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CONDUCTIVITY MEASUREMENTS

A Four-Point Surface Conductivity Probe Suitable for *in situ* Ultrahigh Vacuum Conductivity Measurements, Wiegenstein *et al.*, Rev. Sci. Instrum., 68 (4), 1812-1813, April 1997.



FILMS OR LAYERS ON ITO

Surface electronic properties of self-assembled, oppositely charged macrocycle and polymer multilayers on conductive oxides

Li Lin Song et al. *Journal of Physical Chemistry B* 2000 104/47 (11195-11201)
Using the layer-by-layer self-assembly technique, we have deposited multilayer thin films on conductive indium tin oxide (ITO) surfaces by alternatively dipping ITO substrates in a polymer PDDA or poly(diallyldimethylammonium) chloride solution and a macrocycle NiPc or nickel phthalocyanine solution. In addition to characterizing PDDA-NiPc systems with X-ray reflectometry and cyclic voltammetry, we monitored the growth of PDDA/NiPc multilayers on conductive oxides with Fourier transform infrared (IR) spectroscopy at an external grazing-angle reflection configuration. IR spectra with polarization perpendicular to the conductive ITO surfaces revealed vibration bands at 1227 and 1200 cm^{-1} corresponding to salt bridges of $-\text{SO}_3^- \cdots \text{Me}_2\text{N}^+$ = binding between PDDA and NiPc. An oscillation of the surface electronic potential was observed with a Kelvin Probe as the surface layer alternated between PDDA and NiPc. The average gap of the surface potential difference between NiPc and PDDA monolayers is about 400 mV. Oscillation of surface potential or work function is caused by the modulation in electron affinity of ITO due to the dipolar effect generated by the highly charged layers of PDDA or NiPc.

Preparation and characterization of self-assembled monolayers on indium tin oxide

Yan C et al. *Langmuir* 2000 16/15 (6208-6215) Language: English
Self-assembly of amphiphilic molecules, alkanethiols $\text{CH}_3(\text{CH}_2)_n\text{SH}$ ($n = 15, 17$), carboxylic acids $\text{CH}_3-(\text{CH}_2)_n\text{COOH}$ ($n = 16, 18$) and bifunctional $\text{SH}(\text{CH}_2)_{15}\text{COOH}$ on indium tin oxide (ITO) surfaces was investigated by X-ray photoelectron and near edge X-ray absorption fine structure spectroscopies, contact angle measurements, and atomic force microscopy. These molecules were found to form homogeneous, well-oriented monolayers on ITO. XPS indicates that at low coverages, thiol molecules adsorb as thiolates, whereas at saturation coverage approximately 30% of the molecules adsorb as unbound thiols.

Photoelectrochemistry with integrated photosensitizer-electron acceptor and Au-nanoparticle arrays

Lahav et al. *Journal of the American Chemical Society* 2000 122/46 (11480-11487)
Photosensitizer/electron acceptor molecular cross-linked Au-nanoparticle arrays are assembled on indium-doped tin oxide (ITO) electrodes by a layer-by-layer deposition process. A Ru(II)-tris-(2,2'-bipyridine)-cyclobis(paraquat-p-phenylene) catenane (1) or Zn(II)-protoporphyrin IX-bis(N-methyl-N'-undecanoate-4,4'-bipyridinium) (2) are used as molecular cross-linkers for the generation of Au-nanoparticle (13 ± 1 nm) arrays of a controlled number of layers. The Au-nanoparticle arrays are characterized by absorbance spectroscopy and by electrochemical means. The electrodes functionalized with 1- or 2-cross-linked Au-nanoparticle arrays are used in photoelectrochemical experiments. The resulting action spectra of the photocurrents follow the absorbance spectra of the respective chromophores.

Electrochemical molecular recognition by 2,5-bis(phosphonomethyl) hydroquinone (BPH2Q) ionically bound to indium tin oxide electrodes



Hong Hun-Gi et al. Journal of Electroanalytical Chemistry 2000 489/1 (106-110)

Language: English

A novel derivative of hydroquinone, BPH2 Q, has been synthesized and used for the chemical modification of indium tin oxide (ITO) electrodes pretreated with Zr(IV) ion solutions. Ionic binding of the BPH2Q molecule to the zirconium ion-treated ITO surface produces a layer with a coverage of 2.6×10^{-10} mol cm^{-2} . The modified electrode exhibits electrochemical molecular recognition for alkali metal cations.

Electric field modulated near-field photo-luminescence of organic thin films

Adams David M et al. Journal of Physical Chemistry B 2000 104/29 (6728-6736)

Language: English

The concentrated electric field (E-field) in the vicinity of a voltage-biased near-field optical probe is used to modulate the photoluminescence of organic thin films on the approx. 100 nm scale. The samples are bilayers comprising a self-organized-thin-film (50-500 nm) layer of zinc-octakis (β -decoxyethyl) porphyrin (ZnODEP) on top of an indium tin oxide (ITO) coated glass electrode. The Al coated-optical-fiber-near-field probe functions simultaneously as a noncontacting moveable electrode and a local source of optical excitation (30 - 70 nm aperture). When the ITO electrode is charged positive relative to the probe (yielding a field on the order of 1MV/cm-1), the photoluminescence (fluorescence) intensity decreases approx. 5% and the probe - sample probe - sample distance (under shear-force feedback control) increases approx. 7 angstrom. Opposite effects for both signals occur when the ITO is charged negative.

High electric resistance polymer/lipid composite films on indium-tin-oxide electrodes

Hillebrandt Heiko et al. Langmuir 1999 15/24 (8451-8459) Language: English

We report the design of polymer/lipid composite films on polarizable indium-tin-oxide (ITO) electrodes and the characterization of their electrical properties by impedance spectroscopy. The polymer films separating the solid surfaces and the lipid membranes were composed of 'hairy-rod' macromolecules and provided a fluid and homogeneous ultrathin 'cushion' for the deposition of lipid membranes. Two types of polymer cushions were designed: First, electrically insulating multilayers of cellulose derivatives with substituted alkyl chains forming a fluid hydrophobic 'brush' at the surface. Second, conducting cellulose multilayers exposing hydrophilic surfaces for the deposition of self-healing lipid bilayers. The electrical properties, the defect densities, and the homogeneities of the stratified films were studied by impedance spectroscopy in the frequency range between 90 mHz and 50 kHz. Impedance spectra were analyzed in terms of equivalent circuits with resistances, capacitances, and so-called 'constant phase elements'. Resistances of up to 440 k Ω cm^2 were achieved for the polymer-supported lipid bilayers, which corresponds to about 10% of the value for black lipid membranes containing hexane. The gramicidin channels reconstituted into the supported lipid bilayers exhibited the expected cation selectivity.

Electrochemical properties of TiO₂ coated ITO electrodes prepared by sol-gel method

Murakata T. et al. Journal of Chemical Engineering of Japan 1999 32/6 (825-829)

Language: English

An ITO electrode was coated with layers of TiO₂ by using a sol-gel method. The coated electrodes were calcined to change pore and crystal structure of the TiO₂ layer. For these electrodes, cyclic voltammetry and spectro-electrochemical measurements were carried



out in the absence of a substrate and in the presence of ethyl viologen as a substrate. Significant differences in electrochemical properties were found between the calcined and uncalcined electrodes. When a negative potential was applied to the uncalcined electrode, Ti^{3+} was formed in its TiO_2 layer. The uncalcined electrode reduced irreversibly ethyl viologen while the calcined one did reversibly. These behaviors are discussed on the basis of the porosity and electronic structure of the TiO_2 layer.

Effect of steric hindrance on photoinduced electron transfer of self- assembled monolayers of three isomeric Ru(II)-bipyridine complexes on ITO electrode

Wei T.-X. et al. Physical Chemistry Chemical Physics 2000 2/6 (1333-1337)

Language: English

Three kinds of self-assembled monolayers (SAMs) of isomeric Ru(II)- bipyridine complexes: cis-di(thiocyanato)bis(2,2'-bipyridyl-3,3'- dicarboxylate) ruthenium (dye A), cis-di(thiocyanato)-bis(2,2'-bipyridyl- 4,4'-dicarboxylate) ruthenium (dye B) and cis-di(thiocyanato)-bis(2,2'- bipyridyl-5,5'-dicarboxylate) ruthenium (dye C), were fabricated on hydrophilic transparent indium tin oxide (ITO) electrode. The UV-visible spectra, contact angle, XPS and cyclic voltammetry of these SAMs were measured. The photoinduced electron transfer properties were determined both in propylenecarbonate (PC) electrolyte and KCl electrolyte. A possible mechanism of electron transfer of these systems was proposed.

