Tin (IV) Oxide Nanowires Decorated r-GO Nanosheet Thin Film based Prominent Optical Sensor

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Abstract- **To improve the photodetection performance of SnO_2, hydrothermal route has been adopted as a facile and efficient method to prepare the SnO_2-nanowires and it's composite with Graphene-nanosheets on the basis of the reduction of Graphene Oxide (rGO). Here, we report the unique fabrication method of nanocomposite thin film by using the spray method by placing the mixture solution of the as synthesized SnO_2 nanostructure as well as the reduced Graphene Oxide (rGO), inside the medicine chamber of baby's spray nebulizer. Reduction in the size of the SnO_2 particles or thin films has been liable to enhancement in the Responsivity (as grain size or film thickness approaches to the nanoscales) which led to improvement in the sensor response. Nanocomposite SnO_2/rGO thin film is deposited by direct spraying with illustrated method over the Si/SiO_2, Glass and ITO substrates. The structural property of SnO_2 has been characterized by XRD and SEM, Optical properties are measured by optical micrograph and UV-Vis spectroscopy, and its I-V characteristics have been drawn under influence of different wavelength of lights.**

Keywords: ***SnO_2 photodetector, Nanocomposite with Hydrothermal method, Reduced Graphene Oxide (rGO), SnO_2 nanowire***

1. INTRODUCTION

Tin dioxide (SnO_2) is a very important n-type metal-oxide semiconductor with a wide direct band gap is particularly interesting and having many important applications. It has attracted much interest due to photodetector application and having high quantum efficiency in mainly ultraviolet region. Different nanostructures and thin films of SnO_2 have extensively been studied and used as chemical sensors for environmental and industrial applications. It is having potential applications in many practical devices, including as a transparent conducting electrode for organic light emitting diodes, visible-blind photodetectors and solar cells [1]. In addition, one- dimensional (1D) materials have a high surface-to- volume ratio; the surface of nanorods can influence the conductivity remarkably. On the other hand, 1D nanostructure of semiconductors with a wide band-gap, such as GaN, ZnO, SnO_2 or other metal-oxide nanostructures, also show their potential for high- efficiency UV photodetection [2-4]. Photodetection in the ultraviolet (UV) region has drawn extensive attention owing to its various applications in industry, instrument, and our daily life. UV light is typically divided into four spectral regions: UV-A (320-400 nm), UV-B (280-320 nm), UV-C (200-280 nm), and far UV (10-200 nm). Although most of the UV light which comes from the Sun is absorbed by the atmospheric ozone layer but the solar radiation with wavelength longer than 280 nm penetrate the atmosphere and reach to the Earth surface. Therefore, UV detectors that have high sensitivity to UV-C and far UV radiation compared to radiation with wavelength longer than 280 nm can be called „solar-blind". Moreover, UV detectors find several applications, such as in UV dosimetry, solar UV measurements, flame sensors (fire alarm systems, missile plume detection, combustion engine control), biological and chemical sensors etc. [2].

Narrow bandgap semiconductors such as, Si and some III-V compounds (GaP, GaAsP) have first been used to design UV detection. However, in such applications the insertion of costly high pass optical filters and phosphors are necessary in order to tune the photodetecting system to the appropriate spectral range and for preventing the degradation of materials [5].

2. EXPERIMENTAL WORK

2.1. *Chemicals*:

Graphite flakes were purchased from Alfa Aesar (325 mesh), Sulfuric acid (H_2SO_4, 95–98%), phosphoric acid (H_3PO_4, 85%), potassium permanganate ($KMnO_4$, 99.9%), and hydrogen peroxide (H_2O_2, 30%) has been purchased from Merck. Hydrogen chloride (HCl, 37%) was purchased from Sigma-Aldrich. Tin (IV) chloride pentahydrate ($SnCl_4$ $5H_2O$, 98%) and absolute ethanol were purchased from Merck and Hi-Media Chemicals, respectively. Distilled water was used throughout the sample preparation. All

chemicals were used as received without further purification.

