Charge transport and recombination in bulk-heterojunction solar-cells

Main funding: Academy of Finland

Participating FunMat unit: DPh

The charge carrier mobility in organic solar cells is lower compared to crystalline semiconductors. Thus, to achieve the same power-conversion efficiency it is necessary to photogenerate a higher density of charge carriers. An increased carrier density causes a reduced lifetime due to bimolecular recombination and the efficiency might be reduced. Bimolecular charge carrier recombination has been clarified in thin films of low mobility bulk heterojunction solar cells based on blends of either regioregular poly(3-hexylthiophene) or poly[2-methoxy-5-(3,7-dimethoxyloxy)-phenylene vinylene] (MDMO-PPV) and 1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-methanofullerene [1-3]. We found that the recombination coefficient is reduced with orders of magnitude compared to the expected Langevin-coefficient. This leads to enhanced photogeneration efficiencies and improved transport. The power-conversion efficiency will consequently reach up to 5% as reported.

Fig. The measured mobilities of both the faster and slower charge carriers in a bulk-heterojunction solar cell, as measured using three different techniques, namely carrier extraction (CELIV), double injection (Dol) and time-of-flight (TOF). The measured values all agrees very well with each other.
Main collaboration: Vilnius University, Vilnius, Lithuania, Johannes Kepler University, Konarka Austria

Publications:


*Simulation of charge transport and recombination in disordered materials*

Main funding: Academy of Finland and GSMR

Participating FunMat unit: DPh

F. Jansson and R. Österbacka

Transport and recombination of charge carriers are important processes in electrical devices. We have simulated a dark double-injection transient measurement on an organic bulk heterojunction solar cell. The model used is hopping transport, with many charge carriers simulated simultaneously. Coulomb interactions between all charge carriers are taken into account.

Publications:


Effective temperature for hopping transport

Main funding: Academy of Finland and GSMR

Participating FunMats units: DPh
F. Jansson, S. Baranovskii, F. Gebhard, and R. Österbacka

For hopping transport in disordered materials, the mobility of charge carriers is strongly dependent on the temperature and the electric field. By numerical simulation we have studied the energy distribution and the mobility of charge carriers, as a function of electric field, temperature and carrier concentration. We have shown that both the energy distribution and the mobility can be described by a single parameter, the effective temperature, which is dependent on the magnitude of the electric field. This gives a possibility to describe the field dependence of the mobility at high electric fields.

Main collaboration: Phillips University Marburg, Germany

Publications:


Photoexcitation dynamics in an alternating polyfluorene copolymer

Main funding: Academy of Finland and Lund Laser Center

Participating FunMat units: DPh

Transient photoinduced absorption measurements have been performed on the alternating polyfluorene copolymer, poly[2,7-(9,9-dioctylfluorene)-alt-5,5-(4’,7’-di-2-thienyl-2’,1’,3-benzothiadiazole)] (APFO3) on femto-second to nanosecond timescales.
Further, delayed fluorescence has been measured up to microsecond timescales. Based on these results we have created a model of the photoexcitation dynamics in the polymer. The model includes decay of singlet excitons and intrachain polaron pairs, but also build-up and decay of interchain polaron pairs. The results are modeled numerically and the parameters which govern the generation and recombination processes are extracted.

**Main collaboration:** University of Durham, Durham, United Kingdom, Chalmers University of Technology, Göteborg, Sweden, Lund University, Lund, Sweden

**Publication:**


* 

**A Combined Optical and Electrical Method for Measuring Charge Carrier Dynamics in Bulk-heterojunction Solar Cells**

**Main funding:** Academy of Finland

**Participating FunMat units:** DPh
*M. Nyman, H. Aarnio, G. Sliaužys, and R. Österbacka*

A novel method for measuring charge carrier dynamics in bulk-heterojunction solar cells has been developed and tested. The method combines transient photo-induced absorption (tPA) with charge extraction by a pulsed voltage (CEPV). The transient photo-induced absorption technique is used to optically study the decay rates of excitations on ns – μs timescales. Some of the charges are extracted by a voltage pulse and the subsequent alteration of the excitation decay rates is studied. The amount of extracted charges is measured and compared to the decrease in the photo-induced absorption. The method has been tested on bulk heterojunction solar cells based on the conjugated polymer poly(3-hexylthiophene-2,5-diyl) (P3HT) and the fullerene derivative [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM).

