كليه العلوم التطبيقيه
Faculty of Applied Sciences

Smart Windows

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Abstract

Electrochromic devices are critical important in electronic technology, such as smart windows, which have the ability to change the throughput of light, this paper reviews the construction methods of the tungsten oxide (WO_3) electrochromic device, with regard to film deposition, chemical and physical technique and optical properties.

The main goal is to provide information about the different techniques used in manufacturing (WO_3) electrochromic devices.

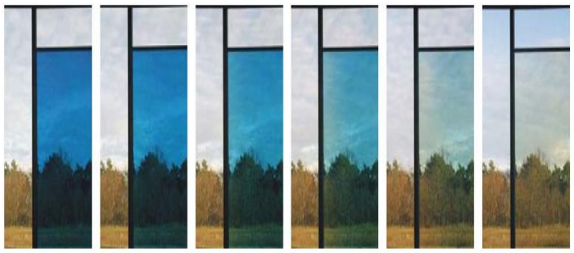
Keywords:
Smart Windows
Electrochromic
Transparent conductor
Electrode
Substrate
Switching time
Response
Electrolyte
Ion reservoir

Contents

1. Introduction

Smart windows have been one of the most important parts of new huge buildings, 98 % of harmful U.V rays can be blocked using smart windows. In smart windows, photovoltaic electrochromic devices are used to change the optical properties of glass through a voltage pulse [1].

In the electrochromic phenomena, an electrochemical redox reaction is used to change the material's optical properties such as the solar factor and the transmission of radiation in the solar spectrum in response to an electric current or to the changing environmental conditions themselves where an example is shown in figure1. The electrochromic devices which used in smart windows have been developed to improve the ratio of contrast, the lifetime and the switching speed. It is expected that electrochromic devices are going to be widely used in sunglasses, warning signs and many other



applications [2].

Figure 1.Switching sequence of an electrochromic laminated glass.

Engineers in all over the world are working to develop smart windows which transparency is controlled as needed in order to use power efficiently. In 1980s, C.Granqvist [3] introduced an optical description of the switchable electrochromic glazing. A group of engineers from Texas state in Aston city made a smart window technology that controls the amount of light passing through it [4].

The most important types of electrochromic devices are

1. Transition metal oxides.
2. Prussian blue.
3. Phalcyanines viologens.
4. Fullerenes.
5. Dyes and conducting polymers[5, 6].

In this paper, we summarized information on the construction of the electrochromic device, its optical properties and the techniques used in making the tungsten oxide (WO_3) layer and analyzed the spectral curves of the (WO_3)Laye.

2. principle of operation

The electrochromic device's principle of operation depends on changing its optical properties by inserting or removing ions from the material in the presence of an electron to preserve charge neutrality.

The electrochromic coating is composed of a multilayer stack and a thin film of tungsten oxide (WO_3) as shown in figure 2[1, 2, 7].

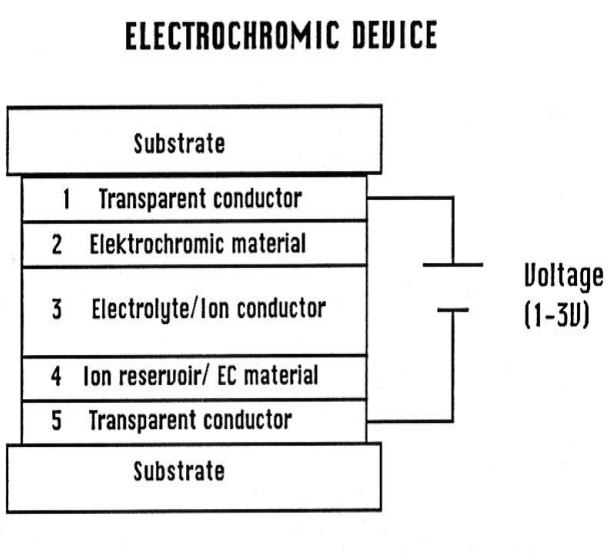


Figure2. The principle set-up of an electrochromic device.

A small bipolar voltage is applied between the two transparent electrodes to force the ions to immigrate to the (WO_3) layers. When a solar photon hits the outer substrate it emits an electron which reaches the (WO_3) film via the transparent conductor.