2.2. Preparation of SnO2 nanowires, rGO and SnO_2- rGO thin-film:

At first SnO2 nanowires were synthesized via a hydrothermal method [6,7]. In a typical process, calculated amount of SnCl4.5H2O and NaOH were mixed with 40 ml de-ionized water under magnetic stirring for 10 min. Next, 40 ml absolute ethanol was dropped slowly into the solution to make the white precipitation. The mixture was stirred for another 24 h. Finally the whole mixture was transferred into a Teflon- linked autoclave of 100 ml volume. The autoclave was placed in an oven maintained at 190–210 ^{0}C temperature. After the reaction was complete, the resulting solid product was filtered and washed several times by de-ionized water, absolute ethanol and finally dried at 120 ^{0}C in air for the duration of 24 h. Then GO was prepared from natural graphite powder through Improved Hummers‟ method [8,9]. As synthesized GO was further undergone to microwave reduction at 700W to form rGO. Thereafter, thin films were prepared on Glass, ITO, Si/SiO_2 substrate by spray method by mixing both solutions i.e. rGO and SnO_2 in 5:1 ratio having concentration of 1mg/ml and placing it into nebulization chamber of baby's Nebulizer and spray coating was performed. The prepared thin films were annealed, at 500◦C for 3h under an atmosphere of nitrogen, to obtain good crystallinity. For making comparison of the properties, SnO_2 thin-film without rGO was also prepared by following the same procedure.

2.5. *Characterizations:*

The resulting hydrothermally synthesized SnO_2 powders were characterized by X-ray diffraction (D 5000, Siemens) using copper Kα radiation (λ=1.5417 Å) having scan rate of 0.021s^{-1}. The morphology of SnO_2/Graphene was examined by using scanning electron microscopy (SEM, Philips, XL30 scanning electron microscope). Optical absorption properties over the spectral region of 200–800 nm were measured by using a dual beam UV–Vis Spectrophometer (Hitachi, U-3010).

3. RESULTS AND DISCUSSION

The XRD pattern of the as-synthesized SnO_2 nanostructures has been measured and it is shown in Fig. 1. All the diffraction peaks are matched with the tetragonal phase of SnO_2 and the calculated values of lattice parameters are a = 4.742Å and c = 3.186Å, which are in well agreement with the standard data (JCPDS no. 77-0450). The relatively higher intensity of diffraction peaks of nanowires reveals the higher crystallinity with the obtained diffraction peaks, broadened by the small diameter of the nanowires [10,11]. No impurity peaks are observed, confirms that final products is of high purity.

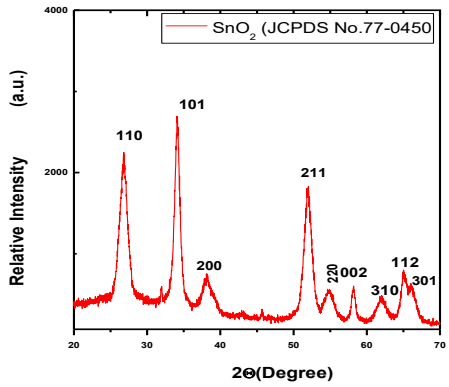

Fig. 1. XRD pattern of SnO_2 nanowires

The scanning electron micrograph (SEM) images of synthesized SnO_2 confirmed that the sample consists of nanowires. Figure 2(a) shows that nanowires are clearly looking over Graphene (blackish layered) in SnO_2/rGO thin film. Figure 2(b) shows the presence of very long undistorted nanowires in Maggi like structure with the average diameter of ~18 nm.

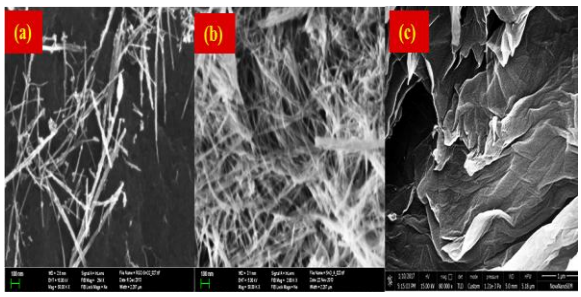

Fig. 2. SEM image of (a) SnO_2/rGO thin film over Si substrate and (b) as-synthesized SnO_2 nanowires (c) as-synthesised r-GO

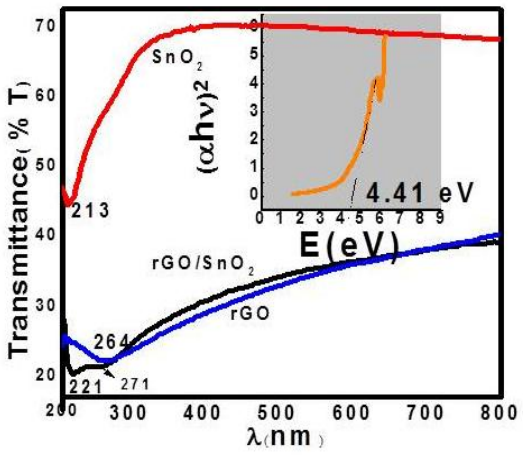

Fig. 3. UV-Vis. Transmittance spectra of SnO2, rGO and SnO2/rGo Mixture.(inset shows band gap energy plot for SnO2

