time, compared to cSi, ZnO nanowires typically exhibit a very limited intrinsic sensitivity to visible and infrared radiation, whereas the sensitivity to short-wavelength photons also tends to be reduced as a result of their small diameter and relative increase in the number of the surface defect states. In this chapter, we provide a brief review on the progress in engineering high-responsivity ZnO nanowire photodetectors operating in an extended, i.e., ultraviolet-visible spectral range. Particular attention is paid to the use and role of transition metal dopants to enhance the light sensitivity of ZnO nanowires/nanorods grown by seeded vapor-transport methods. Detailed consideration is given to several key aspects pertaining to the transport, photoconduction, and time-response characteristics of two-terminal metal-semiconductor-metal nano-photodetectors operating at both pre-avalanche and avalanche regimes. This review might be important to scientists working in with high-sensitivity and multispectral oxide-based nano-photodetectors, optical switches, and sensors.

## 2. Sensing light with ZnO nanowires

The relentless drive towards down-scaling traditional electronics has enabled a new class of devices that operate faster, consume less power, and cost less. This has catalyzed new fabrication approaches to push beyond the limits of conventional lithography. A variety of high-quality, one-dimensional electronic materials have been all synthesized by techniques other than photolithography. Such materials include nanotubes, nanobelts and nanowires in both conventional and non-conventional semiconductors, such as metal oxides. (Chik et al. 2004; Lee et al. 2004; Sen et al. 2007; Gupta et al. 2008; Wischmeie et al. 2008) Among different metal-oxides, wurtzite ZnO, a II-IV compound, has a direct-band gap of  $\sim 3.3$  eV (at room temperature) and one of the largest exciton binding energies of  $\sim 60$ meV, which makes this semiconductor particularly attractive for many advanced short-wavelength device applications, including but not limited to, ultra-small photodetectors, optical switches, and light-emitting diodes.

The UV-light sensitivity of ZnO nanowires produced by various routes including vapor transport methods has been commonly verified and reported. (Fan et al. 2004; Fan et al. 2006; Yong 2006) The group of P. Yang was among the first to report a marked drop in the resistance of multi-terminal ZnO metal-semiconductor-metal detectors exposed to a UV light ( $\sim 365$  nm). (Kind et al. 2002) The device rise and decay times were typically better than  $\sim 1$  s. No change in the current was registered when the devices were exposed to visible radiation (532 nm light). P. Yang's group also found that, in contrast with a conventional semiconductor-based sensor, the photocurrent changed nonlinearly with illumination

intensity, presumably stemming from a complex interplay of electron-hole generation/recombination such as trapping/detrapping processes. Despite an overall good UV photoconduction response, the UV absorption efficiency of most ZnO nanowire-based detectors is to remain small on the whole, especially when the diameter of the nanowire is reduced below  $\alpha^{-1} \sim 150$  nm ( $\alpha$  stands for the intrinsic absorption coefficient of ZnO). At the same time, a relative increase in the number of surface defect states (Shalish et al. 2004) is known to further reduce the device absorption cross-section as defects provide the sites for fast, non-radiative recombinations. The effect becomes especially apparent as the nanowire diameter approaches the limit of tens of nm.

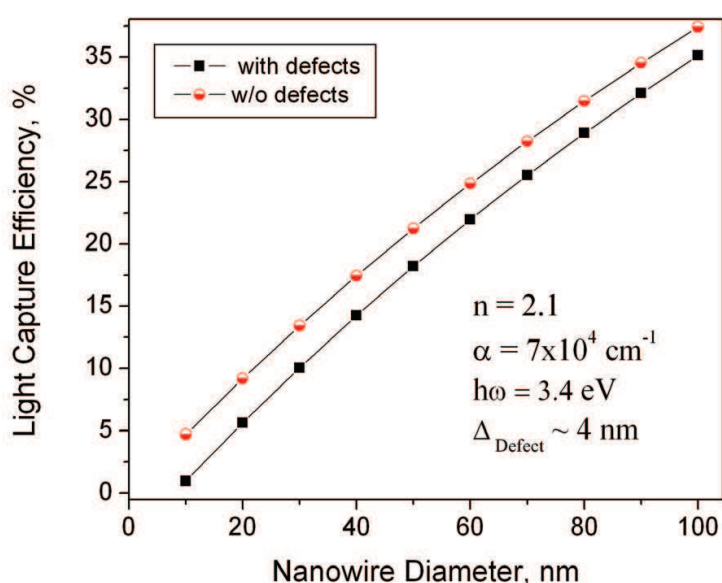


Fig. 1. Plots light capture efficiency as a function of nanowire diameter with and without a defect layer. The light polarization is assumed to be along the nanowire main axis. Reproduced with permission, J. Elect. Mat. 38 (2009).

