

**FA5-MS39-T01****Real-Time X-Ray Studies of the Effect of Chemical Transients on Oxide Thin Film Surface Structure.**

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Modifying the chemical environment (e.g. the oxygen partial pressure) above a complex oxide can induce significant structural and electronic changes in its surface. Surface x-ray scattering studies are uniquely capable of probing the structure and dynamics of these rearrangements because of their ability to penetrate into complex and near-atmospheric pressure environments with time resolution down to nanoseconds, and with sub-micron spatial resolution. We are using these capabilities to explore basic mechanisms of materials synthesis and processing. In this talk, I will present recent results from our research programs at the Advanced Photon Source, including studies of chemical switching of ferroelectric PbTiO<sub>3</sub> where surface structure is strongly coupled to the polarization structure of the entire film, and high temperature structure and segregation in complex oxides such as La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub>. Looking to the future, spatially coherent x-ray sources such as free-electron lasers offer spectacular performance gains over current x-ray sources. I will discuss the fundamental knowledge that new and improved x-ray techniques using these new sources may yield, and how that knowledge might enable creation of high-performance materials with unique properties. Work including use of the Advanced Photon Source and Center for Nanoscale Materials is supported by U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract DE-AC02-06CH11357.

Abstract submitted for oral presentation at the European Crystallographic Meeting, Darmstadt, Germany (ECM-26), August 29- September 2, 2010.

**FA5-MS39-T02****Surface X-ray diffraction on mineral surfaces in environmental conditions.** Uta Magdans, *Department of Geology, Mineralogy and Geophysics, Ruhr-*

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Surfaces reactions and interactions of minerals play an important role in many geological and environmental, as well as in industrial processes, e.g. weathering, biomineralization or heterogeneous catalysis. Most of these surfaces are well characterized in UHV conditions with experimental techniques like STM, XPS or LEED. But are these results comparable to "real" environmental conditions, with ambient temperature and pressure, including the presence of water in the atmosphere?

Surface X-ray diffraction techniques carried out with synchrotron radiation provide an excellent tool to obtain information about the surface and interface structure of minerals in dry and humid atmosphere. With crystal truncation

rod diffraction studies we observed the formation of an laterally ordered hydration layer on the (104) surface of calcite (CaCO<sub>3</sub>) and the (100) fluorapatite (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F) surface with increasing humidity. Both surfaces showed no reconstruction, but a bulk terminated, relaxed surface structure, respectively [1,2].

Crystal truncation rod scattering experiments allow also to determine the water-mineral interface structure of the completely hydrated mineral surface. Here the calcite (104) and the fluorapatite (100) surface were covered with a water film, which leads to a 1-2 monolayers thick ordered water layer above the topmost surface layers, stabilizing dangling bonds and forming a strong hydrogen bond network [3,4].

With the mineral surface in contact with an aqueous solution of small molecules, e.g. simple amino acids like glycine and proline, we were able to resolve the water-molecule-mineral interface structure with surface X-ray diffraction on calcite, fluorapatite and pyrite surfaces [3,5]. This provides a model system to understand the influence of small biomolecules on the formation of biominerals or, as in the case of pyrite, insight in the function of mineral surfaces serving as templates during the emergence of complex biomolecules in the prebiotic world.

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**Keywords:** surface X-ray scattering, surface structure and relaxation, crystal truncation rod scattering

**FA5-MS39-T03****X-ray investigation of the morphology of DCV6T-Bu<sub>4</sub> films for Organic Solar Cells.** Alexandr A.

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Dicyanovinyl-substituted sexithiophene with four butyl chains (DCV6T-Bu<sub>4</sub>), C<sub>32</sub>H<sub>10</sub>N<sub>4</sub>S<sub>6</sub>-(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>, is a new promising photoactive material for organic solar cells. The influence of the film thickness (3.5 nm to 50 nm), the substrate temperature (30 °C or 90 °C) during the film deposition, and the kind of buffer underlayer on the atomic structure, microstructure, and film morphology of the DCV6T-Bu<sub>4</sub> neat layers is investigated by means of X-ray diffraction (XRD) and X-ray reflectivity (XRR) methods. A Si wafer or a Si wafer covered by a 15 nm-thick buffer underlayer of fullerene, C<sub>60</sub>, or 9,9-Bis[4-(N,N-bis-biphenyl-4-yl-amino)phenyl]-9H-fluorene (BPAPF), C<sub>73</sub>H<sub>52</sub>N<sub>2</sub>, is used as substrate.

