

Semiconducting Properties of Thin Anodic WO₃ Films Grown in Different Electrolytes

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Investigou-se as propriedades semicondutoras de filmes anódicos finos de WO₃ crescidos sobre eletrodos de tungstênio policristalino. Estes filmes foram obtidos em soluções aquosas de H₃PO₄, H₂SO₄, HNO₃ e HClO₄ (pH ≈ 1,3), sob condições potenciostáticas (1 V ≤ E_f ≤ 5 V vs. ECS) até que correntes estacionárias fossem atingidas. Dados de impedância eletroquímica (obtidos sob uma ampla variedade de condições de potencial) destes filmes foram analisados com funções de transferência usando rotinas de ajuste não-linear. A interpretação dos resultados assim obtidos mostrou que os filmes de WO₃ comportam-se como um semicondutor tipo n. Daí que os valores da capacitância da carga espacial do óxido (C_{sc}) puderam ser obtidos da região de alta frequência do espectro de impedância. Valores similares de C_{sc} foram encontrados para as camadas passivas crescidas em soluções de HClO₄, HNO₃ e H₂SO₄; os valores menores encontrados para os filmes crescidos em H₃PO₄ podem ser explicados como decorrentes de permissividades relativas mais baixas nesses filmes. Os valores da concentração em número de doadores na região de carga espacial obtidos de gráficos de Mott-Schottky decrescem com o potencial anódico de formação do filme (isto é, espessura crescente do filme) e são levemente influenciados pela natureza das soluções anodizantes. Além disso, os valores estimados para os potenciais de banda plana parecem ser influenciados somente por essa natureza, pois não dependem da espessura do filme.

The semiconducting properties of thin anodic WO₃ films grown on polycrystalline W electrodes were investigated. These films were obtained in aqueous H₃PO₄, H₂SO₄, HNO₃ and HClO₄ solutions (pH ≈ 1.3) under potentiostatic conditions (1 V ≤ E_f ≤ 5 V vs. SCE) until steady-state currents were achieved. Electrochemical-impedance data (obtained under a wide variety of potential conditions) for these films were analyzed with transfer functions using non-linear fitting routines. The interpretation of the results thus obtained showed that the WO₃ films behave as n-type semiconductors. Hence, the values of the capacitance of the oxide space charge (C_{sc}) could be obtained from the high frequency range of the impedance spectra. Similar C_{sc} values were found for the passive layers grown in HClO₄, HNO₃, and H₂SO₄ solutions; the smaller values found for the films grown in H₃PO₄ may be explained as being due to lower relative permittivities for these films. The values of the concentration of donors in the space charge region obtained from Mott-Schottky plots decrease with the anodic film formation potential (*i.e.*, increasing film thickness), and are slightly influenced by the nature of the anodizing solutions. Furthermore, the estimated values for the flat band potentials seem to be influenced only by this nature, *i.e.*, they do not depend on the thickness of the film.

Keywords: tungsten, anodic oxide, semiconducting properties, potentiostatic growth

Introduction

In the last decade, many reports¹⁻⁵ were published on the electrochromic and photoelectrochemical properties of WO₃. The interest in the study of WO₃ is mainly due to its possible use in electrochromic devices and as a photoanode in solar cells. The preparation techniques used to obtain WO₃ films strongly affect their solid-state properties. Many authors have previously reported on the semiconducting properties of WO₃ films prepared in different ways, including chemical vapor deposition⁶, thermal oxidation of the metal⁷, and galvanostatic anodization⁸. Nevertheless, very few data have been reported on the semiconducting properties of anodic WO₃ films grown using potential perturbation techniques.

Gravimetric and SEM studies⁹ of thick anodic films formed galvanostatically have shown that the films start to grow as an amorphous barrier layer (mainly WO₃), part of which dissolves and reprecipitates onto the electrode as an outer porous layer of hydrated oxide whose composition and morphology are dependent on the anodizing solution. Photoelectrochemical and capacitance measurements have shown that the WO₃ films anodically obtained in several acid solutions behave as n-type semiconductors^{1,3,8,10}. The charge carriers were identified as oxygen vacancies injected at the metal/oxide interface. Di Quarto *et al.*¹¹ reported values for the relative permittivity of the passive films grown on W that depended on the electrolyte solution used during the anodization. On the other hand, the number concentration of donors was found to decrease as the film thickness increased, but not to vary with the nature of the anodizing solution⁸.

