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Model of electrochromic and related phenomena in tungsten oxide thin films

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Abstract We have developed a model of electrochromic and related phenomena in tungsten oxide thin films based on the assumption that the constitution of such films is heterogeneous and built up of nanosized particles, pores and adsorbed substances (mainly water). It is discussed why a high-efficiency reversible blue colour is observed in amorphous tungsten oxide films (α -WO₃ films) as well as why such porous thin films with polycrystalline or amorphous constitution and with a variety of particle properties can be easily obtained by a physical vapour deposition process in a low-pressure atmosphere in the presence of water. A substrate temperature in the range 450–550 K corresponds to some plateau on the water desorption curves which divided physically adsorbed water from chemically adsorbed water. Two types of structural units based on tetrahedrally and octahedrally coordinated tungsten ions have the main role in the formation of the film constitution. The tetrahedral structural units have a glass-forming function, but the octahedral ones have a modification function. From the electrochemistry point of view, the internal multiphase interfaces in such films are distributed multiphase electrodes. The adsorbed water together with defects of the oxide particles provide reagents for reversible coloration reactions in the film. The colour centres can be induced thermally (oxygen nonstoichiometry) or electrically (injected ions) or by radiation (photoinjected hydrogen). The electrochromism and related phenomenon of α -WO₃ films can be directly related to ion insertion/extraction processes controlled by external forces.

Keywords Tungsten oxide · Thin films · Physical vapour deposition process · Constitution, composition, structure · Nanoparticles

Introduction

Tungsten oxide thin films are still investigated by many researchers as main cathodic electrochromic materials. A high-efficiency reversible blue colour is observed in amorphous tungsten oxide films. Usually such films are prepared by thermal evaporation of tungsten trioxide powder in the presence of or without H₂O vapour. The classical definition of the amorphous state of a solid material that the sizes of the crystalline regions in solids or particles in a powder with long-range order are not larger than 3 nm is based on X-ray diffraction data.

The same reversible coloration can be induced by different physical or chemical processes (electrical, photo, thermal or chemical). The nature and diversity of such reversible coloration phenomena or polychromism can be connected with the constitution, composition, atomic structure and adsorbed substances in these films. A similar approach is successfully used in glass physics and chemistry to explain the vitreous state of glasses as noncrystalline or disordered systems. The induced optical absorption band in the wavelength range 600–1,000 nm is related to absorption centres of the reduced forms of tungsten ions (possible reactions $\text{WO}_3 + xM^+ + xe = M_x\text{WO}_3$ or $\text{WO}_3 = \text{WO}_{3-y} + 1/2y\text{O}_2$, where $M^+ = \text{H}^+, \text{Li}^+, \text{Na}^+, \text{NH}_4^+, \dots$). From time to time we analysed our experimental data of reversible coloration phenomenon in such films on the basis of the evolution of our understanding and experience over 25 years. We have developed a model of electrochromic and related phenomena in tungsten oxide thin films based on the assumption that the constitution of such films is heterogeneous and built up of nanosized particles, pores and adsorbed substances. The characteristics of coloration should depend on the constitution and the composition of the film as well as on the atomic

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structure and the size of the tungsten oxide particles. The redox processes on the inner surfaces of such films have an important role in the coloration induced by external forces. The influence of the constitution, composition and structure of tungsten oxide films on reversible coloration phenomena has not been sufficiently analysed to explain that. The aim of this paper is to discuss the electrochromic and related phenomena in tungsten oxide thin films on the basis of analyses of the properties of inner surfaces as well as processes on inner surfaces.

Experimental

The main research subjects were amorphous tungsten oxide films (α -WO₃ films) themselves and in cells or in systems of type: indium–tin oxide (ITO)/WO₃/SiO_x·nH₂O//Au and ITO/WO₃//SE//IrO₂/ITO, where SE is an electrolyte based on solid antimony acid hydrates or hydrogen uranyl phosphate. Some investigations of coloration processes of α -WO₃ films have been done in Au/WO₃/Au cells with a planar Au electrode arrangement. The chemichromism was studied in WO₃ films on palladium foil (Pd/WO₃).

