IMPROVEMENTS IN THE STRUCTURAL AND OPTICAL PROPERTIES OF \textit{In}_2\textit{O}_3\textit{NANOSTRUCTURE BY IN-SITU THERMAL ANNEALING}

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Abstract

\textit{In}_2\textit{O}_3/W_2\textit{N} nanocomposites have been successfully grown by a single step deposition technique. The nanostructures were characterized by field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), Ultraviolet-Visible spectroscopy (UV-Vis), and X-ray photoelectron spectroscopy (XPS). The structure deformation of \textit{In}_2\textit{O}_3 nanostructure by an in-situ thermal annealing under ambient nitrogen plasma treatment was investigated. The \textit{In}_2\textit{O}_3 nanostructure demonstrated a decreasing in particle size when it was exposed to in-situ thermal annealing by a hot-filament at temperature of 1700 °C. The in-situ thermal annealing enhances the surface mobility of the N adatoms to reach the nucleation sites to form crystalline W_2N. The formation of chemical composition of \textit{In}_2\textit{O}_3 and W_2N nanostructures presented in the material were analyzed by XPS spectra. The crystallinities of these nanostructures were revealed by XRD patterns showing the cubic, hexagonal and cubic of \textit{In}_2\textit{O}_3 and W_2N structures respectively. The decreasing of the optical energy gap, \(E_g\) from 2.89 to 1.69 eV which is in the visible region could be attributed to the incorporation of nitrogen into the \textit{In}_2\textit{O}_3 and the formation of \textit{In}_2\textit{O}_3/W_2N nanocomposites.

Keyword: Indium oxide, In-situ thermal annealing, Nanocomposite, Optical, Structure deformation

Introduction

\textit{In}_2\textit{O}_3 semiconductor materials have been investigated for their superior properties which include high conductivity (Girtan et al., 2000), high transparency in the visible region and high reflectivity in the infrared region (Zhang et al., 2016a) thus making it a promising material for transparent conducting oxides (TCOs) (Ho et al., 2011). The high conductivity, stability and suitable valence band edge for water oxidation of \textit{In}_2\textit{O}_3 make it a very interesting material for photo-electrochemical (PEC) application (Zhang et al., 2013). Despite of the fact that \textit{In}_2\textit{O}_3 is a well-established material for PEC applications, there are still several ambiguities in the understanding of energy band configuration and fundamental optical absorption in relation to the performance of \textit{In}_2\textit{O}_3 based PEC. Most of the \textit{In}_2\textit{O}_3 nanostructures to be applied in PEC application are limited by its large band gap, \(E_g\) (~ 3.75 eV) (Zou et al., 2013). Besides, it displays a typical of low quantum efficiencies owing to the short diffusion lengths of charge carriers. These could influence the photoexcitation of electron/hole pairs, the migration of charge carriers and the redox capabilities of electrons and holes in the excited state (Scaife, 1980). Moreover, the large band gap comparable to photon energy in the ultraviolet (UV)
region limits the optical absorption of solar radiation spectrum. Generally, only a small fraction of UV (<4%) of total solar spectrum reaches the surface of the earth (Linsebigler et al., 1995) thus only a small portion of solar radiation can be utilized by In$_2$O$_3$. Therefore, band-engineering of In$_2$O$_3$ towards producing direct and narrow bandgap In$_2$O$_3$ are more likely the solution for the material to exhibit high absorbance in the visible region and hence be suitable for the efficient harvesting of low energy photons. However, the band edge positions may not be compatible with the electrochemical potential resulting in the formation of trap states within the crystal structure which can act as recombination centres. Thus, the majority of holes created in the bulk of the material will be lost through recombination before reaching the material (electrode)/electrolyte interface. Therefore, in order to overcome the drawbacks particularly in extending the photo-response of In$_2$O$_3$ towards the visible region, In$_2$O$_3$ is combined in various forms with other narrow band gap semiconductor material. In recent years, development of nano-composites/heterojunction materials like ZnFe$_2$O$_4$/ In$_2$O$_3$ (Zhang et al., 2016), TiO$_2$/ In$_2$O$_3$ (Wu et al., 2015) and Ni-Fe/ In$_2$O$_3$/WO$_3$ (Chaudhari & Singh, 2017) have been reported in attempts by researchers to shift the photo-response of In$_2$O$_3$ towards the visible region for photo-electrochemical process applications.