The band gap energy (E_g) is calculated on the basis of the measured UV-Vis absorption characteristics and by following the method as described below. The relationship between band gap energy E_g and absorption coefficient α is given as-

$$(\alpha h\upsilon)^2 = B(h\upsilon - E_g) \quad \ldots\ldots\ldots(1).$$

Where, B is a constant and hυ correspond to the photon energy. The optical band gap energy is obtained by plotting $(\alpha h\upsilon)^2$ *vs.* hυ and then extrapolating to the $h\upsilon$ axis (plot is shown in the inset of Fig. 3).

The UV-Vis transmittance spectra of SnO_2, rGO and SnO_2/rGO samples dispersed in ethanol are measured at room temperature and those are shown in Fig. 3. FromFig. 3 it is found that SnO_2 nanowires absorb strongly at 213 nm, rGO absorbs at 264 nm. The composite of SnO_2/rGO gives maximum absorbance peak at 221nm and one shoulder peak at 271 nm, which may be due to the presence of rGO leading to increase in the absorbance values in visible region.

These results indicate that these materials may be used for designing UV sensor. From the inset of Fig. 3 the band gap energy for SnO_2 nanowires has been found to be ~ 4.41 eV which is much larger than that of bulk SnO_2 (3.6eV). This enhancement in band gap has occurred due to the quantum confinement effect.

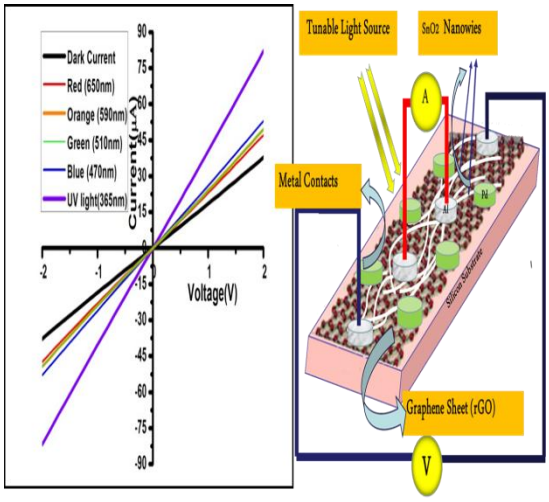

Fig. 4. I-V spectral response of the thin film (on Glass substrate) based device with device schematics (right)

Prepared thin film, mounted with aluminum contacts by using Hind Hivac Vacuum coating unit (Model No.12A4), has been examined for its current– voltage (I–V) characteristics. The I-V characteristics of SnO_2nanowire-based photo detector illuminated with light of different wavelengths and under dark conditions are shown in Fig. 4.

From here it is clear that as the wavelength is increasing from blue to red the current indicating is less this is because the energy of particular light is decreasing which is not enough to create electron hole pair inside the semiconductor material as the wavelength is decreasing that is towards blue its current is increasing so it also implies that if we will provide the UV light on the film it will give much more current.

The value of the current flowing in the device without any light (dark current) is 37.7 μA at the applied voltage of 2V. Under illumination by light, the photocurrent gradually increases with decreasing wavelength i.e. red (650 nm), green (510 nm), Blue (450 nm) and UV light (365 nm) color of the light source. A maximum increase of the photocurrent is detected when light of wavelength 365 nm (UV light) is used, and the photocurrent could approach 80.1 μA for the same applied voltage of 2 V. Such photocurrent obtained from here is comparatively higher than semiconductor nanowire based photodetectors. In some earlier research work done with SnO_2 nanowires based photodetector the dark current of ~19.4nA and maximum photocurrent of 2.1 μA measured at 1.0 V has been reported [12]. The obtained value of large photocurrent validates the effective employment of the present thin film of SnO_2 nanowires with very high surface-to- volume ratio as the building blocks of UV photodetectors. The high spectral selectivity vindicates that the SnO_2 nanowire-based photodetector is intrinsically "visible-blind". Further deposition of thin films on Si/SiO_2 and ITO substrates are also in progress for comparative studies.

