Optical and Structural Properties of Multi-wall-carbon-nanotube-modified ZnO Synthesized at Varying Substrate Temperatures for Highly Efficient Light Sensing Devices

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Abstract: Structural, optical and light detection properties on carbon-nanotube-modified ZnO thin films grown at various temperatures from room to 1173 K are investigated. The optical band gap values calculated from reflectivity data show a hump at a critical temperature range of 873-1073 K. Similar trends in surface roughness as well as crystallite size of the films are observed. These changes have been attributed to structural change from wurzite hexagonal to cubic carbon modified ZnO as also validated by x-ray diffraction, RBS and PIXE of these layers. UV and visible light detection properties show similar trends. It is demonstrated that the present films can sense both UV and visible light to a maximum response efficiency of 66 % which is much higher than the last reported efficiency 10 %. This high response is given predominantly by cubic crystallite rather than the wurzite hexagonal composites.

Keywords: Carbon nanotubes, Zinc Oxide, Light Detection, Optical, Structure, Sensing.
1. Introduction

There has been tremendous interest in ZnO [1-4] as well as carbon materials [5-7]; these are already in various technological devices. Work on the combination of ZnO and carbon materials is gaining interest [8-10] since these composites benefit from the good properties of both popular materials. For instance, carbon modified ZnO materials have been presented for solar cells [11-13] and sensors [14-16, 21, 22] to name a few.

In light sensing, single carbon nanotubes mixed with ZnO have been employed [7-8]. The current-voltage characteristics obtained on the SWNTs-ZnO devices were found to be non-rectifying and Ohmic-like in the dark and when exposed to optical radiation. While the conductivity of SWNTs thin films was observed to increase by ~7% under UV illumination, similarly tested SWNT-ZnO samples consistently exhibited a decrease in conductivity upon exposure to UV radiation yielding a net negative change of ~10% associated with the formation of ZnO-SWNT interface. This effect as well as that of strong optical gating was explained within the model of interface-mediated charging/discharging effects.

In the present study, the aim was to push the UV and visible light sensing efficiency of the multi-wall-carbon-nanotube-modified ZnO (MWCNT-ZnO) to higher values than 10% by developing MWCNT-ZnO materials at varying processing temperatures from 300 K to 1173 K. This ensures that for the same starting MWCNT-ZnO composite, the proportions of MWCNT/ZnO are tuned by the process temperatures. In this work, the structural, morphological and optical properties of MWCNT-ZnO processed at varying temperatures are reported and how the process temperature impinges on structure, surface roughness and optical band gap energy of the MWCNT-ZnO composites calculated from reflectivity as well as the UV and visible light sensing of these composites is also discussed. It is demonstrated the light sensing efficiency can be pushed to above 50%.

2. Experiments

The carbon modified ZnO films were prepared by pulsed laser deposition (PLD). A 3-cm radius pellet of pre-mixed ZnO and CNT powder was first prepared in a press of maximum 10 tonnes equivalent pressure. The pellet was sintered at 473 K for 5 hrs in order to avoid fracturing during laser deposition. PLD was accomplished by employing a KrF excimer laser emitting a pulse of wavelength 268 nm, a pulse repetition rate of 20 pulses per second. Each deposition was carried out on Si substrate and varying the substrate temperatures from 300 K, 373 K, 473 K, 573 K in that order up to 1173 K.

The films were characterized for their structural, morphological and optical properties by respectively employing the following instruments; the XRD using CuKα radiation of wavelength 1.5418 Å recorded in the 2θ range from 5 to 90, SEM (Auriga Cobra FIB FESEM) at a working distance 100 nm and a Varian Cary UV-Vis-IR Spectrophotometer with a diffuse reflectance spectrometer (DRS) attachment respectively.

AFM topography examinations were carried out with the Multimode AFM NanoScope Version (R) IV (VEECO instrument) using a 0.5 – 2 Ω-cm phosphorous (n) doped Si tip with a radius of curvature of 10 nm and the aspect ratio of 1:1. Imaging was done in tapping mode (TM) and varying the scan rates and magnifications.

Rutherford Backscattering Spectrometry (RBS) and Proton Induced X-ray Emission (PIXE) measurements were carried out using a collimated 2 MeV He+ beam at GNS Science. For RBS measurements, the backscattered particles were collected using a surface barrier detector placed at 165° with a target current ~15 nA. PIXE measurements were simultaneously carried out, and the X-rays were detected using liquid nitrogen cooled Canberra detector.