The ion reacts with the (WO_3) layer and changes it to a colored layer as shown in the following equation

$$xM + xe + WO_3 \leftrightarrow MxWO_3$$

where, M: is an alkali metal or hydrogen

When a voltage is reversed the chemical reaction will stop. The ions go back to the ion survivor, the electrons go back to the substrate and the (WO_3) becomes colorless again [2].

3. The Electrochromic cell

The Electrochromic cell consists of five layers: The Electrochromic layer, two Transparent Conductors coating a substrate within them, an electrolyte and an Ion reservoir [2].

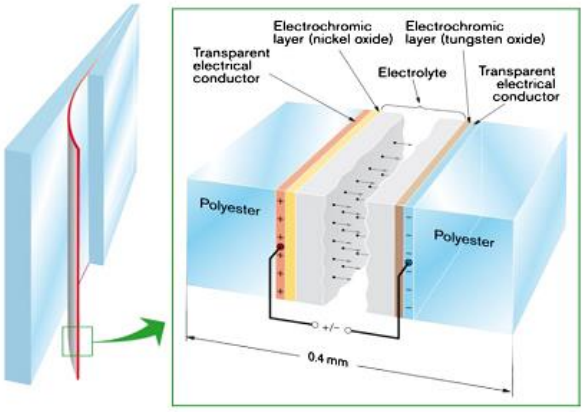


Figure 3 A prototype of the electrochromic cell.

3.1 Electrochromic layer

Switching between oxidized and reduced form is used to change the optical properties of the electrochromic film. Switching speed and durability could be optimized by combining different types of electrochromic and ion conductors, but the most widely used electrochromic layer is the tungsten oxide films and polymers.

Tungsten oxide (WO_3) thin film was the first material in which the electrochromic phenomenon was discovered and still the most promising material till these days, so scientists have written many extensive reviews on (WO_3) films.

In1995 C.Granqvist has written "a case study on tungsten oxide", and in 1999 k.Bange wrote about the coloration of tungsten oxide films and made a model for active coating and it was considered as one of the most comprehensive models[8].

A number of deposition techniques have been used to deposit tungsten oxide thin films, the most widely used techniques are:

1. Chemical vapor deposition.
2. Pulse laser deposition.
3. Electron beam evaporation.
4. Thermal evaporation [9]

3.1.1 Chemical vapor deposition (CVD)

Chemical vapor deposition is used to produce high purity composite materials. A wide range of the periodic table elements have been deposited by (CVD) technique either as elements or as compounds many reviews have covered the development of the (CVD) techniques.

The first one was the classic book by Powelly which covered the work up to1965[9]. Followed by a bibliography by

Hawkins which contain papers in CVD for the 1960-1980 time period [10].

Several books on several applications of CVD were written for example the books that concentrate on silicon applications have been written by Hitchman and Jensen[9]. Books that concentrate on compound semiconductor applications have been written by String fellow and by Jones and books that concentrate on CVD of metals have been written by kodas and Hampden[11].

In CVD technique, a chemical reaction occurs when the gas flows into a chamber that contains an object to be coated. The object surface is deposited by a thin film at a temperature range from 200-1600 C°.

To increase the deposition rate other CVD processes have been used such as using plasma, combustion reaction, photons and filaments or ions.

CVD advantages include:

1. CVD films are conformal (i.e) the films sidewalls thickness make it possible to be applied to sharped pieces.
2. There are a lot of materials which can be deposited.
3. Can be deposited with high purity .
4. high deposition rate .

CVD disadvantages are summarized by the fact that the precursor has to be volatile near room temperature which is non-trivial for some elements in the periodic table but this problem was solved by the use of metal- organic precursors .

The second disadvantage is that CVD precursors can be toxic such as (Ni(Cou)) ,or corrosive such as (Siclu)or explosive such as (B_2H_6)[12].

3.1.2 PLD (pulsed laser deposition)

The use of the PLD technique is reported in the literature since 1965. In 1969, the powders of (SrTio3) and (BaTio3) were used to pulsed laser evaporation.

In 1983, the superconductivity in pulsed laser evaporated (Bapd1-x Bix O_3) was reported by Zaitsev – Zotov and coworker

In 1987, the application of PLD to an in-situ growth of epitaxial high-temperature superconductor films was achieved and considered as a breakthrough for since then PLD has been widely used in high-temperature cuprates and other complex oxides.

