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Nickel-oxide-based electrochromic films with optimized optical properties

Abstract Reactive DC magnetron sputtering was used to grow thin films of Ni (93%)-V (7%) oxide and Ni (62%)-Al (38%) oxide. Both films showed electrochromism in KOH. The addition of Al diminished the luminous absorbance significantly, while the charge capacity was maintained. The Al-containing films are superior to the conventional Ni oxide electrodes as regards applications requiring high-bleached-state transmittance.

Keywords Electrochromic · Nickel-based oxides · Polyester · Sputtering conditions · Transmittance

Introduction

Thin films of nickel oxide possess anodic electrochromic properties [1, 2, 3, 4, 5], with the visual appearance changing between transparent and brown upon charge insertion/extraction. In electrochromic devices incorporating W oxide, the brown colour of Ni oxide is complementary to the blue colour of W oxide, both together yielding a neutral (grey) colour in transmittance in the dark state. While having sufficiently high charge capacity and low transmittance in the coloured state, Ni oxide films have a drawback in their not being completely transparent in the bleached state. This is particularly serious for architectural applications, such as electrochromic "smart windows". The present work focuses on sputter-deposited Ni-oxide-based films and aims to increase the transmittance and the colour neutrality in

the bleached state, without sacrificing other relevant properties. These assets are achieved by adding Al to the Ni oxide.

Experimental

Thin films of Ni (93%)-V (7%) oxide were deposited by conventional DC magnetron sputtering from a metallic target. Vanadium was added for technical reasons; it renders the material non-magnetic and convenient for magnetron sputtering, in contrast to strongly magnetic pure Ni. Depositions were made in atmospheres of Ar/O_2 and $Ar/O_2/H_2$ with varied gas flow ratios at a total pressure of approximately 30 mTorr. Depositions of Ni-Al oxide films were made from a metallic Ni (62%)-Al (38%) target in an atmosphere of $Ar/O_2/H_2$ a total pressure of approximately 30 mTorr. The targets were 99.95% pure, and the gases were 99.998% pure. The films were approximately 200 nm thick, as measured on an Alpha step profilometer. Our substrates were glass plates pre-coated with a transparent and electrically conducting ITO layer. The deposition unit and the relevant procedures are described in some detail elsewhere [6].

Cyclic voltammetry was carried out in a 1 M KOH electrolyte at a scan rate of 10 mV/s in a three-electrode configuration cell with a counter electrode of Pt and a reference electrode of Ag/AgCl, using an AUTOLAB PGSTAT10. Spectrophotometric measurements were made after withdrawing the films from the electrolyte and rinsing with distilled water. A slight spontaneous bleaching was observed upon rinsing of the coloured films, so that the measured coloured-state transmittance is somewhat higher than the electrochemically produced one.

Stoichiometry of the as-deposited samples backed by carbon were determined by Rutherford backscattering spectroscopy (RBS) using 2 MeV He ions.

Results and discussion

When sputtering is carried out in Ar/O_2, three rather distinct deposition regions can be distinguished, depending on the oxygen content. The characteristics are similar for films based on Ni-V and Ni-Al, and we only report data for the former films below. Figure 1 shows deposition rate and luminous transmittance for as-deposited Ni-V-based films. As the amount of oxygen in the sputtering atmosphere is increased, the films evolve

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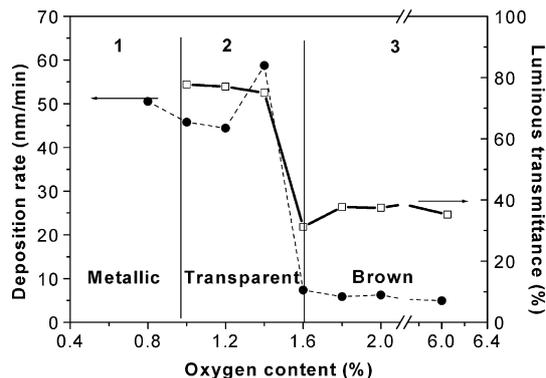
Fig. 1 Deposition rate and luminous transmittance for as-deposited Ni (93%)-V (7%) films versus oxygen content in the sputter plasma. *Vertical lines* separate three intervals; they signify different visual appearances

from nearly metallic (region 1), to transparent (region 2), to brown (region 3). According to RBS, the oxygen-to-nickel ratio in the films increases from 0.63 in region 1 (film deposited at 0.8% O_2), to 1.56 in region 2 (film deposited at 1.2% O_2), to 1.85 in region 3 (film deposited at 2% O_2). The film density is 6.5 g cm^{-3} in region 1, 4.3 g cm^{-3} in region 2, and 4.8 g cm^{-3} in region 3. From a sputtering point of view, regions 1, 2, and 3 roughly correspond to deposition from metallic, partly oxidized, and fully oxidized targets. All the films are expected to contain hydrogen to an extent that is as-yet unknown.

