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ABSTRACT

Mixed vanadium and tungsten oxide films with compositions ranging from 0 to 100% vanadium (metals basis) were prepared by reactive sputtering from metallic vanadium and tungsten targets in an atmosphere of argon and oxygen. The vanadium content varied smoothly with the fraction of total power applied to the vanadium target. Films containing vanadium were more color neutral than pure tungsten oxide films, tending to gray-brown at high V fraction. The electrochromic switching performance of these films was investigated by *in situ* monitoring of their visible transmittance during lithium insertion/extraction cycling in a non-aqueous electrolyte (1M $LiClO_4$ in propylene carbonate). The solar transmittance and reflectance was measured *ex situ*. Films with vanadium content greater than about 15% exhibited a marked decrease in switching range. Coloration efficiencies followed a similar trend.

INTRODUCTION

Mixed metal oxides have been investigated for their potential to improve existing electrochromic films. Possible beneficiary effects on the electrochromic host material are increased coloration efficiency, improved durability, color neutrality, a larger switching potential range or faster reaction kinetics. Both Granqvist and Monk 1,2) recently reviewed mixed metal oxides and gave a useful summary. Binary combinations with WO_3 with oxides of Ag, Ce, Co, Cr, Cu, Fe, Mo, Nb, Ni, Ru, Sn, Ta, Ti, V, and Zn are mentioned. Despite the variety of reported combinations, few have been studied in depth. Ternary mixtures containing V_2O_5 and WO_3 were suggested with additional components MoO_3 (3), Li_2O (4) and VO_2 (5), but due to the large influence of thin film deposition parameters it may be conjectural to what extent the combined properties are affected by the individual components.

From studies on bulk crystals of V_2O_5-WO_3 they are known to consist of regular blocks of corner-sharing octahedra that are connected by edge-sharing octahedra (6-9). The electrochromic properties of V_2O_5 itself are given in (10-15). The most commonly cited advantage of V_2O_5-WO_3 is its potential to provide a neutrally coloring electrochromic electrode (3,16,17). In WO_3 the spectral position of the broad absorption band in the NIR (near infrared spectral region) varies between approximately 1.3 eV for disordered films (18-33) and 0.9 eV for a single-crystalline WO_3 (34). WO_3 therefore exhibits in either case a characteristic bluish tint in the colored state. This work found the effective absorption band of vanadium (7%) tungsten (93%) oxide blue-shifted by 0.5 eV versus pure WO_3, hence providing a more neutral color.

EXPERIMENTAL

Thin film deposition

Films were co-deposited by DC magnetron reactive sputtering using W (99.95%) and V (99.9%) targets. The Ar (99.9995%) flow rate was 220 sccm (standard cm^3/min), delivered into the chamber through the sputter guns, flowing up between the anode shield and the cathode, and then across the target surfaces. The O_2 (99.998%) was delivered through a manifold at the substrate surface. Oxygen flow rates were 50 sccm for the WO_3 and W-V oxides, and 40 sccm for V_2O_5. Deposition pressure was 30 mTorr. The chamber was pumped with a 450 l/s LH turbomolecular pump backed by a LH D40B roughing pump. The as-deposited base pressure (i.e. base with turbo throttled to run pressure position) was below 2.0×10^{-6}, with an ultimate system base pressure of less than 7.0×10^{-7} Torr. Two Angstrom Sciences 2" sputter sources inclined 20 degrees off normal to a common focal point were used for co-deposition. The target-to-substrate distance was 17 cm. Compositional variation was achieved using W powers between 15 and 350 Watts, and V powers between 50 and 375 Watts. Total power for the binary metal oxide runs varied between 250 and 575 Watts. Single oxide runs were done at 200 and 200-350 Watts respectivel for vanadium and tungsten.

