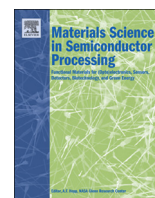




ELSEVIER

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Internal electrochromism in vanadium pentoxide xerogel films



D. Yakovleva, A. Pergament*, O. Berezina, P. Boriskov, D. Kirienko, V. Pikulev

Faculty of Physical Engineering, Petrozavodsk State University, 185910 Petrozavodsk, Russia

ARTICLE INFO

Article history:

Received 22 September 2015

Received in revised form

15 December 2015

Accepted 5 January 2016

Available online 14 January 2016

Keywords:

Vanadium pentoxide

Sol-gel

Ionic conductivity

Electrochromism

Chemical bonds

ABSTRACT

We describe the internal electrochromic effect in V_2O_5 xerogel films caused by the redistribution of hydrogen ions inside the film, instead of insertion from the outside, i.e. from an electrolyte, as in the case of conventional electrochromism. A hypothesis is put forward according to which the mechanism of this electrochromic effect is associated with formation of red-colored hexa- and (or) deca-vanadic acid inclusions inside the vanadium pentoxide layers. This model is supported by the calculated data of energy characteristics of V–O chemical bonds in V_2O_5 octahedra layers of xerogel, as well as by the experimental results of XRD, FTIR, and optical spectroscopy.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

$V_2O_5 \times nH_2O$ xerogel possesses mixed electronic-ionic conductivity [1], which enables its use, particularly, in electrochromic (EC) devices [2] and lithium battery cathodes [3]. EC materials reversibly modulate their optical properties depending on charge (electrons and ions) insertion or extraction. Many transition metal oxides demonstrate the EC properties [4], and the most studied amongst them is WO_3 whose coloration is associated with formation of M_xWO_3 bronzes (where M is hydrogen or an alkali metal, most often lithium, element). V_2O_5 also exhibits EC behavior under Li intercalation [4–8] due to formation of a $Li_xV_2O_5$ bronze [9]. The color change usually occurs toward the green–blue spectrum region because of a decrease in transmittance at wavelengths over about 600 nm [5], and the optical contrast is rather weak as compared to some other EC materials (e.g., WO_3). That is why, as a rule, vanadium pentoxide films are frequently used as just counter electrodes in EC devices [6].

Currently, much research are focused on the study of EC effect in systems with solid electrolytes in order to develop technologies for manufacturing such devices as “smart” glass and “smart” paper, flexible displays and thin film sensors. Previously, we have reported on the internal EC effect [10] in thin films of hydrated vanadium pentoxide, which consists in a reversible color change of the film under the action of electric field. An important feature of this phenomenon is that the EC effect in $V_2O_5 \times nH_2O$ xerogel occurs without an external electrolyte, unlike in conventional EC

materials which modulate their optical properties due to ion insertion/extraction from an electrolyte.

In addition, to produce the films of hydrated V_2O_5 , the sol-gel method is applied, which is regarded as one of the most promising liquid phase deposition processes, especially, for obtaining thin vanadium oxide films [10–12]. Also, the liquid-phase sol-gel process makes it possible to deposit thin-film coatings onto large-area substrates of complex topology and at low temperatures; the latter merit is essential for applications in flexible electronics [11].

In this paper we report experimental results on the internal electrochromic effect and present a qualitative model describing the observed phenomena on the basis of partial electrochemical transformation of V_2O_5 layers of a xerogel film into hexa- or deca-vanadic acid inclusions. This model is further supported by the quantum-mechanical calculations of the strength of vanadium-oxygen chemical bonds.