***Deposition of Oriented Polymer Films for Liquid Crystal Alignment by Pulsed Laser Ablation**, Luo *et al.*, Applied Surface Science, 108, pp. 89-93 (1997).

Electrically Conducting Polymers: Science and Technology, Epstein, Materials Research Society Bulletin, 22 (6), pp. 16-23, June 1997.

Polymer Electroluminescent Devices, Yang, Materials Research Society Bulletin, 22 (6), pp. 31-38, June 1997.

Progress in Electroluminescent Devices Using Molecular Thin Films, Tsutsui, Materials Research Society Bulletin, 22 (6),pp. 39-45, June 1997.

Conjugated Polymer Surfaces and Interfaces for Light-Emitting Devices, Salaneck *et al.*, Materials Research Society Bulletin, 22 (6), pp. 47-51, June 1997.

Stimulation of neurite outgrowth using an electrically conducting polymer, Schmidt *et al.*, Proc. Natl. Acad. Sci. USA, Vol. 94, pp. 8948-8953, August 1997.

Sol-Gel Deposited V_2O_5 Films as Counter Electrodes for WO_3 Based Electrochromic Devices (ECDs), Agnihotry *et al.*, Bulletin of Electrochemistry, 12 (11-12),pp. 756-758, November-December 1996.

A Monolayer-based Lift-Off Process for Patterning Chemical Vapor Deposition Copper Thin Films, Payne *et al.*, Langmuir, 12 (22), pp. 5350-5355, 1996.

Improvement of the Crystallinity in $PbTiO_2$ Films Grown on Indium Tin Oxide-Coated Glass by Metalorganic Chemical Vapor Deposition using the Continuous Cooling Process, Yoon *et al.*, Applied Surface Science, 93, pp. 285-289, 1996.

Preparation of Nanoparticulate CdS Films Suitable for Opto-Electronic Device Applications, Salata *et al.*, Thin Solid Films, 288, pp. 235-238, 1996.



Patterning of Dielectric Oxide Thin Layers by Microcontact Printing of Self-Assembled Monolayers, Payne *et al.*, J. Mater. Res., 10 (12), pp. 2996-9, 1995.

Electrical and Optical Properties of Amorphous BaTiO₃ Thin Films Grown by Metal organic Chemical Vapor Deposition on Indium Tin Oxide-Coated Glass, Yoonet *et al.*, Jpn. J. Appl. Phys., Part 1, 33 (12A), pp. 6663-6666, 1994.

Photocurrent Spectroscopic Study of the Initiation and Growth of Poly(3-methylthiophene) Films on Electrode Surfaces with Different Adsorption Properties, Lukkari *et al.*, J. Phys. Chem., 98, pp. 8525-8535, 1994.

As-Deposited High T_c Superconducting Thin Films on ITO-Coated Glass, Fujino, IEEE Trans. Magn., 27 (2, part 2), pp. 1642-1645, March 1991.

INDIUM TIN OXIDE

Electrodeposited cobalt + copper thin films on ITO substrates

Go´mez et al. Journal of Electroanalytical Chemistry 2001 517/1-2 (63-68)
Cobalt + copper thin films with variable composition were obtained over indium-tin oxide covered glass plates (ITO) by means of electrodeposition, from a citrate bath upon varying both the [Co(II)]/[Cu(II)] ratio in solution and the deposition conditions. The ITO/glass substrate is sufficiently conductive to allow electrodeposition directly onto it, and also allows the measurement of the magnetoresistance without separating the films.

Novel method for the subdivision of ITO glass substrates

Hohnholz et al. Synthetic Metals 2000 111/- (385-386) Language: English
Subdivision of indium tin oxide (ITO) covered glass substrates can be easily carried out by a localized destruction of the ITO under a tungsten needle, applying a voltage between the ITO and the needle tip. The necessary equipment can be set up with commercially available components. The scorched lines almost completely insulate the different segments from each other. Using this method almost, every pattern can be printed into the ITO layer by a computer aided design (CAD) software in combination with a flatbed plotter, by application of a template or by free hand treatment.

Crystallization and electrical property change on the annealing of amorphous indium-oxide and indium-tin-oxide thin films

Morikawa Hiroshi et al. Thin Solid Films 2000 359/1 (61-67)
The relation of the progress of crystallization in indium-oxide thin films to the change of electrical properties was studied and compared with the results on indium-tin-oxide thin films. The resistivity of amorphous indium-oxide thin films was lower than that of indium-tin-oxide thin films, and increased with the progress of the crystallization contrary to the case of indium-tin-oxide thin films. The resistivity change on annealing of the amorphous film was almost the same between annealing in vacuum and in air. By comparison of the carrier concentration in indium-oxide thin films with that in indium-



tin-oxide films, the contribution of ionized Sn to the carrier concentration has been estimated

Separate structure extended gate H⁺-ion sensitive field effect transistor on a glass substrate

Yin Li-Te et al. *Sensors and Actuators, B: Chemical* 2000 71/1-2 (106-111)

In our research, glass was used as a substrate for an H⁺ ion sensitive field effect transistor (ISFET). The sensitive characteristics of five structures for separate extended gate ion sensitive field effect transistors (EGFET) were studied. The components included tin oxide (SnO₂)/aluminum/micro slide glass, tin oxide/aluminum/corning glass, indium tin oxide (ITO) glass, tin oxide/indium tin oxide glass and tin oxide/micro slide glass.

Indium tin oxide (ITO) thin film was first time used as an H⁺ ion sensitive film, which has a linear pH Nerstern response sensitivity, about 58 mV/pH, between pH 2 and 12. In addition, the sensing area effect of the tin oxide/glass, tin oxide/ITO glass and ITO glass structure is discussed. The results show that the tin oxide/ITO glass structure EGFET has the best drift, hysteresis and sensing area characteristics.

Ionic charge-selective electron transfer at fullerene-multilayered architecture on an indium-tin oxide surface

Oh Sang-Yoon et al. *Langmuir* 2000 16/17 (6777-6779)

We report the first observation of the ionic charge-selective electron transfer at the fullerene-multilayered indium-tin oxide (ITO) electrode. The surface of the ITO electrode was modified by three layers of self-assembled fullerene/1,12-diaminododecane. The fullerene concentration in each layer was quantitatively measured by Rutherford backscattering spectrometry and UV spectrometry. Electron transfer was not observed from the electrode to the negatively charged Fe(CN)₆³⁻, but smooth electron transfer was made to the positively charged Ru(NH₃)₆³⁺ in an aqueous solution. At the extremely low concentration of Ru(NH₃)₆³⁺, 2 × 10⁻⁶ M, the bare ITO could not detect the ruthenium complex, but the fullerene-multilayered electrode identified the presence of the cationic ruthenium complex, indicating the enrichment of the ruthenium cationic complex in the vicinity of the electrode.

Effect of substrate temperature on the surface structure, composition and morphology of indium-tin oxide films

de Carvalho C.Nunes et al. *Surface and Coatings Technology* 2000 124/1 (70-75)

Surface properties of indium-tin oxide (ITO) films are sensitive to substrate temperature. ITO films have been produced by reactive thermal evaporation (RTE) of an indium-tin alloy in the presence of oxygen at different substrate temperatures. The surface chemical composition and structure of the deposited films have been examined by X-ray photoelectron spectroscopy (XPS). The surface morphology has been investigated by atomic force microscopy (AFM). XPS results indicate that all the examined ITO films contain amorphous and crystalline phases. The best ITO films for optoelectronic applications show the smallest percentage of oxygen and indium atoms in an amorphous phase, AFM shows that these films have reduced surface roughness (6.265 nm) and grains with almost uniform size and shape. The ITO films deposited on substrates in the lower temperature range are darkened and show an increase in the amount of surface tin associated with a decrease in the amount of indium, leading to the formation of the SnO₂-rich surfaces.



