



Optical and electrochemical characteristics of niobium oxide films prepared by sol-gel process and magnetron sputtering

A comparison

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Abstract

Electrochromic niobia (Nb_2O_5) coatings were prepared by the sol-gel spin-coating and d.c. magnetron sputtering techniques. Parameters were investigated for the process fabrication of sol-gel spin coated Nb_2O_5 films exhibiting high coloration efficiency comparable with that d.c. magnetron sputtered niobia films. X-ray diffraction studies (XRD) showed that the sol-gel deposited and magnetron sputtered films heat treated at temperatures below 450°C , were amorphous, whereas those heat treated at higher temperatures were slightly crystalline. X-ray photoelectron spectroscopy (XPS) studies showed that the stoichiometry of the films was Nb_2O_5 . The refractive index and electrochromic coloration were found to depend on the preparation technique. Both films showed low absorption and high transparency in the visible range. We found that the n , k values of the sol-gel deposited films to be lower than for the sputtered films. The n and k values were $n = 1.82$ and $k = 3 \times 10^{-3}$, and $n = 2.28$ and $k = 4 \times 10^{-3}$ at 530 nm for sol-gel deposited and sputtered films, respectively. The electrochemical behavior and structural changes were investigated in 1 M LiClO_4 /propylene carbonate solution. Using the electrochemical measurements and X-ray photoelectron spectroscopy, the probable electrode reaction with the lithiation and delithiation is $\text{Nb}_2\text{O}_5 + x \text{Li}^+ + x \text{e}^- \leftrightarrow \text{Li}_x\text{Nb}_2\text{O}_5$. Cyclic voltametric (CV) measurements showed that both Nb_2O_5 films exhibits electrochemical reversibility beyond 1200 cycles without change in performance. ‘‘In situ’’ optical measurement revealed that those films exhibit an electrochromic effect in the spectral range $300 < \lambda < 2100$ nm but remain unchanged in the infrared spectral range. The change in visible transmittance was 40% for 250 nm thick

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electrodes. Spectroelectrochemical measurements showed that spin coated films were essentially electrochromically equivalent to those prepared by d.c. magnetron sputter deposition.

Keywords: Niobia; Sol-gel deposition; D.C. magnetron sputtering; Electrochromism; Optical properties

1. Introduction

Niobium oxide has been studied extensively due to its broad industrial applications especially in optoelectronic technology [1–5]. Niobium oxide film is a promising counter electrode material in electrochromic devices. Niobia has excellent chemical stability and corrosion resistance in both acid and base media which makes it useful in a wide range of electrochromic devices. The relationship between microscopic and macroscopic properties, and deposition parameters provides important guidance when optimizing material characteristics for a given application. This is especially true for oxides of niobium, since niobium oxide films exhibit different electrical and optical properties depending on deposition techniques and fabrication parameters [2].

Electrochromism is a phenomenon related to a persistent and reversible optical change induced electrochemically, whose macroscopic effect is a change in color [6]. A niobium oxide film shows a transparent to brownish gray or blue electrochromism with ion injection. The quality of an EC material is measured by its coloration efficiency which is its transmittance contrast between colored and bleached states relative to injected charge, response time, and chemical stability. These properties depend on the materials properties of the Nb₂O₅ films. The best EC properties are observed in porous amorphous niobium oxide films made by sputtering [7]. There are various studies on EC properties of Nb₂O₅ films fabricated by sputtering [8], electron beam evaporation [9], plasma oxidation [10], chemical vapor deposition [2], metalloorganic chemical vapor deposition [11], and sol-gel process [5,12]. Conventional techniques such as vacuum evaporation and sputtering need capital intensive and complicated equipment. Sol-gel process can overcome such drawbacks. Sol-gel process have other technical advantages such as simplicity, good chemical and mechanical stability, high porosity and ease of control of the microstructure and stoichiometry [13]. These factors can influence the kinetics, durability, coloring efficiency and charge capacity in electrochromic electrodes [14].