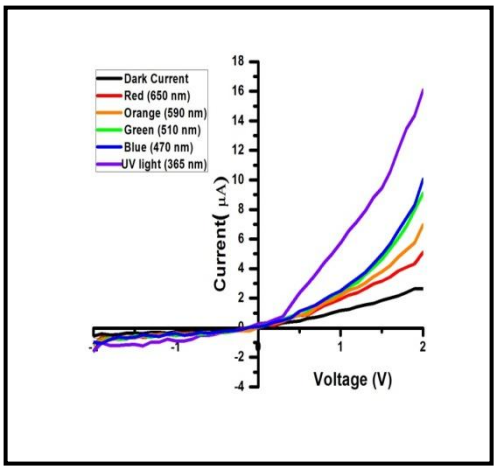

Fig. 5. I-V spectral response of the thin film (on Si/SiO_2 substrate) based device

Furthermore the rGO/SnO_2 thin film on Si/SiO_2 substrate having Palladium contacts was undergone with the same I-V characteristics by using probe station (Everbeing Taiwan) under the illumination of the lights of different wavelengths (UV as well as visible ranges) whose characteristics has

been depicted in the Fig. 5. From here it is confirm that there is a formation of Schottky Contact. This is just because of the work function of the Pd. The similar characteristic (I-V spectral response) of the device has been obtained with highest increment of currenton illumination of UV light (365 nm) as compared to different wavelength of lights (400-700nm) in visible region.

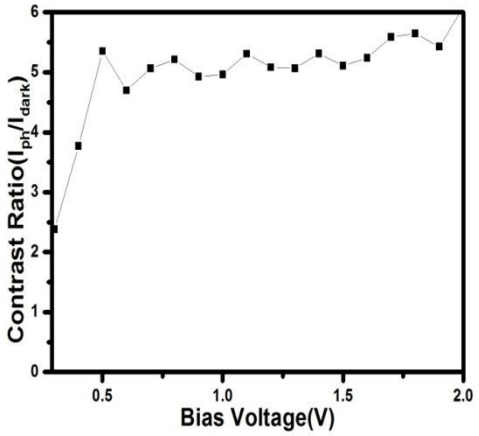

Fig. 6. Contrast ratio plot of the device

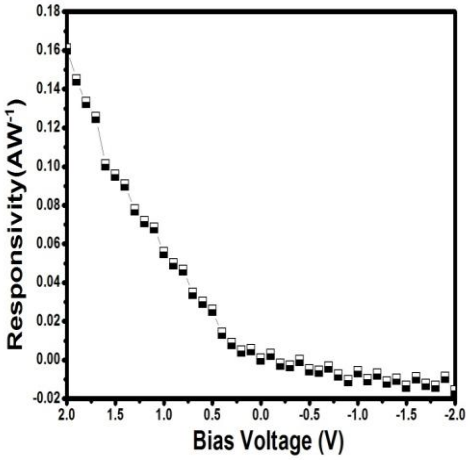

Fig. 6. Responsivity plot of the device

With the help of Fig. 5, the contrast ratio (I_{ph}/I_{dark}) and Responsivity (AW^{-1}) of the device have been plotted in the Fig. 6 and Fig. 7 respectively. From Fig. 6, it is confirmed that device contrast ratio is constant i.e. 5(approx.) with respect to the bias voltage (V). Similarly from fig. 7, it is confirmed that the Responsivity is highest (0.16 A/W) at bias voltage 2 V.

4. CONCLUSION

We have successfully synthesized highly uniform ultra-long SnO_2 nanowires with an average diameter of 18 nm via a simple hydrothermal route. The band gap energy of prepared SnO_2 is calculated and is found to be increased with decrease in size of the prepared nanoparticles due to quantum confinement effect.

We also reported the simple method to fabricate thin film by cost effective spray nebulizer method. Graphene Oxide is also synthesized by improved Hummers method and then further reduction has been done via microwave assisted method which also cost effective and less time consuming. Previously reported papers based on SnO_2 Photo detectors reports to be dark current ~19.4nA and maximum photocurrent is to be 2.1 µA measured at 2.0 Volt [12] .Here we also observed that the current of the device in the dark was ~37.7 µA. Under illumination by light, the photocurrent gradually increases with decreasing wavelength of the light source. A maximum increase of the photocurrent was detected when light of wavelength 365 nm was used, and the photocurrent could approach 80.1 µ A at a low applied voltage of 2.0 V. The linear I –V characteristic indicates a good Ohmic /Schottky contactbetween the nanowire and the electrodes.

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