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Alternative Nb_2O_5-TiO_2 thin films for electrochromic devices

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Thin films of mixed oxides of Nb_2O_5-TiO_2 with molar ratio Nb/Ti = 3, have been prepared by sol-gel sonocatalytic method. The precursor sols consist of a mixture of niobium salt $NbCl_5$, titanium alkoxide $Ti(OPr^i)_4$, isopropanol and acetic acid. After addition of all components the mixture was sonicated. The films were deposited by dip-coating technique on ITO-Asahi Glass and then submitted to a final heat treatment at 560°C during 3 h in atmosphere of oxygen. The electrochromic properties of the films were investigated using *in situ* spectroelectrochemical method. The films exhibit a blue-gray coloration under lithium ions insertion with a reversible variation of the transmittance in the visible and near infrared range between 90% and 20%. The xerogels of Nb_2O_5-TiO_2 also were characterized by X-ray diffraction, thermal analysis (DTA/TGA) and IR measurements. The morphology of the films was observed by scanning electron microscopy (SEM) and the topography by atomic force microscopy (AFM). These films appear suitable for architectural applications, where a minimum performance in depth color is required.

1. Introduction

The energetic control of the edification is an important problem to be solved in countries with colder and tropical weather. The principal problem is the consumption and waste of energy with heating and air-conditioning during the winter or summer months respectively [1]. For the external opaque surface already exist very good solutions, for example, synthetic foams or mineral wool [2]. But the major part of the infrared and visible radiation corresponding for the temperature and visual conditions of the building paste by the windows. With this, the windows are not only the transparent surfaces but they became very important in the energy waste calculation. In some countries the solar problem is partially solve by use of color and reflective glasses. This kind of glasses decreases the transmission of some of wavelength, from ultraviolet to near infrared, giving only this one possibility due to its constant compositions [3, 4]. However, the weather changes frequently from cold to warm and from the sunny to cloudy. With this idea the researcher try to find a new “smart system” that can change alone depending on the weather conditions, decreasing the energetic consume. This system should be rejecting the maximum level of near infrared radiation in the summer to lower air-conditioning cost, and passing as possible near infrared radiation in winter months in order to reduce the heating cost. One of the most promising technical solutions is using electrochromic windows, which are already installed in Stadtsparkasse bank in Dresden, Germany [5]. These electrochromic windows are multi-layer structure formed by glass and thin films with different properties [3, 6]. The working principle of this system is the insertion, by the potential application, of positive ions (e.g., H^+, Li^+) and electrons in the electrochromic coating and changing its coloration from transparent to blue for most of electrochromic layers [7]. Depending on the applied potential the coloration of this device can be more or less intense. The electrochromic films are for example WO_3 [8] that change to dark blue and Nb_2O_5 to blue [9] or brown [10]. But it seems that the very strong coloration is not very acceptable for architectural purposes, being more interesting neutral color [3]. And remember a good comfort of these applications we prepared a new alternative Nb_2O_5-TiO_2 film to use in electrochromic windows.

In this work we report on a preparation of Nb_2O_5-TiO_2 films dip coated on ITO - coated glass from a sonocatalytic sol containing niobium and titanium as a precursors. The xerogels of Nb_2O_5-TiO_2 have been calcinated at different temperatures and characterized by X-ray diffraction, thermal analysis (DTA/TGA) and infrared spectroscopy (FTIR), and the coatings by scanning electron microscopy (SEM), atomic force microscopy (AFM), optical and electrochemical techniques.

2. Experimental procedure

The starting solution to produce Nb_2O_5-TiO_2 films with molar ratio of Nb/Ti = 3 was obtained by dissolving

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$NbCl_5$ salt (CBMM-Brazil) in isopropanol, addition of titanium isopropoxide ($Ti(OPr^i)_4$) and acetic acid with the purpose to stabilize this sol. After the addition of all components, the solution mixture was submitted for a few minutes (∼5 min) to the action of 95 W ultrasonic irradiation from a Sonicator® W385 Heat System-Ultrasonic, Inc. at 20 kHz equipped with a 1/2” Disruptor Horn resulting in a transparent and pale yellow solution. This solution was stable for several weeks when kept in a closed glass recipient at room temperature.