Kelvin probe and ultraviolet photoemission measurements of indium tin oxide work function: a comparison

Kim J.S et al. Synthetic Metals 2000 111/- (311-314)

We report a comparison of the work functions of thin films of indium tin oxide (ITO), carried out by means of ultraviolet photoelectron spectroscopy (UPS) and by measurements of the contact potential difference with respect to a gold reference electrode (Kelvin probe (KP) method). We investigated commercially available ITOs both 'as-received', and after certain surface treatments, such as oxygen plasma. First, we find measurable discrepancies between KP values measured with three different instruments, and between the KP and the UPS values. Secondly, and unexpectedly, we find that the KP, although more sensitive than UPS, does not detect certain differences between ITOs with different surface treatments. We discuss the results in view of the different environments in which the measurements are carried out (UHV for the UPS and air/Ar for the Kelvin method), of the effects which may be induced by the high-energy photon irradiation in the UPS measurement, and of the stability of the gold probe work function in gas ambient. We conclude that UPS is better-suited for absolute work function determination, although KP remains a convenient and inexpensive tool for fast screening of contact potential differences.

Point defects and electrical properties of Sn-doped In-based transparent conducting oxides

Hwang J.-H. et al. Solid State Ionics 2000 129/1 (135-144)

In-based transparent conducting oxides (TCOs) share the prevailing defect structure of indium-tin oxide (ITO), i.e. electrons, isolated SnIn donors, and neutral associates, believed to be $(2\text{SnInO}''\text{i})_x$. The present work reviews the state of the literature, presents calculated Brouwer diagrams vs. oxygen partial pressure and vs. dopant concentration, and reports intermediate temperature electrical property data (thermopower, conductivity) vs. $p\text{O}_2$ and Sn concentration for three systems - polycrystalline bulk ITO, nanocrystalline ITO, and the recently reported ternary cation TCO, $\text{Ga}_{3-x}\text{In}_5+x\text{Sn}_2\text{O}_{16}$. The influence of non-reduceable tin-oxygen complexes at high doping levels is identified for ITO. Ramifications for In-based TCO properties are discussed.

Work function of ITO substrates and band-offsets at the TPD/ITO interface determined by photoelectron spectroscopy

Chkoda L. et al., Synthetic Metals 2000 111/- (315-319) Language: English

Surface compositions and work functions (Φ) of commercially available indium tin oxide (ITO) substrates were measured by photoelectron spectroscopy (UPS/XPS). Whereas substrates cleaned by organic solvents are significantly contaminated and have low Φ values ($3.9\text{-}4.2 \pm 0.1$ eV), substrates cleaned by Ar^+ sputtering typically have values of $\Phi = 4.3 \pm 0.1$ eV. Even higher Φ values (up to 4.7 ± 0.1 eV) are obtained by reactive ion etching with oxygen, likely related to oxygen-containing surface impurities. Evaporated TPD is physisorbed on ITO, but causes a drop of the vacuum potential by 0.2-0.4 eV (depending on the ITO pretreatment) directly at the TPD/ITO interface, in contradiction to the common-vacuum level rule. The TPD highest occupied molecular orbital (HOMO) is found 1.1-1.3 eV below the Fermi level of the ITO, which indicates the presence of a significant barrier for hole injection.

Electrochemical oxidation of water to dioxygen catalyzed by the oxidized form of the bis(ruthenium - hydroxo) complex in H_2O



Wada T. et al. *Angewandte Chemie - International Edition* 2000 39/8 (1479-1482)

Language: English

A structural model of the O₂ -evolving center in photosystem II is provided by complex 1. The two ruthenium - hydroxo units in the complex play a key role in the oxidation of water to O₂. Deposition of the complex on an indium - tin-oxide electrode has enabled 15.0 mL of O₂ (turnover 6730) to be evolved from the controlled-potential electrolysis of water at +1.7 V.

Electrosynthesis and study of carbazole-acrylamide copolymer electrodes

Sarac A.S et al. *Polymer* 2000 41/3 (839-847) Language: English

Polymerization of N-carbazoles in the presence of acrylamide has been studied by electrochemical polymerization onto platinum and indium tin oxide (ITO), electrodes from an acetonitrile solution of the monomers and tetraethylammonium perchlorate-supporting electrolyte. The influence of polymerization conditions such as electrode potential, monomer concentration, type of solvent and supporting electrolyte on the mechanical and electrochemical properties of final polymers have been studied. The redox behaviour of the polymer-coated electrodes was checked in solution containing ferrocene and dopamine solution by cyclic voltammetry. Depending on the conditions the electrode response may be reversible or quasi reversible. Cationic polymerization of monomer is initiated either by the monomer cation radical or by the proton generated by the coupling reaction of the cation radical of carbazole. For the characterization of copolymers Cyclic Voltammetry, UV-vis and FT-IR spectrophotometric, solid state conductivity and SEM measurements were used.

Stepwise assembled photoactive films containing donor-linked fullerenes

Luo C et al. *Angewandte Chemie - International Edition* 2000 39/21 (3905-3909)

Language: English

Stable multilayer systems of C₆₀ -based materials were assembled on photoactive indium tin oxide (ITO) electrodes by supramolecular layer-by-layer organization. The assembled ensembles comprise a positively charged fulleropyrrolidinium salt (see scheme) and a series of positively charged ruthenium(II)-polypyridyl-full-erene donor-acceptor dyads. Upon irradiation with light of an appropriate wavelength generation of photocurrent can be observed, whose intensity increases linearly with the number of deposited monolayers.

Ferredoxin-mediated electrocatalytic dehalogenation of haloalkanes by cytochrome P450(cam)

Wirtz et al. *Journal of the American Chemical Society* 2000 122/6 (1047-1056)

The potential role of cytochrome P450(cam) in bioremediation has been extensively studied because of its ability to carry out the nonphysiological reductive dehalogenation of haloalkanes. The reductive dehalogenation catalytic cycle requires the input of two reducing equivalents, typically delivered to the enzyme from NADH via putidaredoxin reductase and putidaredoxin. In the presence of polylysine, spinach ferredoxin acts as an efficient electron shuttle between an indium-doped tin oxide (ITO) electrode and substrate-bound cytochrome P450 (cam). The ferredoxin-mediated electrochemical reduction of substrate-bound cytochrome P450 (cam) conduces to the reductive dehalogenation of haloalkanes. Consequently, this strategy permits the replacement of NADH and cytochrome P450 reductase, both expensive and fragile species, with an electrode to catalyze dehalogenation reactions.



Postdeposition annealing influence on sputtered indium tin oxide film characteristics

Higgins Masatoshi et al. Japanese Journal of Applied Physics, Part 1: Regular Papers & Short Notes & Review Papers 1994 33/1 A (302-306) Language: English

The influence of post-deposition annealing on sputtered indium tin oxide (ITO) film characteristics were investigated. The annealing experiments were carried out in air or vacuum atmosphere. Both air and vacuum annealing decreased the resistivity up to heat treatment of 200°C. Over 300°C treatment, air annealing increased resistivity whereas vacuum annealing decreased it. It was clarified that the resistivity depended on the carrier concentration.

Concentration and removal of tritium and/or deuterium from water contaminated with tritium and/or deuterium U.S. Patent No. 6,190,531 (T.J. Meyer and P.M. Narula)

Metal oxo complexes, preferably containing a Group VIII met al., are used. Uses ITO electrodes.

***Patterning of Transparent Conducting Oxide Thin Films by Wet Etching for α -Si:H TFT-LCDs**, Lan *et al.*, Journal of Electronic Materials, 25 (12), pp. 1806-1817, 1996.

Estimation and Verification of the Optical Properties of Indium Tin Oxide Based on the Energy Band Diagram, Knickerbocker *et al.*, J. Vac. Sci. Technol., A, 14 (3, Pt. 1), pp. 757-761, May-June 1996.

Microstructural and Electrochemical Aspects of Wet Etching ITO Films, Jacobs, et al., Electrochemical Society Proceedings, Vol. 96-23, pp. 158-173.

ITO Thin-Film Transparent Conductors: Microstructure and Processing, Shigesato *et al.*, JOM, 47 (3), pp. 47-50, 1995.

Damage Free Indium Tin Oxide Contacts to Indium Phosphide Based Devices, Azèma *et al.*, Proc. SPIE - Int. Soc. Opt. Eng., 2397 (Opto electronic Integrated Circuit Materials, Physics, and Devices), pp. 271-275, February 1995.

