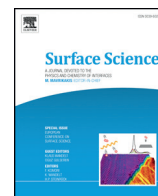




Contents lists available at ScienceDirect

Surface Science

journal homepage: [www.elsevier.com/locate/susc](http://www.elsevier.com/locate/susc)

## Q1 The preparation and chemical reaction kinetics of tungsten bronze thin films and nitrobenzene with and without a catalyst

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### ARTICLE INFO

Available online xxxx

#### Keyword:

Tungsten oxide  
 Tungsten bronze  
 Hydrogenation  
 Macroscopic kinetics  
 UV–vis

### ABSTRACT

Microcrystalline tungsten bronze thin films were prepared using wet chemical techniques to reduce a tungsten oxide thin film that was prepared by thermal oxidation of a sputter deposited tungsten metal film on a quartz substrate. The crystallinity of these films was determined by X-ray diffraction and the surface was characterized by X-ray and Ultra-Violet Photoelectron spectroscopy. The total amount of hydrogen incorporated in the film was monitored using absorbance spectroscopy at 900 nm. The oxidation kinetics of the film and the hydrogenation of nitrobenzene in hexane were measured as a function of film thickness. A satisfactory fit of the resulting kinetics was obtained using a model that involves two simultaneous processes. The first one is the proton diffusion from the bulk of the film to the surface, and the second is a reaction of the surface protons with the oxidants. Finally, the dependence of the reaction rates on the presence of catalytic amounts of first row transition metals on the surface of the film was explored.

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## 1. Introduction

The hydrogen bronzes of molybdenum and tungsten are interesting compounds derived from the reduction of molybdenum or tungsten trioxide with hydrogen or a hydrogen source such as an alcohol [1–6]. These mixed valence oxide species are highly-colored compounds that contain pentavalent metal centers attached to hydroxides. The attached hydroxides have the unusual property of reacting as if they are hydridic rather than in the expected protic manner [2]. This reaction behavior is due to the fact that the transfer of the hydrogen ion is accompanied by electron transfer and reoxidation of the metal ion back to the hexavalent state. In some respects, the bronze can be considered to be a convenient storage medium for reactive hydrogen and this property has been exploited in hydrodechlorination of chlorocarbons [1,7]. A later investigation found that these reagents neutralize both peroxide-based improvised explosives and military explosives (such as RDX and TNT) under ambient conditions during which a dramatic color change is observed [8]. For the military explosives, the process is suspected to occur via a reduction of the nitro groups to amines. To investigate the surface chemistry occurring during the reduction of the nitro-based explosives and oxidation of the bronze, this paper discusses the development of a model system, based on tungsten oxide films that mimic these nanometric materials.

Films of tungsten oxide exhibit a wide spectrum of electrochromic and photochromic properties [9–13]. Chromogenic properties of evaporated tungsten oxide films were first intensively explored by S. K Deb in 1970s [14]. The observed alteration of its optical properties in response to the external stimuli (light, temperature, and applied voltage) makes tungsten oxide one of the most promising chromogenic materials for a wide range of applications [15]. The ability to reversibly change color creates opportunities for its use in emerging technologies, especially for highly energy efficient buildings with incorporated “smart windows” [16]. Other possible applications for optical switching films include sensors for noxious gases [17], hydrogen sensors [18], adjustable surface emissivity devices for satellite applications [19], UV and Co-60 radiation detectors, electrochromic displays, and variable reflectance mirrors [20].