**Main collaboration:** Vilnius University, Lithuania
The construction of a Kelvin-probe setup

Main funding: Academy of Finland

Participating FunMat units: DPh
F. Petterson, K.-M. Källman, and R. Österbacka

The aim of the project was to construct a Kelvin probe measurement setup on a macroscopic scale. This is the “classic” Kelvin probe setup and differs from modern scanning techniques where optical methods are used to monitor how the vibrating tip is affected by atomic forces. Still, both methods are used to measure the same quantity, namely the work function of conducting materials. The project resulted in a Master’s Thesis and also work function measurements, on printed electrode materials in organic transistors and solar cells, for other projects in the ORGEL group were carried out.

Publication:

Molecular Understanding of Printability (MolPrint)

Main funding: TEKES

Participating FunMat units: DPC, LPCC
Carl-Mikael Tåg, Hanna Koivula, Martti Toivakka, Jarl B. Rosenholm

The key challenge originally placed on the MolPrint research partners was to utilize or to develop measurable quantities describing key professional terms, such as mottling.
Then academic criteria derived from theoretical models could be used to produce commonly accepted measurable quality standards for paper manufacturers, but particularly for printing houses.

The liquid spreading of a drop introduced during printing is usually modeled for an ideally smooth (Young) surface, with an average (homogeneous) chemical property. However, coated paper surfaces are both chemically and structurally heterogeneous. The coating color of the sample papers consist of a rich number of components, such as pigments, lattices and binders. Moreover the smoothness is dependent on physical treatment such as calendaring, but remains relatively rough. This feature must be considered when evaluating the wetting with liquids and inks.

A comprehensive account on the equilibrium wetting properties of liquids on solid surfaces has been collected in a review. The work of adhesion (perpendicular interaction) between the ink and the paper surface represents the energy of immobilization (setting) of ink and the work of spreading (horizontal wetting) reflects the blotting tendency of an ink drop. Moreover, references to recent reports on the hydrophobic and polar (acid and base) properties of a range of paper qualities have been published. In these investigations the surface roughness has been corrected for and the chemical heterogeneity is evaluated as a chemical interaction of the surface.

**Main collaboration:** University of Joensuu, University of Jyväskylä, University of Oulu, University of Turku, University of Maine, Omya AG, Top Analytical Ltd

**Publications:**


Molecular Understanding of Printability (MolPrint)

Radial spreading of liquids on heterogeneous polar surfaces

Main funding: TEKES

Participating FunMat units: DPC
Mikael Järn, Carl-Mikael Tåg, Joakim Järnström, Jarl B. Rosenholm

The investigation of liquid spreading on solid surfaces is usually restricted to equilibrium wetting of nearly ideal, smooth polymers. Due to its complexity, less attention has been directed onto dynamic wetting of rough, chemically heterogeneous polar surfaces. The aim in this study is to apply the most common models developed for liquid spreading on pigment coated paper surfaces, for which the equilibrium surface energy components have been determined previously. Two models have been used to model the spreading of liquids on solid surfaces; the hydrodynamic and molecular kinetic model.

Hydrodynamic model describes the energy dissipation is a result of viscous drag within the spreading droplet. The hydrodynamic model has showed the following asymptotic time-dependence:

\[ R \sim t^{1/10} \quad \Leftrightarrow \quad \Theta \sim t^{-3/10} \]

Molecular-kinetic model by Blake and Haynes describes the three phase contact line movement as a stress modified molecular rate process involving adsorption of molecules of the advancing phase and concurrent desorption of molecules of the receding phase, respectively. The molecular kinetic model has showed the following asymptotic time-dependence:

\[ R \sim t^{1/7} \quad \Leftrightarrow \quad \Theta \sim t^{-3/7} \]

Publications:

