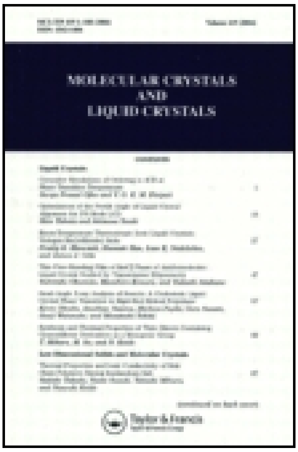

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Sol-Gel Coatings of Nb 2 O 5 and Nb 2 0 5 :Li + :Electrochemical and Structural Characterization

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Sol-Gel Coatings of Nb_2O_5 and Nb_2O_5:Li^+: Electrochemical and Structural Characterization

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ABSTRACT

Thin solid films of Nb_2O_5 and Nb_2O_5:Li^+ were prepared by the sol-gel process using the sonocatalitic method from $NbCl_5$ as precursor and butanol as solvent. The addition of different lithium salt ($LiCF_3SO_3$) quantities to the precursor solution produced films with different electrochemical performance. All the films showed the TT structure and the best opto-electrochemical responses were obtained with the films doped with 10%mol of lithium salt.

Keywords: electrochromism, Nb_2O_5, sol-gel

INTRODUCTION

In recent years, there has been considerable interest in the good use of solar energy. The development of new technologies in this area has been increased in last years [1]. One of them is the development of electrochromic devices like smart windows, display, sunglasses and mirrors based on large class of optically active materials that has shown interest, especially those with transmission, absorption and reflectance controllable. These materials have been known like chromogenous because they change their color when an external field is applied [1].

Pure and doped niobium (V) oxide (Nb_2O_5) are promising cathodic electrochromic materials. Their electro-optical performance depends strongly of its structural morphology. They can be obtained as films by sol-gel process. This well-know process is a good method to achieve such morphology and in combination with dip-coating technique is possible to deposited large area coating at low cost besides of control the microstructure of the films.

Nb_2O_5 films were prepared by the sonocatalytic method [2], using sol obtained from Nb ethoxide coatings by Ohtani *et al.* [3] and Ozer *et al* [4]. In order to improve the bleaching process, Orel *et al.* [5] have prepared films of Nb_2O_5 doped with lithium salt ($LiCF_3SO_3$).

In this work, it was realized a study of electrochemical and optical properties of Nb_2O_5 films pure and doped with $LiCF_3SO_3$ salt using the sonocatalytic sol- gel route and "dip coating" deposition technique.

EXPERIMENTAL

The starting solution to produce Nb_2O_5 films was prepared by dissolving $NbCl_5$ powder (0.005mol) in butanol (0.16mol), acetic acid (0.05mol) and $LiCF_3SO_3$ salt, (0-10%mol). The solution was submitted for ~5min to the action of a 95W, 20kHz ultrasonic irradiation from a sonicator resulting in a transparent and viscous solution.

The layers were deposited by dip-coating method on ITO (Asahi Glass 14Ω/) withdrawing it at rate of 10cm/min, and a final heat treatment was performed at 560°C in air atmosphere during 10 min.

X-ray diffraction measurements have been performed on films with a URD6-VEB-Carl-Zeiss Jena instrument with CuKα radiation.

The electrochemical measurements were realized using Solartron 1286 analyzer and a conventional three-electrode cell. The counter electrode was a platinum foil of 1 cm^2 area and the quasi-reference electrode was a silver wire. The electrolyte was a 0.1 M solution of $LiClO_4$ dissolved in propylene carbonate (PC).

The thickness of the films was measured with a Taylor-Hobson Talystep and the optical spectra in the UV-Vis range were recorded with a Hitashi model U3501 spectrophotometer.

RESULTS AND DISCUSSION

Figure 1 shows X-ray diffraction patterns of ITO and different Nb_2O_5 films deposited on ITO and compared with Nb_2O_5 precipitate heat treated at 600°C.

How it can be seen on this figure the diffractograms of Nb_2O_5 pure and doped with $LiCF_3SO_3$ films deposited on ITO glass show the peaks that correspond to ITO and Nb_2O_5. No other different peaks are observed. The structure of these films compared with the diffractograms of Nb_2O_5 precipitate heat-treated at the same temperature indicates a TT structure (tief-tief or very-low-temperature form) [6,7]. The mean interplanar distances d = 0.393, 0.314, 0.245, 0.196, 0.180 and 0.166 nm, are in good agreement with already reported results [6,7].

The electrochemical measurements of these films presented on the Figure 2 show cyclic voltammograms also typical for this kind of films. However it can be observed on this figure that addition of lithium salt to the precursor increase the value of cathodic current from –0.85 mA/cm^2 for pure Nb_2O_5 film to –1.0 mA/cm^2 for 10%mol lithium salt doped film at –1.5V. The same can be observed with anodic process when the peak at -0.75V increase from 0.35 mA/cm^2 for pure Nb_2O_5 film to 0.57 mA/cm^2 for 10% mol lithium salt doped film.

