STRUCTURE AND PROPERTIES OF WO_3 THIN FILMS FOR ELECTROCHROMIC DEVICE APPLICATION

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Among transition metal oxides, tungsten trioxide is one of the most interesting materials exhibiting a wide variety of novel properties particularly in thin film form useful for advanced technological applications. It exhibits structural transformations and sub-stoichiometric phase transitions, which attracted the attention of researchers over the past few years to explore their potential scientific and technological applications in the fields of display systems and microelectronics. WO_3 is probably the most widely studied electrochromic material, especially in an amorphous state. Crystalline WO_3 displays a change in optical constants over a wide spectral range in the visible and infrared regions when intercalated with Li^+ or H^+ ions. Tungsten trioxide thin films have been deposited by a number of deposition techniques such as thermal evaporation, electron beam evaporation, chemical vapour deposition and laser deposition. Tungsten trioxide exhibits a cubic perovskite like structure based on the corner sharing of regular octahedra with the oxygen atoms at the corner and the tungsten atoms at the centre of each octahedron. The crystal structure of tungsten trioxide is temperature dependent. It is tetragonal at temperatures above 740 °C, orthorhombic from 330 to 740 °C, monoclinic from 17 to 330 °C, and triclinic from -50 to 17 °C. Tungsten oxide is one of the most promising inorganic materials which exhibit excellent electrochromic, photochromic and gasochromic properties and it has been widely investigated to be used in electrochromic, gasochromic, solar energy, optical modulation, writing–reading–erasing optical devices, flat panel displays, gas, humidity and temperature sensors. In this paper the detailed technological aspects of properties, structures and applications of WO_3 are presented.

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1. Introduction

Tungsten has a rich history dating back to its discovery during the 18th century. Peter Woulfe was the first to recognize a new element in the naturally occurring mineral, wolframite. Tungsten was originally known as wolfram, explaining the choice of "W" for its elemental symbol. Swedish chemist Carl Wilhelm Scheele contributed to its discovery as well with his studies on the mineral scheelite. In 1841, a chemist named Robert Oxland gave the first procedures for preparing tungsten trioxide and sodium tungstate. He was granted patents for his work soon after, and is considered to be the founder of systematic tungsten chemistry.

In the last several decades, many transition metal oxides have been exploited in many challenging fields of information science, nano and microelectronics, computer science, energy, transportation, safety engineering, military technologies, optoelectronic, electrochromic devices etc. Among transition metal oxides, tungsten trioxide (WO_3) is one of the most interesting materials exhibiting a wide variety of novel properties particularly in thin film form useful for advanced technological applications. It exhibits structural transformations and sub-stoichiometric phase transitions, which attracted the attention of researchers over the past few years to explore

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their potential scientific and technological applications in the fields of display systems and microelectronics [1].

Among transition metal oxides, tungsten trioxide is one of the most interesting materials exhibiting a wide variety of novel properties particularly in thin film form useful for advanced technological applications. It exhibits structural transformations and sub-stoichiometric phase transitions, which attracted the attention of researchers over the past few years to explore their potential scientific and technological applications in the fields of display systems and microelectronics. It exhibits electrochromic properties which make it suitable for variable reflection mirrors, dazzle free mirrors in automobiles, variable sun protection system usually called 'smart window' (variable transmittance) and surfaces with tunable emittance of thermal control of satellites. It has been recognized as a significant chromic material that can be coloured through electro, photo, gas, laser and thermochromism processes.

