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Effect of post annealing treatment on electrochromic properties of spray deposited niobium oxide thin films

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Abstract

Niobium oxide thin films were deposited on the glass and fluorine doped tin oxide (FTO) coated glass substrates using simple and inexpensive spray pyrolysis technique. During deposition of the films various process parameters like nozzle to substrate distance, spray rate, concentration of sprayed solution were optimized to obtain well adherent and transparent films. The films prepared were further annealed and effect of post annealing on the structural, morphological, optical and electrochromic properties was studied. Structural and morphological characterizations of the films were carried out using scanning electron microscopy, atomic force microscopy and X-ray diffraction techniques. Electrochemical properties of the niobium oxide thin films were studied by using cyclic-voltammetry, chronoamperometry and chronocoulometry.

Keywords: Niobium oxide thin films; Spray pyrolysis technique; Scanning electron microscopy (SEM); X-ray diffraction (XRD); Atomic force microscopy (AFM)

1. Introduction

The transition metal oxides (TMOs) exhibit a wide range of optical and electrical properties. Most of these TMOs are studied as electrochromic (EC) materials. EC materials whose optical properties can be varied reversibly and persistently by a low voltage signal are used in many applications viz. information displays, variable emittance surfaces, variable reflectance mirrors and smart window, etc. Amongst these 'smart window' have captured the interest of researchers as a means to achieve energy efficiency in buildings. It has become clear that 'smart window are able to combine two features that are often thought of as incompatible; energy efficiency (as a result of the curtailing of air conditioning) and indoor comfort (due to less glare and thermal discomfort). Therefore EC materials have been considered as a subset of solar energy materials. [1,2].

Reichman and Bard reported the electrochromic properties of Nb_2O_5 coatings in 1980, for the first time [3]. Thereafter niobium oxide has been studied widely as a promising EC material because of its excellent chemical stability and corrosion resistance in both acid and base media. Also depending on its crystallinity niobium oxide films turns transparent to brown, grey or blue in its reduced state. Subsequently niobium oxide has been studied as a compatible material for EC devices. Several more adequate deposition techniques such as sputtering [4], electron beam evaporation [5], plasma oxidation [6], chemical vapour deposition [7], MOCVD [8], and sol–gel process [9] have been used to prepare Nb_2O_5 thin films.

Earlier we have reported EC properties of Nb_2O_5 thin films synthesized by simple and inexpensive spray pyrolysis technique (SPT) [10]. Properties of a material strongly depend upon its microstructure and one of the post deposition parameters that mainly affect the properties of spray deposited film is annealing temperature. Several changes may occur in the film after annealing, e.g. increased surface roughness, change in stoichiometry and transformation from amorphous to crystalline or from one crystalline phase to other. It is experimentally observed that electrochromic modulation depends on the films crystalline structure. In the present study we have reported the effect of annealing treatment on the structural, morphological, electrical and electrochromic properties of spray deposited Nb_2O_5 thin film.

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2. Experimental

Niobium oxide films were deposited on both glass and FTO coated glass substrates by spray pyrolysis technique. Films deposited on the glass substrate were used for structural and morphological characterization whereas those deposited on the FTO coated glass substrates were used for electrochromic characterization.

The conducting FTO coatings were prepared by using pentahydrated stannic chloride ($SnCl_4{\cdot}5H_2O$) (purity 98%) and ammonium fluoride (NH_4F) (purity 95%) as precursor salts. The solution was prepared in double distilled water. The FTO coated conducting glass substrates with 90–95% transparency and sheet resistance 10–15 Ω/□ were obtained at 500 °C. These FTO coated glass substrates were further used as conducting substrates for the deposition of electrochromic niobium oxide thin films.