The aim of this study is to analyze optical and spectroelectrochemical properties of Nb₂O₅ films prepared by sol-gel spin coating (SG) and d.c. magnetron sputtering (MS) techniques.

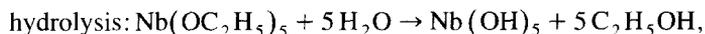
2. Experimental procedure

2.1. Preparation of solution

The niobia coating solutions were prepared by polymerization reactions. Niobium ethoxide (Nb(OC₂H₅)₅, 99.95%, Aldrich Chem. Co. Milwaukee, WI) was used as the molecular precursor. Polymerization occurs by hydrolysis and condensation reactions.

The starting solution was prepared by the acid (CH_3COOH) catalyzed hydrolysis of niobium ethoxide in ethanol. Acetic acid played a specific role in sol-gel processing of niobia both as catalyst for hydrolysis and formed ligands with alkoxide. The stirring of the solution was continued for 15 min. The solution was then diluted with ethanol. A clear light yellow solution was obtained after stirring for 2 hours. The measured pH was 4.5 and the solution viscosity was 1.4 cP. The volume ratio of $\text{Nb}(\text{OC}_2\text{H}_5)_5:\text{CH}_3\text{CH}_2\text{OH}:\text{CH}_3\text{COOH}$ was 1:20:0.003

The overall reaction can be described as follows:



The sol-gel derived Nb_2O_5 layers were spin-coated from this solution. The solution was found to be stable for at least two months at room temperature (55% relative humidity).

2.2. Preparation of Nb_2O_5 coatings

Cleaning of the substrate is important for proper adhesion of the coating. Microscope slides and $\text{In}_2\text{O}_3:\text{Sn}$ (ITO) coated glass substrates ($15 \Omega/\text{cm}^2$, Donnelly Corp. Holland, MI) were ultrasonically cleaned in acetone, rinsed with deionized water, washed with isopropanol, and dried at room temperature. The coatings were deposited by spin coating on an Integrated Technologies Spin Coater (Model P-6000). To produce transparent and uniform SG Nb_2O_5 coatings the polymeric solutions used for spinning must be clear and not cloudy. First, we studied the variation of alkoxide content, catalyst type and solvent in the solutions. Next, we deposited high quality coatings onto both glass and ITO coated glass substrates following the method discussed in subsection 2.1. The thickness of SG Nb_2O_5 coatings was affected by the spinning rate (V_s). Lower spinning rates for solutions with the same viscosity (1.4 cP) produced thicker films. Film thicknesses between 83 and 178 nm were obtained by varying the spinning rate from 3000 to 1000 rpm. A subsequent heat treatment of the films caused a decrease in thickness. The best homogeneity was achieved at spinning rates of 1500 rpm. We formed as many as 15 sequential layers to give the desired thickness. The thickness increment per layer was approximately 124 nm for each deposition cycle. For this purpose it was desirable to have a solution that was stable over a long time period. The films were placed in a furnace for 1 hr. at 150 C before each coating application. Heating of the coatings between spin coating was necessary, because the gel films dried very slowly in air. The dried coatings were transparent, light yellow in color, hard, durable, and stable. All coatings were found to be amorphous by X-ray diffraction analysis up to a firing temperature of 450 C. Above this temperature slightly crystalline structure appeared. The crystallized coating corresponds to the orthorhombic structure of Nb_2O_5 .

2.3. Deposition of d.c. magnetron sputtered films

Nb_2O_5 films for comparative purposes were deposited by d.c. magnetron sputtering. Magnetron sputtered (MS) Nb_2O_5 films were deposited from a Nb target in a mixed

argon–oxygen plasma on unheated substrates. Sputtering power, background pressure, sputtering rate, and plasma flow rate are the important deposition parameters affecting the film stoichiometry and the quality. The power density at the niobium target was 30 W/cm^2 with a 10 cm target to substrate distance. The sputtering rate was 2.5 nm/s and the total pressure during deposition was 2×10^{-2} Torr with 20% oxygen flow. The typical thickness of MS Nb_2O_5 films was 250 nm. These films are typically amorphous with film density of 3.14 g/cm^3 , stoichiometric and low optical absorption.