These In$_2$O$_3$ nanocomposites have been grown by various techniques which include hydrothermal process (Zhang et al., 2016b), chemical vapor deposition (CVD) (Shen et al., 2011a) and pulsed laser deposition (PLD) (Shen et al., 2011b). Most of these techniques involve the use of high growth temperature and tedious multi-step processes in order to obtain high-crystalline nanostructure composites. The first In$_2$O$_3$/TiO$_2$ nanocomposites are developed by electro-deposition method (Chandra & Srivastava, 1989). This technique requires the separate growth of TiO$_2$ and In$_2$O$_3$ as the In$_2$O$_3$ islands are formed by first depositing indium thin film on TiO$_2$ by electro-deposition followed by oxidation.

In this work, In$_2$O$_3$/W$_2$N nanocomposites were grown at low temperature using a single step deposition technique. The nanocomposites were grown by nitrogen plasma assisted in-situ thermal annealing at filament temperatures, $T_f$ of 1700 °C. The effect of thermal annealing on the structural and optical properties of the nanostructures are discussed.

**Materials and Methods**

A home-built plasma assisted reactive thermal evaporation system was used to deposit the In$_2$O$_3$ nanostructures on p-type Si (111) substrates as explained elsewhere (Saroni et al., 2017). The filament used was a ~ 33 coiled tungsten wire (with purity of 99.95 %) with the coil diameter of ~2 mm and coil length of ~2 cm. The filament was hung by two copper electrodes at a height of 1 cm above the substrate. An In wire (with purity of 99,999 %) with diameter of 1 mm and length of 2 mm was used and placed inside the coils. Before the substrates is placed into the chamber, the substrates were cleaned followed the RCA I and RCA II cleaning procedures (Kern, 1970). Prior to the deposition, the substrates were exposed to hydrogen plasma with rf power of 15 W for 10 mins. The hydrogen flow rate and substrate temperature were fixed at 100 sccm, and 200 °C, respectively. The purpose of using the hydrogen plasma is to remove any oxide contaminations on the c-Si substrate (Jeon & Kamisako, 2008). During the deposition, the filament temperature was fixed at approximately 1000 °C in N$_2$ plasma ambient. The rf power, N$_2$ flow rate, deposition pressure and substrate temperature were maintained at 150 W, 40 sccm, 0.4 mbar and 200 °C, respectively. The in-situ thermal annealing was performed after the deposition at $T_f$ of 1700 °C for 30 mins. The rf power, N$_2$ flow rate, deposition pressure and substrate temperature were fixed. Structural morphologies of the In$_2$O$_3$ based nanocomposites was analyzed using Hitachi SU 8000 FESEM at low electron accelerating voltage of 2 kV. Crystalline patterns of the nanocomposites were obtained by PANalytical Empyrean X-ray diffractometer with the X-ray
wavelength of 1.5406 Å and the 2θ range of 20 to 80° at a fixed grazing incidence angle of 0.5°. The step time and step size of the scan was fixed at 2 seconds and 0.026°, respectively. The optical transmittance and reflectance spectra of the nanocomposites were obtained using an UV-Vis–infrared spectrophotometer (Lambda 750, PerkinElmer). The chemical states of the nanocomposites were examined by X-ray photoelectron spectroscopy (XPS, PHI Quantera II) system. A monochromatic Al K-alpha (1486.6 eV) at 25 W (15 kV and 3 mA) was used with incident angle and sample surface under base pressure at 90° and 2 × 10⁻⁷ Pa, respectively.

