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ABSTRACT

There is currently world-wide interest in developing practical electrochromic smart windows. This is because the use of such windows could have significant impact on making buildings more energy efficient, and therefore could significantly influence the world's economy and international politics. This is especially important since more than 1/3 of the energy consumed in the U.S. is used to control the climate of buildings. The Tufts research program has focused on theoretically and experimentally: identifying, designing, depositing, and evaluating thin film materials as individual layers and in multilayer window device structures. The current window device design is based on electrically varying the reflectivity of an EC (electrochromic) layer in a 5-layer structure: [TC (=ITO)|EC (=c-WO_3)|IC (= a-LNO)|CE (=In_2O_3)|TC (=ITO)]; where TC = transparent conducting layer, ITO = tin-doped indium oxide, c-WO_3 = (poly)crystalline tungsten trioxide, IC = ion conducting layer, a-LNO = amorphous lithium niobate, and CE = counterelectrode layer. (The reflectivity of WO_3 is varied by modulating the free electron density via electron and charge-compensating lithium ion injection or extraction.)

During the past year, since demonstrating the world's first completely solid state electrochromic smart window, the Tufts research team has scaled up the window by approximately 20-fold (from 1 cm^2 to 20 cm^2); and has focused on 3 major technical issues associated with smart windows (and especially with their further scale-up and technology transfer): (i) improve the optical properties; (ii) improve the electrical properties; (iii) and identify and attempt to solve other fundamental scale-up problems.

Based on this past year's investigations, we have drawn the following major conclusions: (1) further improvement in reflection modulation in c-WO_3 films for the EC layer should be attainable; (2) further increase in the electronic resistivity of the IC layer is imperative if successful further scale-up is to be achieved, and it is anticipated that this is attainable; (3) In_2O_3 is a satisfactory optically-passive CE layer; (4) $LiCoO_2$ may have too small an optical band gap to be a useful optically-active CE layer; (5) a replacement for ITO as the TC layers is needed because ITO is permeable to lithium, which can cause irreversible lithium loss, (and it appears that ZnO:Al might be suc a replacement); and (6) ion-beam based deposition techniques, and particularly ion-assisted deposition, appear to be very promising deposition methods for achieving a high degree of control of stoichiometry and structure, could allow for the use of low temperature substrates (e.g., plastics)- [and to date, by using an oxygen ion-assisted deposition techinique the Tufts group has successfully deposited crystalline WO_3 films without intentional substrate heating], and such techniques have the potential of providing economically high deposition rates.

1. INTRODUCTION

There is currently world-wide interest in developing practical electrochromic smart windows. This is because the use of such windows could have significant impact on making buildings more energy efficient, and therefore could significantly influence the world's economy and international politics. This is especially important since more than 1/3 of the energy consumed in the U.S. is used to control the climate of buildings. The Tufts research program has focused on theoretically and experimentally: identifying, designing, depositing, and evaluating thin film materials as individual layers and in multilayer window device structures. The current window device design is based on electrically varying the reflectivity of an EC (electrochromic) layer in a 5-layer structure: [TC (=ITO)|EC (=c-WO_3)|IC (= a-LNO)|CE (=In_2O_3)|TC (=ITO)]; where TC = transparent conducting layer, ITO = tin-doped indium oxide, c-WO_3 = (poly)crystalline tungsten trioxide, IC = ion conducting layer, a-LNO = amorphous lithium niobate, and CE = counterelectrode layer. (The reflectivity of WO_3 is varied by modulating the free electron density via electron and charge-compensating lithium ion injection or extraction.)

During the past year the Tufts research program, "Optics and Materials Research on Controlled Radiant Energy Transfer for Energy Efficient Buildings", (Doe Grant DE-FG03-85SF15927), has continued to address the basic question, "What are the current and ultimate limitations associated with practically fabricating commercially-viable, robust, and high-performance electrochromic smart window glass (smart windows)?"