2.4. Characterization of the coatings

Prior to the optical and structural investigations, the deposited films were exposed to the ambient atmosphere. Scanning electron microscopy, X-ray photoelectron spectroscopy, optical spectroscopy, and cyclic voltammetry measurements were made on both Nb_2O_5 films.

Scanning electron microscopy (SEM), JEOL model JSM 6400 was used to examine the surface morphology of the films. A silver coating was deposited on the samples to avoid charging of the surface. The structure of Nb_2O_5 films was investigated by X-ray diffraction (XRD). The XRD study was carried out on a Siemens Kristalloflex X-ray diffractometer with a Ni-filtered $\text{Cu } K_\alpha$ excitation. The X-ray beam was incident at 1 degree and the scan rate was 0.05 degree per step and 6 seconds per step for all measurements.

X-ray photoelectron spectroscopy (XPS) was used to identify chemical composition of the films. XPS spectra were recorded on a PHI 5300 ESCA system with $\text{Mg } K_\alpha$ X-ray source at 1253.6 eV. The background pressure of the system was approximately 5×10^{-10} Torr. The spectrometer was calibrated for each experiment so that C 1s peak occurred at $285 \pm 0.2 \text{ eV}$.

A Perkin-Elmer Lambda 9 double-beam spectrophotometer was used for spectral normal transmittance $T(\lambda)$ measurements. These characteristics were then used to calculate the refractive index $n(\lambda)$, extinction coefficient $k(\lambda)$ and film thickness d . The details of the spectrophotometric transmittance methods used to determine $n(\lambda)$, $k(\lambda)$, and d of a weakly absorbing film are given elsewhere [15].

Cyclic voltammetric measurements were performed with a PAR digital coulometer and a Hewlett–Packard X–Y recorder. The electrochemical cell consisted of a sealed three-electrode cell with quartz windows. The cell was filled with a non aqueous electrolyte consisting from ultra pure (HPLC grade) lithium perchlorate and propylene carbonate (PC). The cell was filled with 1 M LiClO_4/PC and sealed in a dry box immediately before all experiments. Nb_2O_5 deposited on a ITO glass substrate was used as a working electrode, with a lithium metal counter-electrode and reference electrode. A potential scan rate of 20 mV/s was used throughout. Single or multi-scan cyclic measurements were performed within and at the potentials of 1.2 and 4.0 V versus Li.

Film thickness was measured by a Dektak II (Veeco Inst. Inc.) surface profiler having a maximum resolution of $0.5 \text{ nm}/100 \text{ nm}$. Film thickness was 140 nm for a single layer SG Nb_2O_5 coating deposited at a spinning rate of 1500 rpm.

3. Results and discussion

3.1. Chemical and structural analysis of coatings

Scanning electron micrographs of the surface of such films are relatively smooth with few pinholes or microcracks over a large area. SEM cross-section micrographs show that Nb_2O_5 films are very uniform.

The XRD patterns of heat treated SG and MS Nb_2O_5 films on a glass substrate, are shown in Fig. 1. The as deposited SG and MS niobia films were both amorphous. These films crystallize after heat treatments at or above 450°C . XPS measurements revealed that the only impurities seen in the film are sodium (from the glass) and carbon. The stoichiometry of the films, given as ratio of oxygen to niobium (O:Nb) was computed from the area under the XPS peaks. We found for films deposited on different substrates, that the O:Nb ratio were within 2.49 ± 0.1 and 2.53 ± 0.1 for SG and MS films, respectively. The measured binding energies agree very well with standard Nb_2O_5 [16].