The crystalline nature and ordered molecular arrangement of the DCV6T-Bu<sub>4</sub> films are proven by XRD down to 6 nm film thickness. The films grown on heated substrates (90 °C) are characterized by a better crystallinity. With increasing substrate temperature from 30 °C to 90 °C, the size of the DCV6T-Bu<sub>4</sub> crystallites in direction perpendicular to the film

surface increases up to value of the film thickness. Considering the DCV6T-Bu<sub>4</sub> films of the same thickness, use of heated substrates gives rise to the film relaxation, resulting in reducing the interplane DCV6T-Bu<sub>4</sub> distances,  $d$ , (from  $d = 11.29(5)$  Å to  $d = 10.78(5)$  Å, resp., for 50 nm-thick films deposited on Si wafers) closer to the bulk value ( $10.14(1)$  Å) observed for bulk powder material. Similarly, with increasing thickness of the films deposited on heated up to 90 °C substrates, the interplane DCV6T-Bu<sub>4</sub> distances are reduced (on an example of 10 nm- and 50 nm-thick films on Si substrate, from  $d = 10.92(5)$  Å to  $d = 10.78(5)$  Å, resp.) accompanied by a decrease of the microstrain,  $s$ , (from  $s = 1.6(2)$  % to  $s = 0.6$  %). For the same substrate temperature and film thickness, the contraction of the DCV6T-Bu<sub>4</sub> films is reducing for growth on Si to BPAPF to C<sub>60</sub> (compare  $d = 10.92(5)$  Å,  $10.88(5)$  Å and  $10.78(5)$  Å for 10 nm-thick films deposited on corresponding 90 °C-heated substrates). An attempt was performed to index the DCV6T-Bu<sub>4</sub> powder XRD pattern recorded at room temperature. Best results confirmed by comparable rather good quality of the Whole-X-ray-Powder-Pattern-Fitting of the experimental XRD powder pattern using the Pawley approach were obtained in frames of space groups  $P\bar{1}$  (triclinic; unit cell parameters  $a = 11.988(5)$  Å,  $b = 13.645(12)$  Å,  $c = 17.458(9)$  Å,  $\alpha = 125.13(4)^\circ$ ,  $\beta = 57.88(3)^\circ$ ,  $\gamma = 110.58(5)^\circ$ ; number of independent molecules  $Z = 2$ ; calculated density  $\rho = 1.466(3)$  g/cm<sup>3</sup>) and  $P2_1/n$  (monoclinic;  $a = 15.1586(6)$  Å,  $b = 17.2220(5)$  Å,  $c = 14.5872(7)$  Å,  $\beta = 93.845(4)^\circ$ ;  $Z = 4$ ;  $\rho = 1.5228(1)$  g/cm<sup>3</sup>). According to XRR investigations, the thicker films are characterized by smaller density and higher roughness independent on the substrate kind. An up to 6 nm-thick intermediate layer with linear density-gradient is formed at the DCV6T-Bu<sub>4</sub>/C<sub>60</sub> interface for the films with buffer C<sub>60</sub> underlayer.

