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Amorphous vanadium pentoxide thin films prepared by electrostatic spraying-pyrolysis deposition

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Abstract

Vanadium pentoxide thin films were prepared on $Pt/TiO_2/SiO_2/Si$ (1 1 1) substrates by electrostatic spraying deposition at 200 °C for 10 min. As-deposited thin films were finally annealed at 200 °C for 60 min in argon. Crystallinity and surface morphological properties were examined by X-ray diffraction θ–2θ scanning, field emission scanning electron microscope and scanning probe microscope. Electrochemical tests were performed using cycler in a 1 mol $LiPF_6$, EC:DMC = 1:1 liquid electrolyte. Cycling tests were carried out for up 250 cycles in the range of 1.5–3.8 V at constant current density was 20 $\mu A/cm^2$. The relationship between the electrochemical and structural properties are described and discussed.

Keywords: A. Films; C. Optical properties; E. Electrodes; V_2O_5

1. Introduction

Vanadium pentoxide (V_2O_5) has been studied widely in recent years for its semiconducting/electrochemical properties, which can be integrated readily into technological applications such as photochromic and electrochromic devices, color memory devices and positive electrodes of rechargeable lithium batteries [1–3]. The high theoretical capacity of V_2O_5 (~600 mAh/g) makes it an attractive material for application in rechargeable batteries. Due to its unique isotropic structure and faster ion channels over those of crystalline films, the amorphous V_2O_5 film has been widely studied [4,5].

Various physical and chemical methods are used to obtain V_2O_5 films: electron beam evaporation, magnetron sputtering, pulsed-laser deposition, chemical vapor deposition, sol–gel method [1–6]. Among various coating techniques, electrostatic spraying deposition (ESD) was employed to prepare many dense or porous thin films at relatively low deposition temperatures [6,7]. ESD at low temperature of the amorphous and transparent V_2O_5 film will provide a unique route to fabrication of optoelectronic devices.

In this work, we present the results of amorphous and transparent V_2O_5 thin films prepared by ESD. We investigated crystal and chemical structure, surface morphology, transmittance in the visible spectra range, and electrochemical properties of the films.

2. Experimental

A homogeneous precursor solution was prepared by mixing vanadium (V) tri-isopropoxide and ethanol at 25 °C for 120 min in air. Deposition of V_2O_5 films was performed using an ESD setup with a horizontal configuration. The details of the setup used have been reported before [7]. A stainless steel needle (0.1 mm and 0.23 mm inner and outer diameter, respectively) was connected to a syringe pump (KD200, KD Scientific Inc., U. S. A.) using a silicon rubber tube. The flow rate of the precursor sol was kept at 0.05 ml/60 min. The high voltage (20 kV) was applied between the needle tip and ground electrode using DC power supply to obtain a stable con-jet mode. $Pt/TiO_2/SiO_2/Si$ (1 1 1) substrates as well as silica glass to obtain transmittance on the ground electrode were heated at

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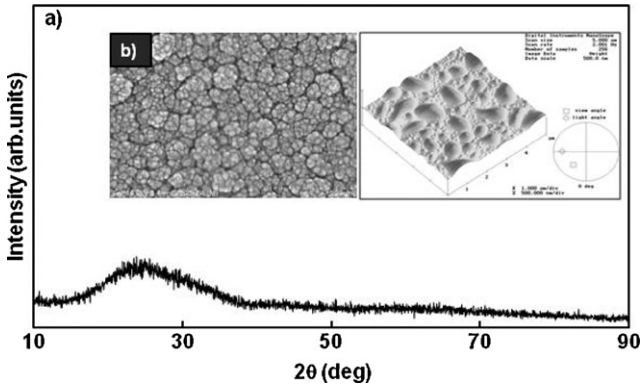

Fig. 1. XRD pattern (a) and FE-SEM and SPM images (b) of V_2O_5 film on Pt/TiO_2/SiO_2/Si (1 1 1) substrates.

200 °C for 10 min in air during spraying. Distance from the nozzle to substrate was kept at 15 cm. Further annealing was performed at 200 °C for 60 min in Ar.