The main purpose of the present work is to investigate the influence of both the anodizing electrolyte and the film thickness on the semiconducting properties of thin WO₃ films anodically obtained on W under potentiostatic conditions.

Experimental

Polycrystalline tungsten rods (99.98% purity, 0.63 cm diameter) included in epoxy resin were used as working electrodes, which, prior to each experiment, were mechanically ground down to 600 grit silicon carbide paper. The counter electrode was a platinum grid symmetrically placed around the working electrode. A saturated calomel electrode (SCE) coupled to a Luggin probe was used as a reference for all potential measurements. The electrochemical cell was fabricated from Pyrex[®] glass.

The experiments were carried out in aqueous H₃PO₄, H₂SO₄, HNO₃, and HClO₄ solutions with a pH of around 1.3. All solutions were prepared from AR grade chemicals and purged with N₂ gas prior to and during each experiment. All experiments were carried out at room temperature (≈ 20 °C).

Thin WO₃ films were grown potentiostatically at the following formation potentials (E_f): 1, 2, 3, 4 and 5 V (vs. SCE), until steady-state currents were achieved (usually *ca.* 1 h), using a PARC 273 potentiostat-galvanostat. The acquisition of electrochemical-impedance data at high frequencies (100 Hz - 10 kHz) was always started at this upper potential limit (E_f), and proceeded in steps of 100 mV towards lower potentials E within the passive region. These data were acquired using a SOLARTRON 1255 frequency response analyzer, coupled to a PARC 273 potentiostat/galvanostat, controlled by a PC using the PARC-M388 software.

Results and Discussion

The impedance profile for passivated W electrodes was found to depend on both the film formation potential and the anodizing solution. The shape of the impedance spectra in the 100 Hz - 10 kHz frequency range corresponds to that of a capacitive semicircle. Spectra obtained involving much lower frequency ranges show that the polarization resistance $R_p = \lim_{\omega \rightarrow 0} [Z(j\omega)]$ is reached at lower frequencies than those covered in this work. Thus, the data can be analyzed in terms of an RC parallel combination in series with an ohmic resistance R_Ω , according to the transfer function

$$Z(j\omega) = R_\Omega + \frac{R}{1 + j\omega CR} \quad (1)$$

where $\omega = 2\pi f$. The high frequency limit R_Ω corresponds to the ohmic resistance of the electrolyte, whereas R and C are the resistance and the capacitance of the passive film, respectively. The experimental impedance spectra are well described by transfer function (1), if an appropriate choice of parameters is made. In order to obtain the values of C , the high-frequency impedance data were fitted to the transfer function (1), using a non-linear least-squares algorithm. The obtained C values decrease with increasing E (see Fig. 1) until a nearly constant value is reached at potentials close to E_f . This constant value was found to be dependent on the film thickness and on the anodizing solution. Such behavior can be explained by assuming that the passive layers formed on tungsten behave as non-stoichiometric semiconducting films. For large anodic polarizations, when the space charge layer encompasses the whole film, its capacity becomes constant if it has a wide bandgap (as is the case for WO₃), being a measure both of the thickness and of the relative permittivity. In this case, the whole thin film is in deep depleted conditions, with surface charges at both the oxide/solution and the metal/oxide interface^{12,13}. Then, the capacitance C of the metal/semiconductor/electrolyte system can be seen as a series combination of the oxide (C_{ox}) and the Helmholtz layer capacitances (C_H), *i.e.*:

$$\frac{1}{C} = \frac{1}{C_{ox}} + \frac{1}{C_H} \quad (2)$$

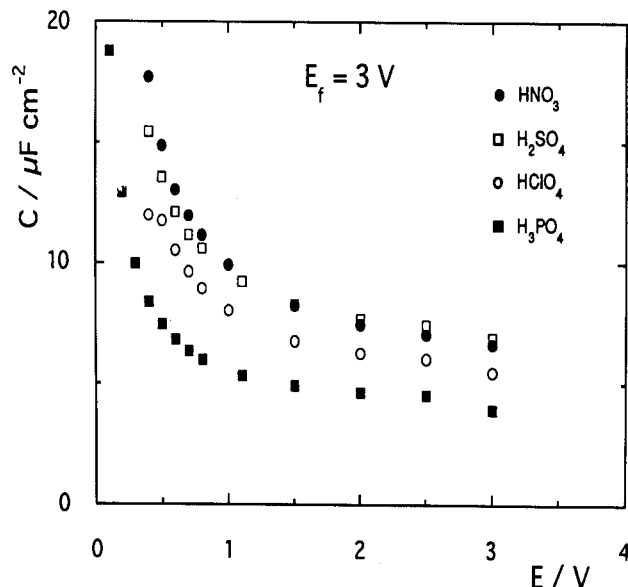


Figure 1. Passive film capacitance vs. electrode potential, for WO₃ films grown at $E_f = 3$ V (SCE) in the indicated aqueous acid solutions of $\text{pH} \approx 1.3$.

