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**Preparation and Characterization
of Optical Multilayered Coatings
for Smart Windows Applications**

Ph.D. Thesis

Sciences

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Anexo 3

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Preparation and Characterization of Optical Multilayered Coatings for

Smart Windows Applications

Abstract

Multilayer films with a tungsten oxide (WO_3) layer were deposited by reactive dc magnetron sputtering onto glass substrates for electrochromic (EC) applications. The configuration of the smart EC devices (ECDs) or window is ITO (Indium-tin-oxide)/ WO_3 /Li⁺-electrolyte/counter electrode film/ITO. Depending on the choice of different counter electrodes such as SnO_2 , V_2O_5 , ZrO_2 and the doped Mo (or Fe) films, a total of 15 different window structures were fabricated and studied. The multilayer ECD between two pieces of glass exhibited maximum optical transmittance of 84 % and minimum of 16% before and after applying 5 V voltages. The change from bleached to coloured state takes two seconds in visible light range, counter to operation it takes 5 seconds. Without glass substrate the multilayer exhibited a maximum of 97 % transmittance at bleached state.

The discussion of the structural model based on hexagonal WO_3 , in which three- and six-membered rings of octahedra are displayed, exhibits suitable kinetic behaviour of ions insertion / extraction functions. The tunnel size data for transition of ions in different structures of the WO_3 film are deduced and given. A forced intercalation model was proposed to explain some EC phenomenon such as no reversibility, and different κ_d (diffusion constant) to a normal κ_d value. A simulation model of ECDs for charge injection was developed. A differential equation was hypothesized and discussed. The model was analyzed for a particular case in the coloration state of the EC devices.

The influence of the deposition conditions and Mo (or Fe) doping concentration on the microstructure and the properties of the films (ITO, WO_3 , SnO_2 , V_2O_5 and ZrO_2) were systematically studied. Suitable conditions for deposition of the films were obtained by changing the following parameters: (i) ratio of O_2 /(Ar + O_2) pressure (P_{O_2} : 0%~80%); (ii) bias voltage (-100~+100 V); (iii) substrate temperature (RT-400 °C); (iv) sputtering power (50~120W); (v) distance between target and substrate (40~70mm) and (vi) post annealing (80-700 °C) in vacuum and air atmosphere. Room temperature (RT) and other temperature depositions of the films were also studied and implemented for possible application. This was done because many materials, such as the electrolyte, do not sustain higher temperature processes in functional multilayer films as well the possibility to deposit on polymeric substrate. V_2O_5 films for ECDs, but also for thermochromic (TC) and thermotropic (TT) applications were proposed and investigated. It can be concluded that V_2O_5 films doped with and without the optimum amount of Mo are potential candidates for advanced TC, TT and EC devices.

The deposited films were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray (EDX), scanning electron microscopy (SEM) and atomic force microscopy (AFM). The films were analyzed in the range of mid infrared (IR), near IR, and visible-ultraviolet (Vis-UV) spectral regions. The transmission, absorption, and reflection spectrum techniques were used to analyse the films. We obtained structural information on the WO_3 , V_2O_5 and their Mo doped films by IR and Raman spectroscopy. Since

glass substrate of EC device has a limited IR transmission range of 2000-4000 cm^{-1} in practical applications, we present a study of the films (WO_3 , V_2O_5 , etc.) by IR reflective absorption spectra using near grazing incidence angle technique. It was found that Raman together with IR spectroscopy is a powerful technique that enables to distinguish the phase and structure of these inorganic thin films.

The roughness (δ) of the film surface is an important parameter, especially for charge transfer in thin film and multilayer material. The roughness was investigated by the following methods: total integrated scattering (TIS); Laser integral micro-topography (LIMT); SEM; AFM; and AFM statistical analysis. The TIS equation is $\text{TIS} = \text{DR}/(\text{DR} + \text{SR})$, in which DR is diffuse reflectance and SR is specular reflectance. The LIMT inspection was used to map a multilayer and its cross section. The two pre-treatment processes before measurement were proposed. From the processes we can obtain the clear micro-photographs of the films. The resulting values of δ and cross section of the film using TIS and LIMT methods are consistent with AFM and SEM respectively. The average δ values of the different films produced are in the range from 3.5 nm to 20 nm.

