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ABSTRACT

During 1989 all the proposed milestones have been met. In particular, the research findings lead us to conclude the following:

* There is no intrinsic difference between the near infrared reflectivities of lithium and sodium tungsten bronzes; rather whatever differences are observed are process-related.

* Films of amorphous lithium niobate and hybrids of lithium nibate and lithium aluminum borate having reproducibly high electron resisitivity (> 10^{11} Ohm-cm) and useful lithium ion conductivity (> 5×10^{-9}S/cm) can be be deposited by rf sputtering techniques.

* Lithium can be reversibly inserted into films of indium oxide, at least up to changes in relative molar concentration, $x = [Li]/[In]$, of greater than 0.3, verifying that indium oxide is likely a useful counterelectrode material for smart windows.

* The band gap of lithium cobalt oxide ($LiCoO_2$) is direct and approximately 2 eV. This limits its usefulness as an anodically-coloring counterelectrode layer in smart windows to smart windows which could employ such a counterelectrode layer having a thickness less than approximately 50 nm.

* Barrier layers could improve the electrical properties of smart windows in at least two ways: (a) prevent mobility degradation in the bottom transparent conducting layer arising from sodium ion migration from the underlying soda-lime glass substrate; and (b) prevent lithium ions from being irreversibly lost, either by leaving the window through the top transparent conductor or by reacting with tin in tin-doped indium oxide transparent conductors. It appears that zinc oxide films could be used either as a lithium barrier layer or as a combination lithium barrier layer/transparent conductor.

* Ion-beam-based-deposition processes are promising for solving scale-up problems for smart windows. That is, they could possibly provide a means to deposit smart windows at high rates, with a high degree of control of composition and microstructure, and allow the use of low temperature substrates.

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, environment, and international politics. This is especially important since more than 1/3 of the energy consumed in the United States 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 smart window device structures. The current window device design is based on electrically varying the reflectance of an electrochromic (EC) layer in a 5-layer structure: [TC(= ITO)/EC(=c-WO_3)/IC(=a-LNO)/CE(=In_2O_3) /TC(=ITO or In_2O_3)], 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 reflectance of WO_3 is varied by reversibly modulating the free electron density via electron and charge-compensating lithium ion injection or extraction.

During 1989 the Tufts research program, "Optics and Materials Research on Controlled Radiant Energy Transfer in 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 smart window glass (smart windows)?" In particular, we have continued to focus on the following 3 major technical issues associated with electrochromic smart windows, and especially with their scale-up and technology transfer:

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

We shall now discuss the major accomplishments related to each of these areas, and particularly how we have met the anticipated milestones for 1989.

2. MAJOR ACCOMPLISHMENTS

2.1 Improvement of 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 reflectance 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 the loss parameter, E_{gam} (eV); the plasma energy, E_p (eV); and the bound electron contribution to the dielectric response function, epsilon_b. As we have previously shown [1], E_p controls the wavelength position of the reflectivity "step"; and the height and transition width (or sharpness) of the reflectivity step are sensitively dependent upon E_{gam}. (e.g., a relatively low E_{gam} yields a high and steeply rising reflectivity step).

The TC layers also contribute to the optical properties of the window in that if their E_p is too high, the tranparency in the near infrared, and possibly in the visible portion of the spectrum, can be reduced (as a result of significant infrared reflectance).