Figure 1 plots the light absorption efficiency of the ZnO nanowire as a function of its diameter, which has been calculated by taking into account the effects of light reflection and absorption. It is apparent that the presence of a  $\sim 4$  nm dead (i.e., surface defect) layer effectively decreases the interband absorption by a factor of five, i.e., down to  $\sim 1\%$  in the nanowires with diameter of  $\sim 10$  nm. While an increase in the spatial confinement of electrons and holes could generally improve the strength of many optical transitions (and thus the absorption in case of ZnO nanowires) owing to a stronger electron-hole wavefunction overlap, the quantum confinement effects are expected to be generally weak as most of the nanowires produced by vapor transport methods have diameters in the range of tens to hundreds of nm, thereby significantly exceeding the exciton Bohr radius in this material system ( $\sim 2$  nm). Therefore, the size quantization effects are unlikely to have any profound influence on the absorption characteristics of ZnO nanowires.

In the case of stoichiometric ZnO, the  $4s^2$  Zn orbital is empty and the  $2p^6$  O orbital is full, making ZnO an intrinsic semiconductor. However, in the case of oxygen-deficient ZnO, the excess  $4s^2$  electrons can be easily ionized ( $\sim 0.05$  eV), which explains why conductivity of

most of as-grown ZnO nanowires is of n-type. As a result, for any solid-state ZnO nanowire-based optical sensors that rely on band-to-band electronic transitions as the primary photocarrier generation mechanism, minimizing the undesired n-type doping effects becomes critical in order to engineer photosensors with improved photosensing characteristics and with a large on/off ratio. (Sen et al. 2007)

In the case of Ohmic contacts, the photoresponse of two-terminal, nanowire-based photodetectors can be calculated by invoking classical considerations, with the collected photocurrent having the following simple expression (Sze 2002):

$$I_{\text{photo}} = q \left( \eta \frac{P_{\text{opt}}}{h\nu} \right) \left( \frac{\tau v_{\text{drift}}}{L} \right) = q G K ,$$

where  $q$  is the electron charge,  $\eta$  is quantum efficiency,  $P_{\text{opt}}$  is incident optical power and  $h\nu$  is photon energy. In this formula,  $G = \eta \frac{P_{\text{opt}}}{h\nu}$  is the number of free carriers generated per

unit time and  $\gamma = \frac{\tau v_{\text{drift}}}{L}$  is the device gain defined as a ratio of the rate at which free

carrier is collected by the contacts to the rate at which it is photogenerated within the device. From the above formula, it is evident that in order to achieve optimum gain/photocarrier collection efficiency, the excess free-carrier lifetime,  $\tau$ , and its drift velocity,  $v_{\text{drift}}$ , must be increased while the device size / carrier travel time must be reduced. At the same time, in contrast with bulk devices, many more free holes are to undergo annihilation on the molecular oxygen that is chemisorbed on the surface of the nanowires – the process that can significantly reduce the rate of bi-molecular recombination of free carriers, especially under high-injection conditions, i.e., when photogenerated excess carrier density  $\Delta n \gg n_0$ ,  $n_0$  is equilibrium majority carrier density. As a result, the lifetime of the photogenerated excess carriers,  $\tau$ , is significantly augmented in ZnO nanowires, making these nanostructures significantly more sensitive to UV optical radiation than their bulk counterparts.

These effects have been held responsible for high gain of  $\sim 10^8$  attained in ZnO nanowire-based UV photodetectors (Soci et al. 2007). For comparison, a gain of  $\sim 10^5$ - $10^6$  is typically considered as an upper-limit in bulk and thin film photoconductor devices. Yet, the main drawback of increased carrier lifetime is slow device response time, also known as persistent photoconductivity. This limits the ability of the device to quickly switch from photoconduction to dark state, which is required in many modern opto-electronic device applications.

While the problem of reduced light absorption by ZnO nanowires can be partially mitigated by increased device gain, most of the metal oxides have another hefty drawback – a very limited sensitivity in the visible-infrared spectral range inherent with their large band gap, Table 1. While the increased visible-blindness represents a critical advantage for engineering visible-blind UV detectors the number of useful device technologies that can be realized with ZnO nanowires remains low, making it difficult for this nanomaterial to compete with commercially established Si-based photodetectors on the cost basis.

A controlled introduction of optically-active defect states within the band gap represents one of the most cost-efficient solutions to improve the photoresponse of ZnO in the sub-band gap optical range. Lin et al., for instance, reported a significant increase in the white light (400-800 nm) sensitivity of ZnO nanowires doped to only  $\sim 1\%$  of Al, with a device

on/off current ratio approaching as high as  $\sim 20$ , whereas for undoped devices the ratio was only  $\sim 1.06$  (Lin et al. 2007). The effect is attributed to an optical excitation of free electrons from the Al-defect levels positioned  $\sim 80$  meV below the conduction band. The photoconduction response of ZnO can be also improved by engineering heterojunctions with other semiconductors or high electronegativity metals such as Pt, Pd, etc., which are known to form Schottky-type junctions at the metal-ZnO interface (Jeong et al. 2003; Heo et al. 2004; Keem et al. 2004; Yong 2006). However, the results of more recent studies performed by us indicate additional possibilities of achieving strong sub-band-gap sensitivity based on avalanche-type photocarrier multiplication effects by intentionally introducing transition metal (TM) centers such as Cu within the core regions of ZnO. This has been found to substantially enhance the light sensitivity of ZnO nanowires in multiple spectral domains, which forms the topic of our next discussion.