The α -WO₃ films were prepared by thermal evaporation of tungsten trioxide powder in the presence of or without H₂O (partial pressure 0.1–0.2 Pa) vapour (physical vapour deposition process, PVD) on glass substrates coated or not with Au or ITO (10–20 Ωsq^{-1}) and for IR spectroscopy on silicon wafers. Standard methods were used for the characterization of α -WO₃ films.

The substrate temperature during deposition of the WO₃ films has a strong influence on their electrophysical properties (Fig. 1), which correlate directly with the water content in the films (Fig. 2). The range of dehydration temperatures for different WO₃ samples (Fig. 2a) and the hydration level of the α -WO₃ films (Fig. 2b) has the same temperature range as substrate temperature, T_s , during deposition of the films. The shifts of the electrical as well as the optical characteristics (Fig. 1a, b) of electrochromic material according to the water content (Fig. 2b) in the WO₃ film influence the coloration efficiency (Fig. 1c). The hydration level of the WO₃ films is more or less high for substrate temperatures up to 200 °C during deposition of the films. In that region the values of the electron and proton conductivity of the films have similar values. Above 200 °C the electronic conductivity prevails over the proton conductivity [1].

From the thermogravimetric analysis, IR absorption spectra and quartz resonator microbalance data (Fig. 2) for WO₃ films from the amorphous to the crystalline state, the weight losses is 7% and the density is in the range 5.6–7.3 g cm^{-3} , but calculated losses of water are 45–55% and the internal surface are greater than 10⁶ cm^2g^{-1} . Part of this surface has to be closed for direct interaction with a gaseous atmosphere or a liquid electrolyte leading to inner and outer interfaces.

Model consideration and experimental data overview

View and concept of the constitution of the films

The model considerations of the constitution of films and the previously mentioned experimental data as well as the dependence of the conductivity (Fig. 1) and the Raman scattering spectra (Fig. 3) of WO₃ films on the H₂O content (Fig. 2) serve as a basis for the assumption about α -WO₃ films being heterogeneous with high porosity.

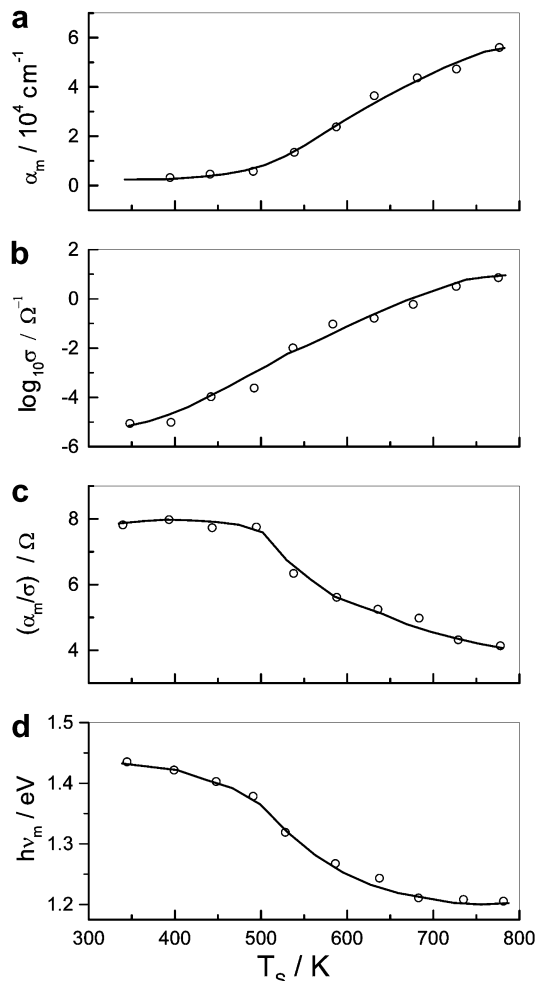


Fig. 1 The changes of electrophysical characteristics of WO₃ film versus the substrate temperature, T_s , during deposition of the film [1]: **a** optical absorption in the maximum of the band at 1.3 eV [$\alpha_m(T_s)$]; **b** conductivity $\sigma(T_s)$; **c** ratio $\alpha_m(T_s)$ to $\sigma(T_s)$; **d** position of optical absorption band $\alpha_m(T_s)$

