



Tantalum oxide film deposited by vacuum cathodic arc plasma with improved electrochromic performance

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ABSTRACT

Inorganic solid-state electrochromic devices (ECDs) based on tantalum oxide (Ta_2O_5) as ion conductor layer were fabricated by vacuum cathodic arc plasma (CAP) deposition. This work focuses on key factor of fabricating Ta_2O_5 film deposited by CAP through four different ratios of oxygen and argon. Our results show that refractive index mostly decreased with increasing oxygen flow rate. Refractive index of 1.9 was achieved for Ta_2O_5 film with $\text{O}_2/\text{Ar} = 2.4$ which provided high ion conduction pathways through a highly porous structure. We also observed higher ionic conductivity $\sigma_i = 3.5 \times 10^{-6} \text{ S cm}^{-1}$ for Ta_2O_5 film at $\text{O}_2/\text{Ar} = 2.4$ which enhanced ion's mobility for ECDs causing rapid coloring/bleaching phenomenon. As a result, excellent optical density and rapid response times were observed in fabricated device with an area of 20 cm^2 , exhibiting optical density of 0.63 (@ 550 nm) and transmittance variation $T = 50\%$ (@550 nm) with the bleaching time = 5 s and transmittance variation $T = 50\%$ (@550 nm) with the coloring time = 13 s.

1. Introduction

Electrochromic devices (ECDs) are based on well-known electrochemical phenomena and are an enabling technology for smart windows, energy efficient building, optical information display, variable-reflectance mirrors, switchable mirrors, electronic paper [1–6]. ECDs are consisting of five layers with an ionic conduction layer (electrolyte) in contact with an electrochromic (EC) layer and an ion storage (complementary) layer, all sandwiched between two transparent conducting layers, which are illustrated in the schematic diagram of Fig. 1.

The EC layer consists of tungsten trioxide (WO_3) electrode film is used for color modulation. The color modulation is reversibly modified by ions and electrons injection which changes the colored or bleached state, hence it needs to be a better electrical conductor and available ions coming from electrolyte layer to be injected into the EC film. The ion storage layer displays complementary electrochromic characteristics to inorganic anodic EC thin films, the popular metal oxide NiO is used for electrode film. WO_3 is known as one of the most popular cathodic electrochromic materials and NiO as one of the widely accepted anodic electrochromic materials, which have been intensively investigated [7] where the optical modulation increases due to the

simultaneous modulation of both electrodes [8]. In this study, we have adopted the usual method of producing electrochromic NiO, and WO_3 films using DC or DC-pulsed sputtering technology.

In particular, switching response time for coloration and bleaching state depends not only on the quality of the electrochromic layer and complementary layer, but also on the ionic conduction layer, which is controlled by the microstructure and composition of the ionic conductor [9]. Nanostructures can have excellent properties for electrochromic device due to enhanced kinetics of ions injection/extraction for electrochromic reaction which may refer to superior EC performances. This can be done by increasing the contact area between the electrode and electrolyte that reduces the diffusion path of ions [10–12]. In general, ionic conductor layer (electrolyte layer) is made up of two kinds of inorganic and polymeric electrolyte [13,14] in the center part of ECDs. Otherwise, polymeric-type materials of ionic conductor layer have better ionic capabilities than inorganic-type, but inorganic-type materials are more stable and durable. The electrolyte layer (Ta_2O_5 thin film) for ECDs has been fabricated using various methods, such as chemical vapor deposition [15], the sol-gel method [18,16,17], electron beam evaporation [19], sputtering [20,21,9], and pulsed laser deposition [22]. Among these methods, reactive sputtering deposition

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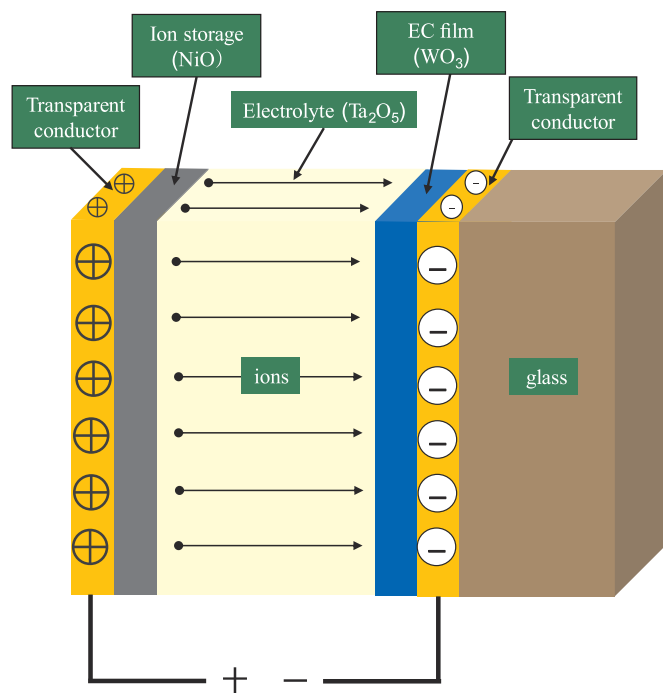


Fig. 1. The typical structure of electrochromic device.