The corresponding peak positions for niobium oxide films deposited by two different techniques are listed in Table 1.

3.2. Optical properties

The optical properties of Nb_2O_5 films were studied to determine the spectral n and k values, transmittance and uniformity. These values helped indicate the deposition–densification conditions to make the best films. The optical parameters (refractive index and extinction coefficient) for as-deposited films were determined from spectral transmittance in the $0.3 < \lambda < 2.1$ μm wavelength range. The refractive index values of SG

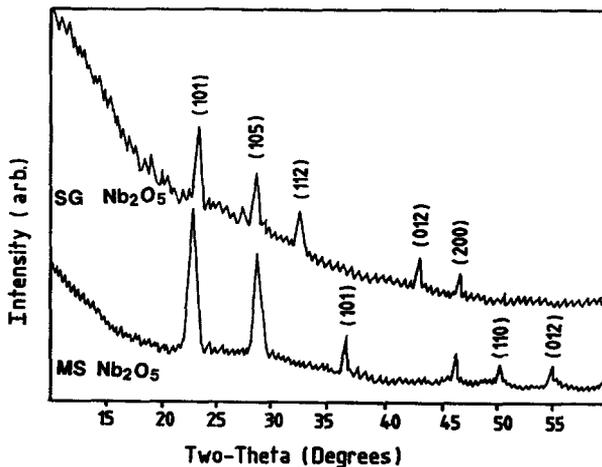


Fig. 1. XRD patterns of MS and SG Nb_2O_5 films: fired at 500°C on soda-lime glass substrate.

Table 1
Binding energies for Nb₂O₅ samples (values ± 0.1)

Parameter	SG film on glass $d = 120$ nm	SG film on ITO $d = 125$ nm	MS film on ITO $d = 270$ nm
Nb 3d _{5/2} (eV)	207.3	207.2	207.2
Nb 3d _{3/2} (eV)	210.1	210.1	210.0
(3d _{3/2} –3d _{5/2})eV	2.8	2.9	2.8
O 1s (eV)	530.6	530.5	530.4
Ratio O: Nb	2.49	2.48	2.53

films were also determined by ellipsometer for comparison with the spectrophotometric analysis.

Fig. 2 shows the transmittance spectra of a 260 nm thick MS niobia coating. The T_0 , T^+ , and T^- curves in this figure correspond to the transmittance of bare substrate and maximum and minimum envelopes passing through the transmittance extrema. The number of interference extrema in a given spectral region is proportional to the film thickness and the refractive index. The separation between the T^+ and T^- and the T_0 and T^+ curves are measures of the refractive index and the absorption of the film, respectively [15]. The SG niobia coatings exhibited to be characteristics similar MS coating. Both films were weakly absorbing beyond 440 nm. For the thicker film we see interference effects between the substrate and film. Fig. 3 shows the spectral dependence of the refractive index value, n of MS and SG Nb₂O₅ films. As can be seen, n increases sharply for $\lambda < 0.4$ μm . The sharp increase in $n(\lambda)$ at shorter wavelengths is connected

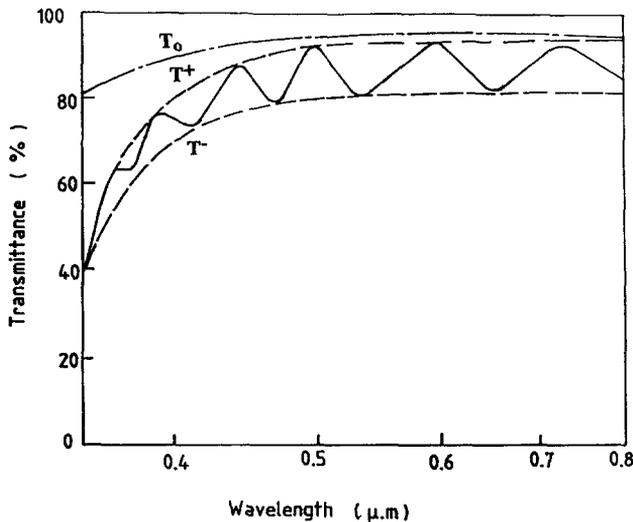


Fig. 2. Spectral normal transmittance for a d.c. magnetron sputtered (260 nm thick) T_0 , T^+ , and T^- curves of this figure correspond to the transmittance of bare substrate and maximum and minimum envelopes passing through the transmittance extrema.