A variety of α -WO₃ films properties in many cases can be explained if one assumes that the films have different constitutions, compositions and structures and that they are composites based on nanosized particles of different oxide phases. The questions are how to present the constitution, composition and structure of an α -WO₃ film and what types of physical and chemical factors or features of oxide phases play primary roles in the formation of the film? There are can be two possibilities for the starting situation, when the formation of the film constitution is driven by structural or composition factors, but in any case the end product has to be analysed in the sequence constitution, composition and structure. The formation factors of the thin film constitution during deposition of physical vapours of oxide on the substrate are the composition and the structure of the oxide phases in the vapours, the partial pressure of H₂O in the vacuum chamber and the temperature of the substrate.

Fig. 2 Water in α -WO₃ films: **a** mass losses versus sample temperature for 1 crystalline H₂WO₄, 2 α -WO₃ film, 3 amorphous high-density pellet of WO₃·1.74H₂O and 4 crystalline WO₃·2H₂O; **b** IR absorption at 1,600 cm⁻¹ (1) and density (2) of α -WO₃ films versus substrate temperature T_s during film deposition

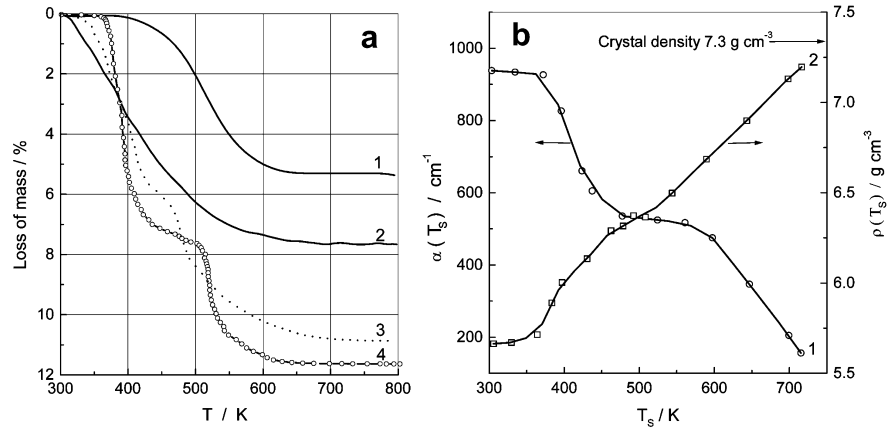
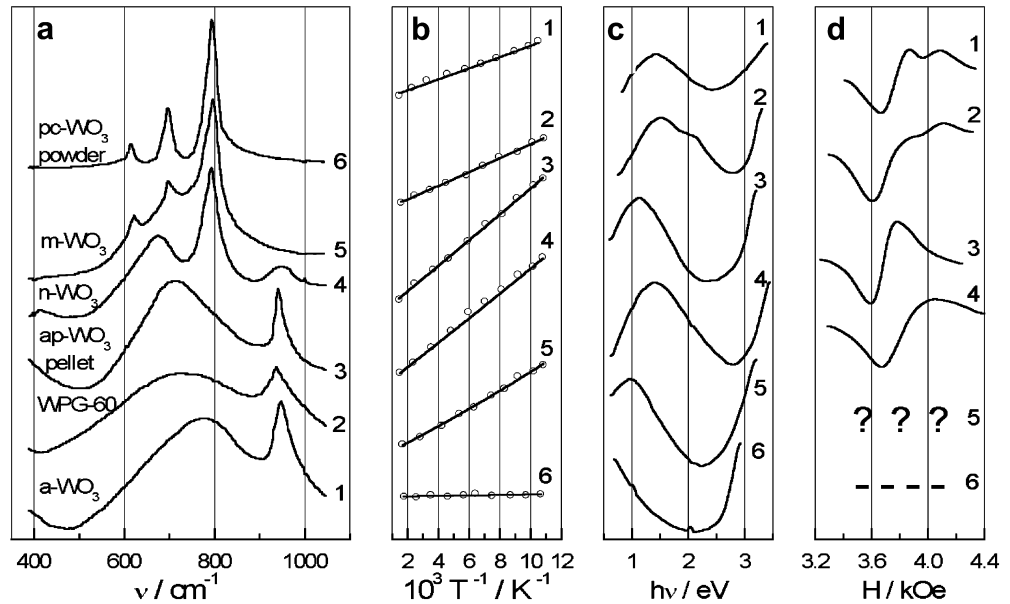