The electrochromic switching behaviour of Ni-V-based films deposited in Ar/O_2 are summarized in Fig. 2. The nearly metallic films did not switch at all. On the other hand, initially transparent films exhibited strong optical modulation with the bleached-state transmittance exceeding 80% and the coloured-state transmittance decreasing considerably within a narrow range of oxygen flow (region 2 in Fig. 2). An increase of the oxygen content within region 2 led to an increase in charge capacity. The optimum performance was found
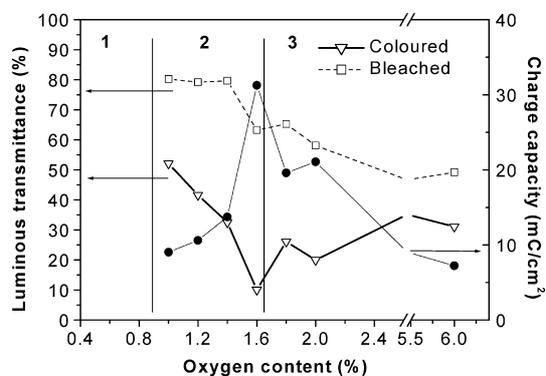
for oxygen concentrations below 1.5%. Both the optical modulation range and charge capacity decreased upon further increase of the oxygen flow (region 3 in Fig. 2).

Addition of hydrogen to the sputtering atmosphere resulted in higher transmittance for the as-deposited state, while the bleached-state transmittance remained the same as in films deposited without hydrogen. The presence of hydrogen during the deposition increased the charge capacity by 20–50%. The optimum gas mixture was found to contain 1.5% of oxygen and 1.9% of hydrogen. A further increase in the hydrogen content decreased the deposition rate with no improvement of the film properties.

It can be inferred from Fig. 2 that Ni-V oxide films provide sufficient charge capacity and luminous transmittance modulation for use in at least some electrochromic devices. A disadvantage, though, is that the films are slightly brownish in their bleached state due to residual absorption in the short wavelengths. Adjustments in the oxygen and hydrogen flows during the deposition could not eliminate this.

However, it was discovered that the short-wavelength transmittance could be increased (i.e. the absorbance could be reduced) by addition of Al to the films. Figure 3 shows an example of spectral transmittance in the bleached and coloured states for films of Ni-V oxide and Ni-Al oxide. The Ni-V oxide film displays a luminous transmittance in the bleached state of 82% and its chromaticity coordinates are $x = 0.331$, $y = 0.341$, and $z = 0.329$ (illuminant D65), where $x = y = z = 0.333$ corresponds to a perfectly colourless film; the concept of chromaticity coordinates has been described [7]. The properties of the Ni-Al films are very different: the luminous transmittance in the bleached state is as high as 85% and the corresponding chromaticity coordinates are $x = 0.314$, $y = 0.337$, and $z = 0.349$. Thus it can be concluded that the addition of Al makes the film more colourless in the bleached state, while the film is still able to yield a brown colour in its dark state. Both films are reported on in Fig. 3; they were coloured/bleached at a potential of 0.6/−0.5 V versus Ag/AgCl. The coloration charge was approximately 12 mC cm^{-2} for the Ni-V oxide film and 15 mC cm^{-2} for the Ni-Al oxide film.

Fig. 2 Luminous coloured-state and bleached-state transmittance and charge capacity for Ni (93%)-V (7%) films versus oxygen content in the sputter plasma. *Vertical lines* separate three intervals; they signify different visual appearances, as shown in Fig. 1. Switching was done in 1 M KOH at a potential of 0.6/−0.5 V versus Ag/AgCl
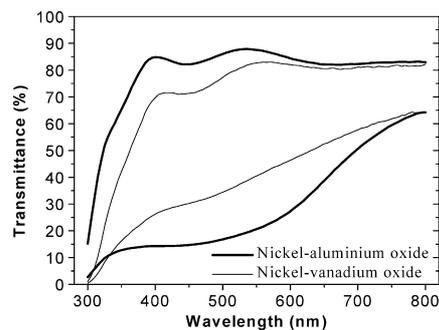
Fig. 3 Spectral transmittance for Ni-Al oxide and Ni-V oxide films in coloured and bleached states. Switching was done in 1 M KOH at a potential of 0.6/−0.5 V versus Ag/AgCl

The difference in the coloured-state spectra in Fig. 3 arises from the coloration charge being higher for the Ni-Al oxide film, rather than from a change in the optical properties due to the Al addition.

We can consider at least two reasons for the decreased short-wavelength absorbance upon Al addition, as follows:

1. Al oxide has a direct band-gap as large as 8.8 eV [8], while fully oxidized V has a direct band-gap of 3.3 eV and also allows indirect transitions at about 2 eV due to the existence of a split-off localized band lying approximately 0.6 eV below the main conduction band [5]; considering that the optical band-gap for Ni oxide is 3.6–4 eV [5, 9], the addition of Al may increase the band-gap of the compound whereas the effect of V may be to diminish it.

2. Alternatively, Al as well V may affect the optical absorption caused by defects such as vacancies, over-stoichiometry, grain boundaries, etc. Thermodynamically stable nickel oxide is a p-type conductor due to excess oxygen [9, 10]. It is then plausible that the p-type conductivity and the residual optical absorption in the bleached state originate from the same electron states. This may then explain why films of pure Ni oxide cannot be made completely colourless. When Al is added, it can act as a donor of electrons and fill the electron (hole) states on Ni, thereby reducing the residual absorption. The addition of V, on the other hand, may provide acceptor states whose effect would be to enhance the residual absorption.

Conclusions

Thin films of Ni (93%)-V (7%) oxide and Ni (62%)-Al (38%) oxide were made by reactive DC magnetron sputtering. Both types of films showed good electrochromism in KOH. An important difference is that the Al addition enhances the luminous transmittance in the bleached state to a significant degree, which renders the Ni-Al oxide films very promising for applications requiring large bleached-state transmittance, such as architectural "smart windows" [11]. We have previously observed similar beneficial effects for Mg additions to electrochromic Ni oxide [12] and Ir oxide [13].

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