SnO_2 Colloidal Nanoparticles Based Ultraviolet Photodetector with High Signal to Noise Ratio

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***Abstract*— SnO_2 nanoparticles possess optical and electrical properties that make them suitable for the fabrication of UV photodetectors. This paper presents the material fabrication and characterization followed by the device fabrication and characterization of a SnO_2 colloidal nanoparticles based ultraviolet photodetector. The fabricated detector exhibits a high signal to noise ratio of 5.8 x 10^3, low dark current of 1.4 nA, responsivity of 307 mA/W, rise time of 16 s and fall time of 5.4 s. The study demonstrates SnO_2 as a favorable material for the development of future optoelectronic devices.**

Keywords—tin oxide, nanoparticles, UV detector, high signal to noise ratio

I. Introduction

Metal oxides nanoparticles (NP) are promising materials for applications in the field of electronics, communications, controls, medicine, and defense. Particularly, their application as optoelectronic devices, energy-harvesting devices, gas sensors, transparent conducting electrodes, photo-catalysts and FETs have been extensively explored [1-3]. In addition to nanoparticles, other nanostructures in the form of nanowires, nanrods, nanospheres and nanobelts have also been developed [4]. Metal oxide nanostructures possess desirable optical and photoelectric properties, high surface-to-volume ratio, and they can be easily doped to tailor the device characteristics [3]. This has promoted their use in the fabrication of ultraviolet (UV) detection sensors. UV detectors find applications in the space and defense industry for the detection of biohazards and fire [5-6].

Metal oxides such as ZnO, Ga_2O_3, In_2O_3, and CeO_2 are significantly studied as potential UV detectors [7]. On the other hand, the application of SnO_2 (tin oxide) has not been thoroughly investigated. SnO_2 is a chemically stable and non-toxic metal oxide with the direct wide band gap in the range of 3.5 eV to 4.6 eV (at 300 K) and exciton binding energy of 130 meV [10]. It is an n-type semiconducting material with high electron mobility [8]. Although, SnO_2 based short-wavelength photo detectors are reported in some recent work [9-12], most of them lack characterization of detector and suffer from low responsivity [10], high dark current [11] and low signal to noise ratio (SNR) [12]. Detectors with SNR from as low as 1.67 for intrinsic SnO_2 nanowires [12] to as high as $5x10^5$ for Sb-doped SnO_2 nanowires [22] have been reported in literature [11].

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In this paper, a SnO_2 NP based photodetector is reported, which is fabricated using the spin coating technique. Material and device characterization is presented along with the fabrication process. The fabricated device possesses superior characteristics such as high signal to noise ratio, low dark current and it is visible blind.

II. Experiments

A. Fabrication

The photo detector, presented in this paper, is fabricated using commercial SnO_2 NP (from Sky Spring Nanomaterials, Inc.) having purity of 99.9% and average particle size in the range of 50 to 70 nm. The NP are first dispersed in ethanol to form a 30 mg/ml suspension before spin coating them on a quartz substrate. The thin film formed on the substrate is then annealed at 150°C for 5 minutes. In the final stage of fabrication, 200 nm thick interdigitated aluminum (Al) contacts are deposited on the film using electron-beam evaporation using a shadow mask. The fabricated detector is wire bonded with Epo-Tek H20E conductive epoxy. Fig. 1 shows the 3D schematic of the fabricated device.

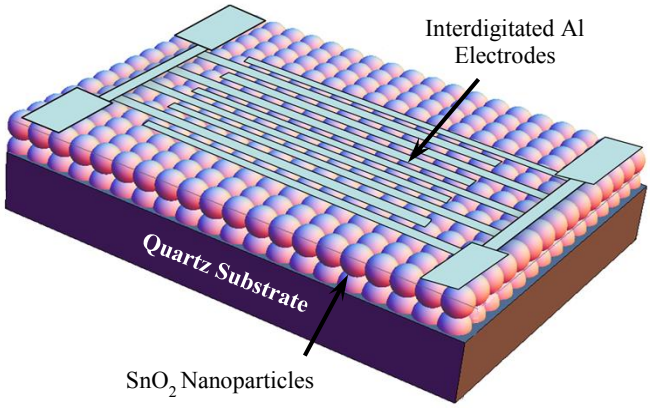

Fig. 1. Schematic of fabricated SnO_2 nanoparticles based photodetector.