M. Järn, C-M. Tåg, J. Järnström, J. B. Rosenholm, “Dynamics of spreading of probe liquids on offset, printing plates and rubber blamkets”, manuscript

C-M. Tåg, M. Järn, J. Järnström, J. B. Rosenholm, “Spreading dynamics of model fountain solutions on offset printing substrates”, manuscript

J. Järnström, M. Järn, C-M. Tåg, J. Peltonen, J. B. Rosenholm, “Spreadings dynamics of probe liquids and ink droplets on ink-jet papers”, manuscript
**Characterisation and Control of Coating Layer Formation**

**Main funding:** KCL and TEKES

**Participating FunMat unit:** DPC

*Rasmus Eriksson, Sami Areva, Thomas Sandberg, Taru Ruohonen, Jarl B. Rosenholm*

Industrially a most interesting question is what the result of interactions between particles in coating slurry is at process conditions. The free formation of the coating layer is of particular importance for, e.g. curtain or spray coating processes. Sediment density and rheology has been utilized for the characterisation of the state of dispersions. However, the parameters for the modelling of these time dependent processes have generally been extracted from dilute model dispersion systems. In the present project the macroscopic effect of the interactions was determined at solids contents comparable to the industrially viable systems. This opens new perspectives to comprehensively investigate homo- and hetero-coagulation and flocculation processes in concentrated dispersions.

However, at high ionic strength the DLVO-model fails to properly represent the experimental results. Therefore, a number of correction terms have been added to the model. Such contributions are: steric repulsion, Lewis acid-base interaction and graininess (packing) of molecules (hydration) close to the surface. From an industrial point of view the extended DLVO-theory, including steric interactions provides the ideal platform to investigate novel alternative coating processes such as curtain and spray coating (casting) processes. However, there is still a critical lack of proper understanding as concerns the interaction under real process conditions. No generally accepted theory covers this range. Another area of restricted research activity is the time-dependent flux phenomena during dewatering and sedimentation i.e. transport of liquid out from consolidating matrices. The latter transport phenomena induces severe strain on the paper which may bending (warping of) the paper and induce cracks and heterogeneities in the coating layer.

**Co-operation:** Helsinki University of Technology, University of Helsinki, VTT

**Publications:**


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**Precipitation and Aggregation of Asphaltene in Organic Solvents**

**Main funding:** Neste Oil Corporation, Technology Centre

**Participating FunMat unit:** DPC

_Bjarne Johansson, Rauno Friman, Jarl B. Rosenholm_

The total combinatorial Gibbs free energy was successfully used to model the solubility of two purified asphaltenes in pure and mixed solvents and the precipitation of the asphaltenes from mixed solvents. Intrinsic viscosity and particle size both sensitively reflected the state of the asphaltenes in homogeneous solution and were used for determining the solubility parameters of the asphaltenes. Phase separation was clearly reflected by a dramatic increase in particle size. The interaction parameter was subdivided into enthalpy and entropy contributions. All parameters indicate an extensive association or secondary phase transition when the phase border was followed by simultaneously varying the temperature and the solubility parameter of the solvent. However, derived in two ways, the enthalpy and entropy contributions lead to conflicting results. These were evaluated on thermodynamic grounds.

**Co-operation:** Neste Oil Corporation, Technology Centre

**Publications:**


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**Characterization and Control of Pigment Coating Structures (C-Coat)**

**Main funding:** TEKES

**Participating FunMat units:** LPCC, DPC
Liisa Sinervo, Thomas Byholm, Marie Käld, Andreas Lemström, Niklas Nylund, Christoffer Stoor, Otto Järvinen, Jani Kniivilä, Joakim Järnström, Jouko Peltonen, Martti Toivakka

Most physical and functional properties pigment coated papers are controlled by the microscopic structure of the coating layer. The objective of the project is to increase our understanding of the interrelations between coating raw materials, the microscopic porous structures resulting from these, and the end-use properties of coated paper. The main areas of research include physical and surface chemical characterization of two and three dimensional coating layer structures, optical properties of coatings and liquid penetration in porous structures. The results of the project range from coating surface characterization on different length scales to computer-based experimentation and prediction of optical and liquid absorption properties of coatings.