Electrochromic (EC) materials have potential to act as emissivity modulators. WO_3 is probably the most widely studied electrochromic material, especially in an amorphous state. Though less studied, crystalline WO_3displays a change in optical constants over a wide spectral range in the visible and infrared (IR) regions when intercalated with Li^+ or H^+ ions. The peak of the room temperature (RT) blackbody spectrum is at 9.7 mm and 94.5% of radiated power from a blackbody falls between 2 and 40 mm. Hence, for thermal control of a RT satellite, the emissivity modulator should be optimized for operation in this range. Some IR devices have been reported, but are usually used in a fairly limited range in the near infrared (NIR) [2]. Among inorganic materials, tungsten oxides have been most extensively studied. Up until now, amorphous WO_3 films have exhibited the highest coloration efficiency (CE) in the visible region of the electromagnetic spectrum. However, because of their high dissolution rate in acidic electrolyte solutions, these films can only be used in lithium-based electrolytes, resulting in slower response times. Furthermore, extended durability, even in Li^+ systems, has not yet been demonstrated. Inexpensive conducting and redox polymers have attracted increased attention for use as electrochromic materials because of their fast response times and high contrast ratios. However, disadvantages include multiple coloration in the visible spectral range and poor UV stability [3].

WO_3 films can be integrated as promising top layers in efficient multi junction hybrid photo electrode systems, providing an oxide/electrolyte interface where oxygen-evolution reactions take place. In these multi junction hybrid photo electrodes, the oxygen-evolution reaction takes place at the illuminated WO_3/electrolyte interface, whereas hydrogen evolution occurs at the back surface "promoted by a suitable catalyst layer". However, the photo electrochemical response of WO_3 has been scarcely reported when compared to investigations of TiO_2. Therefore, studies directed toward optimization of the photo electrochemical response of the WO_3 films are fertile ground for technical exploration [4].

Nanostructured tungsten oxide materials have received tremendous interest in recent years because of their great potential applications as gas sensors, field emission devices and photo catalysts. Nanostructured tungsten oxide based gas sensors have been used for detecting a variety of gases, such as NO_2, CO, H_2, SO_2, H_2 and NH_3. In particular, nanostructured tungsten oxides like nanorods and nanowires can be used as high sensitive gas sensors, which are unattainable by the conventional materials. Nanostructured tungsten oxide nanorods, nanowires, nanotubes, nanoflakes and nanodisks have been synthesized by using high temperature evaporation, precipitation, hydrothermal reaction, and electrochemical or template assisted methods. However, those mentioned methods have some drawbacks in gas sensing devices fabrication, especially for mass production because they require multiples synthesis processes including of (i) growth of nanowires, (ii) collection of nanowires, (iii) dispersal of the nanowires on solution and (iv) deposition or alignment of nanowires on patterned metal electrodes [5].

The rapid diffusion of atoms in mixed conducting materials is of theoretical interest, as well as practical importance in battery electrode materials, electrochromic display devices, coulometers, etc. Using electrochemical methods to measure chemical diffusion coefficients in mixed conducting electrodes, which, combined with the detailed thermodynamic data derived from equilibrium cell measurement, has considerably simplified the acquisition and interpretation of the kinetics and thermodynamics of the electrochemical insertion of lithium into WO_3 thin films. Since the electrochemical intercalation of lithium is, in general, limited by the lithium ion

diffusion in the oxide electrode, the attention of a previous research was focused on the determination of the chemical diffusion coefficient in the electrode material. The interaction between intercalated ions and oxide lattice or between intercalated ions may greatly influence the lithium ion diffusion through the oxide lattice. The primary observation concerning the kinetics of lithium incorporation into WO_3 thin films is that both diffusion and interface kinetics are important. The following considerations are relevant. Firstly, the thermodynamic and kinetic properties of WO_3 thin films are very dependent on the method preparation, and in particular are dependent on the crystallinity degree of the films. The structure of WO_3 host material plays an important role to the thermodynamics and kinetics of lithium intercalation into the oxide [6].