The basic principles of smart windows are discussed in Appendix A, a reprint of our 1988 Solid State Ionics article, "Thin Film Solid state Ionic Materials for Electrochromic Smart Window Glass." (Please refer to Figure 1 of that article for the basic structure.)

During 1987 and 1988, since demonstrating the world's first competely solid state smart window, and scaling it up from ≈ 1 cm^2 to approximately 20 cm^2 area, we have focused on the following 3 major technical issues associated with smart windows (and especially with their further scale-up and technology transfer):

- Improve the optical properties.
- Improve the electrical properties.
- Identify and attempt to solve other fundamental scale-up problems.

We shall now discuss the research that has been carried out on these 3 issues.

2. IMPROVEMENT OF THE OPTICAL PROPERTIES

The optical characteristics of smart windows are primarily determined by the optical modulation properties of the EC and CE layers and by the near infrared reflectivity of the TC layers. According to the Drude free electron model, the reflectance modulation properties of the EC layer (and an optically active CE layer) are characterized by: E_Γ(eV), the loss parameter; E_p(eV), the plasma energy; and ϵ_b, the bound electron contribution to the dielectric response function. As shown in Appendix B, E_p controls the wavelength position of the reflectance "step"; and the height and transition width (or steepness) of the reflectance step are sensitively dependent upon E_Γ, (a relatively low E_Γ yields a high and steeply rising reflectance step). The TC layers also contribute to the optical properties of the window in that if their E_p is too high, the transparency in the near infrared, and possibly in the visible part of the spectrum, can be reduced (as a result of significant infrared reflectance).

2.1 EC Layer:

Our efforts have been directed towards determining both the "intrinsic" lower bound on E_Γ and towards devising a means to lower it in WO_3 films. To these ends our research efforts have been focused on growing, and determining the optical refelectivity properties of, Li_xWO_3 and Na_yWO_3 single crystals. To determine the "intrinsic" lower bound on E_Γ one strategy has been to measure it in single crystals of M_xWO_3, where M = Li or Na. To date our results indicate that E_Γ is usually lower in single crystals than in most of our films (with one important exception, which we are exploring further); and that it is lower in crystals of Na_xWO_3 ($x \geq 0.5$) than in crystals of Li_yWO_3 ($y \approx 0.2$). [For a single crystal of Na_xWO_3, $x \geq 0.5$, $E_\Gamma \leq 0.2$ eV; but for a single crystal of Li_yWO_3, $y \approx 0.2$, $E_\Gamma \approx 0.7$ eV; and generally we have $E_\Gamma \geq 0.8$ eV for Li_xWO_3 films ($x \approx 0.5$). However, in one film, deposited at temperatures in excess of 430°C, $E_\Gamma \approx 0.5$ eV for $x \approx 0.3$.]

To devise a practical method that would allow one to lower E_Γ in films of WO_3, as well as to develop a practical deposition technique for fabricating larger area, high performance smart windows with layers having highly controlled composition and structure, we have begun an investigation of ion-beam based deposition (IBBD) techniques. The first experiments on ion-assisted deposition (IAD) of WO_3 films has led to the synthesis of

crystalline films deposited with the assistance of an oxygen ion beam and without intentionally heating the substrate (glass). We will discuss this further in a section below.

2.2 CE Layer:

Our efforts have also been directed towards attempting to develop an anodically-coloring CE layer [a complementary (or conjugate) EC layer, (or EC* layer), where the EC layer is a cathodically coloring layer]. In particular, films of lithium cobalt oxide (Li_xCoO_2) have been synthesized, both by rf sputtering and by sol-gel techniques. Some of this work was reported at a meeting of the New England Section of the American Chemical Society (July 1988), an abstract of which is in Appendix C. The development of a CE = EC* layer is attractive because it can enhance the reflectance modulation properties of the smart window, thereby improving the window efficiency, and it can improve the lithium stability of the window. The latter arises because for such materials the minimum energy state is the fully lithiated state. Thus, even if the top TC layer is permeable to lithium (as is ITO, the current TC layer material), the Li ions will naturally migrate towards the CE layer, keeping such ions away from the outer surface, where they could irreversibly react with the atmosphere and therefore be lost. We have demonstrated this by incorporating Li_xCoO_2 into a window device, and it has been operating stably in the atmosphere for more than 6 months.