Comparison of ITO Films Produced by Standard D.C. Sputtering and Ion Beam Assisted Sputtering, Grieser, Annual Technical Conference Proceedings - Soc. Vac. Coaters, 38th, pp. 155-162, 1995.

Applications of Electroporation of Adherent Cells in situ, on a Partly Conductive Slide, Raptis, *et al.*, Molecular Biotechnology, Vol. 4, 1995, pp. 129 - 138.

Electrical and Optical Properties of Amorphous Indium Oxide, Bellingham *et al.*, J. Phys.:Condens. Matter, Vol. 2, pp. 6207-6221, (1990).

Evaporated Sn-doped In₂O₃ Films: Basic Optical Properties and Applications to Energy-Efficient Windows, Granqvist *et al.*, J. Appl. Phys, 60 (11), pp. R123-R159, 1 December 1986.



Development of silver-based multilayer coating electrodes with low resistance for use in flat panel displays

Aoshima Yuki et al. Japanese Journal of Applied Physics, Part 1: Regular Papers and Short Notes and Review Papers 2000 39/8 (4884-4889) Language: English
Multilayer coatings consisting of thin silver layers sandwiched between layers of transparent conducting metal oxides were investigated from the view-point of low-resistance electrodes for use in flat panel displays. Optimization of the multilayer coatings resulted in a five-layer coating composed of indium and zinc oxide composite material (IZO) and silver containing 1 wt% of palladium (Ag-Pd). The coatings had satisfactory properties of low resistance, high transmittance, high moisture and alkali resistance, and good patterning.

***Deposition of Oriented Polymer Films for Liquid Crystal Alignment by Pulsed Laser Ablation**, Luo *et al.*, Applied Surface Science, 108, pp. 89-93 (1997).

***Patterning of Transparent Conducting Oxide Thin Films by Wet Etching for a-Si:H TFT-LCDs**, Lan *et al.*, Journal of Electronic Materials, 25 (12), pp. 1806-1817, 1996.

***Glass Substrates for Flat Panel Displays**, Moffatt, Materials Research Society Bulletin, pp. 31-34, March 1996.

Materials in Active-Matrix Liquid-Crystal Displays, Hanna *et al.*, Materials Research Society Bulletin, pp. 35-38, March 1996.

Fast Write and Erase Surface Resistance Induced Nematic Liquid Crystal Display, Monkade *et al.*, Appl. Phys. Lett., 50 (13), pp. 856-858, 30 March 1987.

High Photorefractive Gain in Nematic Liquid Crystals Doped with Electron Donor and Acceptor Molecules, Wiederrecht *et al.*, Science, Vol. 270, p. 1794-1796, 15 December 1995.

ORGANIC LED

Diode Developers: A Bright Future

A.H. Tullo, Chemical & Engineering News, June 26, 2000, Vol. 78, No. 26
A brief review of the market development for organic light-emitting diode (OLED) displays.

Influence of copper phthalocyanine on the charge injection and growth modes for organic light emitting diodes

Forsythe E.W et al. Journal of Vacuum Science and Technology, Part A: Vacuum, Surfaces and Films 2000 18/4 II (1869-1874)
The effect of copper phthalocyanine layer in between indium tin oxide anode and N,N'-bis-(1-naphthyl)-N,N'-diphenyl-1, 1-biphenyl-4,4'-diamine (NPB) hole transport layer on the charge injection and growth modes of organic light emitting diodes (OLEDs) were investigated. The OLEDs were based on tris-8-(hydroxyquinoline) aluminum and NPB. Two properties of the CuPc buffer improved the stability of the OLEDs. Firstly, the improved hole injection from the indium tin oxide to the NPB transport layer. Secondly, the growth of NPB organic molecules in island-like modes on the indium tin oxide.



Interface formation between NPB and processed indium tin oxide

Le Q.-T. et al. Thin Solid Films 2000 363/1 (42-46) Language: English

We have investigated the interface formation between ITO and N,N'-bis-(1-naphthyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB), an organic materials often used as hole transport layer in organic light-emitting devices (OLED), by using X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) and atomic force microscopy (AFM). Acid or base treatment of indium tin oxide (ITO) surfaces can significantly alter the surface work function which, in the case of acid treatment, points to an improved energy level alignment with NPB and, therefore, enhanced hole injection efficiency. We found no significant reactions nor level bending for NPB deposited on standard ITO. In contrast, for acid-treated ITO, reaction of NPB nitrogen with the proton of the dipole layer on the ITO surface is observed. At low NPB coverages, AFM images reveal uniform island growth of NPB on ITO. Further deposition leads to a more complete covering of the ITO surface by NPB layer, corresponding to a laminar growth mode.

Investigation of surface energy for organic light emitting polymers and indium tin oxide

Ma Kui-Xiang et al. Thin Solid Films 2000 371/1 (140-147) Language: English

The contact angles on the thin films of poly(2-methoxy-5-(2'-ethyl-hexyloxy)-p-phenylenevinylene) (MEH-PPV) and indium tin oxide (ITO) were measured by the sessile-drop technique. The surface energies of the films were calculated using the 2-liquid geometric mean and 3-liquid Lifshitz-van der Waals acid-base (LWAB) approaches. The overall total surface energies (γ_S) of MEH-PPV and the as-received ITO were 26.4 and 25.8 mJ/m², respectively. Both approaches yielded almost the same surface energies. The surface energies were mainly contributed to by dispersion interactions or Lifshitz-van der Waals (LW) interactions for both MEH-PPV and ITO. The changes in the contact angles and surface energies of the ITO films, due to different solvent cleaning processes and argon plasma treatments, were analyzed. Experimental results revealed that the total surface energy of the ITO films increased after various cleaning processes. In comparison with different solvents used in this study, we found that methanol is an effective solvent for ITO cleaning, as a higher surface energy was observed. ITO films treated with argon plasma showed the highest surface energy. This work demonstrated that contact angle measurement is a useful method to diagnose the cleaning effect on ITO films.

Modification of indium tin oxide for improved hole injection in organic light emitting diodes

Shen Y. et al. Advanced Materials 2001 13/16 (1234-1238) Language: English

Modification of indium tin oxide (ITO) electrode interface for improved hole injection in organic light emitting diodes (OLED) was investigated. The injection efficiency measurements were carried out to characterize contact between ITO and the organic semiconductor triphenyldiamine (TDP) layer. Coating of ITO with self-assembled ultrathin platinum (Pt) films as interface modification layers, dramatically enhances OLED efficiency and contact with TDP becomes nearly ohmic. The surface morphology of ITO electrodes was investigated by atomic force microscopy (AFM).

All-columnar bilayer light-emitting diode

Seguy Isabelle et al. Synthetic Metals 2000 111/- (15-18) Language: English



The first organic light-emitting diode with both an electron-rich columnar liquid crystal as hole transport material and an electron-deficient fluorescent columnar liquid crystal as electron transport material is presented. Red fluorescence is observed above 10 V from the configuration indium-tin oxide (ITO)/hexabutoxy-triphenylene/tetraethyl perylenetetracarboxylate/Al. The excellent charge transport properties of columnar phases are thus exploited for light-emitting diodes. Both organic materials exhibit their columnar liquid crystal phase well above room temperature and the underlying ordered solid columnar phase is used in the diode. The I(V) and L(V) characteristics are very reproducible from device to device, with an emission peak at 620 nm and an FWHM of 80 nm, a current rectification ratio of about 30, $I \propto V^2$ at low voltages and $I \propto V^7$ at higher voltages. Initial lifetime measurements are encouraging.

Surface wetting properties of treated indium tin oxide anodes for polymer light-emitting diodes

Kim J.S. et al. *Synthetic Metals* 2000 111/- (369-372) Language: English
We report contact angle hysteresis and surface energy of differently treated ITO substrates obtained by measuring dynamic contact angles for liquids with different polar character. We find that the hysteresis and the polar and dispersion component of the surface energy depend strongly on the surface treatments. Oxygen-plasma induces the highest surface polarity and the highest total surface energy, but in contrast, argon-plasma shows the lowest surface polarity and the lowest total surface energy. We suggest that such surface wetting properties of the ITO anodes play an important role in deciding the interface formation with polymers, and therefore the performance of light-emitting diodes. We discuss the results in relation to the ITO surface roughness and chemical heterogeneity modified by the different treatments.