The value of C_{ox} was obtained through Eq. 2, assuming a conservative constant value¹¹ of $20 \mu\text{F cm}^{-2}$ for C_{H} . Figure 2 shows that the C_{ox}^{-1} vs. E_f plots are linear for all the anodizing solutions, having a higher slope value in the case of the data for the film grown in H_3PO_4 ; lower, nearly equal, slope values were obtained for the remaining acids. These results show that C_{ox} can be directly correlated with the thickness d of the passive film, and so the usual formula for the parallel plane condenser can be used:

$$C_{\text{ox}} = \frac{\epsilon_r \epsilon_0}{d} \quad (3)$$

where ϵ_r denotes the relative permittivity of the film, and ϵ_0 is the permittivity of the vacuum. It has been well established by optical methods¹¹ that the thickness d of the anodically grown WO₃ films increases linearly with the applied formation potential E_f , *i.e.*:

$$d = \alpha(E_f - E^0) \quad (4)$$

where E^0 is the potential at which the film starts to grow. If a value of the anodizing ratio $\alpha = 17.8 \text{ \AA/V}$ is assumed¹¹, regardless of the anodizing solutions used in the growth of the film, the estimated film thickness will have an uncertainty of less than 5 per cent⁸.

From Eqs. 3 and 4 one obtains

$$\frac{1}{C_{\text{ox}}} = \frac{\alpha}{\epsilon_r \epsilon_0} (E_f - E^0) \quad (5)$$

Then, the value of the relative permittivity of the passive films can be estimated from the slope of the C_{ox}^{-1} vs.

Table 1. Values of the relative permittivity (ϵ_r) of WO₃ films anodically grown in different electrolyte solutions ($\text{pH} \approx 1.3$), determined using Eq. 5 (see text).

electrolyte solutions	ϵ_r
HNO ₃	45
HClO ₄	33
H ₂ SO ₄	31
H ₃ PO ₄	27

E_f plots shown in Fig. 2. The obtained values (see Table 1) are slightly smaller than the ones previously reported in the literature^{8,11,14}, suggesting that the thin films grown potentiostatically have a lower water content than the thicker ones obtained under galvanostatic conditions. The lower relative permittivity estimated for the passive layers formed in aqueous H_3PO_4 solutions, compared to the ones for the films obtained in the other acids (see Table 1), has also been reported for other valve metals^{15,16}, and has been attributed to the incorporation of phosphate ions into the films¹¹.

On the other hand, at the lower operational potentials, the capacitance C can be assumed to correspond to the space charge capacitance (C_{sc}) of the semiconductor WO₃ film in the depleted region. Accordingly, for films grown at different formation potentials E_f , C increases as the potential E becomes less positive (Fig. 1). The Mott-Schottky plots (C_{sc}^{-2} vs. E) corresponding to WO₃ films formed in HClO₄ are shown in Fig. 3, for E_f values therein indicated; similar plots were obtained for films grown in the other acid solutions. From these results, which clearly characterize an n-type semiconductor behavior of the oxide film, it is possible to determine the number concentration of donors (N_{D}) in the space charge region as well as to estimate the flat band potential (E_{FB}) for films grown in each of the different electrolytes. This was done using the above calculated values of the relative permittivity of the

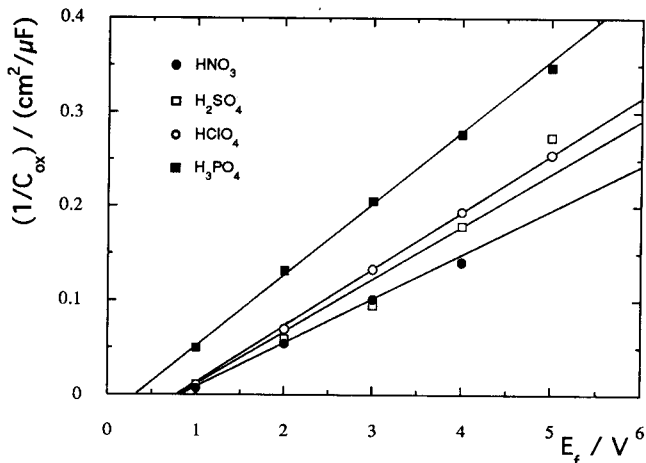


Figure 2. Inverse of the oxide capacitance vs. formation potential, for WO₃ films grown in the indicated aqueous acid solutions of $\text{pH} \approx 1.3$.

