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研究課題名（英文）Understanding and control of the epitaxial multilayer growth of aromatic molecules on single crystalline metal substrates

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研究成果の概要（和文）：
相互作用の異なる金属基板上への有機分子結晶薄膜のエピタキシャル成長を行った。炭素と水素以外の元素を含む分子は、部位特異的に基板と共有結合するが、Cu(110)表面上のオリゴアセンの成長は拡張界面準位により特徴付けられ、基板上の第一層は分子が「寝て」いる。一方でBi(001)やシリセンの様な相互作用の小さい表面上では分子が「立って」いる場合と「寝て」いる場合の両方が観察され、分子結晶との格子整合性が重要であることが明らかとなった。

研究成果の概要（英文）：
The epitaxial growth of single-crystalline-like organic multilayer films on selected metal surfaces, chosen to provide either weak or strong interactions at the hybrid interface, has been studied. In particular, while molecules containing heteroatoms form site-specific covalent bonds, the growth of oligoacenes on the Cu(110) surface is characterized by extended interfacial states and a flat molecular orientation in the first layer. On the contrary, for surfaces providing weak interactions like Bi(001) and silicene, both standing and flat orientations occur and are governed by the specific lattice-matching conditions for various crystallographic planes of the thin film crystals. The results provide a detailed understanding of the influence of the substrate beyond the widely studied first layer in achieving epitaxial growth and uniaxial alignment of the grains.

交付決定額

（金額単位：円）

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2011 年度	800,000	240,000	1,040,000
2012 年度	500,000	150,000	650,000
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年度			
総　計	3,600,000	1,080,000	4,680,000

研究分野：超分子科学、界面物理・化学、光電子分光法
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キーワード：有機エレクトロニクス、光電子分光、エピタキシャル成長

１．研究開始当初の背景

Even if the condition of lattice matching is met, the epitaxial growth of a thin organic film with large (>100 μm) single-crystalline domains is rarely achieved. This is because usually in the sub-monolayer regime, condensation starts from various nuclei (C. Seidel *et al.*, Phys. Rev. B 64, 195418 (2001)) leading often to a Stranski-Krastanov growth of multilayer islands, the occurrence of rotational domains, and subsequently of grains of a very limited size. Molecular aggregation at surfaces is controlled by the temperature-dependent competition between the molecule-molecule and the molecule-substrate interactions, where two-dimensional gas, liquid and crystalline phases can be distinguished (A. Langner *et al.*, Surf. Sci. 574, 153 (2005)). Examples of the very few single-crystalline monolayer films with a horizontal molecular orientation include pentacene on Cu(110) (H. Yamane *et al.*, Phys. Rev. B 76, 165436-1 (2007)) surfaces while pentacene molecules are vertically aligned on Bi(001) surfaces (J. T. Sadowski *et al.*, Appl. Phys. Lett. 86, 073109 (2005)). The latter system provides also the first example of a single-crystalline organic film with vertical orientation and "double- epitaxy" since the Bi(001) film is itself epitaxially grown on the Si(111) surface.

If some gold atoms are deposited on the same Si(111) surface, for very sub-monolayer coverages, a substantial change of the growth mode is observed (G. E. Thayer *et al.*, Phys. Rev. Lett. 95, 256106 (2005)). Obviously, the Au-related electronic states at the very surface play a significant role in the adsorption process. Increasing the film thickness starting from the highly ordered monolayer, it is extremely difficult to achieve a growth of single-crystalline multilayers. Consequently, for highly-studied oligoacenes and to our best knowledge, prior to the present project, there has been known only four cases so far: pentacene (H. Yamane *et al.*, phys. stat. sol. (b) 245, 793 (2008)) and anthracene (F. Bussolotti *et al.*, Phys. Rev. B 80, 153402 (2009)) on Cu(110) and recently pentacene (R. C. Hatch *et al.*, Phys. Rev. B 80, 081411(R) (2009)) and anthracene (Ref.⑦) on Bi(001), where molecules grow as single-crystalline multilayer films with vertical molecular orientation. Note that the growth on Cu(110) proceeds very different from that on Bi(001). For the former surface, the first layer is strongly chemisorbed (with a flat molecular orientation).