Self-assembled nanocomposite polymer light-emitting diodes with improved efficiency and luminance

Bliznyuk Valery et al. *Advanced Materials* 1999 11/15 (1257-1261) Language: English
Indium tin oxide (ITO) transparent anode was modified using self-assembled monolayers and electrostatically assembled SiO₂ nanoparticles. The modification of the ITO electrode with SiO₂ nanoparticles dramatically improved electroluminescence properties of polymer light emitting devices (PLED). The charged nanoparticle surface, which serves as a carrier trap at low current densities, induced a dipole moment across the electrode interface, effectively increasing the local electric field and promoting carrier injection. This effect enabled the ability to improve PLED efficiency with a single monolayer without including additional polymer layers or modifying the electrode work

Molecular-scale interface engineering for polymer light-emitting diodes

Ho P.K.H. et al. *Nature* 2000 404/6777 (481-484) Language: English
Achieving balanced electron-hole injection and perfect recombination of the charge carriers is central to the design of efficient polymer light-emitting diodes (LEDs). A number of approaches have focused on modification of the injection contacts, for example by incorporating an additional conducting-polymer layer at the indium-tin oxide (ITO) anode. Recently, the layer-by-layer polyelectrolyte deposition route has been developed for the fabrication of ultrathin polymer layers. Using this route, we previously incorporated ultrathin (<100 Å) charge-injection interfacial layers in polymer LEDs. Here we show how molecular-scale engineering of these interlayers to form stepped and graded electronic profiles can lead to remarkably efficient single-layer polymer LEDs.



These devices exhibit nearly balanced injection, near-perfect recombination, and greatly reduced pre-turn-on leakage currents. A green-emitting LED comprising a poly(p-phenylene vinylene) derivative sandwiched between a calcium cathode and the modified ITO anode yields an external forward efficiency of 6.0 per cent (estimated internal efficiency, 15-20 per cent) at a luminance of 1,600 candelas per m² at 5 V.

Efficient, blue light-emitting diodes using cross-linked layers of polymeric arylamine and fluorene

Chen J.P et al. *Synthetic Metals* 1999 107/2 (129-135) Language: English
Single-, double- and triple-layer polymer light-emitting diodes (PLEDs) with indium-tin oxide (ITO) anodes and Ca cathodes were fabricated, based on solution processable and thermally cross-linkable hole transporting polyarylamine and blue luminescent polyfluorene; and an electron transporting oxadiazole trimer. Triple-layer PLEDs show the highest efficiency, brightness and saturation of blue emission. These results are interpreted in terms of charge injection balance and electron-hole recombination efficiency. The maximum external quantum efficiencies achieved (>1%) are comparable to the best polymer blue PLEDs.

Indium diffusion in model polymer light-emitting diodes

de Jong M.P. et al. *Synthetic Metals* 2000 110/1 (1-6) Language: English
The diffusion of indium into poly-(phenylenevinylene) (PPV) in model polymer light-emitting diodes (p-LEDs) was studied with Rutherford backscattering spectrometry (RBS), X-ray photoelectron spectroscopy (XPS), low energy ion scattering spectroscopy (LEIS) and particle induced X-ray emission (PIXE). The model p-LEDs consisted of a glass substrate, an indium-tin-oxide (ITO) electrode, a PPV layer obtained by thermal conversion of sulfonium precursor PPV, and a patterned aluminum electrode. From RBS measurements it was concluded that about 0.01 at.% indium was present in the PPV, homogeneously distributed in depth. Annealing at 230 °C for 19 h caused the amount of In in the PPV layer to increase by roughly an order of magnitude.

An alternating copolymer consisting of light emitting and electron transporting units

Jai Kyeong Kim et al. *Journal of Materials Chemistry* 1999 9/9 (2171-2176)
Language: English
An alternating copolymer composed of fluorene-divinylene as the light emitting unit and pyridine as the electron transporting one was synthesized by employing the Wittig reaction. The copolymer, which has conjugation throughout the molecular chain, is soluble in both polar and nonpolar solvents. The copolymer has a band gap energy of 2.85 eV deduced from an ultraviolet-visible absorption spectrum, and ionization potential and electron affinity of -5.67 and -2.82 eV, respectively, deduced from a cyclic voltammogram. The photoluminescence (PL) emission maximum was observed at 440 or 540 nm depending on the solvent used in making the solution for spin-casting. The copolymer was also capable of transporting electrons and could be used as an electron-transporting layer. A light emitting diode (LED) fabricated with a blend of polyvinylcarbazole (PVK) with a fluorene-based light emitting material, and this copolymer as an electron transporting layer, exhibited an electroluminescence (EL) emission maximum at 475 nm with a full width at the half maximum (FWHM) of 50 nm and a quantum efficiency of 0.1%, where indium tin oxide (ITO) and Al were used as the anode and cathode, respectively.



Charge carrier transport in poly(p-phenylenevinylene) light-emitting devices

Forero S. et al. *Physical Chemistry Chemical Physics* 1999 1/8 (1769-1776)

Language: English

The role of doping and trap states for charge carrier transport in light-emitting devices based on unsubstituted poly(p-phenylenevinylene) (PPV) was investigated and charge carrier mobilities were determined by different techniques. Using temperature dependent impedance spectroscopy and thermally stimulated currents, the energetic depth and density of states created by doping of PPV during device fabrication on different substrate materials were determined. It was found that the conversion of PPV on indium-tin oxide (ITO) substrates creates shallow traps with a depth of about 0.1-0.2 eV, which are responsible for the p-type doping of PPV and govern the room temperature device characteristics.

Effect of poly(3,4-ethylene dioxythiophene) on the built-in field in polymer light-emitting diodes probed by electroabsorption spectroscopy

Brown T.M. et al. *Synthetic Metals* 2000 111/- (285-287) Language: English

Here we report electroabsorption (EA) measurements on light-emitting diodes (LEDs), fabricated with poly(4,4'-diphenylene diphenylvinylene) (PDPV) as the emissive layer in indium-tin oxide (ITO)/poly(3,4-ethylene dioxythiophene) (PEDOT):polystyrene sulfonic acid (PSS)/PDPV/Ca-Al and ITO/PDPV/Ca-Al structures. In the latter structure, the built-in potential, determined from nulling the EA signal, corresponds to the difference between the work functions of the electrodes. By incorporating a PEDOT:PSS film between the ITO electrode and the emissive layer we find that such a built-in voltage increases by 0.5 V. The correspondent lowering of the anodic barrier height at the PDPV interface is likely to be responsible for the improvement in device performance.

Self-assembled nanocomposite polymer light-emitting diodes with improved efficiency and luminance

Bliznyuk Valery et al. *Advanced Materials* 1999 11/15 (1257-1261) Language:

English

Indium tin oxide (ITO) transparent anode was modified using self-assembled monolayers and electrostatically assembled SiO₂ nanoparticles. The modification of the ITO electrode with SiO₂ nanoparticles dramatically improved electroluminescence properties of polymer light emitting devices (PLED). The charged nanoparticle surface, which serves as a carrier trap at low current densities, induced a dipole moment across the electrode interface, effectively increasing the local electric field and promoting carrier injection. This effect enabled the ability to improve PLED efficiency with a single monolayer without including additional polymer layers or modifying the electrode work function.

Characteristics of polythiophene surface light emitting diodes

Kaminorz Yvette et al. *Synthetic Metals* 2000 113/1 (103-114) Language: English

Surface light emitting diodes (SLEDs), in which previously microfabricated electrodes were coated with a conjugated polymer, were made with greatly different electrode spacings (250 nm and 10 or 20 μm) and with different electrode material combinations. The fabrication process allowed us to compare several electrode materials. The SLED structures also enabled imaging of the light emission zone with fluorescence video microscopy. Conventional sandwich structures were also made for comparison (electrode separation 50 nm). In this study, the emitting layer was poly[3-(2',5'-bis(1'',4'',7''trioxaocetyl)phenyl)-2,2' ;5'-bithiophene] (EO-PT), a conjugated polymer based



on polythiophene with oligo(ethyleneoxide) side chains. The current-voltage (I(V)) and light-voltage (L(V)) characteristics of the SLEDs were largely insensitive to electrode separation except at high voltages, at which the current in the devices with the largest separations was limited. Sandwich structures had the same light output at a given current. Light could be obtained in forward and reverse bias from indium tin oxide (ITO)-aluminum, gold silicide-aluminum, and gold silicide-gold SLEDs, but the turn-on voltages were lowest with the ITO-aluminum devices, and these were also the brightest and most reliable. Adding salt to the EO-PT increased the current and brightness, decreased the turn-on voltages, and made the I(V) characteristics symmetric; thus, a device with an electrode separation of 10 μm had the extraordinarily low turn-on voltage of 6 V. The location of the light emission was at the electron-injecting contact.