2. Synthesis

Tungsten (VI) oxide, also known as tungsten trioxide or tungstic anhydride, WO_3, is a chemical compound containing oxygen and the transition metal tungsten. It is obtained as an intermediate in the recovery of tungsten from its minerals. Tungsten ores are treated with alkalis to produce WO_3. Further reaction with carbon or hydrogen gas reduces tungsten trioxide to the pure metal [7].

$$2\ WO_3 + 3\ C + \text{heat} \rightarrow 2\ W + 3\ CO_2$$
$$WO_3 + 3\ H_2 + \text{heat} \rightarrow W + 3\ H_2O$$

Tungsten(VI) oxide occurs naturally in form of hydrates, which include minerals, tungstite$WO_3 \cdot H_2O$, meymacite $WO_3 \cdot H_2O$ and hydrotungstite (of same composition as meymacite, however sometimes written as H_2WO_4). These minerals are rare to very rare secondary tungsten minerals.

Tungsten trioxide can be deposited in thin film form using various deposition techniques and finds their effective use in scientific and technological applications. Tungsten trioxide thin films have been deposited by a number of deposition techniques such as thermal evaporation, electron beam evaporation, chemical vapour deposition and laser deposition. Each deposition technique produced different properties on different substrates in terms of composition, structure and morphology [8, 9]. After Deb´ s discovery [10] of the electrochromism of tungsten oxide, it has been one of the most studied electrochromic materials. The characteristics of WO_3 films make them suitable for EC devices or windows. Depending on the deposition conditions and techniques, films may present considerably different structural, optical and electrical behaviours, and consequently different EC behaviours. The sputtering technique is the most widely investigated and large-scale deposition set available. Sputtered WO_3 films deposited on substrates are known to be amorphous or polycrystalline. Using tungsten targets in direct current (d. c.) magnetron reactive sputtering, thin film properties can be improved by controlling the reactive gas atmosphere.

The electrochromic characteristic is a phenomenon in which a colour of metal changes with electric chemical reactions. They usually use as an electrochromic display and an optical shutter using the phenomenon. WO_3 is well known as a material with the electrochromic properties. Usually, WO_3 thin films as electrochromic display have been prepared on the glass substrates. However, a glass substrate is easily damaged and it cannot be bend. If WO_3 thin film can be prepared on the flexible substrates (PET, PEN etc.), various applications may be performed. Therefore, the technology to prepare at low temperature has been required to prepare WO_3 thin films on the flexible substrates with low heat resistance. We have been prepared the WO_3 thin films using the pulsed laser deposition (PLD) method at low temperature on the flexible substrates. Experimental results suggest that WO_3 thin films deposited by PLD method worked as electrochromic display and they show the high transmittance independent of deposition condition. However, uniformity of the films is not high enough for display panel using PLD method [11].

WO_3 is one of the most widely used EC materials owing to its relatively easy synthesis, strong electrical and optical properties. The general EC phenomena of WO_3 is due to the formation of tungsten bronze (M_xWO_3) according to the following equation,

$$WO_3 + xM^+ + xe^- \rightarrow M_x WO_3$$
(Transparent) (Blue)

where for each atom injected an electron enters the conduction band of the host oxide and a deep blue coloration develops. At the same time, the electronic conductivity of the oxide rapidly increases. Thus it remains until now the most promising; most studied and most applied EC material in EC windows and devices. Due to the previous studies have never investigated the filled volume effect of electrolyte on coloured and bleached rate [12].

ZnO and WO_3 are well-known transition metal-oxide materials that have promising gas-sensing performance, primarily due to their catalytic properties. The combination of these metal oxides with an appropriate proportion is a useful approach to enhance gas-sensing performance. Promising results have been reported from recent studies on WO_3/ZnO films prepared by sol-gel method. Preparation technique can considerably affect the physical, chemical and gas sensing properties of the mixed oxide sensor because these peculiarities rely on the essential surface activity of the layers. One of interesting preparation techniques is Flame Spray Pyrolysis (FSP) that is a cost-effective and versatile process for controlling the production of nanoparticle materials. This process has been demonstrated as one-step, suitable for dry synthesis of high surface area and highly efficient for noble metal laden catalysts. Furthermore, the specific surface area increased with increasing oxidant flow rate leading to a reduction in spray flame length, which resulted in shorter residence time and allowed less time for particle growth. Scaling-up of nanoparticles is one of the FSP advantages [13].

