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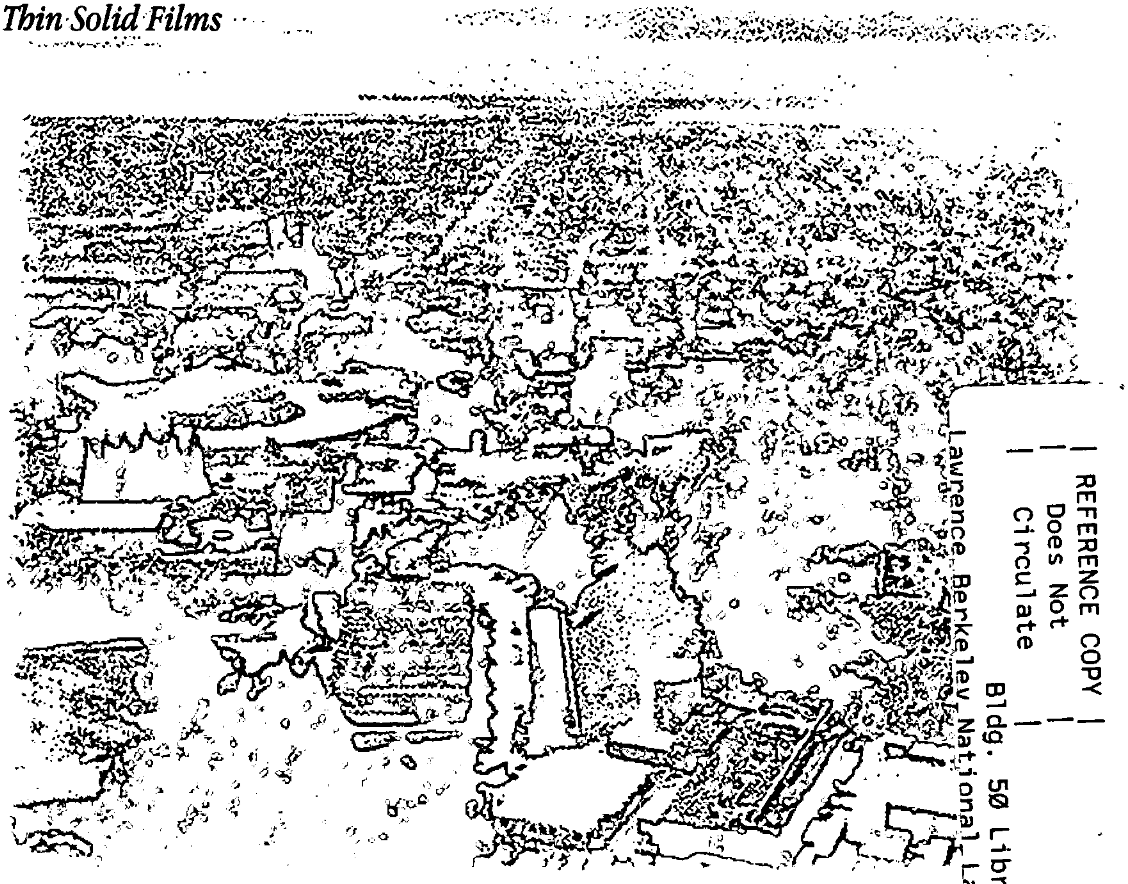

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Analysis of Binary Electrochromic Tungsten Oxides With Effective Medium Theory

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ABSTRACT

Multicomponent oxides are of increasing interest for electrochromic electrodes. To reduce the large number of permutations in composition it would be useful to be able to predict the properties of the mixtures from the pure oxide components. WO_3 mixed with V_2O_5 has been produced by a sol-gel technique in order to increase durability and color neutrality of conventional WO_3 electrochromic coatings. Chemical composition was confirmed by Rutherford backscattering spectrometry. Surface morphology was analyzed by atomic force microscopy. Electrochromic performance of the films was tested by cyclic voltammetry with in-situ transmission control. Optical constants of vanadium tungsten oxides were determined over the whole solar spectrum. The measurements included variable angle spectroscopic ellipsometry and spectral transmittance and reflectance. An attempt is made to treat doped tungsten oxide as an effective medium consisting of a mixture of WO_3 with V_2O_5. In the clear state, comparison of optical constants and thickness directly determined on the samples yields qualitative agreement with results from effective-medium analysis. The resulting component fraction also agrees as long as the film density does not deviate too much from the linearly interpolated value between the pure components. For the colored state, preferential trapping of electrons at one atom species hinders the application of effective medium theory.