Consequently, following layers need to reorient by maintaining an epitaxial relation with the substrate. On Bi(001), on the other hand, the interaction is very weak such that the already the first layer can grow with a vertical orientation. By comparing various materials systems, it has been argued that the electronic properties of the substrate surface play a dominant role in the initial growth and structural ordering of thin organic films (G. E. Thayer *et al.*, Phys. Rev. Lett. 95, 256106 (2005)). For crystals, the substrate electronic density tailing out of the solid into the vacuum has a spatial distribution periodic along crystallographic directions of the surface. Molecules recognize this periodic electronic density, even leading to a surface band formation involving both molecular and substrate wave functions, as observed for a pentacene monolayer on the Cu(110) surface (H. Yamane *et al.*, phys. stat. sol. (b) 245, 793 (2008)). While the importance of the structural motive is in no doubt, details like *e.g.* the involvement of bonding and antibonding orbitals of the molecules and of the substrate surface for the interaction strength has only been partially discussed.

２．研究の目的

For high-performance organic electronics applications, a fast transport of charges across the organic layers and the organic/ electrode interfaces is required. One of the fundamental issues in the engineering of such devices is the achieving a high degree of structural order since any defect will scatter or trap charge carriers. Recognizing the importance of this issue, the research performed in the project was aimed to investigate the *fundamental electronic interactions* at selected organic/metal interfaces leading to the observed epitaxial growth of thin films of oligoacene and related molecules.

In particular, it was the goal of the project

(1) to relate the electronic properties of the substrate surface and of the thin organic films to *particular growth modes* and temperature-dependent phase transitions in mono- and

multilayers of anthracene, tetracene, pentacene and related molecules;

(2) to explore the *epitaxial growth of organic mono- and multilayer thin films* on both single-crystalline metals and on metallic thin films grown on semiconductors;

(3) to measure the *electronic band structure* of the substrate surface and of the organic thin films and to relate it to electronic properties of the substrates;

(4) to find *predictions* for the growth of single-crystalline organic multilayers shall be achieved based on the knowledge of fundamental factors obtained in this study.

３．研究の方法

(1) The experiments have been performed in a costum-built, ultra-high vacuum (UHV) set-up that contains a liquid nitrogen sample cooling and a sample preparation system for the preparation of thin organic films on inorganic substrates (incl. sputtering and high-temperature heating), as well as a high-resolution angle-resolving ultraviolet photoelectron (ARUPS) spectrometer (VG Scienta SES-100 electron analyzer). Structural characterization was performed *in situ* using Reflection High- Energy Electron Diffraction (RHEED) and Low- Energy Electron Diffraction (LEED) instruments.

(2) In order to prepare silicene, thin ZrB2 films have been grown on Si (111) wafers by thermal decomposition of metal-borohydride, using a custom-built UHV chemical vapor deposition system equipped with a RHEED system. Following the transfer on air to the set-up used for the growth of organic films, native oxide was removed by annealing at about 780 $^{\circ}$C under UHV conditions (Ref. ④).

４．研究成果

(1) Strong interactions - Aromatic molecules on Cu(110)

While anthracene forms ordered multilayers on Cu(110) that are characterized by a thickness-dependent reorientation (F. Bussolotti *et al.*, Phys. Rev.B 80, 153402 (2010)), tetracene multilayers on the same surface are disordered, due to a missing epitaxial relation.

In the case of adenine on metals, particular site-specific covalent bonds are formed between the heteroatoms and the metal surface (Ref. ⑩). On the other hand, between oligoacenes and Cu(110) substrates, interfacial states are de-localized (Ref. ⑪).