Deposition rates ranged from 16 Å/sec for WO_3 at 350 Watts, down to 0.2 Å/sec for pure V_2O_5 utilizing 200 Watts V power and 40 sccm O_2. For growth of the mixed oxides with vanadium concentration below 15 %, the most promising range, a rate of 7.5 Å/sec was typical. Deposition rates declined rapidly as the percent of total power contributed by the vanadium source increased. At 68 % vanadium, with 25 Watts tungsten power and 375 Watts vanadium power, the rate was only 1 Å/sec. Growth of WO_3 required substantially higher oxygen pressure than did V_2O_5. A lower oxygen pressure for the pure V_2O_5 run would have resulted in a much higher deposition rate, but would have been a significant departure from the deposition environment used for the mixed oxide runs. Typical film thickness was between 4400 and 5100 Å for films below 15% V, 2900 to 3000 Å for films with intermediate V concentrations, 2000 to 2300 Å for films over 60% V, and 1500 Å for the pure V_2O_5 film.

Films were deposited on TEC 15 (SnO_2:F coated glass) and ITO substrates. Prior to deposition, the substrate holder was heated to 120°C to remove moisture from the substrate surface. Deposition was begun after the holder had cooled to approximately 50°C. The deposition process maintained the temperature at approximately 50°C for the duration of the run. AFM analysis on heated samples was based on a series of high temperature runs in which the substrate holder (aluminum plate, 8.5 x 8.5 x 0.7 cm) was heated to temperatures ranging between 325°C and 525°C. The film composition varied smoothly with the ratio of sputtering power applied to the guns as shown in Figure 1. The W/V ratios were determined by RBS, or by PIXE for V concentration lower than 1 at%. The W/O ratios were obtained after fitting the RBS spectra with an appropriate model.

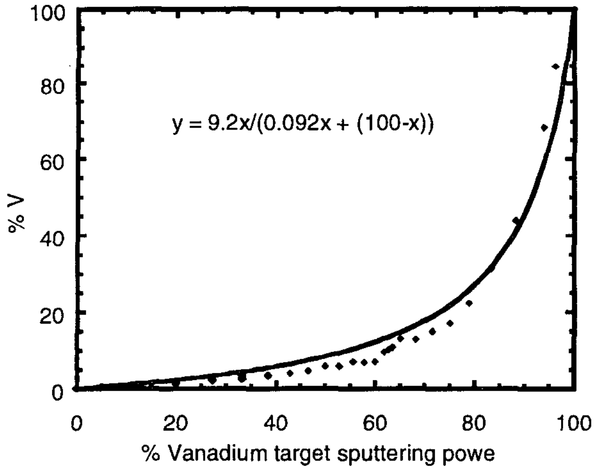

Figure 1. Atomic fraction vanadium in the mixed oxide films as a function of the ratio of sputtering powers: P(V)/[P(W)+P(V)].

Optical measurements

Optical measurements were made with a variable-angle spectroscopic ellipsometer (VASE) from 280 nm to 1700 nm using an instrument from the J. A. Woollam Co. Ellipsometric data were taken at three different angles in order to provide data with good signal to noise ratio at each wavelength as well as to over-determine the system of unknown model parameters. To extend the covered spectral range to the whole solar spectrum, transmittance and reflectance measurements from 250 nm to 2500 nm were added; these measurements were taken at near-normal incidence on a Perkin-Elmer Lambda 19 spectrophotometer.

Atomic Force Microscopy

AFM measurements were performed with a Park Scientific M5 instrument. Typical scans were taken over 2 x 2 μm at a scan frequency of 1 Hz. A silicon tip was operated at F = 50 nN in contact mode. Whole images were corrected for slope in fast and slow scan directions and analyzed without filtering.

Electrochemical cycling

The film samples were transferred to a helium-filled glove box (O_2 and $H_20 < 1$ ppm) in which all electrochemical testing was performed. Lithium insertion and extraction was carried out using an Arbin battery testing system in glass test cells with 1M $LiClO_4$ in propylene carbonate electrolyte and lithium foil counter and reference electrodes. Solar transmittance was measured *in situ* during cycling by means of a fiber optic light source (Oriel) and photometric detectors with appropriate filters (International Light).