Keywords: electrochromic vanadium tungsten oxide, optical constants, effective medium approximation

INTRODUCTION

Compound metal oxides have raised interest for their potential to improve existing electrochromic films. Possible effects on the electrochromic host material are increased coloration efficiency, improved durability, color neutrality and faster reaction kinetics. Sato et al. [1] studied the electrochromic properties of WO_3-V_2O_5 compounds produced by vacuum evaporation. They characterized the spectral changes in the optical density for different compositions. Huang et al. [2] prepared films by a similar method. During electrochemical cycling they observed the induced color change in the film consisting of a mixture of two electrochromic materials to be occurring sequentially in V_2O_5 and WO_3. Granqvist recently reviewed mixed metal oxides and gave a useful collection of which variety of elements was added to either WO_3 and V_2O_5 [3]. So did Monk et al. [4].

To reduce the large number of permutations in multi-component metal oxides it would be very useful to be able to predict their optical properties from the properties of their constituents. In this context we applied effective medium theory to model the optical properties of vanadium tungsten oxide mixtures using the optical constants of thin film V_2O_5 and WO_3 determined on samples that had been produced by the same sol-gel method.

EXPERIMENTAL

The V_2O_5 films were prepared according to [5] from a modified $VO(OPr^i)_3$. precursor. Mixing with tungsten oxide was achieved by adding an appropriate amount of WO_3 precursor based on peroxopolytungstic acid [6]. The resulting clear mixture solution was stable for several weeks. The gelling time of the doped solution decreased with increasing tungsten concentration due to the 1.6 times higher viscosity of the WO_3 sol. The color of the vanadium oxide solution is brownish with tungsten oxide and orange without. Deposition of a mixed oxide is straightforward. Solutions of V_2O_5 and WO_3 can be mixed and the mole ratio in the coating solution ultimately resembles the mole ratio in the deposited mixed oxide coating. The WO_3 fraction tends to be about 10% larger than expected. The films were produced by spin-coating under ambient atmosphere with a spinning rate of 1600 rpm. The supporting silica and TEC15 substrates (Libby Owens Ford) were previously ultrasonically cleaned. TEC15 consists of a multi-layer structure on glass with a SnO_2:F transparent conductor [7]. The coatings were fired at 180°C for one hour to complete hydrolysis, condensation and densification. The film adhered well on both kinds of substrates.

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 was 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.

Composition and thickness of the samples were characterized by Rutherford backscattering spectrometry (RBS) using a 1.95 MeV $^4He^+$ beam in the 165° backscattering geometry. Ellipsometry was used not only as part of the optical analysis but also to measure film thickness. Other types of structural analysis were performed with x-ray diffraction (XRD), infrared spectroscopy and atomic force microscopy (AFM).

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

For XRD measurements bulk powder samples of the tungsten oxide and mixed oxide sols were prepared by heat treating the dried precursor mixtures under the same conditions as those used for the films. X-ray diffraction patterns were collected using a Siemens D5000 powder diffractometer at 0.2° resolution. Fourier transform infrared spectra were obtained in transmission mode on powders pressed into KBr discs using an ATI Mattson Research Series spectrometer.

Electrochemical testing was carried out in a helium-filled drybox. The electrolyte was 1M $LiClO_4$ in propylene carbonate. Counter and reference electrodes were metallic Li. Cyclic voltammograms were recorded for 10 cycles at a rate of 10 mV/s. The first three cycles for each sample are shown. There was little change in either the current or the % transmission after cycle 3.

RESULTS

Ellipsometric and transmittance data were used to extract the optical constants of the vanadium tungsten oxide films in the range of 300 - 2500 nm. A parametric dispersion model [8, 9] assuming a Gaussian broadening was found to fit the data of these amorphous materials more adequately than a Lorentz oscillator model [10]. However, reasonable fits were obtained in both cases. The resulting optical constants for samples of different compositions are shown in figure 1 and 2.

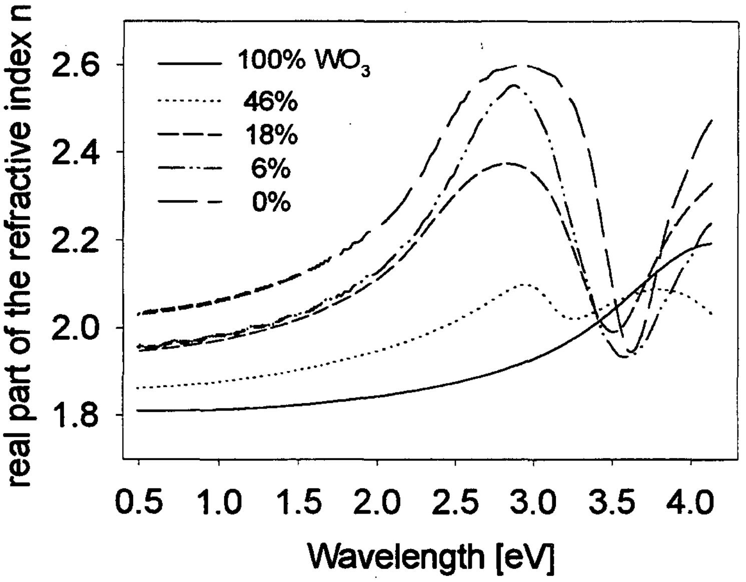


Figure 1. Real part of the refractive index of vanadium tungsten compounds on fused silica obtained from direct fitting