B. Experimental Setup

The morphology of the NP was studied using a Carl Zeiss Ultra 1540 dual beam scanning electron microscope (SEM). X-ray diffraction (XRD, PANalytical) pattern was obtained using Cu Kα radiation. The absorption spectrum was recorded using a

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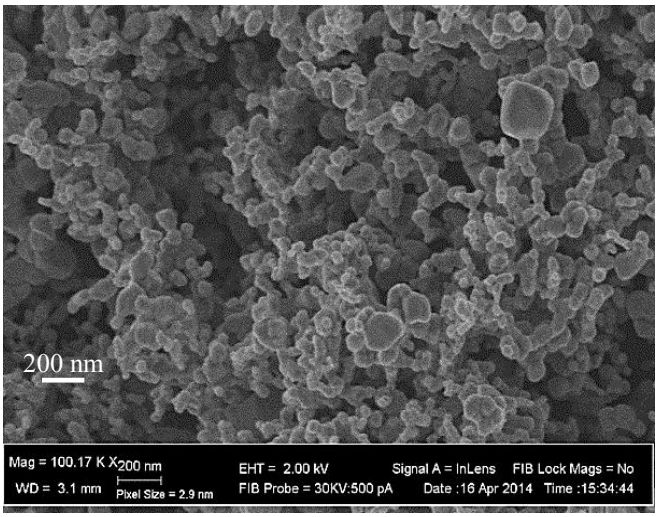
Shimadzu UV–Vis 2550 spectrophotometer with a deuterium lamp (wavelength: 190–390 nm) and a halogen lamp (wavelength: 280–1100 nm). A Spex Fluorolog Tau-3 spectrofluorimeter with a Xenon lamp was used to measure the photoluminescence (PL) spectrum. The excitation wavelength was set to 330nm.

To characterize the electrical properties of the detector, dark current, photo generated current and time response of the fabricated device were measured using an HP4155B semiconductor parameter analyzer and a UV LED with peak wavelength of 340 nm. The responsivity of the device was measured by Shimadzu UV–vis 2550 spectrophotometer, Newport 1928-C optical power meter and Keithley 6487 pico-ammeter. All measurements were performed at room temperature in air.

III. Results and Discussion

Fig. 2a) shows the high-resolution SEM image (scale 200 nm) of the SnO_2 NP film developed on quartz substrate. The XRD pattern of SnO_2 NP is shown in Fig. 2b).



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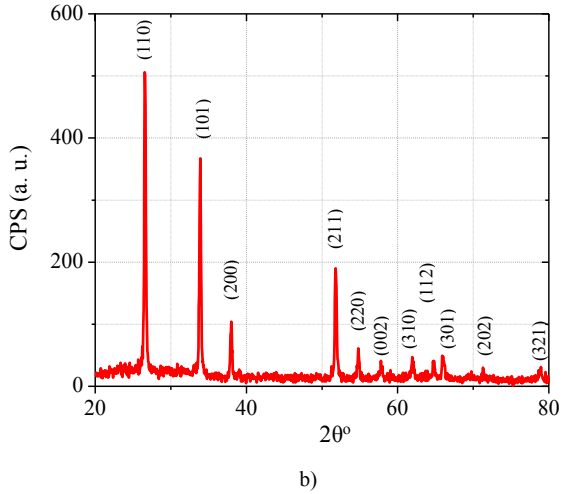
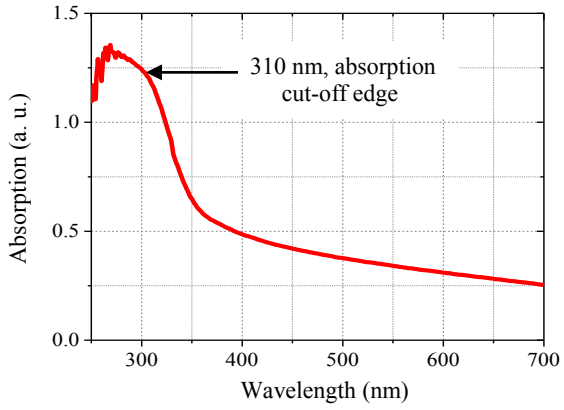


