SYNTHESIS OF In_2O_3 NANOWIRES FOR THE APPLICATION OF LPG SENSOR

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Abstract

In_2O_3 nano-column arrays are synthesized on p-type Si substrate by glancing angle deposition technique (GLAD). Indium Oxide is a wide-band gap Semiconductor which shows prospective potential for gas sensors. After the deposition is completed, the Crystallinity and the Orientation of the as-deposited Indium Oxide Nanowires are observed using the X-ray Diffractometer (XRD). Extrapolation of the linear part of the curve to the hv-axis from E Vs $(\alpha h\nu)^2$ graph from optical absorption spectrum yields a bandgap close to 3.3eV. Silver (Ag) contact is made over In_2O_3 nanowires to form In_2O_3 LPG sensing device. At 2V,under exposure to LPG, the device shows nearly 5 times enhancement in the sensitivity as compared to exposure in ambient atmosphere. This result clearly indicates that In_2O_3 NW device is a very good contender for efficient and cost effective LPG sensor if fabricated commercially on large scale

Keywords: *GLAD,In_2O_3 Nanowire, XRD, SEM, Optical absorption, Photoluminescence (PL), electrical characteristics*

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1. INTRODUCTION

Indium oxide is a wide band gap (~3.6 eV) [1], transparent and highly conducting [2]. Because of these properties it has its application in sensors and detectors [3-6]. There are different techniques for fabricating one dimensional In2O3 nanostructure, they are thermal evaporation [7-8], pulse laser ablation [9], chemical vapour deposition [10], sputtering [11], vapour liquid solid condensation [12], atomic vapour deposition [13]. The main disadvantage with the above mentioned techniques is that the nanostructures obtained are not perpendicularly grown on the substrate. Perpendicular and well patterned [14] NW array is very much essential to obtain high surface-to-volume ratio, which in turn will greatly enhance the sensitivity of the fabricated nanostructure by facilitating large surface area for reaction to take place. With the help of GLAD technique the growth and orientation of nanowire [15] can be controlled effectively. GLAD technique is an effective technique for vertically growing well patterned NW on the substrate. In this study we have synthesized the vertically oriented In2O3 NW arrays on Si substrate by using GLAD technique inside e-beam evaporator. The characterization of the fabricated samples has been discussed.

Liquefied petroleum gas (LPG) is utilized in almost every kitchen all over the world. It is therefore, referred as a town gas or cooking gas. Along with inevitable domestic use, it is utilized in large extent for industrial purposes and in laboratories as fuel. Cooking gas consists mainly of butane and propane, which are colourless and odourless gases [17-19]. It is usually mixed with compounds of sulphur (viz. methyl mercaptan and ethyl mercaptan) having foul smell, so that its leakage can be noticed easily. This gas is potentially hazardous because explosion accidentsmight be caused when it leaks out by mistake. It has been reported that, at the concentration up to noticeable leakage, it is very much more than the lower explosive limit (LEL) of the gas in air. Explosion accidents destroyed many industries, laboratories, kitchens and houses, buildings, societies and what not? Due to the increased awareness of potential explosive in bothindustrial and domestic environments, there is a growing need todetect and monitor LPG. Many researchers are working on LPG sensor, but could not meet the challenges up to the depth of demand by society. So, there is a great demand from the society of detecting LPG for the purpose of safety applications in domestic and industrial fields.

2. EXPERIMENTAL PROCEDURE

2.1 Synthesis of In_2O_3 NW and Device Fabrication

In_2O_3 NW arrays were synthesized on the P-type Si<100> substrate. With the help of GLAD technique In_2O_3 NW were deposited over cleaned 1 cm x 1 cm p-type Si substrate inside E-beam evaporation chamber. The substrate was cleaned successively using electronic grade acetone, methanol and 18 MΩ DI water, rinsed for 10 sec in each solvent. The deposition was carried out at a chamber pressure of around ~1 X 10^{-5} mbar. A constant growth rate of $1.2A^{\circ}s^{-1}$ was maintained throughout the deposition process. For achieving vertical growth of NW, the substrate were kept at 85° with respect to the perpendicular line between the material source and the planar substrate and a separation of 24 cm is kept between substrate holder and E-beam source. Azimuthal rotation of 120° is maintained for synthesis of NW. In_2O_3 LPG sensing device is fabricated by deposition of In_2O_3 TF over the Si substrate, then In_2O_3 NW were grown over the TF using GLAD, Ag (silver) contacts were made over the NW. Ag was evaporated through the aluminum mask having holes of diameter 2 mm on top of In_2O_3 NW to get a schottky contact.