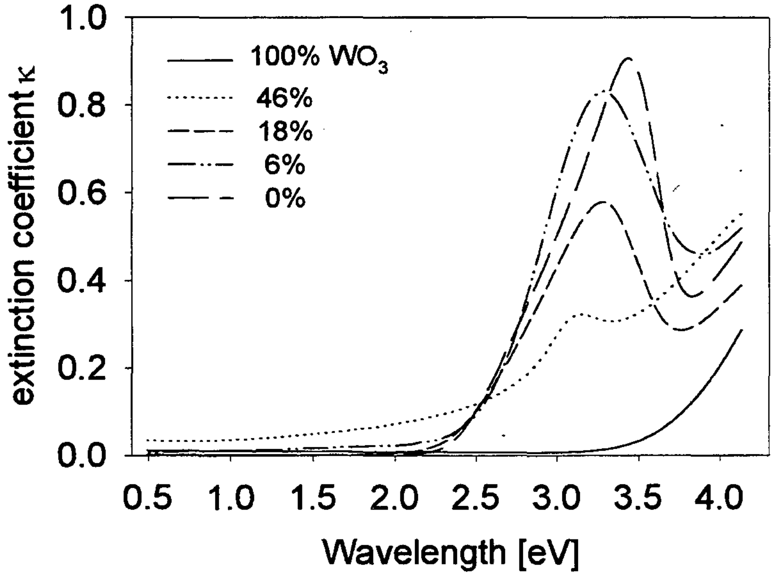


Figure 2. Extinction coefficient of vanadium tungsten compounds on fused silica obtained from direct fitting

Real and imaginary parts of the refractive index are plotted versus light energy to show the transition from WO_3 to V_2O_5 clearer at the absorption edge. It can be seen that with the addition of more V_2O_5 to WO_3 an additional oscillator around 3.45 eV is becoming more pronounced. This represents the band gap absorption of V_2O_5 [11] originating from an electron transition from the O 2p band to the split-off portion of the V 3d band [12]. The real part of the refractive index below the ultraviolet spectral region gradually increases during the transition from WO_3 towards V_2O_5. Sol-gel deposited samples sometimes tend to be considerably carbon contaminated due to the use of isopropoxides in the preparation of the solutions. Such contamination was found to lower the refractive index.

Optical constants of WO_3 and V_2O_5 were used to model the dispersion of the compound materials via effective medium approximation. To be able to do that we have to make sure that the compound material actually exists as a two phase mixture and not as a solid solution, as the term "doping" sometimes employed in the literature may suggest. Results from X-ray diffraction and FTIR measurements, however, both indicate the presence of an additional phase in the mixed sols, rather than elemental substitution in the tungsten oxide. We therefore ascribe the shifts of the absorption peak in figure 2 to irregularities in the sample deposition. However, the presence of a small amount of atomic in addition to two-phase mixing cannot be completely excluded and could explain quantitative deviations between direct and effective medium results.

Since little was known about the microstructure of the V_2O_5-WO_3 films in different compositions, we used Bruggemann effective medium theory which makes a self-consistent choice of the complex dielectric function $\tilde{\varepsilon}$ of the host material equaling that of the effective mixture [13, 14]. Following equation for a mixture of V_2O_5 and WO_3 has to be solved numerically for $\tilde{\varepsilon}$.

$(1-f_{WO_3})\cdot\frac{\tilde{\varepsilon}_{V_2O_5}-\tilde{\varepsilon}}{\tilde{\varepsilon}_{V_2O_5}+2\tilde{\varepsilon}}+f_{WO_3}\cdot\frac{\tilde{\varepsilon}_{WO_3}-\tilde{\varepsilon}}{\tilde{\varepsilon}_{WO_3}+2\tilde{\varepsilon}}=0$, where f_{WO_3} denotes the volume fraction of WO_3.

A more accurate model of the physical reality can be obtained by distinguishing between Maxwell-Garnett theory that describes spherical inclusions of a material in a host matrix for low volume fractions of one component and Bruggemann theory for an aggregate structure [15]. However a consideration of bounds to the dielectric function shows that microstructure is of lesser importance in the case of quite similar optical constants of V_2O_5 and WO_3 [14, 16, 17].

The tungsten oxide volume fraction was allowed to vary in the model and was then compared to results from Rutherford backscattering measurements. RBS however, does not measure volume fractions but the actual density of atoms in the material. Therefore effective medium theory results have to be converted to mole fractions using measured film densities. In our V_2O_5-WO_3 compound films the mole fraction of WO_3 exceeds the volume fraction by a factor of 1.3. As can be seen in figure 3 the agreement between the WO_3 mole fraction obtained from effective medium theory with RBS results is relatively good as long as the film density does not deviate too far from the expected value. That is the value one obtains if the densities of WO_3 and V_2O_5 are linearly interpolated.