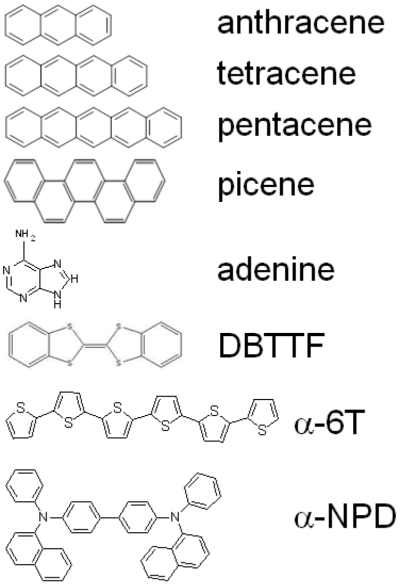

Fig. 1: Chemical structures of the molecules used in this project.

The study was extended to an aromatic molecule that contains both electron donating and accepting functional groups - dibenzotetrathiaful- valene (DBTTF). The molecular orientation of DBTTF molecules grown on the Cu(110) surface and the interactions at the interface have been found to depend strongly on the coverage and on the substrate temperature. The reason is that interactions at the interface are strong but have an opposite effect for different functional groups of the molecule.

(2) Weak interactions - Anthracene and tetracene on Bi(001)

The re-investigation of anthracene/ Bi(001) prepared on non-vicinal Si(111) surfaces proofs the existence of rotational domains. It is now understood that the electronic band structure along high-symmetry directions, shown in Fig. 2, could be measured because band edges provide a higher spectral weight making the turning points visible. Uniaxial alignment of large domains on hexagonal substrates requires therefore the use of vicinal surfaces.

Anthracene multilayer films are isostructural to the “thin-film” phase of pentacene on the same substrate, the intermolecular band structures differ significantly from each other. The evaluation of the relationship between crystal and electronic structures provides important information on the dependence of microscopic charge transport parameters on small deviations of the lattice parameters (Ref. ⑦).

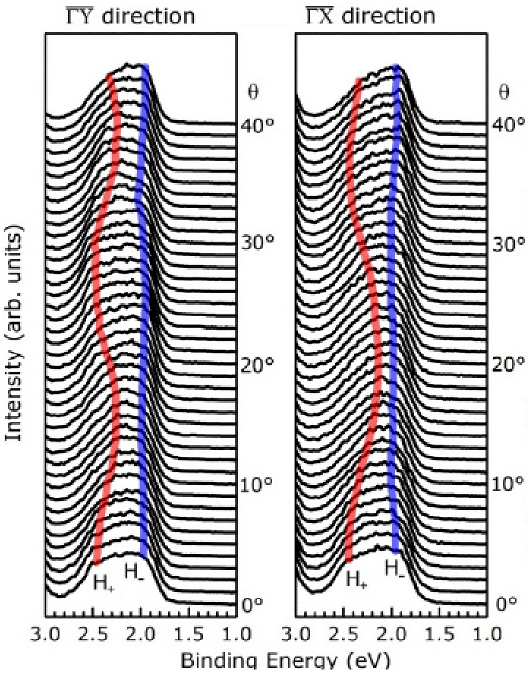

Fig. 2: Ultraviolet photoelectron spectra of anthracene multilayer films on Cu(1100, along high symmetry directions and of as a function of the polar emission angle θ (from Ref. ⑦).

Unlike pentacene (J. T. Sadowski *et al.*, Appl. Phys. Lett. 86, 073109 (2005)) and anthracene, a temperature-dependent growth mode has been observed. Since at 150 K, the flat-lying monolayer exhibits an epitaxial relation with the substrate, it is suggested that epitaxial conditions play an important role when the interaction with the metal substrate and the molecules are weak.

(3) Oligoacenes on silicene

Silicene - the Si version of graphene - has recently been found by us to form epitaxially on thin zirconium diboride, ZrB_2 (0001), films prepared on silicon wafers as substrates (Refs. ①,②,④). In our attempt to characterize the chemical properties of silicene, we have deposited mono- and multilayer anthracene and pentacene films onto silicene, held at different temperatures.

