

Novel control strategies in molecular thin film deposition: from tailoring crystallinity and morphology to patterning of films

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Crystal structure and resulting electronic and optical properties of materials and thin films can increasingly be predicted by theory. However, despite advances in unraveling the mechanistic details of the thin film growth process, film properties such as morphology, grain size and defect density are rarely modelled before film deposition. To take our understanding beyond a recipe-based perspective to that of sound fundamental understanding we use real-time X-ray observation of growth processes (using growth oscillations and small angle scattering) to understand the atomic scale processes. We derive the energy barriers for diffusion and step edge crossing from X-ray data for examples of organic semiconductor thin films (C_{60} and PTCDI- C_8 molecules). Using this detailed understanding of growth processes we demonstrate different strategies to tailor film growth. We will demonstrate how fast temperature modulation instead of a constant substrate temperature can be used to tailor the nucleation phase of each successive monolayer to achieve smoother film growth. As another new control parameter in molecular film growth we show that light can be used to increase phase purity in organic thin films. We will further demonstrate how polarized light can be used for photo-alignment during molecular thin film growth by addressing specific anisotropic absorption bands, such as the lower Davydov component of tetracene films. The illumination allows us to achieve photo-alignment of the otherwise randomly oriented polycrystalline tetracene films and also enables patterning of films, e.g. for photonic meta-films or electronic applications.

ELECTRONIC PROPERTIES OF PPP@ZnO FROM ALL-ELECTRON QUASIPARTICLE CALCULATIONS

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We investigate the electronic properties of poly(*para*-phenylene) (PPP) adsorbed on the non-polar (001) surface of rocksalt (*rs*) ZnO using all-electron density functional theory (DFT) as implemented in the *exciting* code [1] as well as the *GW* method to treat quasiparticle excitations within many-body perturbation theory. A comparison of the derived electronic band offsets at the interface with various mesoscopic alignment methods, such as the Shockley-Anderson approach [2] or the alignment via the electrostatic potential [3] shows the inadequacy of these methods for molecular adsorption even for physisorbed molecules with no charge transfer at the junction.

We discuss the influence of quantum confinement, charge transfer and molecular polarization as well as the impact of electron-phonon coupling on the electronic band discontinuities and the methodological implications for the *ab-initio* description of interface electronics.

Keywords: electronic structure theory; organic-inorganic heterostructures; hybrid systems; band-level alignment

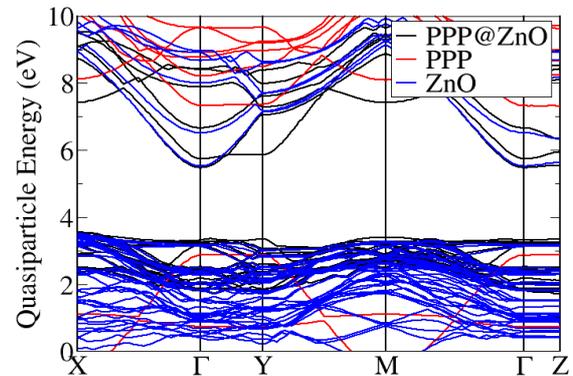


Fig. 1. QP band structure of PPP@*rs*-ZnO

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Chemoselective Reactivity of Bifunctional Cyclooctynes on Si(001)

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Organic functionalization of semiconductor surfaces and its potential for the miniaturization in semiconductor technology has motivated detailed investigations of the adsorption of organic molecules on semiconductors, especially on silicon. However, controlled organic functionalization of semiconductor substrates under well-defined vacuum conditions has not been achieved so far. The challenge is the chemoselective covalent fixation of bifunctional molecules on these substrates leaving the remaining second functional group available for further building up of complex molecular architectures. The main difficulty in achieving the required chemical selectivity on semiconductor surfaces, especially on the technologically most relevant Si(001) surface, arises from the high reactivity of their dangling bonds; typically, a mixture of molecules adsorbed with different functional groups is observed.

In this contribution, we present STM- and XPS-experiments on the adsorption configurations of bifunctional cyclooctyne derivatives with different functional side groups. These molecules show indeed such a chemoselective fixation: The strained cyclooctyne triple bond adsorbs selectively on-top of a silicon dimer while leaving the other functional groups intact. The achieved chemoselectivity is explained taking the distinctly different adsorption dynamics of the separate functional groups into account: Using molecular beam techniques, we demonstrate a direct adsorption pathway for the strained cyclooctyne triple bond. This is opposed to the majority of most organic functionalities, which generally adsorb on Si(001) via a metastable intermediate state. Thus, even if the cyclooctyne derivative first adsorbs in this metastable intermediate, the reaction of the strained triple bond is still accessible and in fact kinetically more favorable than the further reaction of the other functional group.