**Main collaboration:** Helsinki University, University of Jyväskylä, ABB Oy, Ciba Specialty Chemicals Oy, M-real Oyj, Metso Paper Oy, Omya Oy, Specialty Minerals Nordic Oy, Stora Enso Oyj and UPM-Kymmene Oyj.

**Publications:**


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Rheological materials in process industry (ReoMat)

Main funding: TEKES

Participating FunMat units: LPCC
Tomi Kemppinen, Jan Gustafsson, Martti Toivakka

The general goal of the project part was to support the related industrial research by methods development, research networking and technology transfer. The research included three main topical areas: experimental rheology, development of experimental techniques and numerical analysis. During the project a new measurement technique based on helical-flow modified rotational rheometer was developed. The measurement
allows for characterization of strongly sedimenting suspensions, which has not been possible previously. The correction terms commonly used in capillary rheometry were found to be inadequate for particulate suspensions, due to particle migration and slip phenomena.

**Main collaboration:** VTT, University of Jyväskylä, Tampere University of Technology, Kemira Oyj, Outokumpu Research Oy, Metso Paper Oy, M-real Oyj, Stora Enso Oyj, and Premix Oy

* 

**X-ray photoelectron spectroscopy study on polymer/fullerene nanocomposite memory devices**

**Main funding:** TEKES, Nanoscale Memory Unit (NAMU)

**Participating FunMat units:** DPh

*Daniel Tobjörk, Ari Laiho, Jayanta Baral, Himadri Majumdar, O. Ikkala and Ronald Österbacka*

We studied the chemical composition of memory devices as a function of depth by using X-ray Photoelectron Spectroscopy (XPS) and sputtering with argon ions. The depth profile in the figure below shows the slightly oxidized aluminum top electrode, the carbon rich active material consisting of a mixture of polystyrene (PS) and [6,6]-phenyl-C$_{61}$ butyric acid methyl ester (PCBM), the bottom aluminum contact and finally the glass substrate (containing silicon and oxygen).
**Fig.** The composition of an Al/PS:PCBM/Al memory device is shown as a function of sputtering time in this depth profile.

The atomic concentrations were determined from the area of the carbon (C1s), oxygen (O1s), aluminum (Al2p) and silicon (Si2p) peaks in the XPS spectrum. The broader shape of the bottom electrode was explained by the inhomogeneous sputtering process. From the results we could conclude that the thermal evaporation of the aluminum electrodes had not led to any observable inclusion of aluminum (<0.1-1 at.%) into the active material layer. Furthermore, the observation of alumina on the bottom contact gave some clues to the understanding of the device operation principle. We also compared the XPS results with Transmission Electron Microscopy (TEM) images of cross sections of the memory devices.

**Main collaboration:** Helsinki University of Technology

**Publication:**

Multiple layer structures – A case study of district heating and chemical resistant pipes

Main funding: KWH-pipe

Participating FunMats unit: LPT
Tua Sundholm and Carl-Eric Wilén

Multiple layered pipes are an increasingly growing niche on the plastic pipe market. Knowledge and experience in developing multiple layer pipes might give substantial competitive advantages in the future, as the processing equipment is more complex than solid wall extrusion equipment and hence not in use by most players on the pipe market.

The aim of this work was to gain knowledge on multiple layered structures, and study how individual material properties affect the final pipe’s properties. This was done e.g. through mechanical tests, jointing experiments, chemical resistance tests and calculations. This thesis work studied multiple layered pipes through two case studies: district heating pipes and chemical resistant pipes. Altogether six multiple layer structures with three to five layers were studied. The pipe extrusion trials, mechanical tests, simulations and the brief experiments with jointing indicate the most critical parameters: melt/viscosity compatibility between the materials, adhesion and appropriate process equipment. The work also purposes a structure for a multiple layer district heating pipe with better long term insulation capacity than the solid wall polyethylene pipes currently in use.