At 140 K, molecules are found to grow with the long molecular axis aligned parallel to the surface, in a point-on-line commensurate relationship between the bulk-like bc-plane of anthracene and silicene, and with an out-of-plane spacing that is consistent with a layered structure (Fig. 3). At 293 K, molecules adsorb on silicene. This fact indicates that the interactions between anthracene molecules and silicene are stronger than those on the graphite (0001) surface and enhanced by the atomic-site specific charge distribution associated with the buckling of silicene.

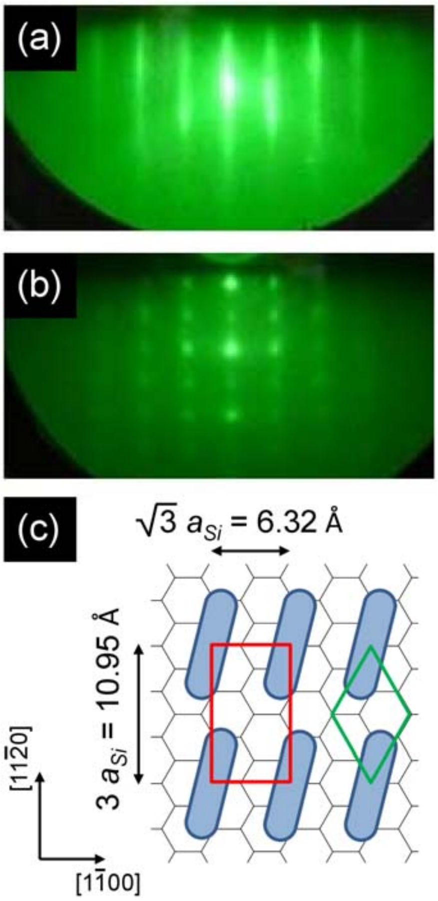

Fig. 3: (a) and (b), RHEED patterns of the silicene/ZrB2(0001) substrate and of the anthracene multilayer film on silicene prepared at 140 K, respectively. (c) Model of the in-plane crystal structure of the anthracene film.

In contrast, for pentacene, the UPS spectra and RHEED patterns are consistent with "flat-lying" and "standing-up" molecular orientations in the surface region of the films, for the low- and high temperature films, respectively. Only a low degree of only local order within the two-dimensional planes of standing molecules exists.

(4) Picene on Ag(110)

Picene is a w-shaped isomer of pentacene. To study this molecule has not been part of the original research plan. However, it has recently been attracted a lot of attention due to remarkable and unusual transport properties like superconductivity (R. Mitsuhashi *et al.*, Nature 76, 464, 2010). In order to understand these properties, it is important to be able to grow highly-ordered films epitaxially. As proven by RHEED, we succeeded to obtain such highly-ordered films on the Ag (110) surface (Ref. ⑧). A model of the as-derived in-plane unit cells of co-existing twin domains shows the length of the unit cell vectors within the *a*-*b* plane of 8.79 Å and 12.12 Å is consistent with a unit cell of an epitaxial monolayer containing four molecules. In subsequent layers, this monolayer unit cell gives naturally rise to a unit cell that would be half the size. Picene thin films on Ag(110) exhibit a “standing-up” orientation from the very beginning. This is markedly distinct to monolayer thin films of pentacene and of other aromatic molecules on the same surface where the molecular plane is parallel to the substrate surface. The orientational difference may indicate a particular molecule-substrate interaction governed by epitaxy conditions.

(5) Organic/organic heterointerfaces

The influence of molecular order on the electronic structure and the charge transport characteristics at an organic/organic heterointerface was investigated. It was found that the molecular orientation of α-NPD molecules changes the ionization energy and leads to a modification of the charge injection barrier at the α-sexithiophene/α-NPD interface (Ref. ③). The full name of α-NPD is α-*N*-*N*-diphenyl-*N'*-bis(1naphthayl)- *1,1'*-biphenyl-*4,4'*-diamine. This molecule has traditionally been considered to form only a disordered aggregation state.

５．主な発表論文等

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〔図書〕(計 0 件)

〔産業財産権〕
○出願状況（計 0 件）

○取得状況（計 0 件）

〔その他〕
ホームページ等
http://www.jaist.ac.jp/ms/labs/friedl/

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