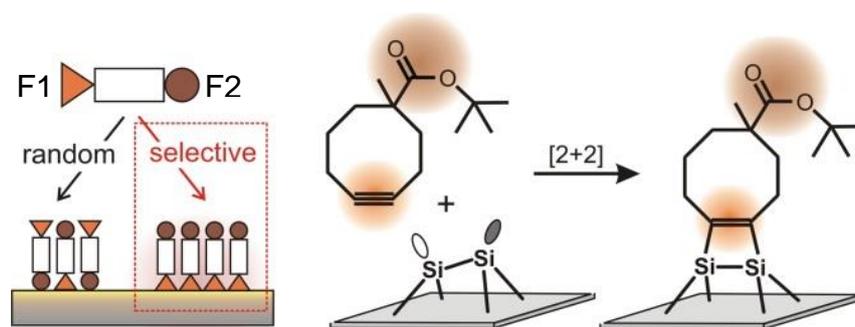


Fig. 1. (left) Schematics of the adsorption process of bifunctional (F1, F2) organic molecules on Si(001). The high reactivity of the surface dangling bonds leads typically to a random adsorption via F1 or F2. (right) In the case of bifunctional cyclooctyne derivatives, a chemoselective adsorption with the strained triple bond is observed; F2 stays intact for further functionalization.

Keywords: Surface Chemistry; Surface Reactions; Reaction Dynamics; Si(001); Cyclooctyne

SUBMONOLAYER ISLAND GROWTH OF ORGANICS: CAPTURE-ZONE DISTRIBUTIONS, GROWTH EXPONENTS, & TRANSIENT MOBILITY*

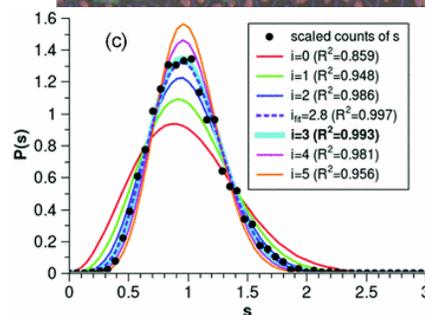
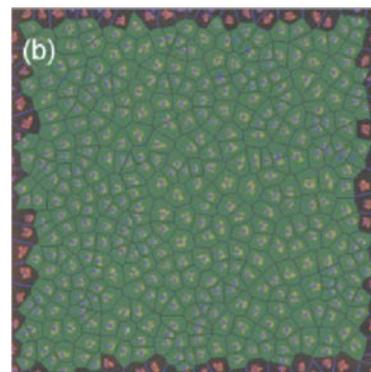
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Analyzing capture-zone distributions (CZD) using the generalized Wigner distribution (GWD) has proved a powerful way to gain insight into epitaxial growth, in particular to access the critical nucleus size i , as reviewed in [1]. The CZ of an island contains all points closer to that island than to any other, a generalization of Wigner-Seitz cells known as a Voronoi tessellation. This approach complements measurements of the growth exponent α from the scaling (with flux F) of island density $N \propto F^\alpha$ and of the distribution of island sizes. We summarize some extensive Monte Carlo simulations and especially experiments on various systems to which the GWD has been applied, emphasizing organic adsorbates. Others include atomic (sometimes with impurities), quantum dots, and colloidal nano-particles. In the case of parahexaphenyl (6P) on sputter-modified mica [2], the value i extracted from CZD (see figures) differs from the [larger] values of i deduced from $N \propto F^\alpha$. Furthermore, the values of i differed considerably at small and large F , which was attributed to DLA and ALA dynamics [2]. To reconcile the CZD and scaling measurements, we took into account long-known transient mobility (hot precursors) [3]. Similar behavior is seen for pentacene adsorbates. We close with applications of the GWD to social phenomena, notably the areas of Voronoi tessellations of subway stations and of secondary administrative units (e.g. French arrondissements and German Landkreise) [4]. In some other cases (e.g. Dutch gemeenten and Turkish ilçeler) a lognormal distribution accounts better for the data. We discuss the source and note analogous behavior in surface phenomena.



b) Voronoi tessellation for islands of 6P on sputtered mica; c) analysis of distribution $P(s)$ of s , cell areas [\pm average area] using GWD [2]

Keywords: Deposition of organic molecules, growth on surfaces, size distributions

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THERMODYNAMIC BALANCE OF PERYLENE SELF-ASSEMBLY ON Ag(110)

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We present a room temperature STM study of perylene adsorption on Ag(110) at the monolayer coverage regime. We found that structure and symmetry of the flat perylene monolayer is determined by thermodynamic balance of the three factors: (i) the site recognition effect, (ii) the intermolecular interaction and (iii) the thermal motion of the perylene molecules. The moderate strength of the site recognition and intermolecular interactions, of the same order of magnitude as $kT \sim 25$ meV, represented a key feature of the thermodynamic balance.

