ARTICLE IN PRESS

Scripta Materialia xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Scripta Materialia

journal homepage: www.elsevier.com/locate/scriptamat

Morphology-inspired low-temperature liquefied petroleum gas sensors of indium oxide

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ARTICLE INFO

Article history:
Received 26 February 2015
Accepted 7 May 2015
Available online xxxx

Keywords:
In_2O_3
LPG sensors
Nanostructures

ABSTRACT

Low-temperature wet chemical method has been applied to produce indium oxide (In_2O_3) nanostructures *viz.* cracked-cubes and the maize-corns which were then employed for their structure, morphology and surface-related measurements and finally envisaged in detection of liquefied petroleum gas (LPG) at different temperatures and concentrations. At 1000 ppm LPG, cracked-cube-based In_2O_3 sensor demonstrated lower operating temperature (135 °C) and gas sensitivity (44.35%) than the maize-corn-type (155 °C, 36.51%). Except moderate difference in sensitivity there was negligible difference in response and recovery periods.

In recent years, gas detection and monitoring (due to serious air pollution globally) have created an increasing concern regarding the awareness of environmental protection and human health. In the field of air pollution, gas sensors play an important role [1]. Liquefied petroleum gas (LPG), one of the flammable gases, presents many hazards to both the humans and environmental issues. LPG is considered as fuel for domestic and industrial purposes. Increasing applications of LPG have caused several accidental explosions due to its leakage problem. This is because combustion accidents might be caused when it leaks out accidentally or by mistake. Thus, the requirements for reliable and sensitive gases detecting instruments have increased for safety at home as well as industries. Therefore, LPG sensor has become the subject of intense research as on today, in view of fundamental research as well as industrial applications. Despite of considerable efforts, developments in improving the performance of existing LPG sensors; quick response and recovery periods and extremely small detection level capacity, are still in progress and scientific community is looking for a reliable, efficient, simple and cost-effective chemical sensors (including LPG, CO_2, NO_2 and H_2S, etc.) for good sensitivity, common term used in scientific community to express gas reactivity with given nanostructure.

Recently, many efforts, in this field, are being devoted for synthesizing novel sensing nanomaterials of various metal oxides/chalcogenides for enhancing the gas detecting level. For example, metal oxides like α-Fe_2O_3 [2], ZnO [3,4], CdO [5], WO_3 [6] and SnO_2 [7,8], etc., have been envisaged greatly because of their abundant nature, low-cost for synthesis, availability in various appearances. Apart from these metal oxides, In_2O_3 has attracted considerable interests due to its remarkable electronic and optical properties; high electrical conductivity is very sensitive to the external environment, wide band gap energy (3.55–3.75 eV) and high free carrier mobility, etc., in addition to high sensing ability with gases including H_2S [9], NH_3 [10], CO [11,12], O_3 [13,14], Cl_2 [15], formaldehyde [16], acetone and toluene [17], H_2 [18], CO [19], and NO_2 [20], etc. On account of different surface areas and potential properties, nanostructures (morphologies) of In_2O_3 play potential role in window heaters, solar cells, liquid–crystal displays, etc. [21–26]. These morphologies exhibit superior gas sensing properties owing to their unique geometry and size- and shape-dependent characteristics. The morphology and structure-mediated gas sensors, undoubtedly, play the vital role in determining their electrochemical and optical properties. In general, low level detection limit of a particular gas should be as low as possible, i.e., parts per million (ppm) and moreover preferred gas (flammable) should efficiently react with available

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http://dx.doi.org/10.1016/j.scriptamat.2015.05.019
1359-6462/

morphology of either metal chalcogenide or oxide. Herein we experimentally proved that the nanostructures would absorb more LPG molecules than planar types. Several morphologies of In_2O_3, converted from indium hydroxide, including nanodots, nano and micro-spheres, nanocubes, multipods, lotus root-like nanocrystals, and one-dimensional nanocrystals, etc., are well-familiar [2]. Investigating gas sensors performance of LPG with new In_2O_3 morphologies, i.e., cracked-cubes and maize-corns, in particular those obtained at low temperatures, would be greatly fascinating and noteworthy. Usually, a smaller pore-size means worse diffusivity for gases, resulting in a lower sensitivity [27,28]. This demonstrates that pore-size and specific surface area of a particular morphology can be correlated with the sensing properties to establish basic morphology-LPG sensing relation [29].

In continuation to our ongoing research activities based on LPG sensors [30,31], herewith, In_2O_3 morphologies *viz.* cracked-cubes and maize-corns were firstly synthesized onto glass substrate with the help of co-ordination chemistry and Pearson's acid–base concept and further envisaged in LPG sensor application. Low-temperature wet chemical method, one of the simple, economic and eco-friendly methods, has been preferred for developing these morphologies. Experiments were set up for the design of LPG sensors based on these morphologies. Prior to measurement of LPG sensors, these samples were characterized for the structure and the morphology confirmations. We believe this work can provide a new insight on the design of morphology-based LPG sensors in the future.

