International Workshop on Interface Science for Novel Physical Properties and Electronics

Date: 9-11 December 2013 Place: lecture room of the first building of Faculty of Science, Okayama University, Okayama, Japan Research Center of New Functional Materials for Energy Production, Storage and Transport, Okayama University The Research Center of New Functional Materials for Energy Production, Storage and Transport (RCNFM), Okayama University will have an International Workshop (International Workshop on Interface Science for Novel Physical Properties and Electronics) on 9 – 11 December 2013 at Okayama University. 19 invited speakers from US, Switzerland, France, Italy, Germany, China and Japan will participate in this workshop and give talks on their recent works. The speakers from Okayama University will also provide their recent topics in this workshop.

In 2012, the RCNFM had an International symposium (International Symposium on Physics and Chemistry of Novel Superconductors and Related Materials); 19 invited speakers participated in it and gave lectures. Subsequently, the RCNFM will have the International Workshop relating to materials science, physics, interface science and chemistry. The RCNFM has an intention to make a new international consortium for solid state physics and applied physics based on the network with oversea researchers as well as researchers at Japanese Universities / Institutes other than Okayama University. In this workshop, we will actively discuss and talk on various topics on solid state physics and applied physics. The main topics on this workshop are follows:

- 1) Superconductivity based on 2D layered materials
- 2) Interface superconductivity and field-effect induced superconductivity
- 3) New superconductors and their physics and chemistry
- 4) Physics of graphene and topological insulators
- 5) Organic electronics: chemistry, physics and interface science
- 6) New energy device: solar-cell application of new materials.

The venue of this workshop is the lecture room of the first building of Faculty of Science, Okayama University. This workshop is partly supported by the program for Promoting the Enhancement of Research Universities, Ministry of Education, Science, Sports and Culture (MEXT); the RCNFM is one of the cores of this program in Okayama University.

@ Organizing Committee of International Workshop, Research Center of New Functional Materials for Energy Production, Storage and Transport (RCNFM), Okayama University International Workshop on Interface Science for Novel Physical Properties and Electronics (9 - 11, Dec. 2013, Conference Room, Faculty of Science, Okayama University)



International Workshop on Interface Science for Novel Physical Properties and Electronics

9 December 2013: Interface Science

9:00 - 9:10 Opening: S. Yamamoto / Y. Kubozono

1-1. Electrostatic carrier accumulation for superconductivity and interface superconductivity based on 2D materials

Chair: Vincent Bouchiat [1] 9:10 - 10:10 Yoshi Iwasa (Tokyo) "2D Electron Systems Produced by Ionic Gating"

[2] 10:10 - 10:55 Xiaodong Cui (HongKong)" Spin-valley coupling in atomically thin dichalcogenides"

10:55 - 11:15 Coffee Break

Chair: Hidenori Goto [3] 11:15 - 12:00 Hiroshi Yamamoto (IMS) "Organic Mott-FET and its phase transitions"

[4] 12:00 - 12:45 Andrea Young (MIT)"Tunable symmetry breaking and helical edge transport in a graphene quantum spin Hall state"

12:45 - 13:45 Lunch

1-2. Materials science for New superconductors I

Chair: Bertram Batlogg [5] 13:45 - 14:30 Eric Spanton (Stanford) "Conductivity, Superconductivity, and Domain Structure in Stronitum Titanate Based Materials" [6] 14:30 - 15:15 Takayoshi Yokoya (Okayama) "High-resolution PES of K doped picene film"

[7] 15:15 - 16:00 Minoru Nohara (Okayama)
"Superconductivity in CaFeAs₂ (112) and CaFe₂As₂ (122) with RE doping"

16:00 - 16:20 Coffee Break

1-3. Materials science for New superconductors II

Chair: Minoru Nohara [8] 16:20 - 17:05 Katsuya Shimizu (Osaka) "Superconductivity onset at very high pressure"

[9] 17:05 - 17:50 Zenji Hiroi (ISSP, Tokyo) "Metal-Insulator Transitions in Transition Metal Oxides"

[10] 17:50 - 18:35 Anvar Zakhidov (Texas)"Low Field Microwave Absorption in Superconducting Fe-Pnictides and Chalcogenides"

18:35 - 18:55 Coffee Break

1-4. Future functional organic FETs

Chair: Antonio Cassinese [11] 18:55 - 19:45 Tatsuo Hasegawa (AIST) "Interface Charge Transport and Device Physics of Organic Transistors"

[12] 19:45 - 20:35 Antonio Fachetti (Northwestern)"Synthesis and Charge Transport Properties of P-N Semiconductor Blends"

21:00 – 22:30 Welcome party

10 December 2013: Organic and inorganic FETs

2-1. Interface control for organic FETs

Chair: Yoshi Iwasa [13] 9:00 - 10:00 Bertram Batlogg (ETH Zurich) "Charge transport and trapping in OFETs :approaching the trap-free limit in single-crystal devices"

[14] 10:00 - 10:50 Jun Takeya (Tokyo) "Materials and devices of high-performance organic transistors"

10:50 - 11:10 Coffee Break

2-2. Organic FET for application

Chair: Yoshihiro Kubozono [15] 11:10 - 12:00 Antonio Cassinese (Napoli) "Interface Charge Transport and Device Physics of Organic Transistors"

[16] 12:00 - 12:45 Yasuhiko Hayashi (Okayama)"Control of molecular orientation for high-performance polymer field-effect transistors by Direct Pen Painting method"

12:45 - 13:45 Lunch

2-3. Topological insulator and superconductor

Chair: Xiaolong Chen [17] 13:45 - 14:30 Andrei Varykhalov (BESSY-Berlin) "Tunable spin-orbit effects in graphene and topological insulators"

[18] 14:30 - 15:15 Guoqing Zheng (Okayama)

"Noncentrosymmetric Superconductors: a possible route to topological superconductivity"

15:15 - 15:35 Coffee Break

2-4. Materials science for New superconductors III

Chair: Guoqing Zheng [19] 15:35 - 16:20 Tatsuo C. Kobayashi (Okayama) "Localized to itinerant crossover of 4f electrons in CeCu₂Si₂ under high pressure"

[20] 16:20 - 17:05 Xiaolong Chen (Beijing)"Some progresses on the study of iron selenide based superconductors"

[21] 17:05 - 17:50 Yoshihiro Kubozono (Okayama)"New organic / inorganic superconductors prepared using liquid NH₃ technique"

17:50 - 18:10 Coffee Break

2-5. Session for young researchers

Chair: Mario Barra [22] 18:10 - 18:40 Hiroki Mori (Okayama) "Synthesis, Characterization, and Transistor Applications of a Phenanthro[1,2-b:8,7-b']dithiophenes (PDT)"

[23] 18:40 - 19:00 Eri Uesugi (Okayama) "Transport properties of graphene edges"

[24] 19:00 - 19:20 Satoki Maeda (Okayama)"Crystal structure and superconductivity in LaPt_{2-x}Ge_{2+x}"

20:30 - 22:30 Banquet

11 December 2013: Materials Science for superconductivity

3-1. Physical properties of organic FETs

Chair: Takayoshi Yokoya

[25] 09:00 - 09:45 Mario Barra (Napoli)

"N-type organic transistors based on Perylene diimide molecules: from bias stress effects to electrical operation in liquid environments"

[26] 09:45 - 10:15 Ritsuko Eguchi (Okayama)

"High performance organic field-effect transistors based on [n]phenacene-type molecules"

[27] 10:15 - 10:45 Thomas Mathis (ETH Zurich)

"Stable organic field-effect-transistors with high mobilities unaffected by supporting dielectric based on π -bridged thienobenzothiophene"

10:45 - 11:05 Coffee Break

Chair: Yasuhiko Hayashi

[28] 11:05 - 11:40 Takashi Kambe (Okayama)

"Dynamics of Carrier Injection in Picene Thin Film FET with Ionic Liquid Sheet and Ionic Liquid Gel Probed by Electron Spin Resonance"

