Characterization of Electrochromic Devices by Spectroscopic Ellipsometry

Céline Eypert - Application Scientist - Thin Film Division

Compounds that change colour visibly and reversibly when subjected to a change in their environment (heat, light, pressure) are known as chromogenic materials. There are four major categories: electrochromic, thermochromic, photochromic and piezochromic. The change in optical properties can be in the form of absorption, reflectance, or scattering. The change can be either in the visible or beyond the visible spectrum.

Electrochromic (EC) materials have been finding several applications in smart windows, anti-dazzling rear view mirrors, switchable motorcycle helmet, for contrast enhancement in some emissive display devices and in non-emissive large area colour displays for information advertisement.

The study of EC materials is an interdisciplinary field. In an electrochemical cell of EC devices the discharged positive ions are free to diffuse into a thin solid film (electrode) of the host material, modifying its electronic structure to create a coloured material. There are two major classes of materials, ion-insertion/extraction type such as tungsten trioxide, and non-insertion groups such as the viologens.

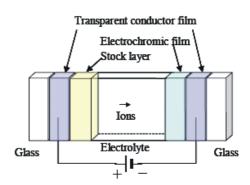
Tungsten trioxide WO₃ is commonly used as it is one of the best choices for the primary working electrode material for EC devices. It provides high charge capacity and has long-term cyclability. It goes blue in insertion of Li or other metals, hydrogen and guest atoms. Viologens are a family of halides of quaternary bases that change from clear to bluish purple.

The refractive index (n), extinction coefficient (k), and thickness (d) are important parameters for predicting the performance of a film in an optical system. These optical parameters are also sensitive to the microstructure, and are often affected by the deposition conditions and doping materials. Spectroscopic ellipsometry is the ideal technique to measure these parameters simultaneously, very accurately and non

Basic Electrochromic Film Device Structures

destructively for the samples under study.

A micrometre-thick multilayer structure contains two transparent electrical conduction layers and two electrodes capable of charge (ion) insertion/extraction. One of the electrode must be electrochromic; and it usually consists of tungsten oxide. The other electrode can either be a complementary colouring EC material or a material that remains transparent upon charge insertion (stock layer or ion storage layer). Examples of ion storage materials are Nb₂O₅, V₂O₅, NiO, IrO₂.



Experimental

Ellipsometric data were collected at an angle of incidence of 70° using the UVISEL NIR (260-2100nm). The full electro-chromic device characterization was successfully carried out by spectroscopic ellipsometry in the spectral range 1-4 eV (1240-310 nm).

For multilayer samples it is always helpful and often necessary to characterize the structure step by step.

The combination of phase modulation technology of the UVI-SEL and the advanced data analysis features included in the DeltaPsi2 software allows very high accuracy for thin film measurements on transparent substrates.

Characterization of Glass/ITO/WO_x device

The following structure has been used to model the sample. The introduction of a very thin interface between the two layers of WO_x and ITO significantly improves the goodness of fit parameter ($\chi^2=9.11\Rightarrow 2.86$). This interface is richer in tungsten and is described by a mixture of 35.5% W + 64.5% WO_x using the effective medium approximation.

Roughness	74 Å
WO _x	2999 Å
35.5% W + 64.5% WO _x interface	22 Å
ITO	1732 Å
Glass substrate	

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Characterization of Glass/ITO/TiVO_x device

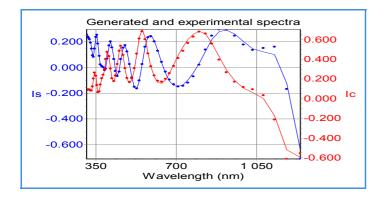
Roughness	44 Å
TiVO _x	977 Å
ITO	1643 Å
Glass substrate	

Characterization of Glass/ITO/TiVO_x/Ta₂O₅ device

Ta ₂ O ₅	596 Å
TiVO _x	977 Å
ITO	1643 Å
Glass substrate	

Characterization of Glass/ITO/TiVO $_{\rm x}$ /Ta $_{\rm 2}$ O $_{\rm 5}$ /WO $_{\rm x}$ device

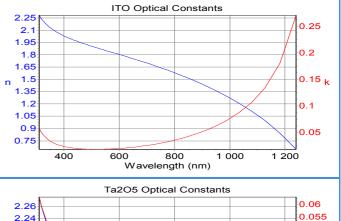
Roughness	57 Å
WO _x	2818 Å
Ta ₂ O ₅	596 Å
TiVO _x	977 Å
ITO	1643 Å
Glass substrate	

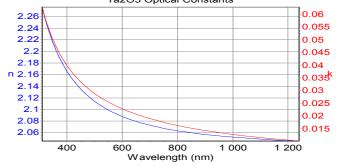


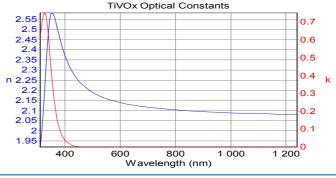
The optical constants have been determined using:

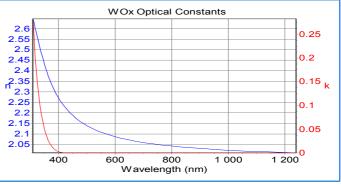
- a combined Lorentz oscillator and Drude term for ITO
- an absorbing Lorentz oscillator for Ta₂O₅
- the new amorphous dispersion formula for WO_x and $TiVO_x$

All these dispersion formulae are included in the DeltaPsi2 software that allows accurate modelling of a large variety of materials as well as describing complex behaviours such as gradient or anisotropy.









Conclusion

The UVISEL Spectroscopic Ellipsometer is a powerful instrument for characterizing complete EC devices with high accuracy and reliability, and provides information on surface roughness or interface layers along with their composition.

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Find us at www.jobinyvon.com or telephone:

USA: +1-732 494 8660 Germany: +49 (0)89 462317-0 China: +86 (0)10 6849 2216

France: +33 (0)1 64 54 13 00 UK: +44 (0) 20 8204 8142 Other Countries: +33 (0)1 64 54 13 00

Japan: +81 (0)3 3861 8231 Italy: +39 02 57603050