Session IX - Thursday, September 3 - afternoon

PL8

THE TWO-DIMENSIONAL OXIDE QUASICRYSTAL AND ITS APPROXIMANTS

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Two-dimensional materials have recently pioneered a new field of materials science. Their peculiar properties are often related to their lower dimensional periodic structure. The recent discovery of a two-dimensional oxide quasicrystal (QC) extends the family of 2D materials by aperiodicity [1]. We report here on the complex growth process of the oxide QC involving a high-temperature wetting process and periodic approximant structures.

The QC is derived from $BaTiO_3$ thin films on a hexagonal Pt(111) substrate and exhibits a sharp twelvefold diffraction pattern [1]. Based on scanning tunneling microscopy the aperiodic atomic structure had been resolved [1]. It is formed by surface atoms arranged in forms of squares, triangles, and rhombi with a next-neighbour distance of 0.69 nm. Using low-energy electron microscopy (LEEM) the preparation and the growth of the QC films on top of the hexagonal Pt(111) is monitored in all details from room temperature up to about 1200 K. LEEM shows that upon high-temperature annealing large 3D $BaTiO_3$ islands are formed with bare Pt(111)-(1x1) in between. At temperatures above 1020 K a wetting layer spreads on the free Pt area. From μ-LEED analysis and darkfield imaging the twelve-fold structure of the wetting layer can be confirmed. Upon annealing in an oxygen atmosphere the QC can reversibly be transformed into smaller $BaTiO_3$ islands as revealed by in-situ LEEM measurements shown in Fig. 1.

Besides the QC itself also various approximant structures have been observed. The simplest one is the 3^2.4.3.4 Keppler approximant. But also more complex very close relatives of the QC exist.

1. S. Förster, K. Meinel, R. Hammer, M. Trautmann, and W. Widdra, *Nature* **502**, (2013) 215.

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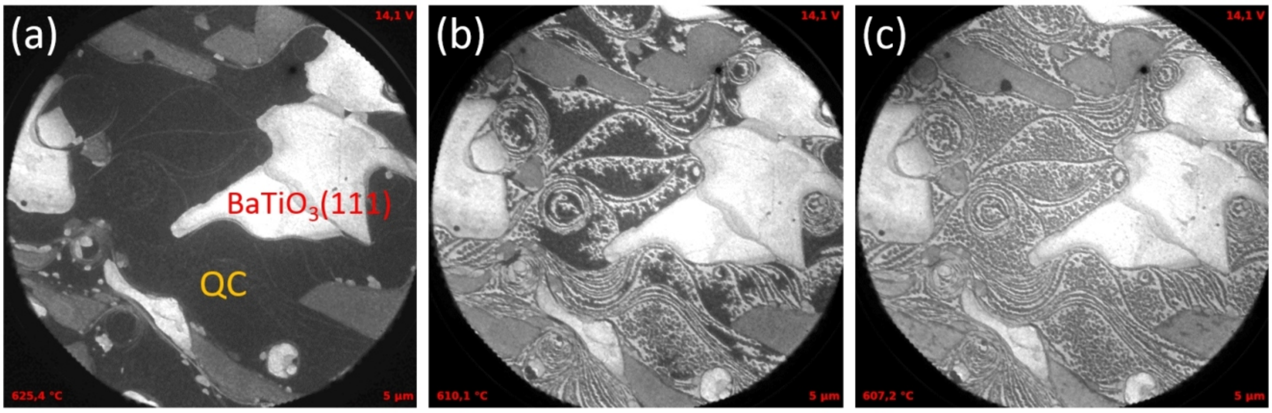

Figure 1. LEEM images showing the coexistence of the 12-fold quasicrystal and $BaTiO_3(111)$ islands on Pt(111) at temperatures between 975 and 1000 K (5 μm field-of-view): (a) as prepared and (b, c) upon in-situ oxidation that finally leads to pure $BaTiO_3(111)$ islands.

