Solid-State Electronics 99 (2014) 16–20

Contents lists available at ScienceDirect

Solid-State Electronics

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

Operation mechanism investigation of electrochromic display devices using tungsten oxides based on solid-state metal–oxide–metal capacitor structures

Chin-Pao Cheng [a,*], Yi Kuo [a], Chun-Hu Cheng [a,*], Zhi-Wei Zheng [b]

[a] Department of Mechatronic Technology, National Taiwan Normal University, Taipei 106, Taiwan
[b] Institute of Microelectronics, Chinese Academy of Sciences, Beijing 10029, China

ARTICLE INFO

Article history:
Received 9 January 2014
Received in revised form 4 April 2014
Accepted 1 May 2014
Available online 2 June 2014

The review of this paper was arranged by Prof. A. Zaslavsky

Keywords:
Electrochromic
Tungsten oxide (WO_3)
Oxygen vacancy
Redox

ABSTRACT

In this work, we investigate the electrochromic effect of WO_3 electrochromic display device and operation mechanism based on a solid-state TaN/WO_3/ITO metal–oxide–metal capacitor. The electrochromic switching mechanism correlated with the oxygen vacancy concentration was proposed and well-predicted. The experimental results reveal that electrochromic device using electrodeposited WO_3 without post annealing exhibits the much better coloration and bleach process than those of annealed sample. The cycling test of WO_3 metal–oxide–metal capacitor also demonstrates that the degradations of current/voltage distributions are mainly originated from randomly distributed connected paths consisting of oxygen vacancies. Thus, oxygen vacancies formed during WO_3 electrodeposition process or post film annealing need to be well controlled.

1. Introduction

The electrochromic materials have attracted more attention because of low cost, low power operation and excellent environmental compatibility, which show the potential for energy saving application, such as smart windows, automobile rear-view, flexible displays and sensors [1–13]. The WO_3 electrochromic material shows high optical contrast on coloration and bleaching switching, which have been reported in previous works [7–13]. The device performance of WO_3 electrochromic (EC) devices depends on the injection efficiency of electrons and oxidation–reduction rate based on electrolyte cation diffusion. Although the coloration and bleaching process can be achieved by appropriate bias conditions, the WO_3 EC devices still suffer from the issues of electrochromic efficiency and cycling reliability due to an unclear operation mechanism [10–13]. Several physical mechanisms have been applied to describe EC mechanism, such as color center mechanism [14], intervalence charge transfer model [15], small-polaron model [16], Hubbard splitting of the conduction band model [17]. Although related operation mechanisms or models are proposed to explain this complex electrochromic system, the redox chemical reaction and corresponding reversible electrochemical behavior are significantly influenced by composition, concentration, and temperature of electrolyte. To address these issues, we investigate the operation mechanism based on a solid-state WO_3 metal–oxide–metal (MOM) capacitor with a simplified device structure. The coloration and bleaching behaviors can be explained by capacitance–voltage (*C*–*V*) and current–voltage (*I*–*V*) hysteresis characteristics of WO_3 MOM capacitor, showing that the oxygen vacancy in WO_3 bulk plays an important role to dominate the switching power and redox reaction.

Further finding was also revealed by WO_3 film annealing. After film annealing, the additional oxygen vacancies are created and contribute to an overdrive leakage current during redox reaction process to lead poor coloring. The switching uniformities for operating voltage and current are also dependence of randomly distribution conduction paths consisting of tungsten ions and complex oxygen vacancies that need to be well controlled during WO_3 electrodeposition process or post film annealing. The presented results show that by controlling the oxygen vacancies in WO_3, the WO_3 EC device based on oxygen vacancy transport mechanism could create high potential in high-performance electrochromic display applications.

* Corresponding authors. Tel.: +886 2 7734 3514; fax: +886 2 2358 3074.
E-mail addresses: cpcheng@ntnu.edu.tw (C.-P. Cheng), chcheng@ntnu.edu.tw (C.-H. Cheng).

http://dx.doi.org/10.1016/j.sse.2014.05.001
0038-1101/

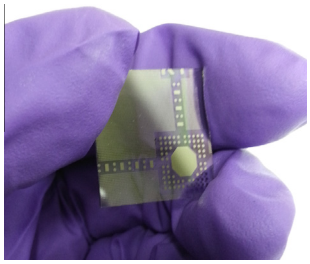

Fig. 1. The photograph of TaN/WO_3/ITO MOM capacitor on glass substrate.