### 3. Fabricating highly crystalline ZnO nanowires doped with Cu.

#### *Role of TM-impurities.*

Advances in nanofabrication now allow growing ZnO nanowires as dislocation-free, highly faceted single crystals (Chik et al. 2004). Consequently, such nanowires possess highly versatile and often refined electrical and optical properties. Following the previous discussion, achieving *p*-type doping in ZnO is critical not only from the standpoint of realizing *p-n* junction-based nanodevices such as electrically driven UV light-emitting diodes or detectors, but also improving the photosensitivity characteristics due to the charge compensation effect. Apart from spintronic applications, doping ZnO with TM impurities has a two-fold advantage. First, previous reports indicate that many TM dopants, including Cu, form deep acceptor states within the band gap of II-VI compounds (Dingle 1969; Heitz et al. 1992), including ZnS, CdS, and ZnO; thus these dopants can partially compensate/offset the *n*-type doping effects. Second, these centers have been found to act as a source of optically-induced charge transfer transitions and photocarrier multiplication effects, which render ZnO nanowires extremely sensitive to both UV and visible radiation and thereby help extend the optical sensitivity range of this metal-oxide.

Theoretical investigations of the electronic configurations of different substitutional TM impurities in groups II-VI and III-V have been undertaken within the framework of local density functional calculations (Gemma 1984), with the results confirming that most of TM dopants, including Fe, Ni and Cu, exhibit a highly rich transitional behavior and form deep multiplet states within the band gap of ZnO. Most of the doubly ( $\text{TM}^{2+}$ ) and triply charged states ( $\text{TM}^{3+}$ ) were also found to be electronically stable in this semiconductor system. At the same time, only Cu has been predicted to exist in a highly stable singly-ionized ( $\text{TM}^+$ ) state in ZnO. Due to the strong ionicity of ZnO, most of TM impurities exhibit a strong 3d electron character (Dietz et al. 1963). The formation of multiplet states within the band gap of ZnO results from the splitting of the TM state into two E and  $T_2$  symmetry states by the internal field of the crystal. In the case of ZnO, using a hole representation, Cu is predicted to exist in three primary electronic configurations/states: a ground state ( $\text{Cu}^{2+}, {}^2T_2$ ) and two excited states ( $\text{Cu}^{2+}, {}^2E$ ) and ( $\text{Cu}^+, h$ ) (Dahan et al. 1998). According to IR-absorption studies, the lowest energy transitions, i.e., involving  $\text{Cu}^{2+} ({}^2T_2 \rightarrow {}^2E)$  states, recently have been confirmed to be infrared-active, with a quantum efficiency approaching  $\sim 30\%$  (Broser et al. 1994)

*VLS Fabrication and Structural Characteristics of Cu:ZnO nanowires.*

Several pathways have been developed and used to produce crystalline nanowires in different materials systems and in large quantities, including physical vapor deposition (Huang et al. 2001, Kong et al. 2001; Omari et al. 2008), electrochemical deposition (Kouklin et al. 2001; Kouklin et al. 2002; Wang et al. 2002), metalorganic chemical vapor deposition (Li et al. 2001), and Vapor-Liquid-Solid (VLS) growth methods (Wu and Liu 2002). The VLS pathway provides many technological advantages such as fast growth rates, low probability/ number of the extended defects such as dislocations, the possibility of diameter, and length control of the resultant nanowires. The VLS pathway also has been proven successful and previously used to produce nanowires in a variety of metal oxides, including but not limited to TiO<sub>2</sub>, CdO, Cu<sub>2</sub>O and ZnO (Huang et al. 2001; Wang et al. 2002; H. Chik et al. 2004; Keem et al. 2004; Fan et al. 2006; Zhao et al. 2007; Wischmeier et al. 2008).

The ability to control the nanowire diameter, density, and location is inherently provided with the use of proper diameter catalyst islands, as well as their precise positioning on the growth substrate. The latter also remains one of the key prerequisites to obtaining nanowires with identical electronic, optical, chemical, and mechanical characteristics (Chik et al. 2004; Kouklin and Sen et al. 2008; Sen and Kouklin, 2008). Finally, the VLS method also provides a simple means of incorporating TM impurities into ZnO nanowires either by time-controlled or the composition-tailored addition of TM precursors to the target (Zhou et al. 2004; Goris et al. 2008). Several TM impurities, including Co, Cu, Fe, and Ni, have been successfully incorporated within the crystalline core of ZnO nanowires (Zhou et al. 2004; Wang et al. 2007; Zhao et al. 2007; Kouklin 2008; Lin et al. 2009). S. Zhou, for example, produced wool-like films of ~65 nm diameter ZnO nanowires doped to 1-5 % of Cu by using intermixed CuI- ZnI<sub>2</sub> powders as the growth precursors. The results of x-ray diffraction and transmission electron microscopy (TEM), selected area electron diffraction, and high-resolution TEM microscopy suggest that the nanowires are single crystals, with the fast-growth direction corresponding with (101).