b)

Fig. 2. Material characterization of SnO_2 nanoparticles, a) SEM image and b) XRD pattern.

All peaks are well matched to the reference JCPDS card no. 41-1445 and they are sharp and clear. This indicates that the SnO_2 film is crystalline. The SnO_2 crystals are in the tetragonal rutile phase. The optical characteristics are studied by obtaining the absorption and the photoluminescence (PL) spectra of the SnO_2 NP. The absorption spectrum is shown in Fig. 3a).

The onset of the absorption edge is at 310 nm, beyond which the absorbance sharply decreases. As the absorbance in the UV range is approximately five times of that in the visible range, it is expected that the detector will be visible blind and will have a large signal to noise ratio. The signal to noise ratio can be defined as the ratio of photo generated current to dark current. The PL spectrum shown in Fig. 3b) peaks at 398 nm and 565 nm, and shoulder at 440 nm; indicating that the spectrum is formed of multiple peaks. The de-convolution of the spectrum shows peaks at approximately 388 nm, 425 nm and 565 nm. The 388 nm peak is in the UV range and can be attributed to near band edge UV emission [13]. The 425 nm peak can be attributed to material defects such as tin interstitials and dangling bonds. They introduce energy states in the band gap of tin oxide and provide alternate paths to charge carriers for transition. The broad peak at 565 nm is the parasitic green luminescence, found in most metal oxide NP [14-15]. This peak can be attributed to oxygen vacancies in SnO_2; formed when oxygen



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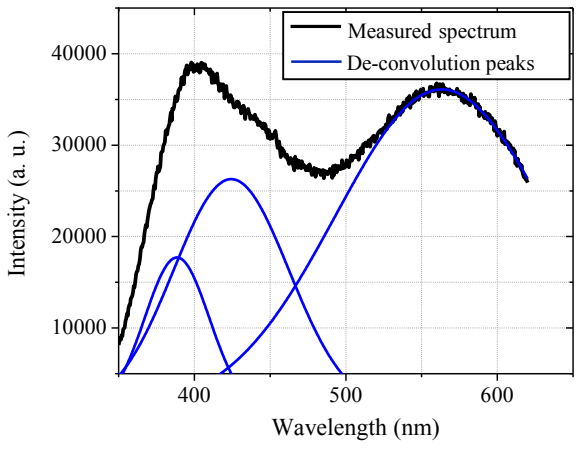

b)

Fig. 3. Optical characterization of SnO_2 nanoparticles, a) absorption spectrum and b) photoluminescence spectrum.

escapes from the host lattice, forming a trap for electrons. These traps act as radiative centers for luminescence and result in green luminescence and are common to metal oxides.

The electrical properties of the detector have been studied by measuring the current-voltage (*I-V*) characteristics, time response and the responsivity. Fig. 4 shows measured photocurrent and dark current of the detector for a voltage sweep from −5 V to 5 V. The photo detector exhibits high signal to noise ratio of 5.8 x 10^3. The dark current density and photo current density are approximately 2.2 x 10^{-2} A/m^2 and 1.3 x 10^2 A/m^2 respectively.