3. CHARACTERIZATION

XRD analysis was done by D8 ADVANCE ECO BRUKER using CuKα radiation. The Photoluminescence (PL) study was carried out at room temperature using F-7000 FL spectrometer. The optical absorption analysis was carried out using UV-Vis spectrophotometer. The electrical characteristics of the device (Ag/In_2O_3-NW/In_2O_3-TF/Si) were studied by using Keithley 2400 source measure unit. The response of the device was studied both in presence and in absent of LPG.

4. RESULT AND DISCUSSION

Figure 2(a) shows the X-ray diffraction (XRD) analysis of the as deposited In_2O_3 NW which shows the presence of different phases i.e. (222),(400) and (004). The phases at (222) and (400)are attributed to In_2O_3 [JCPDS, 06-0416] [20]. The diffraction pattern from 004 is also observed which is due to Si substrate [JCPDS, 27-1402] [21-22]. Therefore, the XRD pattern reveals the polycrystalline nature of the deposited In_2O_3NW.

5. OPTICAL CHARACTERIZATION

Optical absorption measurement was carried out on In_2O_3 NW/Si Nanostructure samples in the wavelength range of 200–800 nm at room temperature. Enhance absorption was observed from In_2O_3 NW sample both in the visible and UV region (Fig 2(b)), which is due to their large surface area to volume ratio of the In_2O_3 NW [23]. Fig 2(c) shows the $(\alpha h\nu)^2$ versus (hν) for the as deposited In_2O_3 NW sample, where hν is the sample energy and α is the absorption of each wavelength which is given by $\alpha = \frac{4\pi k}{\lambda}$, where k = absorption index.. The value of band gap was determined by extrapolating the straight line portion of the $(\alpha h\nu)^2$ on the x-axis. From the graph, we have seen the optical band gap value close to ~ 3.3 eV (375 nm). Multiple scattering of incident photon occurs between consecutive vertically grown NW, as a result the NW absorbed most of the incident photon. Fig 2(d) shows the PL spectrum of In_2O_3 NW grown over Si substrate. The PL measurement has been carried out at room temperature on the as deposited In_2O_3 NW using an excitation wavelength of 250 nm. The band gap of the In_2O_3 can also be estimated from the peaks in the photoluminescence (PL) curve. From the figure, maximum peak is observed at the wavelength λ=346.78 nm (3.57 eV). PL emissions are possibly due to the effect of oxygen vacancy [24].

6. ELECTRICAL CHARACTERISTICS

Fig 3 shows the Plot between Current density and voltage. The black curve indicates the response of the fabricated device when it is exposed to ambient atmosphere. When the device is exposed to atmosphere, atmospheric oxygen (O_2) will get absorbed onto the surface of In_2O_3 NW, thereby forming a layer of O^-(ion) on the NW surfaces. These O^- will become the active sites for the absorption of different constituent of LPG. The red curve indicates the response of the device when exposed to LPG.The turn ON voltage for the device in ambient atmosphere is found out to be 2V, on exposure to LPG it reduces to 0.15V. It is very clear from graph that there is significant improvement in device response when exposed to LPG, this is due to the release of extra electrons, when O^- (ion) attached to In_2O_3 NW react with LPG.

