

Structural and optical studies of nanocrystalline V₂O₅ thin films

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Abstract

We report the structural and optical properties of nanocrystalline thin films of vanadium oxide prepared via evaporation technique on amorphous glass substrates. The crystallinity of the films was studied using X-ray diffraction and surface morphology of the films was studied using scanning electron microscopy and atomic force microscopy. Deposition temperature was found to have a great impact on the optical and structural properties of these films. The films deposited at room temperature show homogeneous, uniform and smooth texture but were amorphous in nature. These films remain amorphous even after postannealing at 300 °C. On the other hand the films deposited at substrate temperature $T_s > 200$ °C were well textured and *c*-axis oriented with good crystalline properties. Moreover colour of the films changes from pale yellow to light brown to black corresponding to deposition at room temperature, 300 °C and 500 °C respectively. The investigation revealed that nanocrystalline V₂O₅ films with preferred 001 orientation and with crystalline size of 17.67 nm can be grown with a layered structure onto amorphous glass substrates at temperature as low as 300 °C. The photograph of V₂O₅ films deposited at room temperature taken by scanning electron microscopy shows regular dot like features of nm size.

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1. Introduction

The fascinating properties and wide range applications of vanadium pentoxide, especially in thin film form, has attracted considerable interest. Multivalency, layered structure, wide optical band gap, good chemical and thermal stability, excellent thermoelectric property, etc., are the characters that make vanadium pentoxide (V₂O₅) a promising material. It can be used as a catalyst, as gas sensors, as a window for solar cell and for electrochromic devices as well as for electronic and optical switches but the growing interest is in fabrication of thin film batteries (TFB) [1]. As the conventional bulk battery consists of aqueous electrolytes, which is responsible for the formation of dendrite phases during charge–discharge process while TFB does not have aqueous electrolytes. As a result its cycle performance is higher even after thousands of cycles. Moreover thin film process can give a very clean and sharp interface between deposited films which leads to a smaller value of

interfacial resistance between electrolytes and electrodes. Furthermore, the ionic conduction of a solid electrolyte is enough for Li⁺ ion diffusion toward a cathode. Vanadium pentoxide has high potential, high energy density, high capacity and good cycle performance so is a fascinating candidate for the fabrication of TFBs. However, the crystalline phase of V₂O₅ has phase transformation during intercalation and de-intercalation process resulting in the formation of irreversible γ and δ phases, which reduces the life time of the battery. While no phase transformation occurs in amorphous V₂O₅ during Li intercalation, and hence amorphous V₂O₅ is a potential candidate for fabrication of TFBs with high cycle performance [2].

V₂O₅ crystallize with an orthorhombic unit cell structure and belongs to P_{mm} space group with lattice parameters $a=11.510$ Å, $b=3.563$ Å, and $c=4.369$ Å [3]. The crystal structure of orthorhombic V₂O₅ is made up of zig-zag ribbons of square pyramidal VO₅ units, which share edges hence building double chains along the *b*-direction. The chains are connected by their corners and the resulting is stacked along the *c*-direction. This results in VO₆ units with three principal V–O distances, which are 1.58 Å (along the *c*-direction); 1.77–2.02 Å

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(bridging oxygen in the basal planes) and 2.79 Å (weak bonds in between the layers). The rich and diverse chemistry and the catalytic performance of vanadium oxides are based on two factors i.e. variety of vanadium oxidation states, ranging from 2^+ to 5^+ , and variability of oxygen coordination geometries [4]. The principal oxides of vanadium occurs as single valency oxides in the oxidation states from V^{2+} to V^{5+} , that is in the form of VO, V_2O_3 , VO_2 and V_2O_5 . The mixed valence oxides are formed by introducing oxygen vacancy defects in to the respective higher oxides. If the number of oxygen vacancies exceeds a certain value, the vacancies tends to correlate and form the crystallographic shear planes, i.e. the vacancies associate along a lattice plane and become subsequently eliminated by reorganization of V–O coordination units. The result is a series of oxides with related stoichiometries, such as the mgnéli phases with V_nO_{2n-1} or the wadsley phases with $V_{2n}O_{5n-2}$ formulas.