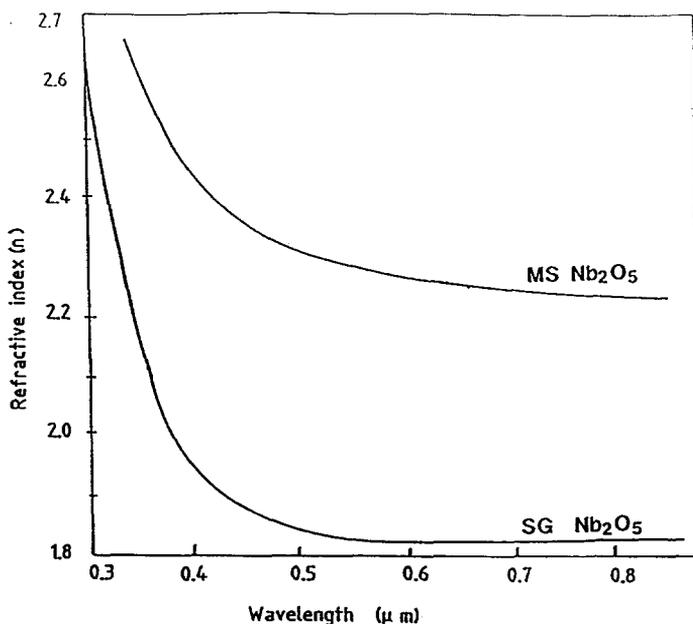


Fig. 3. Wavelength dependence of refractive index of MS and SG Nb₂O₅ films.

with band-to-band electronic transitions. For the MS and SG niobia films, the refractive index and extinction coefficient was $n = 1.82$ and $k = 3 \times 10^{-4}$, and $n = 2.28$ and $k = 4 \times 10^{-3}$ at $\lambda = 0.53 \mu\text{m}$, respectively. An increase in n and k was observed with increasing firing temperatures. In the region of strong dispersion ($\lambda < 0.55 \mu\text{m}$) this model is potentially inaccurate. The n and k values of SG films are lower in comparison to MS Nb₂O₅ films. The n and k values of MS Nb₂O₅ films agree with the literature [6]. The higher index films made by sputtering or heat treatment are known to be more dense [13]. The MS Nb₂O₅ films are denser than SG Nb₂O₅ films. The densification of SG Nb₂O₅ films were controlled by firing. Optical properties near those of MS Nb₂O₅ were achieved in SG Nb₂O₅ film only after heat treatments at or above 400 C.

3.3. Electrochemistry and spectroscopy

Cyclic voltammetry (CV) was performed on Nb₂O₅/ITO/glass electrodes in an electrolyte of 1 M LiClO₄ in PC at room temperature. Fig. 4 shows the cyclic voltammogram of MS and SG Nb₂O₅ films, which are similar to that reported previously for the conventionally deposited Nb₂O₅ [6]. The curves show a single oxidation–reduction cycle. The anodic current peaks were observed at about 1.9 V (versus Li) and 2.1 V for MS and SG Nb₂O₅ films, respectively. The charge capacity values of both films were found to be approximately equal ($1.8 \times 10^{-2} \text{ C/cm}^2$), for a sweep rate of 20 mV/s. We note that the present data are comparable with those in Ref [6]. The Nb₂O₅ film colored to bronze at low positive potentials, e.g. 1.7 V (versus Li). This coloration is the result of Li⁺ and e⁻ insertion into the film. The film bleaches by