2.1.1 EC Layer - As in 1988, our efforts have been directed towards determining both the "intrinsic" lower bound on E_{gam}, and towards devising a means to lower it in WO_3 films. The results for the past year are summarized in Appendix A, (a reprint of an invited paper presented at the Electrochemical Society Meeting at Hollywood, Florida in October 1989). In particular, we have obtained evidence from films and single crystals of the lithium tungsten bronze, Li_xWO_3, and single crystals of the sodium tungsten bronze,Na_xWO_3, that indicates that differences between the near infrared reflectances for the lithium and sodium tungsten bronzes is primarily associated with processing rather than with inherent differences. This reinforces the need to better understand existing deposition processes for films as well as to develop improved, better-controlled deposition processes. Thus, we argue that we have answered, in the negative, one of the important questions that we originally posed, namely, "Is E_{gam} intrinsically lower for the sodium bronze than for the lithium bronze?" That is, the evidence reported in Appendix A indicates that the the near infrared reflectivity for the lithium bronze films could possibly approach or exceed 90%, the value that has been found for crystals of the sodium bronze. Consequently, one of the objectives of our current investigations on deposition processes is to answer the remaining question, "How could one deposit Li_xWO_3 films that would exhibit high (possibly approaching 90%) near infrared reflectivity?" This will be discussed further in section 2.3, regarding research on scale-up issues.

2.1.2 CE Layer - As in 1988, our efforts in 1989 were directed towards attempting to develop an anodically-coloring CE layer (i.e., a complementary EC layer, where the EC layer is a cathodically-coloring layer). In particular we examined further films of lithium cobalt oxide ($LiCo_2$). This research is summarized in Appendix B, (a reprint of an invited paper presented at the Electrochemical Society Meeting at Hollywood, Florida in October 1989). Based on thermopower and optical measurements and their analyses, we have concluded that the band gap of lithium cobalt oxide is direct and is approximately 2 eV. Thus, as we pointed out in the 1988 Annual Report, unless we can significantly reduce E_{gam} in Li_xWO_3 films, lithium cobalt oxide will not be a practical single-layer CE material for smart windows. Again, this provides further impetus to devise means by which one can obtain low E_{gam} for the EC layer.

2.1.3 TC Layers - In order that one be able to obtain TC layers with high electrical conductivity but relatively low plasma energy it is necessary to synthesize the layers so that they have a high electron mobility. One impediment to obtaining a high mobility in ITO deposited at elevated temperatures on soda-lime glass is that sodium can diffuse into the ITO during deposition and substitutionally occupy cation sites. This creates acceptor-like states, thereby creating a double problem: (a) providing recombination, or at least, trapping sites for electrons; and (b) providing extra electron scattering sites. In both cases, the conductivity will decrease from what it might be otherwise; and to increase it requires more free electrons and therefore causing an increase in the plasma energy. Hence we have been exploring the use of thin SiO_2 layers on the glass to act as sodium barriers. This will be discussed further below in section 2.2.2. Likewise, discussed in that section will be our efforts to prevent lithium from diffusing into the top TC layer either during deposition and/or during window operation.

2.2. Improvement of the Electrical/Electrochemical Properties

During 1989 progress has been made regarding improvement of the electrical properties of the IC and TC layers. As in 1988, reproducibly obtaining a high effective electronic resisitivity for the IC layer remained one of the most pressing problems needing solution before further scale-up could be practically attained; and we believe that we are close to its achievement, as will be discussed below. Similarly, for practical large area windows, the TC layers need to have high electronic conductivity (cf. pp. 4-5 of the Sixth Annual Report of Research for a further discussion). We have addressed this problem in two ways: (a) using barrier layers (as mentioned briefly above); and (b) modifying the deposition process so as to obtain high electron mobilities for these layers. Finally, we include under this section the research that we have done on In_2O_3 as a CE layer material. In particular, we have carried out electrochemical experiments on such films - namely cyclical voltammetry and Coulomb titration experiments, together with atomic absorption spectroscopy to determine lithium content. The purpose of this research was to determine how much lithium can be reversibly inserted into differently prepared In_2O_3. We have also begun a collaborative effort with SUNY-Albany (Prof. Wm. Lanford and his graduate student, Carl Shepard), to use nuclear reaction analysis (NRA) [2] to lithium profile our devices (and preliminary results indicate that even in ITO there is a modulation of the lithium concentration with device operation.

