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Nanoporous vanadium oxide network prepared by spray pyrolysis

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ABSTRACT

Interconnected nanoporous vanadium oxide thin films are successfully prepared on glass substrates by spray pyrolysis technique. Deposition was carried out at 673 K using aqueous solution of ammonium metavanadiate by maintaining spray rate at 10 ml/min. prepared samples were characterized by means of structural, optical and morphological characterizations. X-ray diffraction and optical study confirms deposited samples are of orthorhombic crystal structure with 2.25 eV optical band gap. Fourier transform infrared spectroscopic (FTIR) analysis shows bonding of vanadium oxide and supports the XRD results. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images revealed the formation of interconnected nanoporous network and nanorods. Nanorods were 10–20 nm wide and 150–200 nm in average length. A supported growth mechanism for their formation is projected.

1. Introduction

Nanoporous/nanostructured materials with defined size and shape have attracted much more interest in fundamental research due to their particle size, porosity and size distribution on physical and optical properties of the materials [1–3]. Now days V_2O_5 has attracted much interest because of their potential use in rechargeable lithium-ion batteries [4], catalysis [5], actuators [6], sensors [7], optical switching devices [8] and electrochemical supercapacitors [9–11]. However, these applications predominantly depend on the techniques used to grow the films and the material performance linked with the crystallinity and morphology of the films [12]. Microporous V_2O_5 films have been prepared by sol–gel [13], anodic deposition [14], sputtering [15], electron-beam evaporation [16], etc. but literature does not support the preparation of interconnected nanoporous V_2O_5 films by spray pyrolysis technique via aqueous route. Spray pyrolysis technique (SPT) offers good quality and adherence of the material on large area substrates by controlling preparative parameters like spray rate, distance to substrate, solution concentration, volume, air flow rate, etc. It also facilitates precise control over droplets. It offers several advantages over conventional deposition techniques for the control of stoichiometry and film structure. This paper reports preparation of interconnected nanoporus vanadium oxide thin films by the well known spray pyrolysis technique at 673 K deposition temperature. The crystalline structure and optical properties of the prepared nanoporus vanadium oxide thin films have been studied well in detail.

2. Experimental

All the chemicals were used for the preparation of V_2O_5 thin films are of analytical grade (S. d. fine make) and used without further purification. Ammonium metavanadate was used as an initial precursor. In typical preparation, 0.05 M ammonium metavanadate was dissolved in 40 ml of double deionized water under vigorous stirring of mixture for 10 h. Continuous stirring results yellowish solution which was further used for deposition of V_2O_5 samples. Samples were deposited on pre-heated glass substrates (Blue star make) at 673 K using 40 ml resulting solution, at 10 ml/min spray rate using air as a carrier gas with 10 L min^{-1} flow rate. The nozzle to substrate distance was optimized to be 30 cm. Prepared samples were further used for different characterizations.

Samples were characterized by X-ray diffraction using Rigaku (D/max2550Vb+18 kw with CuKα 1=1.54056 Å) X-ray diffractometer, by varying 2θ from 10° to 90° by the step width of 0.2°. The optical absorption and transmittance spectra were recorded using a Shimadzu (UV 3600) spectrophotometer over the wavelength range of 300–1000 nm. Fourier transform infrared spectra were obtained using Perkin Elmer IR spectrophotometer-783 in the spectral range 400–4000 cm^{-1}. Scanning electron microscopy images were obtained using a JEOL Model JSM-6360 microscope and transmission electron microscopy images were obtained using Philips CM30 TEM, at an operating potential of 200 kV. Weight of the deposited material was measured by using

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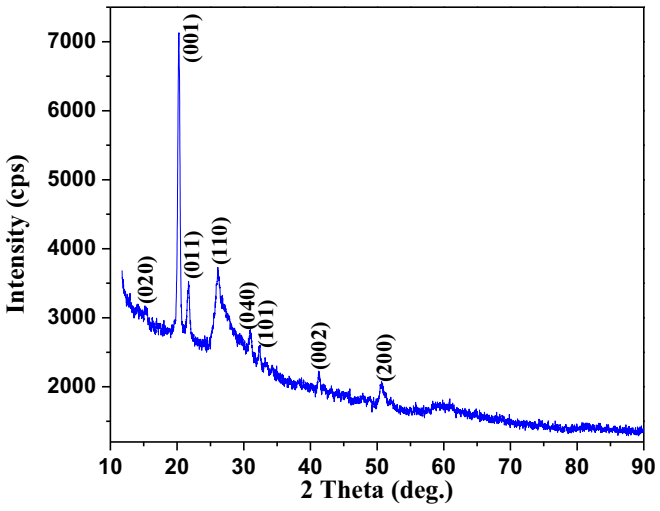

Fig. 1. XRD Pattern of as – prepared V_2O_5.

high accuracy (1×10^{-5} gm) microbalance (Tapson's, Model-100S).

