E-MRS

2014 Spring Meeting Lille, France – May 26th - 30th

SYMPOSIUM L

Chromogenic Materials and Devices

Symposium Organizers:

Aline Rougier, Institut de Chimie de la Matière Condensée de Bordeaux, Pessac, France

Claes G. Granqvist, The Angstrom Laboratory, Uppsala, Sweden

Bernard Dam, Chemical Engineering, Faculty of Applied Sciences Address, Delft, The Netherlands

Martyn Pemble, University College Cork, Ireland

Published in Solar Energy Materials and Solar Cells

PROGRAM VIEW : 2014 Spring

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Symposium : L

Chromogenic materials and devices

26 May 2014 | 27 May 2014 | 28 May 2014

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start at	Subject	Num.
	Thermochromism I : Russel Binions, Bernard Dam	
09:00	**Thermochromics and the Suntuitive® Interlayer** **Authors :** Harlan Byker **Affiliations :** Pleotint, LLC **Resume :** Dynamic windows offer an opportunity to enhance a building environments and occupant sense of wellbeing. However, windows can cause serious energy concerns due to heat loss in the winter and heat gain in the summer. Glare is also a major concern. A thermochromic interlayer in a window can be sunlight responsive and the heat of the sun can provide all the energy required to tint the window. The chemistry that allows this to take place will described and a status update on commercialization will be given.	L-I 1
add to my program	(close full abstract)	
09:30	**Performance limits of thermochromic undoped and Mg-doped VO2 films and nanoparticles for energy efficient window applications** **Authors :** Shuyi Li, Gunnar A. Niklasson, Claes G. Granqvist **Affiliations :** Department of Engineering Sciences, Solid State Physics, The Ångström Laboratory, Uppsala University, Uppsala, Sweden **Resume :** Thermochromic VO2 is a promising material for energy-efficient window applications. It goes through a metal-to-insulator transition at a critical temperature Tc of ~68 °C. This phenomenon also enables transmittance modulation in the solar infrared region and lays a foundation for thermochromic VO2-based energy-efficient fenestration. Historically, high Tc, low luminous transmittance and low solar transmittance modulation have been the three challenges to the performance of VO2-based materials. Doping has been reported to offer a number of solutions: W-doping can reduce Tc effectively, and Mg-doping can reduce Tc and improve luminous transmittance. Furthermore, VO2 nanoparticle composites were found to offer so called nanothermochromic properties, which enable dramatic improvements in luminous transmittance and solar transmittance modulation simultaneously. The study to be presented is focused on undoped and Mg-doped VO2 films and nanoparticle composites. Optical constants were obtained for experimentally prepared VO2 films with Mg contents 0 < Mg/(Mg + V) < 0.21. Luminous transmittance and solar transmittance for films and nanoparticle composites were calculated for varied thickness and Mg-contents. The performance limits of undoped and Mg-doped VO2 films and nanoparticle composites were shown as a relation between luminous transmittance and solar transmittance modulation. Mg-doping was found to improve the optical performance of films but to impair that of the nanoparticle composites. A generally preferable degree of Mg-doping was found to be Mg/(Mg + V) < 0.06. The positive effect of antireflection treatment on Mg-doped VO2 films is discussed too.	L-I 2
add to my program	(close full abstract)	
09:45	**Combined optical and transport measurements during the metal-insulator transition in thin V2O3 films** **Authors :** T. Smets, L. Dillemans, M. Menghini, C.-Y. Su, and J.-P. Locquet **Affiliations :** Department of Physics and Astronomy KU Leuven, Belgium **Resume :** Vanadium sesquioxide (V2O3) is a strongly correlated electron system which exhibits a metal-insulator-transition (MIT) when cooled down below 180K. We study simultaneously the optical and electrical properties of V2O3 thin films over a temperature range covering but not limited to the	L-I 3

transition range. Therefore we measure the material before, during and after the films exhibits the MIT in order to identify the different phases (metallic, insulating) involved in the whole transition process. A combination of in situ optical transmission and transport measurements are performed as a function of temperature. The different simultaneous measurements delivers consistent data: a metallic state at high temperature, an insulating state at low temperature and a broad first order transition visible as a change in electrical as well as optical properties in between these states. Additionally a hysteresis between cooling down and warming up curves, both in the electrical as well as the optical properties, occurs during the transition signaling the first order transition. Both the metallic and the isolating phase are opaque in the near infra red which limits the study to a set of thin (below 100nm) V2O3 films. High crystallinity and good uniformity are required in these thin films in order to observe a sharp MIT and reproducible material properties over multiple temperature cycles. All the samples used in this study were high quality thin epitaxial films films deposited by Molecular Be

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10:00 **Coffee Break**

Electrochromism I : Delia Milliron, Aline Rougier

10:30 **Electrochromic materials: Electronic, ionic and optical properties.**

Authors : Gunnar A. Niklasson

Affiliations : Department of Engineering Sciences, Uppsala University, P.O. Box 534, SE-75121 Uppsala, Sweden

Resume : Electrochromic materials have the ability to change their optical properties, gradually and reversibly, when an electrical potential is applied across them. Thin films of transition metal oxides impart electrochromic functionality to the emerging smart window technology. Together with transparent contacts and a solid or gel-like electrolyte they constitute the building blocks of electrochromic devices. A typical device consists of five layers between two substrates, or alternatively deposited on a single substrate. In the former configuration, each substrate is coated by a transparent conducting layer and subsequently by an electrochromic layer. The two sides of the device are laminated by an ion conductor, preferably a polymer-based one. The electrochromic layers are chosen to be complementary. One of them is cathodic (i.e. it colors under cation/electron insertion) and the other is anodic (coloring under cation/electron extraction). Some of the important performance parameters of an electrochromic device are the optical contrast between transparent and dark states, the charge capacity and the switching speed. Each of these has its roots in the fundamental physical and electrochemical properties of the materials. The optical properties depend on the nature of the electronic transitions and whether the electrons are free or localized. It appears that in many electrochromic materials intervalence transitions between localized states is the most important mechanism. Basically, a good description of the optical properties depends on a good understanding of the electronic band structure. The charge capacity of an electrochromic film depends on the magnitude of the electronic density of states in the reversible potential range. It should be noted that the achievable density of states may be less than the theoretically expected one, since intercalated ions may not be able to penetrate all parts of the material. The switching speed depends on the diffusion coefficient of ions in the electrochromic films, as well as in the electrolyte. The sheet resistance of the transparent conductors is also important in this respect. A number of electrochemical techniques are suitable for studying ionic transport in intercalation materials, such as for example electrochromic films in contact with an electrolyte. Impedance spectroscopy gives the most detailed characterization of the transport processes but measurements are time consuming, and in certain situations more simple techniques such as chronopotentiometry or choronoamperometry may be preferable. Electronic transport may be studied with conventional electrical measurements with the film samdwiched between two metal electrodes. In this contribution we will focus on the determination of the diffusion coefficient and the electronic density of states (DOS) by electrochemical methods, and how to use this knowledge to describe the optical properties. It is shown that the features observed in the ?electrochemical density of states? often show good agreement with the theoretically computed DOS. However, the magnitude of the electrochemical DOS is always lower that

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the theoretical one. It seems that the whole film is not accessible to the ion intercalation process. We also address the question whether the electronic states are extended or localized and how to determine this experimentally. Theories for optical properties are reviewed based on the intervalence transfer concept. In some, but not all, cases the transitions may be identified as polaronic. We also comment on the existence of electrochromism due to free electrons and its possible limitations. Examples are given mainly from our work on WO3, but also results on SnO2, IrO2 and NiO-based films will be discussed.

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11:00 **A monolithic magnetron sputtering fabrication and properties of all-solid-state inorganic multilayered electrochromic transparent and reflective devices**

Authors : 1. Xungang Diao*, Guobo Dong, Fangyuan Gao 2. Qi Wang, Shuo Wang 3. Yudong Feng, Huaping Zuo

Affiliations : 1. Laboratory for Infrared and Solar Energy, School of Physics and Nuclear Energy Engineering, Beihang University, Beijing, 100191, China 2. China South Glass CO. LTD., 301700, Tianjin, China 3. Science and Technology on Surface Engineering Laboratory, Lanzhou Institute of Physics, Lanzhou 730000, China

Resume : All-solid-state inorganic multilayered electrochromic transparent and reflective devices have been developed in our work for potential applications on high energy efficiency smart windows and satellite surface thermal controllers respectively. A typical five multilayered transparent electrochromic device Glass/ITO/WO3/LiTaO3/NiOx/ITO and a flexible reflective device PI/ Al/WO3/LiTaO3/NiOx/AZO have been monolithically fabricated layer by layer with a multi-target magnetron sputtering machine. The maximum transparency and reflectance difference in the visible light spectrum region between coloration and bleaching states reaches as high as 80%. The response time for both coloration and bleaching is as fast as within less than 10 seconds for the first tens of cycles. The cycling life has reached more than 100,000 cycles for the full device but it suffers a very serious degradation especially for the bleaching states that we are continuing to work on in order to overcome. L-II 2

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11:15 **Mixed oxide thin films deposited by magnetr?n sputtering at oblique angles for the development of electrochromic anodes**

Authors : Jorge Gil-Rostra, Francisco Garcia-Garcia, Francisco Yubero, Agustin R. Gonzalez-Elipe

Affiliations : Nanotechnology on Surfaces laboratory, Instituto de Ciencia de Materiales de Sevilla (CSIC-Univ. Sevilla). Avda. Americo Vespucio 49. 41092 Sevilla. Spain. http://www.sincaf-icmse.es/

Resume : In this work we have prepared by magnetron sputtering at oblique angles and room temperature a series of WxSiyOz and CoxSiyOz thin films with different W/Si and Co/Si ratios. 1,2 It is found that this deposition method permits the fabrication of films with a high porosity and excellent optical properties that can be suitable for electrochromic applications. Besides their characterization by a large variety of techniques, their electrochemical behaviour in aqueous and organic media has been ascertained by following the evolution of color and color efficiency when cycling the films from oxidized to reduced states for several thousand times. A precise control over the refractive index in the bleached state of the films and the possibility of tuning the variation of transmittance by adjusting the M/Si ratio are additional advantages provided by this type of thin film materials. 1.-J. Gil-Rostra, M. Cano, J.M. Pedrosa, F.J. Ferrer, F. Garcia-Garcia, F. Yubero, A.R. Gonzalez-Elipe, ACS Applied Matear. Interf. 4, 2012, 5147-5154 2.-J. Gil-Rostra, F. Garcia-Garcia, F. Yubero, A.R. Gonzalez-Elipe, Sol. Energy Mater. Solar Cells, in press L-II 3

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11:30 **Pigment particle based electrochromic coatings and devices**

Authors : Angela Šurca Vuk(1), Mohor Mihelcic(1), Ivan Jerman(1), Aline Rougier(2), Boris Orel(1)

Affiliations : 1 National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia 2 CNRS, UniversitédeBordeaux,ICMCB,87avenueduDr.A.Schweitzer,PessacF-33608,France

Resume : One possibility for reducing the price of solar control products is their mass production on flexible polymer foils. This rules out the possibility of depositing most inorganic electrochromics, which require post-deposition heat-treatment at elevated temperatures (>300 °C). The preparation of an “electrochromic paints” that could be applied on polymer foils has great potential for EC sunroofs and sight control EC plastic film for appliance doors and aircraft cabin windows. We described herein the preparation of “electrochromic paints” from the pre-prepared Ni1-xO pigments and properties of the corresponding L-II 4 electrochromic pigment coatings. The main accent is given on the description of structural changes accompanying colouring/bleaching changes of Ni1-xO; ex situ infrared absorption-reflection spectra were used for these purposes. Results revealed a dominant role of the Ni1-xO grains surface in the colouring/bleaching of the Ni1-xO pigment coatings, extending the possibilities of the use of Ni1-xO coatings for fabrication of organic polymer/inorganic electrochromic devices, i.e. PEDOT/ionic liquid electrolyte/Ni1-xO device. Functioning of the pigment coatings was demonstrated by showing electrochromic response of Ni1-xO based devices with TiO2 or WO3 pigment coatings, assembled with lithium conducting gel type electrolyte.

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11:45 **Lithium-doped nickel oxide and surfactant-assisted tungsten oxide thin films made by USP, toward improved electrochromic performances** L-II 5

Authors : J. Denayer, G. Bister, C. Henrist and R. Cloots

Affiliations : Laboratory GREEnMat, University of Liège (ULg); Environmental and Material Research Association (CRIBC-INISMa); Laboratory GREEnMat, University of Liège (ULg); Laboratory GREEnMat, University of Liège (ULg)

Resume : In the last few years, there has been increasing interest in electrochromic glass due to its potential use as an energy-saving component for buildings, as it could reduce considerably their CO2 emission by decreasing their energy consumption up to 30%. The crucial issues of such devices are the durability, the coloration efficiency and the reversibility upon coloration and bleaching of the electrochromic layers. The combination of NiO and WO3 films affords a good coloration contrast between the colored and the bleached state of the device, since tungsten oxide colors upon ions and electrons insertions while nickel oxide gets colored after their extractions. In order to improve the performances of those electrochromic films, we have investigated a surfactant-assisted deposition process for WO3 layer and the insertion of lithium in the NiO layer. All films have been deposited on FTO substrates by ultrasonic spray pyrolysis (USP), which is a low-cost alternative to industrial vacuum processes for manufacturing high quality thin films. The crystallization and morphology of those films, as well as their optical, electrochromic and electrochemical properties have been investigated. The presence of lithium ions in nickel oxide films has shown improved coloration efficiency compared to the undoped films. The higher active surface of surfactant-assisted tungsten oxide films has led to higher reversibility (89% against 43% without surfactant) and a coloration contrast up to 70%.

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12:00 **Lunch BREAK**

Photochromism I : Yoshimura Makimura, Claes Granqvist

13:30 **Room temperature photochromic effect in Yttrium hydride** L-III 1

Authors : S. Zh. Karazhanov, T. Mongstad, Ch. Ch. You, J. P. M?hlen, and E. S. Marstein

Affiliations : Department for Solar Energy, Institute for Energy Technology, 2027 Kjeller, Norway

Resume : The development of new metal hydride films for optoelectronic applications has been a major field in our research group for several years. One of the investigated materials is YHx, which was selected partly because it is a wide band gap material and can withstand thermal processing at elevated temperatures. It has previously been reported that YHx can exhibit a photochromic effect and persistent photoconductivity at low temperatures (<100 K) if it is capped by Pd. In our experiments, uncapped YHx were investigated. Upon exposing into the air, the films have been oxidized and exhibit a strong photochromic effect and persistent photoconductivity at room temperature. In this presentation, the current status of the research related to understanding the deposition and characterization of the films will be presented. The films have been deposited by industrial magnetron sputtering machine on small and large area glass and plastic substrates using different hydrogen partial pressures. Compositional analysis was performed and presence of O was confirmed. Electrical and optical properties of the films have been studied. We demonstrated that upon exposing into the excitation by light or by time-resolved X-ray beam the films show lattice contraction and no phase transformation has been observed. The time dependence of the lattice contraction resembles the optical signature of the photochromic effect and suggests a relation between the two phenomena.

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14:00 **Solid-state NMR studies of Photochromism in Oxygen-containing Yttrium hydride Thin-films**

Authors : C. Vinod Chandran(a), Herman Schreuders(b), Bernard Dam(b), Jakob Bart (a), J. W. G. Janssen(a), P. J. M. van Bentum(a), Arno P. M. Kentgens(a)

Affiliations : (a) Solid-state NMR, Institute for Molecules and Materials, Nijmegen, The Netherlands (b) Chemical Engineering, Delft University of technology, Delft, The Netherlands

Resume : The photochromic effect of oxygen doped yttrium hydride (YHxOy) thin films is studied by solid-state NMR. The photochromic effect causes changes in optical and conduction properties of the YHxOy film when irradiated with light. We have used the novel NMR strip-line probe technology to investigate this effect. In comparison with pure yttrium hydride (YHx) thin films, the 1H NMR study showed reversible changes for YHxOy before and after light irradiation. Mobility of some hydrogen species was found to be diminishing during the photochromic darkening. The high sensitivity of the strip-line NMR probe helped to observe these changes. With the help of 89Y{1H} Cross-polarization MAS experiment we found some of the yttrium species getting to a metallic state during the darkening process. The 89Y-1H 2D correlation spectrum shows a close proximity of those yttrium atoms with the hydrogen species near the oxygen atoms. Therefore, the static NMR experiments help to observe the dynamics of the system whereas the MAS NMR experiments show the chemical and structural information. With the help of observed NMR data the present work suggests a model for the structural transformation during the reversible photochromic changes in YHxOy thin-films, as a result of illumination.

