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ITO nanowires-embedding transparent NiO/ZnO photodetector

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Ni tipped ITO nanowires (NWs) have been prepared by state-of-the-art method and used as a base layer for NiO/ZnO UV detector. The enhanced opto-electrical properties of the fabricated UV detector were systematically analysed. Ni islands were used as a template to forming vertically grown ITO NWs. The prepared NiO/ZnO/ITO NW UV detector exhibited more than 80% transmittance in the visible and NIR regions. However, as the UV radiation was completely utilized by the device, the transmittance in the UV region was least. The photoconduction mechanism including Schottky contact between NiO and ZnO layers were studied by I–V characteristics and Mott-Schottky analysis. The device showed the lowest reverse saturation current of 0.59 nA, showing good junction quality. The detector showed excellent UV photoresponse time of 7.05 ms. It is suggested that the optical and electrical properties of an UV detector could be enhanced by incorporating the Ni tipped ITO NWs.

1. Introduction

The transparent conductive oxide (TCO) nanostructures employed in photodetectors drastically improve the sensitivity and the response time of the devices due to their high surface to volume ratio, selective spectral responsivity, light trapping mechanism and higher photocurrent generation [1–5]. Among various types of photodetectors, the UV sensing one provides its unique excellence in the fields of light wave communications, bio-labelling, missile-tracking, weather monitoring and flame detection [6–8]. Recently, ZnO [9], ITO [10], ZnS [11], CdS [12] and $W_{18}O_{49}$ [13] nanowires have been used in high sensitive UV detectors. Concerning the viable material for UV detection, the high performed ZnO and NiO are the immediate choices because of their distinctive properties as follows: both ZnO and NiO have the wide energy gaps of 3.37 eV and 3.6 eV respectively and large exciton binding energies of 60 meV [14] and 110 meV [15] which make them as ideal candidates for UV based optoelectronic devices such as UV photodetector, UV laser and UV LEDs. As ZnO and NiO are the intrinsic n and p type TCOs respectively, the combinations of these two TCOs have been studied by various research groups [16–20]. Few researchers have combined ZnO nanowires or nanorods with NiO layer in the UV detectors to demonstrate the UV detectors with quality junction, fast response and high sensitivity to UV radiation [16,21–24]. The admirable photoresponse of NiO/ZnO UV detector has already been demonstrated by our research group [17]. In the present work, our main objective is to fabricate the highly sensitive transparent UV detector since the sensitivity of conventional Si based photodetectors is limited due to its high absorption length at UV region. In order to enhance the opto-electrical properties of NiO/ZnO UV detector further, we have built the device over the renowned ITO nanowires which results in better light trapping, increased carrier collection efficiency, reduced recovering time in photoresponse and suppressed reflection. This is the first time of reporting the fabrication of competent UV photodetector on the ITO nanowires network. The ITO nanowires exhibited the assured transmittance of more than 80%, improved charge collection, very low resistivity in the order of $10^{-4}\,\Omega$ cm and electron density of 2.6×10^{20} cm^{-3} [25,26]. When compared to the ITO thin films and other nanoscale building blocks such as carbon nanotubes, silver nanowires, these properties are superior for ITO nanowires [10].

The NiO/ZnO UV photodetector fabricated on FTO coated glass substrate has been reported in our previous work. In the present work, FTO is replaced by ITO nanowires. ITO nanowires are sequentially grown on the nano-sized Ni islands template by state-of-the-art method. Advantages of this method are, Ni island intrudes into the NW up to the tip during the growth of ITO NWs, the conductivity of NWs increases tremendously due to the higher carrier concentration of Ni and reflection is almost nullified due to

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the inherent properties of Ni and ITO materials. Over the ITO NW network, thin NiO/ZnO layers with Schottky contact are deposited using the appropriate conditions so as to develop the advanced UV photodetector with fast response and high sensitivity. The demonstrated UV detector shows a very quick response to the UV radiation with rise and decay times of 7.05 ms and 17.61 ms respectively.

2. Experimental procedure

2.1. Preparation of ITO nanowires

The quartz substrates were cleaned by Acetone, Methanol and DI water for 5 min each under ultra-sonication process. A 4-in. Ni target was subjected to the DC power of 3.70 W cm^{-2} to deposit a thin Ni layer about 5 nm thickness on quartz substrates under Ar atmosphere. After the deposition, the substrates were undergone rapid thermal processing (RTP) at 600 °C for 10 min. Due to the constant temperature, thin layer of Ni transformed into nano islands over the entire surface which acts as a template for ITO NWs growth. Followed by this process, the substrate was kept back in sputtering chamber and a 4-in. ITO target (99.999%) containing the mixture of In_2O_2 and 10 wt% of SnO_2 was sputtered over the Ni nano-islands for about 20 min at a deposition temperature of 600 °C under 5mTorr of Ar/O_2 ambient. During this process, the ITO NWs are gradually looming.

2.2. Preparation of NiO/ZnO layers with Schottky junction

A thin layer of ZnO was deposited over ITO nanowires by applying the RF power of 3.58 W cm^{-2} on to the 4-in. ZnO target (99.999%) which is kept in RF sputtering system. Then, DC power density of 3.70 W cm^{-2} was given to a 4-in. Ni target (99.999%) to deposit a thin Ni layer of 50 nm thickness over ZnO layer. After that, the prepared sample was undergone the RTP at 500 °C in oxygen atmosphere for about 10 min to convert Ni to NiO. The transformed NiO forms Schottky junction at the interface of NiO and ZnO layers, by this means, working as an effective UV photodetector.