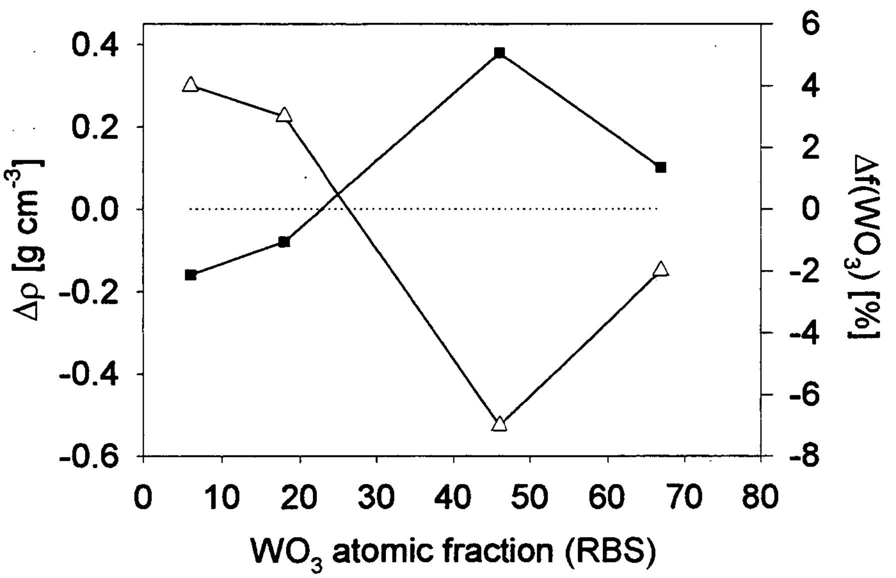


Figure 3. Differences between RBS and EMA mole fractions (triangles) and deviations from linearly interpolated densities (squares)

A higher density for the same composition leads to a higher real part of the refractive index thus approaching closer to the index of V_2O_5. Therefore effective medium approximation on samples that are more dense than expected yields an artificially high V_2O_5 fraction and vice versa.

Plots of optical constants derived from effective medium theory in figure 4 and 5 show certain differences from the ones obtained from the fit of a dispersion model as in figure 1 and 2.

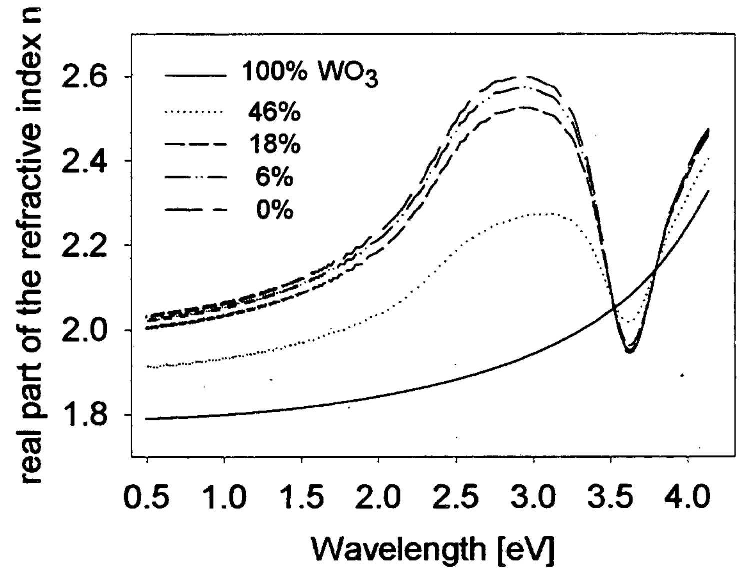


Figure 4. Real part of the refractive index of vanadium tungsten compounds on fused silica obtained from effective medium approximation

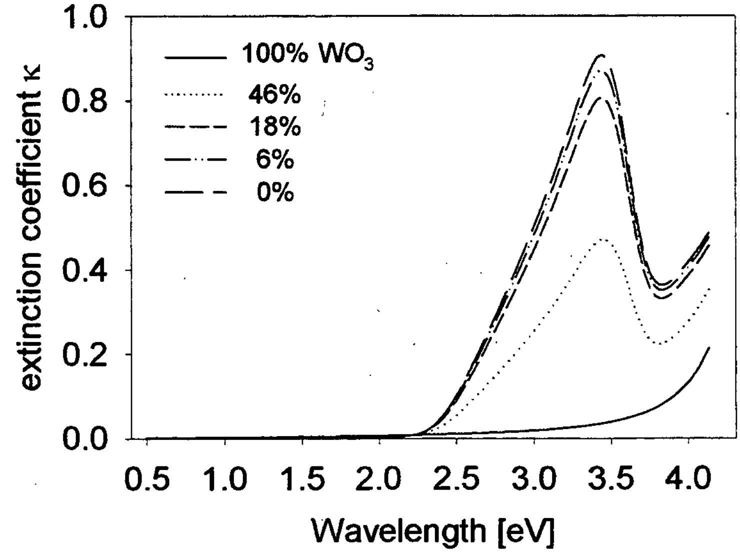


Figure 5. Extinction coefficient of vanadium tungsten compounds on fused silica obtained from effective medium approximation

Those exhibit weaker dispersion at the V_2O_5 absorption edge near 3.4 eV than expected from effective medium theory. Approaching stoichiometric V_2O_5 also the peak position seems to shift towards higher energies. This is something effective medium theory will of course not account for. The differences are especially important for the film with 46% WO_3 content. figure 6 a, b, c, d illustrates the case of worst agreement between EMA and direct fitting.