S9-L1

CLUSTER-PLUS-GLUE-ATOM MODEL OF SHORT-RANGE-ORDER STRUCTURAL UNITS

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Structural description of aperiodic structures such as quasicrystals, metallic glasses, and eutectic liquids is a difficult task because of the involvement of disordering and short-range ordering. We propose here a new structural approach, called 'cluster-plus-glue-atom model', which identifies local characteristic short-range-order units, mimicking molecules for chemical substances. This model regards any structure as being composed of a nearest-neighbor polyhedral cluster part and an outer-neighbor glue atom part situating between the clusters, expressed with universal cluster formulas [cluster](glue atom)$_x$. Such units provide the key clue towards understanding the seemingly complicated composition rules of the alloys phases. Quasicrystals and amorphous phases satisfy cluster formulas with x = 0, 1, and 3. Binary eutectic liquids are expressed as dual-cluster formulas, with the clusters issued from the two eutectic compounds. These simple rules are well verified in binary alloy systems.

S9-L2

PHOTONIC BAND GAP FORMATION IN 2D PHOTONIC QUASICRYSTALS

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Photonic crystals (PCs) are artificial periodic structures of dielectrics with a period comparable to light wavelength. When the structure is appropriately designed, a frequency range, in which light propagation in the photonic crystal is forbidden in any direction, is formed. Such a frequency range of light is called photonic band gap (PBG). In principle, if a PC possesses a PBG, various types of light-controlling devices can be realized by introducing defects in the photonic crystal. Besides PCs, photonic quasicrystals (PQCs) having quasicrystalline structural order have been demonstrated to form PBGs. Though it was theoretically expected that PQCs are generally more favourable for PBG formation than PCs due to high rotational symmetry, numerical and experimental works have not necessarily presented positive results to support it. In addition, the PBG formation mechanism in PQCs is not fully understood. In the present work, we conducted numerical calculations for the purpose of clarifying the PBG formation mechanism in PQCs, and examined under what conditions PQCs are more favourable than PCs for the PBG formation.

We constructed crystal approximant structures to a 12-fold quasicrystal of the arrangement of equilateral triangles and squares. We performed photonic band structure calculations for the TM mode for the structures having dielectric cylinders at the vertices. Here, the parameters changed are the ratio (r/a) between the cylinder radius (r) and the cylinder-cylinder distance (a) and the refractive index of the cylinder (n). In addition, we made the calculations for 4-fold and 6-fold PCs for comparison.

With respect to PBG formation mechanism of 12-fold PQCs, it was revealed that Bragg scatterings work dominantly in the weak scattering conditions (small and large r/a, and/or small n), and that Mie resonances are dominant in the strong scattering conditions (intermediate r/a and /or large n). Comparing with 4-fold and 6-fold PCs, 12-fold PQCs showed a tendency of forming larger PBGs in the weak scattering conditions where Bragg scatterings work. Fig.1 shows n-dependences of normalized band gap widths for the 12-fold PQC and the 6-fold PC. In a region of small n, the gap width is larger for the 12-fold PQC than for the 6-fold PC. Further details will be presented at the conference.

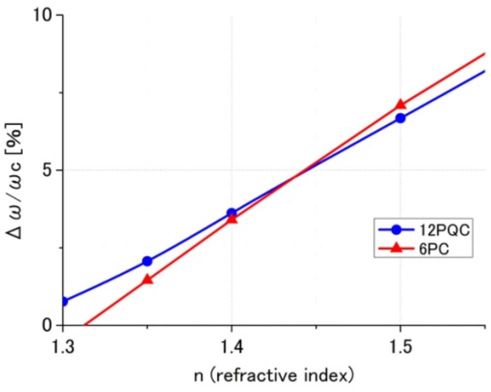

Figure 1. Normalized band gap width plotted against refractive index.

S9-L3

MOLECULAR ASSEMBLY AND 2D ORGANIC FILM GROWTH ON QUASICRYSTALLINE SURFACES

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Nanomaterials for energy and electronic applications draw significant attention of multidisciplinary research. The advantages of these materials are believed to hold the potential for higher process efficiencies and lower device manufacturing costs. However the device performance and efficiencies, in practice, are determined by the properties of surface/interface and structure of the films/surfaces. While the control on fabrication of films having targeted functional structures, remains a challenge.

We extensively studied the role of molecular symmetry and symmetry/structures of wide ranges of substrate-surfaces from non-periodic to periodic to quasi-crystalline [1-4] in nucleation, growth and phase transition in films made of organic molecular materials. Recently, most interest in quasicrystals is due to the generalization of aperiodic ordering to several classes of systems. In periodic materials, the highest degree of symmetry is provided by the cubic system, which is isotropic in six directions. There is no upper limit on the degree of symmetry in quasicrystalline systems. Compared to periodic materials, these provide a closer approximation to an isotropic first Brillouin zone, which is of great importance to the design of new materials for applications.