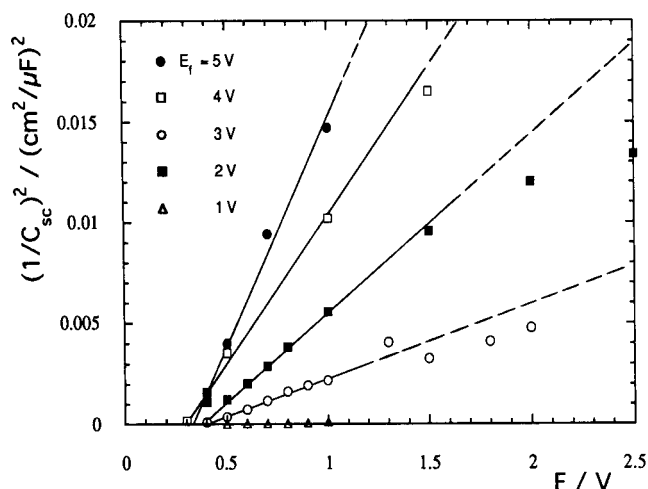


Figure 3. Mott-Schottky plots for WO_3 films obtained in aqueous HClO_4 solution of $\text{pH} \approx 1.3$ at the indicated formation potentials.

WO_3 films grown in different electrolytes, and the well-known Mott-Schottky relationship¹³:

$$C_{sc}^{-2} = \frac{2N_A}{N_D F \epsilon_r \epsilon_0} (E - E_{FB} - \frac{RT}{F}) \quad (6)$$

where N_A is the Avogadro constant, F the Faraday constant, T the thermodynamic temperature, and R the molar gas constant.

As can be seen in Fig. 4, N_D decreases with the anodic potential (*i.e.*, increasing film thickness); at the same time, the values of N_D for films grown in H_3PO_4 are smaller than those for films grown in the other acids. These values are larger than the ones previously reported⁸ for much thicker WO_3 films, and are of the same order of magnitude as the ones reported for annealed WO_3 films³; this could have been predicted from data previously reported in the literature⁸. The smaller N_D values for films grown in H_3PO_4 may be due to the incorporation of anions from the electrolyte into the film, as suggested before by Di Quarto *et al.*¹¹, with

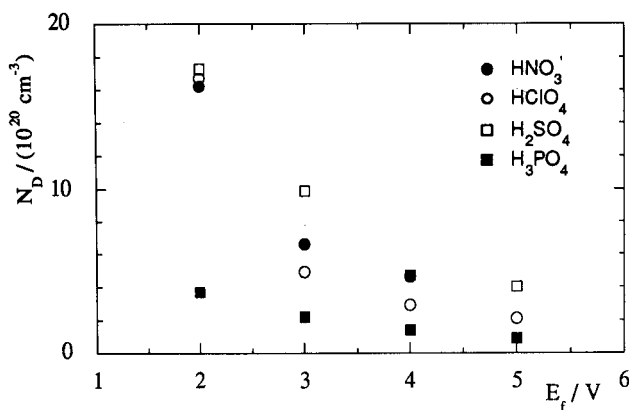


Figure 4. Number concentration of donors vs. formation potential, for WO_3 films grown in the indicated aqueous acid solutions of $\text{pH} \approx 1.3$.

a consequent decrease of donor-like centers in the space charge region.

Finally, the estimated values obtained from the Mott-Schottky plots for E_{FB} are approximately 0.22 V for the WO_3 films formed in H_3PO_4 , 0.35 V in HClO_4 and H_2SO_4 , and 0.45 V in HNO_3 , which are quite similar to those previously reported^{1,8}. It should be noted that the lower value of E_{FB} for films grown in H_3PO_4 suggests that the WO_3 films prepared in the phosphate-containing electrolyte may be more convenient for use in photocells, *i.e.*, a photoanode material less susceptible to corrosion. This possibility still needs to be tested.

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