Sputter deposited electrochromic films and devices based on these:
Progress on nickel-oxide-based films

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Abstract

This paper introduces electrochromic (EC) devices, capable of changing their optical absorption under charge insertion/extraction, and some of the required materials. Special attention is given to EC nickel-oxide-based films, for which we discuss sputter deposition and ensuing optical and structural properties. The paper is concluded with some recent results for practical foil-based devices.

Keywords: Electrochromic properties; Nickel oxide; Tungsten oxide; Optical properties; Sputtering; Thin films

1. Introduction

Materials that are able to change their optical properties as a response to an external stimulus are called “chromogenic” [1]. The change can be effected through irradiation by light (photochromic materials), change in temperature (thermochromic materials), application of an electrical voltage (electrochromic materials), to mention the most common alternatives. Electrochromic (EC) materials were brought to public attention more than 30 years ago in seminal work on tungsten oxide films by Debi [2]. In essence, the optical absorption in the visible range changes between widely separated extrema as charge is inserted or extracted. These materials were immediately considered for application in information display, but they did not stand up to the competition from the then rapidly developing liquid crystal devices.

However, electrochromism has remained an active area for basic and applied research, with large possibilities for applications in emerging technologies. The interest was boosted in the mid-1980s with the realization that electrochromism was of much interest in fenestration technology as a means to achieve energy efficiency in buildings [3], and the concept of the “smart window” [4]—with variable-transmittance of light and solar energy—was coined and captured the interest of researchers and the general public. Since then, EC materials have been considered one subset of the “solar energy materials” [5]. Recently, it has become clear that “smart windows” 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 [6]). Similar assets prevail in the automotive sector. A number of more or less related chromogenic technologies are also available [7,8]. Electrochromism is well known also in polymers [9].

2. Survey of electrochromism

Fig. 1 illustrates a standard EC construction that allows basic features and operating principles to be introduced conveniently. The design embodies five superimposed layers on one substrate or positioned between two substrates in a laminate configuration. Normally the substrates are made of glass or flexible polyester foil. The central part of the five-layer construction is a pure ion conductor (i.e., electrolyte) that can be organic (an adhesive polymer) or inorganic (often based on an oxide film). The ions should be small in order to be mobile; protons (H+) or lithium ions (Li+) are normally preferred. This ion conductor is in contact with an EC film (W oxide being a typical example) capable of conducting electrons as well as ions. On the other side of the ion conductor is a film serving as ion storage, ideally with EC properties complementary to those of the first EC film (Ni oxide being a typical example).
The central three-layer structure is positioned between electrically conducting transparent films; the best material in terms of optical and electrical properties—or at least by far the most well known one—is In\textsubscript{2}O\textsubscript{3}:Sn (referred to as Indium Tin Oxide, or ITO) [10,11], while films of SnO\textsubscript{2}:F are less costly and readily available on large area glass panes. ZnO:Al is still another option. We note in passing that In is often considered a rare and hence inherently expensive metal, but this view has been challenged in a recent study on the geology, mineralogy, and economics of indium, which states that this metal can enjoy virtually infinite growth in use without supply limitations [12].

When a voltage of the order of one volt is applied between the transparent electrical conductors, ions will be shuttled between the ion storage film and the EC film. The electrons injected from the transparent conductors then alter the optical properties. A reversal of the voltage, or short-circuiting, brings back the original properties. The coloration can be stopped at any intermediate level, and the device exhibits open-circuit memory so that the optical changes take place only when charge is moved. It is evident that the EC device can be viewed as an electrical battery with its charging state manifested as optical absorption.

EC materials and devices have been reviewed several times in the past, and the literature up to 1993 is covered in considerable detail in books by Granqvist [13] and Monk et al. [14]. Device-related work until 2002 has been reviewed more recently [15,16]. In order to give a snapshot of the ongoing endeavors on EC oxides we mention below some of the most recent work, confined solely to 2004. Such work has been reported for oxides based on tungsten, iridium, vanadium, and nickel. W oxide colors under charge insertion and is referred to as a cathodic EC material, whereas oxides of Ir and Ni color under charge extraction and are called anodic EC materials; V oxide is of an intermediate nature and displays features of weak cathodic and anodic coloration in different wavelength regions. Specifically:

- W oxide films have been prepared by evaporation, sputtering, spray pyrolysis, sol–gel deposition, and electrodeposition; work has been reported also on W oxide containing Mo, V, Ta, Ti, and P;
- Ir oxide films have been prepared by electrodeposition; work has been reported also on Ir oxide containing Ta;
- V oxide films have been prepared by sputtering; work has been reported also on such films with polymer additives;
- Ni oxide films have been prepared by reactive evaporation, pulsed laser deposition, sol–gel deposition, and electrodeposition; work has been reported also on such films containing Mg, Al, Si, V, Zr, Nb, Ag, Ta, and Au.