$$C_4H_{10} + 13O^- \longleftrightarrow 4CO_2 + 5H_20 + 13e^-$$

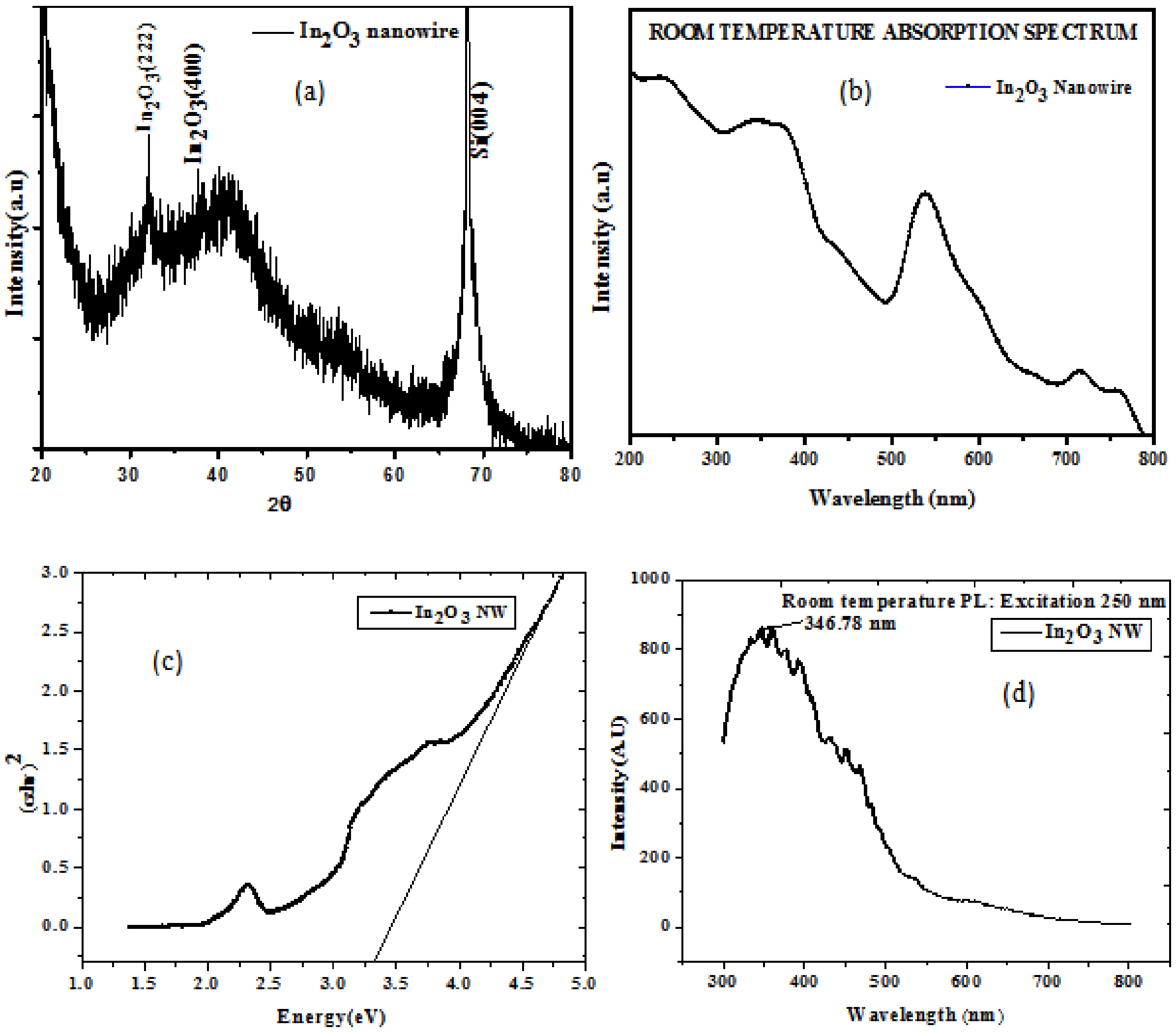


Fig.2: (a) XRD pattern of as deposited In_2O_3 NW/Si nanostructure (b) Room Temperature Optical absorption spectrum of In_2O_3 NW/Si Nanostructure. (c) $(\alpha h\nu)^2$ Vs Energy curve and (d)Room temperature Photoluminescence spectrum of In_2O_3NW.