Our research findings also show that other precursors, particularly high purity powders of Cu, Zn, and graphite mixed in the proportion of Zn:Cu:C=3:1:1 can be also used to produce crystalline Cu:ZnO nanowires. In this case, the growth of the nanowires was achieved at ~800 °C in an Argon atmosphere with an Argon flow rate maintained at 0.12 L/min. Our routine SEM and TEM investigations indicate that the growth mechanism remains self-catalytic VLS, with the average growth rates of 1-2 microns per minute. Figure 2, left, shows the detailed SEM image of the nanowire tip. The presence of the metal nanoparticle at the apex of the nanowire is an attribute of self-catalytic growth. This pathway obviates the need to introduce metal catalyst (typically Au), which should help lower the fabrication cost and avoid potential problems with cross-contamination/uncontrolled doping.

In parallel, the results of Energy Dispersive Spectroscopy (EDS) have confirmed the presence of Cu traces in the samples, Figure 2, right, and agree with the Photoluminescence (PL) measurement results, which are discussed below. According to previous EPR studies, interstitial and substitutional Cu remain a most common defect in bulk ZnO crystals unintentionally/intentionally contaminated with Cu (Dietz et al. 1963; Broser and M.Schultz 1969). In the case of in-situ Cu doping, i.e. during VLS growth, incorporating Cu can be achieved by two separate routes: (1) diffusion through sidewalls and (2) direct deposition via a solid-liquid interface. It is likely that the diffusion-based incorporation will prevail at a

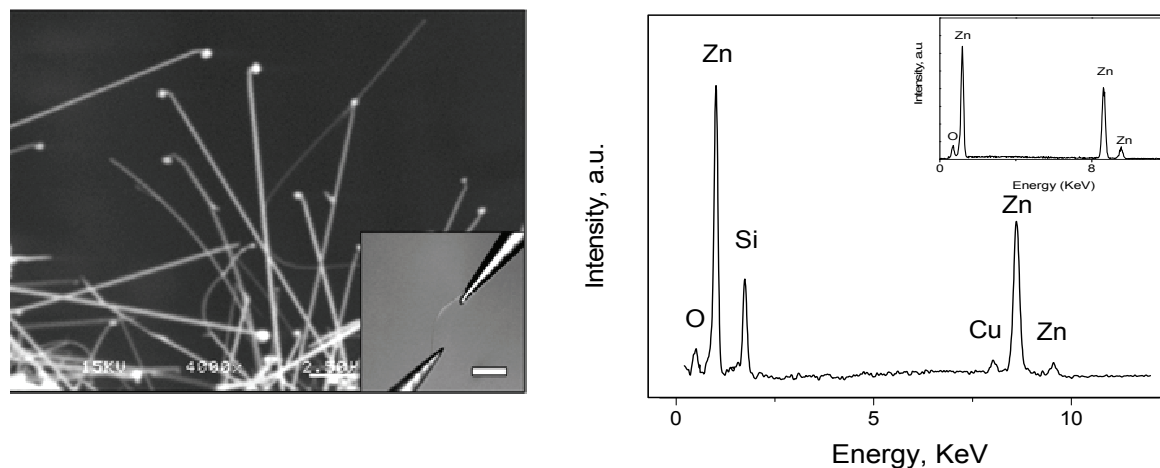


Fig. 2. (Left) A low-resolution side-view SEM image of Cu:ZnO nanowires grown by VLS on top of (111) Si substrate using Zn+Cu+C (graphite) mixture as a target; the inset shows an optical microscope image of ZnO nanowire suspended across the gap between two-terminals, scale bar 50  $\mu\text{m}$ . (Right) EDS spectrum of Cu:ZnO nanowires; the inset shows an EDS spectrum of the ZnO nanowires grown away from the Cu target. Reproduced with permission, *Adv. Mat* 20 (2008).

very high  $T$ , similar to what has been observed in bulk and thin films of ZnO (Zhou et al. 2004). Instead, a direct incorporation pathway (i.e., via the solid-liquid interface) is likely to dominate at low  $T$  regime, as well as during growth initialization and termination stages. Due to an overall low melting point of metallic Zn (419  $^{\circ}\text{C}$ ) compared with that of Cu (1100  $^{\circ}\text{C}$ ), Zn droplets are expected to form first on the growth substrates while becoming saturated with Cu as the temperature is set to increase. According to a binary phase diagram of Cu-Zn alloy, at any growth stage the maximum Cu content is limited to 25% for the growth temperatures of 700-800  $^{\circ}\text{C}$  (Okamoto 2000). This makes the droplet stay saturated with Zn, thereby yielding the growth of ZnO rather than CuO nanowires. Given a close similarity in ionic radii of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ , Cu is expected to precipitate mostly as substitutional or interstitial dopants in case of ZnO nanowires.