For the sake of brevity, the references have been excluded here; a detailed coverage will be given elsewhere [17]. The relevant literature is much larger, though, and includes numerous investigations of similar films for sensing applications, thin film batteries, super-capacitors (electro)catalysis, etc.; a survey of this work is clearly outside the scope of the present article. One impression from this miniature review of today’s literature is that interest is focused on EC W oxide and Ni oxide.

Devices incorporating EC W oxide and Ni oxide films have been subject to much research during the last decade, and detailed work has been reported on rigid (glass-based) devices [18–30] and, recently, also on flexible (polyester-film-based) devices [31,32].

3. Electrochromism in nickel-oxide-based films

3.1. Sputter deposition and film properties

Ni oxide shows anodic electrochromism, as pointed out above. An extensive study of sputter deposited thin films of this material was performed recently [33]. Reactive DC magnetron sputtering was employed, using targets of magnetic Ni and non-magnetic NiV\textsubscript{0.08}, in a plasma of Ar + O\textsubscript{2} + H\textsubscript{2} onto substrates...
of glass pre-coated with ITO (for optical and electrochemical measurements) and graphite (for compositional determinations using Rutherford Backscattering Spectrometry, RBS). The film thickness was ∼200 nm. A range of other Ni-oxide-based films were investigated as well [34,35]. Charge insertion/extraction measurements) and graphite (for compositional determinations of glass pre-coated with ITO (for optical and electrochemical procedures. Optical properties were investigated by spectrophotometry on films that had been withdrawn from the electrolyte.

Three distinct deposition regions—here denoted 1, 2, and 3—can be identified when sputter deposition of nickel-oxide-based films is carried out under reactive conditions in a plasma of Ar with varying amounts of O2 [35,36]. When this content is increased, the films evolve from nearly metallic (region 1) to transparent (region 2), and then from transparent to brown (region 3), as illustrated in Fig. 2. Films in region 1 do not exhibit electrochromism, films belonging to region 2 have a very high electrochemical activity and good charge capacity, and films in region 3 have low activity and poor optical properties. The deposition rate drops precipitously at the transition between regions 2 and 3; it was found to lie between 50 nm/min for a partly oxidized target and 10 nm/min in the over-oxidized mode of the target.

The EC properties are also strongly affected by the amount of oxygen in the sputter plasma, as summarized in Fig. 3. The nearly metallic films did not exhibit any optical modulation whatsoever. The initially transparent films, however, displayed pronounced electrochromism with a bleached state luminous transmittance exceeding 80% and a colored-state transmittance pronounced electrochromism with a bleached state luminous transmittance exceeding 80% and a colored-state transmittance strongly decreasing within a narrow range of oxygen flow (cf. region 2 in Fig. 3). An increase of the oxygen content in this intermediate range also yielded a significant enhancement of the charge capacity. The optimum performance was found at oxygen concentrations somewhat below 1.5%. Larger oxygen contents—corresponding to region 3—led to deterioration of the optical modulation range as well as of the charge capacity.

Elemental compositions were determined by RBS. Defining the composition as Ni1−yVyOy+z, the three regions referred to above correspond to y ≈ 0.11 and z ≤ 0.71 for region 1, 0.05 ≤ y ≤ 0.10 and 1.45 ≤ z ≤ 1.75 for region 2, and y ≈ 0.11 and z ≈ 2.07 for region 3. These results are consistent with those of an independent ion beam analysis [37]. An increase of the O2 flow in the gas mixture increased the oxygen content in the films. Furthermore, an addition of H2 to the gas mixture produced films with improved crystallinity and also increased their charge capacity and transparency.

The density lay between 3.6 and 4.2 g/cm3 in the optimized EC films, obtained with intermediate O2 and H2 flows during the sputtering. At the transition between regions 1 and 2, the density was approximately 6.6 g/cm3, and at the transition to the over-oxidized region 3 it was approximately 4.9 g/cm3. Similar values of the density were found for nickel oxide films made by electron beam evaporation [13,38,39].