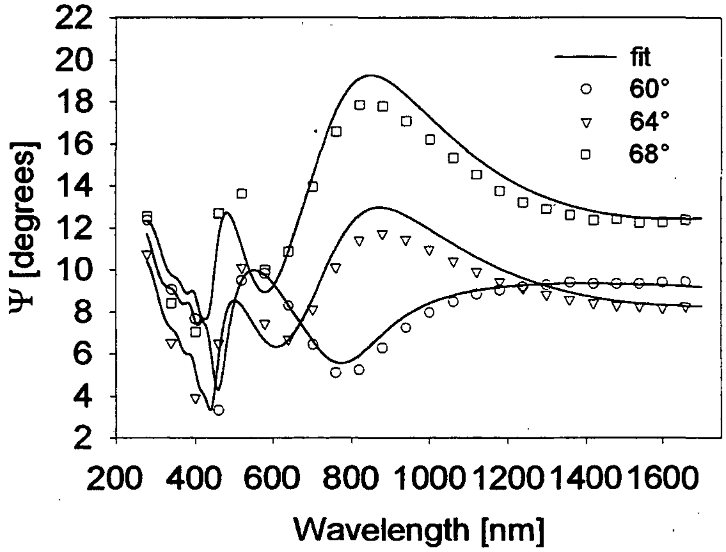


Figure 6a. Direct fit on spectral Ψ-data of $(V_2O_5)_{0.54}$-$(WO_3)_{0.46}$

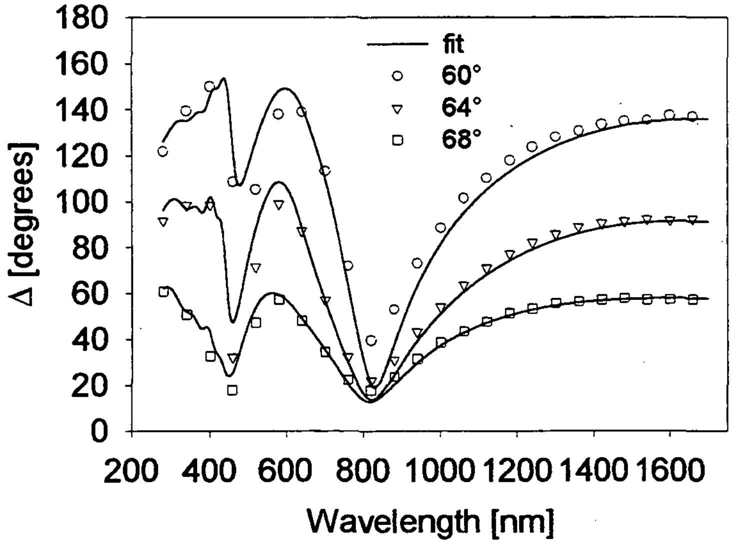


Figure 6b. Direct fit on spectral Δ-data of $(V_2O_5)_{0.54}$-$(WO_3)_{0.46}$

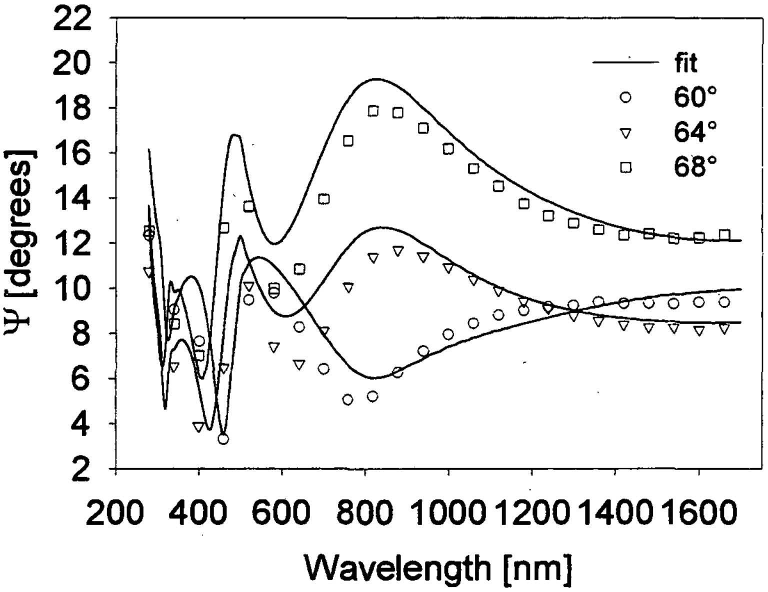


Figure 6c. EMA fit on spectral Ψ-data of $(V_2O_5)_{0.54}$-$(WO_3)_{0.46}$.