[33] 11:40 - 12:10 Takanori Wakita (Okayama)

"Spectroscopic evidence for metallic states in potassium-intercalated picene film on graphite"

[29] 12:10 - 12:55 Naoshi Ikeda (Okayama) "Recent progress in ferroelectric material"

12:55 - 14:00 Lunch

3-2. FET properties of topological insulator and graphene

Chair: Xiaodong Cui [30] 14:00 - 14:30 Hideniori Goto (Okayama) "Electronic properties of few-layer graphene with ionic-liquid gates"

[31] 14:30 - 15:30 Vincent Bouchiat (Grenoble)

"How to make graphene a macroscopic superconductor: from proximity effect to intrinsic superconductivity"

[32] 15:30 - 16:30 Kazuhito Tsukagoshi (NIMS)

"Atomically thin semiconducting channels for future nano-electronics"

16:30 - 16:40 Closing: T. C. Kobayashi

2D Electron Systems Produced by Ionic Gating

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Ionic gating technique has been recognized as a powerful tool for creation and control of high density two dimensional (2D) electron systems, showing superconductivity, ferromagnetism, and Mott transitions [1-7]. This is achieved by field effect transistor (FET) geometry, where charge carriers are accumulated at the interface channels by application of gate voltages though gate dielectrics. Gate dielectrics can be replaced with electrolytes or ionic liquids, which are ionically conducting, but electrically insulating. In this device, which we call electric double layer transistor (EDLT), the capacitance becomes nearly 10 μ F/cm² and the gate coupling is extremely large. Consequently, the operation voltages of the transistor are dramatically lowered and the maximum accumulated carrier density is enhanced up to 1 x 10¹⁵ cm⁻², with which gate control of electronic phases becomes possible.

In this presentation, I will focus on the properties and functionalities on transition metal dichalcogenide (TMD) involving MoS₂ as an archetypal material. TMD based 2D crystals are attracting growing interest because of its functions found in monolayer systems, including high mobility FETs [8], valleytronics [9], and superconductivity [10]. In particular, monolayer or few layer TMDs can be good channel materials for FETs and EDLTs because of their atomically flat surfaces easily available either by mechanical cleavage of single crystals or by chemical vapor depositions. Field effect of superconductivity [10], spin polarization [11], and ambipolar transport [12] on TMDs will be discussed.

References

[1] K. Ueno et al., *Nat. Mater.* 7 (2008) 855. [2] J. T. Ye et al., *Nat. Mater.* 9 (2010) 125. [3] K. Ueno et al., *Nat. Nanotech.* 6 (2011) 408. [4] Y. Yamada et al., *Science* 127 (2011) 1065. [5] J. G. Checkelsky et al., *Nat. Phys.* 8 (2012) 729. [6] M. Nakano et al., *Nature* 487 (2012) 459. [7] T. Hatano et al., *Sci. Rep.* 3 (2013) 2904. [8] B. Radisavljevic et al., *Nat. Nanotech.* 6 (2011) 147. [9] D. Xiao et al., *Phys. Rev. Lett.* 108 (2012) 196802. [10] J. T. Ye et al., *Science* 338 (2012) 1193. [11] H. T. Yuan et al., *Nat. Phys.* 9 (2013) 563. [12] Y. J. Zhang et al., *Nano Lett.* 12 (2012) 1136.

[2]

Spin-valley coupling in atomically thin dichalcogenides

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The monolayers of group VI transition metal dichalcogenides feature a valence band spin splitting with opposite sign in the two valleys located at corners of 1st Brillouin zone. This spin-valley coupling, particularly pronounced in tungsten dichalcogenides, can benefit potential spintronics and valleytronics with the important consequences of spin-valley interplay and the suppression of spin and valley relaxations. Here we report the optical studies of MoS₂,WS₂ and WSe₂ monolayers and multilayers. The efficiency of second harmonic generation (SHG) shows a dramatic even-odd oscillation consistent with the presence (absence) of inversion symmetry in even (odd) layer. Photoluminescence (PL) measurements show the crossover from an indirect band gap semiconductor at mutilayers to a direct-gap one at monolayers. The PL spectra and first-principle calculations consistently reveal a spin-valley coupling of 0.4 eV which suppresses interlayer hopping and manifests as a thickness independent splitting pattern at valence band edge near K points. This giant spin-valley coupling, together with the valley degrees of freedom in these atomically thin 2D materials.

Organic Mott-FET and its phase transitions

Hiroshi M. Yamamoto (Institute for Molecular Science, Japan)

Field effect transistors (FETs) with organic channel materials are under intense studies because of the possibilities of application in flexible, printable, and large-area electronic devices. Despite single-component neutral molecules like pentacene and ruburene are mainly investigated to pursuit high performance organic FETs, few studies are known for FETs based on compound-type organic semiconductors that are composed of two (or more) kinds of molecules. We have been exploiting FET devices with organic charge-transfer salts, more specifically, cation-radical salts of electron-donating molecules such as BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) with counter anions. Among these materials, our focus concentrates in Mott-insulators in which Coulomb interaction among carriers blocks metallic transport. In this 'highly correlated' situation of charge carriers, Mott insulator stays in a fragile semiconducting state, where carrier injection, chemical and/or physical pressure (or strain), and thermal fluctuation can drive it into a metallic state by phase transition (*i.e.* Mott transition). Therefore, one can expect an abrupt change of the conductivity of device due to phase transition that is induced by very small external stimuli such as gate voltage. Recently, we have shown that such an insulator-to-metal transition as well as an insulator-to-superconductor transition can take place at the interface of organic Mott-insulator-based FET (Mott-FET). The details of such electric-field induced phase transition will be discussed.

(Ref.)

1) Y. Kawasugi, H. M. Yamamoto, et al, Phys. Rev. Lett., 103, 116801 (2009).

2) H. M. Yamamoto, M. Nakano, et al, Nature Commun., 4, 2379 (2013).



Figure Device structure of organic Mott-FET. On a Nb-doped SrTiO₃ substrate covered with 28 nm Al₂O₃, a thin crystal of κ -(BEDT-TTF)₂Cu[N(CN)₂]Br (κ -Br) is laminated and cut in a Hall-bar arrangement as shown in the upper right picture taken by optical microscope. Inside the κ -Br crystal, alternating layers of BEDT-TTF and counter anion form a FET channel. Scale bar, 100 μ m.

Tunable symmetry breaking and helical edge transport in a graphene quantum spin Hall state

Andrea Young

MIT Physics Department

Low-dimensional electronic systems have traditionally been obtained by electrostatically confining electrons, either in heterostructures or in intrinsically nanoscale materials such as single molecules, nanowires, and graphene. Recently, a new paradigm has emerged with the advent of symmetry-protected surface states on the boundary of topological insulators, enabling the creation of electronic systems with novel properties. For example, time reversal symmetry (TRS) endows the massless charge carriers on the surface of a three-dimensional topological insulator with helicity, locking the orientation of their spin relative to their momentum. Weakly breaking this symmetry generates a gap on the surface, resulting in charge carriers with finite effective mass and exotic spin textures. Analogous manipulations of the one-dimensional boundary states of a two-dimensional topological insulator are also possible, but have yet to be observed in the leading candidate materials. Here, we demonstrate experimentally that charge neutral monolayer graphene displays a new type of quantum spin Hall (QSH) effect, previously thought to exist only in TRS topological insulators, when it is subjected to a very large magnetic field angled with respect to the graphene plane. Unlike in the TRS case, the QSH presented here is protected by a spin-rotation symmetry that emerges as electron spins in a half-filled Landau level are polarized by the large in-plane magnetic field. The properties of the resulting helical edge states can be modulated by balancing the applied field against an intrinsic antiferromagnetic instability, which tends to spontaneously break the spin-rotation symmetry. In the resulting canted antiferromagnetic (CAF) state, we observe transport signatures of gapped edge states, which constitute a new kind of one-dimensional electronic system with tunable band gap and associated spin-texture.