Unfortunately, it appears that the intrinsic (probably direct) band gap of $LiCoO_2$ is $\leq$2eV. Thus, only very thin films ($\leq$ 500 Å) could be practically utilized in smart windows if one wants high transmission in the visible part of the spectrum when the window is in the clear, or bleached, state; and this would limit the amount of lithium that could be transferred to or from the EC layer. (Note that if $E_\Gamma << 1$ eV in WO_3, then this should not be a problem.)

3. IMPROVEMENT OF THE ELECTRICAL PROPERTIES

Improvement of the electrical properties of the IC and TC layers are currently being investigated. Increasing the electronic resistivity of the IC layer is perhaps the most immediate pressing problem that needs to be solved before further scale-up can be practically achieved.

3.1 IC Layer:

To prevent loss of electrons during and following switching of the windows, [and therefore increase the window switching efficiency and memory, and decrease switching time (which can approach infinity if the

electronic resistivity of the IC layer is too low)], the electronic resistivity of the IC layer needs to be high ($\geq 10^{12}\Omega$-cm for a 1 m^2 window having an IC layer $\approx$ 0.5 µm thick and a memory $\geq$ 24 hours). In addition, to obtain a relatively uniform switching rate, the "transverse" ionic resistance, R_t, of the IC layer should be of the same order as the "lateral" (or "longitudinal") electronic resistance of the TC layer, R_λ. [e.g., for a window of 1 m^2 area, an IC layer thickness of $\approx$ 0.5 µm, a TC layer thickness of $\approx$ 0.2 µm, and electrodes at each edge of the TC layer, to obtain $R_t/R_\lambda \approx 0.2$, the ratio of the TC electronic conductivity to the IC ionic conductivity, $(\sigma_{TC}/\sigma_{IC}) \geq 10^{11}$; and therefore, for $\sigma_{TC} \approx 2\times10^3\ \Omega^{-1}\text{-cm}^{-1}$, $\sigma_{IC} \approx 2\times10^{-8}\ \Omega^{-1}\text{-cm}^{-1}$.]

3.2 <u>TC Layers</u>:

A factor which is important for the window is that the TC layers, and particularly the top TC layer be impermeable to lithium. If the top layer is permeable to lithium and there is no "capping" layer over it, when the window is in its bleaching mode, some lithium can be irreversibly lost at the surface of the top TC layer if it is in contact with an oxidizing atmosphere (e.g., air).

In addition to what has been said above regarding σ_{TC} for building windows, it should be pointed out that, although it is highly desirable to increase σ_{TC} as much as possible, it should not be done by increasing the carrier concentration, but rather the electron mobility. If the carrier concentration is increased there is a consequent increase in the plasma energy of the TC layer which could result in an unwanted permanent infrared reflectance.

Thus our efforts have been focused on developing high mobility, high conductivity, but low E_p ITO films, as well as on developing an alternative material for the TC layer. For the latter we have begun to investigate ZnO:Al (aluminum doped zinc oxide), and it looks promising as regards a TC material that is not permeable to lithium.

Our efforts have been addressing the above matters by investigating alternative materials and materials processing techniques for the IC and TC layers.

3.3 <u>IC Layer Investigations</u>:

Glassy lithium silicates, with and without network modifiers, such as ZrO_2, were investigated by rf sputter deposition over a bi-layer of WO_3 and

ITO. In all cases the resulting films did not have lithium ion conductivity high enough to allow for electrochemical transfer of any measureable lithium to or from the underlying WO_3. This result remains puzzling because others have reported that sputter-deposited films of $Li_2O:SiO_2:ZrO_2$ exhibited room temperature lithium ion conductivity as high as $\approx 10^{-7}$ S/cm [1]. Further work is needed on these silicates, because their electronic resistivity is probably $\geq 10^{12}$ Ω-cm.

