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Observation on structure in the surface region of cocoa butter, POP, SOS and POS by X-ray diffraction

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Cocoa butter, prepared from ground roasted cacao beans, has six polymorphisms characterized by different melting points in thermal analysis. It is known to consist of several oils and fats, e.g., POP (sn-1,3-dipalmitoyl-2-oleoylglycerol), SOS (sn-1,3-dialmitoyl-2-stearoyl-glycerol) and POS (1,3-rac-palmitoyl- stearoyl-2-oleoylglycerol), etc. Since there is some resemblance in molecular structure among them, POP, SOS and POS exhibit six or five polymorphisms like cocoa butter. They are also known to acquire stable structures throughout phase transformation via quasi-stable polymorphisms. In the present study, we observe structures in surface region to a depth of 10nm from the surface and those of thin films of polymorphisms of POP, SOS, POS and natural cocoa butter by surface-sensitive X-ray diffraction techniques. The aim of our research is to clarify the peculiar molecular interactions and structures emerging only in the surface and thin films, which would also serve as basic information on melting and oxidation of chocolate. X-ray reflectivity (XR) and grazing incidence X-ray diffraction (GIXD) were exploited with high precision diffract meters on rotating anode X-ray generators (SLX2000+UltraX, TTR-450, Rigaku Co.). Thin films on Si (100) were prepared by spin-coating method with acetone as a solvent. For cocoa butter, uniform layers were easily formed by annealing, yet dewetted layers are obtained for some oils even after the annealing. A strong surface-induced preferred orientation is shown for all the samples, indicating anisotropy in intermolecular interaction. Furthermore, a distinct transformation from a double-layer structure to a single-layer structure is observed. We consider that those structures might correspond to smectic phases of liquid crystals.

Keywords: X-ray diffraction, surface structure, oil

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The formation of ice nanostructures on Cu(001)

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Nucleation of water into ice is an important process in diversified fields ranging from atmospheric chemistry to astrophysics to biology. The hydrogen-bonded network of water is well-understood in homogenous nucleation but the influence of the substrate in heterogeneous nucleation leaves a lot of open questions to be answered. How does the interaction of water with the substrate affect hydrogen-bonding? To understand this dynamic process, it is essential to study the nano-structure of ice nucleation on the substrate. In this work, we study the structure of water adsorbed on the Cu(001) at 25K by measuring its crystal truncation rods (CTR) using synchrotron-based surface x-ray diffraction (SXRD). The results are compared with water adsorption on Ni(111) to evaluate the substrate effect, whereby lateral relaxation and vertical buckling of the surface atoms are observed in order to accommodate the water in an atop position. We discuss the surface structural factors leading to this phenomenon. High photon intensity synchrotron-source x-ray at Spring-8 provides accurate structural information of the weak interaction of molecules on surfaces even for a small molecule like water.

Keywords: surface X-ray diffraction, water nucleation, copper

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Structure determination of water chain adsorbed on Pt(211)

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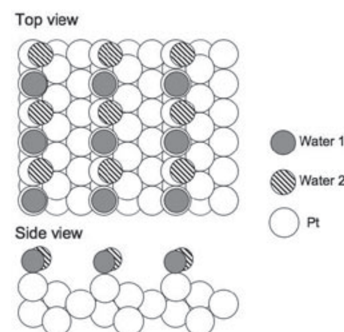
The interaction of water with metal surfaces is of considerable importance in many fields of science. Many studies have focused on the detailed structure of ice-like bilayer. [1] The low-dimensional structure of water on surface remains controversial. We determined the structure of water chain adsorbed on Pt(211) using surface x-ray diffraction (SXD). SXD measurement was performed with UHV chamber at BL13XU for surface and interface structure determination in SPring-8. Structural analysis demonstrates that water is molecularly adsorbed on the step of Pt(211) as shown in figure. Two different kinds of water are found at the top of the step. One is adsorbed on Pt (Water 1), and the other forms hydrogen bond with adsorbed water (Water 2). Pt - O length of adsorbed water is shorter than that on Pt(111), indicating that water binds strongly to the step Pt atom. This result is consistent with previous theoretical and experimental study. [2]



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Keywords: surface X-ray scattering, water, surface structure

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Observation of 1D and 2D nanostructures using the X-ray reciprocal-lattice space imaging method