**Result and Discussion**
The comparison between the XRD patterns of the In₂O₃ nanostructure and In₂O₃/W₂N nanocomposites shown in **Figure 1**. The formation of In₂O₃ nanostructure are confirmed by the appearance of the small diffraction peaks of In₂O₃ observed at 30.5 and 50.9° which correspond to the (100) and (440) orientations, respectively [JCPDS card No. 00-065-3170]. Metallic Indium (In) peaks are also observed at 32.9, 39.2, 54.5, 56.6, and 63.2° corresponding with crystallographic planes of (101), (110), (112), (200), and (103) orientations, respectively [JCPDS card No. 01-085-1409]. The formation of In₂O₃/W₂N nanocomposites occur as the nanostructures are treated by the in-situ thermal annealing at T_f of 1700 °C. A significant sharp diffraction peaks of W₂N are produced at 37.7, 43.9, 63.7, and 76.5° which are indexed to the cubic W₂N crystallographic planes of (111), (200), (220), and (311) orientations, respectively [JCPDS card No. 00-025-1257]. For the as-grown In₂O₃ nanostructures, the presence of metallic in particles indicates that the T_f was not sufficient for the in droplets to react with N or O adatoms and the short deposition time of 5 mins further reduces the possibility of any reaction. In-situ thermal annealing is needed for the as-grown sample so that the adatoms mobility is increased and the surface diffusion mechanism is thermally activated, subsequently forming the composite nanostructures. **Figure 2** shows the FESEM images of the as-grown In₂O₃ nanostructure and In₂O₃/W₂N nanocomposites prepared by plasma assisted reactive thermal evaporation and nitrogen plasma assisted in-situ thermal annealing at filament temperatures of 1700 °C, respectively. The In₂O₃ nanostructure shows the micro-grains are in irregular shape and size as illustrated in **Figure 2a**. The average size ranges from 200-300 nm with shapes of different facets (three, four, five, six, and eight faces) corresponding to triangular, rhombohedral, pentagonal, hexagonal, and octahedral shapes respectively. The formation of the micro-facets indicates that these In₂O₃ micro-grains are mostly crystalline in structure. As the nanostructure treated by the in-situ thermal annealing at 1700 °C, the nanostructure tends to change to a rhomboidal shaped grain with significant crystal facets of the crystallites as depicted in **Figure 2b**. This is attributed to the surface heating effect which initially ejecting the W adatoms from the tungsten filament as reported in our earlier work (Saroni et al., 2017). Moreover, the filament thermal irradiation results in the formation of W₂N on the surface of the In₂O₃ nanostructures.
Figure 1 XRD pattern of In\textsubscript{2}O\textsubscript{3} nanostructure and In\textsubscript{2}O\textsubscript{3}/W\textsubscript{2}N nanocomposite

Figure 2 FESEM images of (a) In\textsubscript{2}O\textsubscript{3} nanostructure, and (b) In\textsubscript{2}O\textsubscript{3}/W\textsubscript{2}N nanocomposite

Figure 3 illustrates the Tauc plot of optical energy gap of In\textsubscript{2}O\textsubscript{3} nanostructure and In\textsubscript{2}O\textsubscript{3}/W\textsubscript{2}N nanocomposites. The result shows that the $E_g$ value of the as-grown samples (2.89 eV) is slightly lower than that of cubic In\textsubscript{2}O\textsubscript{3} nanostructure (3.75 eV) as reported in literature (Girtan et al., 2000). As the In\textsubscript{2}O\textsubscript{3}/W\textsubscript{2}N nanocomposite formed, the $E_g$ value drastically changed to 1.69 eV. Tauc plot is calculated based on transmittance and reflectance value from UV-Vis analysis as reported elsewhere (Saroni et al., 2017). The narrowing bandgap towards visible range of light is due to the presence of W\textsubscript{2}N on the surface of the nanostructure that formed the nanocomposites. The in-situ thermal annealing leads to the increase of heating surface and thermal irradiation from the filament, that provides reactive N ions. As a result, the N ion bombardment effect leads to more N adatoms being incorporated into the nanostructures. Therefore, it tends to form W-N bonds which contributes to the narrowing of the $E_g$ of the nanocomposites.