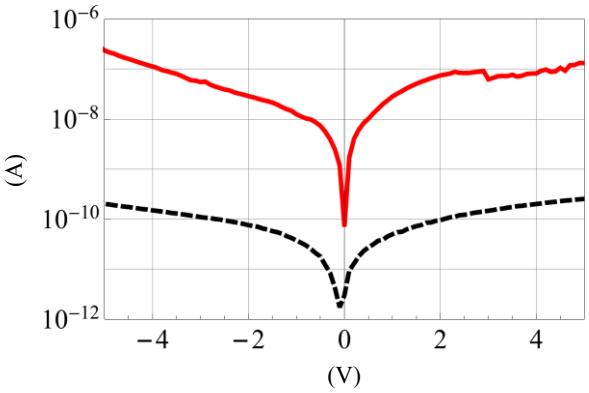

Fig. 4. Measured *I-V* characteristics of SnO_2 nanoparticles based photodetector, photocurrent (solid line) and dark current (dashed line).

The photo generation of current in the SnO_2 NP thin film is caused by oxygen adsorption and desorption on the surface [24]. The NP thin film has high surface to volume ratio implying large number of oxygen vacancy sites on the surface. These vacancies act as electron traps. Oxygen molecules have affinity for the electrons and they combine with them to form ions on the surface defects. Upward band bending occurs and a depletion region with a low conductivity is formed on the surface. When UV light is incident on the film, it produces electron hole pairs. The photo excited holes move up to the oxygen ions leaving behind the photo generated electrons that are now free carriers that contribute to the photo current. The oxygen ions combine with the holes and oxygen desorption takes place which decreases width of the depletion region and increases the conductivity of the material. In addition, the recombination probability of the photo-generated electrons with the holes is greatly reduced, resulting in longer carrier lifetimes. The photogeneration process is shown in Fig. 5.

The transient response of the photodetector is shown in Fig. 6. Time responses are obtained by manually turning on and off a 340 nm UV light stimulus. The photo detector is biased at 10V. The calculated rise time and fall time are 16 seconds and 5.4 seconds respectively. This time response is two times faster than ZnO photodetector [14] and about 100 times faster than In_2O_3 photodetector [15] fabricated by similar process. When the UV light stimulus is removed, the oxygen molecules readsorb after capturing free electrons and the detector goes back to a low conductivity state. Fig. 6b) confirms reliable and repeatable operation of the detector.

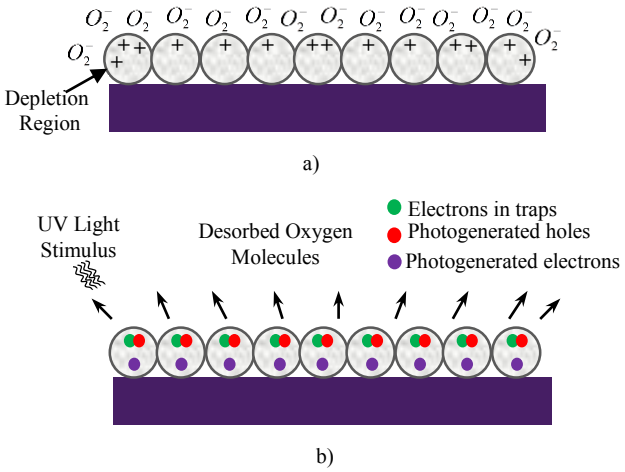

Fig. 5. Schematic representation of photogeneration of current in SnO_2 nanoparticles UV detector in a) absence of UV stimulus and b) presence of UV stimulus.