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14:15 **Compositional and structural control of reversible photochromism in sodalites**

Authors : Edward R. Williams, Jennifer A. Armstrong, Mark T. Weller

Affiliations : University of Bath UK

Resume : Photochromic materials, which demonstrate a reversible colour change when exposed to radiation of various wavelengths, are of increasing interest due to their potential applications as smart coatings for example in windows, sun-screens and build environment. Of particular interest are materials that develop their colour reversibly. One example of such a material is the mineral hackmanite which adopts the sodalite composition and structure, A8 [M’M’’O4]6X2; this undergoes a colour change to a deep pink or violet on exposure to UV radiation, before reverting to colourless in white, red or IR light over time. This property, also known as tenebrescence, can be repeated indefinitely. Synthetic equivalents of hackmanite have been reported previously; however in these materials, direct compositional analogues of hackmanite, the photo-induced colour is restricted to pink/lilac. We have investigated the effect of composition on the colour of the photo-induced, long-lived F-centres in the sodalite structure though the synthesis and characterisation of a range of new phases of the general composition A8[M’M’’O4]6[X,S]2 . The visible-region absorption spectra of these materials, following UV irradiation, shows a broad, strong, absorption whose position correlates with the dimensions of the sodalite cage occupied by the excited electron. Phases that undergo reversible photochromism from white to pink, violet, blue and green have all been obtained.

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14:45 **Fast-responsive photochromic materials**

Authors : Claudio Roscini (1,2), Nuria Vázquez-Mera (1,3), Daniel Ruiz-Molina (1,2), Jordi Hernando (3)

Affiliations : (1) Institut Català de Nanociència i Nanotecnologia (ICN2), Edifici ICN2, Campus UAB, 08193, Bellaterra, Spain; (2) Consejo Superior de Investigaciones Científicas (CSIC), Edifici ICN2, Campus UAB, 08193, Bellaterra, Spain; (3) Universitat Autònoma de Barcelona (UAB), Edifici C/n, Campus UAB, 08193, Bellaterra, Spain

Resume : Since 1950s, T-Type photochromic materials are increasingly finding application in ophthalmic, smart windows and as protective coatings.(1) However, important drawbacks, such as the low fading rates when embedded in polymeric matrices, due to steric restrictions, limit their applicability in these areas. Various strategies have been attempted to enhance the isomerization rate: photochrome embedment in low glass transition polymers(2) or use of photochromes that isomerize without involving conformational changes(3) are just two examples. However, the proposed alternatives may affect the material mechanical properties or are limited to specific families of photochromes. We

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recently developed a new strategy(4,5) to obtain fast responsive photochromic materials based on oil-core polymeric capsules containing photochromic dyes (e.g. spirooxazines). The photochromic molecules, dissolved in the oil core of the capsules, behave as in solution, where the isomerization rate is the highest. Consequently, the polymeric materials (e.g. films) containing the photochromic capsules have solution-like photochromic behaviour: the measured fading kinetics are one order of magnitude faster than those obtained for the same photochrome directly dispersed in the polymeric matrices, reaching the 80% of the initial transparent state in less than 15 seconds. 1.Color. Tech. 2009,125,249. 2.Adv. Mater. 2002,14,1496. 3.J. Am. Chem. Soc. 2009,131, 4227. 4.WO2013132123 A1. 5.Adv. Optic. Mater.,2013,1,631

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15:00

Spiropyran-Polyoxometalate Hybrid Materials with Highly Tunable Solid-State Photo- and Electrochromic Properties

Authors : Rémi Dessapt (a), Khadija Hakouk (a), Stéphane Jobic (a), Anne Dolbecq (b), Olivier Oms (b), Pierre Mialane (b)

Affiliations : (a) Institut des Matériaux Jean ROUXEL, Université de Nantes, CNRS, 2 rue de la Houssinière, BP 32229, 44322 Nantes Cedex 3, France (b) Institut Lavoisier de Versailles, UMR 8180, Université de Versailles Saint-Quentin en Yvelines, 45 Avenue des Etats-Unis, 78035 Versailles cedex, France

Resume : The combination of inorganic polyoxometalates (POMs) with photoswitchable organic molecules such as spiropyrans (SP) and spironaphthoxazines (SN) has recently opened up the way to new hybrid materials with highly tunable solid-state photochromic and electrochromic properties in ambient conditions. Two complementary strategies have been successfully conceived. The first approach consists in assembling POMs with a cationic spiropyran into supramolecular networks [1]. The nature of the POM units and the design of the frameworks impact both the initial color of these charge-transfer assemblies and the SP photoisomerization rates. Pertinent structure/property relationships have been evidenced from the combination of X -ray crystallographic and spectroscopic techniques. Some of these systems are remarkably bistable and are very promising for potential high density optical data recording. In the second approach, neutral SP and SN molecules have been covalently linked onto POM units in new photochromic and electrochromic dyads [2][3]. This grafting allows improving the photoisomerization of the SP and SN moieties, and solid materials with strong photoresponses can be elaborated from spiro-derivative molecules initially nonphotochromic in the crystalline state. [1] K. Hakouk, O. Oms, A. Dolbecq, J. Marrot, A. Saad, P. Mialane, H. El Bekkachi, S. Jobic, P. Deniard, R. Dessapt, J. Mater. Chem. C 2013, DOI:10.1039/C3TC31992J [2] O. Oms, K. Hakouk, R. Dessapt, P. Deniard, S. Jobic, A. Dolbecq, L. Nadjo, B. Keita, J. Marrot, P. Mialane, Chem. Commun. 2012, 48, 12103 [3] A. Parrot, G. Izzet, L.-M. Chamoreau, A. Proust, O. Oms, A. Dolbecq, K. Hakouk, H. El Bekkachi, P. Deniard, R. Dessapt, P. Mialane, Inorg. Chem. 2013, 52, 11156

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15:15

TMTU as alternative redox couple for electrochromic and photoelectrochromic devices

Authors : Shankar Bogati, Helena Orvalho, Carmen Jerg, Andreas Georg, Wolfgang Graf

Affiliations : Fraunhofer Institute for Solar Energy Systems (ISE)

Resume : Electrochromic devices comprising redox couples show the following configuration: TE / EC / RE / Cat / TE, where: TE represents a transparent electrode, like F:SnO2 (Fluorine-doped Tin Oxide on Glass) , EC an electrochromic material, like WO3 (Tungsten oxide), RE a redox electrolyte and Cat a catalytic layer. The redox electrolyte contains a redox couple, like I^- /I_3^- (iodide/tri-iodide), which counterbalances the redox reaction of the double injection into WO3. The electron transfer in between electrochromic material and redox couple should be slow, which may be expressed as a low loss current when applying a constant coloring potential, or as a high charge transfer resistance as characterized by impedance spectroscopy. In contrast to that, the electron transfer in between the catalyst and the redox couple should be fast. The redox couple should be transparent or showing some contrary coloration. Especially for an application in photoelectrochromic or photochromic devices, the redox potential of the redox couple has also to fit the limitations of the system. Therefore, charge transfer resistance or loss currents, optical properties and redox potential have been measured for a set of redox couples, especially I^-/ I_3^-, TEMPO/TEMPO+ (2,2,6,6-tetramethyl-1-piperidinyloxy/oxidised form), K4Fe(CN)6/K3Fe(CN)6, and TMTU/TMFDS+ (tetramethylthiourea/ tetramethyl

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formaminium disulfide), where TMTU/TMFDS+ has to be found to show the most promising redox couple.

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15:30 **Coffee Break**

Photochromism II : Smagul Khazanov, Martyn Pemble

16:00 **The hydrogen photochromism in solids**

Authors : Alexander Gavrilyuk

Affiliations : A.F. Ioffe Physical Technical Institute of the Russian Academy of Sciences

Resume : The hydrogen photochromism in solids Alexander Gavrilyuk A.F. Ioffe Physical Technical Institute of the Russian Academy of Sciences, Sankt-Petersburg, Russia The hydrogen photochromism is a very special type of photochromism because it arises due to hydrogen atoms detached from hydrogen-containing molecules under the action of light. The hydrogen photochromism is in fact the photo-induced doping by atomic hydrogen. Saturated transition metal oxides, such as WO3, MoO3,V2O5 have a whole series of special properties regarding hydrogen, which makes it possible to detach hydrogen atoms from organic molecules previously adsorbed on their surface and to form hydrogen metal bronzes under the action of light. The mechanism and the factors influencing the efficiency of the hydrogen photochromism have been discussed. It has been shown that the control upon the oxide optical parameters can be achieved via the diffusion of the injected hydrogen atoms. It has been inferred that the hydrogen diffusion influence both the oxide photochromic sensitivity and the spectral characteristic of the arising absorption band. Special attention is paid to formation of different color centers: bulk centers and surface centers (paramagnetic and diamagnetic). By switching on or off the hydrogen diffusion one can achieve different absorption bands arising in the oxide under the action of light. Furthermore the diffusion makes it possible for the injected carrier to reach the surface of another material being in the contact with that where the injection of hydrogen had previously occurred. This yields new possibilities for the use of the atomic hydrogen which is an excellent reducing agent, often a latent agent, and capable of playing the role of a dopant or a catalyst, sometimes, combining both functions, which can trigger various secondary processes on the surface of solids. L-IV 1

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16:30 **Photochromism in Mn2+ doped phosphate glasses**

Authors : A.Cemmi, S.Baccaro, Q.Cai, N.Yang, F.Zhou, H.Xu, G.Chen

Affiliations : ENEA, Rome (Italy): A.Cemmi; S.Baccaro. ECUST, Shanghai (China): Q.Cai; N.Yang; F.Zhou; H.Xu; G.Chen.

Resume : Photochromism is the reversible transformation of a chemical species between two forms by incident electromagnetic radiation. Since the discovery of photochromic phenomenon, it is interesting for applications such as optical recording. In this work, photochromism in Mn2+ doped phosphate glasses is investigated using gamma ray as an excitation source. The Mn2+ doped glass sample change its body color upon gamma ray irradiation at the proper doses because of irradiation induced oxidation process from Mn2+ to Mn3+. These two forms have different absorption spectra where Mn2+ is colorless while Mn3+ shows violet coloration due to absorption at around 490 nm. After heat treatment at the temperature higher than Tg of the glass, the colored samples can be bleached completely without any degeneration even after many coloration ↔ bleaching processes. A model was proposed for the photochromism in this glass system. The effects of glass composition as well as Mn2+ doping concentration on the photochromism are discussed. It is also interesting to find that there is a critical irradiation dose beyond which the irradiation induced coloration could not be bleached after thermal treatment even at the higher temperature for longer time. The relevant mechanism is studied. L-IV 2

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16:45 **Understanding of atomic and electronic structure of SnWO4**

Authors : A. Kuzmin1, A. Anspoks1, A. Kalinko2, J. Timoshenko1, R. Kalendarev1

Affiliations : 1 Institute of Solid State Physics, University of Latvia, Kengaraga street 8, LV-1063 Riga, Latvia; 2 Synchrotron SOLEIL, l'Orme des Merisiers, Saint-Aubin, BP 48, 91192 Gif-sur-Yvette, France L-IV 4

Resume : Stannous tungstate SnWO4 is very interesting semiconducting material and is a promising candidate for sensing, photocatalytic and transparent conducting oxide applications. It has two polymorphs, the low-temperature orthorhombic alpha-phase and high-temperature cubic beta-phase, which transform into each other by a diffusion-controlled phase transition mechanism, whose details still require clarification. The crystalline structure of alpha-SnWO4 is composed of distorted SnO6 and WO6 octahedra, which are joined by vertices into 2D-sheets held together by Sn2+ ions. In beta-phase, which is metastable at room temperature, the structure is built up of slightly deformed WO4 tetrahedra interconnected with four strongly distorted SnO6 octahedra. The distortion of metal-oxygen octahedra in SnWO4 is caused by the second-order Jahn-Teller effect, and the type (n or p) of its conductivity can be controlled by changing the Sn:W ratio. In this study we will discuss the above mentioned issues based on the results of synchrotron radiation x-ray absorption spectroscopy, Raman scattering study and the first principles calculations.

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17:00 **Sol-gel derived WO3 layer with photochromic effect**

Authors : Urša Opara Krašovec1, Tjaša Vidmar1, Andreas Georg2, Marko Topič1

Affiliations : 1 University of Ljubljana, Faculty of Electrical Engineering, Tržaška cesta 25, 1000 Ljubljana, Slovenia 2 Fraunhofer Institute for Solar Energy Systems, Heidenhofstr. 2, 79110 Freiburg, Germany

Resume : The most studied smart windows are multilayered electrochromic systems that require electrical control, while photochromic systems respond to the solar illumination. Therefore a photochromic system based on single layer can be considered as a low-cost alternative. In this contribution we report on the photochromism of the WO3 layers processed with different organic additives. We have applied peroxo sol-gel synthesis to prepare WO3 sols which were further modified with different organic additives (e.g alcohols, ethers). Dip-coating and Doctor-blade techniques were used for the layer deposition. Solar simulator (Oriel Class ABA) was used as a light source for the colouration of the layers, while the photochromic response of the layers was analysed by UV-VIS spectroscopy. The modified WO3 layers show good photochromic response; the change in transmittance between 80 and 30 % @ 600 nm upon 1 sun illumination (1000W/m2, AM 1.5) is achieved in 30 minutes. However, the bleaching kinetic in the dark is slow (few hours), but can be enhanced to few minutes if the layers are exposed to the elevated temperatures (120°C). The reversibility of the structural changes in the WO3 layers upon cycling will be analysed with IR-ATR. In addition, the mechanisms associated to the photochromic response of the WO3 layers will be discussed. L-IV 3

add to my program **(close full abstract)**

17:15 **Photochromism of p-type GaN:Eu; a route to the Mg acceptor qubit**

Authors : K. P. O'Donnell, P. R. Edwards,M. J. Kappers, K. Lorenz, E. Alves and M. Boćkowski

Affiliations : Strathclyde U.; Cambridge U.; IST-CTN; Unipress

Resume : Rare-earth-doped III-N semiconductors have been studied for many years on account of their possible role in visible light-emitting diodes (LED) with built-in utility as red (e.g. Europium), green (Erbium) and blue (Thulium) monochromatic light sources [1]. However, to date, no commercial devices have been introduced on the basis of these materials. We have recently discovered photochromism and thermally activated luminescence hysteresis in the emission spectrum of p-type GaN thin films that were co-doped with Mg and Eu [2]. We have also reported an unexpected Zeeman splitting and xray-induced magnetic moment of Eu3+ ions in GaN [3,4]. These findings encourage speculation on taking the study of RE-doped III-N beyond the limited goal of im-proving LED efficiency into the realm of novel quantum-optical and magneto-optic devices, leaving aside their optoelectronic functionality. In this talk I will describe the spectroscopy of ion-implanted and annealed GaN(Mg): Eu samples and discuss the possible exploitation of the Mg acceptor in GaN as a qubit. [1] K. P. O'Donnell and V. Dierolf (eds), Topics in Applied Physics 124, (Springer, Dordrecht, 2010) [2] K. P. O'Donnell, P. R. Edwards, K. Lorenz, E. Alves, and M. Boćkowski, Proc. ICNS10, Washington, 2013, to be published in pss(c) (2014) [3] V. Kachkanov, K.P. O'Donnell, C. Rice, D. Wolverson, R.W. Martin, K. Lorenz, and E. Alves, MRS Proceedings 1290–i03–06 (2011) [4] V. Kachkanov, G. van der Laan, K. P. O'Donnell et al. Scientific Reports 2, 969 (2012) L-IV 5

add to my program **(close full abstract)**

17:30 **Multifunctional information carriers with concealed quick response codes**

Authors : Melanie Ecker, Thorsten Pretsch*

Affiliations : BAM Federal Institute for Materials Research and Testing, Division 6.5, Polymers in Life Science and Nanotechnology, Unter den Eichen 87, 12205 Berlin, Germany L-IV 6

Resume : Shape memory polymers like poly(ester urethanes) (PEUs) may serve as technology platform for switchable information carriers (SICs). Once attached to a product, the triggering of the shape memory effect leads to the release of information stored by the SIC. This behavior can be helpful in view of product verification and identification. Recently, the first generation of multifunctional SICs has been developed, characterized by shape memory and thermochromic properties and color fading quick response (QR) codes at elevated temperatures. Here, we show that SICs can also be prepared with partially decolorizing surfaces. The fabrication of SICs was realized as follows: Firstly, PEU paste containing graphite black was deposited atop PEU samples of cuboid shape in a solvent cast approach. After solvent evaporation, a machine readable QR code was engraved into the resulting film. Finally, PEU paste containing black thermochromic pigments with a color switching temperature of 43°C was used to seal the QR code containing site of the obtained SIC, thus rendering the code both non visible and undecipherable at 23 °C. Herein, we demonstrate that SICs with concealed QR codes are thermo-responsive in terms of shape memory behavior and thermochromism, which enables an uncomplicated reading of the QR codes at elevated temperatures. Beyond this conceptual introduction, we report on the physical properties of the SICs as characterized by thermal analysis and optical methods.

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17:45 **Efficient photochemical isomerization of N,N’-di(t-butoxy carbonyl)indigos – characterization and applications**

Authors : Eric Daniel Głowacki, Dominik Farka, Elisa Tordin, Gundula Voss, Niyazi Serdar Sariciftci

Affiliations : Linz Institute for Organic Solar Cells (LIOS), Physical Chemistry, Johannes Kepler University Altenbergerstrasse 69, A-4040 Linz, Austria

Resume : We report on the photophysics of highly-soluble N,N’-di(t-butoxy carbonyl)indigos (BOC-indigos), finding that reversible photochemical trans-cis and cis-trans isomerization reactions proceed with high quantum yields (0.20 – 0.50). Absorption of wavelengths in the 550-600 nm region induces trans-cis isomerism, while blue light (~420 nm) leads to the reverse cis-trans process. We find that like their parent indigos, trans-BOC-indigos have low fluorescence yields (~1×10-3), while the cis isomers have no measurable emission. Electron donors and proton donors are both found to strongly quench photoisomerization. Observation of quenching by proton donors supports the model of ultrafast proton transfer deactivation of excited states in indigoid molecules. Dissolution of the dyes in glassy polymer matrices does not significantly impede photoisomerization – with this we demonstrate simple photochromic polymeric films. Reversible photoisomerism induced by relatively low-energy photons (~2 eV) is the dominant photophysical process in these materials, making BOC-indigo derivatives interesting for photomechanically-actuated materials.