The thin film materials were exposed to the ultraviolet light (254 nm) for 10 sec responds and 10 second recovery as well as visible light and the resistance of the films were simultaneously collected by the Keithley Semiconductor Characterization System (SCS) model 4200. The sample was placed in a chamber having a window with an aperture that could be opened or closed by sliding especially for the case of visible light sensing. For UV light sensing, a UV source was placed on top of the open aperture and the source could be turned ON or OFF while the resistance of the film is being monitored in time. The schematic of the light sensing system is given in Fig. 1.

![Schematic diagram for the configuration of the experiment during (a) UV light sensing, (b) Visible light sensing.](image)

3. Results

3.1. Morphological Properties

The surface morphology of MWCNT-ZnO thin films deposited on a silicon substrate shows an even and smooth coverage of the ZnO on the silicon substrate. In Fig. 2 are shown scanning electron microscope images of (a) carbon nanotubes mixed with ZnO starting material (pellet surface) showing that the carbon nanotubes and the ZnO powder are...
well mixed (b-d) typical SEM images of deposited substrates showing the carbon nanotubes are not as evenly distributed as expected. The carbon nanotube doped zinc oxide visualised at 100 nm shows the distributed rod shaped particles (Fig. 2 (b-d)). The carbon nanotubes are observed to become more straightened after deposition than before. This suggests that the flimsy carbon nanotubes are coated with stiffer material of ZnO.

3.2. Atomic Force Microscopy

Surface topology of the MWCNT-ZnO thin films is presented in Fig. 3. The surface sections observed by AFM show no obvious evidence of carbon nanotubes distributed evenly throughout the surface. This observation is supported by SEM above where carbon nanotubes are seen in isolated islands on the surface. Apart from the different morphologies seen in the materials as the substrate temperatures are increased, there seems to be a pattern in the increment and decrement of the surface roughness of the samples. The values of RMS roughness are obtained via the following equation

$$R_q = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (z_i - \bar{z})^2},$$

where $N$ is the number of data points, $z_i$ and $\bar{z}$ are the $i^{th}$ position and the average surface level respectively. The values of roughness are summarized in Table 1 along with crystallite sizes from XRD, band gaps from reflectance and other measurements whose results are given in the forthcoming sections. It will be noted that the pattern of surface roughness changes point to the bulk structural changes in the materials which will be discussed.

Fig. 2. (a) SEM image of carbon modified zinc oxide target before pulsed laser deposition (b) deposited at 300 K (c) deposited at 373 K and (d) deposited at 473 K.

Fig. 3. The surface topology of the MWCNT-ZnO materials show a variety of morphologies that indicates that the carbon nanotubes are not uniformly distributed at the surface.
Table 1. Summary of roughness, crystallite size, calculated optical band gap energies, UV and Vis light response results for carbon modified ZnO samples synthesized on Si substrates at various temperatures.

<table>
<thead>
<tr>
<th>Substrate Temp</th>
<th>Roughness, (nm)</th>
<th>ZnO (002) (nm)</th>
<th>Band Gap (eV)</th>
<th>Response (UV)</th>
<th>Response (Vis)</th>
<th>τ(^{90}) (UV)</th>
<th>τ(^{90}) (Vis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>301</td>
<td>4.1</td>
<td>19</td>
<td>2.9</td>
<td>0.05</td>
<td>0.2</td>
<td>0.1</td>
<td>1.3</td>
</tr>
<tr>
<td>373</td>
<td>1.65</td>
<td>43</td>
<td>3.4</td>
<td>0.02</td>
<td>0.04</td>
<td>0.07</td>
<td>1.1</td>
</tr>
<tr>
<td>473</td>
<td>10</td>
<td>22</td>
<td>3.1</td>
<td>0.2</td>
<td>0.01</td>
<td>0.06</td>
<td>1.0</td>
</tr>
<tr>
<td>573</td>
<td>3.47</td>
<td>39</td>
<td>3.1</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.9</td>
</tr>
<tr>
<td>673</td>
<td>4.75</td>
<td>61</td>
<td>3.1</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>1.0</td>
</tr>
<tr>
<td>773</td>
<td>39.9</td>
<td>57</td>
<td>3.6</td>
<td>0.5</td>
<td>0.5</td>
<td>1.0</td>
<td>0.8</td>
</tr>
<tr>
<td>873</td>
<td>13.3</td>
<td>33</td>
<td>4.3</td>
<td>0.5</td>
<td>0.5</td>
<td>1.0</td>
<td>0.8</td>
</tr>
<tr>
<td>1073</td>
<td>1.86</td>
<td>33</td>
<td>4.3</td>
<td>0.5</td>
<td>0.5</td>
<td>1.0</td>
<td>0.8</td>
</tr>
<tr>
<td>1173</td>
<td>12.9</td>
<td>19</td>
<td>2.7</td>
<td>0.05</td>
<td>0.05</td>
<td>0.06</td>
<td>1.0</td>
</tr>
</tbody>
</table>