Effect of ionization potential of hole transport layer on device characteristics of organic light emitting diode with oxygen plasma treated indium tin oxide

Hashimoto Y et al. Source: Japanese Journal of Applied Physics, Part 1: Regular Papers and Short Notes and Review Papers 2001 40/7 (4720-4725) Language: English
We have investigated the contribution of the oxygen ions and electrons, and of the kinetic energy of these species on oxygen plasma treatment of indium tin oxide (ITO) electrode. In the case of the treatment by positive oxygen ions with kinetic energy of 50 eV, the luminance increased markedly with a lowering of the operating voltage in the organic light emitting diode (OLED). The change in the device characteristics was attributed to an effective removal of organic contaminants from the ITO surface, leading to enhanced hole injection from ITO to a hole transport layer (HTL) due to an increase in work function of the ITO. Moreover, the highest luminance and luminous efficiency were obtained in the OLED having HTL with ionization potential of 5.4 eV. These results have suggested that OLEDs fabricated using the oxygen plasma treated ITO can give the best device performance by the selection of an optimum HTL.

Cyclic Voltammetry Studies of Light-Emitting Electrochemical Cells, Heeger *et al.*, J. Electrochem. Soc., Vol. 144 (4), pp. L70-L72, April 1997.

Light-emitting Polymers: Increasing Promise, Holton, Solid State Technology, pp. 163-169, May 1997.

Pyridine-based Polymers: Photoexcitations and Light-Emitting Devices, Polymer Division, Epstein *et al.*, ACS, 37(1),pp. 133-134, 1996.

Light-emitting Diodes Fabricated with Conjugated Polymers -Recent Progress, Baigent *et al.*, Synthetic Metals, 67,pp 3-10, 1994.

Light-emitting Diodes Based on Conjugated Polymers, Burroughes *et al.*, Nature, 347, pp. 539-541, 11 October 1990.

PHOTOCHROMIC DEVICES

Flexible solid-state photoelectrochromic windows

Pichot Francois et al. Journal of the Electrochemical Society 1999 146/11 (4324-4326)
Language: English

Photoelectrochromic 'smart' window technology is extended to include the use of flexible substrates and solid-state electrolytes. This should facilitate their application as retrofit modifications of office windows, where, by blocking incoming solar irradiation, they could substantially lower air-conditioning costs. These devices are based on a dye-sensitized TiO₂ electrode coupled with a 500 nm thick WO₃ electrochromic counter



electrode, separated by a cross-linked polymer electrolyte containing LiI. A novel method for preparing conducting nanoporous TiO₂ films is described that allows for the construction of these devices on flexible organic substrates. Colloidal solutions of TiO₂ free of surfactants were spin-coated onto indium-tin oxide coated polyester substrates, resulting in highly transparent films ranging from 100 nm to 1 μm in thickness. Upon annealing at 100 °C, these films were strongly adherent and displayed excellent photoconductivity as shown by their current-voltage characteristics. The devices typically transmit 75% of visible light in the bleached state. After a few minutes of exposure to white light (75 mW/cm²), the windows turn dark blue, transmitting only 30% of visible light. They spontaneously bleach back to their initial noncolored state upon removal of the light source.

ELECTROLUMINESCENT DEVICES

Improvement of organic electroluminescent device performance by in situ plasma treatment of indium-tin-oxide surface

Ishii M. et al. Source: Journal of Luminescence 2000 87/- (1165-1167) Language: English

Indium-tin-oxide (ITO) surface treated by Ar-50% O₂ plasma has been in situ analyzed using X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS), to investigate the relations between the properties of the ITO surface and the properties of organic electroluminescent (EL) devices. The plasma treatment of the ITO surface lowered the operating voltage of the organic EL device. The UPS measurements revealed that the plasma treatment resulted in the increase of the work function of the ITO surface by more than 1 eV. The XPS measurements showed that the plasma treatment effectively removed carbon contaminants from the ITO surface. The work function was correlated with the surface carbon concentration. From these results, the lowering of the operating voltage in the EL devices is attributed to the increase of the work function resulting from the carbon removal by the plasma treatment.

Influence of thickness of electrochemically deposited hole-transport film on electroluminescent properties

Wang G. et al. Applied Physics A: Materials Science and Processing 2000 71/1 (117-120) Language: English

Polybithiophene (PBTh) film was used as a hole-transport layer in an electroluminescent (EL) device. The PBTh was electropolymerized on indium tin oxide (ITO)-coated glass acting as a working electrode. From the change of full width at half maximum (FWHM) of the EL spectrum with the thickness of the PBTh film, it could be deduced that the PBTh film efficiently blocks the injection of electrons into the ITO electrode. The thickness of the hole-transport layer used in the EL device has a significant influence on the EL intensity and efficiency. Experimental data showed that there is an optimal thickness of the electrodeposited PBTh-hole-transport layer for high-efficiency EL devices.

Alq₃/PVK heterojunction electroluminescent devices

Michelotti F. et al. Synthetic Metals 2000 111/- (105-108) Language: English
We report on the design, manufacturing and testing of Alq₃/polyvinylcarbazole (PVK) light emitting devices. The devices were obtained by spin coating PVK films on indium tin oxide coated glass substrates. Alq₃ films were then deposited by high vacuum thermal



evaporation. The devices were topped by depositing magnesium/silver electrodes by thermal evaporation. After deposition, the samples were stored and operated under a nitrogen atmosphere in order to prevent damage due to oxidation. The thickness of the active layers was purposely chosen to be large in order to study the device with an electro-optic reflectometric technique.

Quantized electroluminescence from Q-CdS films immersed in aqueous electrolytes

Tanno K. et al. Colloids and Surfaces A: Physicochemical and Engineering Aspects 1999 146/1-3 (293-298) Language: English

Quantum dot electrodes (QDEs) have been constructed by deposition of Q- CdS particles onto indium-tin oxide substrates. Upon application of cathodic potentials to the electrodes in electrolytes containing persulfate ions ($S_2O_8^{2-}$), light emission is observed. The emission peak depends on the particle size, with electrolyte electroluminescence (EEL) being observed down to 478 nm (blue light) for CdS with a particle size of 3.6 nm.

Use of tin oxide thin films as a transparent electrode in PPV based light-emitting diodes

Arias A.C. et al. Thin Solid Films 2000 371/1 (201-206) Language: English

Tin oxide (TO) thin films, nominally undoped, have been used as electrodes in poly(p-phenylene vinylene) (PPV) based organic electroluminescent devices. The evolution of the crystallinity and the electrical resistance of TO films submitted to the PPV thermal conversion conditions, have been investigated. It has been found that the electrical resistance is decreased whereas the crystallinity of the film is increased. It is shown in this work, that the photoluminescence of PPV converted on top of TO substrates is not as quenched as it is when converted on top of indium-tin oxide (ITO) substrates. The quantum efficiency of light-emitting diode is 0.07% at 17 V forward bias. It is also shown that the work function of TO films is very stable to different cleaning procedures, in contrast with previous results obtained for ITO films.

White-Light-Emitting Material for Organic Electroluminescent Devices, Hamada *et al.*, Jpn. J. Appl. Phys., Part 2, Vol. 35 (10B) L1339-L1341, 1996.

Materials Used in Electroluminescent Displays, Rack *et al.*, Materials Research Society Bulletin, pp. 49-58, March 1996.

***Transparent Conductive Electrodes for Electrochromic Devices: A Review**, Granqvist, Applied Physics A57, pp. 19-24, 1993.

DNA IMMOBILIZATION/DETECTION

Electropolymerizable film, and method of making and use thereof

U.S. Patent No. 6,180,346 (H.H. Thorp and Ontko; Allyn C.)

DNA immobilized onto poly(ethylene terephthalate) or PET membranes and DNA probes attached directly to Indium-Tin Oxide (ITO) electrodes were used for detection of complementary DNA with application as a PCR amplicon bioassay.