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Chromogenic materials and devices

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start at	Subject	Num.
	Electrochromism II : Xungang Diao, Aline Rougier	
09:00	**Semi-interpenetrating polymer network architecture:Design and tailoring of new IR devices** **Authors :** C. Chevrot, D. Teyssié, F. Vidal, L. Beouch, P-H. Aubert, L. Goujon, N.Roy **Affiliations :** Laboratoire de Physicochimie des Polymères et des Interfaces, Université de Cergy-Pontoise, France **Resume :** Since Interpenetrating Polymer Networks (IPNs) represent interesting materials with tailored properties, it was exciting to examine how the presence of an electronic conducting polymer (ECP) within an IPN could render the obtained semi-IPN an adaptive material. We have developed since several years, electro-adaptive materials involving that a conjugated monomer was polymerized on each side of a thin film of an IPN leading to a self-supported device after swelling with an electrolyte. Upon applying a low voltage between the two sides of the film, this device can work as a mechanical actuator or as an electrochromic device according to the ECP content. Such device possesses some advantages compared with a multilayered device: easier elaboration, perfect adherence between layers, no delamination. The purpose of this talk is to show that the interest of this new electro-adaptive device depends on the type of the IPN (host matrix) and the amount of ECP formed within the IPN. The mechanical and electrical properties of several host matrices will be described: polyethyleneoxide network (PEO), Nitrile butadiene rubber (NBR) network or NBR/PEO IPNs with various NBR/PEO ratios. The incorporation of poly (3,4-ethylenedioxythiophene) (PEDOT) via an oxidative polymerization of EDOT from each side of the host matrix lead to a semi-IPN. After swelling by an ionic liquid such as 1-ethyl, 3-methyl imidazolium trifluorosulfonimide (EMImTFSI), this material can behave as an IR electro-reflective device working without additional electrodes if the PEDOT content is between 1 to 3wt%. Finally, we will show that the IR reflective contrast of these devices can reach high values: up to 26 % and 36% in band II (3-5 µm) and band III (8-12 µm) respectively. These values could be improved since a PEDOT electrodeposited on ITO glass can reach higher values.	L-V 1
add to my program	(close full abstract)	
09:30	**Novel Multicolor Electrochromic Device Based on Localized Surface Plasmon Resonance of Electrodeposited Silver Nanoparticles** **Authors :** Norihisa Kobayashi, Ayako Tsuboi, Kazuki Nakamura **Affiliations :** Department of Image and Materials Science, Chiba University **Resume :** Multifunctional EC materials which control multiple colors, various color density, and specular reflection are expected to be potential candidate for light-modulation device and novel reflective display device. In this paper, we focus on that silver (Ag) nanoparticles exhibit various optical states based on their localized surface plasmon resonance (LSPR). LSPR bands of metal nanoparticles are affected by the size and shape. The control of LSPR, therefore, must enable dramatic changes in color for the surface which nanoparticles are deposited. In order to realize this color variation and to apply for display devices, we investigated here the electrochemical deposition of size-controlled Ag nanoparticles using a voltage-step method which consists of application of two successive different voltages (V1 and V2). The electrochemically deposited Ag nanoparticles exhibit red and blue color depending on the time for V2 voltage application. The color changes between transparent state and colored states are	L-V 2

reversible. Then, we successfully demonstrate the first LSPR-based multicolor EC device in which reversible control of five optical states—transparent, silver mirror, red, blue, and black—is achieved.

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09:45 **An all-organic electrochromic device containing poly(vinylidene fluoride-co-hexafluoropropylene), succinonitrile, and ionic liquid**

Authors : Ting–Hsiang Chang, Chi-Wei Hu, Hsin-Wei Chen, and Kuo-Chuan Ho
Affiliations : Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan ; Institute of Polymer Science and Engineering, National Taiwan University, Taipei 10617, Taiwan

Resume : A high contrast, self-standing thermoplastic electrochromic (EC) layer is fabricated, using N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) and heptyl viologen (HV(BF4)2) as the cathodically coloring and anodically coloring materials, respectively, with plastic crystal succinonitrile (SN) incorporating poly (vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) as the polymer matrix, with or without the addition of ionic liquid. In this study, ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF4) plays a role not only increase the ionic conductivity and optical performance of the electrochromic device (ECD) but also eliminate the crystalline nature of SN. Incorporation of BMIMBF4 in PVdF-HFP/SN polymer matrix changes thermal stability, melting temperature, morphology, and ionic conductivity. The ionic conductivity of polymeric film has been found to increase with increasing concentration of ionic liquid and attains a maximum value of 6 × 10-3 S•cm−1 at 5 wt% BMIMBF4 addition at room temperature. The electrochemical and electrochromic properties of HV(BF4)2 and TMPD molecules are analyzed from their individual perspectives in a 0.1 M electrolyte of tetrabutylammonium tetrafluoroborate (TBABF4) in plastic polymer matrix containing BMIMBF4 with different weight ratios. Electrochemical and electrochromic properties of the electrochromic layer are characterized using cyclic voltammetry (CV), in-situ potential-UV–vis absorption spectra, electrochemical impedance spectroscopy (EIS), and kinetic optical transmittance measurements. The transmittance of the ECD containing the EC layer at 615 nm can be changed reversibly from 70.1 to 10.0%, with the applied potentials of 0 and 1.0 V, respectively.

L-V 3

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10:00 **Coffee Break**

Electrochromism III : C. Chevrot, Aline Rougier

10:30 **Plasmonic metal oxide nanocrystals and their near infrared electrochromism**

Authors : Delia J. Milliron(a,b,c), Anna Llordes(a), Guillermo Garcia(c), Tracy M. Mattox (a)
Affiliations : (a)The Molecular Foundry, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94720 (USA) (b)Department of Chemical Engineering, The University of Texas at Austin, 200 E. Dean Keeton Street, Austin, Texas 78712 (USA) (c)Heliotrope Technologies, 2625 Alcatraz Ave #377, Berkeley, California 94705 (USA)

Resume : Degenerately doped metal oxide semiconductors exhibit plasmonic resonance at wavelengths tunable by varying their composition. We have recently developed robust chemical strategies for incorporating high levels of dopants during colloidal nanocrystal synthesis and thereby fabricated a wide range of dispersible, processible nanocrystals with infrared plasmon absorption features.[1] For example, aluminum-doped zinc oxide nanocrystals exhibit broad absorption peaks in the mid-infrared that change intensity and position systematically as the doping level is synthetically tuned, while plasmon peaks of tin-doped indium oxide (ITO) nanocrystals can be tuned across the near infrared. I will describe our recent efforts to compare the plasmonic behavior of such substitutionally doped nanocrystals to those with interstitial doping, namely tungsten bronzes. These new exemplars are faceted and their plasmonic resonance characteristics are influenced by their shape and size. These plasmonic metal oxide nanocrystals are chemically robust, which has enabled us to study their optical response to electrochemical charging and discharging. Over a few volts of applied bias, the carrier concentration and plasma frequency in a conductive network of ITO nanocrystals were reversibly modulated by nearly 3- and 2-fold, respectively.[2] The result is a strong and selective modulation of near infrared transmittance in visibly transparent films. This effect

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shows promise for energy-saving smart windows, a potential application which is even more compelling when considering the electrochromic properties of inorganic composites containing these nanocrystals. ITO-in-amorphous niobium oxide composites exhibit sequential switching of near infrared and visible transmittance whose dynamic range is enhanced 5-fold by synergistic reorganization at the ITO-glass interface.[3] 1) R. Buonsati and D. J. Milliron, Chem. Mater., 2013, 25, 1305. 2) G. Garcia et al., Nano Lett., 2011, 11, 4415. 3) A. Llordes et al., Nature, 2013, 500, 323.

add to my program **(close full abstract)**

11:00 **Printable materials for low-cost flexible electrochromic devices**

Authors : P.J. Wojcik, L. Pereira, R. Martins, E. Fortunato

Affiliations : Departamento de Ciencia dos Materiais, FCT-UNL, Cenimat – I3N and Cemop-Uninova, Campus de Caparica, 2829-516 Caparica, Portugal

Resume : The growing demand of consumer printed electronics such as smart cards, smart packaging, automotive displays, electronic paper and others led to the increased interest in fully printed electrochemical devices. These components are expected to be developed based on printed thin films derived from cheap and widely accessible compounds. In this talk we present a long stretch of technical research that was performed to realize printed energy efficient concepts such as electrochromic display (passive matrix) and smart-window. Within this broad theme, the overall aim was to develop low-cost material systems (i.e. printable mixtures) at a lab-scale, which would be compatible with large-scale roll-to-roll processing. Presented results concern three main topics: (i) dual-phase inorganic electrochromic material processed at low temperature, (ii) enhancement in electrochromic performance via metal-oxide nanoparticles engineering, and (iii) highly conductive and mechanically stable solid-state electrolyte. In order to extract information from massive computational data, model developed material systems and optimize composition, an efficient mathematical methodology based on statistical techniques was applied. This approach significantly reduces the number of experiments to be realized, while maintaining a high accuracy of the analysis. Coupling of statistical methods with formulation of electrochemically active materials shows the potential to maximize the capabilities of these systems. L-V 2

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11:15 **Electrochromic Devices with Screen Printed Nano-particles on Electrodes for Ultrafast Switching**

Authors : Hojun Ryu, Seong M. Cho, Chil Seong Ah, Tae-Youb Kim, Ju Hee Song, Hye Yong Chu

Affiliations : Electronics and Telecommunications Research Institute

Resume : Electrochromic materials have been widely researched for many applications. The typical respected application areas are energy savings or automobile for safety. Nowadays new application fields have been emerging such as transparent displays and active camouflages. Furthermore electrochromic materials have a good potential to apply to the information display devices because they shows many colors and they control the gray scale very easily in low energy consumption. In this study we fabricated ultrafast switching electrochromic devices using vilogen for electrochromic materials. For cathode electrode we 7 nm TiO2 nano-particles with viologen anchored by phosphates. The other electrode for anodic reaction we used antimony doped tin oxide nano-particle of 10 nm size. The transmettance of the devices show under the 12% transmittance for darkened state measured with 550 nm beam. The band of transmittance change is obtained almost 60% and the transition time from initial to darkened state is 45 msec while the bleaching time which is measured at 90% bleached is 85 msec. After 10,000 cycles transition test the transparency of devices and the transition time do not deteriorated because of the very stable nano structure. So the fabricated devices have very good potential for fast switching optical shutter for transparent display or interior/exterior room mirror for cars relieving the glaring by the other cars. L-VI 3

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11:30 **Towards an all-printed electrochromic device on paper substrate**

Authors : A. Danine, L. Manceriu, C. Faure, A. Rougier

Affiliations : CNRS, University of Bordeaux, ICMCB, 87 avenue du Dr. Albert Schweitzer, 33608 Pessac, France.

Resume : Nowadays electrochromic devices, characterized by a reversible change in optical properties under an electrical stimulation, are more and more present in a wide range of applications including smart windows, rear-view mirrors and more recently as a new functionality for electronic papers. Focusing on displays, WO3 thin films were deposited at room temperature on paper L-VI 4 substrate using a novel synthesis method involving UV-treatment [1]. Electrochromic studies of Paper/Ag/WO3-UV films in three electrodes cell configuration showed high optical performances (Variation in reflectance ΔR ≈ 21% @ 550nm) when cycled in ionic liquid electrolyte (proton and lithium based) between the colored and the bleached state ([-0.1V +0.5V] vs. Hg/HgO). In parallel complete EC devices were assembled in optimized design using a membrane electrolyte based on (0.3 M) LiTFSI BMITFSI. These systems showed a color contrast of 50 (ΔE*, by CIE L*a*b* color space) with short switching times (tcoloration≈ 5s and tbleaching≈ 11s for 90% of contrast, S =2x2cm2) at an operational voltage lower than 1V. Finally, durability studies and lifetime behavior of electrochromic systems will be discussed. [1] A. Danine, L. Cojocaru, C. Faure, C. Olivier, T. Toupance, G. Campet and A. Rougier, Electrochimica Acta, (submitted).

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11:45

New poly(diaryldithienothiophen and alternated copolymers for yellow-to-transmissive electrochromic devices - Influence of the ionic liquide environment

Authors : Zahra Abada (1), Alexia Charron (1), Bruno Schmaltz (2), Corinne Marcel (2), François Tran Van (1)
Affiliations : (1) Université François Rabelais, E.A. 6299. Physicochimie des Matériaux et des Electrolytes pour l'Energie (PCM2E), Par de Grandmont, 37200 Tours, France (2) CEA/DAM Le Ripault, B.P. 16, F.37260, Monts, France

Resume : Chromogenics are included in a wide range of smart materials such as automotive, architectural, aircraft, and information display. Among these chromogenics, electrochromic π-conjugated polymers occupy an important place in various devices such as multicolor displays, smart windows, etc…, with the possibility to realize large surface area onto flexible substrates in using low cost printing techniques [1]. For the realization of multicolor displays, the elaboration of pixels possessing the three primary colors i.e magenta, yellow and cyan are necessary to elaborate color devices. In such a device, any color can be achieved by adjusting the intensity of each colored pixel. If the literature concerning polymers possessing Magenta-to-transmissive and Cyan-to-transmissive electrochromic properties is already largely described, few studies focus on materials with cathodically coloring yellow-to-transmissive properties [2],[3], which limit the development of full color displays. This presentation deals with the chemical synthesis and electrochemical characterization of different polymers (homopolymer and copolymer) showing a yellow color and describes a new way leading to a fine tuning of the chromaticity coordinates (L*a*b*) of the thin polymer films. In particular, poly(diaryldithienothiophene)s prepared by oxidative polymerization and electrochemical polymerization will be presented. CIE Chromaticity coordinates, optical contrasts, commutation times and cyclability will be compared depending on the way/media of synthesis (classical solvents or aprotic ionic liquids). The tuning of the yellow color will be realized by a Suzuki copolymerization of a diaryldithienothiophene and a dialcoxyphenyl moiety leading to well defined alternated structures. The elaboration of devices using ionic liquid based polymer gel and achromatic electrochemically reversible counter electrode (vanadium oxide based) will also be realized and discussed. [1] P. M. Beaujuge and J. R. Reynolds Chem. Rev., 2010, 110, 268–320 [2] C. M. Amb, J. A. Kerszulis, E. J. Thompson, A. L. Dyer and J. R. Reynolds, Polym. Chem., 2011, 2, 812–814 [3] H.-M. Wang and S.-H. Hsiao, Polym. Chem., 2010, 1, 1013–1023

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Electrochromism IV : Agustin R. Gonzalz-Elipe, C. Granqvist

14:00

New opportunities for chromogenic optical interference filters

Authors : B. Baloukas, L. Martinu
Affiliations : Department of Engineering Physics, École Polytechnique de Montréal, P.O. Box 6079, Succursale Centre-ville, Montréal, Québec H3C 3A7, CANADA

Resume : Till fairly recently, optical filters have been, for the most part, passive; meaning that their optical performance could not be modulated by the application of an external source of energy. However, the increasing interest in chromogenic materials has resulted in concepts in which their variable optical properties can be combined with optical interference in order to obtain new and novel active (smart) components reacting to changes in temperature, electric current, light, etc. Particularly, angular-color-shifting features have shown high efficiency in the protection of important documents against counterfeiting. All-dielectric and metal-dielectric filters have both found applications in this respect, and we show how these architectures can be converted into active structures by

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implementing, for example, electrochromic WO3 layers. This has indeed been demonstrated by the use of porous and dense WO3, or WO3/SiO2 composites as well as NiOx in replacement of the porous WO3 films. Much less costly and simpler to fabricate metal-dielectric Fabry-Perot-like devices will also be discussed. All of these solutions present an angular color shift and a voltage-driven color change, thus offering two levels of authentication. The progress in security devices coincides well with advances in other areas such as smart windows. For instance, silver-based low-e coatings have been combined with WO3 as a means of obtaining a variable visible transmittance, decreasing the solar heat gain coefficient and replacing the ITO electrode with silver. In another case, TiO2/VO2 multilayers have resulted in an increase of VO2's intrinsically low luminous transmittance. Clearly, chromogenic optical interference filters have much to offer and are yet to be fully exploited.