3. Result and discussion

To determine the crystal structure, orientation of the planes and crystallite size, XRD pattern of the deposited samples were carried out. Fig. 1 represents the XRD patterns of V_2O_5 samples deposited at 400 °C. Observed diffraction peaks corresponds to the (020), (001), (011), (110), (040), (101), (002) and (200) planes indicated that V_2O_5 has polycrystalline nature with an orthorhombic crystal structure. The obtained '*d*' values were in good agreement with standard '*d*' values taken from JCPDS card no. 85-0601. The same values were reported by Wang et al. by Sol–gel method [17]. The UV–vis absorption spectrum of nanoporous V_2O_5 samples is shown in Fig. 2(a). Spectrum was recorded in the wavelength (λ) range 300 nm to 1000 nm, absorption edge was observed at 360 nm. The observed value of 'α' is in the order of 10^4. It has been observed that absorbance decreases with increase in wavelength and become stable near the band edge. The recorded data was further used to calculate the band gap energies of the deposited samples using Tauc plot [18]. Fig. 2(b) shows the corresponding band gap, and it was calculated to be 2.25 eV. $(\alpha h\upsilon)^2$ vs $h\upsilon$ plot consist of linear portion, which exhibits the presence of direct inter band transition in samples.

Fig. 3(a)–(d) shows typical SEM and TEM images of V_2O_5 sample. Fig. 3(a) and (b) shows the SEM images of V_2O_5 sample, from which interconnected nanoporous network like morphology is apparent at 50 and 10 μm magnification respectively. Fig. 3 (c) conform the interconnected nanoporous network and in inset of Fig. 3(c) gives the SAED pattern conforming the crystalline nature of V_2O_5 sample. Fig. 3(d) shows some nanorods of 10–20 nm wide and 150–200 nm in average length. Calculated thickness of the deposited film is ~300 nm, measured by using weight difference method. The interconnected nanoporous network offers maximum porosity as compared to highly compact surface structure, which is favorable for above reported applications.

Fig. 4 shows FT-IR transmittance spectrum of V_2O_5 sample carried in the wavelength range 400–4000 cm^{-1}. The FT-IR transmittance spectrum gives information about phase, composition as well as the way by which oxygen is bound to the metal ions (M–O structure). Spectrum comprises of three transmittance peaks. The characteristic features of oxides appear below 1200 cm^{-1}. The three broad absorption bands at ~990, ~783and ~548 cm^{-1} were observed for all the samples can be attributed to V=O stretching vibrations of the vanadyl group, asymmetric and symmetric stretching vibrations of V–O–V bands respectively [19]. It is observed that both the V–O–V and V=O stretching vibrations of the terminal vanadyl are present in deposited samples. The conformed structure of V_2O_5 phase is analogous to the data obtained from XRD (JCPDS card no – 85-0601).

4. Conclusions

Interconnected nanoporous network like V_2O_5 samples can be deposited by spray pyrolysis technique. It was found that, V_2O_5 nanoporous samples prepared by spray pyrolysis had a better crystallinity optical properties and morphology. XRD indicated that the V_2O_5 were of orthorhombic crystal structure. SEM and TEM images revealed the formation of interconnected nanoporous network and nanorods. Nanorods were 10–20 nm wide and 150–200 nm in average length. FT-IR study confirms the V_2O_5 phase of prepared sample. A proposed growth mechanism is found

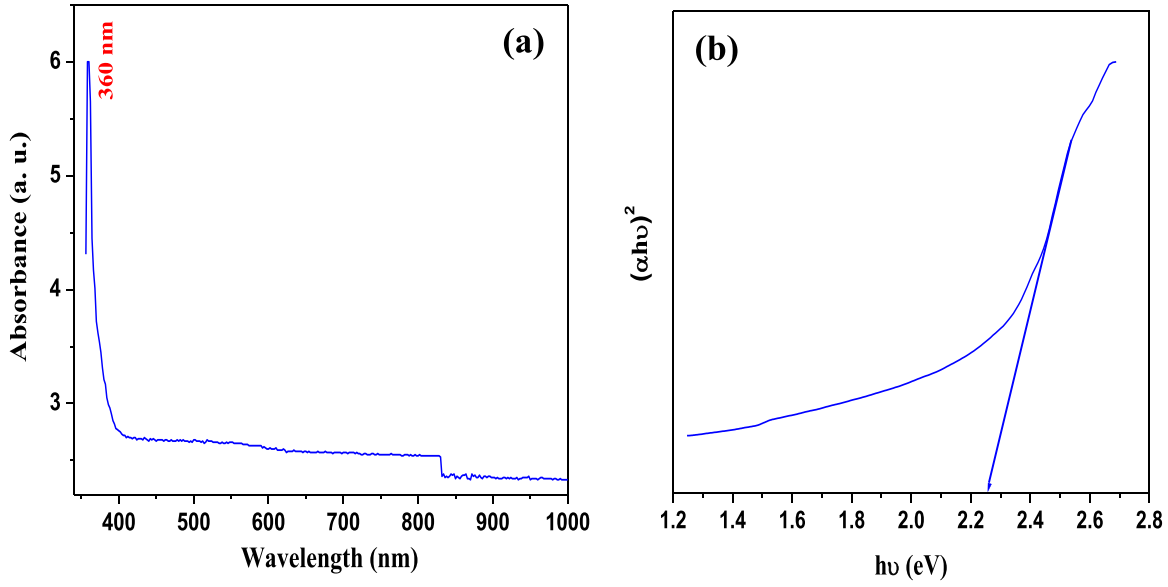

Fig. 2. (a) UV–vis absorption spectrum, (b) Direct band gap plot.