3. Structure

Tungsten trioxide exhibits a cubic perovskite like structure based on the corner sharing of regular octahedra with the oxygen atoms at the corner and the tungsten atoms at the centre of each octahedron. The crystal network is the result of alternating disposition of O and WO_2 planes normally to each main crystallographic direction. Actually, the symmetry of WO_3 is lowered from the ideal ReO_3 structure by two distortions: tilting of WO_6 octahedra and displacement of tungsten from centre of its octahedron. The crystal structure of tungsten trioxide (Fig.1) is temperature dependent [14]. It is tetragonal at temperatures above 740 °C, orthorhombic from 330 to 740 °C, monoclinic from 17 to 330 °C, and triclinic from -50 to 17 °C. The most common structure of WO_3 is monoclinic with space group $P2_1/n$.

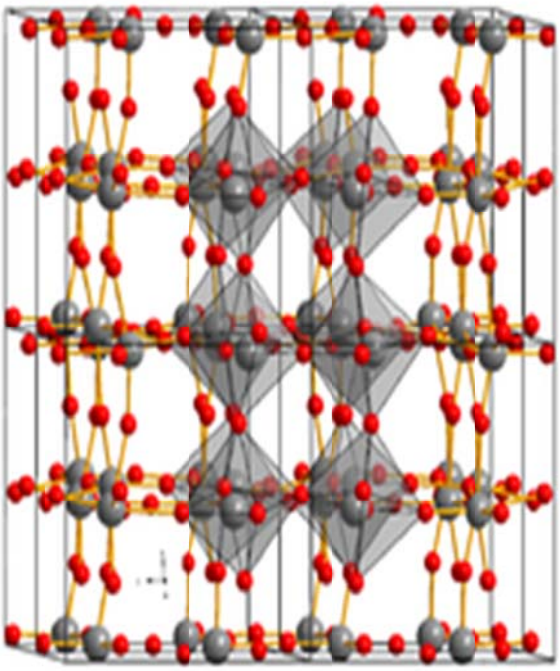

Fig.1. Crystal structure of tungsten trioxide

4. Nanostructured WO_3

Design and controlled growth of semiconductor nanostructures has become a rapidly expanding new field of materials chemistry. Much of this work has focused on optically active II-VI and III-V semiconductors exhibiting quantum confinement effects. In fact, the optical and electrical properties of the latter compounds strongly depend on the size and shape of the corresponding nanoparticles. Accordingly, the prospects of practical application in light-emitting-diodes and in biological labelling rely critically upon control of morphology and size distribution of the semiconductor nanoparticles. On the other hand, studies pertaining to oxide semiconductor nanostructures are mainly aimed at the formation of high surface-area, mesoporous, transparent films in view of their use in solar cells an in the field of photo catalysis [15, 16].

By fabricating EC films from crystalline WO_3 nanoparticles, the state-of-the-art technology of producing EC materials has been profoundly advanced. Crystalline WO_3 nanoparticles have been grown by an economical hot-wire chemical-vapour deposition (HWCVD) process, and a unique electrophoresis technique is employed for the fabrication of porous nanoparticles films. The porosity of the films not only increases the surface area and ion-insertion kinetics, but also reduces the overall material cost, leading to an inexpensive, large-area EC material. Compared to conventional amorphous WO_3 films prepared by vacuum deposition, nanoparticle films deposited by electrophoresis exhibit vastly superior electrochemical-cycling stability in acidic electrolytes, a higher charge density, and comparable CE. This greatly enhanced stability and charge capacity are attributed to the crystalline nanoparticles employed in this work. These initial results will ultimately revolutionize all EC applications. Furthermore, preliminary results show that these advances will impact developing battery technologies [17].