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14:30 **Anodic electrochromic nickel oxide: the role of film composition and working potential**

Authors : Rui-Tao Wen, Gunnar A. Niklasson, Claes G. Granqvist

Affiliations : Department of Engineering Sciences, The Angstrom Laboratory, Uppsala University, Uppsala, Sweden

Resume : Electrochromic (EC) windows incorporating nickel oxide films are of large interest because of their potential for use in energy-efficient and sustainable buildings. Long-term stability and sufficient optical modulation are needed for these windows. In the past, most work has been done on Ni oxide films immersed in aqueous electrolytes, especially KOH. These electrolytes are suitable for understanding the EC mechanism, but they are not appropriate for practical EC windows, and more research is needed for non-aqueous electrolytes. In this paper, we explore the relationship between composition and electrochemical potential for EC films of Ni oxide. Our films were prepared by reactive DC magnetron sputtering in argon and oxygen. Structure, composition and chemical bonding of the films were determined by XRD, RBS and XPS, respectively. Optical modulation, durability and cyclic voltammetry were recorded and correlated with the compositions of the Ni oxide thin films with the object of optimizing durability and optical modulation. L VII 2

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14:45 **Understanding Electrochromic Nickel Oxides/Hydroxides**

Authors : Sing Yang CHIAM

Affiliations : Institute of Materials Research & Engineering

Resume : In this presentation, I will try to highlight some of the efforts in our group to study electrochromic oxides. In particular, I will examine anodic NiO and Ni(OH)2. We show in our work that cycling of NiO or Ni(OH)2 in aqueous medium leads to activation and degradation phenomenon that is associated with intercalated water. This is more pronounced for films with larger surface area (solution grown) in comparison with the more compact sputtered films. For cycling in a dry environment such as lithium based polymers, we found that the optical response is unlike that observed in the aqueous medium. We show that the presence of absorption sites, such as defects is important for enhanced performances and this is demonstrated for both the solution grown and sputtered films. We also explored nanostructuring approach through solution electroplating using alumina templates. Through this exercise, we showed the important of enhanced surface area in improving the modulation capability of the nickel hydroxides. Finally, we will show some studies of the electronic states of NiO using filled and empty states measurement together with theoretical calculations. We propose that in strongly correlated oxides such as NiO, a shift in spectrum weight is accompanied by the cycling in of the ions in creating hole states. This creates empty conduction band states into the band gap that results in a broad band absorption in the visible spectrum. L VII 3

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15:00 **Enhanced lithium electrochromic performance of flexible Ni oxide films by Fe oxide addition with an atmospheric pressure plasma jet for flexible electrochromic application**

Authors : Yun-Sen Lin*, Pei-Ying Chuang, Ping-Shiun Shie

Affiliations : Feng Chia University, Department of Chemical Engineering

Resume : Enhanced lithium electrochromic performances of the flexible organo-nickel oxide (NiOyCz) films by a rapid co-deposition of organo-iron oxide (FeOyCz) onto 40 ohm/□ flexible PET (polyethylene terephthalate)/ITO (indium tin oxide) substrates at a short exposed duration of 32 s using an atmospheric pressure plasma jet (APPJ) at various concentrations of ferrocence [Fe(C5H5)2] precursors added onto nickelocence [Ni(C5H5)2] precursors were investigated. L VII 4

The APPJ-synthesized organo-nickel-iron oxide ($NiFe_xO_yC_z$) films possess notable electrochromic performance for 200 cycles of reversible Li^+ ion intercalation and de-intercalation in a 1 M $LiClO_4$-propylene carbonate electrolyte by the switching measurements of potential sweep from -1.25 V to 1.25 V at a scan rate of 50 mV/s and the potential step at -1.25 V and 1.25 V. The optical modulation (□T) of 30.9% for NiO_yC_z films at a wavelength of 550 nm was highly improved up to of 42.4% for $NiFe_xO_yC_z$ films as co-synthesized with an APPJ at atmospheric pressure and room temperature (~23 oC).

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15:15

Electrochromic Properties of Amorphous Tungsten Oxide a-WO_{3-x} $(0 \le x \le 1)$ Thin Films Studied under Li Ion Intercalation

Authors : C.A. Triana, C.G. Granqvist, and G.A. Niklasson
Affiliations : Dept. of Engineering Sciences The Angstrom Laboratory Uppsala University P.O. Box 534 SE-75121 Uppsala Sweden

Resume : Amorphous tungsten oxide, a-WO_{3-x}, is one of the most important materials for electrochromic coatings in smart window applications. Because of its switchable optical properties, these films exhibit a wide optical modulation from bleached to colored state by application of a voltage. Here we report on a comprehensive study of the optical transmittance modulation of sub-stoichiometric amorphous tungsten oxides thin films, spanning the range from a -WO_2 to a-WO_3, under Li ion intercalation. For this purpose, thin films of a-WO_{3-x} were produced by reactive DC magnetron sputtering from a pure metallic target of tungsten onto glass substrates covered by transparent conductive indium-tin oxide films. Depositions were carried out at equal pressure, power and argon flow ratio, but using different oxygen flow ratios. Stoichiometry and density of the films were determined by Rutherford Backscattering spectroscopy. Amorphous structures of the thin films were confirmed by X-ray diffraction measurements Film thicknesses were obtained by surface profilometry and were found to have mean values between 300 and 318 nm. Subsequent electrochemical intercalation of Li^+ ions was performed in an electrolyte consisting of lithium perchlorate in propylene carbonate. Optical characterization of the a-WO_{3-x} thin films in the as-deposited and Li^+-intercalated state was performed by transmittance and reflectance measurements in the wavelength range from 300 to 2500 nm. Data from optical measurements were used to calculate the complex dielectric function in the phonon energy range from 0.5 to 4.25 eV. Diminished coloration efficiency and smaller optical transmittance modulation were obtained for thin films with low oxygen content. Charge capacity of the films decreased as their oxygen content was reduced.

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15:30

Dynamic modulation of chromatic coordinates in multifunctional dye-sensitized photoelectrochemical devices

Authors : Michele Manca (a); Simone Valente (a); Mehrdad Balandeh (b); Roberto Giannuzzi (a); Fabio Di Fonzo (b) and Giuseppe Gigli (a)
Affiliations : a) Center for Biomolecular Nanotechnologies @ UniLE, Istituto Italiano di Tecnologia, Via Barsanti snc, 73010, Arnesano (LECCE) - ITALY b) Center for Nano Science and Technology @PoliMi, Istituto Italiano di Tecnologia, Via Giovanni Pascoli 70/3, 20133 Milano, ITALY

Resume : A photovoltachromic cell 1 may potentially act as a complex artificial skin, by generating electric energy as a photovoltaic system but even ‘‘perceiving’’ small variations in external radiation and controlling the energy fluxes by means of a smart variation of their optical transmittance. To this aim we recently developed a specifically designed bi-functional counter electrodes made of two physically separated regions, respectively displaying as a catalytic and an electrochromic function. Incoming solar light is partially harvested by a dye-sensitized photoelectrode made on the front glass of the cell which fully overlaps a bi-functional counter. When the cell is illuminated, the photovoltage drives electrons into the electrochromic stripes through the photoelectrochromic circuit and promotes the Li^+ diffusion towards the electrochromic region, which thus turns in its colored state: At the same time an efficient photovoltaic functionality is executed by the catalytic region. Several different combinations of dyes (basically characterized by complementary absorption spectra) and electrochromic materials (both produced by colloidal routes and by plasma enhanced laser deposition techniques) have been explored along with several specific device architectures. These devices can potentially pave the way to the effective development of large-area multifunctional smart windows to be integrated in the next generation of building glass facades.

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POSTER SESSION : Bernard Dam, Claes Granqvist, Martyn Pemble, Aline Rougier

17:00 **Improved Electrochromic Durability of Nickel Oxide by Iridium Doping**

Authors : Rui-Tao Wen, Gunnar A. Niklasson, Claes G. Granqvist

Affiliations : Department of Engineering Sciences, The Angstrom Laboratory, Uppsala University, P.O. Box 534, SE-751 21 Uppsala, Sweden

Resume : Nickel oxide and iridium oxide are well-known anodic electrochromic (EC) materials. A typical application for EC thin films is in smart windows, which can be used to decrease energy consumption and eliminate glare in buildings and automobiles. A large amount of work has been done on nickel oxide films in order to meet the demands for smart window applications, such as compatibility with cathodic EC films and electrolytes, long-term cycling durability and large optical modulation. However, pure nickel oxide films exhibit poor long-term cycling durability and iridium oxide is considered superior because of its excellent electrochemical stability, chemical resistance and EC cycling speed, but an obvious limitation for iridium oxide is its limited global abundance and high price. The aim of our present work is to improve nickel oxide based anodic EC layers for smart windows applications by doping small amounts of iridium into the nickel oxide lattice. Our films were prepared by reactive DC magnetron sputtering in argon and oxygen. Structure, composition and chemical bonding of iridium doped nickel oxide films were determined by XRD, RBS and XPS, respectively. Optical modulation, durability and cyclic voltammetry were recorded and compared with corresponding data for pure nickel oxide and iridium oxide thin films with the object of optimizing the anodic EC layer for smart windows. L VIII 1

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17:00 **Electrical and optical properties of Nb/Nd-codoped TiO2 thin films grown by pulsed-laser deposition**

Authors : C. Tchiffo-Tameko (1), C. Cachoncinlle (1), E. Millon (1), C. Boulmer-Leborgne (1), J. Perriere (2,3), M. Nistor (4)

Affiliations : 1) GREMI, UMR 7344 CNRS-Université Orléans, 45067 Orléans Cedex 2, France; 2) Sorbonne Universités, UPMC Université Paris 06, UMR 7588, INSP, 75005, Paris, France 3) CNRS, UMR 7588, INSP, 75005, Paris, France 4) NILPRP, L 22 P.O. Box. MG-36, 77125 Bucharest-Magurele, Romania

Resume : Titanium dioxide-based thin films find applications on a large number of devices and components: optical waveguides, piezoelectric transducers, gas sensors, transparent conductive electrodes. TiO2 can be doped by rare-earth elements such as Nd, that leads to intense emissions in IR domain under UV excitation making such films very promising candidates as optically active electrodes for photonic conversion by down-shifting process in silicon based solar cells. Nevertheless the electrical conductivity of Nd-doped TiO2 films has to be improved to be used as a transparent conductive electrode. In this work we attempt to increase the conductivity of Nd-doped TiO2 films by doping with a metal element (i.e. Nb). The Nb/Nd-codoped TiO2 films were grown by nanosecond pulsed-laser deposition. The doping concentration, composition, structure, microstructure and morphology of films were precisely studied. These results are correlated with optical (transparency, photoluminescence under UV excitation) and electrical (resistivity, concentration and mobility of charge carriers) properties. L VIII 2

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17:00 **Protons in Electrochromic Switchable Mirror Device Prepared by DC Magnetron Sputtering**

Authors : Kazuki Tajima, Mika Shimoike, Yasusei Yamada, Kazuki Yoshimura

Affiliations : National Institute of Advanced Industrial Science and Technology

Resume : Our developed electrochromic (EC) switchable mirror has a typical structure of Mg4Ni/Pd/Ta2O5/HXWO3/indium tin oxide on a transparent substrate. These layers act as an optical switching, a catalyst, a solid electrolyte, an ion storage layer, and a transparent conductor, respectively. When a voltage is applied to the device, the protons in the ion storage layer move to the optical switching layer where the MgH2 and Mg2NiH4 are formed. These hydride complexes show better transparency, resulting in the transparent state. In our fabrication methods of the device, we chose some kinds of introducing protons into the layer. For examples, one is a process to fabricate tantalum oxide thin film, the as-prepared film included the protons originated from sputtering chamber depended on vacuum conditions. The other is a solution process such as dilute sulfuric acid solution used to inject the protons L VIII 3 into the layer by electrochemically. The process to inject protons into the layer significantly affected to optical switching properties and durability of the device. In this work, we investigated the optical switching properties and surface structures of the device related to the fabrication process of the device. The protons in the layers were analyzed by RBS, and cross-sectional structure of the layer was observed by TEM.

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17:00

Effect of oxygen on active Al doping concentration of ZnO:Al thin films made by PLD

Authors : M. Kodu, T. Arroval, T. Avarmaa, R. Jaaniso, I. Kink, S. Leinberg, K. Savi, M. Timusk

Affiliations : Institute of Physics, University of Tartu, Riia 142, 51014 Tartu, Estonia

Resume : Polycrystalline c-axis oriented ZnO:Al (AZO) thin films were deposited onto amorphous SiO2 substrates by pulsed laser deposition (PLD) method. Films were deposited at 300 oC in vacuum and oxygen environment using targets doped with 1-10 at% Al. The properties of thin films were studied from the standpoint of transparent electrode applications. According to XRD analysis, Al doping level and deposition atmosphere does not have considerable influence on crystalline quality of our AZO films. As determined by XRF analysis, Al concentration in the films was substantially lower than nominal Al concentration in ZnO:Al PLD targets. Compared to the films grown in oxygen, films deposited in vacuum environment had substantially lower resistivity (σ) and showed significantly different σ dependence on Al concentration – oxygen-deposited films had minimal σ at 0.6 % Al doping concentration, compared to 4.3 % for vacuum deposited films. Also, the carrier concentration (ne) and mobility (μ) dependence on Al doping level were considerably different – a) at all doping levels, ne of vacuum deposited films was higher than of films deposited in oxygen, b) carrier mobility of oxygen deposited films decreased steadily with the increase of Al doping from 0.6 to 5.2 % (μmax at 1% Al) but for vacuum deposited films, mobility was highest at 2.8 % doping level. The results can be explained by higher effective solubility of Al for the films deposited in vacuum conditions. Oxygen deposited films showed high optical transmittance in the visible and near-IR region while transmittance of the vacuum deposited films decreased in near-IR region due to increased reflectance caused by larger carrier concentrations in these films.

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17:00

Effect of Temperature of Electrolyte Solution on the Anodic Deposition of Tungsten Oxide Thin Films

Authors : Kentaro NISHIYAMA,Junji SASANO,Seiji YOKOYAMA,Masanobu IZAKI

Affiliations : Toyohashi University of Technology

Resume : We developed new method to directly form tungsten oxide by anodization in aqueous solution. In order to induce the chemical reaction in which WO42- ions are transformed into WO3•H2O at low pH, pH decrease due to oxygen evolution under anodic polarization was utilized in this method. However, when the solution was prepared at room temperature, WO3•nH2O (n>2) deposited. WO3•H2O is thermodynamically stable at high temperature. In this research, we investigated the influence of temperature on the electrodeposition behaviors. The solution was prepared by dissolving 0.025 mol/L Na2WO4 into ultra-pure water. HCl was added to the solution to adjust the pH to be 1.0. Experiments were performed with a three-electrode cell. F:SnO2-coated glass substrate, Ag/AgCl electrode and stainless steel plate were used as a working, reference and counter electrode, respectively. Potensiostatic deposition was performed at 1.55 V vs. Ag/AgCl for 60 minutes in each solution. Temperature was kept at 30, 40, 50, 60 and 70°C, respectively, throughout the processes of preparing the solution and electrodeposition. The results of XRD indicated that WO3•H2O crystal was deposited at 60°C and higher. SEM images showed the crystal size was from 0.5 to 2.0 um. UV-visible spectroscopy showed that the absorption edge of the WO3•H2O was approximately 500 nm. This study revealed that WO3•H2O were directly formed by anodization from the solution containing WO42- by keeping the solution at high temperature.

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17:00

Optical and electrical properties of Nd doped ZnO thin films

Authors : M. Nistor 1, E. Millon 2, C. Cachoncinlle 2, W. Seiler 3, N. Jedrecy 4,5, C. Hebert 4,5, J. Perrière 4,5

Affiliations : 1 National Institute for Lasers, Plasma and Radiation Physics (NILPRP), L22 P.O. Box. MG-36, 77125 Bucharest-Magurele, Romania; 2 GREMI, UMR 7344 CNRS-Université d'Orléans, 45067 Orléans Cedex 2, France; 3 PIMM, UMR CNRS 8006 Arts et Métiers ParisTech, 151 Boulevard de l'Hopital, 75013 Paris, France; 4 Sorbonne

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Universités, UPMC Univ Paris 06, UMR 7588, INSP, F-75005, Paris, France; 5 CNRS, UMR 7588, INSP, F-75005, Paris, France

Resume : The ZnO films properties can be enhanced or new properties can be obtained by the use of well adapted dopants. For example Nd can be used to increase the ZnO conductivity (Nd3+ in substitution of Zn2+) and to convert the solar spectrum (down conversion of UV photons in near IR photons), or to induce magnetic properties. Transparent Nd doped ZnO (ZnO:Nd) thin films were grown either by pulsed-laser deposition (PLD) or pulsed-electron beam deposition (PED) on Si and c-cut sapphire single crystal substrates at various oxygen pressures and substrate temperatures. The composition, surface morphology and structure of Nd doped ZnO thin films were investigated by means of Rutherford Backscattering Spectrometry, SEM and X-ray diffraction analyses. The ZnO:Nd films are smooth, dense, with the wurtzite phase. Epitaxial relationships between films and c-cut sapphire substrates were evidenced by asymmetric X-ray diffraction measurements. These results have been correlated with optical and electrical measurements. A dielectric model including band gap transitions and free electron excitations was used to simulate the transmittance spectra of ZnO:Nd films in 300-2500 nm range. The resulting optical parameters were compared with those obtained by Hall effect measurements for different growth conditions and Nd doping concentrations.