The thermodynamic balance bestowed to this system the unique quality to form a flexible monolayer of epitaxial as well as self-assembling character. The increasing perylene coverage induced gradual crystallization of the initially fluid monolayer (<0.1 ML) into the crystalline $(2 \times 5 \times 3^{-2}) / (2^{-5} \times 3 \times 2)$ monolayer (0.1053 ML). The crystalline monolayer further incorporated extra molecules modifying its structure and symmetry albeit maintaining its true commensurate character. The recognition effect of moderate strength was able to lock some of the perylene molecules into favorable adsorption sites of the (110) lattice providing a skeleton of the crystalline phases. We have found that the crystalline monolayer did not quench thermal motion of the included molecules but rather accommodated it modifying its skeleton by reselecting a new set of available adsorption sites favorable in terms of intermolecular interaction.

The ability of the perylene crystalline structure to accommodate its thermal motion made possible formation of the epitaxial and self-assembled perylene monolayer free of domain boundaries in the whole coverage range.

Key words: perylene, Ag(110), organic monolayer, self-assembly, epitaxy, surface mobility, thermodynamics, fluid phase, STM

Thin Films of Coupled Organic-Inorganic Nanostructures

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The concept of coupled organic-inorganic nanostructures provides a new approach to electronic applications of colloidal nanocrystal (NC) superlattices for power conversion or lighting purposes. [1] A typical superlattice consists of periodically alternating NCs and monolayers of coordinating organic semiconductor (OSC) small molecules, which act as electronic coupling agents to promote charge carrier transport across the lattice of NCs. I will show how the OSC is utilized to guide the self-assembly of semiconducting or metallic nanocrystals into quasi-2D thin films which are conductive and highly ordered at the same time. [2,3] The thin films are obtained as free-floating membranes at the liquid/air interface, transferred to solid substrates and characterized in real space by high-resolution TEM, HAADF-STEM as well as in reciprocal space by GIXD, GISAXS and simultaneous SAXS/WAXS utilizing a nano-beam set-up. The optoelectronic properties inferred from electric transport measurements, optical spectroscopy and transient absorption are discussed in the light of utilizing these hybrid thin film materials for applications in LEDs, photodetectors, sensors and thermoelectrics.

Keywords: Colloidal nanoparticles; hybrid nanomaterials; Optoelectronics

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SEMICONDUCTING OXIDE THIN FILMS: NOVEL RECTIFYING CONTACTS FOR ELECTRONIC AND PHOTONIC APPLICATIONS

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We present a number of novel rectifying material combinations (thin film heterostructure diodes) involving semiconducting oxides that provide excellent rectification [1]. We discuss the interfaces and the physical mechanisms of rectification, device properties and the possible use in applications. Three diodes are discussed in some detail: n-ZnO/p-NiO, n-ZnO/p-ZCO and n-ZnO/p-CuI.

n-ZnO/p-NiO forms a type-II heterostructure due to the conduction band lineup. Optimized structures exhibit high rectification and exhibit photovoltaic energy conversion combined with high transparency in the visible range ("transparent solar cell"). Only the UV part of the spectrum is converted with an efficiency of 3-4% [2,3]. The heterojunction can also serve as gate in transparent junction field effect transistors (JFET) [4].

n-ZnO/p-ZCO involves a p-type electrode made from amorphous zinc cobalt oxide which is fairly insulating as epitaxial ZnCo₂O₄ thin film. In 2014 the high rectification of such diode has been reported for the first time [5]. In the meantime we have reported JFET inverters [6] and JFET ring oscillators (Fig. 1) [7] based on such gate diodes.

CuI was the first transparent material ever reported (1907) [8] and forms together with n-ZnO highly rectifying diodes [9]. The role of the interface in this type-II heterostructure diode is theoretically modeled and analyzed.