RESULTS

Ellipsometric and transmittance data were used to extract the optical constants of the vanadium tungsten oxide films in the range of 280 - 2500 nm. A parametric dispersion model 35,36) assuming a Gaussian broadening was found to fit the data of these amorphous materials more adequately than a Lorentz oscillator model (37), although both gave reasonable fits. The real part of the refractive index at wavelengths longer than in the ultraviolet graduall increases during the transition from WO_3 towards V_2O_5 (Figure 2). The significant scatter of refractive index data in the low vanadium region illustrates the error bars of our deposition process under the same conditions over a period of six months. Among the reasons for the deviations are differences in film thickness and substrate temperature, which was not constrained by external means.

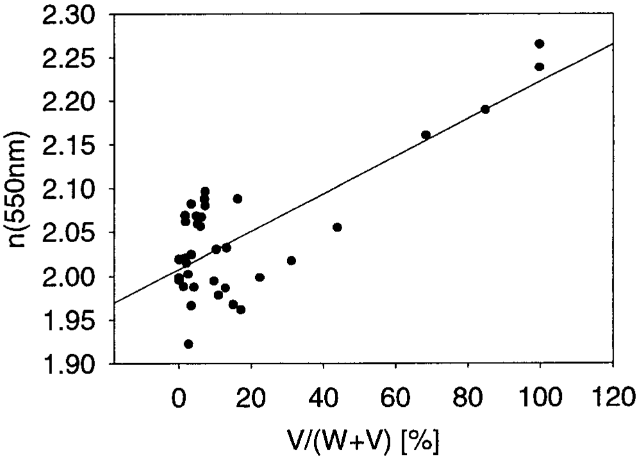

Figure 2. Real part of the refractive index at 550 nm of V-W oxides a a function of vanadium content. The line is drawn for convenience.

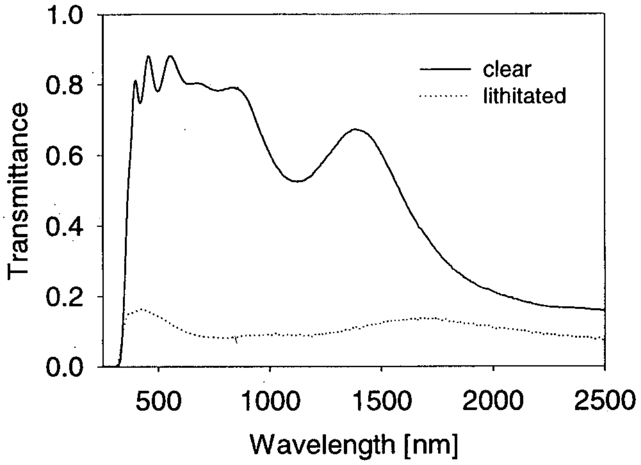

Figure 3. *Ex situ* Spectral transmittance of a V-W oxide film with 7% vanadium in clear (4.0 V vs. Li/Li^+) and dark (2.3 V vs. Li/Li^+) states.

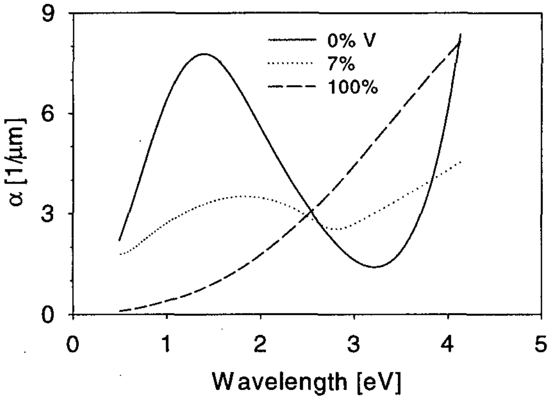

Figure 4. Spectral absorption coefficients (*ex situ*, 2.3 V vs. Li/Li$^+$) for lithiated vanadium tungsten oxides as a function of atomic % vanadium (metals basis).