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17:00 **The Effect of Oxygen Vacancy Defects on Electrochromic Properties of Molybdenum Oxide**

Authors : Binayak Dasgupta, Wai Kin Chim, Eng Soon Tok, Sing Yang Chiam

Affiliations : NUS Graduate School for Integrative Sciences and Engineering, National University of Singapore & Institute of Materials Research and Engineering, A*STAR, Singapore : Electrical and Computer Engineering, National University of Singapore : Department of Physics, National University of Singapore : Institute of Materials Research and Engineering, A*STAR, Singapore

Resume : Molybdenum oxide (MoO3) together with tungsten oxide is one of the limited number of promising inorganic cathodic electrochromic (EC) materials. Together with anodic EC materials such as nickel oxide, it has the potentials to be used in energy saving smart windows technologies. However, unlike tungsten oxide, the colouring mechanism is less explode and understood. This is particular so for understanding how the presence of oxygen vacancy defect and structural properties effects the coloration efficiency and mechanisms. In this work, we present an in-depth investigation of the electrochromisum in MoO3. We investigate how the electronic structure of sputter deposited MoO3 thin films changes during the EC cycling. Also we investigate how different levels of oxygen vacancy defects, from near stoichiometry MoO3 with low level of localised defects to semi-metallic MoO2 with high levels of ordered defect, affect the EC performance. These investigations give us a better understanding of the fundamental EC mechanisms in MoO3 thin films. L VIII 7

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17:00 **Unprecedented Reversible Thermochromic Response of Polydiacetylenes with Molecular Level Understanding**

Authors : Sunhi Park, Songyi Lee, Joonseong Lee, Minji Lee, Yu Kyung Cho, Junwoo Baek, Jinwook Kim, Sungnam Park

Affiliations : Myung Hwa Kim; Rakwoo Chang; Juyoung Yoon

Resume : Polydiacetylenes(PDAs), a family of conjugated polymers, have very unique electrical and optical properties. A variety of sensory systems based on PDAs have suggested because of its distinct colorimetric change. In this study, we prepared a new type of PDA, Bis-PDA-Ph, which contains two PDA moieties and p-phenylene group, and is good at thermochromic system. This PDA-embedded electrospun fibers were prepared by Bis-PDA-Ph and poly(ethylene oxide)(PEO) solution in capillary. The interaction between alkyl chains in Bis-PDA-Ph stimulates it to form electrospun fibers, and those fibers display thermochromic reversibility between 20-120 ℃. It's broad temperature range is a benefit from other reported PDA sensors. Polymer's well-packed structure also induced a clear blue to red colorimetric transition. To elucidate thermochromic response, we have conducted a theoretical simulation of the new PDA. Furthermore, transient absorption(TA) and fluorescence measurements were employed to analyze the temperature-dependent change of the new PDA. Finally, We confirmed that Bis-PDA-Ph undergoes a exceptional change in response to temperature, which is reversible with a blue to red colorimetric transition. References 1) Lee, S.; Lee, J.; Lee, M.; Cho, Y, K.; Baek, J.; Kim, J.; Park, S.; Kim, M, H.; Chang ,R.; and Yoon, J. Advanced Functional Materials, L VIII 8

2014, in press 2) Xu, Q.; Lee, S.; Cho, Y, K.; Kim, M, H.; Bouffard, J.; Yoon, J. J. Am. Chem. Soc. 2013, 135(47), 17751-17754.

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17:00 **Theoretical study of the electronic structure of Cr3+ doped in silicate glasses**

Authors : Olfa Taktak*, Hajer Souissi, Souha Kammoun

Affiliations : Applied Physics Laboratory; Physics Group luminescent materials; Faculty of Sciences of Sfax Tunisia;

Resume : Silicate glasses are used in many applications such as in optics as lenses or beam splitters, in telecommunications as optical fibers, in micro and optoelectronics and in near IR windows due to their low optical attenuation and optical dispersion. The doped transition metal in glasses affect to color and physical proprieties. From the transition metal Cr3+ produces green color in silicate glasses and it is largely used in these glasses due to its favorable absorption and emission properties. A recent work demonstrated that the Cr3+ ion occupy a site with Oh symmetry in these glasses. The spectrum of Cr3+ exhibits two broad and intense bands which impart glasses their characteristic green color. These bands are assigned to the spin-allowed, d-d transitions of octahedral Cr3+ , 4A2g(4F) → 4T2g(4F) and 4A2g(4F) → 4T1g(4F). Additional weak feature occur in the low energy side of the 4T2g(4F) band and is assigned to the 4A2g(4F) → 2Eg(2G) transition. In this work, we present a detailed crystal-field analysis of the electronic energy levels of Cr3+ in alkalin silicate glasses. This analysis based on the Racah theory was carried out for the Chromium (III) centre with a Oh site symmetry. The objective of this theoretical analysis is to determine the Racah and the crystal field parameter. Therefore, to deduce the Stark levels which are not observed experimentally. The interference dip observed in the 4T2g(4F) band is also studied.

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17:00 **Influence of the Cr doping technique on light-emission properties of ZnSe crystals**

Authors : I. Radevici, K.Sushkevich, H. Huhtinen, D. Nedeoglo, P. Paturi

Affiliations : Wihuri Physical Laboratory, Department of Physics and Astronomy, University of Turku, FI-20014, Turku, Finland; Faculty of Physics and Engineering, Moldova State University, Mateevici str. 60, MD-2009, Chisinau, Republic of Moldova

Resume : Diode-pumped tunable solid state lasers for the infrared (IR) spectral range on the base of Zn and Cd chalcogenides, doped with transient metals, for example, Cr2+ and Fe2+, have many advantages comparing to another tunable generators of IR emission, e.g. low production cost, flexible pulse format. One of the main obstacles on the way of mass production of the laser systems based on zinc selenide crystals doped with Cr is well known troubles in equilibrium doping of large band-gap II-VI compounds. Luminescent properties of the 4 series of ZnSe:Cr crystals with various concentrations of the doping impurity in 0.03 – 0.30 at. % range within the temperature interval from 6 K to 300 K are studied. Chromium doping is performed in various technological processes: during the growth by chemical vapor transport method; during the growth from melt; by thermal diffusion from the Bi+Cr melt or by thermal diffusion from gas. It is shown that a broad IR band, located at ~2 μm and characteristic for the emission spectra of ZnSe:Cr crystals, is complex. It was argued that this band consists of both intrashell emission of Cr2+ ions, which are activators for mid-IR emission band, and emission caused by complexes based on zinc vacancies and background impurities. Obtained results show that emission of ZnSe:Cr crystals is determined not exclusively by the doping impurity, but strongly depends on structural defects of the doping crystals, their concentrations, and sets of background impurities.

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17:00 **Influence of the d- and f- doping impurities interaction on light-emission properties of ZnSe:Cr:Yb crystals**

Authors : I. Radevici, K.Sushkevich, H. Huhtinen, D. Nedeoglo, P. Paturi

Affiliations : Wihuri Physical Laboratory, Department of Physics and Astronomy, University of Turku, FI-20014, Turku, Finland; Faculty of Physics and Engineering, Moldova State University, Mateevici str. 60, MD-2009, Chisinau, Republic of Moldova

Resume : Recently, materials doped with rare-earth elements (REE) are of renewed interest, mostly because of their potential application as solid-state lasers active media. Co-doping of laser crystals with chromium and REE allows combination of the functionality of the active media and Q-switching into the single functional element of the laser system, this lead to intensive research of YAG:Cr:Yb and GGG:Cr:Yb crystals. Main disadvantage of the garnet-like materials is the need of optical pumping, but this may be avoided in the case of co-doping of wide band-gap semiconductors with d- and f- ions. The

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luminescent properties of ZnSe, ZnSe:Cr, ZnSe:Yb and ZnSe:Cr:Yb crystals, doped during the growth process by the chemical vapor transport method, were studied within the temperature interval of 6 - 300 K. At the liquid helium temperature a band with maximum close to 1.7 µm is observed in the mid-IR PL spectrum of the ZnSe:Cr:Yb crystal. This band overlapps with the complex band in the mid-IR spectral range, which is characteristic for the chromium doped crystals. Large FWHM of the IR band in the PL spectrum of ZnSe:Cr:Yb crystals, as well as its approximately unchanged intensity within 1.6 — 2.4 µm range, shows that this emission may be used for development of the tunable solid state lasers for the IR spectral range. A model which explains formation of this band as a result of emission transitions between Cr+ (stabilized by Yb3+) and Cr2+ is proposed.

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17:00 **Intrinsic optical and structural properties of VO2 films on 2D hexagonal substrate** L VIII 12

Authors : Hyeongkeun Kim1, Yena Kim1,2, Seung Ho Han1, Dae Ho Yoon2, and Woo Seok Yang1

Affiliations : 1 Electronic Materials and Device Research Center, Korea Electronics Technology Institute 2 School of Advanced Materials Science and Engineering, Sungkyunkwan University

Resume : Vanadium dioxide (VO2) is a metal-insulator transition (MIT) material, displaying a reversible switch in optical transmittance/reflectance in the infrared range near room temperatures. This property makes VO2 potentially useful for ‘smart’ optical switches. Large-scale fabrication of VO2 on mechanically flexible substrates is critical to the realization of flexible smart window films that can respond to environmental temperatures to modulate light transmittance. The 2D hexagonal substrate such as graphene and h-BN effectively function as an atomically thin, flexible, yet robust support which enables the formation of stoichiometric VO2 crystals with temperature-driven phase transition characteristics. In this paper, we report a new method for the production of VO2 films on a flexible substrate using 2D hexagonal substrate. For this work, we made VO2/graphene (or h-BN) hybrid film by utilizing chemical vapor deposition (CVD) and sputtering processes. The morphologies of the VO2 film were examined by field-emission scanning electron microscope (FE-SEM), atomic force microscope (AFM), laser scanning microscope (LSM), and transmission electron microscopy (TEM). Identification of the structural phase was performed using Raman spectroscopy, X-ray diffraction (XRD).

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17:00 **Comparison of EC devices based on sprayed and sol-gel processed WO3 electrodes** L VIII 13

Authors : G. Bodurov, Y.E. Romanyuk, A.N. Tiwari, E. Jung, D. Nadargi, M. Koebel

Affiliations : EMPA - Swiss Federal Laboratories for Materials Science and Technology

Resume : Sprayed and sol-gel deposited WO3 thin films are promising low-cost cathodic electrode materials for electrochromic (EC) devices used in “smart windows”. Although numerous sprayed and sol-gel WO3 thin films have been investigated, only a limited number of reports on EC devices exists in the literature. This is mainly because of the inherent challenges of spray and sol-gel deposition methods, such as film uniformity, the need of post-treatment leading to a rather complex interplay of technological parameters. In this paper WO3 thin layers were deposited by sol-gel and spray methods from poly-tungstic acid precursor solutions, and subjected to a high temperature annealing at 450°C. Average film thicknesses of 300 nm were tailored. SEM analysis confirmed the desired values and gave evidence for good film quality and adhesion to the substrate. XRD measurements confirmed the desired WO3 crystal phase, whereas UV-Vis spectrophotometry was used to determine transmittance and reflectance of the films. Electrochromic devices were fabricated in the configuration Glass/FTO/ WO3/Electrolyte/Pt/FTO/Glass with both, model liquid and solid electrolytes. The EC performance of sprayed and sol-gel-based prototypes was compared in terms of their optical switching modulation, transmittance/reflectance, response time, and coloration efficiency.

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17:00 **Low toxicity electrolytes for electrochromic devices** L VIII 14

Authors : Laura Manceriu, Abdeladine Danine, Aline Rougier

Affiliations : CNRS, Universit? de Bordeaux, ICMCB, 87 avenue du Dr. Albert Schweitzer, F-33608 Pessac, France

Resume : Lately the interest for low cost and non-toxic electrolytes has been growing especially for applications such as electrochromic (EC) devices or lithium batteries. In this category the natural polymers such as gelatin, chitosan or starch are ideal candidates because they are biodegradable and easy accessible. Already these natural polymers have been used to obtain Li and H based electrolytes with ionic conductivities (σ) in the range of 10-5 S/cm-1 and their functionality in EC devices has been proven. In this work aqueous based gels were prepared from cellulose nanofibers, glycerol, gelatin and NaCl/LiCl as precursor for ions using a facile synthesis method. The concentration of each component has been varied in order to optimize the gel stability and conductivity. AC conductivity measurements have been carried at room temperature by using stainless steel as blocking electrodes. The optimized gel electrolyte has been successfully used in the assembly of an EC device. The coloration/bleaching kinetics and contrast were correlated with the gel electrolyte ionic conductivity.

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17:00 **Low-haze optically passive powdered coatings on the basis of cerium oxide**

Authors : M. Mihelčič, A. ?urca Vuk, B. Orel

Affiliations : National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana, Slovenia

Resume : The electrochromic society was during recent years engaged with the preparation of EC devices on polymeric substrates. Since these are light-weight and flexible wet chemical roll-to-roll deposition seems the most suitable option to produce commercial smart windows at an acceptable price. In case of transition metal oxides, the crystalline coatings with reversible intercalation properties have usually been produced by sintering above 300?C. Since such temperatures overwhelmed the thermal stability of polymeric substrates, we developed a simple two-step process for deposition of so-called ?electrochromic paints?, which has already been reported for substoichiometric Ni1-xO pigmented coatings1,2. In the first step we produce crystalline particles via peroxo or sol-gel route at temperatures >300?C, followed by milling of crystalline particles in the presence of appropriate dispersant to obtain a nanocrystalline dispersion. Thermal treatment can be accomplished at 150?C, which corresponds to polymeric substrate. Since the preparation of any low-haze functional coatings from pigments on polymeric substrates is not trivial, in this work we present the applicability of the described preparation process to various cerium oxide-based coatings (CeO2, Ce/Ti-oxide,?). The deposited coatings were investigated with the aim to observe their haze and electrochemical characteristics. 1 Mihelčič et al., Sol. Energy Mater. Sol. Cells 107 (2012) 175. 2 Mihelčič et al., Sol. Energy Mater. Sol. Cells 120 (2014) 116.

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17:00 **Optical Properties of Photochromic Oxygen-containing Yttrium hydride Thin-films**

Authors : N. Law, H. Schreuders, B. Dam

Affiliations : MECS, Chemical Engineering, TU Delft, Netherlands

Resume : In a recent study the photochromic properties in reactively sputtered yttrium hydride thin films were reported [1]. The incorporation of a substantial amount of oxygen appeared vital for the observation of this effect. Exposure to visible and ultraviolet (UV) light at moderate intensity triggers a uniform decrease in the optical transmission of visible and infrared (IR) light. The reaction is reversible and samples that are left in the dark return to the initial transparent state. Potential applications range from smart windows to sunglasses. The effect observed in YOyHx is unique, since it shows reversible photochromism induced by light from the visible part of the optical spectrum and displays colour neutrality: The transmission decreases for all wavelengths with energies E < Egap. This suggests some opto-electronic phase segregation of metallic entities in a dielectric matrix. Here, we investigate the wavelength dependence of the photochromism on samples with slightly varying bandgaps. We observe in all case a substantial darkening at wavelengths below the gap. References 1. T. Mongstad, C. P. Bjorkman, J. P. Maehlen, L. P. A. Mooij, Y. Pivak, B. Dam, E. S. Marstein, B. C. Houback, S. Zh. Karazhanov, Sol. Energy Mater. Sol. Cells 95 (2011) 3596.

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17:00 **Effect of Al oxide top coatings on the durability of thermochromic VO2 thin films**

Authors : Yu-Xia Ji, Shu-Yi Li, Gunnar A. Niklasson, Claes G. Granqvist

Affiliations : Department of Engineering Sciences, The Ångström Laboratory, Uppsala University, P.O. Box 534, SE-75121 Uppsala, Sweden

Resume : Thermochromic VO2 films deposited by sputtering was exposed to heat treatment under harsh dry and humid conditions. In the harsh ambient conditions, the VO2 films, 80-nm-thick, converted to non-thermochromic V2O5 rapidly. It was found that good protection of the thermochromic VO2 film was achieved by applying a protective top coating consisting of 30-nm-thick

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sputtered aluminium oxide. The top coating delayed the oxidation for more than one day upon heating in dry air at 300 °C. The protection of the thermochromic properties of the VO2 film occurred for several days at 95% relative humidity and 60 °C. The thickness of the Al oxide protective layer is of importance and, expectedly, increased thickness yields an enhanced protection. Our results are important for TC fenestration as well as for other technical applications.

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17:00 **Growth of copper oxide thin films by reactive sputtering: control of the texture and structure-properties relationship** L VIII 18

Authors : Y. Wang1, J. Ghanbaja1, S. Migot1, P. Boulet1, P. Miska1, D. Horwat1, F. Soldera2, F. Mücklich2, J.F. Pierson1

Affiliations : 1 Institut Jean Lamour, Université de Lorraine, Nancy, France 2 Department of Materials Science, Saarland University, Saarbrücken, Germany

Resume : The binary Cu-O system contains two stable phases (Cu2O and CuO) and one metastable phase (Cu4O3) that may be suitable as p-type TCO. These three copper oxides can be deposited by adjusting the oxygen flow rate introduced into the sputtering chamber. Although some of the properties of the Cu4O3 phase have been described, the relationship between the film microstructure and their properties is scarcely described. This presentation aims to study the effect of the deposition conditions on the films microstructure and on films properties. As a function of the oxygen flow rate and the total pressure, 3 main deposition zones corresponding to the 3 oxides have been evidenced by X-ray diffraction and Raman spectrometry. Within these domains, the films exhibit a columnar microstructure. Pole figure analyses show that the texture of the 3 oxides can be tuned by adjusting the deposition parameters. For Cu2O films, the preferred orientation changes from [100] to [111] by increasing the total pressure. At the border of the 3 zones, a biphased domain has been systematically evidenced by Raman spectrometry (Cu2O + Cu4O3 or Cu4O3 + CuO). The relationship between the microstructure and the electrical and optical properties of the films is discussed. Finally, a homoepitaxial growth of Cu2O has been evidenced by transmission electron microscopy observations in cross section.