#### 4. Light emission and photoconduction response of Cu:ZnO nanowires.

##### *PL and PLE studies.*

Light emission from Cu:ZnO nanomaterials can be categorized similarly to that from bulk ZnO, with the emission highly dependent on the nature of the physical mechanisms that control radiative recombinations, including free and donor/acceptor bound excitons, both shallow donor-acceptor pair recombination, and deep defect associated emission (DAP-emission), effectively covering the UV-IR optical range. Figure 3, left, lists some of emission lines that were experimentally obtained from ZnO samples. A typical near band-edge RT PL spectra collected from Cu:ZnO nanowires at room temperature is presented in Figure 3, right. The emission is dominated by two peaks centered at  $\sim 382$  nm and  $\sim 493$  nm, which are attributed to free exciton and blue-green (BG) emission bands, respectively. The peak positions of both bands were further found to be slightly red shifted by  $\sim 7$  nm and  $\sim 3$  nm



with respect to their known positions in undoped ZnO nanowires. At the same time, an increase of  $\sim 2$  orders of magnitude in the ratio of BG- to-excitonic intensities for Cu:ZnO samples is observed. An appearance of high-intensity BG band accompanied by quenching of the excitonic emission is a typical attribute of Cu:ZnO samples, i.e., similar trends were reported for thin film and nanowire samples in ZnO containing Cu impurities (Garces et al. 2002; Xu et al. 2004).

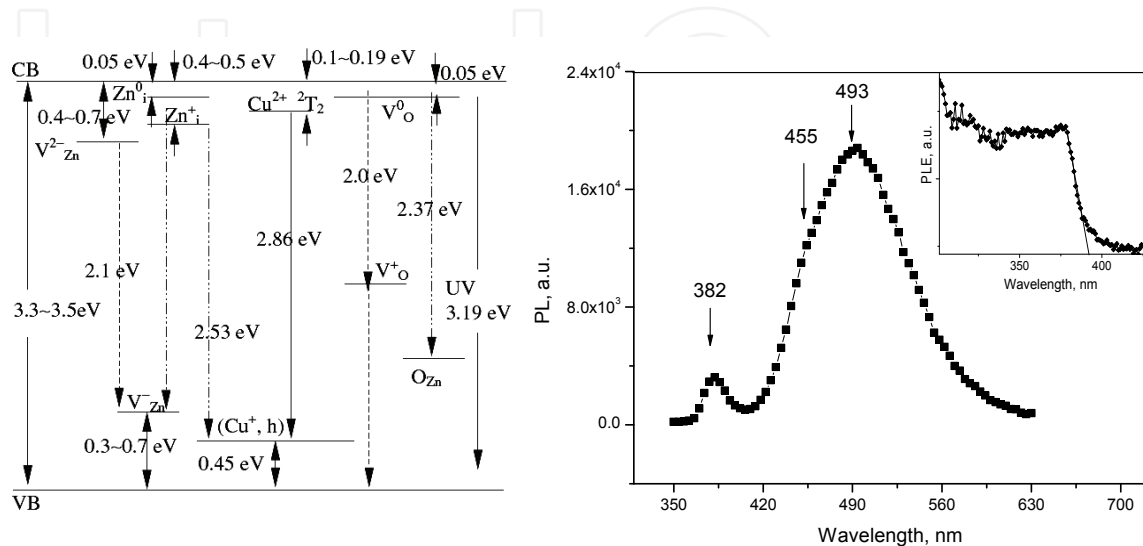


Fig. 3. (Left) Energy diagram of different defect states within the band-gap of ZnO and related optical transitions, reproduced with permission, *Nanotechnology*, **15** (2004); (right) room temperature micro-PL spectrum of Cu:ZnO nanowires, excited with a 325 nm light source. The inset displays the PLE spectrum with the emission monitored at 493 nm. Reproduced with permission, *Adv. Mat* **20**, (2008).

The DAP recombination involving  $Zn^+$  and  $Cu^+$  states is known to yield BG emission with a peak centered around  $\sim 493$  nm ( $\sim 2.51$  eV) (Garces et al. 2002). On the other hand, a weak shoulder peak centered at  $\sim 455$  nm ( $\sim 2.72$  eV) has been observed and assigned to  $Cu^{2+}$ - $Cu^+$  transitions, in which the hole remains localized on the  $Cu^+$  center (Hausmann et al. 1979; Robbin et al. 1981).

Figure 3 right the inset, further shows PL-excitation (PLE) spectra obtained on Cu:ZnO nanowires at room temperature by monitoring the PL emission at  $\sim 493$  nm. A step-like shape of PLE spectra can be observed and attributed to a strong increase in the light absorption by nanowires at the wavelength of  $\sim 390$  nm. The extrapolated intercept on the  $\hbar\omega$ -axis yields an effective band-gap of  $\sim 3.17$  eV, which is again slightly red shifted (by  $\sim 50$  meV) compared with that of undoped ZnO nanowire samples. No light emission could be obtained for photons with energies  $< E_{gap}$  in accordance with the previous works on Cu:ZnO materials. (Heitz et al. 1992)

#### *Photoconduction in preavalanche regime.*

The UV-photocurrent-voltage characteristics of Cu:ZnO metal-semiconductor-metal photodetectors engineered by precisely placing nanowires across the gap between two metal contacts were investigated in the low-intermediate voltage regime. For this, the central part of the nanowire devices was excited with a UV light of the wavelengths: 254, 302, and 365 nm. In the dark, the IV characteristics were typically found to be linear,