Main collaboration: KWH-pipe

Publication:
Tua Sundholm, “Multiple layer structures – A case study of district heating and chemical resistant pipes”, (Diploma thesis), Åbo Akademi University (2007).

* Optimisation of Blade Geometry for Coating of Fine Paper Using Wear-Resistant Blades

Main funding: Industry

Participating FunMat units: LPCC
Parvez Alam, Christoffer Stoor, Prem Kumar Seelam, Martti Toivakka

The project aims at understanding the blade mechanics in the blade coating of paper, and proposing new, improved blade geometries for coating of board and fine paper. A
A computer-based complex inter-coupled multi-physics model was developed to account for backing roll, base paper, pigment filter cake and, if desired, polymeric blade surface compression. Based on numerical simulations of pigment coating suspensions modelled with one-phase fluid of non-Newtonian rheology, a better understanding of the blade mechanics have been obtained.

**Main collaboration:** Industry

**Publications:**


*

**Microscopic Modeling of Coating Layer Consolidation**

**Main funding:** KCL

**Participating FunMat units:** LPCC

*Anders Sand, Martti Toivakka*

The project aims at (a) clarifying what kind of microscopic structures exist in pigment coating colors during consolidation, and (b) predicting how the wet state coating structure is reflected in the final dried coating layer structure and related coated paper end-use properties. The project utilizes numerical tools developed at the laboratory to model concentrated colloidal suspensions and to follow the microscopic motion of individual particles in the consolidating coating layer. The results have clarified relevance of the various theories proposed in literature to control consolidation of pigment coating layers.

**Main collaboration:** VTT

**Publications:**


*Printability on paper and board*

**Main funding:** Industry

**Participating FunMat units:** DPC, LPCC

*Petri Ihalainen, Jouko Peltonen*

The aim of the project is to carry out versatile surface characterization for paper and board samples. Of special interest have been topographical and thermal properties of polymer films.

**Publications:**


4.6. **Utilization**

The main focus of FunMat is to produce hierarchic intelligent structures. The interactive material is functionalized by printing of devices (indicators, sensors, transistors) making it responsive to external stimuli. However, considering the broad competence of FunMat partners on materials manufacturing also other functionalities may be demonstrated by utilization in products.

**NanoEar**

**Main funding:** EU

**Participating FunMat units:** DPC

*Alain Duchanoy, Boris Ufer, Jessica Rosenholm, Mika Lindén*

Millions of people suffer from hearing loss, and the number is increasing every year when the life expectancy increases. Therefore there is an obvious need for new medical treatments aiming at regenerating hearing loss. This integrated EU funded project aims at developing novel drug carrier systems for delivery of therapeutic agents to the inner ear. The round window membrane has small pores with pore diameters in the range of 100+ nm, which puts an upper limit to the physical size of any carrier system to be applied in a non-invasive form. This project brings together a wide range of research groups and European companies with activity areas ranging from nanoparticle synthesis and functionalization, synthesis of specific targeting ligands, and *in vitro* and *in vivo* testing.

The specific task of our research group is the synthesis and functionalization of silica based mesoporous particles to act as drug carriers. Within the framework of this project we have developed robust syntheses allowing reproducible preparation of mesoporous silica particles with a very narrow particle size distribution. The particle size can be fine tuned in the size range 60 nm – 500 nm. Furthermore, we have developed surface functionalization protocols which make it possible to selectively introduce functional groups onto the inner or outer surface of the particles, making it possible to fine-tune the interactions between the cargo and the host particle on the one hand, and those between the particle and the surrounding biological media on the other hand. The interactions between the cargo and the inner pore surfaces are important for keeping the cargo inside the particles until the particle reaches its target, while the interactions between the particles and the surrounding media is important both from a dispersion stability point and a biological recognition point of view. Successful labeling of the particles with fluorescent dyes and by targeting ligands has been demonstrated, and the particles will soon enter into the *in vivo* testing stage.
Main collaboration: RWTH, Aachen, Germany, Royal Institute of Technology, Stockholm, Sweden, Tampere Technical University, Finland, University of Helsinki, Finland, Uppsala University, Sweden, University of Rostock, Germany, Medical University of Innsbruck, Austria, University of Southampton, Great Britain