Semiconductor metal oxide nanostructures are highly attractive, so more attention has been paid, because of their obvious optical and electronic applications. Tungsten trioxide is one of the n type indirect wide band gap materials. It is a fundamental functional material having interesting physical properties and wide range of applications. Due to its high work function, it was used as a charge injection layer. Because of its higher catalytic activity, it can be used in photocatalytic and electro catalytic applications. It serves as a good host for ions, so it can be used successfully in electrochemical Li ion batteries, electrochromic, thermochromic and photochromic devices. Many methods have been developed to synthesize 1-D WO_3 nanostructures, such as template assisted growth, anodization, conventional thermal evaporation, hot wall chemical vapour deposition, arc discharge, pulsed laser deposition and hydrothermal method. Among the various methods, hydrothermal method is a facile, dominant tool for the synthesis of anisotropic nanoscale materials. Significant advantages of this method are controllable size, low temperature growth, cost-effectiveness and less complicated. Number of attempts was paid to synthesize controlled WO_3 nanostructures by hydrothermal method with the help of structure-directing chemicals like Na_2SO_4, Rb_2 SO_4, K_2SO_4, Li_2SO_4 and Na_2S [18].

5. Properties

The physical properties of a material are greatly affected by its structural order and morphology. Different preparation methods have their specific advantages in viewpoint of the film quality and production cost of materials for the different applications. Thin films of tungsten oxide have two extreme structural orders like amorphous (α-WO_3) and polycrystalline (c- WO_3). The structural configuration of the WO_3 crystal lattice is the distorted rhenium trioxide (ReO_3) structure. Though the tungsten oxide was known as a promising candidate for electrochromic devices, it was not popular because of the fast developments in the liquid crystal displays (LCDs). Tungsten oxide films are presently used in sunglasses and automotive rear-view mirrors, sun roofs, variable-tinted windows for automotive glass and building windows. Many researchers have built and tested whole electrochromic devices with promising results [19, 20].

The WO_3 film is quite porous and smaller alkali ions can be easily intercalated and deintercalated into it. The density of the films starts to increase significantly up to a deposition temperature of 200 ºC and up to a post annealing of 300 ºC. Moreover, the electrochromic device performance of WO_3 films basically depends on their structural, surface morphological,

compositional and optical properties. It is important that the improvement of materials properties requires a closer inspection of preparation conditions and also the above mentioned properties of the films. In this regard, a large number of techniques for preparing WO_3 films were employed. Out of which the electron beam evaporation technique, one of the physical vapour deposition methods, has been considered largely for the growth of device quality thin films. Indeed, a systematic characterization of the above mentioned properties is of great interest and is necessary to understand the electrochromic properties of the WO_3 films. Fig. 2 shows the crystal structure of monoclinic WO_3 thin film [21, 22].

