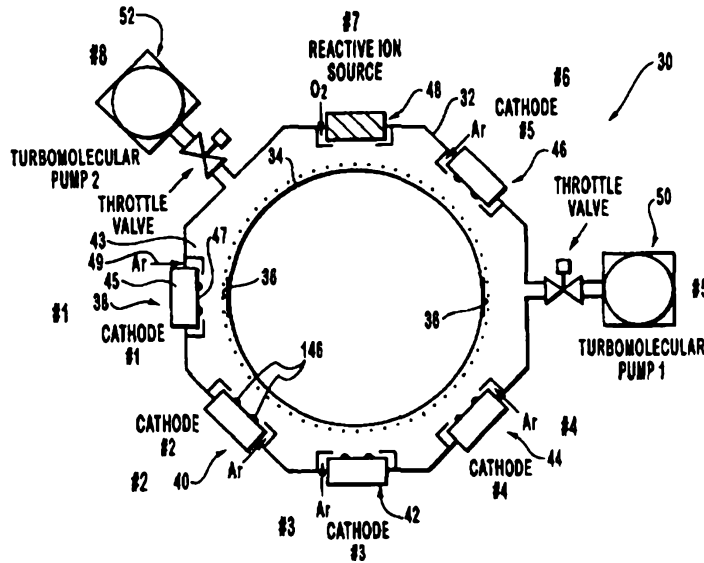




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(54) Title: ELECTROCHROMIC MATERIALS AND DEVICES, AND METHOD



(57) Abstract

A process for manufacturing electrochromic layers/devices at high rates and low deposition temperatures is described. The method utilizes the magnetron enhanced sputtering technique in which a substrate (36) is rotated past sputter cathodes (38, 40, 42, 44, 46) and past a reactive ion source (48) in order to deposit a layered electrochromic device. The process uses high system pressure and large reaction gas flow rates, but relatively low reactive gas partial pressures at the sputter cathodes (38, 40, 42, 44, 46) to reproducibly form electrochromic materials and devices which exhibit excellent optical and physical properties.

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ELECTROCHROMIC MATERIALS AND DEVICES, AND METHOD

1. BACKGROUND OF THE INVENTION

5 **A. Field of the Invention**

The present invention relates to electrochromic and electrochromically active materials and devices and to methods and processes for making such materials and devices.

10 **B. Description of the Related Technology**

Electrochromic or electrochromically active (EC) materials change their refractive index (real and imaginary) as the result of a voltage potential-induced injection (or rejection) of ions induced by the application of an electric potential. Charge neutrality is maintained by a balanced and oppositely directed flow of electrons from the potential source. The change in refractive index results in a change in the transmission and/or the reflection characteristics of the film, often resulting in a visible change of color. So-called anodic and cathodic electrochromic materials/devices color when a positive or negative voltage of appropriate magnitude and duration is applied.

Because ion transfer is required to induce the change in the index of refraction, reversible electrochromic devices contain both a source of ions and a sink. Typically, this necessitates a multiple-material, multi-layer structure comprising electrochromic and ion conductive materials. See for example, Large Area Chromogenics: Materials and Devices for Transmittance Control, Ed. C.M. Lampert and C.G. Granqvist, SPIE 1990. The typical device structure used and the associated electrochemical processes are equivalent to those of a rechargeable battery for which the degree of color is an indication of the state of charge. Consequently, many of the electrochromic materials, fabrication methods and analysis techniques are similar or identical to those used for the manufacture of batteries.

FIGS. 1A and 1B (collectively, FIG. 1) schematically depict key components of two common types of reversible EC devices. Please note, these figures are not to scale. Layer thicknesses are chosen in part for ease of illustration and to help in distinguishing adjacent layers. Furthermore, except as noted, the cross-hatching is selected primarily merely to visually distinguish adjacent layers.

Referring initially to FIG. 1A, there is shown a typical laminated device 1 which incorporates polymer ion conducting material. The laminated device 1 comprises supportive substrates 2 and 8, of material such as glass, at the opposite ends or sides

thereof. Conductor layers 3 and 7 on the interior sides of the substrates apply voltage from source 9 across the EC structure which is positioned therebetween. The EC structure comprises an EC layer 6 next to the conductor layer 7, a so-called ion storage layer 4 next to the conductor layer 3 and polymer ion conducting layer 5 sandwiched between the EC and ion storage layers. Suitable ion conductor polymer materials include proton conducting polymer such as polyAMPS (2-acrylamido-2-methylpropanesulfonic acid), and Li^+ conducting polymer such as PMMA (poly methyl methacrylate) doped with LiClO_4 .

