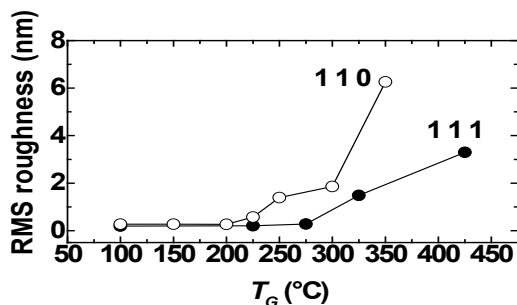


range order [2]. Different types of superlattice reflections are sensitive to different types of disorder. The image of the (222) reflection is more homogeneous than the one of the (111) reflection, indicating that the $B2$ order is more widespread compared to $L2_1$ order in the film. In the $\text{Co}_2\text{FeSi}/\text{GaAs}$ system, an almost perfect interface can be prepared. However, the films still exhibit lateral fluctuations of the compositional order, which may be connected to the formation of magnetic domains.



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Keywords: magnetic material, semiconductor, MBE

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The Surface Structure of Nano-Materials: Combining In-situ PDF Analysis and IR Spectroscopy

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Interfaces are important for the functionality of catalysts, sensors and materials for separations and sequestration. Understanding the structure of the interface, at an atomic scale, is key to controlling the functional behavior of these systems. The reactivity of catalysts, for example, can be directly derived from the structure catalytic centers at the surface of the material. Further, functional properties can be strongly dependent on the size and morphology of the particles; the surface structure of nano-particles may vary significantly from the structure of bulk materials.

What is surface structure of a nano-particle? How does it interact with molecular species? These are the questions we aim to answer by simultaneously combining the pair distribution function (PDF) method with infra-red spectroscopy. The structural characterization of nano-particle surfaces and the resulting interfaces they form can be challenging to probe, as the structures can deviate from that of the bulk; coordinately unsaturated metals, and defects are common. The surface structure may also change with the size of particles. The pair distribution function (PDF) method has shown great promise for providing quantitative insight into the structure of nano-materials. Recent advances in experimental methods have improved the sensitivity of X-ray PDF measurements allowing the correlations of molecules bound to nano-particle surfaces to be selectively recovered. We have developed an approach that allows simultaneous measurement of a secondary probe, namely infrared (IR) spectroscopy. IR enables the differentiation between molecular binding sites and brings molecular restraints to the PDF modeling. The structural insights from the combined PDF and IR data allow the surface structure and binding sites on nano-materials to be quantitatively determined.

Keywords: PDF, infra-red, surface

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Hysteresis effects of weak E fields on the domain structure in thin PbTiO_3 films

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Thin films of PbTiO_3 (PTO) of thickness ranging from 2.4 to 41.5 nm deposited by RF magnetron sputtering on SrTiO_3 (STO) single crystal (0 0 1) faces have been studied by X-ray scattering to explore the impact of weak electric fields on domain structure. In this thickness range c -oriented 180° domains of very high perfection are formed in the PTO film, *i.e.* with the polar c -axis aligned in the growth direction. Electric fields of varying magnitude and either direction (up and down) were applied along the polar c -axis employing a new sample holder [1]. To a film of thickness 50 unit cells (uc) or 20.7 nm was applied potential differences of magnitude up to 1200 V. This corresponds to a nominal field strength of ~ 100 V/cm over the film, $< 0.05\%$ of the estimated coercive field.

Bragg reflections $1\ 0\ 3$ and $0\ 0\ 3$ were examined by scans in $\dot{\omega}$ with step length 0.01° using SR of energy 12.763 keV. Images were recorded for steps of 200 V in applied voltage within the range +1200 to -1200 V. Reciprocal space reconstructions show diffuse scattering in the shape of an annular ring or cylinder centred on the Bragg truncation rod (BTR). This is consistent with domain 'stripes' in a nearly random in-plane orientation. Very similar patterns, in some cases developing into square patterns of diffuse intensity reflecting stripes being arranged with increasing perfection along the tetragonal axes a and b , have been reported by several groups, *e.g.* [2], [3], [4], [5].

In the present study we have found in addition 1) Increasing positive fields (E direction from substrate into film) instigate an increase in the diffuse intensity of the ring with a concomitant decrease in intensity of the BTR. The process reaches a maximum at $\sim +1000$ V. A reduction in magnitude and subsequent change in polarity of E initiates a reversal of this process. With increasing negative fields, the annular ring gradually vanishes with a parallel increase in intensity of the BTR. There is a hysteretic relationship between the development of these intensities and changes in E . 2) An offset in c^* between the centres of the annular ring and of the film Bragg reflection relays a contracted c for the material that gives rise to the diffuse scattering. A small hysteretic variation in $\text{\AA} c^*$ with E is mainly due to small changes, of the order 0.1%, in c for PTO. 3) At the present level of accuracy the domain period \tilde{E} that can be retrieved from the diameter of the annular ring seems to be dependent on E , increasing slightly with increasing positive field. These results appear to be novel, not previously discussed in the literature.

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Keywords: synchrotron X-ray scattering, perovskite oxides, thin ferroelectric films

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The pyrite (100) surface structure in dry and aqueous ambient conditions

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Pyrite (FeS₂) is one of the most abundant sulphur minerals on earth and plays an important role in many natural processes, e.g. acid mine drainage and heterogeneous catalysis. Its surface adsorption properties to organic molecules in hydrothermal setting were shown by Lindgren et al. [1] and are important in the iron-sulphur world scenario published by Wächtershäuser et al. [2].