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17:00 **Tungsten-oxide-based monolithic solid-state electrochromics deposited on single substrate** L VIII 19

Authors : Seung Ho Han1, So Hee Kang1,2, Sang Jiun Lee1,3, Hyeongkeun Kim1, Dae Ho Yoon2, Sahn Nahm3, Woo Seok Yang1

Affiliations : 1Electronic Materials & Device Research Center, Korea Electronics Technology Institute, Korea 2School of Advanced Materials Science and Engineering, Sungkyunkwan University, Korea 3Department of Materials Science and Engineering, Korea University, Korea

Resume : Electrochromic materials, which can reversibly change their optical properties under an applied electric field, have attracted in various applications such as smart windows, optical displays and rear-view mirrors. Electrochromic devices (ECDs) contain an electrochromic film in contact with an electrolyte adjacent to an ion storage layer, and these three layers are sandwiched between the two transparent conducting films. For the simple and large-scale fabrication, ECDs which consist of all solid-state materials are advantageous. In this study, monolithic solid-state form of ECDs was fabricated on single glass substrate by magnetron sputtering. The ECDs exhibited the multilayer structure of ITO/WO3/Ta2O5/NiO/ITO on glass substrate. The WO3, Ta2O5 and NiO were used as electrochromic, solid electrolyte and ion storage layer, respectively. Sputtering conditions, such as DC/AC power, Ar/O2 gas flow rate and deposition time were optimized for the enhanced performance of ECDs. The cyclic voltammetry was performed using a potentiostat with a standard three-electrode configuration. The WO3 and NiO films were deposited on ITO glasses served as the working electrodes, respectively. Pt was used as the counter electrode, Ag/AgCl was the reference electrode and the electrolyte was 1M LiPF6/PC. The transmittance spectrum of as prepared and after colored ECDs was characterized by a UV/VIS/NIR spectrophotometer.

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17:00 **Thickness dependence simulations of the optical properties for a suspended particle device derived from scattering and absorption coefficients** L VIII 20

Authors : David Barrios a, b,*, Ricardo Vergaz b, Jose M. Sanchez-Pena b, Braulio Garcia-Camara b, Claes G. Granqvist c, Gunnar A. Niklasson c

Affiliations : a Facultad de Inform?tica y Electr?nica, Escuela Superior Polit?cnica de Chimborazo, Riobamba, Ecuador b Grupo de Displays y Aplicaciones Fot?nicas, Departamento de Tecnolog?a Electr?nica, Universidad Carlos III de Madrid, C/Butarque

15, E-28911 Legan?s, Madrid, Spain c Department of Engineering Sciences, The Angstrom Laboratory, Uppsala University, P.O. Box 534, SE-75121 Uppsala, Sweden

Resume : Suspended particle devices (SPDs) constitute an electrically powered chromogenic technology, in which the active layer quickly switches from a bluish -black dark color to a clear grey color when an AC electric field is applied. Refractive index and extinction coefficients, in addition to scattering and absorption coefficients, were derived from four flux and two flux models. They were used in model calculations to predict the direct and the total (and hence the diffuse) components of the transmittance and the reflectance, together with the color appearance and the haze, as a function of thickness of the active layer. The optimum thickness for the SPDs performance can be determined in this way.

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17:00 **Transparent p+-TiN:SnO2/n+-ITO tunnel diode**

Authors : Chih-Yi Hsieh, Chin-Han Liao, and Cheng-Yi Liu

Affiliations : Department of Chemical and Materials Engineering National Central University, Jhong-Li, Taiwan

Resume : Many invisible electronic devices have been developed in recent years, such as, transistors and p-n junctions. Yet, so far, no transparent tunnel diode has ever been reported. In this work, we demonstrate an unique approach to fabricate a transparent p+-TiN:SnO2/n+-ITO tunnel diode. The p+-TiN:SnO2 thin film formed by annealing a SnO2/TiN multi-layer structure. The hole carriers in the p+-TiN:SnO2 thin film are mainly generated by the N3--O2- substitution reaction. The p+-TiN:SnO2 thin film has low resistivity (0.2 Ω•cm) and high hole concentration (1.52×1019 cm-3). The I-V characteristics of the p+-TiN:SnO2/n+-ITO junction exhibits distinct tunnel diode characteristics. In addition, the overall transmittance of the p+-TiN:SnO2/n+-ITO tunnel diode is higher than 80% in the visible region. The transparent p+-TiN:SnO2/n+-ITO tunnel diode can be further applied in transparent tunnel field-effect transistor (TFET) and other invisible electronics.

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add to my program **(close full abstract)**

17:00 **Nanocomposite WO3-TiO2 material with electrochromic responses**

Authors : Mateja Hocevar1, Andreas Georg2, Marko Topic1, Ursa Opara Krasovec1

Affiliations : 1 University of Ljubljana, Faculty of Electrical Engineering, Trzaska 25, SI-1000 Ljubljana, Slovenia; 2 Fraunhofer Institute for Solar Energy Systems, Heidenhofstr. 2, 79110 Freiburg, Germany

Resume : We have successfully developed electrochromic (EC) nanocomposite material via the peroxo sol-gel synthesis. Stable WO3-TiO2 sols were realized by the addition of Ti-alkoxide to the peroxotungstic acid solution, which were further modified with different solvents in order to obtain suitable sols for dip-coating deposition of transparent crack-free layers. We will present systematic study of the WO3-TiO2 sols formulation by varying the amount of Ti in WO3 and report the influence of sol composition on layer structure and consequently on the EC properties of the layers. It will be shown how the integration of Ti into the WO3 influences the crystal structure of the WO3. We assume two alterations: (i) the change of the WO3 crystalline structure or/and (ii) the formation of two phase system. Newly developed WO3-TiO2 layers will be thoroughly characterized. IR spectroscopy will be employed to monitor the sol-gel synthesis processes. The structure and morphology of the layers will be analyzed by the SEM, while the XRD will be used to record the crystalline structure of the WO3-TiO2 layers. The EC properties of the layers will be evaluated using in-situ UV-VIS electrochemical set-up. In addition, we will study the possibility of integration of the developed layers into photoelectrochromic system, which combines EC and photoactive layer1. The first results reveal that the addition of Ti in WO3 layer improves its EC properties. 1. A. Hauch et al., Electrochim. Acta 46 (2001) 2131.

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add to my program **(close full abstract)**

17:00 **Thermochromic Oxides for 150 to 500 °C Range**

Authors : Isil Top1, Halime S. Kocadag, Elif Kilic, and Mehmet A. Gulgun

Affiliations : 1Isil Top, Faculty of Engineering and Natural Sciences, Sabanci University, Tuzla, Istanbul, 34956, TURKEY. Halime S. Kocadag,Faculty of Engineering and Natural Sciences, Sabanci University, Tuzla, Istanbul, 34956, TURKEY. Elif Kilic, Faculty of Engineering and Natural Sciences, Sabanci University, Tuzla, Istanbul, 34956, TURKEY. Mehmet A. Gulgun, Faculty of Engineering and Natural Sciences, Sabanci University, Tuzla, Istanbul, 34956, TURKEY. Halime S.Kocadag,Elif Kilic, Mehmet A. Gulgun,

L VIII 23

Resume : Oxides of certain transition metals show reversible colour change as a function of temperature. The so-called thermochromism was observed in CoAl2O4-Bi2O3 blends, in TiO2- V2O5 and V2O5-Nb2O5 systems. The three separate systems studied in this work show reversible thermochromism in the temperature range of 150 °C to 500 °C. All three systems exhibited hysteresis behaviour in their transition temperature. CoAl2O4-Bi2O3 blends allowed a certain degree of tuning for the transition temperature. As the ratio of the CoAl2O4:Bi2O3 was increased, the temperature of perceived colour change shifted to higher temperature from 200 °C to 400 °C. The V0.48Ti0.52O2 oxide system show reversible colour change (yellow to deep orange) in the temperature range 150-160 °C with the smallest hysteresis in the transition temperature. The phase analysis of the oxide powders were done by using XRD and electron diffraction studies. The origin of thermochromism was investigated with the help of the UV-VIS Spectroscopy and electron microscopy.

add to my program **(close full abstract)**

17:00 **Deposition and properties of electhrochrommic Tungsten and Molybdenum oxide thin films** L VIII 24

Authors : Z. Labadi, A. Subrahmanyam (*), Cs. Major, M. Takács, A.L. Toth, I. Bársony

Affiliations : Research Centre for Natural Sciences, Institute for Technical Physics and Materials Science (MFA) P.O.B. 49, H-1525 Budapest, HUNGARY; * Indian Institute of Technology, Madras Dept of Physics, IIT Madras 600036 Chennai, INDIA

Resume : Electrochromism is defined as the ability of a material to change its optical state in response to an applied DC voltage. The requirement towards electro-chromic materials is high coloration efficiency (~ 150 cm2/ Coulomb) and quick response time (~ seconds). The main physical properties that control the charge movement in the lattice are: density and porosity of the lattice. Amorphous lattice is preferred for high coloration efficiency. Tungsten oxide (WO3), due to its multiple oxidation states, is the most widely studied EC material. Relatively less attention is paid however to the properties of industrially viable sputtered layers. Molybdenum Oxide films were deposited by reactive DC magnetron sputtering while Tungsten Oxide films were made by sol-gel deposition technique. Deposited films were characterized by ellipsometry, SEM and TEM microscopy, van der Pauw measurements and by cyclic voltammetry for electrochromic properties. The present study aims to establish optimized parameters for the depositions, together with an ellipsometric model enabling in situ process control. Correlation between the sputtering parameters (oxygen pressure, power), the sol-gel methodology and the density and porosity of the lattice will be analyzed for establishing enhanced electro-chromic performance.

add to my program **(close full abstract)**

17:00 **Prototype Vanadium Dioxide Nanoparticle Thermochromic Smart Window** L VIII 25

Authors : Rafaël Sibilo, Alaric Taylor, Michael Powell, Ivan Parkin, Ioannis Papakonstantinou

Affiliations : UCL; UCL; UCL; UCL; UCL

Resume : For energy efficient glazing purposes a small-scale prototype nanoparticle smart window is fabricated and tested. Thermochromic phase changes of the embedded nanoparticles facilitates highly-efficient solar-thermal transmission modulation while maintaining glazing transparency. Finite Difference Time Domain (FDTD) simulations are conducted in order to formulate design rules and predict the optical behaviour of the VO2 nanoparticle system. Subsequently, VO2 nanoparticles are incorporated into a plastic host. Comprehensive optical studies are presented.

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17:00 **Chirality control in mixed system of achiral bent-core mesogen and photo-reponsive rod-like molecule** L VIII 26

Authors : Ki-Beom Kim, Myoung Hoon Song, Seong Jun Kang, Suk-Won Choi

Affiliations : Department of Advanced Materials Engineering for Information and Electronics, Kyung Hee University, Yongin, Republic of Korea: School of Mechanical and Advanced Materials Engineering, UNIST, Ulsan, Republic of Korea

Resume : Enantioselective segregation has been obtained in the Bx phase of mixture consisting of an achiral bent-core molecule and photo-responsive rod-like molecule without introducing any chiral species. This mixture exhibits liquid crystal (LC) polymorphism; the higher temperature nematic (N) phase, and the lower temperature Bx in which spontaneous chiral segregation with (+) and (-) chiral domains occurs with equal probabilities. The imbalance between the chiral domains in Bx was achieved by following method; the mixture was irradiated in the N phase with right- or left circular polarized light, and while maintaining the irradiation, the B2 phase was allowed to cool below the N-Bx phase transition temperature.

add to my program **(close full abstract)**

17:00

Coupled excited states in Nickel (II) complexes probed by absorption spectroscopy

Authors : Nour Gharsallah*, Hajer Souissi, Souha Kammoun

Affiliations : Laboratoire de Physique Appliquée, Groupe de physique des matériaux luminescents Faculté des Sciences de Sfax, B. P ; 802, 3018 Sfax, Tunisie.

Resume : Absorption spectra with weak spin-forbidden and more intense spin-allowed transition bands are observed for many different octahedral transition metal complexes. The simplest electron configurations showing these two different types of transitions are d2 and d8 with singlet and triplet excited states. The optical absorption spectrum of [Ni(H2O)6]2+ was performed and shows a three spin allowed transition bands. The middle transition 3A2g → 3T1g (3F) shows a complicated band shape with two maxima and an interference dip. Based on the Racah theory, the theoretical crystal field analysis was established. This study leads to deduce the [Ni(H2O)6]2+ electronic structure . The interaction origins between excited states with different spin multiplicity were investigated with modern theoretical models based on coupled potential energy surfaces.

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17:00

Electrochromic properties of non-stoichiometric Nickel oxide (NiO) thin films in various electrolytes

Authors : M. Da Rocha, L. Manceriu, H. Moulki, A. Rougier

Affiliations : ICMCB- CNRS, 87 av. Du Dr. Schweitzer, 33608 Pessac, France

Resume : NiO is a well known anodic electrochromic (EC) material showing optical modulation in the visible under electrochemical oxidation and reduction [1]. Commonly associated in inorganic EC devices, the WO3/NiO combination still suffers from the different stabilities of both oxides in acidic and basic media. In our group, unusual reactivity for non-stoichiometric Ni1-XO thin films cycled in various electrolytes was recently reported opening the choice of materials for complete devices [2]. Ni1-XO thin films were deposited by sputtering and pulsed laser deposition on ITO-glass substrate. The influence of various deposition parameters on the stoichiometry, morphology and crystallinity of Ni1-XO thin films was studied and correlated to their EC behavior. The comparison of the electrochemical properties of Ni1-XO films cycled in aqueous (KOH), lithium based and lithium free ionic liquid electrolytes, shows various mechanisms whereas optical contrast from colorless to brownish remains in all cases. Herein, the relationship between the physico-chemical properties and EC performances of non-stoichiometry Ni1-XO thin films will be discussed. Finally, behavior in full devices will be reported. [1] C.G. Granqvist, Handbook of inorganic electrochromic materials, Elsevier, Amsterdam, Netherlands, 1995 [2] Moulki, H., Faure, C.,Mihelčič, M., Vuk, A.S., Švegl, F., Orel, B., Campet, G.,Rougier, A. Electrochromic performances of non-stoichiometric NiO thin films, Thin Solid Films, http://dx.doi.org/10.1016/j.tsf.2013.10.154

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17:00

Origin of the photochromic properties of PbMoO4 and Pb2MoO5 crystals

Authors : S. Nedilko (1), Yu. Hizhnyi (1), V. Chornii (1), M. Trubitsyn (2), I. Volnyanskaya (2)

Affiliations : (1) Taras Shevchenko National University of Kyiv, Volodymyrska Street 64/13, 01601, Kyiv, Ukraine; (2) Oles Honchar Dnipropetrovsk National University, Naukova Street 9, 49050, Dnipropetrovsk, Ukraine

Resume : Under irradiation by the UV light, the lead molybdate crystals reveal in some cases a strong photochromic effect related with creation of multiple color centers [1]. In this work, the origin of photochromic effects in PbMoO4 and Pb2MoO5 crystals, namely the origin of additional bands in their optical absorption spectra is revealed in complex experimental and computational studies. The set of PbMoO4 and Pb2MoO5 single-crystalline samples was grown by the Czhochralskii technique with stoichiometric composition of initial components as well as with excess of MoO3 oxide in initial batch. The effect of irradiation by the UV ligth and high-temperature annealing on the optical absorption spectra of synthesized samples is studied. The electronic structures and optical constants of PbMoO4 and Pb2MoO5 crystals are calculated by the FLAPW method [2]. Besides crystals with perfect lattices, the oxygen-deficient compounds PbMoO4:Vo and Pb2MoO5:Vo are considered in geometry-optimized calculations. Origin of irradiation- and temperature-induced color centers in both types of lead molybdate crystals is revealed in comparative analysis of experimental and computational results. It is assumed that additional bands in optical absorption spectra of PbMoO4:Vo and Pb2MoO5:Vo are formed by electronic transitions in the oxygen-deficient molybdate groups of the crystals.

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[1] T.M. Bochkova, et al, Phys. Sol. St. 45 (2003) 244-247. [2] P. Blaha, et al, 2001. ISBN 3-9501031-1-2.