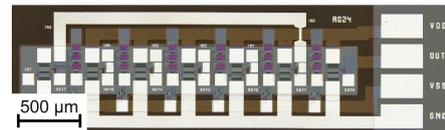
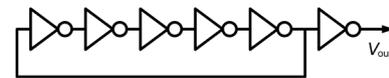


Fig. 1. Schematic and optical image of ZnO JFET-based ring oscillator (ZnO/ZCO gate diodes)

Keywords: diodes; oxide semiconductors; JFET; rectification; interface; transparent electronics

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IMPLEMENTATION OF SILICON NATIVE OXIDE AS A TUNNEL BARRIER FOR SPINTRONICS

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The integration of ferromagnetic and semiconductor materials offer unique possibilities to develop a powerful and reliable method of injecting and detecting spins in the semiconductor material at room temperature. However a strong obstacle for the development of this technology is associated with the large impedance mismatch existent between both types of materials, which limits the spin injection from high conductive ferromagnetic material to high-resistive non-magnetic semiconductor. The use of extremely thin tunnel barriers has been recently proved to be the solution to this problem [1,2]. The use of SiO₂ as a barrier is very promising due to its high dielectric constant. However the main problem concerns with the difficulty in stabilizing extremely thin layers of SiO₂ on silicon substrates while deposition of the ferromagnetic material.

Within this context, we have successfully grown thin layers of Fe₃O₄ on Si/SiO₂ substrates by PLD, with thicknesses ranging between few nm to 80 nm, in order to determine the applicability of FM-semiconductor integration using SiO₂ native oxide as a tunnel barrier. A complete morphological, compositional, electronic, magnetic and transport characterization has been performed by synchrotron based X-ray reflectivity, high and low energy XPS, Raman spectroscopy, SEM, Magneto-Optic Kerr effect and in-plane transport techniques. Special attention has been paid on the quality of the buried interfaces, thickness of the tunnel barrier and absence of other iron oxide phases or silicate phases. The results showed Fe₃O₄ single phase character without silicate formation, ferromagnetism at room temperature, well-defined metal to insulator transition, high quality interfaces and low tunnel barrier thicknesses.

Keywords: Tunnel barrier; Spintronics.

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A STUDY OF THE ELECTRONIC STRUCTURE OF ENGINEERED SOI MATERIAL

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The extreme demand for the miniaturization and increased performance of electronic devices have led to a search for low dimension, high performance and reliable materials. Silicon has been the preferred choice for decades. Silicon-on-insulator (SOI) consists of a thin Si layer known as the device layer, usually several tens of nanometres in thickness, bonded to a bulk Si wafer with an intermediate insulating oxide layer. When the silicon device layer is very thin, the effective number of atoms contributing to its physical properties are finite and small compared to the bulk. This leads to new electronic, mechanical and thermodynamic phenomena [1]. In order to study the confinement of electrons in SOI, engineered SOI structures were characterized with low-temperature scanning-tunnelling-microscopy (STM) and spectroscopy (STS).

SOIs were cleaned and thinned using plasma techniques [2] and patterned using electron beam lithography. Various scanning tunneling spectroscopic techniques such as field emission [3] and variable height spectroscopy [4] were used to study the varying density of states (DOS) of SOI structures. Significant variation in LDOS were observed for the engineered SOIs. Interestingly, apart from the effects due to low dimension of the structures, parameters such as doping concentration and annealing affects the STM and STS measurements significantly [5]. Further, using electrical measurements and kelvin probe force microscopy (KPFM) we have been able to distinguish and understand these effects. In this work we demonstrate the influence of dopant concentration and quantum confinement in SOI structures.

Keywords: Silicon-on-Insulator (SOI); Scanning tunneling microscopy (STM); Scanning tunneling spectroscopy (STS); Local density of states (LDOS);

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Optical Studies on Flash Lamp Annealed Doped and Undoped β -Ga₂O₃ Thin Films Prepared by Spray Pyrolysis

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With its wide band gap of around 4.9 eV, β -Ga₂O₃ is a promising transparent semiconductor for (opto-) electronic applications. Besides the established techniques for the preparation of β -Ga₂O₃ layers, for instance chemical vapor deposition, electron beam deposition, molecular beam epitaxy, and pulsed laser deposition, low cost techniques such as ultrasonic nebulization and spray pyrolysis are also of great interest. With the latter we prepared β -Ga₂O₃ thin films on silicon substrates.

For the preparation of β -Ga₂O₃ a solution of Ga(NO₃)₃ in water or in a water/ethanol mixture was employed. Rare earth elements, like Er³⁺, Sm³⁺, and Gd³⁺, and Al and Mg were used as dopants. The β -Ga₂O₃ thin films were investigated by scanning electronic microscopy (SEM), X-ray diffraction, Raman spectroscopy, as well as imaging and spectroscopic ellipsometry.