2.2.1 IC Layer - To prevent the leakage of electrons between CE andEC layers during and following switching of smart windows, and therefore obtain smart windows with high switching efficiency, long memory times, and short switching times, (which can approach infinity if the electronic resistivity of the IC layer is too low), the effective electronic resisitivity of the IC layer needs to be high (> 10^{12} Ohm-cm for a 1 m^2 window having an IC layer approximately 0.5 micrometers thick and a memory > 24 hours). For similar reasons, and as previously discussed in the 1988 Annual Report (p.5), the lithium ion conductivity for the IC layer should be > 10^{-9} S/cm.

We have carried out two major investigations on the IC layer during 1989: (a) Determine and minimize the causes of non-reproducibility of the electronic resistivity of rf sputter deposited lithium niobate (LNO); and (b) investigate the properties of hybrid IC layers composed of rf sputter-deposited LNO and variously doped lithium borates, and, in particular, lithium aluminum borate (LABO).

The results for LNO alone indicate that rf sputter deposited stoichiometric amorphous,(a),-LNO has a resisitivity > 10^{11} Ohm-cm and a lithium ion conductivity > 10^{-11} S/cm; and that the primary reason for lack of reproducibilty of the electronic resisitivity is due to rf sputter deposition conditions - especially, "dust particles" coming principally from the target.

The results for hybrid layers of LNO and LABO indicate that effective electronic resistivities as high as 10^{15} Ohm-cm can be achieved with such hybrid layers. More research is needed to determine the lithium ion conductivities for these hybrids.

What remains to be solved is how to scale up these layers - i.e., how to devise a process by which the layer stoichimetry is highly controlled, allow for much higher deposition rates than are currently being attained (< 0.1 nm/sec), and still reproducibly obtain high electronic resistivity and high lithium ion conductivity.

We have carried out two other efforts related to obtaining a more fundamental understanding of the IC layer materials: (a) In-situ and ex-situ impedance spectroscopy measurements and analysis; and (b) Raman spectroscopy studies. This is in addition to open circuit voltage decay measurements on device structures. All these are on-going studies.

2.2.2 TC Layers - During 1989, we have carried out three investigations to optimize the performance of the TC layers. We investigated the feasibility of: (a) using ZnO:Al as a TC material; (b) using ZnO as a combination lithium barrier layer and a transparent conductor; and (c) increasing the in situ mobility of the bottom layer ITO (in contact with the substrate).

Our investigations of rf sputter deposited ZnO:Al have led us to conclude that it could be a substitute for ITO, but that it would require more research to obtain high enough mobility and conductivity to replace ITO or undoped In_2O_3.

As a result of a study on the effects of a thin SiO_2 layer on soda-lime glass we conclude that such a layer does appear to prevent Na ions from diffusing into the ITO layer during deposition of the latter. That is, there is negligible degradation in the electron mobility for ITO deposited on such a coated glass substrate, whereas there is a noticeable degradation of mobility for ITO deposited on an uncoated glass substrate.

As a result of similar experiments on the effects of a ZnO layer between ITO and WO_3 we have concluded that such a layer does serve as a barrier to lithium insertion into the bottom

ITO; and we conjecture that such a barrier layer could likewise prevent lithium insertion into the top ITO layer of the smart window.

These three investigations lead us to conclude that: (a) ZnO could be a useful TC layer material, but more research is needed before it is recommended that it be used; (b) ZnO films are useful as barrier layers to prevent unwanted lithium insertions; and (c) a thin (approximately 20 nm) layer of SiO_2 (or equivalent material, such as Si_3N_4) on window glass would serve to preserve the electron mobility of the bottom TC layer, particularly if the latter is ITO. What remains to be done is to incorporate these barrier layers into a complete device.

In addition to investigating the use of barrier layers we have begun to explore the use of alternate deposition processes to obtain higher mobility. These studies are in their initial stages, and we plan to complete them during 1990.