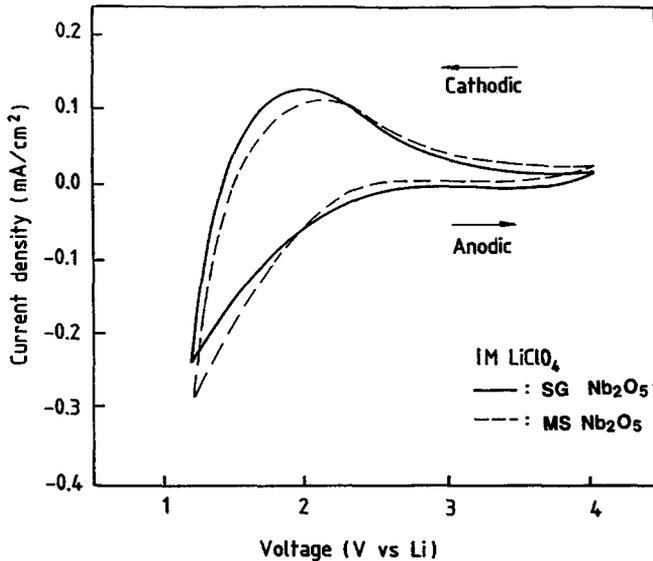


Fig. 4. Cyclic voltammograms for MS and SG Nb_2O_5 film on ITO coated glass electrode in IM LiClO_4 / PC solution with a Li reference after 1000 cycles (scan rate 20 mV/s).

application of an anodic potential which results in Li^+ and e^- extraction. The coloration process began around 2.2 V (versus Li) and deepened at lower voltages. The films started to bleach at around 1.5 V (versus Li). Long term cycling (1200 cycles) at room temperature show that Nb_2O_5 films were quite stable; a change less than 2 mC/cm^2 in the spectra compared to the as-deposited film. This shows that the electrochemical Li^+ insertion/extraction is reversible. The voltammetry indicates that Nb^{5+} is reduced to a lower valence state Nb^{4+} by lithiation, which returns to the original valency through delithiation [17]. The presence of Nb^{5+} and Nb^{4+} also has been confirmed by XPS analysis in the bleached and colored states.

The optical transmittance spectra of Nb_2O_5 /ITO/glass electrodes in the reduced and oxidized states are shown in Fig. 5. The MS and SG Nb_2O_5 films become bronze under an applied potential of 1.3 V (versus Li). The electrode was colored at 1.8 V (versus Li). A decrease in transmittance between 0.35 mm and 0.80 mm occurs under this applied potential. Using the weighted ordinate method, the photopic response for the colored and bleached states of MS and SG films were found to be $T_p = 0.41$ and $T_p = 0.78$, and $T_p = 0.44$ and $T_p = 0.79$, respectively. A deeper coloration ($T_p = 0.31$) can be obtained at 1.25 V (versus Li). The films became transparent again when the bleaching potential of 3.6–3.8 V (versus Li) was applied for 18 s.

3.4. Chemical analysis of cycled films

The XPS binding energy curves for SG niobia films cycled 1200 times are shown in Figs. 6 and 7. Curves are shown for the reduced and oxidized states. In Fig. 6 are the