Since Gallium oxide, like we prepare it, needs a high annealing temperature to form the β -modification (higher than 800 °C), we use flash lamp for the annealing. There for we use energies from 10 J/cm² to 60 J/cm² and apply some additional heat with a heat plate (room temperature to 600 °C). With this we want to prepare the thin films for the application in (opto-)electronic devices.

In this work we compare by using optical investigations the characteristics of β -Ga₂O₃ thin films, which had been flash annealed and thermal annealed.

FUNCTIONAL THIN FILMS BY DESIGN: EMPLOYING RESONANCE BONDING TO TAILOR THERMOELECTRIC AND PHASE CHANGE MATERIALS

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Phase change and thermoelectric materials utilize remarkable property portfolios, which have made it difficult to design such materials, other than employing trial and error approaches. In this presentation, an alternative is discussed. Phase change materials are characterized by the ability to rapidly switch between the amorphous and crystalline state, which differ significantly in their properties. This material combination makes them very attractive for data storage applications in rewriteable optical data storage, where the pronounced difference of optical properties between the amorphous and crystalline state is used. This unconventional class of materials is also the basis of a storage concept to replace flash memory. This talk will discuss the unique material properties, which characterize phase change materials. In particular, it will be shown that only a rather small group of materials utilizes resonance bonding, a particular flavour of covalent bonding, which can explain many of the characteristic features of phase change materials. This insight is employed to predict systematic property trends and to explore the limits in stoichiometry for such memory applications. It will be demonstrated how this concept can be used to tailor the electrical and thermal conductivity of phase change materials. It even can be utilized to identify thermoelectric materials with large figures of merit. Yet, the discoveries presented here also force us to revisit the concept of resonance bonding and bring back a history of vivid scientific disputes about 'the nature of the chemical bond'.

IN SITU RAMAN STUDIES OF LASER-INDUCED TRANSFORMATIONS IN Cd-DOPED As_2Se_3 FILMS

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Amorphous As_2Se_3 is a semiconductor material with numerous possible applications related mostly to reversible or irreversible photoinduced effects. Contrary to the extensively investigated amorphous As–Se systems with different As and Se content ratio, studies of doped As_2Se_3 , except for the Ge–As–Se systems, are rather rare. Here we report on a study of thin As_2Se_3 :Cd films grown by a thermal evaporation technique using atomic force microscopy (AFM), energy-dispersive X-ray spectroscopy (EDX), and micro-Raman spectroscopy.

Thin (1–2 μm) Cd-doped As_2Se_3 films with nominal Cd content of 1 to 10% were grown by thermal evaporation on silicate glass and Si substrates. AFM studies (Agilent AFM 5420) reveal a uniform film surface with a roughness of 0.4–0.8 nm.

EDX measurements (NovaSEM microscope) performed at different electron energies (5–30 keV) show that the content of cadmium gradually decreases from the surface into the film depth. For instance, for As_2Se_3 film with nominal 10 % Cd the cadmium content in the surface layer is 18 %, decreasing down to 2.5 % with probing deeper into the film.

Micro-Raman measurements performed at 295 K using a LabRAM spectrometer and a $\lambda_{\text{exc}}=514.7$ nm or a $\lambda_{\text{exc}}=632.8$ nm laser show that at low laser power densities P_{exc} the observed Raman spectra of the Cd-doped films basically reproduce that of the undoped As_2Se_3 films with a dominating broad feature near 225 cm^{-1} that is a clear evidence of their amorphous structure. With increasing P_{exc} a new sharp peak appears at $204\text{--}209\text{ cm}^{-1}$ as well as a smaller maximum near $410\text{--}420\text{ cm}^{-1}$. The new peak positions and intensities depend on the Cd content, P_{exc} , and λ_{exc} .

The new peaks in the As_2Se_3 :Cd film Raman spectra appear, as a rule, within an acquisition time below 1 min, meaning that the local photostructural changes in the film are quite fast. At relatively low P_{exc} the evolution of the new Raman features with the illumination time can be traced. These changes are irreversible: the new peaks do not disappear after the excitation power is lowered again. This can be explained by the formation of CdSe nanocrystals in the laser spot area: the corresponding LO and 2LO phonon frequencies for CdSe are 210 and 420 cm^{-1} , respectively. The bands are observed in the As_2Se_3 :Cd film spectra at slightly lower frequencies because of tensile strain undergone by the nanocrystals due to a photo-plastic effect (radial mass transfer from the laser spot) in the films.