The coatings were deposited by dipping ITO coated glass substrates (Asahi-Glass, 14Ω/□) previously cleaned and rinsed with bidistilled water, ethanol and then dried at 50° C, into the solution in ambient atmosphere (RH < 60%) and withdrawing it at a rate of 12 cm/min. The samples were subsequently dried in air at room temperature for few minutes. The uniform gel films were then calcinated at 450°C for 5 min and kept the final temperature in oxygen atmosphere at 560°C for 3 hours. The resulting coatings with a thickness of about 100 nm for 1 dip were transparent and homogeneous without any visual cracking.

Differential Thermal Analysis (DTA) and Thermal Gravimetry Analysis (TGA) were performed on xerogel sample with Thermal Analysis TA 2000. All analyses were executed in air atmosphere at a heating rate of 10°C/min.

X-ray diffraction measurements have been performed on samples of xerogels obtained from the same sols and heat treated at different temperature form 400 to 600°C for 3 hours with a URD6-VEB-Carl Zeiss Jena with the CuK_α radiation.

The electrochemical measurements were realized using a Solartron 1286 analyzer and a conventional three-electrode cell placed in a dry-box under dry N_2. 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 cell was previously purged with dry N_2 gas.

The thickness of the films was measured with a Taylor-Hobson Talystep and the optical spectra in the UV-VIS range were recorded *in situ* with a Hitashi U-3501 spectrophotometer. The coated substrate was placed in a special electrochemical cell built with two flat fused quartz windows and the UV-VIS spectra were measured before and after insertion of Li^+ cations at fixed potentials.

3. Results and discussion

The structural changes of Nb_2O_5-TiO_2 sonocatalytic xerogels were accompanied by thermal analysis (DTA and TGA) showed on Fig. 1. The strong endothermic peak at 100°C accompanied by weight loss of 17% correspond to water and organic compound liberation, that are present in the original sol. The second endothermic peak at about 370°C accompanied by weight loss of 23% can correspond to the water and organic residues from the gel network. The final weight loss was about 32%. At 450°C start a crystallization process of niobium visualized by an exothermic peak. This process is confirmed by X-ray diffraction showed on Fig. 2, where until 400°C the structure seems to be amorphous, without any peak. Above this temperature start the crystallization process of both components, niobium and titanium, confirmed by peaks at 500°C. These peaks can be attributed to the Nb_2O_5 TT phase, what shows the X-ray diffractogram and the peaks of TiO_2 anatase phase with the mean interplanar distances of $d = 0.354$; 0.243; 0.231 and 0.190 nm. Above this temperature the both very well definite structures disappears and occurs a formation of a new mixed structure. The formation of this new structure with the interplanar distances of $d = 0.370$; 0.345; 0.277; 0.230; 0.203; 0.190 and 0.167 nm can be a result of fusion of both initial structures.

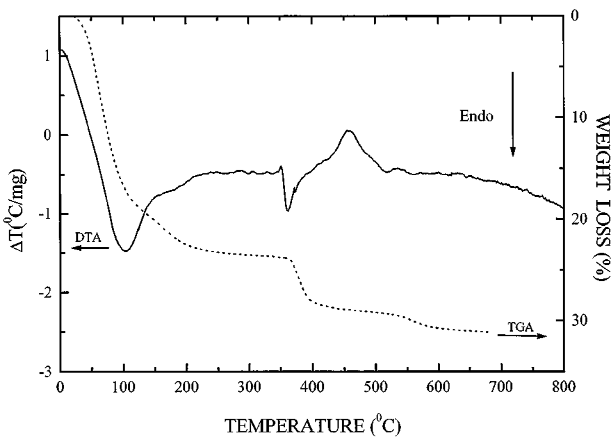


Figure 1 DTA/TGA of niobium-titanium xerogels (10°C/min, air atmosphere).