**Keywords: organic thin films, X-ray reflectometry, X-ray diffraction**

#### FA5-MS39-T04

**Theory of phonons in 2D, 3D crystals and multilayers of hexagonal boron nitride.** K.H. Michel, B. Verberck. *Department of Physics, University of Antwerp, Belgium.*  
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Starting from an empirical force constant model of valence and van der Waals interactions and calculating by Ewald's method the ion-ion force constants, we derive the dynamical matrices for two-dimensional (2D), three-dimensional (3D) and multilayer crystals of hexagonal boron nitride (h-BN). The phonon dispersion relations in h-BN are calculated and the evolution of the spectra from 2D to multilayer and 3D crystals is studied. The interplay between valence and Coulomb forces is discussed. It is shown by analytical and numerical methods that in the 2D crystal the longitudinal and transverse optical (LO and TO) phonon frequencies for in-plane motion are degenerate at the  $\Gamma$ -point of the Brillouin zone. Away from  $\Gamma$ , the LO branch exhibits pronounced overbending. It is found [1] that the nonanalytic Coulomb contribution of the dynamical matrix causes a linear increase of the slope of the LO branch with increasing wave vector  $q$  starting at  $\Gamma$ . In the multilayer case, the LO and TO branches are still degenerate at  $\Gamma$ , away from  $\Gamma$  we obtain a phonon band where the number of LO branches is equal to the number

of layers. The slope of the highest LO branch increases steeply with  $q$ . In 3D h-BN the highest LO and TO modes are split, in agreement with the Lyddane-Sachs-Teller theory for ionic crystals. The splitting at  $\Gamma$  is found to be  $61$  cm<sup>-1</sup>. Away from the  $\Gamma$ -point the LO branch in 3D h-BN can be considered as the envelope limit of the highest mode of the multilayer band for a large number of layers. Since 2D and 3D h-BN are ionic crystals where the lattice points are not centers of symmetry, the mechanical and electrical properties are coupled. The phonon spectra calculated by the present theory for 3D h-BN are reasonably close to the results of inelastic X-ray scattering experiments [2]. Piezoelectric effects are found to be important in two ( $e_{1,11} = -1.19 \times 10^{-12}$  C/cm) [1] and in three ( $e_{1,11} = -0.357 \times 10^{-4}$  C/cm<sup>2</sup>) dimensions.

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**Keywords: 2D crystals, multilayers, piezoelectricity**

#### FA5-MS39-T05

**Investigation of the Water-Pyrite-(100)-Interface with GIXRD.** Sandrina Meis, Uta Magdans. *Department of Geology, Mineralogy and Geophysics, Ruhr-University Bochum, Germany.*  
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Pyrite surface reactions play an important role in many geological, biological and environmental processes, e.g. acid mine drainage, heterogeneous catalysis. Pyrite could also serve as a template for complex reactions and the formation of amino acids in the iron-sulphur-world scenario under prebiotic conditions [1]. The knowledge about the adsorption processes of H<sub>2</sub>O under ambient conditions is essential to understand the surface reactions and template properties of the pyrite surface. The three-dimensional pyrite surface and the interface structure of the (100) pyrite surface and water were investigated using grazing incidence X-ray diffraction (GIXRD) under ambient conditions. The measurement of non-specular crystal truncation rods (CTR) provided information about the periodic order of the vertical and lateral surface and the interface structure on atomic scale, using integrated and corrected intensities in a least square fit.

A general structure model for H<sub>2</sub>O adsorption was found by refining models with different start parameters for the site occupation factors of the surface cell of FeS<sub>2</sub>, the occupancy of O-atoms mimicking water molecules and their positions. The pyrite surface is terminated by the bulk structure, it shows no reconstruction and only small relaxations of  $<0.1$  Å for the bottom FeS<sub>2</sub>-layers and up to  $0.5$  Å for the topmost layer. The cubic surface cell with the dimensions  $a_1=a_2=5.417$  Å is extended in z-direction to  $a_3=8.748$  Å. We found a defect structure resulting from an increasing amount of S and Fe vacancies for the topmost layers.

In good agreement with results from molecular dynamic simulations of a water film on the pyrite surface [2], three layers of H<sub>2</sub>O molecules adsorbing on the pyrite surface were found at distances of  $1.9(1)$  Å,  $3.0(3)$  Å and  $5.4(4)$  Å from the topmost Fe-layer. Additionally, part of O-atoms occupies the Fe-vacancies of the topmost layers, so that we found another O position in  $3$  Å distance above the 2<sup>nd</sup> Fe layer of the pyrite surface. Between the adsorbate structure and the bulk structure of H<sub>2</sub>O, a transitional zone of up to  $8$  Å above the topmost Fe