Keywords: amorphous thin films; nanocrystals; Raman scattering

THE LATERAL DISTRIBUTION OF OPTICAL PROPERTIES OF CHALCOGENIDE GLASSES MEASURED BY SPECTROSCOPIC IMAGING ELLIPSOMETRY

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Chalcogenide glasses exhibit a variety of properties applicable to optical devices. The vast majority of them are based on photoinduced changes created with band-gap illumination. In particular, the photodarkening, photoinduced surface corrugations and refractive index change are of renewed interest, especially for fabrication of diffractive optical elements or optical fibers.

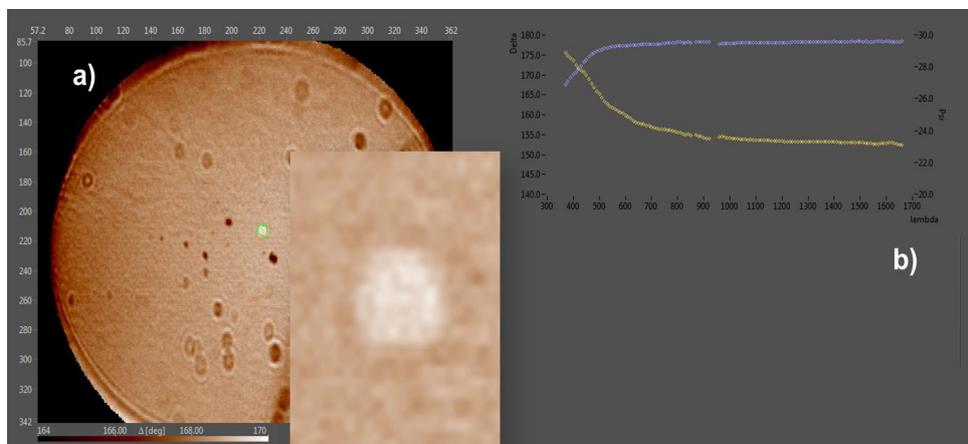


Fig. 1. Delta map (a) and Delta, Psi spectra (b) of As_2S_3 -Fiber with a core size of $6 \mu\text{m}$.

Chalcogenide fibers with core sizes down to $6 \mu\text{m}$ and holographic gratings with different phase profiles depending on the exposure conditions were characterized by imaging ellipsometry. Ellipsometric enhanced contrast micrographs were used for fast surface inspections. Optical properties of distinctive surface areas were obtained based on regions of interest (ROI) concept. Pattern and profiles of the optical properties were obtained from Delta- and Psi-maps.

To express the dispersion function of chalcogenide glasses mainly a Tauc-Lorentz term was used. In case a roughness layer must be taken into account, a Bruggemann effective medium layer containing chalcogenide glass as host was applied. A main point of view of the work was the characterization of diffraction gratings prepared under parameters that differ from the optimal procedure.

Keywords: Chalcogenide glasses, Imaging Ellipsometry

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REALIZATION OF ORDERED PHASE CHANGE MATERIALS AND THEIR INVESTIGATION VIA ELECTRICAL TRANSPORT, TERAHERTZ AND RAMAN SPECTROSCOPY

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Phase Change Materials (PCMs) are unique compounds employed in non-volatile random access memory thanks to the rapid and reversible transformation between the amorphous and crystalline state that display large differences in electrical and optical properties. In addition to the amorphous-to-crystalline transition, experimental results on polycrystalline alloys evidenced a Metal-Insulator Transition (MIT) attributed to disorder in the crystalline phase.

Here we make use of fundamental advance in the fabrication by molecular beam epitaxy of ordered alloys and heterostructures. We assess the degree of ordering by X-ray diffraction and explicitly correlate it with the MIT by means of electrical transport [1]. We further tune the ordering in a controlled fashion attaining a large range of resistivity. A combination of Terahertz and Raman spectroscopy is employed to investigate vibrational modes and the carrier behavior in amorphous and crystalline ordered epitaxial alloys [2].

Finally, superlattices made of alternating layers are studied by micro-Raman spectroscopy. A structural irreversible transformation into ordered alloys is induced by high power laser light exposure. The absence of this configuration after *in situ* annealing even up to 300°C evidences an electronic excitation induced-transition which brings the system into a different and stable crystalline state [3].