2. Experimental procedure

The WO_3 EC devices and corresponding TaN/WO_3/ITO MOM capacitors were prepared on the ITO glass substrate. First, the ITO glass substrate was pre-cleaned by acetone and deionized water for 10 min. Subsequently, the 200-nm-thick WO_3 films were electroplated on the ITO glass as electrochromic layers. The solution syntheses process for WO_3 films preparation was described as follows. The peroxotungstic acid solution was synthesized by dissolving the tungsten powder in a cooled beaker containing a 30 ml hydrogen peroxide aqueous solution for 24 h. Then the 30 ml glacial acetic acid was mixed with peroxotungstic acid solution and heated at 55 °C for 12 h. After that, the 30 ml alcohol was added to stabilize the solution. To evaluate WO_3 film property, a 200-nm-thick TaN was deposited by sputtering a tantalum target with 4 inch size under a mixing gas of Ar and N_2 as the top electrodes of TaN/WO_3/ITO MOM capacitors. The TaN/WO_3/ITO MOM capacitors with annealed WO_3 at 200 °C under a vacuum was also fabricated for film property comparison. The photograph of the finished MOM capacitors is shown in Fig. 1. This solid-state TaN/WO_3/ITO MOM capacitor can be used for evaluating electrochromic properties of WO_3 and studying the switching mechanism under different applied voltages. The electrochromic testing is carried out in a conventional two-electrode environment. The appropriate biases from 1 to 3 V were applied to on the ITO electrodes of WO_3 EC samples. A lithium electrolyte was used as ionic conductor to test electrochromic property. The forward and reverse biasing of WO_3 films in lithium ion-containing electrolytes result in reversible coloration and bleach behaviors through Li^+ interaction. The surface morphology and composition of WO_3 film were analyzed by high-resolution field emission scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) analysis. All electrical characteristics of the WO_3 devices were measured by Agilent 4156 semiconductor parameter analyzer and 4284 LCR meter. The optical property including transmission and absorption spectrum were recorded by using a VIS spectrophotometer (Perkin Elmer Lambda 900).

3. Results and discussion

Fig. 2 shows *I–V* swept curves of TaN/WO_3/ITO MOM capacitors with and without post dielectric annealing. The *I–V* characteristics of MOM capacitors were evaluated by applying bias sweeps under different polarities. The ramp rate of 60 mV/s was performed to measure the leakage current behavior. To avoid device hard breakdown, the *I–V* measurement is limited by a current compliance of 10 mA. From the measured results, TaN/WO_3/ITO MOM capacitor shows the apparent hysteretic *I–V* curves at both forward and reverse bias sweep. The change of leakage current is believed to be related to interface resistance change between electrode and WO_3 dielectric, which have been demonstrated in currently developed resistive memory [18–22]. Here, the hysteretic *I–V* curve accompanying with resistance change may be responsible for coloration and bleach behaviors. Thus, a deep investigation on switching mechanism of WO_3 electrochromic device is necessary. Under a forward bias sweep (from 4 V to −4 V), we can measure a lower leakage current (high resistance state), which is mainly defect-induced leakage from tungsten oxide film. The high resistance value of ~1 kΩ can be measured at an operating voltage of 2 V, which is preferred to the occurrence of hopping conduction in oxidized WO_3 with less oxygen vacancies. However, a larger leakage current (red color) is measured when a reverse bias sweep (from −4 V to +4 V) is applied. The change of operating current from negative to positive bias depends on $W^{6+} \rightarrow W^{5+}$ reduction process and the magnitude of leakage current (low resistance state) is determined by the number of local connection paths consisting of low valence tungsten ions and complex oxygen vacancies [18–22]. The schematic plots of corresponding switching mechanism are shown in Fig. 2(b).

The significant *C–V* hysteresis characteristic is shown in Fig. 3(a), where *C–V* hysteresis loop represents the change of charges by $\Delta Q = \Delta C \times V$. The capacitance change may be originated from the modification of interface barrier height and space charge capacitance [17]. Under a reverse bias sweep (from −4 V to +4 V), the charged oxygen vacancies can be formed by injected electrons from top TaN electrode, resulting in a higher capacitance (top *C–V* curve). In the opposite bias direction (from +4 V to −4 V), the bottom injected electrons from the ITO electrode can break the weakly connected paths by the recombination with charged vacancies:

$$V_{WO_x}^{2+} + 2e^- + WO_x \rightarrow WO_x^* \tag{1}$$

Here, the ${V_{WOx}}^{2+}$ represents oxygen vacancy in tungsten oxide film. Thus, the concentration change of oxygen vacancy caused by electron injection in turn lowers the capacitance value to form an oxidized WO_3 (bottom *C–V* curve). Compared to an annealed condition in Fig. 3(b), the annealed sample provide a much larger leakage current and a smaller hysteresis window, indicating that the resistance modification cannot be reached by local electric filed due to excess oxygen vacancies in the annealed film. Therefore, it is important to note that the oxygen vacancy plays an important role to dominate the operating current and switching power, and thus needs to be well controlled during film deposition process. Although the operation mechanism based on oxygen vacancy in MOM capacitor is similar to EC mechanism [14] proposed under an electrochemical system involving the reaction of electrolyte, the basic reaction mechanism in WO_3 film can be clarified in this simplified MOM capacitor structure. Furthermore, the reduced WO_x with higher concentration oxygen vacancies are responsible for the coloration state that directly affects the coloration efficiency of electrochromic device.

To further investigate related operation mechanism based on oxygen vacancy transport, the XPS analysis for as-deposited and annealed WO_3 films was performed, as shown in Fig. 4. From the O 1s spectrum for as-deposited tungsten oxide film in Fig. 4(a), the main peak of 530.5 eV is assigned to the oxygen atoms in the stoichiometric WO_3 [23], indicating that the as-deposited film is W^{6+} preferred and has less oxygen vacancies. It agrees with the electrical results (Fig. 2) where the initial state exhibits a low leakage current. The small peak at 532.5 eV is regarded as the contribution of absorbed water molecule on WO_3 surface [22]. However, a main peak of 531.5 eV with higher binding energy, which is attributed to nonlattice oxygen ions, is observed in annealed film, as shown in Fig. 4(b). The nonlattice oxygen ions and related oxygen vacancies play the critical role in operating current of coloration state. Excess oxygen vacancies in tungsten oxide film would lead to an overdrive current and thereby damage the tungsten oxide film during cycling operation.