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Effect of annealing temperature on the supercapacitor behaviour of β-V_2O_5 thin films

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ABSTRACT

Vanadium pentoxide thin films are prepared via sol–gel spin coating method. The films coated on FTO and glass substrates are treated at different temperatures ranging from 250 °C to 400 °C. The structural, optical and electrochemical investigations are made. X-ray diffraction analysis shows the film to be composed of V_2O_5 in β-phase up to annealing temperature of 350 °C and at 400 °C the structural transformation to α-phase is observed. FTIR spectrum shows the formation of V–O bond. The SEM images reveal the formation of nanopores. Optical absorption studies indicate a band gap of 2.2–2.4 eV. The supercapacitor behaviour is studied using cyclic voltammetery technique and electrochemical impedance analysis. The vanadium pentoxide films annealed at 300 °C for an hour exhibits a maximum specific capacitance of 346 F g^{-1} at a scan rate of 5 mV s^{-1}.

1. Introduction

Electrochemical capacitors are divided into two categories based on their energy storage mechanism as electrochemical double layer capacitor (EDLC) and pseudocapacitors or redox supercapacitors [1]. EDLC is based on storing electrical energy at the interface between the electrode and electrolyte, while the pseudocapacitors involve Faradic redox reactions. Electrochemical capacitors may be differentiated based on the electrode material utilized, the electrolyte or the cell design. There are three main categories of EC's based on the electrode materials. Carbon based, transition metal oxide based and conducting polymer based. Some of the key factors of electrode materials for EC's are high specific surface area, suitability to enhance the capacitance by additional faradic redox reactions and low ohmic resistance. Transition metal oxides are considered to be the best candidates for EC applications. The high specific capacitance with low resistance makes the transition metal oxide electrodes useful in various commercial applications. Moreover transition metal oxides posses several oxidation states and are reasonably conducting. Transition metal oxides such as RuO_2 [2], MnO_2 [3], NiO [4], V_2O_5 [5] have been studied for possible supercapacitor applications due to their higher energy density. Vanadium pentoxide is an important material due to its interesting properties and applications in various fields like batteries [6], supercapacitors [5], electrochromic devices [7], etc. Electrochemical nature of vanadium pentoxide is mainly decided by its redox property.

V_2O_5 thin films are prepared by various techniques such as sputtering [8], vacuum deposition [9], sol–gel process [10], and electro deposition [11] method. Among these techniques sol–gel method is a low cost method and has several advantages such as provision of large surface area coating and ease of adding dopants [12]. Hwan Kim et al. [13] have reported that the $V_2O_5{\cdot}xH_2O$/CNT film electrode show a specific capacitance of 910 F g^{-1} at 10 mV s^{-1}. Jayalakshmi et al. [14] reported the SnO_2–V_2O_5–CNT composite electrode to exhibit a specific capacitance of 121.4 F g^{-1} at a scan rate of 100 mV s^{-1}. Lao et al. [5] have reported a specific capacitance of 262 F g^{-1} in the case of V_2O_5 powder in 2 M KCl as an electrolyte at a working voltage of 0.7 V. V_2O_5 nanowires have been reported to exhibit a specific capacitance of 146 F g^{-1} in 1 M Na_2SO_4 aqueous solution in the working potential of 2.2 V [1]. We have carried out optimization of thickness of V_2O_5 films for EC applications. In continuation of the same work, we have tried to optimize the temperature of annealing. This paper reports and discusses the results obtained on 8 layer V_2O_5 films treated at different annealing temperatures.

2. Experimental details

0.1818 g of vanadium pentoxide powder is dissolved in 12 ml of conc. HCl and the solution was heated at 120 °C for an hour. This results in the formation of a green powder (vanadyl chloride). The powder is cooled in a water bath overnight and then dissolved in

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25 ml of 2-methoxyethanol with addition of 0.3 ml of conc. HCl. The solution is stirred at a temperature of 50 °C for 30 min. The solution is aged for 5 h at room temperature to obtain the sol–gel. The sol–gel is then coated on fluorine doped tin oxide coated (FTO) substrate of 6 $\Omega\ \square^{-1}$ at a spin rate of 2500 rpm for 25 s. Each layer is thermally treated at the corresponding temperature from 250 °C to 400 °C for 3 min. After coating the required numbers of layers the final films are annealed for 1 h at their corresponding temperature in air. For example the film annealed at 250 °C would mean that each layer was treated at 250 °C for 3 min and that the final multilayer film was treated at 250 °C for 1 h in an atmosphere of air. Totally 8 layers has been coated. The X-ray diffraction (XRD) pattern of the films were recorded using CuKα (λ = 1.54 Å). The transmission spectrum of the films was recorded in the range of 190–1100 nm using a Perkin-Elmer Lambda-35 UV–vis spectrometer. The thermogravimetric (TG) and differential thermal analysis (DTA) measurements were made using SDT Q600 V8.3 Build101, thermal analyzer instrument at a scan rate of 20 °C/min in air. The thickness of the films was calculated by weight gain method. Cyclic voltammograms were recorded using CH-electrochemical workstation (CHI660D) in a three electrode cell with platinum wire as counter electrode, saturated calomel electrode (SCE) as reference electrode and the non aqueous 1 M $LiClO_4$ in propylene carbonate as the electrolyte. The AC impedance spectra were analyzed in the frequency range of 100 kHz to 0.01 Hz and an open circuit potential of 0.5 V.