Keywords: PCM; MBE; Raman

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SURFACE PHYSICS BY NODAL LINES IN ALKALINE EARTH METALS

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In the presentation, we study surface physics characteristic in a nodal-line semimetal, which is one of the topological semimetals. We show by ab initio calculations that fcc Ca, Sr, and Yb have topological nodal lines near the Fermi level when the spin-orbit interaction is neglected (Fig.1(a)) [1]. These nodal lines (Fig.1(b)) are purely topological, characterized by the π Berry phase. Because of the topological nature of the nodal lines, the Zak phase, defined as an integral of Berry connection along a reciprocal vector, becomes π within the region (Fig.1 (c)) encircled by the nodal lines. This π Zak phase is related with charge polarization, and it means that there is an excess charge of $e/2$ or $-e/2$ within this wavevector region. This charge is screened by bulk carriers, leaving behind a large dipole at the surface and a potential dip at the surface. Eventually, this tends to cause a large Rashba spin-orbit coupling, when atoms with large spin-orbit coupling are added at the surface. It is demonstrated in Bi/Sr(111) surface, as well as in Bi/Ag(111) surface [1].

If time allows, we also show our results on Weyl semimetals (WS) [2], which are topological semimetals with nondegenerate 3D Dirac cones in the bulk. In the presentation we show that if the gap of an inversion-asymmetric system is closed by a change of an external parameter, the system runs either into (i) a Weyl semimetal phase or (ii) a nodal-line semimetal, but no insulator-to-insulator transition happens [3]. This transition is realized for example in tellurium (Te). Tellurium has a unique lattice structure, consisting of helical chains, and therefore lacks inversion and mirror symmetries. At high pressure the band gap of Te decreases and finally it runs into a Weyl semimetal phase, as confirmed by our ab initio calculation [4].

Keywords: Nodal-line semimetal, Rashba splitting

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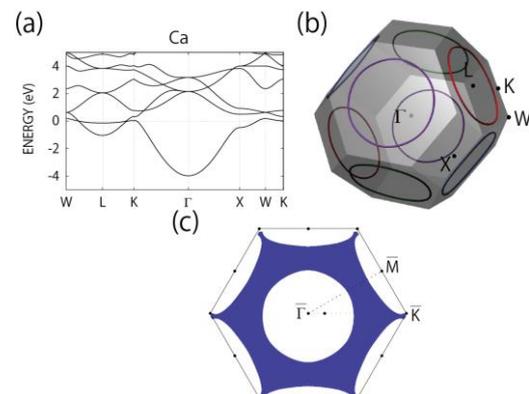


Fig. 1 (a) Band structure of Ca, (b) nodal lines of Ca, and (c) region with π Zak phase on the (111) surface

UNCONVENTIONAL SPIN TEXTURE IN A QUANTUM SPIN HALL INSULATOR

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Quantum spin Hall (QSH) insulators are materials that let electric current flow across their edge without backscattering while keeping it from passing it through their bulk. This exotic property makes QSH insulators very promising for spintronic devices[1]. Because the predicted QSH insulators have a small bandgap allowing that the bulk states contribute to the electronic transport, the observation and control of topologically protected edge states are one of the major challenges in the current condensed matter physics. We find that, in a nanoribbon of a QSH insulator, both bulk and edge states can be protected by the time-reversal symmetry. Thus, the backscattering is forbidden at any energy plane for both edges, allowing the construction of a spintronic device with less energy consumption. This behavior is a consequence of an unconventional spin texture and the presence of topological properties ($Z_2=1$) and the lack of bulk inversion symmetry and Rashba and Dresselhaus effects[2]. That is, the bands have the same spin for both edges. We also find a new stable QSH system with this spin texture. This system has a large nontrivial band gap of 0.4 eV and a spin splitting of 60 meV, which could allow the observation of the edge states.

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Keywords: Topological insulators, Quantum spin Hall insulators, spin-orbit coupling.

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CANCELED

ANNEALING-INDUCED Bi BILAYER ON Bi_2Te_3 INVESTIGATED VIA QUASI-PARTICLE-INTERFERENCE MAPPING

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Topological insulators (TIs) have much potential for use in practical applications because of their unique electronic properties, which are mainly related to two-dimensional (2D) topological surface states (TSS) and their linear dispersion. Since the TSS of TIs reside within the topmost atomic layer of the surface, its precise characteristics depends on surface structure. Hence detailed knowledge of the surface top atomic layers is essential.

Here we present the morphology changes of Bi_2Te_3 surfaces that are freshly cleaved in air, upon subsequent systematic annealing in ultra-high vacuum and the resulting effects on the local and global topological properties of the surface states, which are investigated by scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), and Auger electron spectroscopy (AES) experiments with density functional theory (DFT) calculations.

Our findings demonstrate that systematic annealing induces the formation of a Bi bilayer atop the Bi_2Te_3 surface. The atomic topography of the sample is shown in Fig. 1. The adlayer region is highlighted in red, and the atomic size of the Bi atoms is indicated by the red circles. The centers of the Bi_2Te_3 surface atoms are indicated by the blue circles. We investigated the topological properties of the surface states via quasi-particle interference (QPI) mapping.