Publications:


The effects of metal impurities in an organic semiconductor on field-effect transistor properties

Main funding: Academy of Finland

Participating FunMat unit: DPh

We have used Particle Induced X-ray Emission (PIXE) analysis and Particle Induced Gamma-ray Emission (PIGE) analysis to determine the elemental impurity concentrations in thienol[2,3-b]thiophene samples that have undergone different washing and extraction procedures to remove impurities. Field-effect transistors (FETs) were fabricated from the materials and their electrical characteristics show no
significant differences between the devices made from different material samples. Reducing the metal residue levels below the one measured in the starting material (300 mg/kg Fe, 7 mg/kg Zn, 3000 mg/kg Pd and 12000 mg/kg Sn) does not improve the FET performance. This suggests that it is not necessary to completely remove metal residues in semiconducting polymers used in FETs.

**Fig.** Typical field effect mobilities for the different materials. The linear mobilities where measured at a constant drain voltage of $V_d = -5$ V and the saturated at $V_d = -50$ V. The error bars show the maximum deviation between the measured mobility values and average mobilities.

**Main collaboration:** Merck Specialty Chemicals Ltd, United Kingdom.
Organic memory using polarizable nanoparticles

Main funding: Academy of Finland and TEKES

Participating FunMat unit: DPh
J. K Baral, H. S. Majumdar, A. Laiho, H. Sandberg, M. Vilkman, R.H.A. Ras, J. Ruokolainen, O. Ikkala and R. Österbacka

We demonstrate a simple memory device in which the fullerene-derivative [6,6]-phenyl-C_{61} butyric acid methyl ester (PCBM) as well as metallic nanoparticles mixed with inert polystyrene (PS) matrix is sandwiched between two aluminum (Al) electrodes. Above a threshold voltage of <3V, independent of thickness, a consistent negative differential resistance (NDR) is observed in the devices of thickness range from 200nm to 350nm made from solutions with 4 wt% to 10 wt% of PCBM in PS. We found that the threshold voltage ($V_{th}$) for switching from high impedance state to low impedance state, the voltage at maximum current density ($V_{max}$) and the voltage at minimum current density ($V_{min}$) in the NDR regime are constant within this thickness range. The current density ratio at $V_{max}$ and $V_{min}$ is more than or equal to 10, increasing with thickness. Furthermore, the current density is exponentially dependent on the average hopping distance longest tunneling jump between two PCBM molecules, suggesting a multiple tunneling mechanism between individual PCBM molecules. This is further supported with temperature independent NDR down to 240K.

![Fig.](image)

Fig. The J-V curves of a PS-PCBM device as a function of PCBM concentration (a) showing the exponential dependence of the inter-hopping distance indicative of tunneling.
Main collaboration: Helsinki University of Technology, VTT

Publications:

Development of an inorganic binder based on a cheap sol-gel precursor

Main funding: TEKES

Participating FunMat unit: DPC
Janne Puputti, Qian Xu, Mika Lindén

Currently, organic resins are used as binders for fibermats in insulation applications. However, the limited thermal stability of organic polymers makes them less effective as binders in high-temperature applications. Inorganic oxides, on the other hand, have a high thermal stability, but to date the large-scale industrial use of such binders has been hampered by the high cost of the commonly used metal alkoxide precursors. The aim of this project was therefore to develop a binder solution based on cheap metal oxide precursors.

As the precursor a mixed metal oxide precursor was used, which is soluble under acidic conditions. Formic acid was used for pH adjustments, as mineral acids are highly corrosive, and organic acids can be easily thermally decomposed during the drying of the fiber mat. A small amount of other organic acids, like citric acid and lactic acid, was also added in order to prevent extensive crystallization of metal formiates not taking part in the gel network formation. Different means for hydrophobic surface modification of the dried binder was also investigated, in order to enhance the water stability of the binder. The developed binder has been tested on an industrial scale.