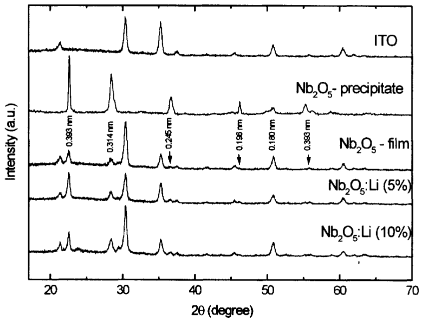

Figure 1: X-ray diffraction of pure and doped with lithium salt Nb_2O_5 films deposited on ITO and compared with Nb_2O_5 precipitate diffractograms.

The changes in cyclic voltammograms of 10%mol $LiCF_3SO_3$ doped films are observed also as a function of number of deposited layers (Figure 3). It will be stated here that the film thickness measurements by Talystep indicate about 70 nm per layer. Figure 3 shows the increase of cathodic and anodic current densities values withincrease of layers number. For the cathodic current the value increase from –0.33 mA/cm^2 for 1 layer films to –1.0 mA/cm^2 for 4 layers film and for the anodic current from 0.18 mA/cm^2 for 1 layer to 0.57 mA/cm^2 for 4 layers film. It can be also observed that between 3 and 4 layers films there are not significant difference in the current densities values.

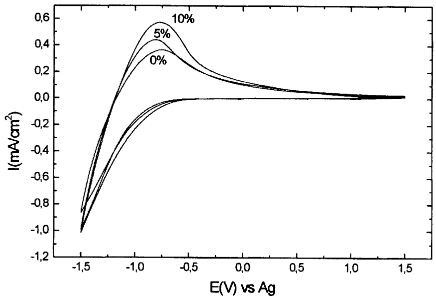

Figure 2: Cyclic voltammograms of pure and doped Nb_2O_5 3 layers films with 5 and 10% mol of $LiCF_3SO_3$. Electrolyte 0.1M $LiClO_4$/PC, scan rate 50 mV/s.

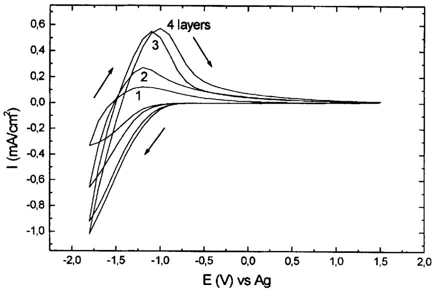

Figure 3: Cyclic voltammograms of different thickness Nb_2O_5:Li (10%mol) films.

The films under scan potential application exhibit intensive coloring/bleaching changes from transparent to gray blue. Moreover the doped films seem to be a darker during color process when compared with undoped films. The doped 3 layers film reach the values of transmittance of 72% at 475 nm and undoped films the values of 36% in the UV-Vis spectra (Figure 4). This electrochromic performance corroborates the results already reported by Orel *et al* [5]. Both kinds of films showed excellent performance where its original transmitting value in transparent state were restored.

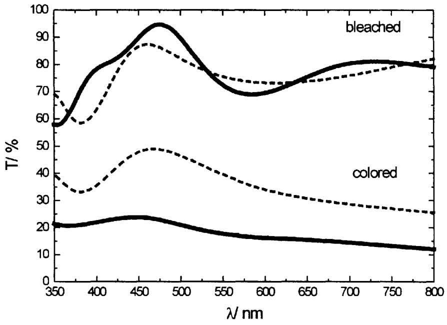

Figure 4. UV-Vis spectra observed during electrochromic switching in the bleached (+2.0V) and colored state (-1.8V) of 3 layers Nb_2O_5 films undoped (…) and doped with $LiCF_3SO_3$ 10%mol (-).

CONCLUSIONS

It was observed that sonocatalytic method makes easy the preparation of stable sol to obtain pure and doped with $LiCF_3SO_3$ niobium oxide films. The structural measurements showed that these films exhibit TT structure. It was stated also that the addition of lithium salt to the sol-gel precursor for Nb_2O_5 films increases the current values obtained from cyclic voltammograms for the films with 10%mol of $LiCF_3SO_3$. These values increase also with the layer numbers from 1 to 3 and no significant difference was observed between 3 and 4 layers films that presented the best results. All the films show the reversible gray blue coloration under applied scanning potential where the doped films are darker than those compared with undoped films. The presented results confirm that the sonocatalytic route to prepare sols for different niobium oxides thin films is easy, cheap and both kinds of films are promising candidates to be used in electrochromic devices.

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