To prepare the starting solution for the deposition of niobium oxide thin films initially powder of niobium pentoxide (Fluka AG. Buchs SG. Niobium (V) oxide Switzerland, 99.99% pure) was fused with potassium pyrosulphate in silica crucible at 500 °C and subsequently the product was dissolved in tartaric acid. The resulting solution was then diluted to 5 mM. The prepared 5 mM solution was further pulverized pneumatically by means of a specially designed glass nozzle on to the preheated glass substrates maintained at 400 °C (optimized temperature). The sprayed droplets undergo evaporation, solute condensation and thermal decomposition thereby resulting in the formation of niobium oxide thin film. Following reaction may take place during the solution preparation:

$$2[NbO_4(CHOHCOO^-)_2]^5 \xrightarrow[400^\circ C]{} Nb_2O_5 + 4H_2O \uparrow + 8CO_2 \uparrow$$

The as deposited films were further annealed at 500 °C for 1 and 3 h. The as deposited (Nb_0), 1 h annealed (Nb_1) and 3 h annealed (Nb_2) samples were further characterized by different techniques and the effect of annealing temperature on the structural, morphological, electrical and electrochromic properties of Nb_2O_5 thin film is reported in the present manuscript.

Film thickness was measured using a gravimetric method. The structural and morphological characterization were carried out using a Philips PW 3710 X-ray diffractometer with Cu Kα radiation (wavelength 1.5432 Å) and scanning electron microscopy (SEM) JEOL JSM-6360, respectively. The optical characterization was carried out using UV–VIS Systronic spectrophotometer in the wavelength range 350–850 nm. Electrochemical impedance measurements were carried out at room temperature by frequency response analyzer attached with potentiostat PGSTAT AUTOLAB 20 (Echo Chemie Netherlands) at 0.7 V bias voltages using a small ac signal of 10 mV peak to peak in the frequency range 0.1 Hz–700 kHz. Electrochemical measurements of the niobium oxide films were performed using EG and G make VersaStat-II model, controlled by electrochemistry software M270. The three dimensional morphology of the growth was examined by using atomic force microscopy (AFM), Nanoscope instruments, USA in contact mode, with V shape silicon nitride cantilever of length 100 μm and spring constant 0.58 N/m.

3. Results and discussions

Niobium oxide films deposited below 400 °C were slightly brownish and do not exhibit redox behaviour, may be due to incomplete decomposition of the precursor solution leading to inadequate stiochiometry. Niobium oxide films deposited at 400 °C exhibited redox behaviour resulting in electrochromism.

3.1. Thickness measurement

Film thickness, measured by the gravimetric method was 480 nm for as-deposited films and decreased to 452 nm for annealed films.

3.2. X-ray diffraction studies

The Nb_2O_5 phase formation was confirmed by X-ray diffraction study. The diffracting angle 2θ was varied between 10° and 100°. The observed XRD pattern is compared with the standard JCPDS data (file number 74-0298). Fig. 1 shows the X-ray diffraction pattern of as deposited and annealed Nb_2O_5 thin films. It is observed that all the samples belong to monoclinic crystal structure exhibiting well defined reflections along $(\bar{8}\,0\,2)$ and $(\bar{8}\,0\,1\,0)$ planes. After annealing the increase in the intensity of peaks owing to improvement in the crystallinity of Nb_2O_5 thin film is observed. In order to determine the crystallite size, a slow scan of XRD pattern between 24° and 27° was carried out within the step of 0.02 min^{-1} for all the samples. The size of the crystallites oriented along $(\bar{8}\,0\,2)$ plane can be deduced using Scherer's formula:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where D is the size of crystallite, β the broadening of diffraction line measured at half of its maximum intensity in radius and λ

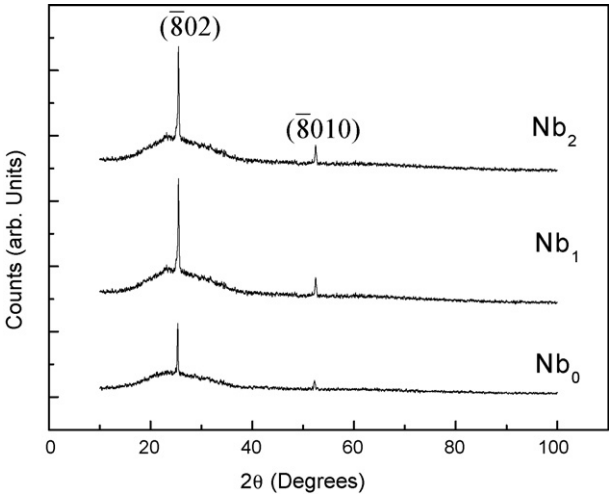

Fig. 1. X-RD spectra of Nb_0, Nb_1, and Nb_2 samples.