One important layer for the EC system is the transparent electrodes. Generally it is a transparent conducting oxide (TCO) and in this study ITO layers were selected as the TCO. The prepared transparent and conductive ITO films yield the lowest sheet resistance (R_s) 26.5 $\Omega/\text{Sq.}$ and highest transmission 94% at low P_{O_2} (10%). The equations of the dielectric function and photon energy were derived by using a physical model (Drude theory, Section 5.3). The refractive index (n), the extinction coefficient (κ) and energy band gap (E_g) were derived and calculated from the measured spectra under hypothesized physical models such as Swanepoel model (Section 3.6), scattering model (Section 5.2), direct transition semiconductor model (Section 3.7). The expression and calculation of electric charge density (n_c) and carrier mobility (μ) from optical measurements are given. The micro electrical characterization parameter n_c and μ were investigated by experimental measurements and by theoretical calculation using Mathematica-4.1 software. Both measured and calculated values are in agreement in magnitude. The ITO films which exhibit high optical transmittance and conductivity are suitable for many technological applications. Depending on the requirements of the application, both amorphous and polycrystalline ITO film could be obtained by controlling the sputtering deposition conditions.

The bi-layer CdS/ITO films were also deposited using physical and chemical methods. The CdS was grown using the ultrasonic colloid deposition (USCD) method. The USCD technique has been proposed to produce bar-shaped ultra fine particle films of cadmium sulfide via a simple, low cost process. The CdS/ITO film is a promising system to produce high efficiency photovoltaic (PV) solar cells. These bi-layer and the other studied films have potential application in ECDs and integrated PV self-powered EC windows. This thesis also provides a preparation and characterization data and references for both research and industrial production.

Preparação e Caracterização de Revestimentos Ópticos Multicamada para Aplicações em Janelas Inteligentes

Resumo

Revestimentos multicamada à base de óxido de tungstênio (WO_3) foram depositados por pulverização DC reactiva em magnetron sobre substratos de vidro para aplicações electrocrómicas (EC). A configuração das nossas janelas inteligentes é de forma ITO/ WO_3 / Li^+ -electrólito/eléctrodo contrário/ITO. No total foram fabricadas e estudadas 15 estruturas diferentes dependendo da escolha dos eléctrodos contrários depositados (SnO_2 , V_2O_5 , ZrO_2) e da quantidade de dopante (Mo ou Fe) utilizada nesses revestimentos. A estrutura multicamada aplicada entre dois vidros exibe uma transmitância óptica máxima de 84% e mínima de 16% na região visível do espectro electromagnético, antes e após a aplicação de um potencial de 5V (ou em estado de descoloração e cor). Estas estruturas multicamada apresentam uma transmitância de 97 % sem o efeito do substrato e quando não têm potencial aplicado.

Foi discutida a formação do modelo estrutural baseado na estrutura hexagonal WO_3 , em que três e seis células unitárias se ligam em forma de anel, exibindo um comportamento cinético apropriado para a função de inserção e/ou extracção de iões. As dimensões dos túneis de transmissão de iões nas diferentes estruturas dos filmes de WO_3 são deduzidas e apresentadas. O modelo da interligação forçado foi proposto. O modelo pode explicar o fenómeno da EC tal como a não reversibilidade e dá um efeito forte para a constante de difusão normal κ_d . Foi também desenvolvido um modelo de simulação para a carga e descarga nos revestimentos EC. Equações diferenciais da física matemática são desenvolvidas e discutidas. A aplicação do modelo a estruturas de EC para o estado colorido é apresentada para um caso particular.