2. Experimental

Vanadium pentoxide gel solution was prepared by the quenching method [12]. V_2O_5 powder was placed in a ceramic crucible and heated in air at 900 °C for an hour (above the melting point, 690 °C), and then quenched by pouring the molten oxide into room temperature distilled water. Using the obtained sol, the xerogel films were deposited onto glass, silicon and glass-ceramic substrates as described previously [10,12] and excess solvent was allowed to evaporate at room temperature for 24 h. These xerogel films had a layered structure [1,12]: V_2O_5 layers were formed by cross-linked fibers and separated by water with the interlayer spacing of about 11 Å for $n=1.6$ –1.8. The film thickness δ varied

* Corresponding author.

E-mail address: aperg@psu.karelia.ru (A. Pergament).

from 0.5 to 3.5 μm .

The samples were characterized by means of X-ray diffraction (XRD) analysis using a DRON-4 diffractometer with Mo K α radiation, $\lambda=0.7107$ Å. Optical (transmittance $T(\lambda)$ and reflectance $R(\lambda)$) spectra) measurements for the xerogel films on glass substrates were performed using an SF-56 spectrophotometer in the wavelength range of 190–1100 nm. The absorption coefficient α was calculated from the formula:

$$\alpha = \frac{1}{\delta} \ln \frac{(1 - R)^2}{T} \quad (1)$$

The films for IR measurements were grown on lightly doped silicon substrates (for they possess an ideal transmittance for IR measurements in the used spectral interval), and the measurements were performed in air at room temperature with a FTIR (Fourier Transform Infrared) FT-801 spectrometer. The spectral range of measurements was 400 to 4000 cm^{-1} , and a resolution was 0.05 cm^{-1} .

For the electrical (DC I - V characteristics) measurements, a power supply with a maximum voltage of up to 250 V, connected in series with the sample and an ammeter, was used. In this case, films on glass substrates were also used. The details of measurement techniques, as well as the equipment used, were also described in detail elsewhere [10–12].

3. Results and discussion

3.1. Optical and electrical properties: experimental results

To study the internal EC effect, we have used a two-electrode planar system (Fig. 1a) where the distance between contacts (gilded wires) is 5 mm. When the current flows, a red spot (Fig. 1b), gradually increasing in diameter, is observed. The time of the spot appearance, as well as its diameter, depend on the voltage applied and on the overall duration of the electric-field treatment. At the reverse polarity, the spot disappears, i.e. the process of bleaching takes place. The applied voltage for the coloration process commencement is about $V_0=10$ V (for $\delta \approx 3$ μm), and the coloration time t_0 is typically 5–30 s. These parameters depend on the film thickness: both the values V_0 and t_0 increase as the thickness increases. At a voltage lower than this threshold value V_0 , no change in optical properties ($T(\lambda)$ spectrum) occurs.

The optical transmittance spectrum of the as-prepared $\text{V}_2\text{O}_5 \times n\text{H}_2\text{O}$ film on a glass substrate is presented in Fig. 2a (curve 1). As one can see from the figure, the spectra exhibit a characteristic absorption band at a wavelength of about 570 nm. For the colored samples, an increase in T (approximately from 50% to 80%) and a shift of the absorption edge towards longer wavelengths are observed.

The absorption edge at 2.3–2.5 eV in vanadium–oxygen compounds is ascribed to $\text{O}2\text{p} \rightarrow \text{V}3\text{d}$ electron transitions and it is consistent with the energy gap of V_2O_5 , $E_g=2.35$ eV [1,12]. For our xerogel films $E_g=2.3$ eV in the pristine state, and it changes to 2.1 eV in the colored state (Fig. 2b). By analogy with the standard EC effect (i.e. with that occurring in an electrolyte), one could assume that the coloration mechanism is associated with formation of an $\text{H}_x\text{V}_2\text{O}_5$ bronze type compound.