We have also begun an investigation of glassy lithium borates. Levasseur et.al. [2] have reported relatively high σ_{Li} at room temperature ($\approx 10^{-6}$ S/cm; and an activation energy $\approx$ 0.5 eV.) for rf sputter deposited films of lithium borate with and without halogen "dopants." Most significant is that they reported the electronic resistivity to be $> 10^{11}$ Ω-cm. Our initial efforts have been with thermally evaporated films which seem to suffer from a considerable built-in strain. Our current work is directed towards developing a capability to fabricate glassy sputter targets of various compositions. Our major concerns and uncertainties are associated with the meaterial's mechanical stability (strain), the reactivity of the materials with the other layers, and the effects of water vapor (at least in a research laboratory environment). However, the above-mentioned report of Levasseur, et.al. on films and reports on bulk lithium borate glasses by Tuller, et.al. indicate that films of the lithium borates hold much promise for the IC layer.

3.4 <u>TC Layer Investigations</u>:

As we have previously reported, (cf. Appendix A), In_2O_3 has an intrinsic structure which should provide for reversible Li insertion. Likewise, ITO is permeable to Li, as we have previously reported [3]. However there is a triple concern with ITO for the TC layers. As mentioned in an earlier section, if Li diffuses through the top layer, it can irreversibly act with an oxidizing atmosphere, leaving the window permanently bleached in the region where the Li was lost. On the other hand, at the bottom TC layer, because the substrate is likely impermeable to lithium, the Li can "pile up" in the bottom TC layer and reach a critical concentration at which Li clusters might form. [This might be occurring when we "over-color" the window (i.e., leave the window in a color excitation state for too long and/or for too high a voltage - e.g.,> 3 Volts), and a "browning occurs, which in some cases appears to be irreversible (i.e., the brown region cannot be bleached, even for bleaching voltages applied for times longer than and for magnitudes larger than that of the original coloring voltage)]. Alternatively, or additionally, "excess lithium" might react irreversibly with the Sn_xO_y in ITO.

The third problem associated with lithium insertion in ITO as the TC layer is that it can lead to a dynamic junction-like effect (whereby a redistribution of Li leads to an n-n^+ type of junction barrier), as we have sometimes observed with ITO as the top TC in our window devices.

To avoid these problems we have begun to investigate films of aluminum-doped zinc oxide (ZnO:Al). The objective of the research is to determine if we could rf sputter deposit ZnO:Al films which have an electronic conductivity, $\sigma_e \geq 2\times10^3$ S/cm, an electron mobility, $\mu_e \geq 20$ cm^2/V-sec., and which are not permeable to lithium. Other researchers [4] have reported being able to sputter deposit ZnO:Al films with conductivities close to our goals; and we conjecture that, because of its intrinsic close-packed wurtzite structure ZnO will probably not be permeable to lithium. One peculiarity associated with sputter-deposited ZnO:Al films is that the highest conductivity films occur when the substrate deposition surface is oriented 90° or 180° from the target surface. This effect is not clearly understood; some investigators attribute it to the fact that less damage probably occurs from bombardment of energetic particles when the deposition surface does not face the target surface. Our initial investigations have confirmed the phenomenon, and we are attempting to understand it further. The results strongly suggest that an ion beam based depostion technique might be valuable for obtaining ZnO:Al films with the desired electrical and optical properties needed for the TC layers.