3.3. Structural Properties

Pure ZnO wurzite hexagonal structure show XRD strong peaks at \(2\theta\) values (and Miller (hkl) indices) of 31.7° (100), 34.422° (002) and 36.253° (101) as referenced from the International Crystal and Crystallography Data (ICCD) powder diffraction file (PDF) number 36-1451. For pure cubic ZnO, the PDF file 65-0523 shows three major peaks: 36.415° (111), 42.298° (200) and 61.360° (220) and PDF 13-0311 presents 31.927 (111), 37.024 (200) and 63.355 (311).

Fig. 4 shows the XRD diffracto-grams of nanostructured carbon nanotubes modified zinc oxide. It is clear that the samples prepared at substrate temperatures from 300 K to 773 K present a wurzite hexagonal structure. There are major shifts in the MWCNT-ZnO spectra from the pure ZnO: for instance in the pure ZnO the strongest alignment of the crystallite is in the (102) plane direction whereas in the carbon modified samples [300-773 K] the preferential alignment is in the \{002\} direction. This preferential orientation starts to disappear when the MWCNT-ZnO are prepared above the temperature of 873 K and this peak completely disappears at a temperature 1073 K. A new preferential orientation emerges at this temperature which matched the cubic ZnO structures with PDF numbers 65-0523 and 13-0311.

It should be noted that the intensity peak at \(2\theta = 28^\circ\) corresponds to \{111\} crystal plane of the silicon substrate which is observed in all the materials except 673 K. Also the intensity peak of carbon at 35° corresponds to (311).

![X-ray diffraction spectra for carbon-modified ZnO thin films prepared at various substrate temperatures](image)

Fig. 4. X-ray diffraction spectra for carbon-modified ZnO thin films prepared at various substrate temperatures show a first class: from 300 K to 773 K assigned to the wurzite ZnO structure and new peaks when the films are prepared beyond 873 K which are assigned to cubic ZnO structure with carbon segregated to the surface.

XRD points to the substrate temperature between 873 K and 1073 K at which there is a transformation from hexagonal to cubic orientation in these carbon modified ZnO materials.

The crystallite sizes for all the sample were estimated using Scherrer equation given by

\[
D = \frac{(K\lambda)}{(\beta\cos\theta)}
\]

where \(D\) is the volume weighted crystallite diameter, \(K\) is constant which is taken to be equal to 0.9; \(\lambda\) is the wavelength of the X-ray photons,
\( \beta \) is the full width at half maximum of the peak and \( \theta \) is the Bragg angle in radian. The results are summarized in Table 1.

### 3.4. Rutherford Backscattering Spectrometry (RBS)

Fig. 5 shows a representative RBS and RUMP simulated spectra of MWCNT-ZnO on Si (100). The Zn surface peaks were found to be at around channel number 620 [9-10], whereas, O and C surface peaks were observed at around channel numbers 290 and 205, respectively, overlapped with backscattering peak from Si substrates.

From RBS spectra it appears that substrate temperature had a pronounced effects on the film thickness, which resulted in significant evaporation of ZnO layer at 1173 K. A significant fraction of Zn atoms migrated towards the interface of the film, which is evident on samples synthesized a substrate temperature of 1074 K and 1173 K. Fig. 6 illustrates PIXE spectra obtained for MWCNT-ZnO nanocomposite films with ZnO K\( \alpha \) and K\( \beta \) X-ray lines appearing at 8.638 and 9.572 keV, respectively. X-ray lines from Si substrate were also observed at 1.739 keV [16] arising from K\( \alpha \) transition followed by a double peak of K\( \alpha \) lines at 3.476 keV. The PIXE spectra also showed no evidence of X-ray peaks associated with Zn in 1073 K and 1173 K grown films, which is consistent with the RBS spectrometer.