Fig. 3 Comparison of properties of WO₃ films and some bulk compounds based on WO₃ [1, 18, 19, 20, 28]: **a** Raman scattering spectra; **b** magnetic susceptibility; **c** optical absorption spectra; **d** electron spin resonance spectra for samples 1 amorphous WO₃ film, 2 tungsten phosphate glass (WO₃ 60 mol%), 3 amorphous powder of WO₃·zH₂O, 4 nanocrystalline WO₃ film, 5 microcrystalline WO₃ film and 6 polycrystalline powder of WO₃



The composition and the structure of the oxide phases in the vapour are determined by nonstoichiometry. Nonstoichiometry is a general feature of transition-metal oxides [2, 3]. That is the reason why tungsten oxides have a variety of different oxide phases and this has an influence on the formation of oxide particles with different compositions and structures in the thin film.

The thermal deposition processes of a WO₃ film on a substrate has two stages: the formation of clusters in the vapour phase and condensation of tungsten oxide vapour or clusters on the substrate at the temperature T_s . In the vapour phase, the smallest and prevailing structural (molecular) unit is the trimer W₃O₉ [2]. These easily form clusters in vapours or particles during condensation on the substrate without a regular, periodic arrangement. The nonstoichiometry and different sharing types (corners, edges, planes) of [WO₆] octahedrons are source of the different crystalline patterns of the oxide particles which can be formed or transformed in WO₃ films during deposition as well as coloration and bleaching. The sharing type of the [WO₆] octahedron

and the structure of different nonstoichiometric phases of the particles depend on the oxygen partial pressure in the film deposition chamber. In amorphous films the size of such particles has to be smaller than 3 nm. Transmission electron microscopy, scanning tunnelling microscopy and atomic force microscopy show that the size of the grains and clusters in the α -WO₃ films are in the range 20–110 nm [4, 5]. The surface of the particles with different composition and structure has a selective adsorption capability for different chemical substances.

Bulk WO₃ can be obtained with a constitution ranging from monolithic glass [6] or amorphous powder to a single crystal, including poly-, micro- and nanocrystalline bulk materials or powders. The difference between the amorphous state and the polycrystalline state can be seen in Raman and near-IR/vis spectra (Fig. 3a, c).

The crystalline WO_{3-y} as a bulk material has a wide range of nonstoichiometric phases with crystal structures ranging from monoclinic to cubic ones. In glass systems, WO₃ has two types of structural units based on

tetrahedrally and octahedrally coordinated tungsten ions [6, 7]. The tetrahedral structural units have a glass-forming function, but the octahedral ones have a modification function. The ratio of octahedral units to tetrahedral ones in glasses is 4–9.