Conductivitity, Superconductivity, and Domain Structure in Strontium Titanate Based Materials

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Strontium titanate is ubiquitous as a substrate for many different classes of materials, including high T_c superconducting films and complex oxide heterostructures. Strontium titanate (STO) is a band insulator, and is an incipient ferroelectric at low temperatures, which leads to a high dielectric constant and allows for the application of large electric fields. Complex oxide heterostructures, and specifically the interface between 4 or more unit cells of lanthanum aluminate (LAO) and strontium titanate has been shown to be conducting, superconducting, and magnetic. Here I will present recent scanning SQUID images of 2D current flow in the LAO/STO interface. We find that more current flows along narrow paths indicating locally enhanced conductivity on the paths (See Figure). These paths are aligned along crystallographic axes and the pattern of current we observe changes only when cycling above STO's cubic to tetragonal transition at 105 K. We attribute these features to enhanced conductivity due to the tetragonal domain structure of the STO substrate. These results show that the properties of electrons at the LAO/STO interface are strongly sensitive to the local crystal structure, and taking these effects into account may be important for interpreting transport results. Additionally, I will present data on superconductivity in both LAO/STO and Nb delta-doped STO, showing that the tetragonal domain structure at low temperatures also influences superconductivity.



Images of magnetic fields generated by current flowing in an LAO/STO interface. More current flows in narrow paths, indicated by the pairs of dark/light lines. These paths are related to the STO's tetragonal domain structure.

High-resolution PES of K doped picene film

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Potassium-doped picene is the first aromatic hydrocarbon superconductor (superconducting transition temperature of 7 and 18K for K concentration (x) of ~ 3, reported by Kubozono and co-workes [1]. Following the discovery, several aromatic hydrocarbon superconductors with the highest transition temperature as high as 33 K have been reported [2-4]. Although determination of the crystal structure has not been made due to the low superconducting shielding fraction of the samples, understanding of the new superconductors has gradually developed [5-7]. Regarding electronic structure, our previous photoemission spectroscopy (PES) study reported change in the electronic structure between the pristine and K-doped solid picene ($x \sim 1$) films: non-rigid band modification of electronic structure and appearance of states close to the Fermi level(E_F) in K-doped solid picene [8]. On the other hand, recent PES studies reported absence of states near E_F [9,10], calling for further investigations. Therefore, it is crucial to perform further PES study in order to check existence or absence of metallic states in K-doped picene films. In this presentation, we will report results of high-resolution PES of K-doped picene films, which shows appearance of states near E_F with a clear Fermi edge [11]. We discuss the correspondence of the obtained results to reported physical properties and theoretical calculations.

Reference

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Superconductivity in CaFeAs₂ (112) and CaFe₂As₂ (122) with RE doping

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Superconductivity in novel 112-type (Ca_{1-x}La_x)FeAs₂ will be presented [1]. The compound crystallizes in a monoclinic structure (space group P2₁), in which FeAs layers alternate with CaAs spacer layers such that monovalent arsenic forms zigzag chains. Superconductivity at 34 K was observed for the x = 0.1 sample, while trace superconductivity was observed at 45 K for the x = 0.21 sample, demonstrating the potential of the 112-phase for higher transition temperature.

Another way to realize higher T_c is co-doping of lanthanum and phosphorus in 122-type CaFe₂As₂, which results in superconductivity at 45 K [2]. Superconductivity with a substantial shielding volume fraction was observed at $0.12 \le x \le 0.18$ and y = 0.06 in Ca_{1-x}La_xFe₂(As_{1-y}P_y)₂. In this doping range, the system exhibits crossover of the lattice collapse transition, which is characterized by the formation of As₂ dimers between the adjacent FeAs layers.

[1] N. Katayama, K. Kudo, S. Onari, T. Mizukami, K. Sugawara, Y. Sugiyama, Y. Kitahama, K. Iba, K. Fujimura, N. Nishimoto, M. Nohara, and H. Sawa, J. Phys. Soc. Jpn. **82**, 123702 (2013).

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[8]

Superconductivity onset at very high pressure

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Superconductivity is generally known as a rare phenomenon: superconductivity can be seen in a few compounds, which made by special treatments, however here we suppose it is rather common phenomenon in material but caused through variety of the mechanism. All elements can be superconductive? It has been already revealed that not a few elements that are not the superconductor at ambient pressure became superconductive at high pressure. The number of elements superconducting materials, include elements, show a negative pressure effect; the superconducting transition temperature, T_c , decreases by applying pressure. However some elements show the positive effect at high pressure. We have been studied on superconductivity in elements not only for understanding the mechanism of superconductivity but also for searching the unrevealed possibility of the material. Furthermore, some light elements were found to exhibit relatively high- T_c ; in the case of calcium, T_c increases with pressure and almost reaches 30 K at pressure above 200 GPa. In my presentation, pressure-induced superconductive elements that show the T_c of around 20 K and positive pressure effect are reviewed.

Metal-Insulator Transitions in Transition Metal Oxides

Zenji Hiroi

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The metal-insulator transition (MIT) is one of the most dramatic phenomena for many electrons in crystals. Some historical examples are found in transition metal oxides like Fe_3O_4 , V_2O_3 , VO_2 , etc. It can occur purely electronic in origin, such as a transition from a correlated metal to a Mott-Hubbard insulator, which is caused by Coulomb repulsions among strongly correlated electrons, or a transition driven by a certain Fermi-surface instability like a charge/spin-density wave or a Peierls transition. The former does not require crystal symmetry breaking, while, in the latter, a structural transition that can remove a certain electronic instability associated with a specific band structure is always accompanied. In general, both an electronic MIT and a structural transition take place simultaneously, because electrons that are going to localize owing to Coulomb repulsions may feel more electron-phonon interactions or those to be captured by a lattice may feel more Coulomb repulsions. Thus, actual phenomena at MITs are always complex and difficult to interpret within a simple scenario; to specify the mechanism of an MIT has always been found to be troublesome and can be a chicken–egg problem among two or more factors. In this context, I would like to discuss the MIT of VO₂ briefly in this talk.

The MIT of the pyrochlore oxide $Cd_2Os_2O_7$ was discovered by Sleight in 1974 [1] and still remains mysterious as is the cases for other MITs. Since electron correlations are weak in 5d transition metals, the Mott-Hubbard mechanism may not be the case. Recently, Mandrus *et al.* [2] proposed a mechanism based on the Slater transition. On the other hand, Koda *et al.* found a static internal magnetic field in their μ SR experiments and suggested the appearance of an incommensurate SDW phase [3]. However, Singh *et al.* disputed the Slater transition because of the absence of a nesting feature in the band structure [14].

For understanding the mechanism of the MIT of $Cd_2Os_2O_7$, it is crucial to decide the magnetic structure realized in the frustrated pyrochlore lattice in the insulating state. By using the resonant X-ray scattering method in a high-quality single crystal, we observed commensurate magnetic peaks that indicate a q = 0 order below $T_{MI} = 227$ K. X-ray and electron diffraction and Raman scattering experiments confirm that the transition is not accompanied by any spatial symmetry breaking. Discussion in terms of the irreducible representation reveals that the ordered magnetic structure is most likely a noncollinear all–in/all–out spin arrangement with a zero net moment on the Os tetrahedron. More recent ¹⁷O NMR experiments by the Takigawa group confirmed this order unequivocally. Based on these results, we suggest that the transition is not caused by the Slater mechanism as believed earlier but by an alternative mechanism: the formation of the specific tetrahedral magnetic order on the pyrochlore lattice triggers a Lifshitz transition in the semimetallic band structure. Possibly, as the magnetic order is approached from high temperature, electron and hole bands shift down and upward, respectively, so that an overlap between them is removed at the transition. A microscopic mechanism is under debate.