![Fig. 6. PIXE spectra of as-deposited and MWCNT-ZnO films synthesized at varying substrate temperatures on Si (100).](image)

The reflectance data obtained can be used to acquire some information on the proportion of incident photons that are absorbed and hence the band gap energy of the material in the sample. The Kubelka-Munk equation [17] which relates the reflectance to absorption coefficient and scattering coefficient was use and is given here as

\[
\frac{\alpha}{S} = \frac{(1-R)^2}{2R}, \tag{2}
\]

where \( \alpha \) is the absorption co-efficient, \( S \) is the scattering coefficient and \( R \) is the reflectance. In order to elucidate band gaps we employ the well know Tauc equation [18] given as

\[
(ch\nu)^n = E_g - h\nu, \tag{3}
\]

where \( h \) is the Planck’s constant, \( E_g \) is the optical band gap of the material in the thin film and \( n \) can be with equal to 2 (for direct band gap material) or equal to \( \frac{1}{2} \) (for an indirect band gap material). Combining Equation 1 and 2, one can get

\[
\left(\frac{S(1-R)^2}{2R}\right)^2 = E_g - h\nu \tag{4}
\]

Note that the scattering coefficient, \( S \), can be wavelength dependent. However it is known that for particle size greater than 5 \( \mu \)m, \( S \) can be wavelength independent [17]. In this analysis we also assumed that \( S \) is wavelength independent since the beam size impinges on larger than 1 mm in the far field and therefore the detector in the DRS observes a
wavelength independent scattering from the nanostructured surface. The reflectance-versus-wavelength data are plotted for all substrate temperatures in Fig. 7 (a). In comparison the Si substrate, all MWCNT-ZnO samples have a higher reflectance in all visible and infrared wavelengths. However in this range, the Si substrate influences the reflectance spectrum as there are two humps between 600 nm and 700 nm in all spectra emanating from Si. For MWCNT-ZnO surfaces, there is a downward step around 320 nm indicating an absorption edge.

In order to pursue the absorption edge study and calculation of the optical band gap energies of each sample, a Tauc plot based on Equation 4 is displayed in Fig. 7 (b). Coloured lines are inserted in each spectrum in order to guide the reader’s eye; these lines are the linear plots of Equation 4 when \( n = 2 \) as it well known that ZnO is a direct band gap material assuming that the allotrope of carbon in ZnO is mostly graphitic or simply carbon nano-tube which are also known to be direct band gap materials.

### 3.6. Ultra Violet and Visible Sensing

The functionalised MWCNT-ZnO sensors synthesised at substrate temperatures of 300, 373, 473 up to 1173 K were tested using UV light (254 nm) and visible light as a stimuli for the interval of 10 second during exposure and 10 second during recovery (Fig. 8). The response, \( S \), has been defined as \( S = \frac{[R - R_0]}{R_0} \) [19-20]. It was found that all the materials respond to both the UV light and visible light except for the sample synthesized at a substrate temperature of 773 K. In addition, for the MWCNT-ZnO material synthesized at 1173 K, response to visible light is negligible; the streaks in the almost flat time profile could be due to changes in pressure as the light chopper is opened and closed.

![Fig. 7](image_url)

**Fig. 7.** (a) Reflectance vs wavelength for all samples compared to the Si reflectance as the substrate. The arrows show the main absorption edge. (b) The Tauc plots for all samples including the Si reference calculated from the Kubelka-Munk function. The arrows indicate where on the photon energy axis the linear fit the optical band is extracted from for each sample.

![Fig. 8](image_url)

**Fig. 8.** Temporal response to (a) UV light and (b) Visible light of the MWCNT-ZnO samples synthesized at different temperatures show the variation of response when the light is ON and OFF.
The response and recovery time of MWCNT-ZnO sensor films towards UV and visible light were extracted from the fitting of the following exponential association curve in Origin™ software:

\[ S(t) = A \left[ 1 - \exp \left( -\frac{t}{\tau} \right) \right], \quad (5) \]

where \( S(t) \) is the response (or recovery) of the sensor to (or from) the exposure as a function of time, \( A \) is the amplitude of the response and \( \tau \) is the response (or recovery) lifetime of the response when the response equals \( A(1-e^{-1}) \approx 0.65A \).