Indium nitrate (0.1 M) and indium chloride (0.1 M) were separately dissolved in de-ionized water (25 mL), poured in falcon tubes of 50 mL capacity. To each of these solutions, 25 mL of 0.4 M urea was separately added. Two glass substrates were placed vertically and then tubes were sealed tightly and kept in a water bath maintained at 80 °C. After completion of reactions (indicated by white deposit on the wall of tube as well as at the bottom) after 12 h, the tubes were taken out from the baths, allowed to cool naturally and washed with tap-water connected to distilled water plant. It was found that the substrates were covered with white coating of indium hydroxide. These substrates with white product were washed with water, dried in a stream of air and annealed in furnace at 400 °C for 30 min for converting them into In_2O_3.

Crystal structure was determined using X-ray diffractometer (Rigaku D/MAX 2500 V, Cu-Kα, $\lambda = 0.15418$ nm). The surface contents with existing bonds on sample surfaces were obtained by X-ray photoelectron spectroscopy (XPS) measurement. Surface morphologies were confirmed with field-emission scanning electron microscope (FE-SEM, Hitachi S-4200) digital photoimages. The specific surface areas were measured from the Brunauer–Em mett–Teller (BET) analysis. The pore diameters were obtained from the adsorption branch of the isotherms, obtained from the Barrett–Joyner–Halenda (BJH) method. The sensor response was determined using Eq. (1) as LPG possesses the properties of reducing gas.

$$S = |R_a - R_g/R_a| \times 100\% \quad (1)$$

where R_a is the resistance of the form in air and R_g is that upon exposure to LPG.

Fig. 1(A) and (C) present cubes and maize-corn morphologies of indium hydroxide obtained from indium chloride and nitrate solutions, respectively. It is seen that Fig. 1(A) is smooth in appearance whereas after annealing smooth cubes turned into cracks and voids (Fig. 1B), called hereafter cracked-cubes indicating that during process of annealing hydroxide is converting into oxide by developing voids and cracks. Fig. 1(D) presents the FE-SEM image of maize-corns after air annealing onto glass substrate. Despite of identical deposition conditions, except change in indium precursor, cracked-cubes and maize-corns type morphologies were grown from indium chloride and indium nitrate precursors respectively, indicating that the type of metal salt, used in reaction, played an important role during a process of particular nanostructure growth. Before annealing and annealing there was no empty space indicating uniform growth for both morphologies. After annealing cubes were broken completely whereas maize-corns were narrowed slightly without developing cracks. The cubes were around 2 μm in lengths and about 500 nm in widths whereas, maize-corns were 1.66 μm in lengths. Each maize-corn was broad at its center and narrow at its one end. After annealing it was difficult to trace out the exact dimensions of cracked product, i.e., for cracked-cubes whereas maize-corns were relatively contracted from diameter side (∼1 μm). Under close inspection it was revealed that all cubes were not of same dimensions before annealing and edges were relaxed on one another. The maize-corns were rough in appearance before and after annealing. Due to smaller dimensions of cracked-cubes than relatively large-sized maize-corns superior sensing performance was anticipated on account of excess LPG molecules adsorption.

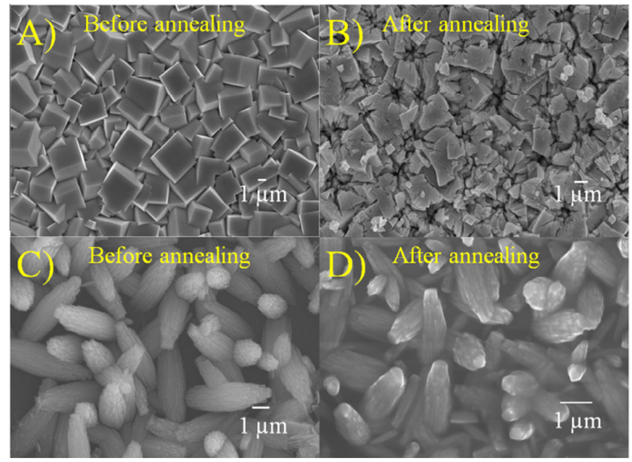

Fig. 1. FE-SEM images of In_2O_3. Cubes; (A) before annealing and (B) cracked-cubes after annealing (obtained from indium chloride) and maize-corns; (C) before annealing and (D) after annealing (from indium nitrate).

Fig. 2 shows the XRD spectrums of In_2O_3 cracked-cubes (Fig. 1B) and maize-corns (Fig. 1D). Qualitatively it was confirmed that the morphologies of In_2O_3 deposited onto glass substrate after annealing were changed to faint yellow from white, suggesting the formation of In_2O_3 from respective hydroxide. After annealing, both products demonstrated reflection planes corresponding to the cubic In_2O_3 with a lattice constant of $a = 10.11$ Å, consistent with JCPDS Card No. 71-2194 [32]. The intensities of the reflection peaks

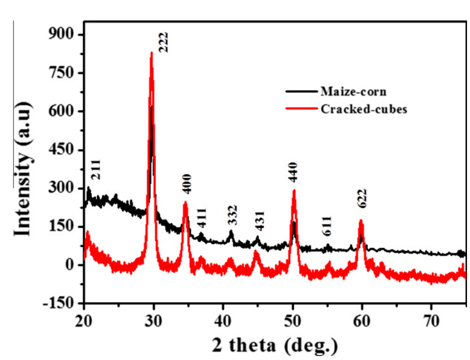

Fig. 2. XRD patterns of In_2O_3 cracked-cubes and maize-corns.