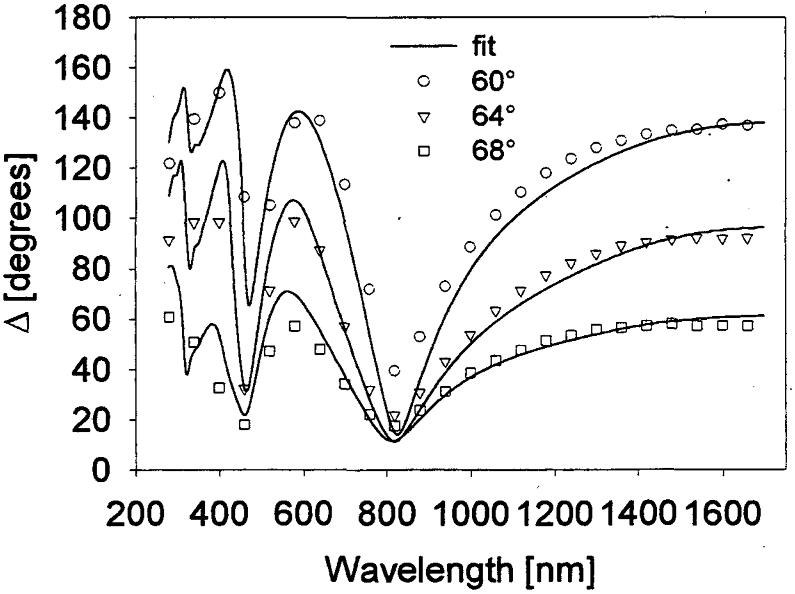


Figure 6d. EMA fit on spectral Δ-data of $(V_2O_5)_{0.54}$-$(WO_3)_{0.46}$

Resulting biased mean square errors are 25.4 and 38.2 for the direct fit and the effective medium approximation respectively. To obtain better fits it is necessary to include a vertically graded index profile in the model with the real part of the refractive index slightly decreasing towards the surface. For our purpose, however, we deliberately chose a simple one layer model to minimize fit parameter correlation. As can be seen the fits do not differ very much in the visible and infrared region, because there the refractive indices of WO_3 and V_2O_5 are very similar.

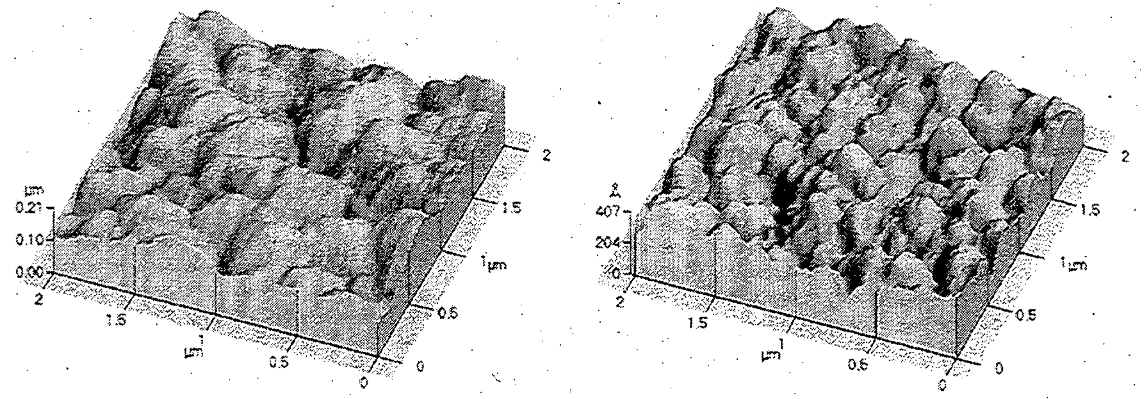
In the literature sometimes thickness values are used that were obtained by RBS. Table 1 shows a comparison of the thickness values obtained by ellipsometry and RBS.

V_2O_5- 67%WO_3	274	233	23
V_2O_5- 46%WO_3	242	210	22
V_2O_5- 18%WO_3	206	200	6
V_2O_5- 6%WO_3	230	210	4
V_2O_5	224	200	8

Table 1. Film thickness values obtained by ellipsometry and RBS, roughness values obtained by AFM

The films appear to be thicker by ellipsometry. It should be kept in mind that ellipsometry does not actually measure thickness, but fits it using the relation between reflected and incident electric fields, which depends on the sample structure. Rutherford backscattering, however, measures the number of atoms per area and calculates the thickness by making assumptions for the atomic density of the material (typically $6\ 10^{22}$ atoms per cm^3) and the penetration depth dependent energy loss of scattered particles. As our sol-gel derived films are of very low mass density, the conversion of RBS results to thickness results in systematically smaller values.