Claims directed to electrodes useful for the electrochemical detection of a nucleic acid for the electrochemical detection of a preselected base in a nucleic acid.

Microelectronic device

U.S. Patent No. 6,132,971 (Thorp; Johnston; Napier; Loomis; Sistare; Kim)



A method of detecting a nucleic acid (e.g., DNA, RNA) that contains at least one preselected base (e.g., adenine, guanine, 6-mercaptoguanine, 8-oxo-guanine, and 8-oxo-adenine) comprises (a) reacting the nucleic acid with a transition metal complex capable of oxidizing the preselected base in an oxidation-reduction reaction; (b) detecting the oxidation-reduction reaction; and (c) determining the presence or absence of the nucleic acid from the detected oxidation-reduction reaction at the preselected base. The method may be used in a variety of applications, including DNA sequencing, diagnostic assays, and quantitative analysis. Uses modified ITO electrodes.

Monolayer and electrode for detecting a label-bearing target and method of use thereof

U.S. Patent No. 6,127,127, (Eckhardt; Mikulecky; Napier; Thomas; Thorp)

An electrode for detecting interactions between members of a binding pair. The electrode is modified by formation of a non-conductive self-assembled monolayer. When contacted with a target nucleic acid, an oligonucleotide probe coupled to the self-assembled monolayer reacts with the target nucleic acid to form a hybridized nucleic acid on the modified electrode surface. The hybridized nucleic acid is reacted with a transition metal complex capable of oxidizing a preselected base in the hybridized nucleic acid in an oxidation-reduction reaction, the oxidation-reduction reaction is detected, and the presence or absence of the nucleic acid is determined from the detected oxidation-reduction reaction.

Polymer-electrodes for detecting nucleic acid hybridization and method of use thereof

U.S. Patent No. 5,968,745 (H.H. Thorp, R. Carson and M.E. Napier)

A polymer-electrode (i.e., a polymer layer on a substrate having a conductive working surface) is used with an oligonucleotide probe. The probe attaches to the polymer layer and is available to capture target nucleic acid. A soluble mediator can diffuse freely and transfer electrons from a preselected base in the hybridized nucleic acid to the conductive working surface of the substrate. An electronic signal generated from the electron transfer reaction is detected and quantitated. (uses ITO electrodes)

Electrochemical detection of nucleic acid hybridization

U.S. Patent No. 5,871,918 (Thorp; Johnston; Napier; Carson; Sistare; Kim)

A method of detecting a nucleic acid (e.g., DNA, RNA) that contains at least one preselected base (e.g., adenine, guanine, 6-mercaptoguanine, 8-oxo-guanine, and 8-oxo-adenine) by reacting the nucleic acid with a transition metal complex capable of oxidizing the preselected base in an oxidation-reduction reaction. The method may be used in a variety of applications, including DNA sequencing, diagnostic assays, and quantitative analysis.

SENSORS

Sensing of Fe(CN)₆⁴⁻

Maizels M et al. *Electroanalysis* 2000 12/17 (1356-1362) Language: English
A spectroelectrochemical sensor that has trimodal selectivity (selective partitioning, electrochemistry, and spectroscopy) is evaluated for the determination of ferrocyanide in solution. The sensor is based on attenuated total reflection spectroscopy at an indium-tin oxide optically transparent electrode coated with a cationic PDMDAAC-SiO₂, where PDMDAAC means poly(dimethyldiallylammonium chloride) film into which anionic



Fe(CN)₆⁴⁻ partitions. Fe(CN)₆⁴⁻ loaded into the film is subjected to spectroelectrochemical modulation, and the absorbance change at 420 nm associated with cycling Fe(CN)₆⁴⁻/Fe(CN)₆³⁻

Simulation of sensor response for different excitation potential waveforms

Slaterbeck A.F. et al. Analytical Chemistry 2000 72/22 (5567-5575) Language:

English

The simulation of the optical response in spectroelectro-chemical sensing has been investigated. The sensor consists of a sensing film coated on an optically transparent electrode (OTE). The mode of detection is attenuated total reflection. Only species that partition into the sensing film, undergo electrochemistry at the potentials applied to the OTE, and have changes in their absorbance at the wavelength of light propagated within the glass substrate of the OTE can be sensed. A fundamental question arises regarding the excitation potential waveforms employed to initiate the electrochemical changes observed. Historically, selection has been based solely upon the effectiveness of the waveform to quickly electrolyze any analyte observable by the optical detection method employed. In this report, additional requirements by which the wave-form should be selected for use in a remote sensing configuration are discussed.

Specific set of the time constants for characterization of organic volatile compounds in the output of metal oxide sensors

Galdikas A. et al. Sensors and Actuators, B: Chemical 2000 68/1 (335-343)

Language: English

The time dependence of the resistance response to a steep change of gas composition in the atmosphere is investigated for the gas sensors based on tin oxide and indium oxide thin films. The dependence is assumed to pertain to the exponential decrease with three time constants for the slope. The leading edge of the response is analyzed for the sensors with the aim of characterizing the target smell using a set of time constants instead of the equilibrium response signal. The sets are applied for the characterization of the volatile substances emitted from the model solutions based on glucose and glycine in which Maillard's browning reaction took place. In the sets, the collection of the time constants is shown being characteristic of the odor produced by the target solutions. Based on the sets, volatile compounds could be recognized in the aroma.

Electrical and optical characterization of thrombin-induced permeability of cultured endothelial cell monolayers on semiconductor electrode arrays

Hillebrandt H et al. Applied Physics A: Materials Science and Processing 2001 73/5 (539-546) Language: English

Impedance spectroscopy and phase-contrast microscopy are combined to monitor the electrical and morphological properties of human umbilical vein endothelial cell monolayers. The cells were cultured on optically transparent indium-tin-oxide (ITO) semiconductor electrode arrays coated with collagen IV, and the effect of the inflammatory mediator thrombin on monolayer permeability was monitored in real time. ITO electrodes provide several advantages for these kinds of experiments, because they are optically transparent, polarizable and highly sensitive due to the absence of insulating oxide layers. A qualitative correlation between the thrombin-induced gap formation and the electrical parameters of the cell layer is established.

Optoelectrochemical sensor for lead based on electrochemically assisted solvent extraction



Wilson R. et al. Sensors and Actuators, B: Chemical 2000 63/1 (115-121) Language: English

A thin film containing the complexing agent 2-(5-bromo-2-pyridylazo)-5-(diethylamino)phenol (BrPADAP) deposited on the surface of an indium tin oxide (ITO) electrode has been used as a colorimetric sensor for lead. The sensor is based on a new electrochemically assisted solvent extraction method. When a cathodic potential was applied to the thin-film sensing layer, lead ions were extracted from the aqueous solution into the film resulting in an increase of absorbance at 550 nm. The magnitude of the absorbance change was linearly dependent on the concentration of lead in the range 0-5 ppm with an estimated limit of detection for a simple spectrophotometric method better than 250 ppb.

Remarkable enhancement of photocurrent generation by ITO electrodes modified with a self-assembled monolayer of porphyrin

Yamada H et al. Chemical Communications 2000 6/19 (1921-1922) Language: English
Quantum yield of the photocurrent generation by an ITO electrode modified with a self-assembled monolayer of porphyrin was remarkably enhanced by a factor of ca. 280, as compared to that of the corresponding porphyrin monolayer on a gold electrode.

Spectroelectrochemical sensing based on multimode selectivity simultaneously achievable in a single device. 4. Sensing with poly(vinyl alcohol)-polyelectrolyte blend modified optically transparent electrodes

Gao L et al. Analytical Chemistry 1999 71/18 (4061-4068) Language: English
The feasibility of using polymer blend thin films covalently attached to indium tin oxide-glass, via the silane coupling agent (3-aminopropyl)triethoxysilane, for performing spectroelectrochemical modulation is demonstrated in aqueous solutions. The polymer blends were formulated by entrapping three polyelectrolytes- poly(vinylbenzyltrimethylammonium chloride) (PVTAC), poly(acrylic acid), and Nafion- in cross-linked poly(vinyl alcohol) (PVA) matrix for the purpose of selectively incorporating solution-phase anions and cations. $\text{Ru}(\text{BiPy})_3^{2+}$ (BiPy = 2,2'-bipyridine), $\text{Ru}(\text{CN})_6^{4-}$, and $\text{Fe}(\text{CN})_6^{3-}$ were chosen as the analytes for their suitable optical and electrochemical properties.