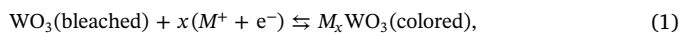
can be independently controlled and stability has been obtained with relatively high ion conductivity ($\geq 10^{-7} \text{ S cm}^{-1}$) [23] and relatively low electronic conductivity ($< 10^{-12} \text{ S cm}^{-1}$). Unfortunately, the above methods do not meet the requirements of low sputtering time and low produce cost for fabricating a solid electrolyte Ta_2O_5 thin film. Here we provide a simple and effective way to synthesize tantalum-oxide film which exhibits enhanced EC performance. In this study, fast fabrication of columnar arrays of Ta_2O_5 film is synthesized by using vacuum cathodic arc plasma (CAP) technique. This deposition technique is unique and can be used to synthesize a variety of transition metal-oxides nanostructures having diverse morphological features. CAP technique owns a high deposition rate, produces good adhesion between the deposited film and substrate, and offers low-cost advantage, thus providing simple commercial opportunities. In general, the Ta_2O_5 thin film has high transparency in the visible and UV range, having high ionic conductivity, and good chemical, thermal stability, and stabilized environment durability [14,23,24].

This work focuses on fabricating Ta_2O_5 film as a solid-state electrolyte deposited by CAP deposition through four different ratios of oxygen and argon. Here, we focus on how to fabricate nano-structure with high specific areas and porosity, so as to enhance fast ions insertion/extraction. In this report, we demonstrate a high-performance ECD composed of ITO/ WO_3 / Ta_2O_5 / NiO /ITO/glass, in which ion conducting layer (Ta_2O_5 film) exhibits much improved electrochromic properties in terms of fast coloration/bleaching response speed, greater optical modulation, and cycle stability.

2. Experimental

2.1. Principle of ECD test

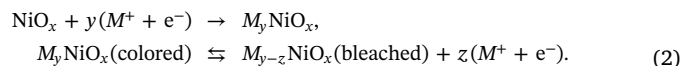
Essential physics of coloring of WO_3 can be represented by the following the redox equations [13,25,26]



where M stands for the lithium ions (Li^+) or hydrogen ions (H^+) ions. From (1), thin film of WO_3 can be colored from a transparent state to deep blue, colored by ions and electrons insertion under a low negative

voltage bias. The film returns to their transparent state (bleached state) by ions and electrons extraction. Coloration is caused by photo-effected inter valence electron transfer from W^{6+} to W^{5+} sites [27].

The electrochromic mechanism of NiO electrode film in lithium ions (Li^+) can be expressed with two chemical processes. The redox reaction against ion insertion/extraction in NiO electrode layer is as follows [28],



The reduction of Ni^{3+} to Ni^{2+} leads to the bleaching of NiO film during the cathodic scan, and the oxidation of Ni^{2+} to Ni^{3+} causes coloration phenomenon in reverse processes. When applying the negative voltage on the NiO electrode film (ion storage layer), electrons and Li^+ ions were inserted into NiO film causing the oxidation of Ni^{2+} ions to Ni^{3+} . When applying the positive voltage on the NiO electrode film (ion storage layer), electrons and Li^+ ions were deserted into NiO film, which causes the reduction of Ni^{3+} ions to Ni^{2+} , so the bleaching state is dominated by reverse scanning. The operational voltage is typically 3.5 V (bleached state) and -4 V (colored state) in EC cell.

2.2. Device fabrication

The solid-state electrolyte Ta_2O_5 film was fabricated using CAP deposition technique and DC-pulsed sputtering technology. Ta_2O_5 film was fabricated by using CAP deposition with pure (99.99 wt%) Tantalum (Ta)-metal target, the deposition temperature was fixed at 100°C . In CAP technique, a Ta-metal disk was used with 3 in. in diameter and 3 mm in thickness as the target size. The base chamber pressure was set to less than $1 - 3 \times 10^{-5}$ Torr using a turb pump. The argon insert flow and oxygen reactive flow were controlled individually by mass flow controllers. By CAP deposition, we consider four different oxygen mass flow of 150 sccm, 200 sccm, 240 sccm and 350 sccm with a fixed 100 sccm argon mass flow for the reactive gasses, and the corresponding working pressure are 2.9×10^{-2} torr, 3.4×10^{-2} torr, 4.6×10^{-2} torr, and 6.3×10^{-2} torr respectively. For DC-pulsed sputtering, we consider oxygen mass flow of 13 sccm with 100 sccm argon mass flow for the reactive gasses, and the corresponding working pressure are 2.0×10^{-2} torr. The 60 nm-thick NiO thin film has been deposited at room temperature on the ITO coated glass substrates by reactive DC-pulsed sputtering technique with the pure (99.99%) nickel (Ni) target, as shown in Fig. 1. The 170 nm-thick ITO coated glass with the low sheet resistance of 6.2 ohm/square and high visible light transparency of 82% was used. After 130 nm thick Ta_2O_5 film was deposited on NiO /ITO/glass substrate, we injected lithium ions (Li^+) or hydrogen ions (H^+) ions into NiO film (ion storage layer) by applying a voltage of -2.5 V in the electrolyte composed of lithium perchlorate (LiClO_4 , $M_w = 106.39$, Sigma-Aldrich) and propylene carbonate (PC, $\text{C}_4\text{H}_6\text{O}_3$, Sigma-Aldrich) + Deionized water solution, the resulting weight ratio is 1.06:20:5. After the sample Ta_2O_5 / NiO /ITO/glass was cleaned in distilled water and dried, we continued to the WO_3 (160 nm) and ITO (100 nm) layers deposition using reactive magnetron sputtering (Table 1).

3. Results

CAP deposition has been widely utilized in various kinds of thin film due to the excellent characteristics of the arc plasma produced from cathode spots. In CAP process, the macro-particles (MPs) are emitted due to the violent plasma-liquid pool interactions in the cathode spots, and MPs adhering to the prepared films deteriorate the quality of thin films. The infamous macroparticle problem is the main reason why CAP deposition is not broadly used in high-tech application. In general, the plasma (electrons, ions, and neutral particles) tends to plume in the normal direction from the cathode surface toward the anode, and

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