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The conventional surface x-ray diffraction method [1] allows us to determine atomic arrangements of crystal surfaces and interfaces. While x-ray diffraction intensities distributed within a reciprocal lattice space are usually measured with a finetooth comb using the method, an overall image of the diffraction intensity profile is difficult to get until after such lengthy and time consuming measurement is completed. We proposed x-ray reciprocal-lattice space imaging method (X-ReSI) for straightforward understanding of 1D nanostructures such as NiO nanowires [2]. The X-ReSI is a single-exposure diffraction technique which records the reciprocal-lattice pattern of a fixed crystalline nanostructure using a 2D detector. The fundamental idea behind the method is that the reciprocal lattice of 1D or 2D structures are an array of sheets or rods, respectively. Thus the reciprocal-lattice space can be recorded for a fixed sample with a 2D x-ray detector fixed. The typical exposure time is a few seconds to a few minutes using the 3rd generation x-ray source. We applied the method to structural evaluation of Bi nanolines being 1/8 monolayers in coverage on average. The results of the application reveal that Bi nanolines embeded in Si was found to have a 2 x n superstructure having Bi dimer bonds [3]. On the other hand line structures in samples capped with an amorphous Si layer and having no cap layers still remained with a non-detectable amount of the 2 x n atomic structures. Other applications are structural determination of a $Bi_4Ti_3O_{12}$ thinfilm and in-situ observation of a Au electrode in H_2SO_4.

Keywords: surface x-ray diffraction, baried 1D Bi line, $Bi_4Ti_3O_{12}$ thinfilm

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Precise determination of crystal orientation for surface X-ray diffraction using Kossel line

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We have devoted our efforts toward developing transmission X-ray diffraction (TXD) for surface to realize more time-effective and precise surface structure analysis than the conventional surface X-ray diffraction (Tajiri et al., 2004). The direction of the development is to enlarge a research field by surface X-ray diffraction, e.g. a complex periodic-structure of surface with a large unit-cell which should have a fascinating physical and chemical properties, and not only inert prototypical surfaces but also practical surfaces with a short life-time. In TXD, we observe diffracted X-rays from surface as a pattern by area detector without rocking a sample, as is common with electron diffraction for surface. In this diffraction geometry, it is very reasonable to keep a sample stationary even during determination of crystal orientation from the viewpoint of high-throughput measurement. We report here a stationary determination of crystal orientation using Kossel line (Kossel et al., 1935), which is diffraction by inside source. The experiments were performed at the beamline BL13XU for surface and interface structures in SPring-8. We detected Kossel patterns from a silicon thin substrate by area detector, e.g pixel-array detector (Eikenberry et al., 2003), simultaneously with crystal truncation rod (CTR) scatterings and surface super-structure reflections. By a simultaneous observation of Kossel lines with CTR scatterings and fractional-order reflections, we cat determine crystal orientation necessarily for indexing X-ray diffraction from surface by a single shot.

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Keywords: surface crystallography, surface diffraction, synchrotron X-ray diffraction

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Three-dimensional imaging of interface atoms using crystal-truncation rod scattering

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It is well known that the measurement of X-ray Crystal Truncation Rod (CTR) scattering gives structural information on surface and interface atoms with respect to the substrate crystal. Usually the X-ray intensities observed are compared with the intensities calculated from structural models until the best-fit model is obtained. In this work we study a holographic method to reconstruct three-dimensional images of interface atoms directly from X-ray CTR scattering. The method utilizes the interference effect between the object wave and the reference wave in holography [1]: the object wave corresponds to the X-ray scattering from the known structure and the reference wave to the unknown interface structure to be determined. In the case of hetero-epitaxially grown thin films, the structure of the thin film as well as the substrate crystal is usually known, but the interface structure is a target to be determined. In the present work, we apply the holographic method to study the interface structure of iron-silicide thin films grown on the Si(111) substrate crystal[2]. The calculations show that the interface atoms reconstructed are stable for the structural changes.

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Keywords: interface structure, phase determination methods, crystal truncation rod scattering

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Studies of $FeSi_2$/Si quantum dot nano-structures by X-ray Bragg-surface diffractions (BSD)

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The method of using Bragg surface diffraction (BSD) for structural investigation of thin film/substrate systems has recently been introduced and demonstrated successfully for interfacial strain analysis. With the BSD method, the strain field can be determined by