2.2.3 CE Layer - Two parallel materials investigations were carried out on improving the electrical properties of the CE layer: (a) an investigation to determine the maximum reversible lithium concentration modulation for films of the anodically-coloring material, lithium cobalt oxide; and (b) an investigation to determine the maximum reversible lithium concentration modulation for films of In_2O_3 which has a very low (cathodic) coloration efficiency.

2.2.3.1 Lithium Cobalt Oxide - The results of measurements on these films indicates that changes in $x = [Li]/[Co]$ more than 0.3 can be achieved readily. These studies were limited by lack of a good strong oxidizing agent. (Attempts were made to use an oxidizing agent reported by Wizansky et.al. [3] but were unsuccessful.) However, theoretically, and based on results on bulk powder as reported by the Oxford group [4], reversible changes in x from 1 to nearly 0 should be attainable. We are temporarily suspending this research until a significant reduction in E_{gam} can be reached in WO_3 films. [As discussed above, the band gap of lithium cobalt oxide is 2 eV, and unless very thin (< 50 nm) films could be used, the visible transmittance would be too highly attenuated for useful smart windows.]

2.2.3.2 Indium Oxide - To determine the maximum amount of lithium that can be reversibly inserted into films of indium oxide, we have carried out three investigations: (a) cyclical voltammetry; (b) Coulomb titration; and (c) atomic absorption spectroscopy. In particular, the cyclical voltammetry investigations (more than 1000 cycles) indicate that lithium can be reversibly inserted into such films up to a change in the molar ratio, x = [Li]/[In], of at least 0.3. This result confirms what we have previously observed for indium oxide as a counter-electrode in a smart window device which was deep cycled for more than 3000 cycles [5]. It is also in agreement with results reported by Golden and Steele [6] for films of tin-doped indium oxide. Further research is planned to correlate both the maxiumum change in x and the lithium diffusion constant with deposition conditions of the indium oxide films.

2.3 Research on Scale-Up Problems

There are three important issues that need to be addressed regarding scale-up, and they all relate to deposition process research. The three issues are to devise a deposition process which allows one to simultaneously : (a) control the stoichiometry and microstructure of each of the layers (e.g., tungsten trioxide should be highly crystalline, whereas lithium niobate should be amorphous); (b) deposit each layer rapidly (> 2nm/sec); and (c) deposit each layer on to relatively low temperature substrates (including plastics, which would be useful for smart window retrofit applications).

During 1989 we began a research program aimed at investigating ion-beam-based-deposition processes to determine their feasibility to achieve these three demands and therefore provide a practical means to scale-up the smart window. In particular, we have carried out experiments on ion-assisted deposition (IAD) of crystalline tungsten trioxide and of indium oxide.

In Appendix C are copies of 2 articles, summarizing the results of the IAD of tungsten trioxide. What should be noted is that low temperature depositions resulted in a high degree of crystallinity and reflection modulation for the films. We have also carried out succesful IAD on mylar substrates of high quality indium oxide films as well as tungsten trioxide films, thus indicating that ion-beam-based deposition processes are very promising for scaling up smart windows.

3. Summary

In summary, during 1989 we met all the proposed milestones, (which were aimed at further developing economical, high performance smart windows). In particular:

* Optical studies on single crystal of Li_xWO_3 and Na_xWO_3 and on polycrystalline films of Li_xWO_3 indicate that there is no intrinsic difference between the near infrared reflectances of the lithium and sodium tungsten bronzes; rather any observed differences are process-related.

* Oxygen-ion-assisted deposition of WO_3 films on to low temperature substrates (including mylar) indicate that ion-beam-based deposition processes are viable means for obtaining improved quality EC layers, and very likely for also depositing the other layers with improved properties. Therefore, we conclude that such processes could very well be used to scale-up smart windows.

* Use of a sputter-up configuration (substrate above target) and appropriate control of electrical fields has led to the deposition of amorphous lithium niobate films with reproducibly high electronic resisitivity (> 10^{11} Ohm-cm) and usefully high lithium ion conductivity (> $5x10^{-9}$ S/cm).

