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ScienceDirect

Thin Solid Films 516 (2008) 789 – 793

www.elsevier.com/locate/tsf

Developments in hot-filament metal oxide deposition (HFMOD)

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Available online 10 July 2007

Abstract

Hot-filament metal oxide deposition (HFMOD) is a variant of conventional hot-filament chemical vapor deposition (HFCVD) recently developed in our laboratory and successfully used to obtain high-quality, uniform films of MO_x, WO_x and VO_x. The method employs the controlled oxidation of a filament of a transition metal heated to 1000 °C or more in a rarefied oxygen atmosphere (typically, of about 1 Pa). Metal oxide vapor formed on the surface of the filament is transported a few centimetres to deposit on a suitable substrate. Key system parameters include the choice of filament material and diameter, the applied current and the partial pressures of oxygen in the chamber. Relatively high film deposition rates, such as 31 nm min^{-1} for MoO_x, are obtained. The film stoichiometry depends on the exact deposition conditions. MoO_x films, for example, present a mixture of MoO_2 and MoO_3 phases, as revealed by XPS. As determined by Li^+ intercalation using an electrochemical cell, these films also show a colouration efficiency of 19.5 cm^2 C^{-1} at a wavelength of 700 nm. MO_x and WO_x films are promising in applications involving electrochromism and characteristics of their colouring/bleaching cycles are presented. The chemical composition and structure of VO_x films examined using IRRAS (infrared reflection–absorption spectroscopy), RBS (Rutherford backscattering spectrometry) and XPS (X-ray photoelectron spectrometry) are also presented.

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Keywords: Hot-wire CVD; Electrochromism; Tungsten oxide; Molybdenum oxide; Vanadium oxide; Thin films

1. Introduction

Changes in colour induced by heat, light or an electric field are known as thermochromism, photochromism and electrochromism, respectively. In modern use, however, the last term is applied to materials that change colour in a persistent yet reversible manner under an electrochemical reaction. Electrochromism therefore is the reversible and visible change in transmittance or reflectance or both associated with an electrochemically induced oxidation–reduction reaction, resulting from the generation of different visible region electronic absorption bands [1].

Among the electrochromic materials are Prussian blue (iron (III) hexacyanoferrate (II)), metal phthalocyanines, such as lutecium *bis*(phthalocyanine), viologens (that is, 4,4′-dipyridinium compounds), conducting polymers such as polypyrrole, polyaniline and polythiopene, and transition metal oxides (TMOs). The present study discusses recent developments in the fabrication of three TMOs, namely MO_x, WO_x and VO_x using a novel variant of hot-filament chemical vapor deposition (HFCVD) denoted hot-filament metal oxide deposition (HFMOD), details of which are given later in this section.

Aside from the theoretical interest in defining the specific mechanisms responsible for electrochromism, the electrochromic effect has been pursued for application in displays, smart windows and mirrors [1]. Each of the oxides of the three metals considered in some detail here (Mo, W and V) is

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0040-6090/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2007.06.183

electrochromic. In addition, MoO_x and WO_x films are used in catalysis and as gas sensors; MoO_x and VO_x films are used in microbatteries [2,3].

Electrochromic effects in many TMOs have been investigated and attempts were made to optimize their optical performance. Among others, anodic electrochromic nickel oxide films have been produced by pulsed laser ablation [4,5] and sol–gel technique [6]. It is also known that annealing strongly influences electrochromic responses of NiO films [6]. A disadvantage of such films is their low durability but this may be improved in more complex systems such as Ni–Co–O (5% Co) and Ni–Ta–O (10% Ta). Tantalum oxide films produced by spin coating showed good abrasion resistance [7], while Ta_2O_5 films produced by rf-magnetron reactive sputtering exhibited transferred charges of up to 70 mC cm^{-2} [8]. Other electrochromic oxides investigated include those of iridium, obtained by sol–gel [9], reactive sputtering [10], and spray pyrolysis [11], and of niobium [12–14]. Films with the Nb_2O_5 stoichiometry have been produced by sol–gel [12] and rf sputtering [13]. The colouration efficiency upon Li^+ insertion was 16.68 cm^2 C^{-1} at 550 nm. A reversible redox reaction between Nb-V and Nb-IV with a double injection/extraction of Li^+ and electrons is responsible for the electrochromism in such films [13]. Titanium oxide films have been produced by immersion in aqueous solutions [15], reactive thermal evaporation and ion-assisted deposition [16], and rf sputtering [17]. Films of TiO_2 with a lithium ion (Li^+) capacity of 7.6 mC cm^{-2} and greater than 10^6 colouring/bleaching cyclic stability have been obtained [16]. Amorphous TiO_2 thin films have also been fabricated by the PECVD of tetraisopropoxy-titanium [18].