Surface morphology of the vanadium tungsten oxide films at the transition from WO_3 to V_2O_5 was monitored by atomic force microscopy (figure 7).



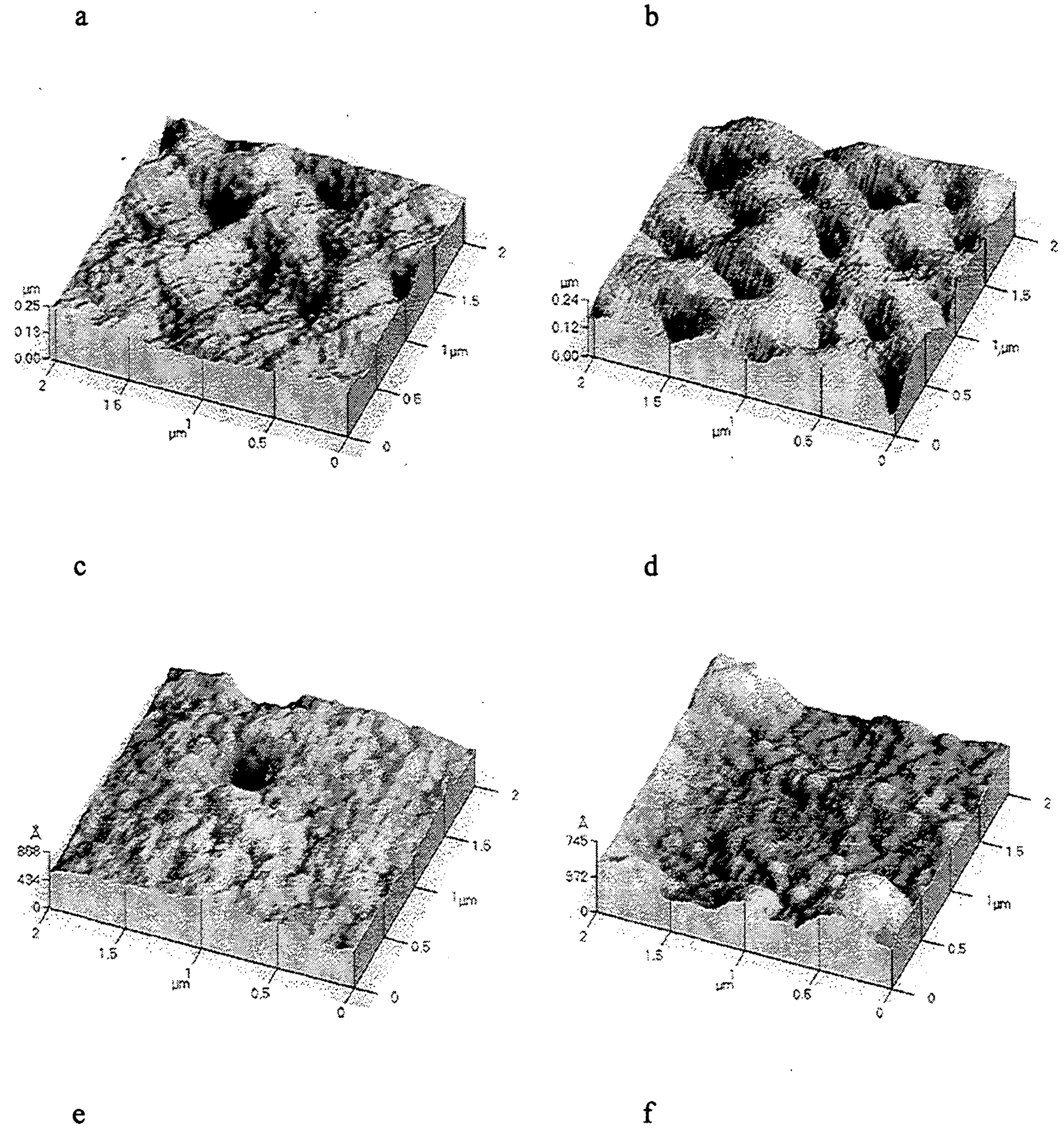


Figure 7. AFM scans of a) WO_3, b) $(V_2O_5)_{0.16}$-$(WO_3)_{0.84}$, c) $(V_2O_5)_{0.33}$-$(WO_3)_{0.77}$, d) $(V_2O_5)_{0.54}$-$(WO_3)_{0.46}$, e) $(V_2O_5)_{0.82}$-$(WO_3)_{0.18}$, f) V_2O_5

It can be clearly seen that the grainy character of the WO_3 gradually decreases with increasing V_2O_5 content. Since all samples were heat treated at 180°C, this has to be expected a priori due to the crystallization point of this sol-gel WO_3 lying about 100°C lower in temperature than that of V_2O_5 [5, 6]. This suggests larger surface roughness for the WO_3 rich films as is confirmed in the results of table 1.