In PLD technique, the pulse laser beam removes a material from a solid target and from an energetic plasma plume [13, 14].

3.1.3. Electron beam evaporation

In Electron beam evaporation technique a filament, generate an electron beam which is steered via electric and magnetic fields to hit source material and vaporize it.

As the strived source material is heated the atoms on its surface will have enough energy to leave and this will traverse the vacuum champer at less than (1 ev) thermal energy and could be used in coating the substrate which is put on the evaporating material. The electron beam evaporation sources are

1. Single pocket
2. Rotary pocket
3. Linear pocket [13].

3.1.4 Thermal evaporation

The most widely used technique in the deposition of thin films is thermal evaporation.

In this technique manufacturers use resistive heating to evaporate the tungsten

oxide material in a high vacuum. This reduces the effect of impurities from the residual gas. The films are deposited under 10^{-6} Torr with a thickness range

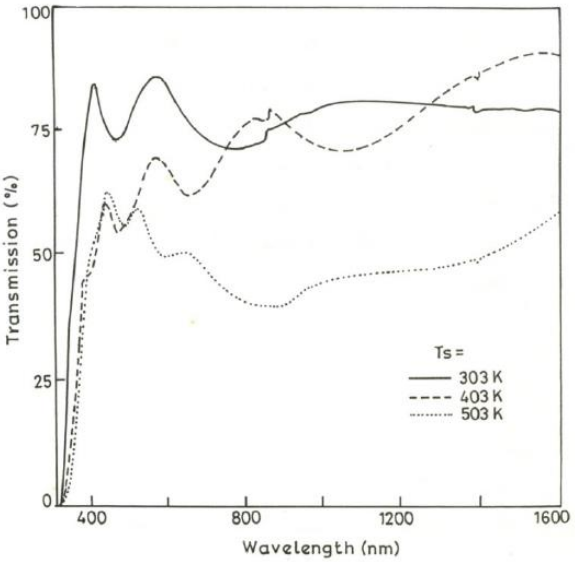


Figure 4 shows the optical transmission spectra of (WO_3)thin films[15].

3.2 Transparent electrical conductors and substrate

In this paper, we will pay attention to indium oxide-based transparent electrical conductors. This type of transparent electrical conductors is the most important one because it is used in many applications such as electrochromic, thin film solar cells, light emitting devices and many other applications.

Many reviews have been done on this field in 2008 Ellmer, k klein studied the use of zinc oxide in a transparent conductor that can be used in electronic devices and discussed the deposition technologies, electronic proportion and optical properties of the zinc oxide (ZNO)[16].

In (2010) Ginley wrote a handbook of transparent conductors and provided some expectation about the flume of this device[17].

In (2012) Ellmer kiein wrote another review about the past achievement and the expected future challenges in the world of transparent electrodes development [18].

In this paper, we will concentrate on transparent conductors that are suitable for a flexible substrate.

3.2.1 Semiconductors - based film

The semiconductors which are used in electrochromic devices must have a wide band gap and must be heavily doped such as In2o3 : Sn , In2o3 : Zn , ZNO : AL …. Etc.

These oxides have low resistivity ~1x $10^{-4}\Omega$cm and high luminous transmittance. If the bending radius of the substrate is less than few centimeters there will be a risk for cracking and delamination and lower electrical conductivity.

The fracture behavior depends on the thickness of the film and the direction of bending.

The disadvantage of this technique is so expensive[16].

3.2.2 Metal based films

The electrical conductivity of metal based transparent conductors is two orders of magnitude higher than that of oxide-based transparent conductors which make it able to make them thin enough so that the luminous absorption is just a few percent.

Metal - based films properties are affected by the peculiarities of thin film growth so through depositing the metal on the substrate, the condensate must pass through a number of growth stages. The thickness of the film is 5-10 nm[19, 20].

3.2.3 Nanowire – based coating and other alternatives

Carbon – based materials are on one of the several alternatives to transparent conductors based on thin films of oxides and metal. Carbon-based materials are either graphite or Graphene layers.

Meshes of metal based nanowires can be prepared and applied to the substrate by electro spraying and brush painting.

The disadvantages of this technique are that diffuse light scattering may occur because of the physical dimensions of the individual nanowires [20].