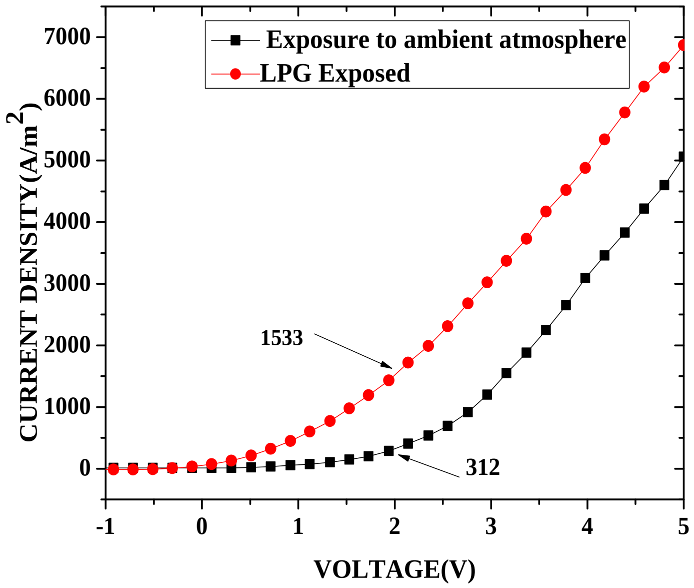


Fig.3: Current density versus Voltage

7. LPG SENSING MECHANISM

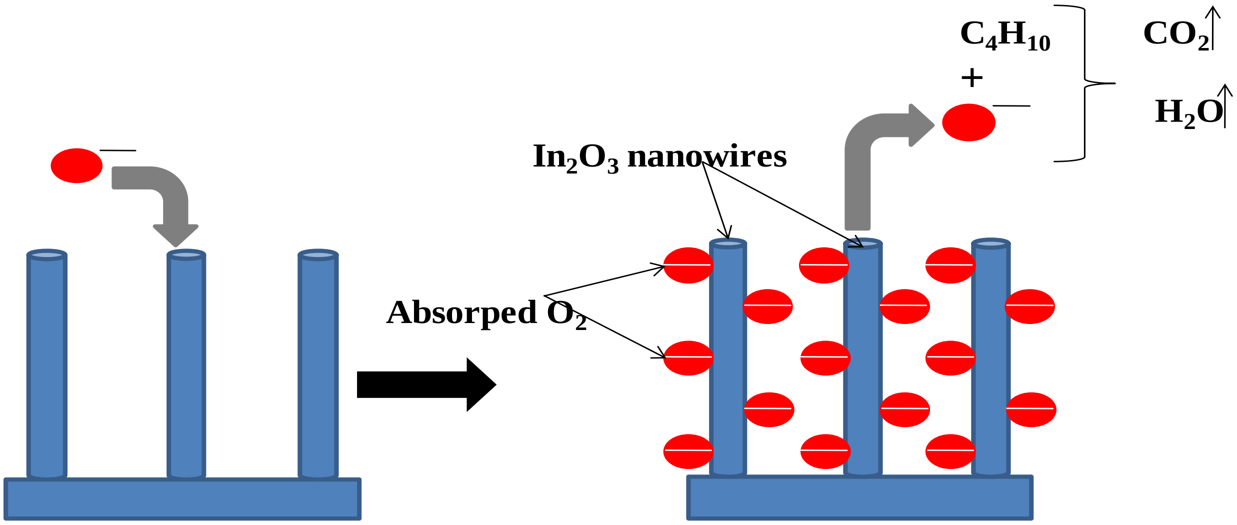
The gas sensing mechanism (fig.4) can be explained in terms of conductance by absorption of atmospheric oxygen on the surface of the In_2O_3 NW with the LPG [25]. The atmospheric oxygen absorbs on the surface by extraction of electrons from conduction band are mainly responsible for the detection of LPG which can be shown as:

$$O_{2(\text{air})} + 2e^-_{(\text{cond. band})} \longrightarrow 2O^-_{(\text{NW surface})}$$

It would result in decreasing conductivity of the device when LPG reacts with the absorbed oxygen on the surface of the NW, LPG constituent gases are oxidized to CO_2 and H_2O following a series of intermediate stages. This liberates free electrons in the conduction band. The final reaction takes place as

$$C_4H_{10(\text{gas})} + 13O^-_{(\text{NW surface})} \xrightarrow[\text{(cond. band)}]{} 4CO_{2(\text{gas})} + 5H_2O_{(\text{gas})} + 13e^-$$

These generated electrons contribute to a sudden increase in conductance of the fabricated device.



$$C_4H_{10} + 13O^- \longleftrightarrow 5H_2O + 4CO_2 + 13e^-$$

Fig 4: Oxygen absorption mechanism

8. CONCLUSION

In summary, we have fabricated the In_2O_3 nanowires by using e-beam evaporation method with the help of GLAD technique.. XRD analysis reveals the polycrystalline nature of the nanostructure. And the absorption spectrum reveals that the nanostructure exhibited a wide range of absorption ranging from 330- 400 nm wavelength due to the presence of In_2O_3NWwhich makes it suitable for a UV-Viz detectionalso. It is also found that at 2 V there is 5 times device response improvement when exposed to LPG. This result clearly indicated that In_2O_3 NW based device is a very good contender for efficient and cost effective LPG sensor if fabricated commercially on large scale.

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