Here, we present results obtained from our ongoing study of interface mediated molecular assembly extended on quasi-crystalline surfaces with specific example of pentacene (Pn) and fullerene (C_{60}) thin films on Al-Ni-Co QC surface. We employed in-situ real-time low-energy electron microscopy (LEEM) for investigation of the processes in assembly and film growth and post-growth STM study to understand structural details. Experimentally observed surface processes could not be accounted from conventional atomistic models. Rather it could rationally be accounted for attachment-detachment kinetics limited by transition state/structure (TS), in which the large energy barrier for reorientation/attachment of ad-molecules results in the TS limited mechanism in molecular assembly and film growth.

Our observed TS limited mechanism in organic molecular system, we believe, is quite general in nanomaterial growth and stabilizing their surfaces, where a group of atoms collectively involves in kinetic growth-decay processes.

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S9-L4

PHASE BEHAVIOUR OF A TWO-DIMENSIONAL QUASICRYSTAL FORMING SYSTEM

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We report the formation of a stable random tiling dodecagonal quasicrystal in a two-dimensional system of disks interacting with a simple isotropic two-length scale potential. The inter particle potential is described by a hard-core and repulsive square shoulder potential. We study the system using Monte Carlo simulations. We introduce a correction term in the free energy of the quascirystal to account for its configurational entropy. Further, we determine the phase diagram of the system at a square shoulder width of 1.4. Under these conditions, the system exhibits a rich phase behaviour consisting of fluid, square, quasicrystal, low- and high-density hexagonal phases. The dodecagonal quasicrystal observed in the system consists of random tiling of square and triangle. We find that the random tiling quasicrystal is thermodynamically stable for a wide range of conditions, and that it is more stable than its crystalline approximant due to the configurational entropy.

S9-L5

SURFACE STUDIES OF Cd-Yb TYPE QUASICRYSTALS AND RELATED APPROXIMANTS

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Our research in the last few years focuses on surface studies of the Cd-Yb type quasicrystals and related approximants. The bulk atomic structure of these systems is well understood [1]. Being different from commonly used Al-based quasicrystals, these sysem are found to be promising for the exploration of new epitaxial phenomena. Several observed interesting results include three dimensional quasicrystalline growth of single elements [2], quasicrystalline monolayers of molecules [3] and five-fold-twinned islands with magic heights influenced by quantum size effects [4]. Here we will present our extended research on various approximants (Ag-In-RE, RE: Yb, Tb and Gd) and high symmetry surfaces of Ag-In-Yb quasicrystal. These systems are isostructural to Cd-Yb, where Cd is replaced by Ag and In. The building block of these systems is rhombic triacontahedral (RTH) cluster.

The growth of Pb on the fivefold surface of i-Ag-In-Yb yields a film which is quasicrystalline film in three-dimension [2]. Using scanning tunnelling microscopy (STM) and theoretical calculations of adsorption energies, we find that lead atoms occupy the positions of atoms in the RTH cluster. This observation is evidenced in other systems, namely Pb on the threefold Ag-In-Yb and In, Sb, In on the fivefold Ag-In-Yb surface.

We also found that Pentacene molecules adsorbs at tenfold-symmetric sites of Yb atoms around surface-bisected RTH clusters, yielding quasicrystalline order [3]. Similarly, C-60 growth on the fivefold surface of i-Al-Cu-Fe at elevated temperature produces quasicrystalline layer, where the growth is mediated by Fe atoms on the surface [3]. It would be interested to examine whether the sites selectivity for adsorbates is applicable in the related approximants. Therefore, we have started studying the surface structure of various approximants.

The surface of the 1/1 Ag-In-Tb and Ag-In-Gd approximants is founded to be rather complicated, compared to the 1/1 Ag-In-Yb approximant. The surface develops facets along seven different crystallographic directions. Interestingly though, there are some common features in all facets. The facet surfaces are In-rich and In-atoms are likely to be bonded with surface or subsurface Yb. This observation is consistent with STM simulation on the 1/1 Ag-In-Ca approximation [5], which showed that the sp-d hybridization between the Cd-5p states and the low-lying d-states of Yb/Ca plays an essential role for stability of surface. We will compare the growth of thin films on these approximant surfaces with the growth on quasicrystal surfaces outlined above.

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