This is the work done by J. Yamaura, K. Ohgushi, I. Yamauchi, M. Takigawa from ISSP, Univ. of Tokyo, H. Ohsumi, S. Takeshita, A. Tokuda, M. Takata, K. Sugimoto from RIKEN and JASRI, SPring-8, T. Hasegawa, M. Udagawa from Hiroshima Univ., H. Harima from Kobe Univ. and T. Arima from Univ. of Tokyo.

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[10]

Low Field Microwave Absorption in Superconducting Fe-Pnictides and Chalcogenides

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Non-resonant magnetically modulated microwave absorption has been used extensively to study properties of HTSC of YBCO and BSCO families, and successfully used for search of new superconducting phases in fullerides and organic SCs. The low-field MW absorption (LFMA) is an extremely sensitive tool: it can detect nanogram amounts of SC (~100 times more sensitive than SQUID) and is quite sensitive to layered or granular structure and particularly for presence of weak links.

In this presentation we demonstrate applications of LFMA to some classes of pnictide 122 (doped Ca, Ba and Eu systems) and Fe-chalcogenide superconductors (films of FeSe, FeSeTe and FeTe on STO, glass and Carbon nanotubes). So angle dependent LFMA in electronically doped Ca122 (by Pr, Nd, Ce and La doping) shows two clearly distinct signals: a hysteretic type LFMA for lower Tc phase and a narrow positive phase peak for higher Tc =45 K phase, which we associate with interfacial superconductivity.



Examples of hysteretic LFMA signal below lower Tc1 and narrow peak, associated with interface superconductivity at higher Tc2

When anisotropic high temperature superconductors are confined in lower dimensions, interesting effects have been observed. Superconductivity has been shown to persist even in monolayers of such materials and, Tc can be increased significantly. We will show the LFMA of several layers of FeSe, demonstrating the sensitivity of LFMA method. We have found that LFMA spectrum of FeSe also can exhibit two distinct features in different T-regions: a hysteretic LFMA below 8K and non-hysteretic narrow LFMA at higher T, with negative phase (as opposed to narrow signal in doped Ca 122). Angle dependences of both types of LFMA signals are analyzed and the origin of the higher Tc LFMA signals will be discussed in FeSe in terms of non-superconducting MW dissipation on magnetic domains in non-SC FeSe phase.

The recent advent of Fe-based SC has shed new light on Ferromagnetism/Superconductivity coexistence, as is the case with the presently discussed EuFe2(As1-xPx)2 system. Using the techniques of LFMA and ESR, we can simultaneously investigate both the SC and FM present in this family of pnictides at T < 20 K.

[11]

Interface Charge Transport and Device Physics of Organic Transistors

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Studies over the last decade have revealed that most of high-performance organic thin-film transistors (OTFTs) is attainable with non-doped, single-component π -conjugated materials that exhibit high *layer crystallinity*, as associated with the large intermolecular π - π interactions both for small-molecules and polymers. The layer crystallinity is quite suitable to afford two-dimensional channel transport layers interfaced with gate dielectric layers in the field-effect devices. Here we discuss our recent investigations into the understanding of microscopic charge transport [1-4] as well as novel film processing technologies [5-8] for high performance OTFTs.

We first discuss the microscopic charge transport in the OTFTs, as investigated by field-induced electron spin resonance (FESR) measurements and by charge modulation spectroscopy (CMS). These techniques are quite useful, because tiny amount of field-induced carriers, accumulated at the semiconductor-insulator interfaces, can be sensitively probed. The following important aspects are presented and discussed; 1) Carrier motion within the crystalline domains can be understood in terms of the multiple trap-and-release (MTR) transport, 2) charge trap states are spatially extended over several sites depending on the trap levels, and 3) the intra- and inter-domain transport can be discriminated by anisotropic FESR measurements.

We also discuss print production technologies for the semiconducting organic materials with high layer crystallinity. The concept of "printed electronics" is now regarded as a realistic paradigm to manufacture light-weight, thin, and impact-resistant electronics devices by the use of printing technologies, although the production of semiconducting thin films of high crystallinity may be incompatible with conventional printing processes. We here present a couple of novel printing techniques for manufacturing high performance OTFTs; 1) double-shot inkjet printing (DS-IJP) for small-molecule semiconductors, and 2) push-coating for semiconducting polymers. We demonstrate that both processes are useful to manufacture high quality semiconductor layers with high layered crystallinity.

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Synthesis and Charge Transport Properties of P-N Semiconductor Blends

Antonio Facchetti

Polymer-polymer blends are some of the most challenging organic semiconductor systems because of their complex thermodinamics of mixing and unique processing. In this presentation we will describe therationale to the synthesis of several polymeric hole- and electron-transporting semiconductors and their characterization in single-component devices (Fig. 1).



Figure 1. Building blocks used to synthesized several semiconducting materials for TFTs and OPVs.

Next, we will report on results comprising blending two polymers in terms of structural, charge transport, optical, and photophysical characterization. In conclusion, we report their implementation in thin-film transistors, diodes, and solar cells (Fig 2).



Figure 2. Chemical structures of P3HT and P(NDI2OD-T2) (a). Schematic representation of the four types of devices used in this work: (b) PSC, (c) hole-only device, (d) electron-only device and (e) bottom-gate/bottom-contact FET.

Charge transport and trapping in OFETs : approaching the trap-free limit in single-crystal devices

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In the quest to elucidate the charge transport mechanism in van-der-Waals bonded molecular organic semiconductors, the masking effects of charge trapping needs to be minimized. We have studied extensively bulk and interface trap density of states (DOS) in p- and n-type semiconductors, developed means to measure and reduce them, and intentionally induced traps by exposure to chemicals, ion beams and Xrays. Thin films and single crystals are compared with each other, and with inorganic semiconductors. In order to explore intrinsic limits in single crystals, we have produced rubrene single crystal FETs with textbook like transfer characteristics and unprecedentedly low subthreshold swing (65meV/dec). This corresponds to a very low trap DOS of ~ $D_{it} = 3 \times 10^9$ cm⁻³eV⁻¹ at ~ 0.65 eV above the valence-band, a density as low as in best crystalline Si/SiO₂ FETs, highlighting the high level of purity and the intrinsic potential.

Materials and devices of high-performance organic transistors

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Development of functional materials and understanding of the microscopic mechanisms mutually benefit through their close interaction. To accelerate development of organic semiconductor devices for industrial application to flexible and printed electronics, it is essential to understand mechanisms of charge transport in conjunction with molecular-scale charge transfer. Here, we examine the idea that high-mobility charge transport, using several different molecular systems as the active semiconductor layers. These materials, which potentially realize the highest-speed organic transistors, can be categorized as "high-end" organic semiconductors characterized by coherent electronic states and high values of mobility close to or even exceeding 10 cm²/Vs, being essentially different from conventional lower-mobility organic semiconductors with basically incoherent hopping-like transport as studied in the previous century. We employ Hall-effect measurement which differentiates the coherent band transport from site-to-site hopping.

Various materials are crystalized to fabricate high-mobility organic field-effect transistors (OFETs) and their charge transport is investigated through temperature dependent four-terminal conductivity, Hall-effect and pressure-dependent measurements. The measured materials range from conventional polyacenes such as pentacene and rubrene, recently developed high-mobility heteroacenes. Furthermore, we developed solution processes for inch-size single-crystalline films of high-mobility organic semiconductor to provide a platform for high-speed integrated devices. We present a method of continuously growing large-domain organic semiconductor crystals to fabricate multi-array high-mobility organic transistors.

To demonstrate possible practical applications of the high-mobility printed organic semiconductors, high-speed liquid-crystalline displays will be exhibited.



Fig. 1. Transfer and output characteristics of a high-mobility solution-crystallized organic transistor.