Main collaboration: Trondheim University of Technology, Norway, AB Paroc Oy
Publication:

“Inhibition of crystallization during drying in gels derived from a cheap, sol-gel precursor by complexation”, J. Sol-Gel Sci. Tech., in press

Degradable Bioactive Composites

Main funding: TEKES

Participating FunMats units: LPT
Eeva Orava and Ari Rosling

The main polymers tested have been different polylactide copolymers. Preparation processes for different composites have been developed to a routine level. A dozen different SiO₂-based materials (with or without additives such as Ca & P and drugs) has been used to prepare polylactide composites and tested in vitro for ion release profiles and bone mineral-like calcium phosphate formation (bioactivity) on the composite surface. In addition, composites have been treated with gas in order to control their porosity. The pore size can be optimized to support cell/tissue ingrowth into the material. Moldable, PLA-PCLA-bioactive glass composite has been tested in vitro. The results from extended in vivo experiments suggest that the material is compatible with bone and dentin and has the potential to be developed to a resorbable bone filler or temporary filling material in teeth.

Main collaboration:

Publications:


**Memory effect in ionic liquid matrix containing single walled carbon nanotubes and polystyrene**

Main funding: TEKES

Participating FunMat Unit: DPh  
Di Wei, Jayanta K. Baral, R. Österbacka, and Ari Ivaska

In this work we use an ionic liquid (IL) gel matrix containing single walled carbon nanotubes (SWNTs) and polystyrene (PS) as a potential memory device. SWNTs and PS beams were mixed at room temperature IL, 1-butyl-3-methyl-hexafluorophosphate ([BMIM][PF₆]). The composite gel was sandwiched between a bottom ITO glass and a top aluminum electrode. With merely change of concentrations of SWNTs in the inert insulating PS matrix, we observed several distinct device electrical properties, such as an insulator, a memory in terms of switching and negative differential resistance (NDR) and a conductor. The electric bistable switching hops between a higher impedance (OFF) state and a lower impedance (ON) state which is approximately equal to 5 orders of current decays.

Main collaboration: Process Chemistry Center, Analytical Chemistry, Åbo Akademi University

Publication:


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**Study of Half-metallic manganite La_{0.67}Sr_{0.33}MnO_3 (LSMO) thin films made by Pulsed laser deposition for spintronic applications.**

Participating FunMat unit: DPh  
S. Majumdar, H. Huhtinen, R. Laiho and R. Österbacka

La_{0.67}Sr_{0.33}MnO_3 (LSMO), a well-known half-metallic manganite has been successfully used as a spin injecting electrode in many inorganic/organic spintronic devices. The advantage of LSMO over the conventional 3d magnetic metals is, classical 3d magnetic metals like Fe, Co, Ni etc., have conduction electrons with mainly 4s character where the
polarized electrons are the 3d ones. This electronic structure results in only 40% SP carriers at the Fermi level ($E_F$) for Fe. In LSMO, there is no electrons and the band of oxygen 2p character lies 2eV below $E_F$, which results in a fully polarized conduction band of 3d character. However, although the Curie temperature ($T_C$) of bulk LSMO lies well above room temperature, the surface spin polarization start decreasing at a much lower temperature due to the presence of a large number of paramagnetic clusters at 300K giving much less SP carriers at the LSMO - barrier interface in spintronic devices. Now, the Double – Exchange (DE) mechanism in manganites, which controls the charge carrier movement, is significantly modified by structural defects and substrate induced strains and also on the growth mechanisms. This makes it necessary to grow the LSMO films on different substrates starting from highly lattice mismatched MgO (MGO) (~9%) to most closely matched SrTiO$_3$ (STO) (0.87%) and NdGaO$_3$ (NGO) (-0.2%) to obtain the best spin injector for our devices. In MGO and STO the strain is compressive while that in NGO is compressive. So, the growth mechanisms in these three kinds of substrates are very different and thus we studied the effect of differently strained films, evolution of strain with film thickness and modification of their spin injection properties. Also using different pulsed laser deposition (PLD) parameters like temperature and laser repetition rate, the growth and oxygen content of the material is modified and from the study of their surface morphology, atomic structures, magnetic and transport properties, we optimized the parameters for achieving maximum SP injection at room temperature.