2.3. Characterization procedure

A field emission transmission electron microscope (FETEM, JEOL, JEM-ARM-200F) was used to record the cross-sectional insight of the prepared NiO/ZnO UV detector and the specially prepared ITO nanowires. The elemental composition and depth profile of a single ITO nanowire were studied using an energy dispersive spectroscopy (EDS) attachment to the FETEM. Optical characterization was carried out using a UV–vis spectrophotometer (Shimadzu, UV-1800) by recording the transmission spectra of the prepared device in the range 300–1100 nm. In order to investigate the junction properties and photoresponse performances, NiO/ZnO/ITO NW photo detector was fabricated. Electrical characteristics of the fabricated UV detector were achieved using a probe station with current–voltage (I–V) measuring instruments (Keithley 2400). Mott–Schottky analyses (C–V characteristics) of the Schottky junction device were obtained by applying an AC signal (0.1 mV) at 2 kHz by sweeping the DC bias in a range from −3 to 3 V using the Potentiostat/Galvanostat from Won A Tech (model, ZIVE SP1). Photoresponses of the UV photodetector were obtained using a quantum measurement system (K3100, McScience) with an on and off pulsed light of a 400 nm monochromatic LED lamp. The LED source was calibrated with a power meter (KUSAMMECO, KM-SPM-11).

3. Results and discussions

The important feature of the described NiO/ZnO UV detector is that it is packed or linked with Ni intruded ITO nanowires. The schematic representation of the prepared device is shown in Fig. 1(a). A small portion of ITO NWs is kept free from the deposition of ZnO and NiO layers with the intention of using it as bottom ohmic contact. The cross sectional and top view FESEM images of ITO NWs are shown in Fig. 1(b) and (c) respectively. It is observed that the grown ITO NWs are not orderly aligned but randomly oriented in vertical direction. And, the thickness of each NW is gradually decreased from bottom to top which confirmed the self-growth of NWs. In the cross sectional view of the NiO/ZnO/ITO NW UV detector (Fig. 1(d)), the uniform growth of each layer is observed with clear boundaries. Thickness of each layer is calculated from the deposition rate and deposition time as ≈180 nm, 200 nm and 60 nm for ITO NW, ZnO and NiO layers, respectively. The calculated thickness is correlated to the thickness roughly estimated from Fig. 1(d). As mentioned earlier, in the course of sputtering ITO over Ni islands, the substrate was maintained at a temperature of 600 °C. This thermal process made Ni to progressively penetrate into the ITO NWs and thereby triggering the NW growth. To measure the quantity of Ni throughout the length of ITO NWs, the depth profile of a single ITO NW is studied by EDS which is shown in Fig. 1(e) along with its HRTEM image. At the bottom and middle portions of ITO NW, the signals corresponding to Ni are comparatively too low whereas the signals of In primarily dominated the other elements such as O and Sn in this region. However, at the top portion, the situation is just reversed ie., the counts corresponding to Ni is suddenly increased than that of other elements. This implies that very small quantity (≈10%) of Ni is distributed along the body of NW and about 90% of Ni is remained at the tip of NW. Hence, this analysis clearly depicts that Ni is grown inwardly via oxygen vacancies and accumulated at the tip of ITO NW. This is also confirmed from HRTEM image (Fig. 1(e) bottom) which shows the accumulation of Ni in the shape of sphere at the tip of ITO NW is evidently observed. The ITO NWs having Ni tip is a remarkable structure that can enhance the properties of existing functional nano-scale devices because of the inherent properties of both ITO and Ni. The transmittance of ITO film (60.27%) is increased when it changes from planar structure to nanowire form and its electrical conductivity and career concentration are increased as a consequence of Ni intrusion. The highly ordered crystal planes corresponding to ($2\bar{2}2$) lattice space of 0.292 nm along the center of the ITO NW, which reveals the [110] directional growth of ITO NW, as shown in the magnified HRTEM image (Fig. 1(f)) of ITO NW. Typically, the nano structured ITO shows the better crystallinity than the conventional ITO films [27,28].

To compete with the advanced photoelectric devices, an UV detector should be optically and electrically beneficial. The optical transmittance profile of the NiO/ZnO/ITO NW UV detector is presented in Fig. 2. The device showed the maximum transmittance of ≈90% in the NIR region and average transmittance of 80.98% in the broad spectral range of 400–1100 nm. The Ni inserted planar ITO, AZO and ITO/AZO films provided optical transmittances of 60.27%, 77.14% and 67.35% respectively. And, the photodetector consisting of NiO/ZnO layers deposited on FTO substrates exhibited the average transmittance of ≈76% [28,29]. However, the Ni tipped ITO NWs have particularly increased the transmittance to ≈81% [17]. Therefore, Ni tipped ITO NW structure has suppressed the surface reflection and enhanced the transmittance of the NiO/ZnO detector in the visible and NIR regions. Since NiO and ZnO have large binding energies and band gaps, the wavelengths corresponding to UV region is not transmitted. In other words, the