The $[\text{WO}_6]$ octahedrons in crystalline compounds based on tungsten trioxide can be interconnected through corners, edges or plains in a spatial network with a short-range order (structure pattern) of the corresponding crystalline compounds [2]. The short-range order of nonstoichiometric compounds or phases of WO_3 is characterised by a strong perovskite arrangement of tungsten and oxygen ions [2, 3]. The smallest crystalline clusters of perovskite short-range order consist of 6–9 $[\text{WO}_6]$ octahedrons (size less than 1 nm). On the basis of glass-forming models we can suggest that the tungsten oxide cluster in an $\alpha\text{-WO}_3$ film has tetrahedral nuclei surrounded by distorted octahedral units. The tetrahedral nuclei may be the trimer W_3O_9 , which is formed in the vapour phase. During condensation of vapours on the substrate, the trimer W_3O_9 is surrounded by clusters of $[\text{WO}_6]$ octahedrons and the size of such disordered particles can be larger than 3 nm. The sharing type plays the main role for obtaining $\alpha\text{-WO}_3$ films, the constitution of which is based on nanosized particles with long-range order of certain crystalline nonstoichiometric phases of tungsten oxide. The surface of all these compounds has a high adsorption capability for different chemical species and a high catalytic activity.

Two types of nonstoichiometry

One of the structural peculiarities of tungsten oxide, related to oxygen-based nonstoichiometry, is a variety of phases based on $[\text{WO}_6]$ octahedron sharing in structural units of pure tungsten oxide compounds with crystalline patterns. The sharing type of the $[\text{WO}_6]$ octahedron and the structure of different nonstoichiometric phases depend on oxygen deficiency.

In general, the basic mechanism of oxygen deficiency of transition-metal oxides ($T_x\text{O}_\beta$) is crystallographic shear (CS) [2]. Removal of oxygen vacancies is the driving force for the formation of a regular block structure of ideal stoichiometric $T_x\text{O}_\beta$ crystals separated by CS planes. In that way nonstoichiometry has an influence on the formation of particles of tungsten oxide compounds in the thin film during thermal evaporation of WO_3 and deposition on substrate.

The ion insertion or extraction phenomenon (ion-insertion-based nonstoichiometry) is another basic common peculiarity of tungsten oxide phases.

Reducing the atmospheric pressure results in a series of homologous phases (Magneli phases) of transition-metal oxides – stoichiometric blocks separated by distances of 14–24 $[\text{TO}_6]$ octahedrons: the widths of the blocks are 5–10 nm. The ion insertion in transition-metal oxides generates an intergrowth structure [8], i.e. $MT_x\text{O}_\beta$ in $T_x\text{O}_\beta$. In the bulk of the crystal, the CS and

intergrowth are extended defects ending on the surface [9, 10].

The electrochromic tungsten oxides can be considered as compounds $M_xY_{1-x}\text{WO}_{3-y}$ with anion- and cation-based nonstoichiometry against oxide-forming tungsten-ion networks (x : inserted ion, y : oxygen deficiency, Y : empty sites) [2, 3]. The ion-insertion phases of tungsten trioxide have the homogeneity range of nonstoichiometry $x=0\text{--}1$, but for oxygen $y=0\text{--}0.3$.

For the tungsten trioxide particle, the local structure can be represented as ABO_3 perovskites with empty cation sites $A=Y$ and in case of the stoichiometric WO_3 can be represented by the formula $Y\text{WO}_3$. The empty sites Y have different atomic and electronic structures on the surface and in the bulk. The oxygen-based nonstoichiometry or oxygen deficiency of tungsten trioxide cannot be represented as an empty oxygen site (oxygen vacancies $[\text{O}]^{2+}_y$) alone, but also as some type of long-range as well as short-range order extended defects based on CS with oxygen deficiency $\text{O}^{2-}_{y'}$ (general oxide formula $Y\text{WO}_{3-y'-y}[\text{O}]_y\Delta_{y'}$). The electronic structure of $[\text{O}]^{2+}_{y'}$ is a combination of perovskite B and O sites: $[B, \text{O}]_{y'} = [\text{O}]^{(2-\delta)+}_{y'} = \Delta_{y'}$.