X-ray diffraction (XRD) was used to study the structure of the as-deposited films. Specifically, bleached and colored films, made so that they belonged to region 2, exhibited cubic nickel oxide (Bunsenite) patterns, which is in agreement with previous work on NiO [13,40,41]. No evidence of phases containing hydrogen was found in any of the films. This at first sight surprising result can be understood if only the outermost part of the grains—that were too thin to be detectable [33]—take part in the EC coloration.

Effective grain size and strain function were determined from the XRD data. The effective grain size lay between 10 and 25 nm depending on the H2 content during the thin film deposition. Small grain size, implying a large surface-to-bulk ratio, may be beneficial for the EC activity, as pointed out before [20,36,40].

Earlier work of ours [42] used extended X-ray absorption fine structure spectroscopy on films similar to the present ones and demonstrated that the vanadium atoms substitute nickel in a NiO-type structure, i.e., Ni and V appeared to form a mixed-oxide phase in the film.

3.2. Electrochromic properties

Transmittance and reflectance were recorded by spectrophotometry in the as-deposited, colored, and bleached states. The
Fig. 4. Coloration efficiency (CE) vs. wavelength $\lambda$ for Ni$_{1-y}$V$_y$O$_z$ films prepared with the shown fractions of O$_2$ and H$_2$ in the sputter plasma. Also shown are O/Ni ratios determined by RBS.

The main differences between these states are most prominent in the spectral transmittance within the visible region. Combining optical and electrochemical measurements, the spectral coloration efficiency (CE) was obtained from a standard relation [43]. Fig. 4 shows spectral CEs. The main effect of the electrochromism takes place in the ultraviolet and visible, whereas the coloration is small in the near-infrared. Three main peaks can be distinguished in Fig. 4: two prominent ones are located at wavelengths being 340 and 445 nm, and a third very broad peak can be discerned around 600 nm. This last peak was confirmed in other recordings of the CE. It is interesting to observe that the coloration efficiency is very high compared to values reported in other work [13,39,41,44], which is an important result with regard to applications. The influence of the sputtering conditions on the CE is strong at short wavelengths and weak at long wavelengths. The CEs correlate with the crystallinity of the films. The behavior supports the notion that the large inner surface area of the films is connected to the EC activity, and that the coloration process takes place in the outermost parts of the grains.

The luminous transmittance—especially in the state of maximum transmittance—and the perceived color are very important properties for architectural windows, including “smart” ones [45]. Quantitative assessments can be performed in several different ways; specifically we employed the CIE Colorimetric System [46,47]. Fig. 5 reports the luminous transmittance for films of pure Ni oxide as well as for films containing various additives, including V as reported on above. We notice, in particular, the beneficial effect of Al and Mg. Detailed results on the colorimetric analysis were presented elsewhere [34].

### 3.3. Coloration mechanism

Extensive work was carried out to ascertain the coloration mechanism. This work embraced X-ray photoemission spectroscopy (XPS) using synchrotron radiation [48], several electrochemical analysis techniques including galvanometric intermittent titration [49], and infrared spectroscopy [49]. Fig. 6 shows an XPS spectrum for the Ni 2p states of a film in colored and bleached state. The difference is small but unambiguous and demonstrates that the optical changes correspond to Ni$^{2+} \leftrightarrow$ Ni$^{3+}$ transitions in parts of the film.

The analysis to elucidate the coloration mechanism is too lengthy to be given in detail here but the net result can be given as follows: the transition to the colored-state is consistent with a structural phase transition from $\alpha$-nickel hydroxide to $\gamma$-nickel oxy-hydroxide, in full accordance with the Bode...
reaction scheme [50,51]. Presumably this reaction is confined to thin sheaths on the grain surfaces, as emphasized above.

4. Conclusion and application to foil-type devices

This paper has introduced EC devices and the materials for making such with emphasis on nickel-oxide-based films. The films were sputtered onto polyester substrates with pre-deposited ITO layers having values of the resistance/square down to 10 Ω. The films were discharged in ozone [52] in order to make them ready for device incorporation. Similarly, tungsten oxide films were made by sputtering onto identical substrates; the deposition was performed in the presence of H2 in order to make appropriately charged films. The nickel-oxide-based and tungsten-oxide-based films were then laminated together by use of a proprietary polymer electrolyte, and the EC foil device was sealed, contacted, and ready for testing and use.

Figs. 7 and 8 show EC foils mounted in a variable-transmittance visor for a motorcycle helmet and in a “smart window” prototype with four 30 cm × 30 cm panes, respectively. The upper two panes are in their dark state and the lower two in their fully bleached state. The maximum range of optical modulation is, typically, 40–50%.

References