One clearly sees a blue shift of the absorption peak when adding vanadium to tungsten oxide. At 7% vanadium, the absorption peak has shifted from 1.3 eV to 1.8 eV, which is responsible for the more neutral grayish color of vanadium tungsten oxide compared to the typical bluish tint of pure WO_3. Because only 7% of vanadium was added to the tungsten oxide, the spectral absorption in the lithiated state does not agree with an effective mediu theoretical treatment of the film as a mixture of lithiated WO_3 with lithiated V_2O_5 (11). The reason for the large effect of the small vanadium fraction can be found in the preferential occupation of V3d sites upon lithiation as was reported before (11,38).

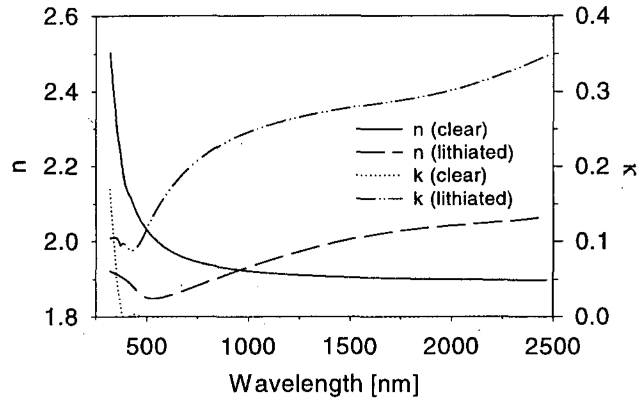

Figure 5. Real and imaginary part of a W-V oxide film with 7% vanadium in clear (4.0 V vs. Li/Li$^+$) and lithium intercalated (2.3 V vs. Li/Li$^+$) states.

Atomic force microscopy (AFM) was used to determine the root-mean-square roughness of tungsten vanadiu oxide films in the low vanadium regime. Disordered films of about 450 nm thickness on ITO substrate were found to have a rather constant surface roughness of about 5 nm. Measurements on crystalline films deposited at 400°C on ITO revealed that a 7% vanadium addition increased the average grain size from 175 nm to 250 nm (Figure 6). AFM was also used to investigate the effects of post-deposition treatment on WO_3 films. Samples heat-treated in air after deposition were found to degrade rapidly upon electrochemical cycling. Devices based on this material shorted out.

Examination by atomic force microscopy revealed cracks in the films as the likely cause for failure leaving the transparent conductor partly exposed to the electrolyte (Figure 7).

Similar measurements on films *deposited* at 400°C did not show cracks in the surface. Electrochemical cycling of those crystalline films did not result in surface roughening detectable by AFM in contrast to films deposited at roo temperature. The influence of the substrate was significant. About 400 nm thick films of WO_3 deposited at 400°C on ITO resulted in surface roughness in the order of 6 nm, whereas films on TEC15 (essentially SnO_2:F (39)), resulted in a roughness of 18 nm. The roughness of the bare substrates was about 3 nm for ITO versus 30 nm for TEC15.

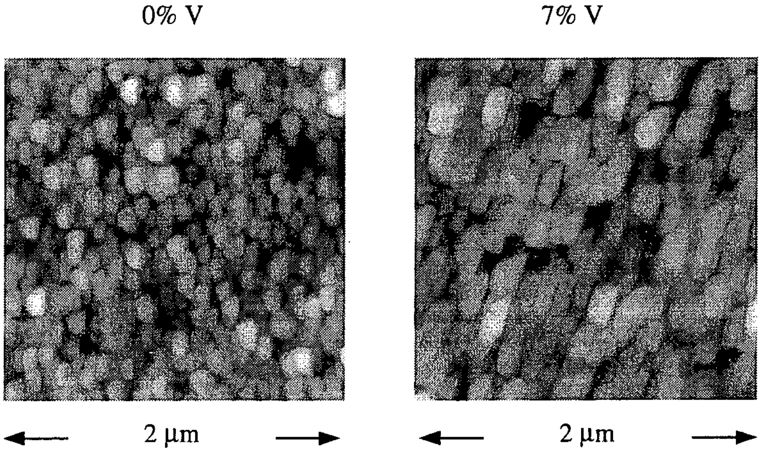

Figure 6. AFM images of tungsten vanadium oxide films on ITO deposited at 400°C.