The crystal structure of the films was characterized by X-ray diffraction (XRD, X'pert PRO, Philips, Netherlands). The morphology of the films was examined by a field emission scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan) and a scanning probe microscope (SPM, XE-200, PSIA, Korea). Optical properties of the films were analyzed by UV spectrophotometer (Cary 500 Scan, Varian, Australia) and Fourier transform infrared (FTIR, FTS-60, BIO-RAD Digilab, U. S. A.) spectrophotometer. Data for half-cell (Li anode) charge–discharge experiments was obtained with a WBCS3000 (Wonatech, Korea) cycler operating at constant current. Molar LiPF6 in 1:1 ethylene carbonate (EC):dimethyl carbonate (DMC) as the electrolyte was used in all the cells tested.

3. Results and discussion

Fig. 1 shows XRD pattern (a) and surface morphology (b) of V_2O_5 film after heat treatment at 200 °C for 60 min. The film showed only very broad and diffuse patterns, which indicate their characteristic amorphous nature. The surface morphology of an amorphous V_2O_5 thin film was studied using FE-SEM and SPM. Fig. 1(b) shows the FE-SEM and SPM images of V_2O_5 film after heat treatment at 200 °C for 60 min. As shown in Fig. 1(b), the V_2O_5 film shows a relatively smooth surface morphology, although FE-SEM picture showed the presence of agglomerates but they were smaller. The growth of defect-free electrode film is very critical in achieving a high performance device, because the smooth surface of a film plays an important role in the fabrication of optoelectronic devices.

The optical properties of the film in the IR and visible range have also been examined. Fig. 2(a) shows the transmittance versus wavelength (300–900 nm) of V_2O_5 film on silica substrate. A relatively high transmittance in the visible spectra range and clear absorption edge of the film were observed. The high transmittance of the film is attributed to the small particle size and homogeneous surface structure, which eliminate light scattering [8]. The blue shift of the optical band gap has been found in non-crystalline vanadium oxide materials such as low temperature deposited V_2O_5 thin films [9]. Further, Dultsev et al. [10] observed a shift of the optical band gap accompanying changes in the thickness of films. Thicker films showed nearly equal value (2.25 eV) for the bulk V_2O_5. Thus we suggest that both factors, an amorphous thin structure with small grain size evidenced by XRD and FE-SEM, are also the cause of the optical band gap blue shift occurring in our ESD derived V_2O_5 film. The film transparency found here (~80%) is suitable as a window for solar cells and a transmittance modulation in smart windows with potential applications in architecture and automotive.

Fig. 2(b) shows the FTIR spectra of V_2O_5 films. An indication for the structural quality of the films is the peak position of the vanadyl mode located at 1020 cm^{-1} in the crystal [11]. This vanadyl mode was observed at about 1012 cm^{-1} [12] for the films deposited at room temperature. The IR active mode located at about 820 cm^{-1} [12] is