The films were cycled in $LiClO_4$ in propylene carbonate and their optical properties measured in the lithiated state. Effective medium approximation does not work according to Huang et al. [2] in a sense that optical indices of WO_3 and V_2O_5 in the colored state could be used to model lithiated compound materials. The V_2O_5 incorporated in WO_3 dominates the optical response. In a simplified picture the injected electrons are trapped first at the V^{5+} 3d orbitals that lie lower in energy than the W^{6+} 5d orbitals. If one compares figure 8 with figure 9 one sees that while the transmission of the $(V_2O_5)_{0.54}$-$(WO_3)_{0.46}$ film exhibits strong WO_3-character in the clear state, the colored state is very similar to the colored state of V_2O_5. However, application of effective medium theory using the optical constants of lithiated V_2O_5 and clear WO_3 did not produce unambiguously good fits on all samples.

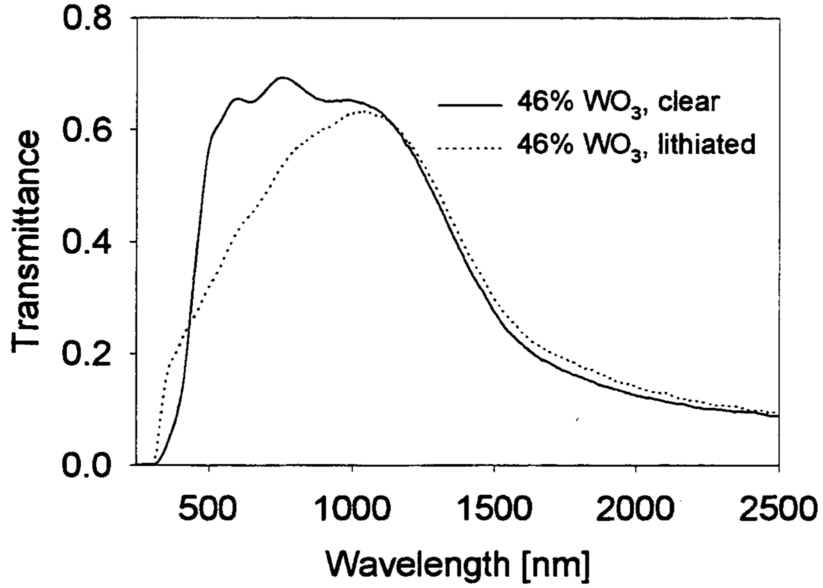


Figure 8. Transmittance of $(V_2O_5)_{0.56}$-$(WO_3)_{0.46}$ in the clear and colored state

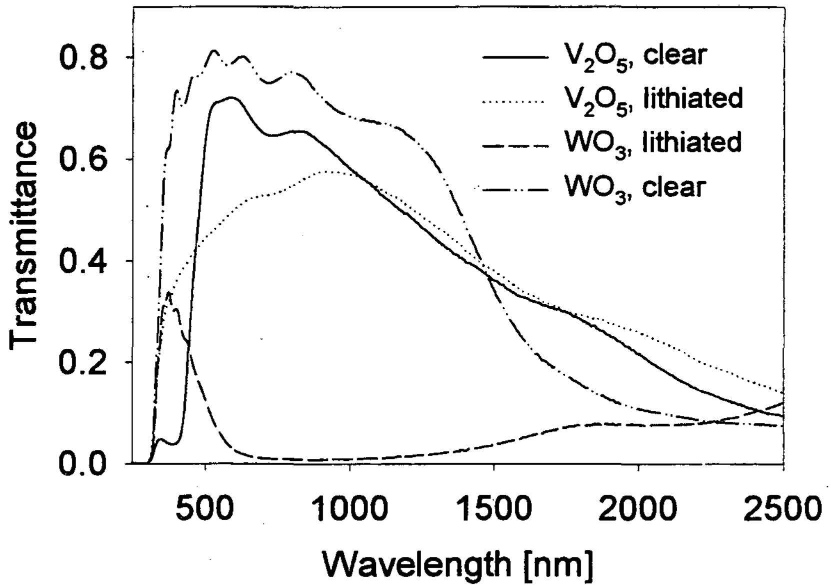


Figure 9. Transmittance of WO_3 and V_2O_5 in the clear and colored state

CONCLUSIONS

The optical properties of sol-gel-derived V_2O_5-WO_3 compounds were investigated in different compositions. In the clear state, comparison of optical constants directly determined on the samples yields qualitative agreement with results from effective-medium analysis. The resulting component fraction also agrees as long as the film density does not deviate too much from the linearly interpolated value between the pure components. In this case, structural irregularities resulting from the growth process cause such deviations from this simple model. Upon coloration the agreement between effective medium theory and optical measurement deteriorates. We believe that injected electrons are trapped at the energetically lower sites thus giving the compound the character of the preferred component, possibly the one with smaller atomic number [2]. Generally good agreement was found for thickness and volume fraction between ellipsometry and Rutherford backscattering with ellipsometric thickness being systematically higher.

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