Because the system under study is “dry” (completely solid-state) and the process is rather slow, we have not conducted standard electrochemical potentiometric measurements, but the conventional current–voltage characteristics of the coloration process has been measured instead (Fig. 3). Due to the mixed electronic-ionic nature of conductivity, the I - V curve is non-linear. Initial (near zero) region of the curve corresponds to Ohmic

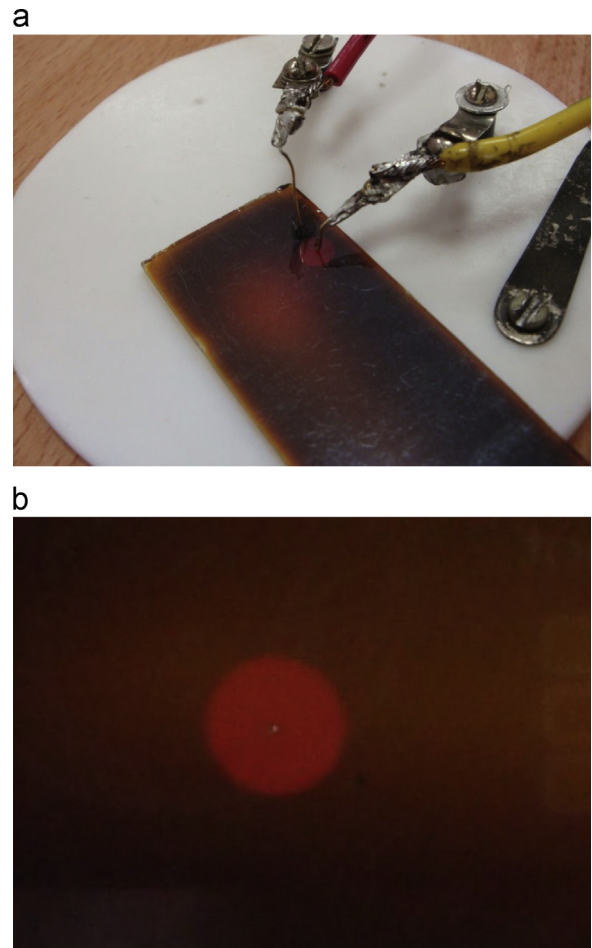


Fig. 1. (a) The process of coloration and (b) colored region (~5 mm in diameter).

behavior, while an instability at V between about 7 and 15 V corresponds to the coloration process commencement which is followed by a saturation region. This region is associated with the ambipolar diffusion-drift motion of electrons and protons and accumulation of abundant hydrogen under cathode. One can suppose that these extra hydrogen ions might intercalate inside V_2O_5 layers causing the observed effect of coloration. It should be emphasized however that unlike conventional EC coloration (with an external electrolyte) of V_2O_5 , the color change in our case is not “yellow \rightarrow green” [5,6,14], but it is quite the reverse, i.e. “yellow \rightarrow red”.

To explain such a difference, we assume that no $\text{H}_x\text{V}_2\text{O}_5$ bronze is formed during coloration. The red color could be ascribed to appearance of polyoxovanadate ions [15], e.g., hexa- ($\text{H}_4\text{V}_6\text{O}_{17}$) or deca- ($\text{H}_6\text{V}_{10}\text{O}_{28}$) vanadic acids which are known to be red in solutions. This transformation must lead to not only a color change, but also to an increase in resistivity of the colored region (because of destruction of V_2O_5 layers partially interrupted by vanadic acid molecules) which is observed in experiment [10].

Higher vanadic acids are unstable and not observed in a free state (and they only virtually appear in solutions [15]), yet $[\text{V}_6\text{O}_{17}]^{4-}$ complexes have been reported to be stable in metal–organic compounds [16,17]. For example, dark red block crystals of $[(2,2'\text{-biphen})\text{Co}]\text{V}_3\text{O}_{8.5}$ has been synthesized in [16]. Therefore we surmise that such a situation might also take place in our case. Note also that, although both deca-vanadate and hexa-vanadate ions might lead to red color, formation of hexa-vanadic acid molecules seems to be more preferable because of their smaller size

Download English Version:

<https://daneshyari.com/en/article/727813>

Download Persian Version:

<https://daneshyari.com/article/727813>

[Daneshyari.com](https://daneshyari.com)