The M^+ ion-insertion-based nonstoichiometry of tungsten oxide compounds can be represented as an occupied cation site $Y_x = M_x^+$ in the perovskite structure, i.e. $Y_xY_{1-x}\text{WO}_3 = M_xY_{1-x}\text{WO}_3$. Now, both nonstoichiometry types of tungsten oxide particles can be represented by the site formula

$$M_xY_{1-x}\text{WO}_{3-y'-y}\text{O}_y\Delta_{y'}, \quad (1)$$

where $x=0\text{--}1$, $y=0\text{--}0.28$ and $y'=?$. WO_3 single crystals, which are grown in a reducing atmosphere, can be obtained as a series of homologous phases according to the formula $\text{W}_n\text{O}_{3n-m}$ or $\text{WO}_{3-m/n}$ ($n=14\text{--}20$, $m=1\text{--}5$, $y'=m/n=0.05\text{--}0.35$) [2, 8, 9, 10, 11, 12].

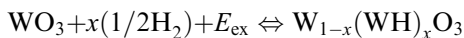
Role of nonstoichiometry

The nonstoichiometry changes the oxidation state of some fraction of the tungsten ions and at the same time changes the colour of the oxide. That can be seen in the optical absorption spectra (Fig. 3c). The $\alpha\text{-WO}_3$ films prepared by the PVD process have thermally induced colour centres in the range 0.9–1.4 eV. Such different absorption band positions are connected with different short-range structural patterns and interaction with adsorbed water.

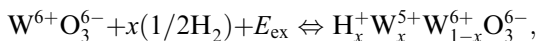
The ion insertion/extraction can cause both types of nonstoichiometry relating to the central tungsten ion in the Eq. (1), i.e. it can cause simultaneous extraction of M^+ and oxygen by a redox reaction on the surface or interface. Equation (1) serves as a general ionic site model of active centres for the formation of colour centres. The different schemes and types of electrochemical reactions have been analysed for some electrochromic systems in Refs. [13, 14, 15, 16, 17].

Model of reversible coloration

The absorption band in the wavelength range 600–1,000 nm is related to an absorption centre of type $[H^+W^{5+}O_6^{6-}]$ or $[WHO_6]$ in surroundings of $[WO_6]$ octahedrons. The formation of such centres is based on some general redox reactions:

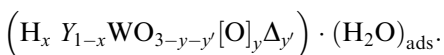


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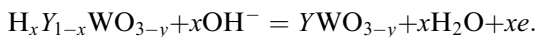
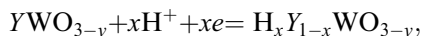
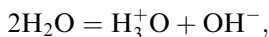


where E_{ex} is some energy for producing and transfer reagents (hydrogen) and the change of the oxidation state of the tungsten ions.

Polychromic phenomena are related to ion–electron reactions induced by external excitations, E_{ex} , of the interface on the particles with transfer of ions (H_3^+O , OH^-) and electrons between of one of the phases with different values of x , y , y' and absorbed water:



The basic polychromic or coloration/bleaching reaction of α - WO_3 films is a reversible ion-insertion/extraction reaction through the interface to the oxide surface region:



The driving forces or the energy source, E_{ex} , of these reactions are the applied voltage, the electron beam, photons, phonons, H_2 spillover and catalysis, which control the direction of the redox reactions, i.e., the direction of coloration/bleaching of a tungsten trioxide film.

Analyses of some experimental data

The adsorbed gases and water in pores on the surface of the particles of the different tungsten oxide phases form different interfaces. The adsorbed water serves as a source of hydrogen ions (protons, H_3^+O) and electrolyte for the ion transfer inside the film. Any adsorbed substance interacts with electronic and ionic defects on nanoparticles and changes the total conductivity of the film. This means that in the α - WO_3 film different types of multiphase interfaces can appear on tungsten trioxide particles as distributed electrochemical electrodes. The boundary between the adsorbed water (liquid phase)–oxide (solid phase) interacts with the gas phase. For the

investigation of polychromic phenomena in α - WO_3 films such a model is useful for analyses of experimental data.

The chemical and physical characteristics (Figs. 2, 3) of bulk (polycrystalline powders) and thin films are similar, but have a strong dependency on the constitution of the samples [18, 19].