Spectroelectrochemical sensing based on multimode selectivity simultaneously achievable in a single device. 3. Effect of signal averaging on limit of detection

Slaterbeck A.F. et al. Source: Analytical Chemistry 1999 71/6 (1196-1203)
The effect of ensemble averaging on the response of a new spectroelectrochemical sensor has been investigated. The sensor consists of a selective film coated over an optically transparent electrode (OTE). The mode of detection is attenuated total reflection (ATR). For an analyte to be detected, it must first partition into the sensing film, second be electroactive at the applied potential, and third have a change in its absorbance at the wavelength of light monitored by ATR. Four different excitation potential waveforms were investigated: pulsed, step, triangular, and sinusoidal. A model sensor consisting of a cationically selective sol-gel-derived Nation composite film coated on an indium tin oxide OTE is employed to demonstrate the signal acquisition techniques under investigation. Tris(2,2'-bipyridyl)- ruthenium(II) chloride was used as a model analyte.

Nitric oxide sensor

U.S. Patent No. 5,603,820 (Malinski; Wink; Younathan; Murray; Sullivan; Meyer; Christodoulou)



An electrode sensor for the measurement of nitric oxide. A nitric oxide (NO) microsensor comprising a thermally-sharpened carbon fiber is disclosed. A larger scale sensor uses porphyrin and cationic exchanger deposited on larger fibers or wires, platinum mesh or indium tin oxide layered on glass, can also be employed when measurement of NO concentration in chemical media, tissue or cell culture is desired.

Electrode materials, systems and methods for the electrochemical detection of nitric oxide

U.S. Patent No. 6,280,604 (Allen; Coury; and Piantadosi)

Nitric oxide-specific electrodes are useful for in situ detection of nitric oxide in biomedical applications and have at least a surface region capable of forming complexes with nitric oxide. The nitric oxide complexes formed at the surface of the electrodes apparently increase the concentration of nitric oxide available for detection, leading to significantly improved relative responses as compared to other known nitric oxide electrode materials. The electrode has at least an exterior surface region which contains ruthenium and/or at least one oxide of ruthenium.

Uses modified ITO electrodes.

A New Planar Device based on the Seebeck Effect for Gas Sensing Applications,

Papadopoulos *et al.*, Sensors and Actuators, B34, pp. 524-527, 1996.

Disubstituted Poly(Bithiophene)s: Syntheses and Applications, Chan, et al., Prog. Pac. Polym. Sci. 3, Proc. Pac. Polym. Conf., 3rd, pp 237-46, 1994.

Preparation of Enzyme Multilayers on Electrode Surface by Use of Avidin and Biotin-Labeled Enzyme for Biosensor Applications, Osa *et al.*, Materials Science and Engineering, C2, pp. 103-106, 1994.

BIOSENSORS

A photoelectric method for analyzing NO-induced apoptosis in cultured neuronal cells

Zhang C. et al. Electroanalysis 2000 12/17 (1414-1418) Language: English

A photoelectric method for analyzing NO-induced apoptosis in cultured neuronal cells is presented. By integrating ITO (a transparent electrode of indium-tin oxide coated with borosilicate) with a layer of primary rat cerebellar granule cells and a photoelectric-current-measuring system, a cytosensor for measuring photoelectric current of neuronal cells was formed. The cells generated an anode photoelectric current under white light (200-800 nm). The amplitude of the photoelectric current was related to the cell number, the light intensity and the cell viability. During neuronal apoptosis, the decrease of the photoelectric current was in accordance with the decrease of the cell viability, the loss of mitochondrial transmembrane potential, and the fragmentation of DNA. This photoelectric method may provide a simple and sensitive way to study electron-transfer mechanism during NO-induced apoptosis.

Voltammetric studies of guanine and its derivatives by Ru(bpy)(2+/3+) mediator on indium tin oxide electrode

Kim J. Bulletin of the Korean Chemical Society 2000 21/7 (709-711) Language: English

Oxidizing metal complex mediates the electrochemical oxidation of guanine nucleotides. This catalysis results in an enhancement in cyclic voltammograms that yield the rate



constant for the oxidation of guanine by the metal complex via digital simulation. The rate constant of oxidation of guanine by $\text{Ru}(\text{bpy})_3^{3+}$ is $6.4 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$. The rate constant and the enhanced current depend on the number of phosphate groups on the sugar of nucleotide. Also the modified guanine bases show different oxidation rate constants following the trend guanine-5'-monophosphate (GMP) > 8-bromo-guanine-5'-monophosphate (8-Br-GMP) > xanthosine -5'- monophosphate (XMP) > inosine-5'-monophosphate (IMP). The guanine bases derivatized differently are all distinguishable from one another, providing a basis for studying electrochemistry of DNA and RNA and developing electro-chemical biosensors.

Soft-lithography-mediated submicrometer patterning of self-assembled monolayer of hemoglobin on ITO surfaces

Fang Aiping et al. *Langmuir* 2000 16/12 (5221-5226) Language: English

The recent direct fabrication of micropatterned arrays of active biomolecules has received overwhelming attention due to its potential applications in biosensors and medical diagnostics. Here, we report an indirect soft-lithography-mediated method of fabricating hemoglobin (Hb) patterns in the submicrometer length scales region on indium-tin-oxide (ITO). Scanning electron microscopy, quartz crystal microbalance, and cyclic voltammetry studies reveal the formation of a self-assembled monolayer of Hb on an ITO surface. The present approach provides an easy and reliable means for simultaneous and defectless passivation and submicrometer patterning of proteins, thus indicating its potential application in biological assay.

SOLAR APPLICATIONS

Semiconductor-sensitized solar cells based on nanocrystalline $\text{In}_2\text{S}_3/\text{In}_2\text{O}_3$ thin film electrodes

Hara Kohjiro et al. *Solar Energy Materials and Solar Cells* 2000 62/4 (441-447)

Language: English

A possibility of semiconductor-sensitized thin film solar cells have been proposed. Nanocrystalline In_2S_3 -modified In_2O_3 electrodes were prepared with sulfidation of In_2O_3 thin film electrodes under H_2S atmosphere. The band gap (E_g) of In_2S_3 estimated from the onset of the absorption spectrum was approximately 2.0 eV. The photovoltaic properties of a photoelectrochemical solar cell based on $\text{In}_2\text{S}_3/\text{In}_2\text{O}_3$ thin film electrodes and I-/I₃- redox electrolytes were investigated. This photoelectrochemical cell could convert visible light of 400-700 nm to electron. A highly efficient incident photon-to-electron conversion efficiency (IPCE) of 33% was obtained at 410 nm. The solar energy conversion efficiency, η , under AM 1.5 (100 mW cm^{-2}) was 0.31% with a short-circuit photocurrent density (J_{sc}) of 3.10 mA cm^{-2} , an open-circuit photovoltage (V_{oc}) of 0.26 V, and a fill factor (ff) of 0.38.

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MISCELLANEOUS

On the structural properties and optical transmittance of TiO₂ r.f. sputtered thin films

Mardare Diana et al. Applied Surface Science 2000 156/1 (200-206) Language: English

Pure and doped TiO₂ thin films were obtained by r.f. sputtering method. The samples were deposited onto glass and glass covered with indium tin oxide (ITO) substrates. Phase and surface morphology were investigated using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The structure of TiO₂ thin films is influenced by the substrate used and also by doping with Ce, Nb and Fe impurities. Consequently, the transmittance will also be modified.

Shaped and fired articles of TiO₂

U.S. Patent No. 4,166,147 (R.W. Lange and H. G. Sowman)

Titania sol gels are prepared and used to form solid, shaped and fired refractory articles, such as fibers and microspheres. Fibers are made by extruding in air a viscous aqueous titania sol, and heating and firing the resulting green fiber to remove water, decompose and volatilize undesired constituents, and form a refractory fiber of polycrystalline titanium dioxide. Microspheres are made by dispersing droplets of an aqueous titania sol in an organic dehydrating liquid.

Commercially available sols: Nalco Chemical Company (Oak Brook, IL)

For further patent information see: <http://www.uspto.gov>