In order to confirm the chemical composition and purity of the as-grown In\textsubscript{2}O\textsubscript{3} nanostructure and In\textsubscript{2}O\textsubscript{3}/W\textsubscript{2}N nanocomposites, XPS characterization was further analysed. Figure 4 shows the wide scan and typical deconvolution of In\textsubscript{3d\textsubscript{5/2}} and W\textsubscript{4f} spectra of the In\textsubscript{2}O\textsubscript{3}/W\textsubscript{2}N nanocomposites. The wide scan shows the appearance of W4f peak at range 28 - 42 eV for the In\textsubscript{2}O\textsubscript{3}/W\textsubscript{2}N nanocomposites while no W4f peak was observed for In\textsubscript{2}O\textsubscript{3} nanostructure. This further confirms that in-situ thermal annealing leads to the formation of W\textsubscript{2}N resulting the formation of In\textsubscript{2}O\textsubscript{3}/W\textsubscript{2}N nanocomposites. Three deconvoluted peaks of In\textsubscript{3d\textsubscript{5/2}} band located at 443.3, 444.5, and 445.3 eV corresponding to In-In, In-N and In-O bonds respectively.
(Barick & Dhar, 2015) are observed in Figure 4b. The high intensity In-O peak observed from XPS in the nanocomposite annealed suggests that this peak is produced by the In$_2$O$_3$ nanostructures since In$_2$O$_3$ peak in XRD is absent for the annealed sample. This may be due to the lower crystallinity of the In$_2$O$_3$ nanostructure as confirmed by the decrease in crystallite size with introduction of in-situ thermal annealing (Saroni et al., 2017). The formation of In$_2$O$_3$/W$_2$N nanocomposites are further confirmed by the presence of the W4f band shown in Figure 4c. The W 4f band is well resolved into three component peaks in this figure. These component peaks appear as doublet peaks at 32.4 and 34.4 eV corresponding to the W4f$_{7/2}$ and W4f$_{5/2}$ respectively of the W$_2$N phase (denoted as W–N bond) (Jiang et al., 2006). The W4f doublet peaks at 33.2 and 34.9 eV, and 36.2 and 38.2 eV are associated to WO$_2$ and WO$_3$ phases respectively (Jiang et al., 2006).

**Figure 3** Tauc plot of the In$_2$O$_3$ nanostructure and In$_2$O$_3$/W$_2$N nanocomposite

**Figure 4** (a) Wide scan XPS spectra of In$_2$O$_3$ nanostructure and In$_2$O$_3$/W$_2$N nanocomposite, (b) Typical XPS deconvolution of In3d$_{3/2}$, and (c) Typical XPS deconvolution of W4f
Conclusion

Simple growth technique of In$_2$O$_3$ nanostructure and In$_2$O$_3$/W$_2$N nanocomposites have been successfully demonstrated using the plasma assisted reactive thermal evaporation and nitrogen plasma assisted in-situ thermal annealing technique, respectively. Formation of In$_2$O$_3$/W$_2$N nanocomposites was shown to result in a substantial decrease in the optical energy gap towards visible range from 2.89 eV to 1.69 eV of In$_2$O$_3$ nanostructure and In$_2$O$_3$/W$_2$N nanocomposites, respectively. The in-situ thermal annealing enhances the surface mobility of the N adatoms to reach the nucleation sites to form crystalline W$_2$N. This work presents a promising photoelectrochemical behaviour of In$_2$O$_3$/W$_2$N nanocomposites that could be applicable for photoelectrochemical applications and bring new insights into the simple growth technique of nanocomposites with superior visible light induced photoelectrochemical activity.

Acknowledgement

This work was supported by the University of Malaya High Impact Research Chancellery Grant of UM.C/625/1/HIR/237 and the University of Malaya Postgraduate Research Fund (PPG) of PG073-2015A. One of the authors, Azianty Saroni is also grateful to the Ministry of Higher Education (MOHE) and MARA University of Technology (UiTM) for the scholarship support.

Conflict of interests

We declare there is no conflict of interest.

References