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Interface Charge Transport and Device Physics of Organic Transistors

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Abstract

Here we report on the observation of an interfacial charge transfer effect in high quality Sexithiophene (T6)/ N,N'-bis (n octyl)-dicyanoperylenediimide (PDI-8CN₂) heterostructures, fabricated *in-situ* by a controlled sequential evaporation of T6 and PDI-8CN₂ thin films on Si/SiO₂ substrates investigated both by electrical characterization and UPS measurements. The electrical characterization of several heterostructures as function of the thickness of each film shows that the hole and electron transport cannot be explained by invoking only the properties of the individual layers. Electrical characterization give clear indications of charge transfer between T6 and PDI-8CN₂ layers, accompanied by band offset and interfacial charge accumulation (heterojunction effect). at the organic/organic interface. Gate voltage-tunable negative transconductance has been also observed for heterostructures composed by thin T6 layers and explained in terms of gate voltage tunable recombination phenomena occurring in hole/electron accumulation layer. Moreover, Bilayer with different T6 and Pdi-8CN2 thicknesses have been realized and characterized by means of ex-situ Ultraviolet Photoemission spectroscopy (UPS, with HeI and HeII photons). Bulk films of T6 showed HOMO and (calculated) LUMO energy positions basically aligned to literature results, while PDI-8CN₂ energy levels differ from the expected configuration, with the HOMO being 2.8eV below the Fermi edge, in principle making possible the matching between the T6-HOMO and PDI-8CN₂.LUMO levels. Different configurations will be discussed, ranging from bulk thin films of materials on device substrate, to different interfaces and bi-layers: the energy level scheme constructed from UPS data will be presented together with a possible implication of different phenomena at surfaces, as interface dipoles or band bending. Finally, in order to better understand the properties of PDI-8CN₂ preliminary measurements of single molecule measurements, investigated by break junctions technique will be reported. Our analysis reveals that the molecular bindings are perturbed when molecules come in direct contact with the gold surface and, at molecular level, two conducting states have been observed.

Control of molecular orientation for high-performance polymer field-effect transistors by Direct Pen Painting method

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The performance of organic field-effect transistors (OFETs) based on conjugated polymers has improved greatly in recent years and received considerable attention because it can be fabricated at low temperature and potentially reduced cost. We have developed a low-cost, high-throughput "Direct Pen Painting (DPP)" method that uses a pen tip, like a white board maker, to deliver polymer to a patterned substrate surface in a "direct paint" manner. Among a wide variety of processing methods, DPP allows to control the average orientation and the azimuthal molecular alignment of polymer to improve performances of polymer OFETs.

The source and drain electrodes were pre-patterned and deposited Au/Cr. The poly(3-hexylthiophene) (P3HT) was dissolved in dichlorobenzene and filled it inside the ink cartridge. The surface of SiO_2 was treated with octadecyltrichlorosilane (ODTS). The painting speed and pressure of the pen were mainly varied in the experiments in the air.

The average mobility and the on/off ratio of OFETs fabricated by painting *across* the channel are about 40 times higher and 10 times higher than those of OFETs fabricated by painting *along* with the channel, respectively. The threshold voltage of TFTs fabricated by painting *across* the channel is about -5 V. It is found that the thickness of films showed extremely thin. Based on results, it is necessary to reduce the film thickness below few nms to obtain high performance of P3HT OFETs. The polymer backbones are orientated along the painting direction confirmed by grazing-incidence X-ray-diffraction measurements. DPP solution-process is an effective method to fabricate the well-controlled molecular alignment of the P3HT film and its OFETs. The observed improvements of OFETs due to painting direction may be because of fewer barriers to neighboring molecules which have to be overcome.

The high-reproducibility OFETs based on the P3HT film exhibits high-performance of mobility up to 0.43 cm²/Vs and the on/off ration of 10^7 , which is much higher than the best values of 0.3 cm²/Vs and 10^4 reported by A. J. Heeger et al., using dip coat method. The results provide a powerful technique for exploring intentionally controlled molecular orientation to enhance the charge transport properties of conjugated polymer field-effect devices.

[17]

Tunable spin-orbit effects in graphene and topological insulators

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Results of recent experiments performed with spin- and angle-resolved photoemission which reveal different approaches allowing for control of Rashba-type electronic states in graphene and topological insulators will be presented and discussed.

In the first part of the presentation it will be shown how the spin-orbit split surface state of Ir(111) [1] can be tuned through the modulation of structural properties of a graphene overlayer grown on top of the iridium sample [2]. A substantial binding energy shift of the Ir(111) surface state is achieved either through enhancement of the graphene corrugation by a superlattice of deposited clusters or through increasing the thickness of the graphene overlayer. The resulting effects are assigned to the alteration of the graphene-Ir separation. The magnitude of the surface state Rashba splitting, however, remains preserved in both cases.

The second part of the talk is devoted to a specific Rashba effect in graphene, which can be induced extrinsically though the contact of graphene with high-Z materials. A giant (~100 meV) spin-orbit splitting of the Dirac cone in quasifreestanding graphene intercalated with Au will be demonstrated and analysed in terms of electronic hybridization between graphene and Au atoms [3,4]. A similar effect will be revealed for graphene on Ir(111), although it will be shown that the magnitude of the Rashba splitting in this system is very sensitive to even small rotational displacements of the graphene with respect to the Ir substrate [5]. Finally, a possibility to tune the magnitude of the Rashba splitting in the Dirac cone through co-intercalation of graphene on Ni(111) with different materials will be demonstrated.

The last part of the presentation is devoted to effects of dynamic tuning of the spin properties of topological surface states by photons with different energy and polarization [6]. It will be shown that circularly polarized low energy photons (6 eV) allow for flipping of the electron spins due to final state effects, while ultraviolet photons (50-70 eV) preserve the initial state spin texture of the topological surface state in the photoemission signal.

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Noncentrosymmetric Superconductors: a possible route to topological superconductivity

Guo-qing Zheng

The effect of spatial inversion-symmetry breaking has received considerable attention in various sub-fields of physics such as superconductivity, spintronics and multiferroics. In this talk, I will discuss the novel superconducting properties due to strong spin-orbit coupling and the topological aspects of non-centrosymmetric (NCS) superconductors, with an emphasis on the exotic electron pairing in $Li_2(Pt_{1-x}Pd_x)_3B$ (Ref.1-2), $Mg_{10}Ir_{10}B_{19}$ (Ref.3) and LaPtBi (Ref.4). We propose a new strategy for searching NCS superconductors with large spin-triplet component.

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Localized to itinerant crossover of 4f electrons in CeCu₂Si₂ under high pressure

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The pressure dependence of the localized/itinerant nature of 4f electrons in CeCu₂Si₂ has been investigated by means of the X-ray diffraction and NQR measurements.[1, 2] The X-ray powder diffraction experiment under high pressure and low temperature was carried out for CeCu₂Si₂ and CeCu₂Ge₂. The precise measurement under well-controlled pressure has been carried out successfully through the selection of the gasket material of a diamond anvil cell. The jump of the unit cell volume, reported previously in CeCu₂Ge₂, was not observed within the present experimental accuracy, indicating the absence of first-order valance transition. The pressure dependence of Cu-NQR frequency v_Q measured in CeCu₂Si₂ is compared with that calculated from the measured lattice parameters. The pressure dependences of v_Q were calculated in two cases of LaCu₂Si₂ and CeCu₂Si₂, corresponding to the localized and itinerant cases for 4f electrons, respectively. The whole slopes dv_Q/dP in the measured and calculated v_Q 's show good agreement. The tiny but significant anomaly in the pressure dependence of v_Q can be observed at 4.0 GPa, suggesting the existence of valence crossover in relatively narrow pressure range or another electrical transition. Recent results of Hall effect under high pressure are also reported.