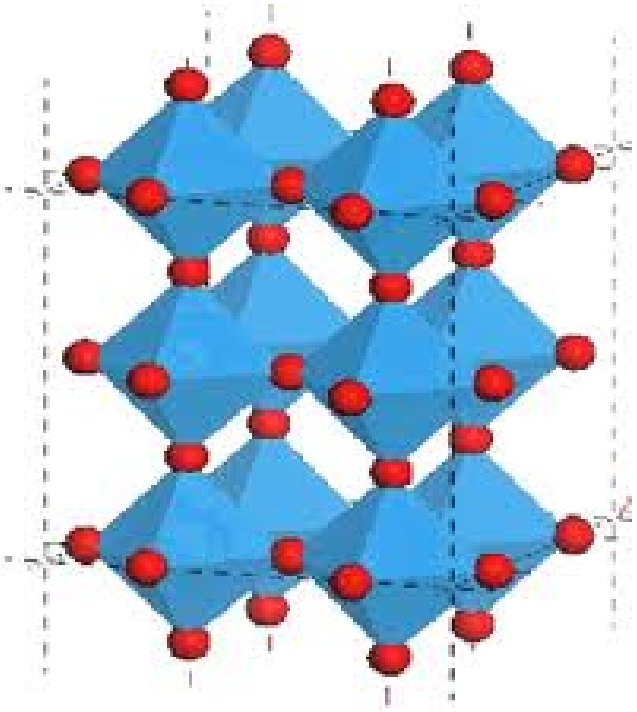

Fig.2. Crystal Structure of monoclinic WO_3

6. Applications

Tungsten trioxide is used for many purposes in everyday life. It is frequently used in industry to manufacture tungstates for x-ray screen phosphors, for fireproofing fabrics and in gas sensors. Due to its rich yellow color, WO_3 is also used as a pigment in ceramics and paints. In recent years, tungsten trioxide has been employed in the production of electro chromic windows, or smart windows. These windows are electrically switchable glass that change light transmission properties with an applied voltage. This allows the user to tint their windows, changing the amount of heat or light passing through [23].

For the improvement of the photo catalytic activity of TiO_2, TiO_2 has been coupled with other semiconductors such as SnO_2 which can induce effective charge separation by trapping photo generated electrons. TiO_2 coupled with other semiconductors has been reported to perform both the abovementioned functions. This has been realized by coupling the WO_3 semiconductor with TiO_2. Because of its band gap (E_g = 2.6 eV to approximately 3.0 eV), WO_3 mainly absorbs in the near ultraviolet and blue regions of the solar spectrum. As a basic function, WO_3 has a suitable conduction band potential to allow the transfer of photo generated electrons from TiO_2 facilitating effective charge separation [24].

Tungsten oxide is one of the most promising inorganic materials which exhibit excellent electrochromic, photochromic and gasochromic properties and it has been widely investigated to be used in electrochromic, gasochromic, solar energy, optical modulation, writing–reading–erasing

optical devices, flat panel displays, gas, humidity and temperature sensors and so forth. It has been known that TiO_2 is an attractive material with excellent photo responsive properties and some researchers have attempted to improve the colouration performance of WO_3 thin-films by doping TiO_2. Most of the studies on WO_3/TiO_2 have been reported on composite thin films (Fig. 3), which can be used in photo electrochromic devices, gas sensors and photo catalysis, etc. However, investigations on nanoarrays of WO_3/TiO_2 composite are still few, due to lack of preparation methods for such materials, particularly WO_3/TiO_2 composite nanotubes. Oxide nanotube arrays of materials containing W and Ti are of great interest for their application in a variety of fields such as photocatalysis, chemical sensors, solar cells and so on [25].

Fig.3. WO_3/TiO_2 Composite film formation

7. Conclusions

Tungsten oxide is one of the most promising inorganic materials which exhibit excellent electrochromic, photochromic and gasochromic properties and it has been widely investigated to be used in electrochromic, gasochromic, solar energy, optical modulation, writing–reading–erasing optical devices. Nanostructured tungsten oxide materials have received tremendous interest in recent years because of their great potential applications as gas sensors, field emission devices and photo catalysts. WO_3 is probably the most widely studied electrochromic material, especially in an amorphous state. Crystalline WO_3displays a change in optical constants over a wide spectral range in the visible and infrared regions when intercalated with Li^+ or H^+ ions. Tungsten trioxide thin films have been deposited by a number of deposition techniques such as thermal evaporation, electron beam evaporation, chemical vapor deposition and laser deposition. The crystal structure of tungsten trioxide is temperature dependent. It is tetragonal at temperatures above 740 °C, orthorhombic from 330 to 740 °C, monoclinic from 17 to 330 °C, and triclinic from -50 to 17 °C. Oxide nanotube arrays of materials containing W and Ti are of great interest for their application in a variety of fields such as photocatalysis, chemical sensors and solar cells.

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