A influência dos parâmetros de deposição bem como a concentração dos materiais dopantes (Mo ou Fe) na microestrutura e propriedades dos filmes (ITO, WO_3 , SnO_2 , V_2O_5 and ZrO_2) foi sistematicamente estudada. As condições optimizadas para a deposição dos filmes foram encontradas variando os seguintes parâmetros: (i) A razão de pressões $\text{O}_2/(\text{Ar}+\text{O}_2)$, (P_{O_2} : 0~80%), (ii) Polarização Bias (-100~+100v), (iii) Temperatura do substrato, (iv) Potência de deposição (50~120 W), (v) Distância entre o substrato e o alvo (40~70mm), (vi) Temperatura de recozimento (80-700°) ao ar e em vácuo. Os filmes estudados e obtidos para aplicações práticas foram depositados à temperatura ambiente e a baixas temperaturas (inferiores a 200°C). A deposição a estas temperaturas deve-se ao facto de alguns dos materiais utilizados como é o caso do electrólito não suportarem temperaturas elevadas assim como a possibilidade de deposição sobre substratos poliméricos.

Foram também propostos e estudados, os revestimentos de V_2O_5 para aplicações termocrómicas (TC) e termotrópicas (TT). Deste estudo pôde concluir-se que os filmes de V_2O_5 dopados com e sem a quantidade desejada de Mo são potenciais candidatos para este tipo de aplicações e também para aplicações em estruturas EC avançadas.

Os filmes produzidos foram caracterizados por Difracção de Raios-X (XRD), Espectroscopia de Fotoelectrões de Raios-X (XPS), Microanálise de Raios-X por Dispersão de Energias (EDX), Microscopia Electrónica de Varrimento (SEM) e Microscopia de Força Atómica (AFM). Foram também analisados por espectrofotometria Raman de onde se obtiveram para estudo espectros de transmissão, absorção e reflexão na gama que vai desde o ultravioleta à região do infravermelho próximo do espectro electromagnético.

Foi ainda obtida informação estrutural dos filmes de WO_3 , e V_2O_5 simples e dopados com Mo por Espectroscopia de Infra-Vermelho (IR) e Raman. Dado que em aplicações práticas o WO_3 deve ser depositado em vidros normais para janelas inteligentes e estes vidros devem ter uma área de transmissão limitada de $2000\text{-}4000\text{ cm}^{-1}$ no infravermelho, apresentam-se estudos de filmes por espectros de absorção reflectiva de infravermelho usando ângulos incidentes rasantes. Foi demonstrado que as técnicas Raman e Espectroscopia de IR são poderosas para a distinção de fases e estruturas de filmes finos inorgânicos.

A rugosidade superficial (δ) dos revestimentos é um parâmetro importante para o estudo das multicamadas e em especial da transferência de carga. A rugosidade foi estudada pelos seguintes métodos: Dispersão Total Integrada (TIS ou cálculo espectral), Microtopografia Laser Total Integrada (LIMT), SEM e AFM (análise estatística). A equação TIS é deduzida como $\text{TIS} = \text{DR}/(\text{DR}+\text{SR})$, onde DR é a reflectividade difusa e SR é a especular. A inspeção de LIMT foi utilizada para avaliar a multicamada em secção transversal transparente. Dois processos de pré-tratamento antes da medida foram propostos (secção 9.4.5). Destes processos, nós podemos obter imagens topográficas das camadas. Os resultados da inspeção superficial obtidos pelos métodos TIS e LIMT estão em concordância com os obtidos por AFM e SEM, respectivamente. Os valores médios de rugosidade variam entre 3.5 nm e 20 nm.

Uma camada importante para o sistema do EC é o eléctrodo transparente. Geralmente é um óxido condutor transparente (TCO) e neste estudo as ITO camadas foram seleccionadas como o TCO. Os revestimentos transparentes e condutores preparados, de óxido de índio-estanho (ITO), apresentam a mais baixa resistência (R_s), cerca de 26.5 Ohm/Square e a mais elevada transmissão (94%) a baixa PO_2 (10%). As equações sobre a função dieléctrica e foto energia foram derivadas por um modelo físico baseado na teoria de Drude (secção 5.3). O índice de refração (n), o coeficiente de extinção (k) e a banda de energia (E_g) foram calculados a partir dos espectros medidos segundo modelos físicos hipotéticos tais como o modelo de Swanepoel (secção 3,6), o modelo de dispersão (secção 5,2), modelo directo do semiconductor da transição (secção 3,7). A expressão e cálculo da concentração de carga eléctrica (n_c) e a sua mobilidade (μ) foram obtidos a partir dos parâmetros ópticos. As características micro eléctricas n_c e μ foram determinadas por medidas experimentais e cálculos teóricos usando o software Mathematica-4.1, sendo os valores obtidos coincidente em ambos os casos na amplitude. Os filmes de ITO que exibem elevada transmitância e condutividade servem para muitas aplicações. Dependendo da necessidade de aplicação (película amorfa ou policristalina), o ITO foi obtido em filme controlando as condições de deposição.