Films of direct interest in the present paper are oxides of Mo, W and V. A number of techniques such as rf sputtering [19] and atmospheric pressure CVD [20,21] have been employed to produce MoO_x; dc magnetron sputtering [22], sol–gel technique [23], organo-metallic CVD [24], dip coating [25] and hot-wire CVD [26] used to produce WO_x; rf reactive sputtering [27], dip coating with subsequent heating [28], and evaporation [29] used to produce VO_x. Table 1 shows some colour changes induced in thin films of transition metal oxides. The oxidation/reduction mechanisms responsible for electrochromism in MO_x, WO_3 and V_2O_5 films are given in Eqs. (1) (2) and (3), which are essentially the same with the salvo that Eq. (1) is specifically for Li^+ intercalation. We used Li^+ intercalation in all of our electrochromism studies.

$$MoO_x + ye^- + yLi^+ \leftrightarrow Li_yMoO_x \quad (1)$$

$$WO_3 + xe^- + xM^+ \leftrightarrow M_xWO_3, \quad (2)$$

where M^+ is H^+, Li^+, Na^+, or K^+

$$V_2O_5 + xe^- + xC \leftrightarrow C_xV_2O_5, \quad (3)$$

where C is H^+ or Li^+.

A HFMOD system is similar to a conventional hot-filament CVD apparatus used to fabricate diamond thin films. Fig. 1 shows a schematic of our system. A filament of the metal whose oxide is to be deposited is mounted in a conventional vacuum chamber pumped by a 150 m^3/h roots pump, backed by a mechanical pump, and fed gases (purity>99.99%) via precision mass flow controllers. Instead of hydrogen/hydrocarbon mixtures, however, which are typical feeds used to deposit diamond, oxygen is employed. A current of about 5 to 20 A is passed through the filament, and a film forms on substrates placed nearby (1 to 3 cm). The filament is heated by an ac current measured by an ammeter. A quartz viewport in the chamber wall allows the filament temperature to be measured using a precision optical pyrometer. A chromel alumel thermocouple is used to measure the temperature of the water-cooled copper substrate holder. The films originate from the vaporization of oxides formed on the filament surface. Thus unlike conventional HFCVD of diamond where oxidation of the filament must be avoided to prevent contamination of the film, in HFMOD this difficulty is exploited. As already mentioned, control parameters include the filament current and the partial pressure of the oxygen. Owing to the film formation processes, a filament of small dimensions (diameter 0.5 to 1 mm) that can be raised to a suitably high temperature by resistive heating, and which forms oxides that show a significant vapor pressure under these conditions is required to obtain a thin film by HFMOD. If the vapor pressure of the metal is too high or the partial pressure of the oxide is too low or both, either predominantly metallic films will be produced or no significant oxide deposition rate will be observed. Thus while it is shown in

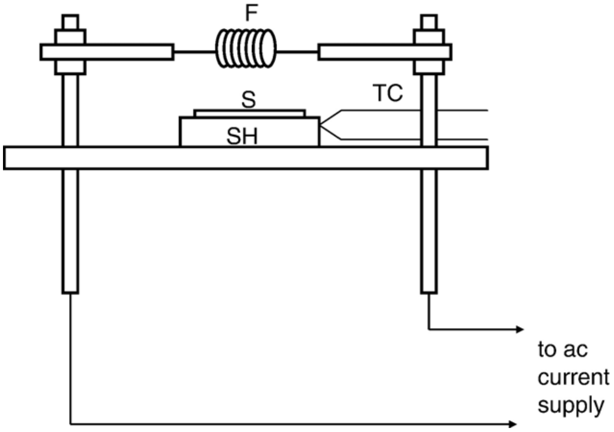

Fig. 1. Hot-filament metal oxide deposition (HFMOD) system.

Table 1
Examples of electrochromic transition metal oxides

Cathodically ion insertion materials	Anodically ion insertion materials	Colour: Oxidized state	Colour: Reduced state
MoO_3		Transparent	Blue
WO_3		Transparent	Blue
V_2O_5		Yellow	Blue–black
Nb_2O_5		Yellow	Blue
	$Ir(OH)_3$	Blue–black	Transparent
	$Ni(OH)_2$	Brown–bronze	Transparent or pale-green

Adapted from Somani and Radhakrishan [1], with permission of Materials Chemistry and Physics (Elsevier).

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