3. Result and discussion

3.1. Thermal and structural properties

Fig. 1 shows the thermogravimmetric and differential thermal analysis curve of the dried xerogel powder. The initial weight of the xerogel was 5.1010 mg yielding 2.426 mg of residue after heat treatment up to 1000 °C. Dehydration and phase changes have been observed at different temperature as shown by the exotherm and endotherm curves. On the TG-curve a weight loss of 9% up to 133.90 °C accompanied by an endotherm at 84.99 °C and an exotherm at 137.10 °C on the DTA curve probably corresponding to the loss of weakly bound water molecules could be observed. In the second step from 133.90 °C to 220.85 °C, there is a major weight loss of 33% in the TG accompanied by endotherm at 188.19 °C and exotherm at 314.57 °C could be observed. This is suggestive of the evaporation of chlorine [15], decomposition of the organic phase, deformation of intermediate phases and loss of surface and bound

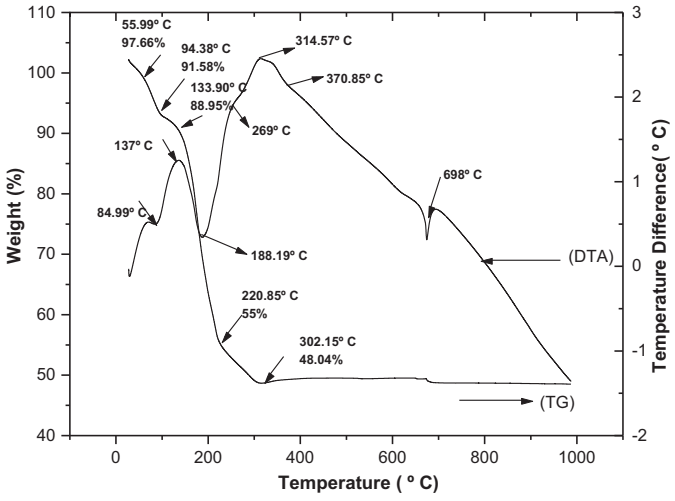

Fig. 1. TG-DTA curve of V_2O_5 xerogel.

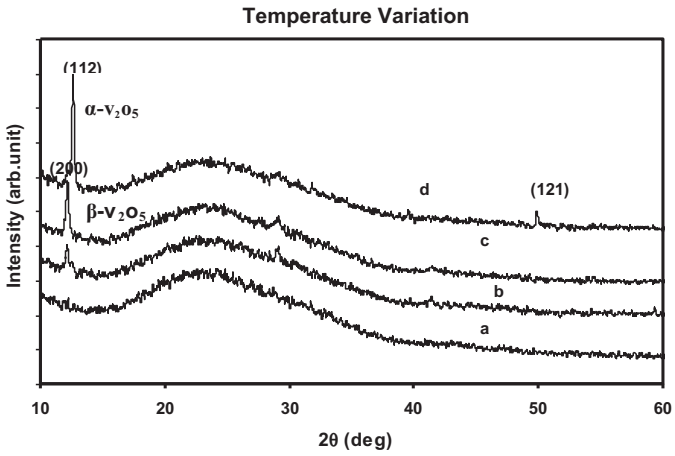

Fig. 2. X-ray diffraction spectra of V_2O_5 films annealed at different temperatures.

water molecules. Zampronio et al. [16] have reported a similar thermogravimetric analysis for PVC/V_2O_5. In the third step there is a weight loss of 7% between 220.85 °C and 302.15 °C showing the removal of bound water molecules and organic phases with the conversion to crystalline vanadium pentoxide. The detailed analysis of the process that are taking place during a thermal process are discussed along with FTIR results.

Fig. 2 shows XRD pattern of the films deposited and annealed at different temperature ranging from 250 °C to 400 °C in air for an hour. The XRD pattern reveals that the films annealed at 250 °C are amorphous in nature. Increase in annealing temperature increases the crystalline nature with the preferred orientation along the (2 0 0) plane corresponding to β-V_2O_5 tetragonal system phase [JCPDS-card no. 45-1074]. At 400 °C a phase change is observed corresponding to the formation of V_2O_5 orthorhombic structure (α-V_2O_5) [17]. The grain size has been calculated using Debye–Scherrer formula and the result shows an increase in the grain size with increase in temperature from 300 °C to 400 °C [18]. The grain size varies from 26 nm to 68 nm. Table 1 gives the grain size of the films anneals at different temperatures.

The FTIR spectrum of the V_2O_5 xerogel (KBr pellet method) treated at different temperatures (150 °C, 250 °C, 300 °C, 350 °C, 400 °C) is shown in Fig. 3. Table 2 gives the list of bands observed in each case and their assignment. The vibrational frequencies corresponding to vanadium oxygen bond, CH and OH at different temperatures could be observed in the FTIR. The V_2O_5 xerogel treated from 150 °C to 400 °C exhibits vibration modes corresponding to vanadium oxygen bond between 1000 cm^{-1} and 426 cm^{-1}. The V–O–V bridging mode observed at 426 cm^{-1} appears in spectrum up to 250 °C [19]. The bands at 656 cm^{-1} [20] and 796 cm^{-1} [21] correspond to V–O–V stretching mode and ν_{as} (V–O–V) respectively, observed in the spectra up to 300 °C. The appearance of new peaks at 524 cm^{-1} [23], 732 cm^{-1} [24] and 810 cm^{-1} [24] in the spectra of 350 °C and 400 °C is attributed to ν_s (V–O–V) mode. The bands observed at 874 cm^{-1} [19] and

Table 1
Variation of film parameters with annealing temperature.

Annealing temperature (°C)	Thickness (nm)	Grain size (nm)	Band gap (eV)	Specific capacitance (Fg^{-1})
250	177	Amorphous	2.40	241
300	202	26	2.36	346
350	212	48	2.29	226
400	224	68	2.22	177