Os filmes bicamada de CDS/ITO foram depositados em substratos de vidro e de quartzo usando em conjunto métodos físicos e químicos. O filme de CDS foi produzido através de deposição ultra sónica coloidal (USCD) mergulhando e retirando os substratos na solução. A técnica de USCD é uma boa técnica para produzir filmes ultra-finos de sulfeto de cádmio a baixo custo. Os filmes de CDS/ITO são filmes promissores para aplicações em células solares foto voltaicas (PV) de elevada eficiência. Estes revestimentos em bicamada, bem como todos os filmes referidos, poderão ser aplicados em ECDs e em janelas EC com integração PV (janelas EC auto-alimentadas). Estes estudos de preparação e caracterização de filmes fornecem informação e referências detalhadas tanto para a produção industrial como para futuro trabalho de pesquisa.

PUBLICATIONS RESULTED FROM THIS THESIS WORK

1. Journal Articles - Papers in international scientific periodicals with referees

- 1.1 **Hai Ning Cui**, V. Teixeira, L. J. Meng and H. J. Zhang, "Studies on microstructure bilayer film of ultrasonic Dipped cadmium sulfide and d.c. sputtered indium tin oxide", *Thin Solid Films* (Elsevier Science Limited), 447/448(2004)663-668.
- 1.2 **Hai-Ning Cui**, Shu Jia, L J Meng, V. Teixeira, X-ray Analysis of Multi-film for Electrochromic Device Application, *Microchimica Acta* (Publisher: Springer Verlag Wien, Vol. 145 (2004)19-23.
- 1.3 **Hai-Ning Cui**, V. Teixeira, A. Monteiro, E. Fortunato, R. Martins, E. Bertran, Physical Properties of Sputtered ITO and WO₃ Thin Films, *Advanced Materials Forum II*, Volume 455&456 (Trans Tech Publications Ltd, Switzerland, ISBN:0-87849-941-5, (2004) PP7-11.
- 1.4 **H. N. Cui**, M. F. Costa, V. Teixeira, I. Porqueras, E. Bertran, Electrochromic coatings for smart windows, *Surface Science*, Vol. 532(2003) 1127-1131.
- 1.5 **Hai Ning Cui**, V. Teixeira, A. Monteiro, "Microstructure study of indium tin oxide thin films by optical methods", *Vacuum*, 67(2002) 589-594.
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2. Chapters in Books

- 2.1 Li-jian Meng, R. Silva, **Hai Ning Cui**, V. Teixeira and M. P. Sos Santos, "Residual stress effects on Raman spectra of RuO₂ thin films", *Materials Science Forum Vols. 490-491* (2005) pp. 583-588, Trans Tech Publications, Switzerland, online at <http://www.scientific.net>.
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- 2.3 **Hai Ning Cui**, V. Teixeira, "Study of Low Temperature Annealing of DC Sputtered ITO Films by

Optical Methods”, Mechanics and Material Engineering for Science and Experiments, Edited by Y. Zhou, Y. Gu, Z.Li, Science Press New York Ltd (New York, USA), (2001) 292-295.