The mechanism of  $\text{WO}_3$  hydrogenation (reduction) follows the scheme:



The reverse reaction occurs upon reaction with an oxidizing agent. Given that chemical reactions occur at the surface, a relevant parameter is the diffusion coefficient for hydrogen to migrate from the bulk of the sample toward the surface. A diffusion constant ( $D$ ) can be written that includes both diffusion of the  $\text{H}^+$  ion and the electron. It is shown that diffusion coefficient varies both with hydrogen content [21,22] and deposition parameters as well as the density of the films [23]. The diffusion coefficient turns out to depend on the crystallinity and the hydrogen

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concentration of the bronze. In different electrochemical experiments, the reported values lie in the range of  $1.5 \times 10^{-9}$  to  $3 \times 10^{-12}$  cm<sup>2</sup>/s for approximately 500-nm-thick WO<sub>3</sub> films deposited by evaporation [13,23]. The diffusion coefficient for hydrogen atoms in crystalline films is estimated to be several orders of magnitude greater than that in amorphous WO<sub>3</sub> films [24]. Indeed, NMR kinetic studies resulted in an extrapolated value for D of  $7 \times 10^{-6}$  cm<sup>2</sup>/s at room temperature [25]. The rate of hydrogen insertion is also related to the presence of water in the reaction (reduction) media. Bludska et al. reported that water increases the rate of hydrogenation and that the rate also becomes greater with an increase in the number of reduction–oxidation cycles [26].

## 2. Experimental

Three different preparative methods were explored: sputter deposition followed by oxidation, evaporative deposition and sol–gel deposition. As discussed later, the sputter deposition oxidation method was chosen for all the kinetic studies in this paper. For this method, quartz slides measuring 0.5 cm × 2 cm were pretreated by heating in a solution of 1:3 ratio of 30% (v/v) hydrogen peroxide and 18.0 M sulfuric acid. This process removes any organic matter and hydroxylates the surface. We found that organic residues result in poor adhesion of the initially sputtered metal coating. The ion beam sputtering was performed in a vacuum chamber under a vacuum of  $1 \times 10^{-6}$  Torr. Pure argon gas for 2.5 cm × 22 cm linear ion source and a plasma bridge neutralizer were controlled by a GFC-1000-U gas flow controller (Ion Tech, INC.) at 4.0 sccm and 2.0 sccm, respectively. The energy for the argon ion beam voltage was 900 V during deposition, controlled by MPS-3000 power supply (Ion Tech, INC.). A Maxtek thickness monitor (TM-350/400) was used with a crystal-based microbalance to measure the rate of deposition. The sputtering rate of the described apparatus was measured to be 2.0 Å/s. The substrates were rotated at 10 rpm during the deposition and were positioned 20 cm from a tungsten metal target. The resulting tungsten metal films were then annealed in a Thermolyne 21100 tube furnace under an oxygen atmosphere at 600 °C for 4 h to create tungsten oxide films. X-ray diffraction (XRD) patterns recorded using a Bruker Advance D8 diffractometer (copper K<sub>α</sub> radiation) of these films showed only one broad peak, implying an amorphous film. The samples were oxidized within a quartz tube by a stream of gaseous oxygen at one atmosphere and heating up to 450 °C for 3 h to produce slightly yellow WO<sub>3</sub> films on the quartz substrate. The oxidation step was the main reason for the use of a quartz substrate as opposed to cheaper borosilicate glass slides due to the tendency of the tungsten oxides to pull impurities out of the glass slides during oxidation. The final thickness of the oxide film was calculated using the thickness reported by the crystal-based microbalance corrected for the rotation of the sample during disposition and the density difference between the W metal and its oxide. The assumption is that the film's surface length and width was constant and the only change upon oxidation was in the thickness.

The colored H<sub>x</sub>WO<sub>3</sub> films were created via the reaction of tungsten oxide films with nascent hydrogen released using zinc metal and hydrochloric acid. As a result, colored tungsten bronze are produced. For most preparations, the slide was placed in a container with 5 ml of 1 M hydrochloric acid. Approximately 1 g of powdered zinc metal was added and the inhomogeneous mixture was swirled by hand until the reaction between the acid and the zinc was complete. The samples formed using the wet chemistry method were compared to tungsten oxide films reduced by atomic hydrogen generated by splitting molecular hydrogen on a hot filament in an UHV-chamber for 3.5 h. During deposition, the temperature of the sample was recorded to be 369 K and pressure of hydrogen in the chamber was equal to  $1 \times 10^{-5}$  Torr. Both methods resulted in the formation of stable blue H<sub>x</sub>WO<sub>3</sub> films.