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17:00 **Structural Properties of MBE-Grown Epitaxial Cr2O3 Thin Films on Al2O3**

Authors : Chen-Yi Su, Leander Dillemans, Ruben Lieten, Pía Homm, Tomas Smets, Mariela Menghini, Jean-Pierre Locquet

Affiliations : Department of Physics and Astronomy, Katholieke Universiteit Leuven, Celestijnenlaan 200D, B-3001, Leuven, Belgium

Resume : Cr2O3 is an interesting material for various applications, such as spintronics and bipolar switching devices. The common corundum structure also makes it an interesting candidate for epitaxial growth on sapphire. In this work, we investigate the effect of the growth temperature and the oxygen pressure on the crystallinity of Cr2O3 thin films. 65 nm Cr2O3 films were deposited on (0001)-Al2O3 substrates by MBE. Cr was evaporated at a rate of 0.1 Å/s, and reacted with O2 in the range of 7 x 10-7 to 2 x 10-6 Torr. The substrate temperature varied from 620 to 820 °C. Structural properties were characterized by X-ray diffractometry. X-Ray diffraction showed a high intensity Cr2O3 (0006) peak with finite size oscillations around it, which indicate a high degree of flatness of the epitaxial film. Increasing the temperature and oxygen pressure during growth both result in negative shifts of the Cr2O3 main peak in the θ-2θ spectra. The out-of-plane lattice spacing reveals small tensile strain along the c-axis. The Cr2O3 thickness was confirmed to be between 61.3 and 68.3 nm from X-ray reflectivity with a density in agreement with that of the bulk phase. The results of the single layers were then compared with bilayers consisting of a similar Cr2O3 layer and a thin V2O3 layer. In conclusion, we demonstrate smooth epitaxial Cr2O3 films grown on Al2O3, which is an essential step for the further integration of additional functional oxides towards multi-functional devices. L VIII 30

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17:00 **Self-Supported Electroreflective Devices in the Mid Infrared using PEDOT, PProDOT-Me2 or their blend**

Authors : Layla Beouch, Nela Roy, Pierre-Henri Aubert, Frédéric Vidal, Claude Chevrot

Affiliations : Laboratoire de Physicochimie des Polymères et Interfaces (LPPI), Université de Cergy-Pontoise 5 mail Gay Lussac, Neuville sur Oise, 95031 Cergy-Pontoise Cedex, France

Resume : A promising alternative to multi-layered devices showing variable electroreflective properties in the MIR results from the design of a self-supported semi-interpenetrating polymer network (semi-IPN) associating a polyethylene oxide / Nitrile Butadiene Rubber (PEO/NBR) semi-IPN (matrix) and an electronic conductive polymer (ECP) formed within. This presentation relates to the elaboration of such semi-IPN in which a linear ECP : poly(3,4-ethylenedioxythiophene) (PEDOT), poly(2,2-dimethyl-3,4- propylenedioxy-thiophene) (PProDOT-Me2) or a blend of PProDOT-Me2 and PEDOT is formed symmetrically and selectively as very thin layers to the two faces of a film matrix. After swelling in an ionic liquid 1-ethyl-3-methylimidazolium bis-(trifluoromethyl-sulfonyl)imide (EMImTFSI), a low voltage (-1.6 and +1.6 V) is applied between the two main faces of the film to induce the switching of the electroreflective device. These semi-IPNs present interesting optical reflective properties in the Mid Infrared region (MIR): band II (3-5µm) and band III (8-12µm). For example the reflectivity is adjustable between 18% and 51% in band III for the semi-IPN obtained with a mixture of ProDOT-Me2 and PEDOT. With the PProDOT-Me2 containing semi-IPN, the values are between 20% and 44%.High value of optical contrasts ranging from 13% to 22% for band II and 24% to 33% for band III are obtained by MIR spectroscopy. L VIII 31

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17:00 **CHROMOGENIC GAS SENSORS FOR MEAT FRESHNESS ASSESSMENT**

Authors : A.M. Iordache, S.M. Iordache, C. Nichita, C. Ceaus, L. Popovici, I. Stamatin*

Affiliations : University of Bucharest, Faculty of Physics, 3Nano-SAE Research Centre, 405 Atomistilor Str., P.O. Box. No 38, Bucharest-Magurele, Ilfov, Romania. *Corresponding author: istarom@3nanosae.org

Resume : The need for fast and reliable sensors for food safety is an important research field in health and security. Actual food testing and evaluation is carried out by specialized laboratories, often with expensive and time-consuming equipment. Here, we propose a chromogenic gas sensors array for the fast evaluation of meat freshness. The volatile organic compounds (VOCs) and biogenic amines (BAs) released during microbial growth induce an irreversible color shift in the sensitive layer. The chromogenic dyes were imprinted on a porous, flexible substrate by ink-jet printing and placed close to L VIII 32 the sample in a tight gas chamber; the sensor array was coupled to a digital camera to record the color shift and the VOCs were collected and analyzed by mass spectrometry. The results open a new path for developing fast and cheap control instruments.

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17:00 **Study of structural and optical properties of W- and Mg-co-sputtered VO2 thin layers, for thermochromic applications**

Authors : M.Panagopoulou1, E.Gagaoudakis3,4, N.Boukos2, E.Aperathitis3, G.Kiriakidis3,4, D.Tsoukalas1, Y.S.Raptis1, G. Iliadis5

Affiliations : 1 School of Applied Mathematical and Physical Sciences, National Technical University of Athens, GR 157 80, Zografou Campus, Athens, Greece 2 IAMPPNM, Department of Material Science, National Center of Scientific Research 'DEMOKRITOS', GR 153 10, Agia Paraskevi,Athens, Greece 3 Institute of Electronic Structure & Laser (IESL), Foundation for Research and Technology –FORTH-Hellas, Heraklion GR 71110, Crete, Greece 4 Physics Department, University of Crete, GR 71003 Heraklion, Crete, Greece 5 Uniglass Lts,31st Vouliagmenis Avenue, GR 16675, Athens, Greece

Resume : Thermochromic materials are suitable for a wide variety of optical applications due to the reversible metal-to-insulator transition (MIT) they exhibit. Energy efficient smart windows is one of these applications. For this purpose, vanadium dioxide is mainly used since it exhibits a transition temperature (~68°C) fairly close to the room temperature. Initially vanadium dioxide films with thermochromic properties have been fabricated using RF magnetron sputtering at temperatures of 400°C and 300°C, with and without TiO2 anti-reflecting coating. Next, two types of dopants (W and Mg) were introduced using simultaneous co-sputtering with two targets, namely of metallic vanadium and each one of the two dopants. Tungsten and Magnesium have been reported in bibliography as a way to modify the transition temperature, aiming to its reduction closer to the room temperature. Different dopants concentration percentance affects the critical temperature of the MIT transition. In these work XRD and micro Raman studies of the films deposited on SnO2 coated glass (k-glass provided by Uniglass), ZnO coated glass and Si as reference will be presented. Furthermore, the lower transition temperature achieved will be determined, through T-dependant micro Raman and transmittance measurements. L VIII 33

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17:00 **THERMOCHROMIC MATERIALS WITH A LOW METAL-INSULATOR TRANSITION TEMPERATURE DEPOSITED BY THE MAGNETRON SPUTTERING TECHNIQUE**

Authors : T. Venot*, H. Boquet, C. Marcel

Affiliations : CEA le Ripault, BP16 37260 Monts, France

Resume : The study of a thermochromic material at low transition temperature (Tt) based VO2 crystallized was performed. The layers were deposited by magnetron sputtering technique. Vanadium oxide (VO2) changes its structure with temperature and passes reversibly to an infrared transparent state (monoclinic) at room temperature to an infrared reflector state (tetragonal) beyond 68 °C. At first, the study of classical material VO2 was performed. In order to obtain the correct stoichiometry from a target of vanadium metal, the reactive gas flow rate (O2) must be determined. From these deposition conditions, the influence of the annealing conditions of the layer is studied. A study by XRD, RBS was conducted to confirm the correct phase of VO2 and confirmed by IR spectroscopy. In a second step, a doping of the VO2 layer with tungsten (V1- xWxO2) to decrease the metal-insulator transition temperature below room temperature is achieved. For the doping, a very thin tungsten layer is deposited on the VO2. Then, Tungsten diffuses into the layer during annealing. The doping of tungsten was quantified by RBS analysis and the samples were measured by infrared spectroscopy. VO2 V1-xWxO2 ΔTMIR (%) 55% 50% Tt 68°C ≈20°C Modulation of the transmission and metal-insulator transition temperature L VIII 34

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17:00 **Reactive Magnetron Sputtering Deposition of Nickel Oxide Thin Films for Electrochromic Devices**

Authors : Vytautas Astasauskas, Aleksandras Iljinas, Vytautas Stankus, Brigita Abakeviciene

Affiliations : Department of Physics, Kaunas University of Technology, Studentu str. 50, LT-51368 Kaunas, Lithuania L VIII 35

Resume : Nickel oxides thin films and especially one form NiO (bunsenite) are very promising and useful material due it interesting properties which allow to use it in such applications as antiferromagnetic films, chemical and gas sensors, cathodes of batteries, catalyst, varistors and electrochromic devices, called “smart glass”. Our work is focused on synthesis NiO thin films, which could be useful for one of these devices elements. Problems to get quality NiO films using magnetron sputtering are lying in some aspects. The main is that Ni cathode is ferromagnetic. It complicates sputtering process due to shortening magnetic field lines on magnetron surface and causes instabilities in plasma processes. The synthesis of nickel oxide thin films using reactive magnetron sputtering technique and post annealing in atmosphere as deposited films were analyzed in this work. Nickel oxide electrical, optical, crystallographic and surface morphology properties before annealing and after were measured and analyzed. Comparing as deposited properties of films before annealing and after the conclusions were made, that nanocrystal Ni2O3 phase grows during deposition, but after annealing in 550oC temperature (50 min) this phase transforms to quality nanocrystal NiO films.

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17:00 **Electrospun fibers of tungsten oxide via different precursors and investigation of their chromogenic properties**

Authors : Amin Tabatabaei Mohsenia, Esra O. Zayim*a, b, A.Sezai Sarac a, c

Affiliations : aNanoscience & Nanotechnology Program, Istanbul Technical University, Maslak, Istanbul, Turkey bIstanbul Technical University, Faculty of Science and Letters, Physics Department, Istanbul, Turkey cIstanbul Technical University, Faculty of Science and Letters, Chemistry Department, Istanbul, Turkey

Resume : Tungsten oxide is well-known for its diverse applications in daily life and industry such as gas sensors, electrochromic, photochromic windows and smart windows application. Tungsten oxide nanofibers are novel research issue according to their significant benefits for molecular biology [1] and gas-sensing [2] applications beside chromogenic advantages. Tungsten oxide fibers can be produced by electrospinning technique using various precursors such as tungsten hexachloride and tungsten metallic powder. The obtained fibers are investigated to find out the differences and similarities. Surface and structure characterizations such as SEM, XRD, XPS and FTIR are performed to demonstrate the crystallity and elemental structure of the fibers before and after calcination of polymer. Tungsten oxide prepared via tungsten hexachloride allows fabrication of films and microfibers, exhibiting reversible color change upon exposure to ultraviolet light known as photochromic effect. Tungsten oxide fabricated via this procedure as nanofibers, microfibers and films can be applied to numerous types of surfaces (e.g. paper, glass, metal, textile and so forth) with different techniques (such as electrospinning, spin coating, droplet drawing, casting and writing ink). These materials have large optical modulation and possess short switching time with superior life-time. [1] http://pubs.acs.org/doi/abs/10.1021/es402364w [2] Polycrystalline tungsten oxide nanofibers for gas-sensing applicatio L VIII 36

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17:00 **Silica-based photonic crystals embedded in a chitosan/TEOS matrix: preparation, properties and applications**

Authors : C.C. Ryan1, A. Pavinatto2, O. N. de Oliveira Jr.2, M.E. Pemble1,3, M. Bardosova1*

Affiliations : 1 Tyndall National Institute, University College Cork, Lee Maltings, Prospect Row, Cork, Ireland 2 Institute of Physics São Carlos, University of São Paulo, CP369, São Carlos, SP Brazil 3 Department of Chemistry, University College Cork, Cork, Ireland *corresponding author, e-mail: maria.bardosova@tyndall.ie Tel: +353 21 490 6010

Resume : Chitosan (Chi) is a long chain cationic polysaccharide formed by deacetylation of chitin, the second most abundant polymer produced in nature. Chitosan is soluble in diluted acids, non-toxic and biocompatible. We have studied a range of so-called Interpenetrating Polymer Networks (IPNs) based on chitosan, with the aim to prepare materials with a controlled porosity and degree of crosslinking. Such materials are capable of forming membranes, which we have used for the production of a range of hybrid organic/inorganic composites consisting of silica-based colloidal photonic crystals (PhCs) surrounded by chitosan/TEOS IPN matrices. These systems swell in acidic conditions due to the protonation of amino groups and conversely shrink in neutral to basic conditions due to the loss of excess protons. Based on the swelling studies, several Chi-TEOS-SiO2 composites were produced, in which the ordered PhC structures remained intact after the composite was subjected to multiple pH-changing cycles. From the photonic crystal perspective, we have achieved a variable non-close packed geometry, suitable to be used in devices such as pH sensors. We discuss other possible applications of these composites as well as photonic band gap properties of the described unique structures. L VIII 37

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17:00

Irreversible thermochromic paints and shock-detection paints

Authors : M. Gaudon*, V Blanco-Guttierrez*, A. Demourgues*
Affiliations : * CNRS, University of Bordeaux, ICMCB, 87 avenue du Dr. Albert Schweitzer, 33608 Pessac, France

Resume : Our researches are focused on the CuMoO4 and CoMoO4 X-chromic materials. These compounds exhibit an abrupt color modification due to a severe structural rearrangement associated to a first order transition which can be produced by pressure or temperature. For both families, the high temperature / low pressure modifications exhibit [MoO4] tetrahedra while the low temperature / high pressure modifications exhibit [MoO6] octahedra. Two ways can be used in order to tune the Xchromic transition temperature/pressure: (i) the doping of the (Cu/Co)MoO4 oxide with various transition metals (Mg, Ni, Zn…), (ii) the control of the oxide morphology, especially its crystallite size. Also for the piezochromism phenomenon, the application mode of the pressure (isostatic / uniaxial) affects the pressure answer. The results of the chemical/morphological impacts on the transition parameters can be discussed thanks to X-Ray/Neutron diffraction, optical characterizations, calorimetric measurements and microscopic observations... Such materials receive attention due to their potential applications as convivial temperature/pressure indicators, especially as piezosensors while the oxide powder is incorporated into a paint/varnish, for the shock detection on fragile substrates.

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	Thermochromism II : Harlan Byker, Bernard Dam	
09:00	**Electric Field Assisted Chemical Vapour Deposition of Thermochromic Thin Films** **Authors :** Michael E.A. Warwick, Russell Binions **Affiliations :** Warwick Department of Chemistry, University College London, Christopher Ingold Laboratories, 20 Gordon Street, London, WC1H OAJ, United Kingdom. & UCL Energy Institute, Central House, 14 Upper Woburn Place, London, WC1H 0HY, UnitedKingdom. Binions School of Engineering and Materials Science, Queen Mary University of London, Mile End Road, London, E1 4NS, United Kingdom. **Resume :** Thin films of thermochromic vanadium dioxide were deposited using a novel electric field assisted chemical vapor deposition methodology at atmospheric pressure onto glass substrates. Electric fields were generated during the deposition reaction by applying a potential difference across the inter-digitated electrodes of the gas sensor substrate or buy applying an electric field between two transparent conducting oxide coated glass substrates. The deposited films were analyzed and characterized using scanning electron microscopy, Raman spectroscopy, X-ray diffraction, atomic force microscopy, variable temperature optical spectroscopy and contact angle measurements. It was found that applying an electric field led to large changes in film microstructure, preferential orientation and changes in the film growth rate. This led to significant changes in materials properties such as decreased crystallite size, nano-structuring, increased surface roughness and enhanced wetting behavior. The deposited films were evaluated using Energy Plus for their energy demand reduction characteristics in a variety of architectural settings and compared against existing glazing products. It was found that thermochromic thin films can offer significant energy demand reduction benefits.	L-IX 1
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09:30	**LUMINESCENT MECHANOCHROMIC AND THERMOCHROMIC MATERIALS BASED ON COPPER IODIDE CLUSTERS** **Authors :** Quentin Benito (a), Sandrine Perruchas (a), Alain Polian (b), Xavier F. Le Goff (c), Alain Garcia (d), Lucio Martinelli (a), Jean-Pierre Boilot (a) and Thierry Gacoin (a) **Affiliations :** (a) Laboratoire de Physique de la Matière Condensée (PMC), CNRS – Ecole Polytechnique, route de Saclay, 91128 Palaiseau Cedex, France; (b) Institut de Minéralogie et de Physique des Milieux Condensés (IMPMC), CNRS –Université Pierre et Marie Curie, 4 place Jussieu, 75005 Paris Cedex, France; (c) Laboratoire Hétéroéléments et Coordination (DCPH), CNRS - Ecole Polytechnique, route de Saclay, 91128 Palaiseau Cedex, France; (d) Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB) - CNRS, 87 Avenue du Docteur A. Schweitzer, 33608 Pessac Cedex, France; **Resume :** Controlling or tuning the photo-luminescence properties by means of external stimuli is particularly attractive in order to obtain photofunctional materials. In this context, luminescent mechanochromic compounds, characterized by emission wavelength change upon mechanical grinding or pressing of the solid sample, are good candidates [1]. The development of such materials requires a deep understanding of the mechanochromism mechanism. Herein we report on the mechanochromic luminescence of molecular copper(I) iodide clusters presenting a great reversible change of their solid state emission and also modification of their thermochromic luminescence upon grinding [2]. Comparative studies of different crystalline polymorphs of the clusters give important information into the mechanism involved and especially correlation between molecular structures and emission properties has been established. In	L-IX 2

order to get straightforward information on the origin of the phenomenon, pressure in-situ X-ray diffraction and luminescence experiments have been conducted. From these results, the mechanochromic luminescence arises from modification of the cluster core geometry. The processing of these clusters as thin films and their incorporation within polymeric matrices have been also studied to synthesize pressure-responsive materials. [1] Y. Sagara et al., Nature Chemistry 1 (2009) 605 [2] S. Perruchas et al., J. Am. Chem. Soc. 132 (2010) 10967