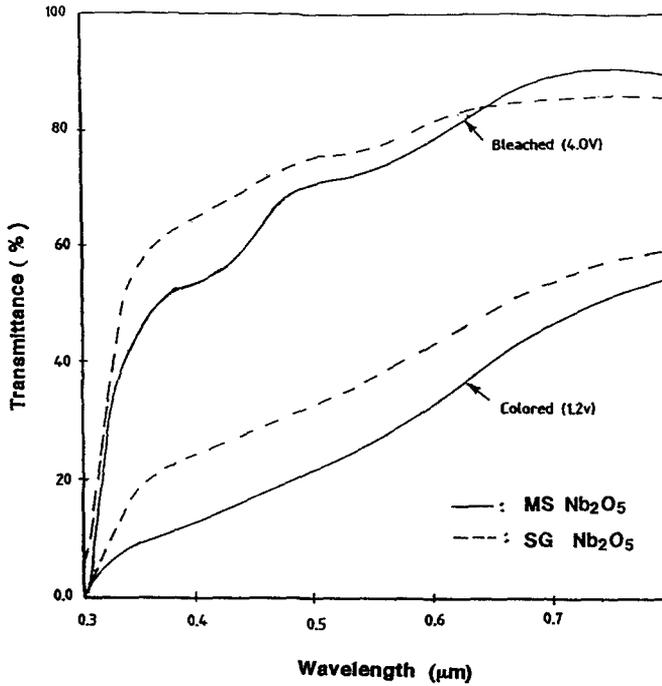


Fig. 5. Transmittance spectra of MS and SG Nb₂O₅ films on ITO coated glass electrodes: oxidized (bleached) at 4.0 V and reduced (colored) at 1.3 V (versus Li).

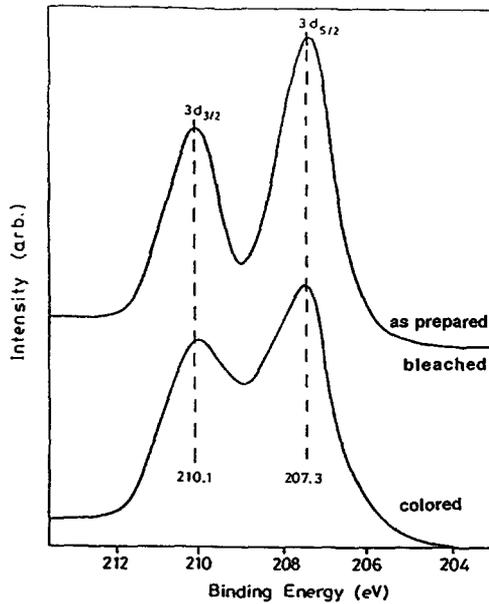


Fig. 6. XPS spectra of SG Nb₂O₅ film in the Nb(3d) region at colored and bleached states.

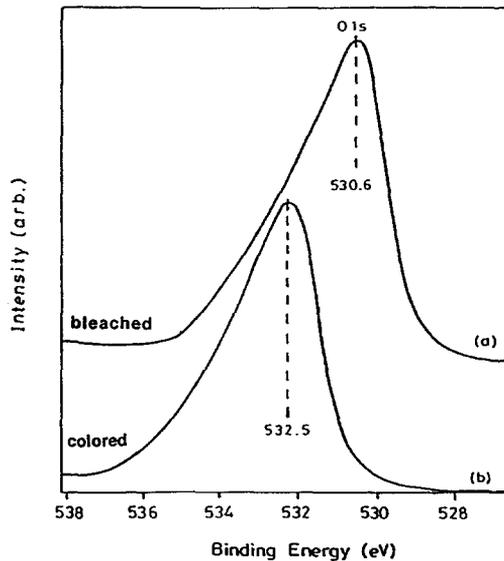


Fig. 7. Typical O (1s) spectra of colored and bleached SG Nb₂O₅ film.

curves for Nb (3d) and in Fig. 7 are the O (1s) spectra. The corresponding peak positions for MS and SG films are summarized in Table 2. For SG niobia films, a pair of peaks are observed at the binding energies of 210.1 ± 0.1 and 207.3 ± 0.1 eV, and can be attributed to Nb 3d_{3/2} and 3d_{5/2} core levels, respectively. Literature data of binding energies for Nb 3d_{3/2} and 3d_{5/2} core levels lie from 210.2 to 209.9 eV, and 208.1 to 207.2 eV for Nb₂O₅ [16]. For SG films subjected to ion intercalation (colored), the Nb 3d_{3/2} and 3d_{5/2} are observed at 209.8 ± 0.1 and 207.0 ± 0.1 eV. Electrochemically reduced SG and MS niobia films had a tendency that the Nb (3d) peaks were shifted toward lower energy. After bleaching, the Nb (3d) peaks are again observed at 210.1 ± 0.1 eV and 207.3 ± 0.1 eV. This shift has been observed in battery electrodes during charge–discharge reactions and corresponds to the colored and bleached conditions of the electrode [17].