The EC layer 6 is the primary electrochromic layer in that most of the color change occurs within this layer. The ion conducting layer 5 which separates the EC layer and the ion storage layer functions both as an ion conducting layer and an electronic insulator. Ion storage layer 4 functions as a sink and as a source of ions for the primary EC layer 6. In fact, the ion storage layer 4 often is an EC material whose color change augments that of the primary EC layer 6. This can be achieved using an EC layer 6 that colors as the result of the injection of ions and an ion storage layer 4 of different EC material that colors upon the loss of the transported ions.

FIG. 1B schematically illustrates a so-called solid state stack EC device 10. (This device is of the greater interest here, because the components can be formed using the techniques developed for forming optical thin film coatings.) The thin film device 10 comprises a substrate 12 of material such as glass; first conductor layer 13 on the substrate; ion storage layer 14 formed next to the conductor 13; electrochromic layer 16; ion conducting layer 15 between the electrochromic layer and the ion storage layer; second conductor 17; and a substrate 18 formed on the opposite end/side of the device from the substrate 12. As indicated in the figure, one or both the substrates may be used. Voltage source 19 is connected to the conductors 13 and 17 for supplying the required voltage across the EC structure. The arrows (see also FIG. 1A) indicate a typical potential-induced flow of electrons (e^-) and ions (M^+) during coloring. Examples of suitable ion conductor thin film materials include Ta_2O_5 , MgF_2 , LiNbO_3 , etc.

In so-called window (optically transmissive) versions of the devices 1 and 10, both conductors 13 and 17, FIG. 1B (also 3 and 7, FIG. 1A), are transparent layers of material such as tin oxide SnO_2 , indium tin oxide ($\text{In}_2\text{O}_3:\text{Sn}$ or ITO), fluorine-doped tin oxide ($\text{SnO}_2:\text{F}$), aluminum-doped zinc-oxide ($\text{ZnO}:\text{Al}$), etc. In mirror (reflective) devices, one of the transparent conductors 13 or 17 (3 or 7) typically is replaced with a reflective conductor layer, for example, a metal such as aluminum. In both window and mirror devices, the other constituent layers preferably are transparent. Examples of

suitable materials for the electrochromic (electrochromic and ion storage) layers 14 and 16 (4 and 6) include WO_3 , MoO_3 , Nb_2O_5 , V_2O_5 , Cr_2O_3 , TiO_2 , IrO_2 , NiO , Rh_2O_3 , etc.

One suitable construction for device 10 uses a glass substrate; an ITO (indium tin oxide) ion storage layer; a nickel oxide (NiO) ion storage layer; a tantalum pentoxide (Ta_2O_5) ion conducting layer; and a tungsten oxide (WO_3) electrochromic layer.

Several processes are reported to have been used to manufacture electrochromic materials, including the electrochromic components of the exemplary EC devices 1 and/or 10. These processes include sol-gel deposition, electrodeposition, and vacuum deposition techniques such as plasma-enhanced chemical vapor deposition (PECVD), electron beam evaporation, reactive ion plating, and reactive sputtering.

U.S. Patent No. 5,277,986 describes sol gel deposition of the tungsten oxide. Reported advantages include low cost of operation, at least in part because the process can be effected at ambient atmospheric pressures, thus eliminating the time and expensive apparatus required for vacuum processing. However, sol gel deposition requires the use of high temperatures to evaporate and decompose the solvent and organic materials, respectively. As a result, this approach is unsuitable for temperature-sensitive materials such as many plastics and for coating electrochromic layers/devices on plastics.

U.S. Patent No. 4,282,272 describes the use of reactive evaporation for forming on a heated substrate a film of electrochromically active, amorphous WO_3 or of WO_3 containing TiO_2 , Ta_2O_5 , Nb_2O_5 , V_2O_5 , or B_2O_3 . Reactive evaporation has the advantage of high deposition rates, here about $5\text{\AA}/\text{sec.}$, but requires heating the substrate to elevated temperatures ranging from about 250°C to 350°C , which prevents coating electrochromic layers/devices on plastics.

Plasma-enhanced chemical vapor deposition of electrochromic transition metal oxide materials is described in U.S. Patent No. 4,687,560. PECVD has the advantage of being a very high deposition rate process. The '560 patent reports a deposition rate of about $4.75\text{\AA}/\text{sec.}$ for tungsten trioxide, WO_3 using this technique. The '560 patent suggests the PECVD process may be used to coat electrochromic materials on temperature sensitive substrates such as plastics, because of the inherently low substrate heating associated with the process. However, this capability is unlikely. Despite the lack of need of "intentional" heating to deposit electrochromic materials, exothermic reactions often occur in the deposition chamber during PECVD processing, causing substrate heating. Perhaps the primary disadvantage of PECVD is the use of poisonous and corrosive gases such as WF_6 , MoF_6 , and $\text{W}(\text{CO})_6$ whose gaseous byproducts are hazardous and corrosive, and which thus present problems of equipment design and maintenance and are subject to stringent safety regulations.

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