Non-specular crystal truncation rods (CTR) of the pyrite surface under ambient conditions, that provide information about the periodic order of the vertical and lateral surface and the water-pyrite interface structure, were collected with grazing incidence X-ray diffraction (GIXRD) at the ESRF, Grenoble, France. The surface/interface structures of the (100) face in dry and aqueous ambient conditions were investigated using integrated and corrected intensities in a least square fit.

Different models for the surface cell dimensions and the site occupation factors (sofs) were tested. The (100) face in dry conditions shows a defect structure resulting from S and Fe vacancies with sofs of 0.1-0.3 for the topmost atom layer, decreasing with increasing depth. The surface cell is bulk structure terminated with only small relaxations in the topmost surface layers.

For the (100) face covered with a water film a pyrite/water interface model was ascertained by refining models with different start parameters: site occupation factors, positions and occupation factors of O-atoms mimicking water molecules. The pyrite surface is also bulk terminated with a defect structure resulting from S- and Fe-vacancies. It shows only small relaxations of <0.1Å for the bottom and 0.5Å for topmost surface layers without reconstruction.

In good agreement with results from molecular dynamic [3] and ab initio [4] simulations three layers of H₂O molecules are adsorbed to the surface. Additionally, water molecules occupy the Fe-vacancies of the topmost Fe-layer and a transitional zone up to 8Å, above the topmost Fe-layer, between adsorbed and bulk water can be found. The first H₂O-layer is located 1.9(1)Å above the topmost Fe-layer and is bound to the iron atoms. The second layer interacts with the topmost sulphur layer and is located 3.0(3)Å above the topmost Fe-layer. The third layer interacts with the second H₂O-layer and the transitional zone and can be found at a distance of 5.4(4)Å to the topmost Fe-layer. There is an electrostatic interaction in x-direction, whereas the interaction in y-direction is more dynamic, because of the surface anisotropy of the (100)-face of pyrite.

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Keywords: surface_X-ray_diffraction, pyrite_surface, crystal_truncation_rod

MS21.P12

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X-ray characterization of sol-gel TiO₂ thin films

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TiO₂ thin films deposited on a Ti-6Al-4V alloy by means of the sol-

gel dip-coating technique were characterized using X-ray synchrotron radiation. The crystalline structure and thickness of the films were obtained and related to the parameters of the sol-gel process.

The process involves immersing the substrate (Ti-6Al-4V) in a colloidal dispersion (sol), withdrawing the substrate at constant low velocity, drying of the coating and heat treatment. For the dispersion preparations, titanium butoxide, isopropanol, ethyl acetoacetate, HCl and distilled H₂O were used. Several withdrawing velocities and number of layer were used, these ranged from 1 to 3 cm/min and from 1 to 3, respectively. Two values of titanium butoxide/isopropanol molar ratio were used in the dispersions: 1/20 and 1/10. Dispersions with aging times ranged from 1 to 10 days were used. The samples received a heat treatment for 1 h at a fixed temperature of 500 C to each layer of coating and heated to 10 C/min and cooling inside the furnace. The morphology of the coatings was observed by optical microscopy and SEM. The crystalline structure was determined by X-ray diffraction with a glancing incidence angle of 1° and the thickness was determined by the X-ray reflectometry technique. These experiments were carried out at the D12A-XRD1 beamline of the LNLS (Campinas, Brazil).

The coatings were homogeneous, compact and smooth to the optical microscope, and of different colors according to their thickness. With increase of the withdrawing velocity, the number of layers, the titanium butoxide/isopropanol ratio or the aging time of the dispersions, the thicknesses of the coatings increased, all in a range from 25 nm to 142 nm. Cracks were observed on films with thicknesses thicker than 100 nm. By X-ray diffraction of the monolayer and multilayer coatings was determined the presence of anatase and rutile.

The results show a relation between thickness and structure. In the thinnest films no crystal structure was detected, while for films with intermediate thickness rutile phase was detected, and for the thickest films both rutile and anatase phases were detected. The brookite structure was not detected in any film.

Keywords: sol-gel, film, synchrotron

MS21.P13

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Characterization of TiO₂ nano-films obtained by anodic oxidation of Ti-6Al-4V

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Anodic oxidation of Titanium and Titanium alloys produce a TiO₂ coating with better mechanical properties and corrosion resistance than the substrate. In addition, this TiO₂ coating is a film with biocompatible properties [1], [2].

In the present report, we determined and analyzed the effects of different acid electrolytes on the color, thickness, morphology and crystalline structure of the coating. The electrolytes used were sulfuric acid (H₂SO₄) 0.1M to 4M and phosphoric acid (H₃PO₄) 1M, and the substrates were plates of Ti-6Al-4V alloy; the oxidation voltages used ranged from 10V to 100V.

The thicknesses of the films were determined by X-ray reflectometry with synchrotron radiation (D12A-XRD1 beamline of the Brazilian Synchrotron Light Laboratory, LNLS). The morphology of the films was observed using optical and scanning electron microscopy and the crystalline phases of the oxides formed were determined by the glancing incidence angle X-ray diffraction technique with a glancing angle of 1°.

The oxide films produced different interference colors depending