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Synthesis of vanadia nanorod arrays and their novel applications as alco-sensors

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ABSTRACT

Vanadia (V_2O_5) nanorod arrays were grown by oxidizing vanadium foil at five different voltages for 3 h through electrochemical anodic oxidation method. Dense aligned nanorods with L/D ratio 4.75-4.88 (diameter D ≈ 40–45 nm and length ≈ 190–220 nm) were grown at the optimized voltage 55 V. The dominant existence of V_2O_5 phase and its layered structure were verified by XPS and Raman spectrum analysis respectively. Linear I–V characteristic curve of the sensor based on V_2O_5 nanorod arrays confirms its Ohmic contact with the electrodes. Gas sensing investigations of the sensor reveals its n-type behavior with the average response magnitude of 6.13 in N_2 atmosphere, which signifies the industrial application of the sensor in a gaseous atmosphere. The sensor shows remarkable static response towards ethanol with lower detection threshold of 800 ppb and a maximum response magnitude of 7.27 at 500 ppm. Based on variable resistance model, a suitable gas sensing mechanism is also established.

1. Introduction

Being a volatile organic compound (VOC), ethanol has numerous utilizations in everyday life, such as a fuel additive, as a universal solvent in laboratories and industries, as an antibacterial, used in alcoholic beverages etc. Necessity of ethanol gas sensors is stipulated on the basis of their essential usage in many industries like transportation, nourishment, biomedical and securities [1]. Based on this crucial significance of ethanol detection, continuous efforts are in line to synthesize effective materials for its detection in biosensors, Schottky based sensors and conductometric gas sensors etc [1–3]. Among these, conductometric gas sensors (also called as semiconductors gas sensors or chemiresistors) are noteworthy, because they offer wide range of applications due to their simple configuration, facile device fabrication, and relatively understandable mechanism [4–6].

One dimensional (1-D) nanostructures (nanorods, nanowires, nanotubes etc.) of various metal oxides exhibit unique gas sensing behavior towards certain oxidizing and reducing gases. A few familiar 1-D metal oxides nanostructures have been enlisted in Table 1 [7]. Due to the exclusive structural flexibility, good catalytic behavior, and facile availability, vanadium pentoxide (V_2O_5) has been under-investigation for conductometric gas sensors since last decade. In particular, its 1-D nanostructures have shown VOCs' detection ability with reasonable response [8–15]. However, the issues of long term reliability, limited selectivity and inadequate realization of certain sensing parameters such as working temperature and sensitivity, have restricted the practical applications of conductometric gas sensors based on 1-D V_2O_5 nanostructures [4,6]. Incessant efforts are being made to remove these short comings and develop the gas sensors with near-to-ideal characteristics.

One such research methodology is based on the growth of 1-D nanostructures in 2-D or 3-D arrays geometries, which result in remarkable gas sensing properties due to the provision of a uniform and enlarged contact area of gas sensors devices with the electrodes of the gas sensing measurement system. Owing to Ohmic contacts of the 1-D nanostructures arrays, lowering in working temperature (upto room temperature) is foreseeable, which certainly outcomes in minimum power consumption. Array of 1-D nanostructures can be likened with the natural olfactory system of human nasal cavity to achieve the desired selectivity. Earlier, this kind of geometrical scheme has already been designed/grown forseveral metal oxides (ZnO, TiO_2, Co_3O_4, and CuO etc.) through template based electrodeposition, hydrothermal and CVD synthesis methods, respectively, which were investigated for batteries and supercapacitors appli-

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Table 1
Gas sensors based on quasi 1-D metal oxides nanostructures [15].

Material	Nanostructure type	Target gases	Media	Detection limit	Response time	Remarks
ZnO	nanorods	NO_2, NO, N_2O	Air	10 ppm (125 °C)	30 s	High W.T
	nanowires	HCHO, NH_3, LPG, CO	Air	50 ppm (min.), 330 °C	N/A	High W.T and High D.L
In_2O_3	Single nanowire	CO, H_2	Air	10 ppm	<60 s	Selectivity issue
				500 ppm 275 °C		
		H_2S, HCHO, CH_4	Air	50 ppm, 250 °C	N/A	High W.T
	Multi-wires	NH_3, NO_2	Air	500 ppm	6 min, 16 min	High t_{resp}
				5 ppb		
		Acetone	Humid air	25 ppm (400 °C)	6 min	High W.T and high t_{resp}
WO_3	nanowires	NO_2, NO, N_2O	Air	0.1 ppm (250 °C)	10 s	Oxidizing target gas sensor
SnO_2	Single nanowire	CO	Air	25 ppm, 280 °C	N/A	High W.T
		NH_3		100 ppb, 300 °C		
		CO	Humid	0.1 ppm, 400 °C	N/A	High W.T
		NO_2	Air			
TiO_2	Nanotubes	H_2	N_2	1000 ppm, 290 °C	150 s	High W.T, High D.L
CuO	Nanoribbons	HCHO	Air	5ppm	N/A	Selectivity issue

W.T; Working temperature, D.L; Detection limit, N/A; Not available.

cations [16–18]. ZnO and CuO nanorods arrays (as synthesized by hydrothermal and template based electrodeposition, respectively) have also been investigated for sensing of various gases [19,20]. Besides this, single crystalline V_2O_5 nanorods arrays, Ni-V_2O_5 core–shell nanocable arrays and V_2O_5-TiO_2 composite nanorod arrays have been grown through template based electrochemical deposition, and investigated for energy storage purposes [21–23]. Earlier, our group has also synthesized the aligned hydrated V_2O_5 nanorod arrays through a template based solution approach that have shown good field emission properties [24].