The comparative analyses of the investigations of the samples based on tungsten oxides [1, 16, 18, 19, 20] was carried out by physical methods sensitive to the composition and the structure and is presented in Fig. 3. These data together with data in Figs. 1 and 2 provide good evidence for the proposed model of α - WO_3 films based on nanoparticles with different composition phases of $WO_{3-y} \cdot zH_2O$. There are similarities in the Raman scattering spectra of the samples. Each spectrum presents a gradual change of particle sizes and of the degree of structural order in the particles. The conclusion about the constitutional, compositional and structural similarity of α - WO_3 films and amorphous $WO_3 \cdot zH_2O$ powder is based on the similarity of the Raman scattering spectra (Fig. 3a, curves 1, 3). The similarity between the Raman (Fig. 3a, curves 1, 2), near-IR/vis (Fig. 3c, curves 1, 2) and electron spin resonance (ESR) (Fig. 3d, curves 1, 2) spectra of α - WO_3 films and tungsten phosphate glass means a similarity of the structural units and patterns with the same spatial distribution of three types of sharing of $[WO_6]$ octahedrons. The differences in these spectra are related to the dominant kind of structural units and crystalline patterns.

The magnetic susceptibility, ESR and near-IR/vis spectra (Fig. 3) display the changes in the degree of localisation for electrons involved in the coloration processes.

For coloured and uncoloured WO_3 films it has been shown from the extended X-ray absorption fine structure that the differences in the interion distances in the radial distribution function are 0.072 Å, but for crystalline and amorphous uncoloured films this difference is only 0.012 Å [21, 22]. The ion-insertion changes locally short-range order.

The inner interfaces on oxide particles and electrolyte (adsorbed water) and environmental gas form distributed multiphase electrodes. The obvious case of this is the coloration of the gap between planar electrodes (Au) on an α - WO_3 film, where the inner interfaces and the coloration front are controlled by external electrodes. The interfaces in the α - WO_3 -film with sandwich electrodes and liquid or solid electrolyte is a more complicated case. In the electrode processes the three-phase (metal layer or particles of Au or Pd, oxide and water or gas) and four-phase (metal layer or particles of Au or Pd, oxide, water and gas) electrodes can be involved [1, 13, 14, 15, 23, 24, 25].

The interface areas of a WO_3 film with liquid or solid electrolyte are different. The exchange current for a WO_3 film electrode in 0.1M H_2SO_4 electrolyte (about 10 mAcm⁻²) is 20–30 times larger than that on the solid electrolyte (hydrogen uranyl phosphate) for equal values

of the proton diffusion coefficient (about $10^{-10}\text{cm}^2\text{s}^{-1}$) in the WO_3 film for both electrolytes [26]. This can be explained by the fact that a liquid electrolyte has a much larger physical interfacial area with respect to the geometric area of a WO_3 film than a solid electrolyte.

Some general consequences of the film constitution model

The consequences due to the nonstoichiometry and which concern the composition, constitution and structure as well as the variety of the particle properties of tungsten oxide compounds are that the thermal evaporation technique produces porous thin films with polycrystalline or amorphous constitution (heterogeneous systems with developed inner surfaces and adsorbed substances). The adsorbed gases and water in pores on the surface of the oxide form different interfaces.

The distribution of nanoparticles with different structural units or patterns is responsible, on one hand, for three induced absorption bands (Fig. 3c) with different optical absorption cross-sections in the spectral region 1.0–2.5 eV of the WO_3 film [20, 27, 28, 29], but, on the other hand, for different redox potential levels at interfaces with the electrolyte as well as with the adsorbed species inside the WO_3 film [16].

The adsorbed water serves as a source of hydrogen ions (protons, H_3^+O) and electrolyte for ion transfer inside the film. Any adsorbed chemical compound interacts with electronic and ionic defects on nanosized crystal particles and changes the surface conductivity of the oxide phase. The boundary between the adsorbed water–oxide interacts with the gas phase. The processes on the surfaces and the interfaces between different phases are controlled by external forces (voltage, light, temperature, partial pressure of active gases).