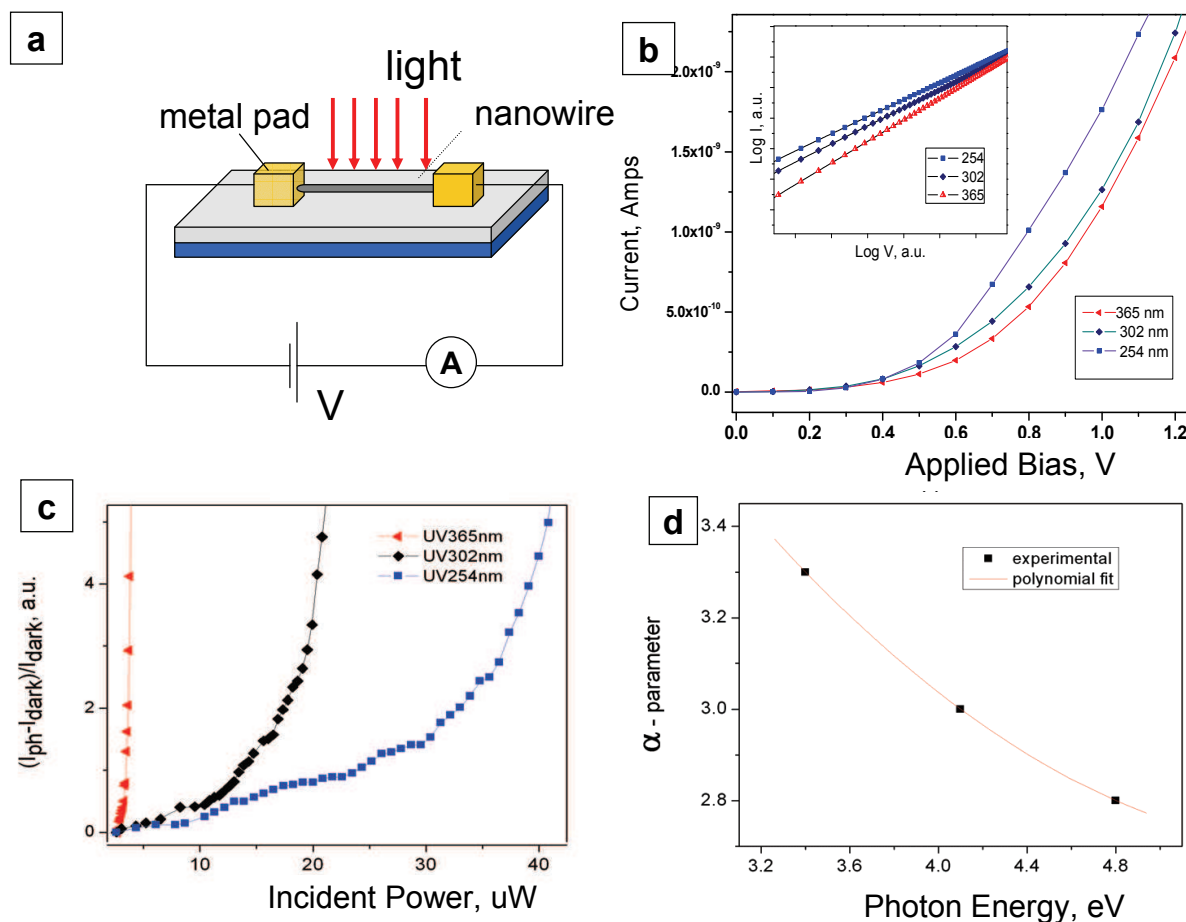


Fig. 4. (a) Schematics of Cu:ZnO-nanowire photodetector (b) Photo-I-V characteristics of Cu:ZnO photodetector obtained for applied biases up to  $\sim 1.2$  V for excitation wavelengths of 254, 302, and 365 nm and power densities of  $\sim 5$ -10 mW/cm<sup>2</sup>. The inset shows a log-log plot of UV photo-IVs plotted for an intermediate part of applied biases yielding power-law dependences of  $I \sim V^{3.3}$ ,  $I \sim V^{3.0}$  and  $I \sim V^{2.8}$  for wavelengths of 365 nm, 302 nm, and 254 nm, respectively. (c)  $(I_{ph} - I_{dark})/I_{dark}$  ratio as a function of excitation powers for different excitation wavelengths of 254, 302 and 365 nm. (d)  $\alpha$ -parameter as a function of photon energy, fitted with a polynomial function  $\alpha \cong 6.2 - 1.2x + 0.1x^2$ . Reproduced with permission, J. Elect. Mat. 38 (2009).

whereas the dark currents were very small, i.e., approaching only few pA at applied bias of a few volts. In contrast, in the case of UV illumination, the photocurrent in the devices showed a strong increase whereas the conductance also changed with the applied bias. A shift from linear to nonlinear photo-IVs is attributed to a shift in the role of interface and bulk-limited currents invoked by the illumination. According to the results of more detailed investigations conducted by some of us (Kouklin 2008), the response at low biases (i.e.,  $< \sim 0.5$  V) is controlled by a Schottky barrier formed at the interface. On the other hand, at the intermediate bias regime, i.e., for bias falling in the range of  $\sim 0.5$ V-4.5 V, the response is power-law dependent as being trap-limited (Figure 4). In this regime, the photocurrent is found to change with voltage as  $I \sim V^{3.3}$ ,  $I \sim V^{3.0}$  and  $I \sim V^{2.8}$  for excitation wavelengths of 365, 302, and 254 nm, respectively.