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[20]

Some progresses on the study of iron selenide based superconductors

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Following FeSe superconductor, the discovery of superconductivity at about 30 K in K_{0.8}Fe₂Se₂ and then in other alkali metals and thallium intercalated iron selenide has aroused a surge of research interests as these iron chalcogenides possess distinct characteristics of crystal structure and electronic structure from their iron pnictide counterpart superconductors. Considerable progresses have been made in the study of this class of superconductors since then. In this talk, I will report our recent progresses and new insights on the structural and physical aspects, covering the synthesis of smaller alkali metals, alkaline earths and some rare earths intercalated iron selenide superconductors through an ammonothermal route, crystal growth, identification of the superconducting phases, the structural stability, doping effects and other properties as well. Finally I will summarize the problems to be addressed and possible research trend in the future.

New organic / inorganic superconductors prepared using liquid NH₃ technique

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We report new superconductors prepared by metal intercalation into two-dimensional (2D) layered inorganic crystals (FeSe, $FeSe_{1-x}Te_x$, MOS_2 and MoSe) as well as organic hydrocarbons (phenacene: picene, [6]phenacene and [7]phenacene), in which liquid NH₃ technique is utilized. Metal atoms are intercalated into the space between 2D layers in the crystals after dissolving metals in liquid NH₃. Cs doped FeSe prepared using liquid NH₃, (NH₃)_vCs_{0.4}FeSe, shows a superconducting transition temperature, T_c , as high as 31.2 K, which is higher by 3.8 K than the T_c of non-ammoniated Cs_{0.4}FeSe.¹ Pressure dependence of T_c and lattice constant, c, determined by X-ray diffraction shows a clear relationship between FeSe-layer distance and T_c , suggesting an importance of Fermi nesting for this type of superconductivity. A new superconducting phase of Na_{0.5}FeSe ($T_c = 33$ K) with being lower than the T_c of previous phase ($T_c^{onset} =$ 46 K) has been discovered, and the c in the former phase is lower than that of latter one. suggesting that the T_c increases with an increase in c.² Moreover, we have fabricated new metal intercalated crystals, (NH₃)_vM_zFeSe_{0.5}Te_{0.5} (M: Li, Ca and Na), which show clear superconducting transitions. This is the first discovery of superconductivity in metal intercalated FeSe_{1-x}Te_x system. In this workshop, we further report metal intercalated MoS₂ / MoSe₂ systems and metal intercalated phenacene solids, exhibiting clear superconducting transitions.

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[22]

Synthesis, Characterization, and Transistor Applications of Phenanthro[1,2-*b*:8,7-*b*']dithiophenes (PDT)

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[Introduction]

Recently, thin film devices using organic semiconductors, for example, organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs) and organic photovoltaics (OPVs), have been actively studied because of their potential utilization in flexible and printable electronics. Picene has been reported as superior organic semiconductors that show high carrier mobility up to 3.0 cm² V⁻¹ s⁻¹ in the OFET devices [1]. Focused on its superior hole-transport ability and excellent chemical stability in air, we designed phenanthro[1,2-*b*:8,7-*b*']dithiophene (PDT), which is a new picene analogue by replacing terminal benzene rings with thiophene rings. In this study, we synthesized PDT and characterized its electronic properties. Furthermore, its FET characteristics were evaluated to demonstrate a potential as an OFET material.

[Results and Discussion]

Suzuki-Miyaura coupling of 3-folmyl-2-thienylboronic acid with 1,4-dibromobenzene, followed by epoxidation with MeSI afforded the PDT precursor in a good yield. PDT was successfully synthesized via acid-catalyzed intramolecular cyclization. The electronic structure of PDT estimated by its optical absorption spectrum together with theoretical calculation based on density functional theory (DFT) was almost the same with that of picene, which expected to have high air stability. In addition, PDT thin film fabricated by vacuum thermal evaporation on Si/SiO₂ formed a highly ordered layer-by-layer structure elucidated by out-of-plane X-ray diffraction analysis. These results suggested that the present PDT have a high potential as a hole-transporting material for OFETs. Thus, fabricated bottom-gate top-contact OFET devices using PDT as an active layer (Si/HMDS-treated SiO₂ (400 nm)/PDT/F4-TCNQ (3 nm)/Au (50 nm)) showed high hole mobility up to 0.11 cm² V⁻¹ s⁻¹. We demonstrated that PDT is a good candidate for p-type semiconductors and building blocks as the semiconducting polymers in organic electronic devices [2]. Further functionalization including polymeric materials is currently underway in our group.

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[23]

Transport properties of graphene edges

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Graphene is a two-dimensional honeycomb lattice of carbon atoms. This lattice structure has two kinds of edges named armchair and zigzag, which have different electronic properties. The armchair edge has no carriers at the charge neutrality point (CNP) as in bulk graphene, while the zigzag edge has an edge state resulting from flat band at the CNP [1]. The singular density of states originating from the flat band induces strong electron correlation which may lead to ordered states such as spin polarization [1] and superconductivity [2]. These phenomena can be identified and explored with a charge transport technique, although most experiments on graphene edges have been carried out so far using microscopic and spectroscopic methods such as scanning tunnelling microscopy / spectroscopy [3], Raman spectroscopy [4], and transmission electron microscopy [5]. In this study, we prove the presence of flat band at zigzag edge with transport measurement.

We have fabricated graphene edge field-effect transistors (FETs) using an ionic-liquid side-gate [6]. The side-gate voltage, V_{sg} , was applied to only the edge, which enabled selective detection of the electronic states at the edge. The geometry of edges could be characterized with Raman spectroscopy; the presence (absence) of D peak at 1350 cm⁻¹ indicates the armchair (zigzag) edge. Two different characteristics were observed in graphene edge FETs. The zigzag-dominant-edge graphene FET, in which graphene possesses zigzag edge, exhibits the conductance peaks around the CNP as seen from figure 1, while the armchair-dominant-edge

graphene FET, in which graphene possesses mainly arm-chair edge, shows no conductance peak. These results show that the flat band at zigzag edge absolutely affects the charge transport so that conductance peaks are observed. In order to clarify the transport mechanism at graphene edge, temperature dependence of the conductance curve was measured. The intensity of the conductance peak diminished with decreasing temperature, indicating that carrier conduction results from the hopping transport between zigzag edges.



Figure 1. Conductance peak at a zigzag-dominant edge.

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Crystal structure and superconductivity in $LaPt_{2-x}Ge_{2+x}$

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The compounds in the formula of MT_2X_2 (M=rare earth or alkaline earth metals T=transition metals X=Si or Ge) can crystallize in several different type structures. Most of them crystallize in the body centered tetragonal ThCr₂Si₂ type structure, but some with heavy T (T=Ir, Pt) crystallize in the primitive tetragonal CaBe₂Ge₂ type structure. There are SrPt₂As₂[1] and LaPt₂Si₂[2] which crystallize in CaBe₂Ge₂ type structure. It can be considered that CaBe₂Ge₂ type is suitable for both CDW and superconductivity because CDW and superconductivity coexist in these two compounds.

LaPt₂Ge₂ is a superconductor ($T_c=0.55$ K) which crystallizes in monoclinic distorted CaBe₂Ge₂ type structure at room temperature. Two candidates were reported for the crystal structure of this compound. One of them is a structure without inversion

symmetry (space group: $P2_1$) and the other is a structure with inversion symmetry $(P2_1/c)$ and the cell volume is doubled compared with CaBe₂Ge₂ type. In addition, CDW and superconductivity probably coexist in LaPt₂Ge₂ because LaPt₂Ge₂ shows structural phase transition at 386 K, and has high temperature phase with undistorted CaBe₂Ge₂ type structure.

We synthesized non-stoichiometric $LaPt_{2-x}Ge_{2+x}$ and measured the electrical resistivity and the ac susceptibility. As a result, we discovered that a tetragonal



Temperature dependence of the electrical resistivity and ac susceptibility of LaPt_{1.8}Ge_{2.2}.

phase can be stabilized where T_c increases by increasing *x*. We succeeded in increasing T_c more than three times compared with stoichiometric LaPt₂Ge₂[3]. In this presentation, the speaker reports about the superconducting properties of LaPt_{2-x}Ge_{2+x}.