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09:45 **Multifunctional thermochromic particles**

Authors : N. Vazquez-Mera [a,c], F. Novio [a,b], C. Roscini [a], J. Hernando [c], D. Ruiz-Molina* [a,b]

Affiliations : a. Institut Catala de Nanociencia i Nanotecnologia, Campus UAB, 08193 Bellaterra (Barcelona), Spain b. Consejo Superior de Investigaciones Cientificas, ICN2 Building , Campus UAB ,08193 Bellaterra (Barcelona), Spain c Chemistry Department, Universitat Autònoma de Barcelona, 08193 Bellaterra (Barcelona), Spain

Resume : Switchable coordination complexes, like spin crossover (SCO) or valence tautomeric (VT) systems, are of growing interest in the area of functional materials. They present two electronic isomers with different spin states and, consequently, distinct optical and/or magnetic properties. Therefore, when the reversible interconversion between those isomers is thermally induced, these complexes exhibit thermochromism accompanied with changes in other physical properties. This multifunctional behaviour makes them promising materials for sensing and information storage, which requires controlled fabrication of robust micro- and nanostructures with high potential device integration. Significant advances have been made in this regard[1]; however, limitations still arise from the changes observed on this scale with respect to the well-established behaviour of these systems in solution or bulk. Here we report the successful fabrication of thermochromic micro/nanoparticles based on the encapsulation of VT compounds inside organic polymers, structured as solid beads[2] and liquid-filled capsules[3]. These systems represent robust platforms to integrate VT on composite materials. Moreover, liquid-filled capsules allow the solution-behaviour of these complexes to be retained, thus providing direct transfer of their properties to the solid state. [1] Chem. Soc. Rev., 2011, 40, 3313 [2] Sci. Rep., 2013, 3, 1707 [3] J. Am. Chem. Soc., 2014, submitted. L-IX 3

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10:00 **Coffee Break**

Thermochromism III : Manuel Gaudon, Bernard Dam

10:30 **Sputter deposited thermochromic VO2 thin films on tin-doped indium oxide-coated glass: electrical, structural and optical properties**

Authors : J. Montero, C. G. Granqvist, G. A. Niklasson

Affiliations : Department of Engineering Sciences, The Ångström Laboratory, Uppsala University

Resume : VO_2 is a thermochromic material, i.e., it changes reversibly from infrared transmitting to infrared reflecting when its temperature is below or above a critical value, respectively. This fact offers possibilities for applications in thermochromics-based smart windows. In the present work we investigated the growth of VO_2 thin films by reactive magnetron sputtering from a pure V metallic target onto $Sn:In_2O_3$ (ITO)-coated and uncoated glass substrates. Preliminary results show that the ITO coating facilitates the VO_2 growth under a wide variety of sputtering conditions. Our work demonstrates how the electrical, structural and optical properties, and also the critical temperature, are affected by the nature of the substrate. L-X 1

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10:45 **Growth and crystallization of vanadium dioxide thin films: comparison between in situ and ex situ processes**

Authors : A. Corvisier, F. Capon, J.F. Pierson

Affiliations : Institut Jean Lamour, Université de Lorraine, Nancy, France

Resume : Vanadium dioxide (VO_2) is a thermochromic material that presents an abrupt first order phase transition at the critical temperature (Tc) of 68 °C. VO_2 thin films have been deposited using reactive sputtering on silicon substrates using three kinds of processes. In the first one, the films have been deposited at high temperature as usually encountered in the literature. In the L-X 2 second process, the VO2 coatings have been synthesised in a two steps method: deposition at room temperature followed by an ex situ annealing in air. Finally, the last process studied can be described as the deposition at room temperature of a VO2 layer covered by a thin film of silica and the air annealing of this bilayer. High temperature deposited films are well crystallized and exhibited a pronounced metal insulator transition at 68°C. On the other hand, the films deposited at room temperature are X-ray amorphous and do not exhibit a thermochromic effect. Furthermore, an oxidation of the films occurs during the air annealing of the vanadium oxide layer. Such oxidation step is avoided by the use of the silica layer that acts as a barrier for oxygen diffusion. The monitoring of the bilayer crystallization by X-ray diffraction shows that the crystallisation occurs at temperature as low as 330 °C and that the crystallisation is governed by a two dimensional growth mechanism. The crystalline bilayer films clearly exhibit switching properties in the infrared domain at a temperature close to 68 °C.

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11:00 **Spectroscopic studies of CocCu1-cWO4 solid solutions**

Authors : A.Kalinko 1, A. Anspoks 2, J. Timoshenko 2, A. Kuzmin 2, P. Roy 1

Affiliations : 1 Synchrotron SOLEIL, l'Orme des Merisiers, Saint-Aubin, BP 48, 91192 Gif-sur-Yvette, France; 2 Institute of Solid State Physics, University of Latvia, Kengaraga street 8, LV-1063 Riga, Latvia

Resume : The 3d metal tungstates represent a large class of compounds with numerous physical properties, which are interesting from practical point of view. Particularly AWO4 (A=Co, Cu) tungstates are attractive because of their catalytic activity and possibility of use in water oxidation processes and as a photoelectrode in photovoltaic electrochemical cell. Upon mixing, the two tungstates readily form CocCu1-cWO4 solid solutions, which have been scarcely investigated until now. In this study polycrystalline CocCu1-cWO4 powders were prepared by co-precipitation technique and characterized by x-ray diffraction. Spectroscopic studies of pure tungstates and their solid solutions were performed using complementary techniques as Raman scattering and far-/mid-infrared spectroscopies. The synchrotron-based far-infrared measurements of pure CoWO4 and CuWO4 in the low temperature range (10-300 K) did not reveal any structural phase transition. The behaviour of phonon modes is consistent with that upon thermal expansion of the crystal lattice. The monoclinic (CoWO4, P2/c) to triclinic (CuWO4, P-1) phase transition in CocCu1-cWO4 solid solutions was observed as a function of composition at room temperature by Raman scattering, far- and mid-infrared spectroscopies. We found that the symmetry lowering occurs in the range of c=0.5-0.8, whereas the triclinic structure becomes dominant at c<0.2. The obtained results will be discussed based on the results of the first-principles phonon calculations. L-X 3

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11:15 **Motheye Smart Windows**

Authors : Alaric Taylor, Ivan Parkin, Clemens Tummeltshammer, Mark Brown, Rafael Sibilo, Ioannis Papakonstantinou

Affiliations : UCL, UCL, UCL, UCL, UCL, UCL

Resume : A novel class of thermochromic 'motheye smart window' is presented. We have found that the optical properties of vanadium dioxide are enhanced when coated in thin layers over a nano-structured surface. Graded refractive index 'motheye' antireflection surface structures, inspired by nature, are chosen for both their optical and wetting enhancements. Wide-angle, polarisation-insensitive and highly-efficient transmission of visible light is possible whilst maintaining strong solar-thermal energy modulation. In addition, the high aspect ratio structures improve the hydrophobicity of the surface making it robust and super-hydrophobic which lends the window surface the ability to self-clean. We will discuss both the theoretical aspects underpinning the dimensions of the nano-structures and our recent work in their fabrication on glass. In addition, the super-hydrophobic self-cleaning properties of the surface will be demonstrated and our optical measurements presented and discussed. L-X 4

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11:30 **Thermochromic properties of rare earth perovskites**

Authors : Capon F., Boileau A., Haye E., Barrat S., Pierson J.F.

Affiliations : Institut Jean Lamour

Resume : Thermochromism is a phenomenon in which electrical and optical properties of a substance change with temperature. Researchers have found a variety of thermochromic materials such as thermochromic liquid crystals, thermochromic dyes, cuprous mercury iodide (Cu2HgI4), vanadium dioxide L-X 5

(VO2), and rare earth (RE) perovskite-type oxide REMO3 (M: transition metal). The thermochromic effect in REMO3 is due to the lanthanum contraction, along the 4f rare earth series of the periodic table, which produces profound effects with the progression of various transport properties. We present the electrical and optical properties of three families of perovskites: nickelates, cobaltites and manganites. They have been synthetized by PVD method (sputtering) and characterized using the four-point probe method and a FTIR spectrometer at various temperatures in the range 80-900K. These perovskites can be utilized to create a large variety of smart devices, for example they can be fitted on a spacecraft surface or on thermal solar captor in order to automatically control the emissive heat transfer without assistances of any electrical instrument.

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12:00 **Lunch Break**

Gasochromism/Electrochromism : Angela Surca Vuk, Aline Rougier

13:30 **Switchable Mirror Sheet using New Gasochromic Method**

Authors : K. Yoshimura, K. Tajima, Y. Yamada

Affiliations : National Institute of Advanced Industrial Science and Technology (AIST)

Resume : Swithchable mirror thin film can be switched between transparent and mirror states. There are two switching methods; electrochromic and gasochromic. Although, gasochromic is preferable for window use from the view point of cost and switching seed, there is the strict limitation that gasochromic window should be used as a pair glass, and safety concerns have been raised about the hydrogen gas used for the switching. Recently, we developed an innovative gasochromic method and resolved these problems. By this method, switchable mirror thin film (Pd capped Mg-Ni thin film or Mg-Y thin film) is deposited on a transparent sheet, and this sheet and a transparent glass are bonded together without a spacer, an air gap with an average thickness of about 0.1 mm is formed naturally. We invented a special method to make gasochromic switching in the narrow gap. By using this method, the attached sheet can be switched between transparent and mirror states like a conventional gasochromic method using pair glass. In addition, because the switching can be performed with a very small amount of hydrogen, the moisture (water vapor) in air can be used as the source of hydrogen. In this case, the new gasochromic sheet uses only air and it can be operated by applying a voltage of about 3 V to the electrolyzer like an electrochromic window. Because the thin film structure of gasochromic is very simple and this new technique has a possibility to raise a cost revolution for switchable sheet. L XI 1

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14:00 **Metal-Organic Frameworks as Novel Electrochromic Materials**

Authors : Chung-Wei Kung1,2, Timothy Chiaan Wang1, Joseph E. Mondloch1, David Fairen-Jimenez3, Daniel M. Gardner1, Wojciech Bury1,4, Jordan Matthew Klingsporn1, Jonathan C. Barnes1, Richard Van Duyne1, J. Fraser Stoddart1, Michael R. Wasielewski1, Kuo-Chuan Ho2,5*, Omar K. Farha1*, and Joseph T. Hupp1*

Affiliations : 1- Department of Chemistry, Northwestern University, Evanston, Illinois, United States; 2- Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan; 3- Department of Chemical Engineering and Biotechnology, University of Cambridge, United Kingdom; 4- Department of Chemistry, Warsaw University of Technology, Warsaw, Poland; 5- Institute of Polymer Science and Engineering, National Taiwan University, Taipei, Taiwan

Resume : Over the last few decades, several materials have been applied for electrochromic devices. Although electrochromic thin films show the advantages of faster switching rate and optical memory compared to soluble electrochromic materials, ions must be transported through the film during the redox reaction to maintain electroneutrality. Thus, facile ion transport in electrochromic thin films is the key to achieve fast switching rate. Herein, metal-organic frameworks (MOFs) thin films are introduced as a new series of electrochromic materials. MOFs are a class of crystalline porous materials constructed from organic linkers and metal-based nodes. Due to their regular and tunable pores, MOFs become attractive candidates for electrochromic thin films. In this study, a MOF constructed from Zr-nodes and pyrene-based linkers is selected. The uniform thin film composed of free-standing one-dimensional (1D) nanorods of that MOF is grown on a conducting glass. The redox reaction of the pyrene-based linkers leads to the reversible color change of the MOF film between yellow and dark L XI 2 blue during potential switching. The crystal structure of the MOF is composed of diamond-shape 1D channels with the pore size of 2.9 nm on the length and 1.2 nm on the width, which is expected to provide fast ion transport through the whole film. Transmittance change of the MOF film at 587 nm is 62% during potential switching, with the bleaching time and the coloration time of 5 and 12 s, respectively.

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14:45 **Improve in optical properties of switchable mirrors based on Mg-Y alloy**

Authors : Y. Yamada, M. Miura, K. Tajima, M. Okada, K. Yoshimura

Affiliations : National Institute of Advanced Industrial Science and Technology

Resume : Smart windows using metal hydride switchable mirrors are expected to reduce cooling load because the window can block solar radiation by reflecting the sunlight. One of the candidate materials of switchable mirrors is a Mg-Y alloy because the switching durability between reflective and transparent states is extremely high of over 10,000 cycles. However, the visible transmittance of the mirrors using the alloy in the transparent state was not so high of ~ 35%. The reason in low transmittance was due to thicker Pd layer of ~7.5 nm to maintain high switching durability. To reduce the Pd thickness, Ta thin layer with the thickness of ~2 nm was inserted between Mg-Y and Pd layers. As a result of insert, Pd thickness can be reduced from 7.5 nm to 3 nm and the transmittance increased to ~41%. Furthermore, by covering the film surface with a TiO2 thin film, which worked as antireflection, the transmittance improved to ~62%. L XI 3

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15:00 **Electrochemical evaluation of vanadium pentoxide coatings grown by AACVD**

Authors : D. Vernardou 1, D. Louloudakis 1 2, N. Katsarakis 1 3 4, E. Koudoumas 1 3, I. I. Kazadojev 5, S. O'Brien 5, I. M. Povey 5, M.E. Pemble 5

Affiliations : 1 Center of Materials Technology and Photonics, School of Applied Technology, Technological Educational Institute of Crete, 710 04 Heraklion, Crete, Greece; 2 Department of Physics, University of Crete, 710 03 Heraklion, Crete, Greece; 3 Electrical Engineering Department, Technological Educational Institute of Crete, 710 04 Heraklion, Crete, Greece; 4 Institute of Electronic Structure and Laser, Foundation for Research & Technology-Hellas, P.O. Box 1527, Vassilika Vouton, 711 10 Heraklion, Crete, Greece; 5 Tyndall National Institute, University College Cork, Lee Maltings, Prospect Row, Cork, Ireland.

Resume : The interest in electrochromic vanadium oxide coatings has increased during the last few years, because of their use in windows that can control the solar light transmission, contributing therefore significantly to energy saving in buildings. Large area uniformity, low production cost and durability of the coatings can play a very important role in the fabrication of such "smart" windows. In that respect, an aerosol assisted chemical vapor deposition process is more advantageous over the other conventional techniques, which are already used in industry for the fabrication of these coatings. Since, it is easily integrated to float glass plants, no expensive vacuum systems are required and high production rates may be realised. In this paper, the effect of the growth parameters and coating thickness on the structural and morphological characteristics of vanadium pentoxide are considered. Finally, their electrochemical activity, comprising charge storage capability and corresponding specific capacitance, reversibility and repeatability of the charge transfer through the as-deposited and annealed vanadium oxides are investigated. L XI 4

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15:15 **Synthesis and modeling of π-conjugated donor-acceptor copolymers with cyan, blue and green colors: Application to electrochromic devices**

Authors : S. Fagour, D. Thirion, A. Vacher, X. Sallenave, J.F. Decarreau, P.H. Aubert, F. Vidal, C. Chevrot, G. Sini

Affiliations : Laboratoire de physicochimie des Polymères et Interfaces (LPPI), Université de Cergy-Pontoise, 5 Mail Gay Lussac, Neuville sur Oise, 95031 Cergy-Pontoise Cedex, France

Resume : Getting polymers with cyan, blue or green colors in the neutral state requires specific spectral features. Indeed, two absorption peaks located at well-defined wavelength are needed: the first centered on 400nm and the second between 640 and 720nm. In the scope of our work, we have taken interest in copolymers ranging from blue to green colors. We hereby report an attempt at tuning the color of donor-acceptor conjugated polymers through controlling their bandgap. This bandgap control relies on the association of two electron-rich propylenedioxythiophene units (ProDOT(EtHex)2) with different aryl-substituted quinoxaline units in a D-A-D structure. Substituting the phenyl units borne by the quinoxaline with functional groups of different electron-donor and electron- L XI 5

acceptor properties allows a fine tuning of the overall acceptor strength of the quinoxaline moiety. Considering a non-substituted phenyl derivative of quinoxaline, we have synthezised four other monomers and their corresponding polymers. To assess the properties of the copolymers, we used spectroscopic techniques, from which the colorimetric data were derived. Modeling based on monomers and trimers with B3LYP and TD-B3LYP led us to interesting trends showing the relationship between the LUMO level of the species and the resulting optical properties. Finally, based on the results, a relationship between energetic levels and color control in D-A-D polymer structures will be proposed.

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15:30 **Coffee Break**

16:00 **PLENARY SESSION**

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