V_2O_5 is especially interesting in thin-film form because of the possibility of integration into micro-electronic circuitry and its application in optoelectronic devices. V_2O_5 films have been prepared by a variety of physical and chemical vapor deposition techniques such as sputtering [5,6], chemical vapor deposition [7], sol gel method [8], pulsed laser deposition [8] and evaporation [10–12]. The properties of the V_2O_5 films are mainly dependent on the deposition technique and the deposition conditions such as vacuum, deposition temperature, deposition rate, residual gases in the vacuum chamber during deposition, etc. It is difficult to grow the oriented films via evaporation because of stoichiometry problem, which leads to the partial dissociation [12]. Earlier reports on V_2O_5 thin films via evaporation technique has shown either amorphous or polycrystalline films [10–12]. In the present study, we have deposited highly oriented V_2O_5 thin films on amorphous glass substrates by evaporation technique at the deposition temperature of 300 °C. We are also able to synthesize homogeneous and uniform V_2O_5 films even at room temperature with high deposition rates via this technique. The aim is to study the effect of deposition temperature on the micro-structural and optical properties of these films.

2. Experimental details

V_2O_5 thin films were prepared in vacuum coating unit over amorphous glass substrate. The substrates were initially cleaned thoroughly in an ultrasonic bath with the mixture of distilled water and trichloroethylene in 4:1 ratio and then washed with boiled acetone. As a source material V_2O_5 powder of 99.998% purity was evaporated from a molybdenum boat. During each deposition the pressure in the chamber was better than 10^{-4} Pa and the distance between the substrate and the molybdenum boat was kept approx 7 cm. Deposition rate was about 0.25 $\mu\text{m}/\text{min}$. Specially designed digital substrate heater from Excel Instruments with temperature controller, which gives very fine control over the deposition temperature with ± 1 °C was used. In addition special geometry was made inside a vacuum chamber to control the evaporation rate, which in turn decides the stoichiometry of the films. At least five number of samples were prepared for each of the tested substrate temperatures.

Structural characterization of the films was carried out using a Bruker X-Ray Diffractometer of $\text{CuK}\alpha$ radiation (1.54 Å) with the scanning speed $2\theta = 1^\circ/\text{min}$ in the angle range between 10° and 60° . To obtain a profile fitting with good signal, a polycrystalline Si powder was used for instrumental correction. Optical properties of the deposited V_2O_5 films were studied using Perkin Elmer Lambda 25 UV–Visible spectrometer with specular reflection attachment in the range between 200 nm and 1100 nm with the scan speed 120 nm/min. The film thickness was measured using multiple-beam Fizeau fringes at reflection with monochromatic light. The surface morphology of the films was investigated using scanning electron microscopy (SEM) with an operating voltage of 20 keV and NTMDT atomic force microscopy (AFM) in semi-contact mode with silicon nitride (Si_3N_4) tip of 10 nm radius. Electrical resistance of the films at room temperature was studied using digital electrometer (Keithley) via standard two-probe technique.

3. Results and discussion

3.1. Structural properties

Fig. 1 shows the X-ray diffraction (XRD) pattern of V_2O_5 thin films deposited at various deposition temperatures in the range from room temperature to 500 °C. XRD pattern of the films deposited at room temperature indicates that the film is amorphous in nature. Even postannealing of these films at temperature of 300 °C in air does not make them crystalline. It is observed that the crystallinity of the film increases with increase in deposition temperature. XRD patterns of V_2O_5 thin films deposited at T_s of 300 °C exhibits the predominant (001) peak of the orthorhombic V_2O_5 phase. This shows that crystallization starts in V_2O_5 films grown onto amorphous glass substrate at the deposition temperature as low as 300 °C. Further the dominance of the (001) peak in the XRD patterns suggests that the texture of the V_2O_5 thin film is oriented along the c -axis perpendicular to the surface of the substrate with its a -, b -axis parallel to the surface. The preferred orientation is related to the in plane organization of the V–O–V chains. The layer-like

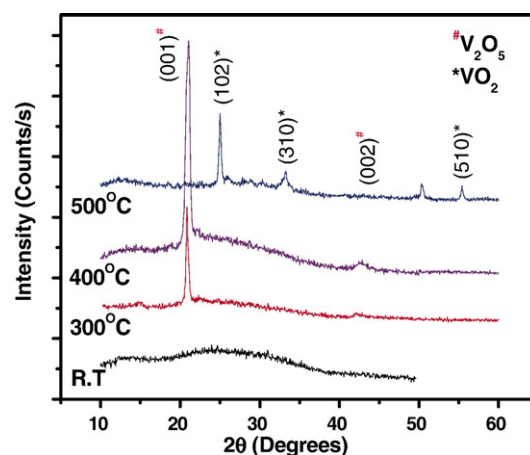


Fig. 1. XRD patterns of the V_2O_5 thin films grown on glass substrate at various deposition temperatures.

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