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N-type organic transistors based on Perylene diimide molecules: from bias stress effects to electrical operation in liquid environments

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In the field of Organic Field-Effect Transistors (OFET), Perylene tetracarboxylic diimide (PDI) molecules functionalized with cyano groups in the bay region (PDI_CY) are undoubtedly among the most interesting electron-transporting (n-type) compounds, thanks to the combination of excellent self-assembling properties, providing high charge carrier mobility values, and improved air-stability, given by their low-lying LUMO levels. In the last 10 years, all these features have motivated several scientific groups to deeply investigate the basic charge transport properties of these organic semiconductors [1].

In line with this interest, the first part of this talk deals with a wide analysis about the Bias Stress (BS) phenomena affecting the electrical operation of both single-crystal and thin-film OFET based on N.N'-bis(noctyl)-1,6-dicyanoperylene-3,4:9,10-bis(dicarboximide) (PDI8-CN₂) and N,N0-1H,1H-perfluorobutyldicyanoperylenediimide (PDIF-CN₂) molecules. Indeed, despite the BS phenomenon is recognized to be the main source of OFET operational instability and has been widely investigated for hole-transporting (p-type) devices, few experimental data are still today available about the occurrence of this effect in n-type organic transistors. In our work, when the BS effect was analyzed in PDIF-CN₂ single-crystal transistors with Cytop gate dielectric, the amount of stress was found to be very small, with performances overcoming those of most p-channel organic transistors studied in the past [2]. In particular, for the first time, we observed that in vacuum the BS effect in these devices tends to saturate over periods larger than 1-2 days, while, in air, $I_{DS}(t)$ decreases by only 10% even when the transistors are driven in the accumulation regime for an entire week. On the other hand, the experimental data concerning PDI8-CN₂ thin-film devices fabricated by evaporation [3] and inkjet-printing [4] techniques demonstrate that the chemical properties of the interface between dielectric barrier and semiconductor play a major role in the BS effect. These findings strongly suggest that the BS physical origin in these devices is mainly related to the occurrence of electrochemical reactions involving water, oxygen and free charge carriers.

In the second part of the presentation, the possibility to use PDI_CY molecules for the development of devices suitable to be applied in the bio-sensing field will be discussed. To this aim, the cellular biocompatibility of PDI8-CN₂ [5] and PDIF-CN₂ [6] films was tested by analyzing the adhesion and viability of three different cell lines (Human epithelial HeLa, Murine neuronal F11, Chinese hamster ovary CHO) when cultivated on their surfaces. Our studies reveal that these films allow the survival of cells on their surfaces but, depending of their hydrophobic nature, can considerably slow down the formation of confluent cellular layers. Finally, low-voltage (-5, 5V) transistors were also fabricated in order to investigate the electrical stability of PDI_8CN₂ and PDI_FCN₂ active channels when operated in liquid environments (namely, bi-distilled water and DMEM cell cultivation medium). According to our tests, an appropriate choice of the electrically-active compound allows getting n-type OFET able to operate steadily in liquid ambient [6].

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High performance organic field-effect transistors based on [n]phenacene-type molecules

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The field-effect transistors (FETs) based on [n]phenacene-type ([5]phenacene (picene), [6]phenacene, and [7]phenacene) molecules have been fabricated and their excellent FET characteristics are reported so far.

[6] phenacene thin films were fabricated with a SiO_2 gate dielectric. These FET devices exhibit field-effect mobility in the saturation regime as high as 7.4 cm²V⁻¹s⁻¹, which is one of the highest reported values for organic thin-film FETs. The two- and four-probe mobilities in the linear regime display nearly similar values, suggesting a negligible contact resistance at 300 K. The FET device fabricated with a parylene gate dielectric on polyethylene terephthalate possesses both transparency and flexibility, feasibility practical application [6]phenacene implying of of **FETs** in flexible/transparent electronics. N-channel FET characteristics are also achieved in the [6]phenacene thin-film FETs using metals that possess a small work function for use as source/drain electrodes.

Recently, a new [n]phenacene-type molecule, [8]phenacene, has been successfully synthesized. The X-ray diffraction pattern of [8]phenacene thin film on SiO₂/Si shows a systematic extension of the c^* -axis (the out of plane lattice constant) compared with other [n]phenacene thin films. This result indicates that [8]phenacene may forms the herringbone structure, which is found in picene as well as other [n]phenacene molecules. We have also fabricate the [8]phenacene thin film FETs and the details of their FET characteristics will be discussed.



Devise structure of [8]phenacene thin film FET with SiO₂ gate dielectric and transfer curve.

[27]

Stable organic field-effect-transistors with high mobilities unaffected by supporting dielectric based on π -bridged thienobenzothiophene

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We report on the electrical properties of organic field-effect transistors (FET) based on a new class of organic semiconductors. The molecules consist of the same thieno[2,3-b][1]benzothiophene (TBT) building blocks, connected by different π - bridge spacers (ethylene, phenylene and fluorophenylene). Molecular orbitals and HOMO/LUMO energies were calculated and compared with results from cyclic voltammetric and UV-vis absorption measurements. In order to study the influence of the bridge groups on the molecular arrangement and surface interaction, the transistor performance on a wide range of dielectrics has been investigated in detail.

These include as grown SiO₂ and Al₂O₃ and also treated with OTS and ODPA, as well as Cytop and Parylene C. An extended study of the multitude of combinations of these materials revealed mobilities up to $\sim 1 \text{ cm}^2/\text{Vs}$, measured for devices made of the phenylene-bridged compound. Surprisingly the mobility was quite independent of the supporting gate dielectric. Stability over time has been observed with no degradation after 5 month. By eliminating the hysteresis using Cytop we were able to show that some of the molecules form films without long-term charge carrier trapping. These are interesting features for practical industrial processing of organic electronics.

[28]

Dynamics of Carrier Injection in Picene Thin Film FET with Ionic Liquid Sheet and Ionic Liquid Gel Probed by Electron Spin Resonance

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Electronic-double-layer field-effect transistor (EDL FET) is a powerful tool for high-density carrier-accumulation into various materials, where only carries are accumulated without any chemical doping. This allows ones to selectively extract physical phenomena that are induced by carrier accumulation into materials, that is, by a shift of Fermi level. Recently, this technique is effectively applied for semiconductors, superconductors and metals, so that interesting physical properties not only emerge but also are precisely controlled. However, both control and emergence of novel physical properties have never been achieved so far in any organic materials. Actually, EDL FET technique was applied for many organic materials, but only superconductivity was observed in C_{60} . However, in the case of C_{60} , electrochemical doping of electrolyte ions was accompanied. This is intrinsically different from electrostatic carrier doping. In particular, the surface of thin films and single crystals of organic materials is so soft / flexible that electrolyte ions in electrolytes and ions in ionic liquids used as EDL capacitors can easily penetrate from the surface into bulk. Thus, electrochemical doping should be more serious in organic materials than inorganic materials.

A detailed investigation of processes of electrostatic carrier-doping and electrochemical doping is indispensable in organic materials in order to know how the carriers are accumulated and further to realize a pure electrostatic doping. In this study, we have investigated process of gate-induces carrier accumulation in organic thin films using electron spin resonance (ESR). The target organic material is picene, which consists of five benzene rings. Here we used two types of EDL capacitors, ionic liquid gel (ILG) and ionic liquid sheet (ILS), because two EDL capacitors produce the difference in the process of carrier accumulation. The alkali-metal intercalated picene showed superconducting transitions at 7 and 18 K. Therefore, a study on carrier accumulation by picene EDL FET is of much interest from view of solid state physics and materials science.