![Magnetization vs. temperature plot of LSMO films on different substrates showing different spin polarization at room temperature.](image)

**Main collaboration:** University of Turku
Organic Spintronics

Participating FunMat unit: DPh  
* S. Majumdar, H.M. Majumdar, R. Laiho, and R. Österbacka

Until recently, the spin of the electron was ignored in mainstream charge-based electronics. Spintronics (or spin-based electronics) is a technology where instead of electronic charge, the electron spin carries information. This opens the possibility for adding multifunctionality to the existing devices and higher integration densities and lower power consumption as the spins can be manipulated much faster and easily than charges. Major challenges in this field of Spintronics include the optimization of electron spin lifetimes, the detection of spin coherence in nanoscale structures, transport of spin-polarized carriers across relevant length scales and heterointerfaces, and the manipulation of both electron and nuclear spins on sufficiently fast time scales. Until very recently no attention was paid to use organic small molecules and conjugated polymers as the spin transporting medium. There have been some encouraging experimental results and some theoretical proposals which show organic molecules are more promising than their inorganic counterparts in transporting spins and that opens up new domains of research. We fabricated the polymeric spin-valve devices for the first time and obtained 80% magnetoresistance (MR) at 5K and 1.5% MR at room temperature and tried to explain their spin injection and transport properties.

![Schematic diagram of a spin – valve device and its operation.](image-url)

**Fig.** Schematic diagram of a spin – valve device and its operation.

Main collaboration: University of Turku
Polymeric spin-valves: The effect of LSMO-polymer interface

Participating FunMat unit: DPh
S. Majumdar, H.M. Majumdar, P. Laukkanen, I.J. Väyrynen, R. Laiho, and R. Österbacka

We have fabricated and characterized polymeric spin valves with the conjugated polymer regio-regular and regio-random (poly 3-hexylthiophene) (RRP3HT and RRaP3HT respectively) as the spacer layer. The device structure is La$_{0.67}$Sr$_{0.33}$MnO$_3$ (LSMO)/polymer/Co, with half-metallic, spin-polarized LSMO acting as the spin-injecting electrode. The spin valve shows behavior similar to a magnetic tunnel junction though the non-magnetic spacer layer (~100 nm) is much thicker than the tunneling limit. We attribute this behavior to the formation of a thin spin-selective tunneling interface between LSMO and the polymer caused by chemical reaction between LSMO and the polymer as observed by x-ray photoelectron spectroscopy measurement. This gives rise to ~80% magnetoresistance (MR) at 5K and ~1.5% MR at room temperature. We found that by introducing monolayer of different organic insulators between LSMO and RRP3HT the spin-selective interface is destroyed and spin injection is reduced. Our results show that organic materials are promising candidates for spintronic applications.

Fig. (a) Magnetic hysteresis loop of the two ferromagnetic electrodes LSMO and Co at 5K. (b) Magnetoresistance (MR) of three different SVs as a function of magnetic field (B)
at 5K showing 80% MR for device A, 20% for device B and no MR in device C. The red line indicates average of 10 scans taken at the same time.

**Main collaboration:** University of Turku

**Publications:**


* Development of paper for inkjet printing

**Main funding:** Industry

**Participating FunMat units:** LPCC, DPC

_Carl-Mikael Tåg, Jarl B. Rosenholm, Jouko Peltonen_

Papers available on the market for high speed inkjet printing can roughly be divided into treated grades and high quality specialty paper grades. The treated grades usually perform well in 1-color printing, printing of barcodes etc., but not so well in 4-color printing. The very expensive high quality specialty papers perform well in 4-color printing, but not always so well in printing bar codes. Currently the high quality specialty paper grades are mainly produced on small paper machines, due to limited production possibilities.

The aim of the Inkjet paper project is to develop paper grades which perform well in high speed inkjet printing, but with less complex structure and at a lower cost than current specialty inkjet papers. To do this, evaluation of what makes a paper good or bad for high speed inkjet printing will be carried out. Additionally the aim is to decrease the paper waviness which causes problems in the post handling process of the printed product.