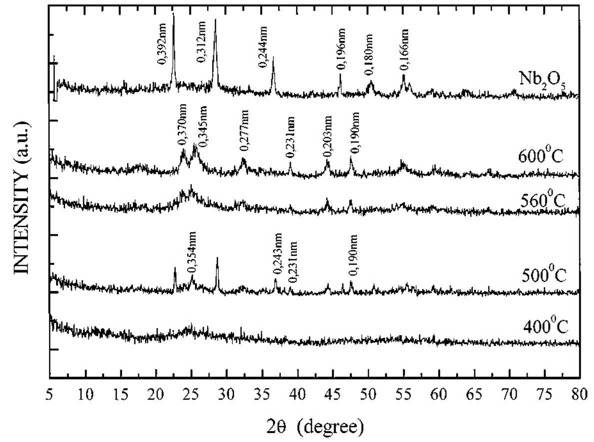


Figure 2 X-ray diffraction of Nb_2O_5-TiO_2 xerogels heat treated from 400 to 600°C in air during 3 hours.

Fig. 3 present IR measurements of xerogels heat treated at 400, 500, 560 and 600°C. In all spectra appear a very small and a large band at 3300 cm^{-1} and 1630 cm^{-1} that correspond to −OH vibration from air adsorbed water. The characteristic bands of inorganic compounds are localized between 1000 and 300 cm^{-1}. The bands of Nb-O locate at 600 and 950 cm^{-1} and are covered by Ti-O bands locate at 540, 780 and 1010 cm^{-1}. However, this large band changes for different heat treatment of the sample and confirms the change of the structure showed by X-ray diffraction. The small band at 2360 cm^{-1} that appears in all spectra is due to atmospheric CO_2.

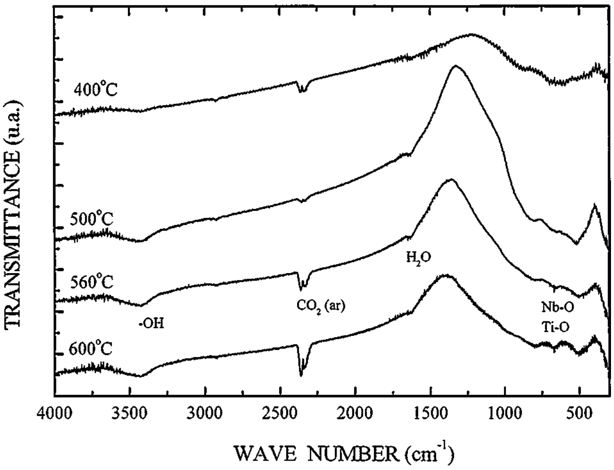


Figure 3 Infrared spectra of: a) niobium-titanium sol, b) niobium-titanium xerogel at air and c) niobium-titanium xerogel heat treated at 600°C during 3 hours.

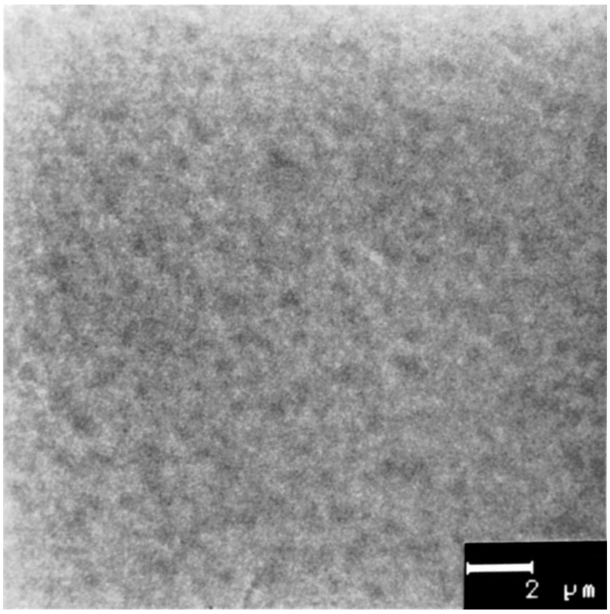


Figure 4 SEM micrograph of Nb_2O_5–TiO_2 film heat treated at 560°C.