[33]

Spectroscopic evidence for metallic states in potassium-intercalated picene film on graphite

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The first aromatic superconductor was reported in potassium-doped picene (K_x picene, K_xC₂₂H₁₄) with critical temperatures of 7 and 18 K in 2009.^[1] Regarding spectroscopic studies, photoemission spectroscopy (PES) using multilayer films on different substrates has provided growing evidence for absence of states near the Fermi level (EF),^[2-4] which contradicts the observation of superconductivity. Considering that the physical properties of aromatic hydrocarbon molecule films synthesized on substrates have been known to be markedly dependent on the specific conditions of the substrate,^[5] searching for metallic films on different substrates is one of the research directions toward understanding superconductivity in doped picene. In this study, we report potassium concentration x dependent PES measurements of K-doped picene films on highly oriented pyrolytic graphite (HOPG) using He I and Xe I resonance lines, which exhibits a clear Fermi edge indicative of metallic character. The appearance of a clear Fermi edge is in contrast with the absence of clear Fermi edges in multilayer films on Au, SiO₂ and Ag(111) substrates.^[2-4] This discrepancy proposes that the emergence of the metallic states for K_x picene films depend on the aspect of the molecular orientations in the films on different substrates, which may shed light on the metallicity leading to superconductivity in doped picene.

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Electronic properties of few-layer graphene with ionic-liquid gates

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An ionic-liquid gated field-effect transistor (FET) forms an atomically thin electric double layer (EDL) at the liquid / active-layer interface, which enables high-density carrier accumulation owing to large geometrical capacitance, C_g . This technique, however, is inefficient for single-layer graphene (SLG) FETs. The reason is that the actual capacitance, C_{EDL} , between the ionic liquid and SLG consists of not only C_g but also quantum capacitance C_q , as $C_{EDL}^{-1} = C_g^{-1} + C_q^{-1}$. Here, C_q is introduced to compensate the shift of Fermi energy due to the carrier accumulation, and is proportional to the density of states, D(E). Since SLG has small D(E), C_{EDL} is limited by C_q , which prevents efficient carrier doping.

In order to clarify the factors affecting the carrier accumulation, we measured C_{EDL} between the ionic liquid (bmim[PF₆]) and few-layer graphene (FLG) by changing layer number, *n*, systematically. C_{EDL} increased up to saturation with an increase in *n*. The maximum C_{EDL} was observed at n = 4. This result is consistent with a simple theory describing how the charge distribution in FLGs affects C_q and C_g . With increasing *n*, C_q increases, but C_g decreases. The saturation of C_{EDL} means that induced charges at a few layers completely screen the electric field. In this way, we found that the ionic-liquid gate technique is not effective for the high-density carrier doping in the graphene system.

We also discuss the parity-dependent electronic states with n from the measurement of C_{EDL} . Since C_{EDL} is proportional to D(E), the detailed band structure can be studied from the capacitance measurement. According to the theory, FLGs with even n have only quadratic bands, while FLGs with odd n have linear bands in addition to quadratic bands. From the measurement, the presence of linear bands was observed as the enhanced gate-voltage dependence of C_{EDL} . This parity effect indicates that FLGs with odd n are unique materials that have massless relativistic carriers as well as SLG.

How to make graphene a macroscopic superconductor: from proximity effect to intrinsic superconductivity

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Graphene has a great potential for implementation of tunable and high temperature 2D superconductor. I will first make a short review of 3 possible ways to make graphene able to transport superconducting current at the macroscopic scale : by stress combined with doping, by intercalation of alkali and by coupling to arrays of superconducting dots.

Indeed easily accessible 2D electron gas offered by graphene provides an ideal platform on which to tune, via application of an electrostatic gate, the coupling between adsorbates deposited on its surface. This situation is particularly interesting when the network of adsorbates can induce some electronic order within the underlying graphene substrate, such as magnetic or superconducting correlations [1]. We have experimentally studied the case of macroscopic graphene decorated with an array of superconducting tin clusters [2], which induce via percolation of proximity effect a global but tunable 2D superconducting state which Tc can be tuned by gate voltage. By adjusting the graphene disorder and its charge carrier density on one side, the geometry and size of the superconducting dot network on the other side, the superconducting state can exhibit very different behaviors, allowing to test different regimes and quantum phase transition from a granular superconductor to either metallic or insulating states [3]. We will show recent experimental results involving a set of dot deposited according to triangular arrays sparcely distributed on graphene, in which superconductivity is suddenly destroyed for a critical gate value caused by quantum fluctuations of the phase giving rise to an intermediate metallic state [4].

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Atomically thin semiconducting channels for future nano-electoronics

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Using atomic-scale thin film of metal chalcogenide layered material, we investigated transport properties, particularly scattering property of carrier transport. We reveal that the carrier scattering from interfacial Coulomb impurities is greatly intensified in extremely thinned channels, resulting from shortened interaction distance between impurities and carriers. Thus, we fabricated MoS₂ field-effect transistors on crystalline hexagonal boron nitride (h-BN) and SiO₂ substrates. Temperature dependence of these transistors shows distinct weak temperature dependence of the MoS₂ devices on h-BN substrate. At the room temperature, mobility enhancement and reduced interface trap density of the single and bilayer MoS₂ devices on h-BN substrate further indicate that reducing substrate traps is crucial for enhancing the mobility in atomically thin MoS₂ devices. More detail of carrier scattering in the atomic-scale thin channel will be discussed. Furthermore, we have developed field effect transistor using high-k flak dielectric with layered structure.

Acknowledgments: We like to thank Dr.H.Miyazaki, Dr.Songlin Li, Dr. A.A.Ferreira, Dr. M.-Y. Chan, Dr.W.Li, Dr.Y.-F.Lin, Dr.S.Nakaharai, Dr.K.Wakabayashi, Dr.M.Osada, Dr.T.Sasaki and Prof.K.Ueno for the collaboration to proceed this research. This work was supported in part by the FIRST Program from the Japan Society for the Promotion of Science and JSPS- KAKENHI Grant Number 25107004.

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The second secon	ベラゾールHTシリーズ品目	Verazol [®] HT Series	Grade
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Grade	Mw	Mw /Mn	Regioregularity
Verazol [®] HT-005	40 - 70K	1.5 - 2.5	≧ 97 %
Verazol [®] HT-010	90 - 130K	1.5 - 3.0	≧98 %
Verazol [®] HT-030	400 - 700K	2.0 - 3.5	≧ 98 %

新規材料開発への取り組み Development of new materials

当社独自製法を応用した高性能な材料開発を推進しております。 We are developing high performance and unigue products by the original synthesis technologies.

> チオフェン改良品 (Improved thiophene-based polymers)

電子吸引性置換基を導入したポリチオフェン
Poly thiophenes having electron-withdraw groups

縮環系ポリマ・

(Polymers having

ring-fused structures)

新規D一A系 (New donar-acceptor polymers)

 新規D-A(ドナー・アクセプター)系ポリマー New Donor-acceptor polymers

低

(Low)

4.7eV

(High)

低

(Low)

イオン化ポテンシャル(eV) Ionized potential

- 縮環構造を導入したポリチオフェン Poly thiophenes having ring-fused structures
- $R \cdot \frac{1 \times 2 \times 2 \times 2}{Formulation of semiconductor inks}$ HTシリーズ (Verazol HT) 次自日



(Solutions of various organic

semiconductors)

有機半導体インク (Organic semiconductor inks)

その他サービス Other services

エネルギーギャップ (eV)

Energy gap

• 有機半導体材料の受託合成 Synthesis of organic semiconductor materials by commissioning

高

(High)

- 材料開発共同研究 Collaborative development of materials
- ・ 有機薄膜太陽電池・有機トランジスタの性能評価 Performance evaluation of organic photovoltaics and organic field effect transistor



問い合わせ Reference

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New analyzer DA30





VG Scienta Highlights New Analyzer for ARPES

Latest Results





3D Spectra of ${\rm Bi}_2{\rm Se}_3.$ Data courtesy of Xingjiang Zhou, IOP, Chinese Academy of Sciences, Beijing.

Spin Scan

Can measure Spin-resolved ARPES for any point in the spectrum, without tilting the sample