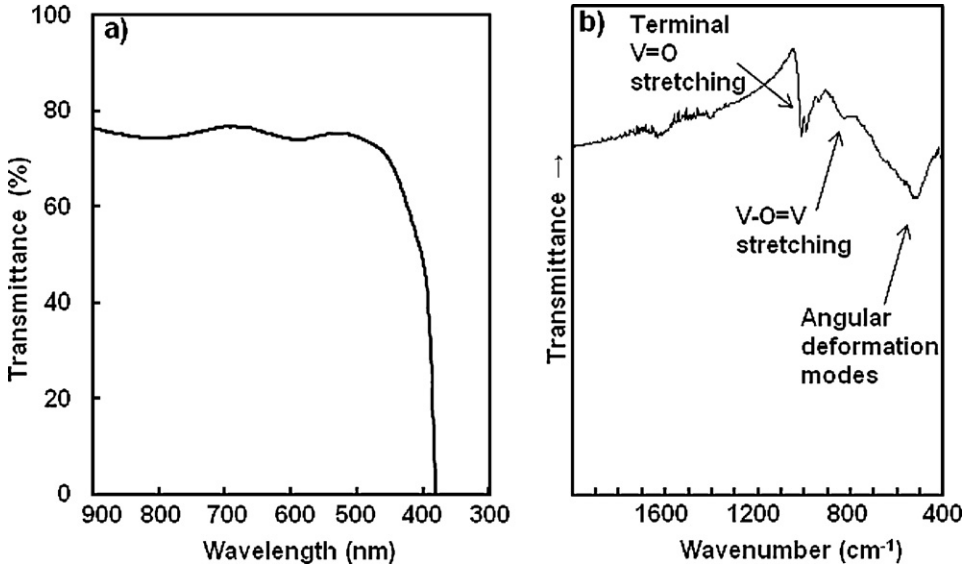

Fig. 2. UV–vis spectrum (a) of V_2O_5 film on silica glass and FTIR spectrum (b) of V_2O_5 film on Pt/TiO_2/SiO_2/Si (1 1 1) substrate.

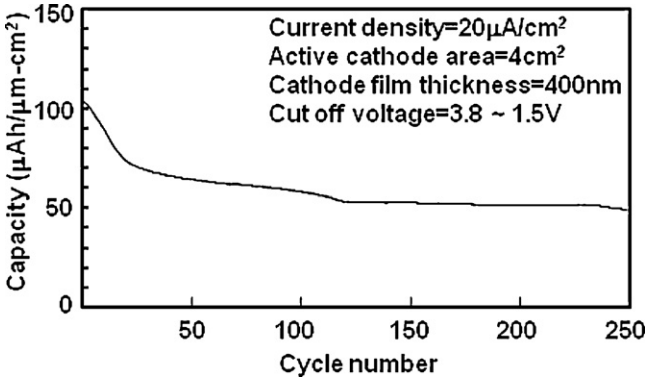

Fig. 3. The discharge capacities of the V_2O_5 film on Pt/TiO_2/SiO_2/Si (1 1 1) substrate as a function of the cycle number.

characteristic of vibrations of the bound oxygen atoms which are shared by two vanadium atoms. The band at 500 cm^{-1} [12] corresponds to the angular deformation modes which are related to the V–O bonds mainly contributing to the edge sharing between square pyramids of VO_5. However, the IR spectrum of amorphous V_2O_5 film is broad and poorly resolved. It was observed that the line width is much larger in amorphous films owing to the random potential fluctuations associated with the amorphous state. Our result is consistent with the results obtained by Sanchez et al. [13] for amorphous V_2O_5 films prepared by vacuum evaporation.

The cyclability of the fabricated Li/V_2O_5 cell was investigated by galvanostatic discharge/charge cycling in a 1 mol $LiPF_6$, EC:DMC = 1:1 liquid electrolyte. Fig. 3 shows the discharge capacities for the amorphous V_2O_5 films as a function of cycle number. The amorphous V_2O_5 film grown on Pt/TiO_2/SiO_2/Si (1 1 1) substrates at 200 °C shows an initial discharge capacity of approximately 100 μAh/μm cm^2 and show discharge capacity retention of 60% after 250 cycles.

Comparison of the present results with the previously reported works of the V_2O_5 films prepared by various methods [1–6] indicates that the ESD used in this work is more economical. Our results show that transparent amorphous V_2O_5 film prepared by ESD method at 200 °C can be one of the promising candidates for optoelectronics and other special applications on flexible plastic substrates.

4. Conclusions

In this work, we have demonstrated the synthesis of amorphous V_2O_5 films using an ESD method. Amorphous V_2O_5 film confirmed by XRD showed relatively high transmittance in visible spectra range. The FTIR spectra of amorphous thin films are broad and poorly resolved owing to the random potential fluctuations associated with the amorphous state. When cycled between 1.5 and 3.8 V, the discharged capacity of this film was approximately 100 μAh/μm.cm^2. The film exhibits negligible capacity fade from the 25 cycles to more than 250 cycles. These results indicate it should be possible to cheaply and easily fabricate V_2O_5-based optoelectronic devices at low temperature, below 200 °C, in the future.

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