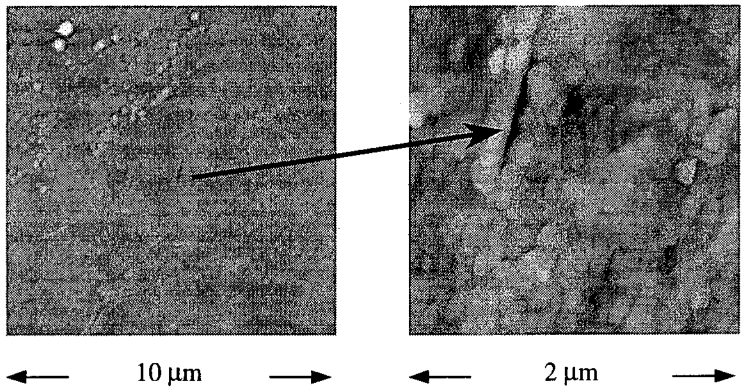

Figure 7. AFM scans of sputtered WO_3 heat-treated at 400 °C and electrochemically cycled (measured in bleached state). The line pattern in the 10 µm scan is identified as a crack in the 2 µm scan.

Electrochemical tests

Figure 8, 9, and 10 show cyclic voltammograms for a series of tungsten vanadium oxides samples with compositions ranging from 0% to 100% vanadium. For compositions between 0% and 10% vanadium, the CVs look like those of amorphous, pure tungtsen oxide thin films. The CVs for vanadium rich samples, i.e., vanadium content higher than 68%, look very similar to CVs of pure vanadium oxide sputtered thin films.

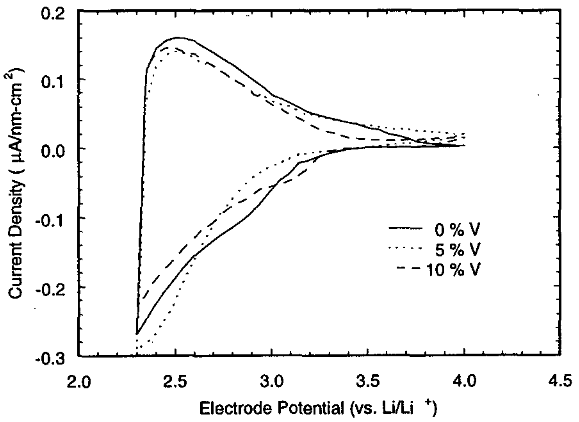

Figure 8: CVs (2mV/s) of tungsten vanadium oxide for samples containing 0%, 5% and 10% vanadium (metals basis).

Samples with composition between 15% and 44%, however, are very different one to another as shown in Figure 9 and 11, showing a steady progression to lower insertion and extraction peak potentials with increasing vanadium content. For this range of composition, both the tungsten and the vanadium oxides can be detected in the CV. The optical properties, however, relate more to those of vanadium oxide, i.e., low coloration efficiency. For lower vanadium content, in the range 0 to 7 at% , the coloration efficiency remains high, between 30 mC/cm^2 and 40 mC/cm^2.