Fig. 7 shows the photoresponsivity of the detector when it is biased at 10V. The high responsivity below 310 nm wavelength confirms with the absorption cut off edge from the absorption spectrum. The responsivity peaks to 307 mA/W at 250 nm. Oshima et al have reported responsivity of 0.023 A/W [9]. Kumar et al have reporter high responsivity of 23A/W but poor SNR of 10 [23]. It should be noted here that from the reported

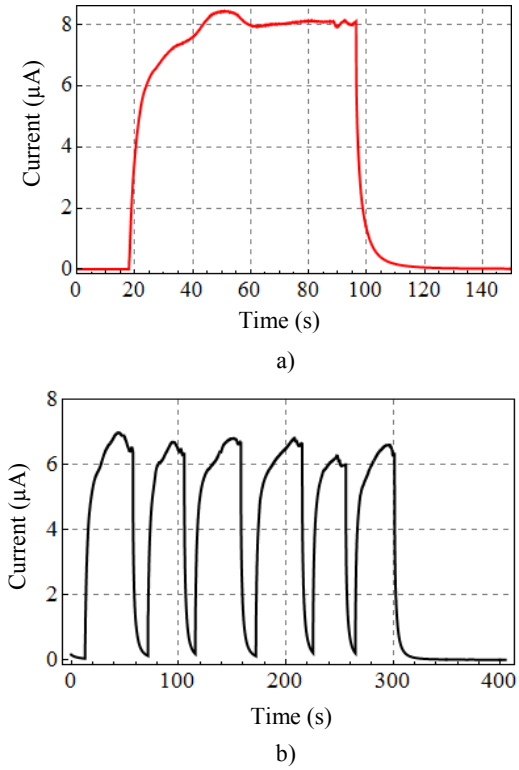

Fig. 6. Time response of photodetector, a) rise and fall time calculation and b) repeatable performance, when UV stimulus is applied intermittently.

band gaps (3.5 to 4.6 eV), the peak responsivity should lie in the wavelength range of 354 nm to 270 nm. At energies higher than the band gap, a decrease in the photoresponsivity is expected. However, it is observed that the responsivity continues to increase beyond this range. Similar behavior is seen in results reported in [16-18]. As the size of the particles in the present study is much higher than the critical exciton Bohr radius of SnO_2 (2.7 nm) [19], this behavior cannot be attributed to the quantum confinement effect. Geraldo et al. [18] have proposed that this behavior can be explained by the effect of adsorbed oxygen on the recombination process. Since the adsorption and desorption require the capture of an electron and a hole by the oxygen molecule, the process is much slower and continues beyond the point of generation of photo excited charge carriers. However, further investigation is required to fully explain this phenomenon in SnO_2 NP based detectors and it will be explored in more details in our future work.

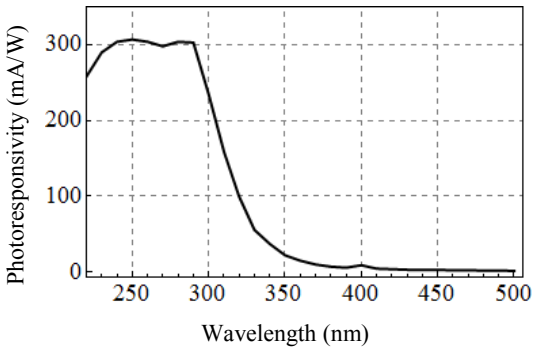

Fig. 7. Photoresponsivity of the detector at a bias of 10V.

IV. Conclusion

This paper discussed the fabrication and the characterization of a SnO_2 nanoparticles based UV photodetector. The fabricated detector is shown to exhibit high signal to noise ratio and photo current, low dark current, high responsivity, and relatively faster time response when compared to other metal oxide nanoparticles based detectors. The response time can be further improved by carrier transfer mechanisms with nanocomposites like graphene and hole or electron blocking polymers [20-21]. The ability of the detector to reject visible light and to generate large photocurrent in the UV range can find significant application in the field of high sensitivity photodetection and photoelectronic switching applications. Future work will explore surface passivation, creating SnO_2 nanocomposites for carrier transport to a highly conductive material, and investigation of other nanostructures to achieve further improvement in the signal-to-noise ratio and the time response of SnO_2 based materials.

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