* Investigations have been made on hybrid combinations of rf-sputter deposited films of amorphous lithium aluminum borate with rf-sputter deposited films of amorphous lithium niobate. These hybrid IC layers have electronic resisitivities as high as 10^{15} Ohm-cm, with lithium ion conductivities exceeding $5x10^{-9}$ S/cm.

* On the basis of cyclical voltammetry (more than 1000 cycles), we conclude that lithium can be reversibly inserted into indium oxide films, at least up to changes in relative lithium molar concentrations, $x = [Li]/[In]$, of approximately 0.3. This supports previous studies on completed window devices using indium oxide as the CE layer (in which there were only negligible changes in the electrical and optical characteristics after deep cycling the window devices for more than 3000 cycles [5]).

* Films of lithium cobalt oxide ($LiCoO_2$) have been prepared which appear to be single phase, but nonstoichiometric (there is a lithium and oxygen deficiency). However, the x-value, ([Li]/[Co]), can be modulated by at least 0.2. The optical band gap for these films appears to be direct, and approximately 2 eV. This latter property limits the utility of lithium cobalt oxide as a CE layer for smart windows. That is, for smart windows which employ tunsten trioxide films that have a Drude loss parameter, E_{gam}, > 0.3 eV, the lithium cobalt oxide layer would have to be thinner than approximately 50 nm, in order that the optical attenuation in the visible part of the spectrum be small enough for practical use. Thus, until tungsten trioxide films having sufficiently low E_{gam} can be developed, we need to use the wider optical band gap indium oxide (In_2O_3) instead of lithium cobalt oxide as a single material counterelectrode layer.

* Investigations of rf-sputter deposited aluminum-doped or undoped zinc oxide films suggest that such films could be fruitfully used to block the transport of lithium ions and yet not appreciably reduce the surface conductance of tin-doped indium oxide (ITO); however, more research is needed to determine if such films could also be used alone as the transparent conductor layer (i.e. replace ITO or undoped indium oxide films).

4. References

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5. Papers Published/Presented During 1989

1) R.B.Goldner, et.al.,"Completely Solid Lithiated Smart Windows," Solar Energy Materials 19, 17(1989).

2) F.O.Arntz, et.al., "Electrochromic Crystalline WO_3 Films Prepared at Ambient Temperature by Ion-Assisted Deposition," Proc. SPIE 1149, (1989).

3) R.B.Goldner, et.al., "Reflectance Modulation with Electrochromic Li_xWO_3 Films," (invited paper), Proc. Electrochemical Society Conference on Electrochromic Materials, Hollywood, Fla (Oct.1989).

4) G.Wei, et.al., "Lithium Cobalt Oxide Thin Film and Its Electrochromism," (invited paper), Proc. Electrochemical Society Conference on Electrochromic Materials, Hollywood, Fla (Oct.1989).

5) F.O.Arntz, et.al., "Near Infrared Reflectance Modulation with Electrochromic Crystalline WO_3 Films Deposited on Ambient Temperature Glass Substrates by an Oxygen Ion-Assisted Technique," to appear in Journal of Applied Physics (Mar.1990).

PROPOSED MILESTONES FOR 1990

- Determine if near infrared reflectances >75% can be achieved routinely with EC layers of polycrystalline lithiated tungsten trioxide.

- Determine if IC layers having electronic resistivities $>10^{11}$ Ohm-cm and lithium ion conductivities $>5\times10^{-9}$ S/cm can be achieved routinely with IC layers based on amorphous lithium niobate.

- Determine if practical CE layers based on indium oxide, can be prepared routinely to exhibit a high degree of reversible lithium ion insertion for more than 10^4 cycles.

- Determine if high performance smart window devices can be fabricated by one or more processes which are practical for scale-up.

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