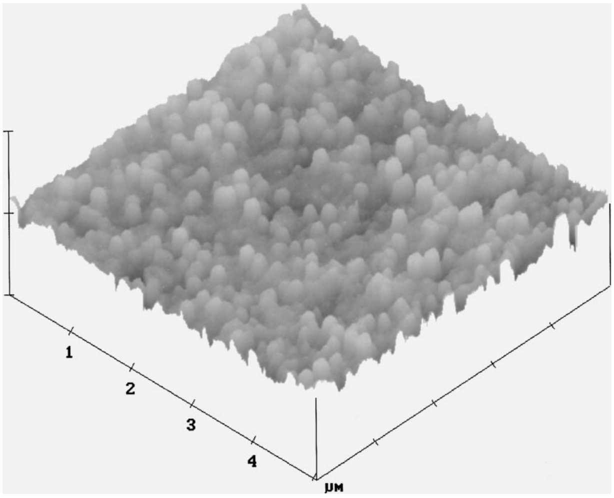
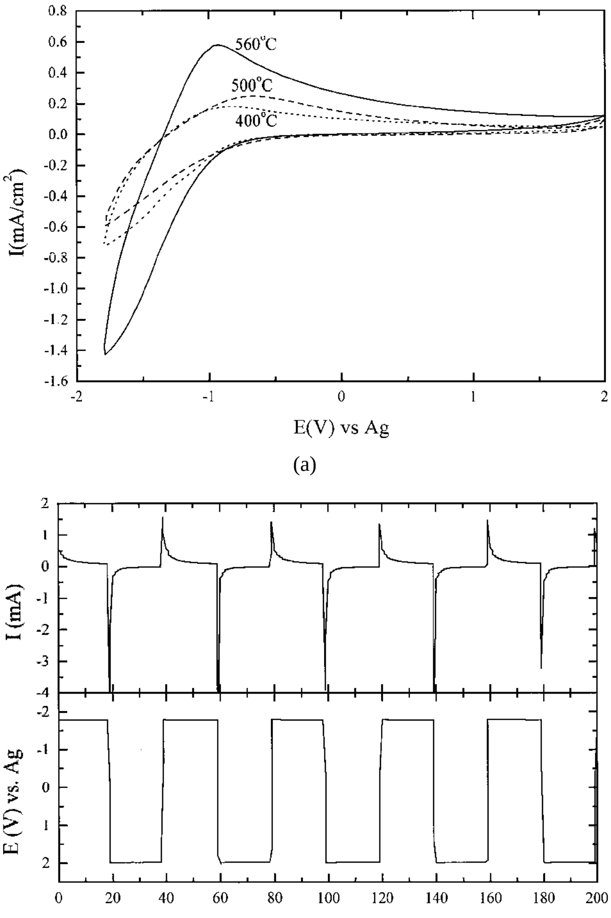


Figure 5 AFM image of Nb_2O_5–TiO_2 films heat treated at 560°C.



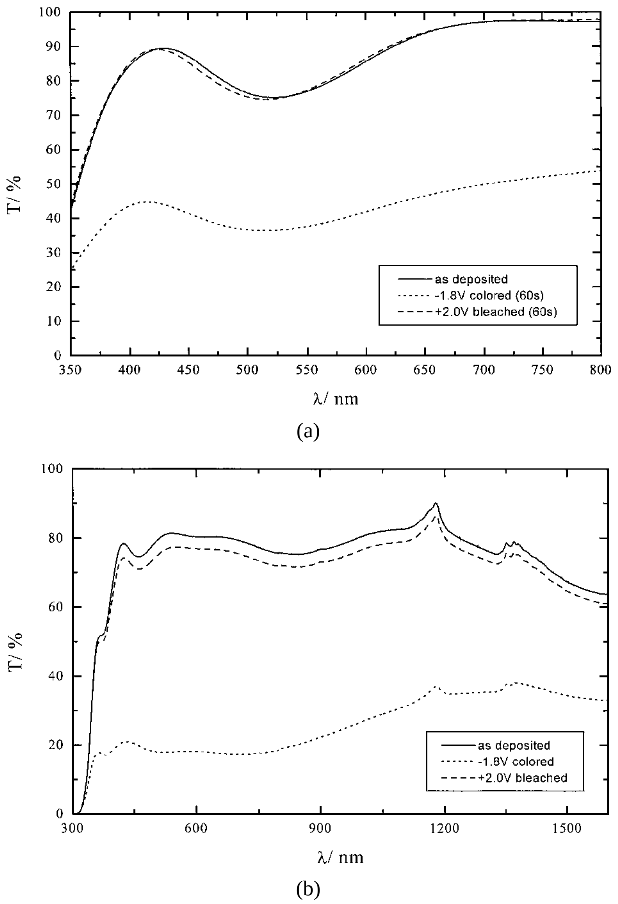
(a)