The corresponding O 1s spectra of SG Nb₂O₅ is shown in Fig. 7. The O 1s spectra exhibit a single peaks centered at 530.1 ± 0.1 eV and 530.5 ± 0.1 eV for MS and SG

Table 2
Binding energies for lithiated/delithiated niobia films (values ± 0.1 eV)

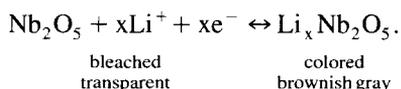
Parameter	As-prep. MS-SG	Colored SG	Colored MS	Bleached MS-SG
Nb 3d _{5/2} (eV)	207.2–207.3	207.1	206.4.0	206.9–207.3
Nb 3d _{3/2} (eV)	210.0–210.1	209.9	209.2	209.6–210.2
D 3d (eV)	2.8–2.8	2.8	2.8	2.7–2.9
O 1s (eV)	530.1–530.6	532.5	532.4	530.1–530.5
Li 1s (eV)	no peak	54.5	54.9	54.3–53.9

niobia films. These binding energy values can be assigned to O^{2-} . The binding energies of 530.1 ± 0.1 eV 530.5 ± 0.1 eV fits well with data in the literature, and corresponds to the O^{2-} anion in niobium oxides [16]. After lithiation and charging the O 1s peaks are shifted to a higher binding energies of 531.9 ± 0.1 eV 531.6 ± 0.1 eV for MS and SG films, respectively. After delithiation, the O 1s peak is observed at 530.1 ± 0.1 eV, and 530.5 ± 0.1 eV the same value before lithiation. From the Li 1s spectra of the bleached films, we observed that the Li 1s peaks are located at 54.3 ± 0.1 eV and 53.9 ± 0.1 eV for MS and SG films respectively. After lithiation, the peaks shifts to a higher binding energy by about 0.6 eV. The small quantity of lithium is detected in the delithiated (bleached) films The Nb:O atomic ratio of the niobia film did not changed after 1200 cycles. The XPS spectra for the uncycled films was almost identical to the bleached films after 1200 cycles. Also, the spectra of colored film remained the same over 1200 cycles.

4. Conclusion

Amorphous and transparent electrochromic Nb_2O_5 films were prepared successfully by a sol-gel spinning and d.c. magnetron sputtering technique. The best film uniformity was observed at the spinning rate of 1500 rpm for SG niobia films. The lithiation and delithiation process in MS and SG films in 1 M $LiClO_4$ -PC solution resulted in desirable changes ($\Delta T_{vis} = 40\%$) in optical transmittance. XPS examination showed that the film consisted of $Li_xNb_2O_5$ in the colored state. Electrochemical cycling experiments have shown that both niobia films were stable for at least 1200 cycles with no change in performance. Oxidized MS and SG Nb_2O_5 films are transparent, and reduced form is brownish gray.

Electrochemical measurements combined with XPS examination confirm that the reduction and oxidation reactions with lithiation (coloration) and delithiation (bleaching) can be represented by:



During lithiation Li^+ ions are incorporated into the oxide and at the same time that Nb^{5+} is reduced to Nb^{4+} by accepting an electron. This process forms a colored intercalation compound, $Li_xNb_2O_5$. The reverse process reforms Nb_2O_5 . The high reversibility, stability and optical properties of lithium insertion make Nb_2O_5 thin films useful for transparent electrochromic devices as a counter electrode, particularly in nickel oxide devices.

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