3.3 Electrolyte layer

During the years, many different types of electrolytes have been used. A thin gold layer is used by Satyenk Deb as a catalyst to produce proton from air humidity and make the Tungsten oxide film becomes colored, but it wasn't so efficient because it depends on the humidity of air which fluctuates when the weather changes [4].

Tungsten oxide films dissolve in water so scientists turned to use hydrous based on other solvents as dimethyl form amid (DMF) and propylene carbonate (pc) An alkali metal salt is used to obtain the Ions needed [5].

4. Discussion and results

For a ($WO3$) electrochromic device the spectral normal transmittance shown in Figure 5, shows that the transmittance falls from about 90% in the bleached state to about 35% in the colored state at 400nm wavelength and the difference in transmittance increases as wavelength increase.

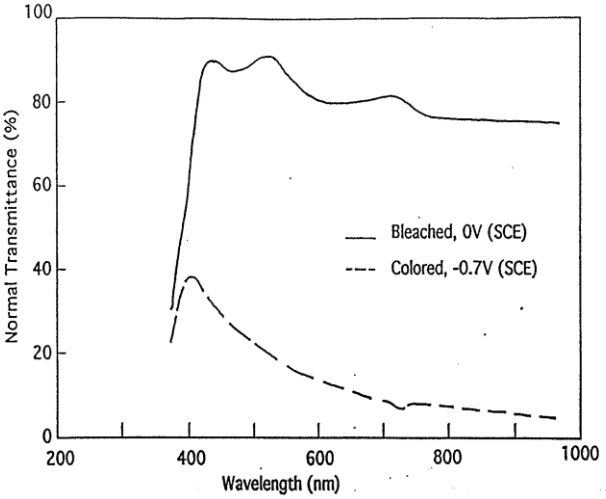


Figure 5. Spectral normal transmittance for an electrochromic WO_3:Mo/TTO/glass electrode in a liquid cell (0.1 M H_2SO_4) in the bleached and colored states. Coloration occurs at a voltage of -0.7 volts vs. S.C.E.

Figure 6 shows the current-voltage characteristic of the WO_3 electrochromic device

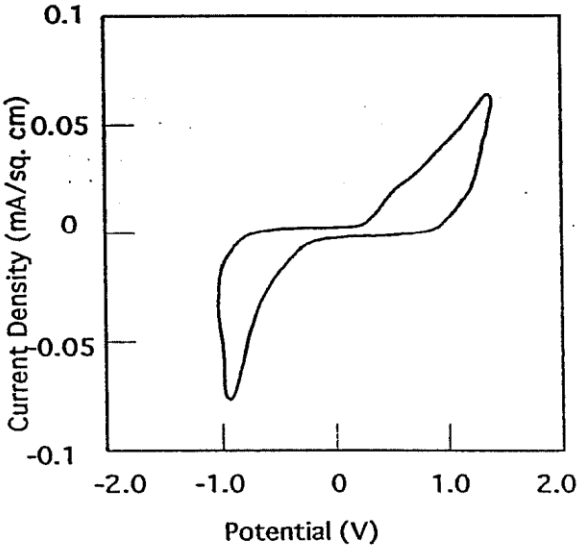


Figure 6 Current-voltage characteristic of an electrochromic device with a WO_3:Mo electrode, a-PEO solid electrolyte, and ion storage later containing the lithium dithiolate salt of 2.5-dimercapto-1,3,4 thiadiazole.

As the voltage reaches -1.3-volt current flows and thus lithium ions Li+ intercalate

into the wo3 layer, and colors it to a deep blue-green rapidly.

At the same time, the dithionate salts which exist in the ion reservoir are oxidized and Li+ ions are released when -1v potential is
Applied a rapid bleaching to the yellow occurs. The switching time for the above process is less than 1 minute [21].

5. Conclusion

The review has discussed the construction of the electrochromic device layers and the various techniques used in making the electrochromic layer and the electrodes to a achieve porosity in order to make bleaching/ coloration dynamic fast.

The review also discussed the advantages of the used techniques in manufacturing the different layers. An electrochromic device is a blend of chemistry and basic physics, thin film science and device technology. If these features are combined with the smart windows, glass facades and intelligent building, we can suppose that electronics will remain as a vital field for endeavors of different kinds for many years in the future.

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