It should be mentioned that the shift of the transport from the Schottky to power-law dependent regime is generally expected in our devices as an increase in the electric field strength is to be accompanied by a reduction in the width/height of the Schottky barrier. This, in turn, helps the photogenerated carriers to tunnel through the barrier, which lowers the contact resistance and the voltage drop across the contact, with the transport thus becoming bulk-limited. Likewise, the barrier height associated with the shallow impurities/traps is to be also reduced, implying that the current should now be controlled by the trapping/detrapping of carriers on deep Cu states. It is also known that deep traps that are only distributed non-uniformly within the bandgap yield power-law dependent IV curves. For the trap density that changes exponentially within the band gap, i.e., when  $n_t \propto e^{-E_t/kT_c}$ , where  $T_c$  is some characteristic temperature reflecting the steepness of the trap distribution and  $E_t$  is the energy of the trap measured from the top of the conduction band, the device current is to change nonlinearly with applied bias given by the following equation  $I \sim V^{\alpha+1}$ , where  $\alpha = T_c/T$  for  $T_c > T$  (Rose 1955). Experimentally, the power-law dependent IVs only have been obtained under UV illumination with  $\alpha$  typically falling in the range of  $\sim 1.8 - 2.3$ . The result confirms the existence of optically-activated, exponentially-distributed deep-trap states in Cu-doped ZnO nanowires.

A dependence of the exponent on excitation wavelength is also observed to be polynomial, Figure 4d. The dependence of  $\alpha$  on the excitation energy/wavelength is invoked by a shift in role different defect states play behind photocarrier transport. More specifically, as the excitation energy increases, the role of upper lying states behind trapping/detrapping weakens, which should yield smaller values of  $T_c$  and thus  $\alpha$ , in accordance with the experimental findings. An interesting aspect is that this trend remains valid also for photon energy well exceeding  $E_g$ , which we attribute to the fact that some excitation processes are likely to originate on surface defect states positioned well outside the band gap.

According to intensity-dependent photocurrent measurements, the photocurrent is also found to change non-linearly with excitation powers in case of all UV wavelengths, Figure 4c (Kind et al. 2002). Finally, the on/off photocurrent measurements have been carried in this bias regime. The photocurrent changes exponentially with time, with the rise and decay time constants approaching  $\sim 10$  and  $39$  s, respectively. The slow response is associated with overall slow trapping/detrapping processes that dominate the photoconduction response in the intermediate bias regime.

*Photoconduction in avalanche, photocarrier-multiplication regime.*

At high applied biases of  $\sim 4.5$  V and above, a drastic shift in the photo IVs is observed, with the current becoming an exponential function of the applied bias, as seen in Figure 5, right. At a bias of  $10$  V, the device UV on/off factor,  $\eta$  has been seen to approach  $\sim 10^4$ . At the same time, undoped ZnO nanowire sensors measured similarly have yielded  $\eta \sim 7$  at best at a bias of  $\sim 1.7$  V, as shown in Figure 5, left, the inset. Likewise, and more importantly, a very strong decrease in the device resistance was also observed in the Cu:ZnO samples irradiated with a white light produced by an incandescent light source with a cut-off wavelength of  $\sim 440$  nm. Under white-light excitation and bias exceeding  $\sim 4.5$  eV the photocurrent also exhibited a strong, exponential-like increase with bias as in the case of UV illumination. At a bias of  $\sim 10$  V, the obtained  $\eta$  was similarly large and approaching  $\sim 10^4$ . The responsivity of photosensor engineered using a nanowire with a length of  $\sim 100$   $\mu\text{m}$  and diameter of  $\sim 100$  nm was further measured to be  $\sim 500$  A/W for both white and UV lights, which significantly exceeds the

sensitivity levels reported previously for ZnO nanowires for sub-band-gap photons. (Fan et al. 2004; Lin et al. 2007)