The response times are traditionally defined as time taken by the sensor output to reach 90% of its saturation after applying or switching off the target analyte and it is called \( \tau_{90} \). With the above fitting, \( \tau_{90} \) values are obtained through calculated \( \tau \) from Equation 5 as follows:

\[ \tau_{90} = -\frac{\tau}{\ln \left( \frac{1 - S_{90}}{A} \right)} \quad (6) \]

The response time of the materials calculated from Equation 6 are plotted Fig. 8 from the results the material that is synthesised at 600°C has the longest response time which means slowest of them all.

The extracted responses and response time values (\( \tau_{90} \)) are summarized in Table 1, alongside calculated band gap energies from reflectivity (Eqs. 4, 5) and from Fig. 7 as well as crystallite size from XRD and roughness from AFM.

When band gap energies, crystallite size and roughness of the MWCNT-ZnO materials are plotted against substrate temperature, it is found that band gaps are in the range from 3.1 eV to 3.4 eV which is acceptable for wurzite hexagonal structure of ZnO up to about 600 K. Above this temperature (800 K – 1073 K), the optical band gap energies drastically increase to above 4 eV only to subside into the 2.6 eV range at 1173 K. This may suggest that at around 800 K there is a transition from one structure to another type of structure. This has been confirmed by XRD which suggests a transition from hexagonal to cubic structure of ZnO between 773 K and 873 K. Similar trends are seen in this Fig. 9 for crystallite size as well roughness although the transition temperature are slightly shifted to lower temperatures.

In addition, plots of response versus substrate temperature in Fig. 10 reveal that there is low sensitivity in the MWCNT-ZnO synthesized at lower than 673 K which is the range of temperatures that gave rise to the wurzite hexagonal structure. However there is an abrupt rise in response in the MWCNT-ZnO materials synthesized at substrate temperatures in the range 800 to 1073 K in which range the cubic structure of ZnO dominates. The response in the range reaches the maximum value of 50% which much higher than the reported values for MWCNT-ZnO materials [13-14]. There is another abrupt and sharp decrease in response as the substrate temperature is increased from 1073 K to 1173 K. This may indicate that there are some changes on the surface of the sample synthesized at 1173 K and the present RBS results confirmed a drastically reduced thickness in the deposition of the film at this temperature. This suggests that either the sample loses its integrity as MWCNT-ZnO and becomes zinc carbides or the ZnO actually start to evaporate from the coating leaving behind very little material for good conduction and hence meaningful sensing.
response times in both UV response and visible light response as the substrate temperatures are increased from 300 K (1.3 s in Vis and 0.1 s in UV) to 1173 K (0.8 s for Vis and 0.03 s for UV). This indicates that the MWCNT-ZnO materials become faster in light response as the substrate temperatures are increased from 300 K up to 600 K. Above 600 K the response times are more or less constant (0.8 s for Vis and 0.03 s for UV). In the constant regime, there is a small hump at 873 K which confirms the transition temperature from hexagonal to cubic structures of ZnO as already shown through XRD, optical band gap energies as well as morphological properties of roughness.

**Fig. 11.** A plot of response time as function of the substrate temperature of MWCNT-ZnO nanomaterials showing longer response times (or slower response) when the MWCNT-ZnO is hexagonal than when the MWCNT-ZnO transforms into cubic form.

### 4. Conclusions

The present report has shown that MWCNT-ZnO thin films on Si have been prepared by pulsed laser deposition of a ZnO/carbon-nano-tube pellet. The films were obtained at varying substrate temperature from 300 K to 1173 K in increments of 100 K. XRD has shown that the wurzite hexagonal structure of ZnO transforms into cubic structure in the temperature range of between 774 K and 873 K. This temperature range has been found to be display drastic changes in optical band gaps (3.1 eV → 4.0 eV), surface roughness (10 nm → 40 nm) as well as crystallite sizes (20 nm → 60 nm). Similar changes in UV and visible light sensing properties such as response (10 % → 50 %) and response times (1.2 s → 0.8 s for visible light and 0.1 s → 0.03 s for UV sensing) are witnessed at these temperatures. The paper has shown that it is possible to enhance the light sensing efficiency in MWCNT-ZnO materials from the current efficiency of 10 % to a new maximum of 50 % by varying the substrate temperatures. And these maxima are obtained in materials that were synthesized at substrate temperatures in the ranges between 873 K and 1073 K.

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