Our present work has three motives. Firstly, the template based synthesis methods have certain limitations. Particularly in the sense of feasibility for bulk production, because these are relatively time consuming, costly and deliver low yield. Designing of facile and economic template free methods are always favored for large mass scale production on industrial level. Secondly, V_2O_5 nanorods arrays are rarely studied for gas sensing applications. Finally, due to versatile features of V_2O_5, anticipation of significant gas sensing performance exists.

In this work, we report the growth of V_2O_5 nanorod arrays via electrochemical anodic oxidation. This is a template free, economic and time-saving synthesis method, is therefore very feasible for bulk production. Sensors based on V_2O_5 nanorod arrays are investigated for sensing of ethanol in air and nitrogen atmospheres. Optimized geometries of the V_2O_5 nanorod arrays exhibit interesting sensing characteristics, which could be explained on the basis of variable resistance model effectively. A schematic gas sensing mechanism has also been suggested.

2. Experimental

2.1. Growth of V_2O_5 nanorods arrays

Prior to anodization reaction, the surface of the commercial vanadium foils was polished by abrasive papers, followed by successive ultra-sonication in acetone, ethanol and deionized water for 10 min each, respectively. Finally, the foils were dried at 80 °C for 30 min.

Electrochemical anodic oxidation (EAO) was accomplished as reported by our group earlier [25]. In a typical procedure, the pretreated V-foil and graphite plate were used as anode and cathode, respectively. The electrolyte solution containing 300 mL ethylene glycol, 4.5 mL deionized water (1.3% V/V) and 400 mg ammonium fluoride was used. Anodization was performed at five different voltages (30, 40, 50, 55 and 60 V) for 3 h. After completion of oxidation reaction, the anodized V-foils were soaked in deionized water three times, dried at 80 °C for 30 min and were finally annealed at 350 °C for 2 h. The samples were marked as AV-30, AV-40, AV-50, AVO and AV-60, corresponding to respective anodizing voltages (30, 40, 50, 55 and 60 V), respectively. It is worthy to be mentioned that for the sample AVO (selected as optimum after FESEM testing), the surface of V-foil was studied at four stages; i.e. after pre-treatment, after 1 h anodization, before annealing and after annealing. Anodization setup is shown in Fig. 1(a).

It was observed that the colour of electrolyte solution changes during anodization process. Prior to the growth, continuum thin film develops on the surface of V-foils by oxidation and electrolyte solution turns its colour to light blue. These surface thin films, on primary anodization, will eventually crop growth to the nanorods rooted inside the thin film. During the roots generation, the electrolyte will turn its colour to light yellow, which indicates the obvious foundation of V_2O_5 phase. Further anodization will result in the aligned nanorods transpiring out of the roots, populated throughout the vanadium surface. Annealing of the anodized vanadium foil on 350 °C merely burns the impurities attached to the nanorod walls from the electrolyte solution and have no effect upon the structure or phase of nanorods. Colour changes as observed during anodization process are shown in Fig. 1(b).

2.2. Characterization

The samples were characterized for crystal structures and morphology through X-rays diffraction (XRD, PertPro, PANalytical, Netherlands) and field emission scanning electron microscopy (SEM, Zeiss Ultra Plus, ZEISS, Germany), respectively. CuK_α line ($\lambda = 1.54$ Å) was applied in X-rays diffraction. Oxidation states of the V_2O_5 were found by X-rays photoelectron spectroscopy (XPS, Al 300W, PE 100 eV). Raman spectroscopy (INVIA; RENISHAW, UK) was performed to investigate the states and modes of orientation. Gas sensing measurements were taken by using WS-30A, and Keithley 4200 in connection with thermal probe station.

2.3. Fabrication of gas sensing devices

Gas sensing devices based on V_2O_5 nanorods arrays were fabricated by RF magnetron sputtering technique [26]. Typically, Pt electrodes were coated on the top of nanorod arrays film, which was grown on the surface of vanadium foil. Inter-electrodes' distance was maintained as 1 mm and current of 50 mA was applied. Gas sensor devices of dimensions $6 \times 10\,mm^2$ were fabricated by this method. Top view of the sensor device is shown in Fig. 2. RF-magnetron sputtering has the advantages that it avoids the interaction of electrodes with the target gases and increases the lifetime.