In addition to films made using sputtering followed by oxidation, films were also created using either direct thermal evaporation of the oxide or sol–gel chemistry. For thermal evaporation, tungsten (VI)

oxide (99.8%, Alfa Aesar) was deposited directly onto cleaned (as described above) 3" × 1" × 1 mm microscopic slides (Fisher Scientific) by performing repetitive conventional thermal evaporation technique under a vacuum of  $1 \times 10^{-5}$  Torr. For direct thermal evaporation of the oxide, an electrically heated tungsten-coated foil boat (MDC) was fixed 10 cm directly below the substrate. The manually manipulated deposition rate is a function of applied voltage and ranges from 10.0 to 30.0 Å/s. For the sol–gel approach, a colloidal tungsten oxide film was produced using tungstic acid generated from sodium tungstate by an ion-exchange column. A solution of 1.0 M sodium tungstate dihydrate (99%, Sigma-Aldrich) was eluted through a column containing analytical grade cation exchange resin AG 50W-X2, 50–100 mesh in its hydrogen form (Bio-Rad). This produces a tungstic acid solution that was deposited onto cleaned 3" × 1" × 1 mm microscope slides (Fisher Scientific). The sol–gel films were dried at room temperature for 24 h and were usable for a few days. The bronze films were prepared with hydrogen released by the oxidation of zinc metal with hydrochloric acid as described above.

The XPS and UPS equipment used in this investigation has been previously described [27]. Briefly, it consists of a surface analysis system with a typical base pressure of  $2 \times 10^{-10}$  Torr measured using an uncorrected nude ionization gauge. The XPS measurements were performed using the Mg anode of a PHI 300 Watt Twin Anode X-ray source. The resulting photoelectrons were detected by a PHI double-pass cylindrical mirror analyzer (CMA) with a pass energy of 50 eV. UPS was implemented using a differentially pumped He discharge ultra-violet source (UG Microtech) to provide He(I) radiation. The same double-pass cylindrical mirror analyzer with a pass energy of 5 eV was used to detect the resulting photoelectrons. A copper foil provides the Fermi level reference for the UPS photoelectron energies. XRD measurements were performed using a Bruker D8 Advance X-ray powder diffractometer with indexing, crystallite size, search/match, and quantitative analysis capabilities. Finally, UV–vis spectra were recorded manually using a DMS-200 Dual-Beam Spectrophotometer with a beam size of 2 × 8 mm.

Control experiments showed that impurities in the hexane slowly reacted with the bronze films. Therefore the hexane was purified by shaking with concentrated sulfuric acid followed by vacuum distillation under nitrogen from sodium benzophenone ketyl solubilized with tetraglyme. Once purified, the H<sub>x</sub>WO<sub>3</sub> films were indefinitely stable immersed in the hexane. It was also found that continuous exposure to the 900 nm light from the spectrometer source also impacted the rate measurement. For this reason, the hydrogen bronze samples were stored in the dark after their preparation and were exposed to the 900 nm radiation only for the time needed to obtain an absorbance measurement (less than 1 min).

## 3. Results and discussion

### 3.1. Film preparation

The synthetic method used for the preparation of tungsten oxide films can strongly influence their properties. For example, thin films produced using one method can have an electrochromic sensitivity extremely different from that of films produced by other methods [28]. Surface defects, oxygen vacancies and interstitials may be responsible for optically active materials obtained under different deposition conditions [29]. In addition, absorbed water can increase the surface conductivity and thus enhance the proton mobility required for efficient electrocoloration [30]. To understand how the properties are affected by different deposition methods, tungsten oxide films were produced by sputter deposition followed by oxidation, evaporative deposition and sol–gel deposition. Films of tungsten oxide formed using sol–gel or thermal evaporation were found to be significantly less reactive in comparison to films prepared by sputter deposition followed by oxidation. Although the colloidal films had excellent electrochromic

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