The surface topography is shown in Fig. 1. The adlayer region is highlighted in red, and the atomic size of the Bi atoms is indicated by the red circles. The centers of the Bi_2Te_3 surface atoms are indicated by the blue circles. We investigated the topological properties of the surface states via quasi-particle interference (QPI) mapping. The surface topography is shown in Fig. 1. The adlayer region is highlighted in red, and the atomic size of the Bi atoms is indicated by the red circles. The centers of the Bi_2Te_3 surface atoms are indicated by the blue circles. We investigated the topological properties of the surface states via quasi-particle interference (QPI) mapping.

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Annealing in ultra-high vacuum offers a facile route for tuning of the topological properties and may yield similar results for other topological materials.

Keywords: Topological insulators; Bi_2Te_3 ; Scanning tunneling microscopy; Density functional theory

Non-equilibrium Surface Dirac Fermion Dynamics of Topological Insulators

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Three-dimensional topological insulators (3D TIs) with surface Dirac fermions in a bulk energy gap induced by a strong spin-orbit coupling have attracted much attention as key materials to revolutionize current electronic devices. A spin helical texture of surface Dirac fermions, where the electron's spin is locked to its momentum, is a manifestation of a 3D TI. To unveil its Dirac fermion dynamics is crucial for the future development of (opto-)spintronic devices incorporating topological insulators. Angle-resolved photoemission spectroscopy implemented by a pump-and-probe method is powerful tool to study both occupied/unoccupied states as well as hot carrier dynamics [1]. Here, the surface Dirac fermion dynamics in the “carrier tuned” topological insulator $(\text{Sb}_{1-x}\text{Bi}_x)_2\text{Te}_3$ have been explored. Sb_2Te_3 ($x=0$) has a Dirac node completely located above the Fermi energy [Fig.1 (*left*)]. The excited electrons in the upper Dirac cone are found to stay longer than those below the Dirac node to form an inverted population. This is attributed to a reduced density of states near the Dirac node [2]. Once the Fermi energy gets into the bulk energy gap by an appropriate Bi doping ($x=0.43$), the duration of the nonequilibrium surface electronic state exceeds >400 ps. The keys for the prolonged nonequilibrium are the bulk insulation and further tuning of the Fermi level to the Dirac point of the topological surface state. These findings expand the pathways to high-mobility opto-spintronic applications.

The experiments were performed at ISSP, the University of Tokyo (Proposal No. H26/A180, H26/B277, H27/259) in collaboration with K. Sumida, Y. Ishida, S. Zhu, M. Ye, K. A. Kokh, O. E. Tereshchenko, S. Shin. This work was partly supported by the bilateral collaboration program between RFBR (Russia) and JSPS (Japan) and also by KAKENHI No. 26247064.

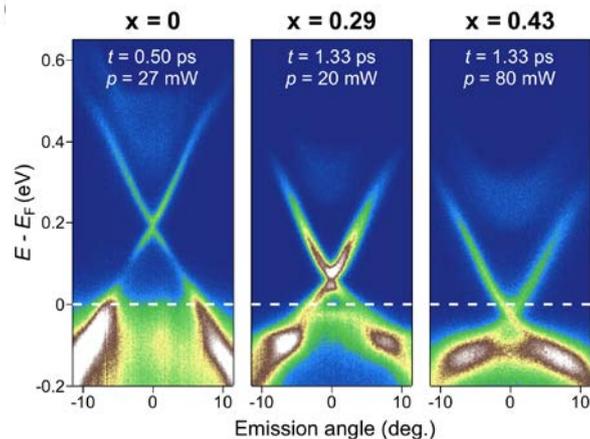


Fig. 1. Band dispersions of $(\text{Sb}_{1-x}\text{Bi}_x)_2\text{Te}_3$ ($x = 0, 0.29, 0.43$) acquired at certain pump-and-probe delay times.

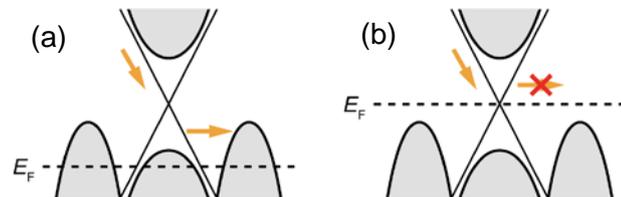


Fig. 1. Schematics of the relaxation processes in bulk metallic (a) and bulk insulating (b) TIs.

Keywords: Topological insulators; Nonequilibrium surface Dirac fermion dynamics

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