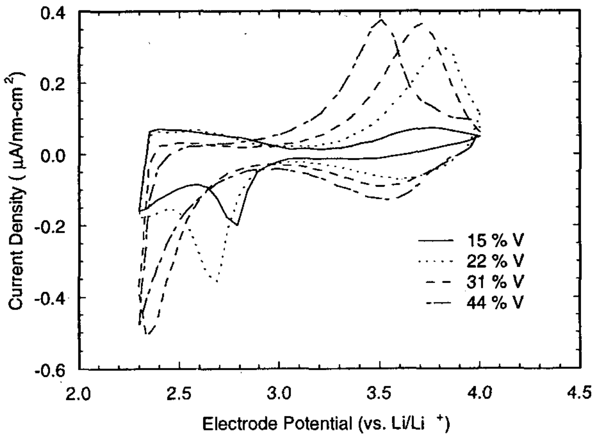

Figure 9: CVs (2mV/s) of tungsten vanadium oxide for samples containing 15%, 22%, 31% and 44% vanadium (metals basis).

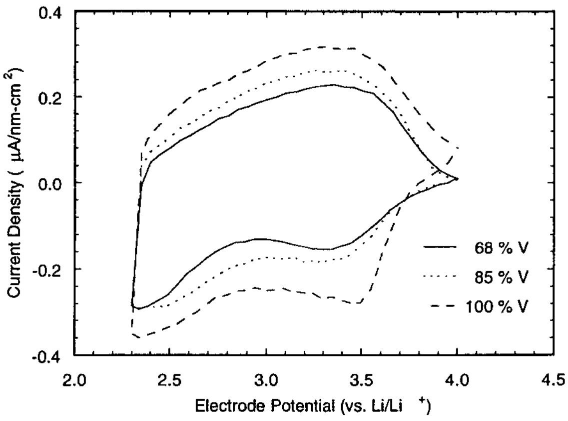

Figure 10: CVs (2mV/s) of tungsten vanadium oxide for samples containing 68%, 85% and 100% vanadium (metals basis).

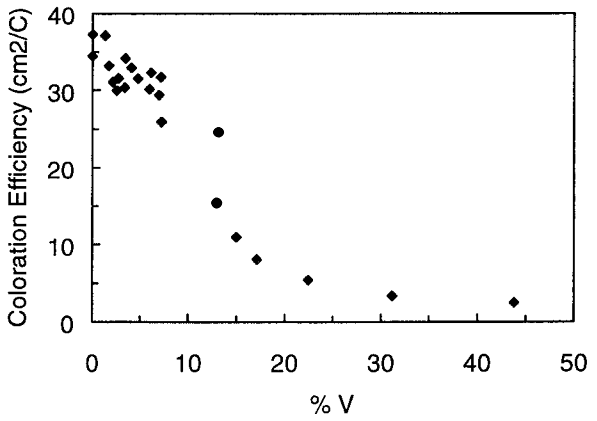

Figure 11. Coloration efficiencies (photopic) of W-V oxides as a function of vanadium content.

CONCLUSIONS

Mixed tungsten-vanadium oxide films were deposited by reactive DC magnetron co-sputtering from metallic tungsten and vanadium targets. The composition of these films ranged from 0 to 100 at% vanadium, as determined by RBS. The composition varied smoothly with the ratio of applied power to the guns. For a given power level, the tungsten sputtering efficiency was about 11 times that of vanadium. The optical absorption band in lithiated films shifted from 1.3 eV for pure tungsten oxide to 1.8 eV for a film containing 7 at% vanadium. The color of the latter film was, therefore, more neutral than that of pure tungsten oxide. The cyclability was good for all levels of vanadium content, but the coloration efficiency decreased rapidly when the V content rose above 7 at%. Although no strong evidence for solid solution formation was found, the cyclic voltammograms of the mixed oxide films were quite similar to those of pure WO_3 for vanadium contents up to 10 %, and to those of pure V_2O_5 for vanadium content greater than 68 %. Intermediate compositions were clearly two-phase mixtures. For pure tungsten oxide films, substrate heating during deposition was found to give more stable and crack-free films than post-deposition heat treatment. Due to their color neutrality, mixed tungsten-vanadium oxide films may be desirable components for electrochromic window applications.

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