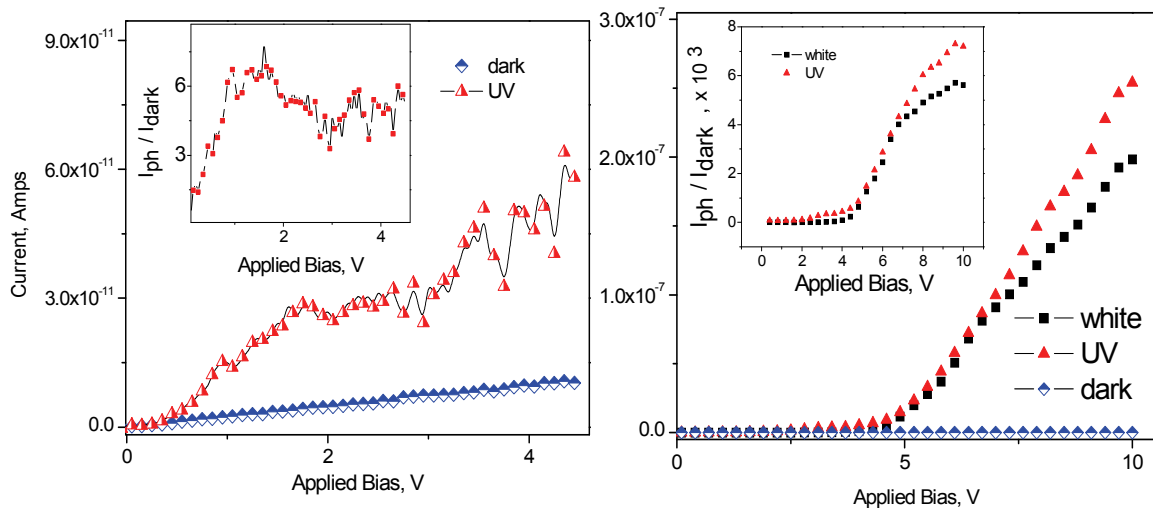


Fig. 5. (left) I-V characteristics of ZnO nanowire for dark and UV-illumination conditions, white-light I-Vs were similar to dark, the inset shows the ratio of photocurrent to dark current as a function of bias, at  $\sim 8$  V the ratio was  $\sim 6$ ; (right) I-V characteristics of similarly-configured Cu:ZnO nanowire sensors for dark, UV and white light illumination conditions, the inset shows the ratio of photocurrent to dark current as a function of bias for white and UV light. Reproduced with permission, Adv. Mat 20, (2008).

By extrapolating the intercept with the voltage-axis yields a threshold voltage,  $V_{th} \sim 4.5$  eV for both UV and white light photo-IVs as presented in Figure 5. The obtained value of  $V_{th}$  ( $\sim 1.4 E_g$  of Cu:ZnO) closely corresponds with the threshold energy of  $1.5 E_g$  required for an avalanche multiplication to initiate in this nano-semiconductor (Sze 2002). A multiplication factor,  $M$  calculated as a ratio of the avalanche photocurrent at a given voltage to that obtained by extrapolating the low-voltage photocurrent to the same voltage, was  $\sim 2 \times 10^2$  and  $7 \times 10^2$  (at a bias of 10V) for UV and white light, respectively, which is taken as evidence that the photo-generated carriers undergo a strong multiplication in this, higher-voltage regime. Since no avalanche multiplication was present in similarly configured, undoped ZnO nanowire-based sensors for voltages of up to 10 V, the introduced Cu centers are likely to play a critical role behind avalanche photocarrier multiplication observed in case of Cu:ZnO nanowires.

In the case of visible excitation, the mechanism responsible for the photoconduction enhancement is likely to be associated with the processes of hole photogeneration, i.e., involving  $Cu^{2+}/Cu^+$  charge transfer transitions, whereas most of the photogenerated holes are expected to be trapped on the impurity centers. A fraction of these holes will be set free via thermoionic emission at RT, therefore giving rise to a weak, linear-like response observed at a low voltage regime. Yet, as the drift velocity of holes increases with the bias, eventually the holes are to gain enough energy to ionize the host lattice atoms as to initiate avalanche free carrier multiplication effects. This process is held responsible for an exponentially enhanced white light and UV sensitivity of Cu:ZnO nanowires for  $V > V_{th}$ .

## 5. Conclusion.

ZnO nanowires have recently emerged as an important class of materials that hold a strong promise for developing low-cost, multi-spectral, and highly sensitive opto-electronic sensors. The intentional introduction of TM impurities such as Cu has been shown to uniquely enhance the photosensitivity in the UV-visible spectral ranges of ZnO nanowires as a result of avalanche photo-multiplication effects. However, additional studies will be required to address the problems with slow response times in order to improve the switching speed of such optical sensors. In general, the highly crystalline character of the core of the Cu:ZnO nanowires grown by high T vapor transport methods is essential to achieving high photocarrier drift velocities in Cu:ZnO nanowire devices, thereby enabling faster photoconduction response without sacrificing gain. While in the near term ZnO photo-detectors are unlikely to replace UV-enhanced Si detectors, they hold many strong prospects in areas such as high-T, radiation-hard, and harsh environment light optical sensing, detection, and monitoring.

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## **Nanowires Science and Technology**

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This book describes nanowires fabrication and their potential applications, both as standing alone or complementing carbon nanotubes and polymers. Understanding the design and working principles of nanowires described here, requires a multidisciplinary background of physics, chemistry, materials science, electrical and optoelectronics engineering, bioengineering, etc. This book is organized in eighteen chapters. In the first chapters, some considerations concerning the preparation of metallic and semiconductor nanowires are presented. Then, combinations of nanowires and carbon nanotubes are described and their properties connected with possible applications. After that, some polymer nanowires single or complementing metallic nanowires are reported. A new family of nanowires, the photoferroelectric ones, is presented in connection with their possible applications in non-volatile memory devices. Finally, some applications of nanowires in Magnetic Resonance Imaging, photoluminescence, light sensing and field-effect transistors are described. The book offers new insights, solutions and ideas for the design of efficient nanowires and applications. While not pretending to be comprehensive, its wide coverage might be appropriate not only for researchers but also for experienced technical professionals.

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