There are two processes with opposite influences on the injected charge which have been changed by oxidation (the electrical resistance to the electron current increases) and by desorption of water. The water desorption from pores increases the electrical resistance to the ion current and causes a decrease of the injected charge. The oxidation in the presence of water, probably, narrows the pores near the oxide surface in contact with the electrolyte. The H_2O molecules shield some of the active sites in the structure units of the oxide particles (Eq. 1), where injected electrons can be located, and reduce the formation of colour centres. The higher concentration of mobile electrons enhances the optical absorption cross-section of the colour centres. The origin of the colour centres is different and can be induced by thermal or chemical [23], electrical [1, 27], electrochemical [13, 15], photochemical or photoelectrochemical [30, 31] reactions (injected charge, increase of nonstoichiometry).

Photoanodic polarisation (irradiation of the anode with laser light during polarisation to excite the electronic state band gap edge) enhances the electrochromic

efficiency of the WO_3 film by 1.5 to 2.0 times [30]. These phenomena can be connected with an increase in the concentration of active sites for electrically induced colour centres. This means the dehydration of the WO_3 film, and in such a way the coloration efficiency of degraded films can be optically regenerated and similar data concerning regeneration of coloration efficiency can be explained [31].

The observed wide spectrum of the physical and chemical properties of WO -films [13, 14, 15, 16, 17, 20, 23, 30, 32, 33, 34, 35, 36] can be related to variations in the composition, constitution and structure of the films as well as to the interaction these films with the environment.

Conclusions

Our model of electrochromic and related phenomena in tungsten oxide thin films is based on the constitution of tungsten oxide thin films, multiphase interfaces on tungsten trioxide particles as distributed (dispersed) electrochemical electrodes and reversible ion insertion by external influences (voltage, current, light, gases).

If $\alpha\text{-WO}_3$ films are prepared by the PVD process, the reversible coloration phenomena (polychromism) in the amorphous tungsten oxide thin films can be understood if assume that the $\alpha\text{-WO}_3$ films are specific composites formed by oxide particles, pores and adsorbed substances, and can be related to peculiarities of the thin films. The oxide particles in $\alpha\text{-WO}_3$ films are amorphous with sizes 20–100 nm. From an electrochemistry point of view, the internal multiphase interfaces in such films are distributed multiphase electrodes.

The previous discussion gives reasons why porous thin films with polycrystalline or amorphous constitution (heterogeneous systems with developed inner surface and adsorbed chemical substances) and with a variety of particle properties in the WO_3 films can be easily obtained by the thermal evaporation technique.

The WO_3 films with heterogeneous composition and constituted by nanoparticles, pores and adsorbed substances together with defects (disordered atomic structure of oxide particles) provide reagents for reversible coloration reactions.

The water has double role in coloration processes: passive and active. The adsorbed water in the film not only leads to a faster electrochromic reaction, but also reacts gradually with WO_3 . The temperature range 450–550 K corresponds to some plateau on the water desorption curves which divides physically adsorbed water from chemically adsorbed water.

The assumption that WO_3 films are composites is useful for investigation of coloration phenomenon. The colour centres can be induced thermally (oxygen nonstoichiometry) and electrically (injected ions) and by radiation (photoinjection of hydrogen). The polychromism of $\alpha\text{-WO}_3$ films can be directly related to ion-insertion/extraction processes controlled by external

forces. The oxygen nonstoichiometry, injected ions and interaction of adsorbed species with oxide particles or solid-state redox reactions in α -WO₃ films are sensitive to external forces such as voltage, light and temperature, which induce a reversible blue colour.

The nanocrystalline clusters or particles in the α -WO₃ films have some distribution of the orientation of crystallographic plane on the surface. In such cases the ion-insertion/extraction process produces particles with different composition. Such nonhomogeneously intercalated oxide particles mean that the some of the particles can undergo metal–nonmetal transitions.

The effects caused by the composition, constitution, structure and products of interaction with the environment, as well as effects on the surfaces, interfaces and defects, can be used for experimental study of the basic properties of α -WO₃ films. The external forces, which induce reversible optical effects, control ion-insertion/extraction processes on internally distributed multiphase interfaces.

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