(b)

Figure 6 Typical cyclic voltammetry of a Nb_2O_5-TiO_2 two layers film deposited on Asahi ITO coated glass heat treated at 560°C (—), 500°C (– – –) and 400°C (· · · · ·) for 3 hours. Electrolyte (0.1M) $LiClO_4$/PC, scan rate 50 mV/s (a) and five chronoamperometric cycles of 20/20s at −1.8 V/+2.0 V (b).

The scanning electron microscopy micrographs (Fig. 4) show the surface morphology of Nb_2O_5-TiO_2 films heat treated at 560°C. This micrograph shows that the structure of the film is very homogeneous and uniform without defects. The topography was visualized by atomic force microscopy measurements showed on Fig. 5. From AFM images it was detected too an uniform agglomeration of well defined small particles with mean average size of about 150 nm.

The cyclic voltammogram of mixed film of Nb_2O_5-TiO_2 showed on Fig. 6a present a visible change on potential versus current graph. Initially the sample is transparent and the electrode potential is cycled between −1.8 V and +2.0 V. When a negative potential is applied, an increase of the cathodic current is observed being this process associated with oxide reduction and lithium intercalation from $E = -0.8$ to -1.8 V. After the limit reversibility potential at $E = -1.8$ V start the extraction process with the maximum anodic wave at $E = -1.2$ V. The best anodic and cathodic charge densities, measured from integration of cyclic voltammograms between −1.8 and +2 V at a rate of 50 mV/s are 18 mC/cm^2 for two layers film. The cronoamperometry measurements (Fig. 6b), performed by applying during 20s the alternated potentials of −1.8 V and +2.0 V, show that the extraction process has a faster kinetics when comparable with the insertion one. This result is in concordance with the results obtained for Nb_2O_5



(a)

(b)

Figure 7 UV-VIS spectral variation observed during electrochromic switching before and after polarization at −1.8 V of two (a) and three (b) layers Nb_2O_5-TiO_2 films as deposited (——), bleached (- - - -) and colored (· · · ·).

films [11]. This figure shows also good reversibility of the Li insertion/ extraction process.

The changes of the color of the Nb_2O_5-TiO_2 film were analyzed by *in situ* visible transmittance measurements in the wavelength range from 350 to 800 nm, (Fig. 7a) and from 300 to 1600 nm (Fig. 7b). The results show that the films exhibit a different spectral transmission for the colored and bleached states. For the both (two and three layers) films (Fig. 7a and b), the transmission value is about 80–90% for the bleached state and after coloration decrease to 40% for two layers film (Fig. 7a) and to 20% for three layers film (Fig. 7b) at 680 nm. This variation is compatible with the results obtained for pure Nb_2O_5 films [11] but the difference is in the color, where for the pure niobium penthoxide is deep blue and for the Nb_2O_5-TiO_2 film is gray-blue. In the near IR region (Fig 7b) it can be observed also decrease in the transmission values from 80% (bleaching state) to 30% for colored state indicating that the film bloc the electromagnetic spectra range responsible for heat conditions in building interior. This figure shows also the small difference (4%) between transmission for the new (as deposited) and bleached film that does not appear for two layers film (Fig 7a). These films appear suitable for architectural applications, where a minimum acceptable in depth color and interior heat comfort is required.

4. Conclusions

Thin mixed films of Nb_2O_5-TiO_2 prepared by sol-gel sonocatalytic method are promising candidates to use in electrochromic windows. They present undefined mixed structure above 500°C showed by the X-ray diffraction. They show also a good reversibility during 25 cycles and charge density of 18 mC/cm^2 for two layers film. Its coloration during the voltammetric recycling changes from about 80% for transparent to 40% (two layers film) and 20% (three layers film) for gray-blue. Optical properties of the films for architectural purpose have been analyzed.

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