3. Conference Proceedings

- 3.1. V. Teixeira, **Hai Ning Cui**, E. Fortunato, R. Martins, E Bertran, “Characterization of Magnetron Sputtered ITO and WO₃ Films for Transparent Smart Devices”, 47th Annual Technical Conference Proceedings, ISSN 0737-5921, Published by Society of Vacuum Coaters (SVC), Dallas, Texas, USA, April 24 –29 (2004), www.svc.org.
- 3.1 **H. N. Cui**, Manuel F. Costa, Vasco M. Teixeira, I. Porqueras, E. Bertran, Electrochromic tungsten oxide multilayer thin films for use in smart windows, Proceedings of SPIE Volume: 4829, 19th Congress of the International Commission for Optics: Optics for the Quality of Life, Editor(s): Giancarlo C. Righini, Anna Consortini (Publication Date: Nov 2003; 1234 pages; p.522).
- 3.2 **H. N. Cui**, V. Teixeira, M. F. Costa, E. Fortunato, R. Martins, Influence of substrate temperature on the properties of DC-sputtered ITO films for electrochromic applications, in Advanced Coatings on Glass & Plastics for Large-Area or High-Volume Products, ed. C.P. Klages, H.J. Gläser, M. A. Aegerter, Braunschweig, Germany, p. 693-695, 2002.
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List of Symbols and Abbreviations

AFM:	atomic force microscopy
ATR:	attenuated total reflection
a.u.:	arbitrary units, or Arb.
CBD:	Chemical bath deposition
CE:	counter electrode
d:	thickness of film
d_e :	thickness got by fitting of ellipsometric parameter
D:	relative density
DR:	diffuse reflectance
D_T :	turning point of relative density
EDX:	energy dispersion of x-ray
EC:	electrochromic
ECDs:	electrochromic devices
E_g :	energy band gap
Eq.:	equation
Fig. :	figure
FWHM:	full width half maximum
GIXD:	graze incidence X-ray diffraction
IR:	infrared
IRE:	internal reflection element
ITO:	In_2O_3 and 1.0 wt % SnO_2 -doped
IS:	ion storage
LIMIT:	Laser integral microtopographic
MeO_6 :	Me=metal; O=oxygen
m- WO_3 :	monoclinic WO_3
Min.:	minute
n:	refractive index
n_c :	carrier concentration
NGIA:	near graze incidence angle
NIR:	near infrared
PC:	photochromic
PVD:	Physical vapour deposition
P_{Ar} :	argon partial pressure
P_{O_2} :	(ratio of) oxygen partial pressure
P_T :	total pressure of sputtering
rms:	root-mean-square = S_q
RT:	room temperature
R_a :	mean roughness
R_{2p} :	resistance of two points
R_s :	sheet resistance
Samp.:	sample
SEM:	scanning electron microscope
SR:	specular reflectance
S_q :	rms

T:	temperature
TC:	thermochromic
TCOs:	transparent conducting oxides
TIS:	total integrated scattering
T _a :	annealing temperature.
T _c :	critical temperature.
T _l :	transmission of light
T _M :	the maximum transmittance of the envelope of interference
T _m :	the minimum transmittance of the envelope of interference
T _{mp} :	melting point of material temperature
T _{max} :	maximum transmittance of spectrum
T _{min} :	minimum transmittance of spectrum
T _{ts} :	transmittance of spectrum
T _s :	substrate temperature
TT:	thermotropic
T _d :	deposition time of the film
T _{pa} :	post annealing temperature
Tα:	the interference-free transmission, $T\alpha = (T_M / T_m)^{1/2}$
UFP	ultrafine particle
USCD:	ultrasonic colloid deposition
UV:	ultraviolet
U _{bias} :	a bias potential
Vis:	visible
XPS:	x-ray photoelectron spectroscopy
XRD:	x-ray diffraction
α-WO ₃ :	amorphous WO ₃
α _a :	absorption of light
α _e :	extinction loss
α _s :	scattering coefficient
δ:	surface roughness
δ':	spin-orbit splitting constant
δ ⁰ :	in-plane bending vibrations
γ:	out-of plane wagging
v:	stretching vibrations
v _a :	anti symmetric stretching vibrations
v _s :	symmetric stretching vibrations
Φ _{max} :	Figure of Merit, $\Phi_{max} = T_{max}/R_s$
κ:	extinction coefficient

κ_d : diffusion constant (or coefficient) of ions
 μ : carrier (or Hall) mobility
 ρ : resistivity
 Ω/\square : ohm/square or Ω/sq .

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