4. <u>Other Scale-up and Technology Transfer Problems</u>:

Probably the remaining most significant scale-up and technology transfer problem is to develop a deposition process(es) which will provide economical, high performance, large area smart windows. This translates into developing a process which will: (i) provide high deposition rates; (ii) permit low substrate temperatures; and (iii) provide for a high degree of control of the composition and microstructure of trhe deposited films. A high deposition rate is obviously imprtant for economical reasons. A low substrate temperature is desirable for at least 3 reasons: (a) prevent crystallization of the IC layer (which needs to be amorphous to maintain high lithium ion conductivity); (b) avoid building in strain; and (c) alllow for the use of low cost, flexible substrates such as plastic which, in turn, could provide for retrofitting existing building windows. Finally a high degree of control of composition and microstructure is needed to reproducibly obtain desirable properties (e.g., low E_Γ EC layers; high μ_e TC layers; etc.). As described above, under, "Improvement of Optical Properties," we have succeeded in using an oxygen ion assisted deposition technique to deposit crystalline WO_3 films which exhibit good reflectance modulation (≈50%

colored state infrared reflectance), and the deposition was done without intentional heating of the substrate. This is a significant result because it implies that not only might one be able to obtain improved crystallinity for WO_3 films at low temperatures, but also for the other layers; and thus low temperature materials such as plastic could be used as substrates. Additionally, the result suggests that a constant, relatively low temperature could be used for deposition of all the layers, thereby easing the heating-cooling production schedule as well as possibly avoiding a built-in strain. We plan to model IAD and other IBBD processes in order to gain additional insights into the processes; and with additional IBBD equipment we will be able to experimentally investigate using such techniques for depositing the other layers of the smart window.

In addition to the research summarized above, there has been an ongoing effort to improve our analytical capabilities. This includes further development of means to better measure: structure (by X-ray, Raman spectroscopy and infrared spectroscopy techniques); composition [by wet chemical, electrochemical, optical, electro-optical (including Auger analysis), and nuclear techniques (esp. nuclear reaction analysis)]; charge transport properties (by immittance spectroscopy and by diffusion modelling); and optical properties.

5. CONCLUSIONS

As a result of our research during the past year we have identified and are investigating four key problems associated with the further scaleup and technology transfer of smart windows. These problems and the solutions being investigated are:

(a) Increase the reflectance modulation of the EC (and CE=EC*) layer(s) - By decreasing the electron scattering, (E_Γ in the Drude model), for the EC [and optically-active CE (=EC*)] layer(s), very high reflectance modulation is predicted. Our investigations have followed 2 routes - (i) single-crystal growth and characterization studies; and (ii) thin film studies. The results to date suggest the feasibility of obtaining a further significant increase in the reflectance modulation of c-WO_3 films. The results for $LiCoO_2$ as the CE=EC* layer are not yet conclusive; however, it appears that the band gap is too narrow (< 2 eV).

(b) Increase the electronic resistivity of the IC layer - For a 1 m^2 window to have a practically long memory and, of the utmost importance, a practical, finite switching time, the electronic resistivity of the IC layer should be $\geq 10^{12}$ Ω-cm. Two principal approaches that are being investigated are: (i) improve the stoichiometry of a-$LiNbO_3$ films; and (ii) sputter deposit alternative materials such as the lithium borates. Based upon the research reported by others on the lithium borates, we are optimistic that the latter approach will lead to successful results.

(c) Develop a TC layer which is impermeable to lithium, has a low plasma energy, and a high electronic conductivity - It is necessary that the TC layers be impermeable to lithium to presvent the irreversible loss of lithium and the unwanted permanent discoloration of the window. A low plasma energy is needed to prevent a fixed near infrared reflectance, and a high conductivity is needed for switching a large area window in a practical, finite time. We have identified and are investigating ZnO:Al films as a possible alternative to ITO films, and results to date are inconclusive as to whether ot would be a good substitute for, or companion to, ITO.

(d) Develop a deposition process(es) which will: (i) provide high deposition rates; (ii) permit low substrate temperatures; and (iii) provide for a high degree of control of the composition and microstructure of trhe deposited films - Ion beam based deposition (IBBD) techniques have been identified, and results using ion assisted deposition (IAD) of c-WO_3 films suggests the likelihood that such techniques will be practical for fabricating economical and robust smart windows.

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