MS26-O5 The incommensurately modulated phase in (2-methylimidazolium) tetraiodobismuthate(III) thermochromic organic-inorganic hybrid

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(2-methylimidazolium) tetraiodobismuthate(III) (abbreviated as (2-MIm)BiI_4) is a thermochromic, semiconducting hybrid. It undergoes structural first-order phase transition to incommensurately modulated phase at 308 K. The symmetry changes form $C2/c$ to $C2/c(0,\beta,0)s0$; the modulation wave vector $\mathbf{q}=0.575(2)\mathbf{b}^*$ [1]. The incommensurate phase is stable down to 100 K. The non-modulated structure consists of polymeric chains of $[BiI_4^-]_n$ anions propagating in the c direction and stacks of 2-MIm^+ counter-ions that couple to the anionic substructure via weak hydrogen bond interactions. The polymeric $[BiI_4^-]_n$ anions comprise of distorted BiI_6 octahedra that form zig-zag chains by sharing the *cis* edges. The cations are dynamically disordered over two equivalent positions that are related by the two-fold axis. The transformation to incommensurate phase is triggered by a collective, sinusoidal displacement of bismuth and iodide atoms from their high-temperature positions. The intra-chain bonds in modulated phase do not differ considerably from their high temperature counterparts. Much significant deviations are observed between the chains which may be shifted up to ~0.4 Å relative to each other along the *c* direction. Substantial variations within the inter-chain Bi...Bi distances may have an impact on the semiconducting and thermochromic properties of this material. 2-MIm^+ counter ions order in the incommensurate phase. In each cavity the 2-MIm^+ adopts one of the two positions that were equivalent in the high-temperature phase. At 220 and 150 K the reorientation movements between the sites are blocked which is confirmed by dielectric response. DOS calculations together with asymmetric local environment of bismuth ions imply the presence of the stereochemically active bismuth lone pair $6s^2$ electrons in both phases. The change of the lone pair activity may play the foreground role in the phase transition mechanism as far as the increased contribution of bismuth states in total DOS in the incommensurate phase is noted. This interpretation is consistent with structural data that show greater deformation of the bismuth coordination geometry in the modulated structure.

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Keywords: modulated structure, organic-inorganic hybrid, phase transition

MS27. Electron crystallography methods

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MS27-O1 Deformation mapping in theTEM by dark holography,nanobeam diffraction,geometrical phase analysis and precession electron diffraction. A comparison of the different techniques

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In the last few years there has been an explosion in the number of transmission electron microscopy based (TEM) techniques that can be used for strain mapping with nm-scale resolution. These include dark field electron holography, the geometrical phase analysis of high-resolution images, nanobeam diffraction and more recently precession electron diffraction. In order to benchmark the different techniques a calibration specimen containing 10-nm-thick SiGe layers with different Ge concentrations has been grown by chemical vapour deposition. Due to the epixatial growth, the lattice parameter of the SiGe will be expanded relative to the Si in the growth direction. Figure 1(a) shows a HAADF STEM image of the calibration specimen indicating the concentration of Ge present in each layer and deformation maps for the growth direction acquired by (b) GPA of HAADF STEM (c) dark field electron holography (d) precession electron diffraction and (e) finite element simulations are shown. The HAADF STEM deformation mapping has a spatial resolution of 1.5 nm which is imposed by the size of the mask used in Fourier space during the reconstruction and a measurement sensitivity of 0.25 % was determined by taking a standard deviation of the deformation measured in the unstrained silicon substrate. For the dark holography the spatial resolution imposed by the fringe spacing of the interference pattern is 6 nm with a measured sensitivity of 0.05 %. For precession diffraction, the spatial resolution imposed by the diameter of the electron probe is 2 nm and a sensitivity of 0.02% measured. While it is relatively straightforward to apply all of these techniques to simple calibration specimens where both large values of deformation are expected and the experiment is simplified due to the 1D nature of the strained layers. All of the techniques have been applied to a range of different specimens each with different complications, such as a 35-nm gate SiGe recessed source and drain pMOS device, a nMOS device tensily strained using a nitride film, to state of the art SOI-based semiconductors and a III/V superlattice. The advantages and disadvantages the

different strain mapping techniques are discussed.

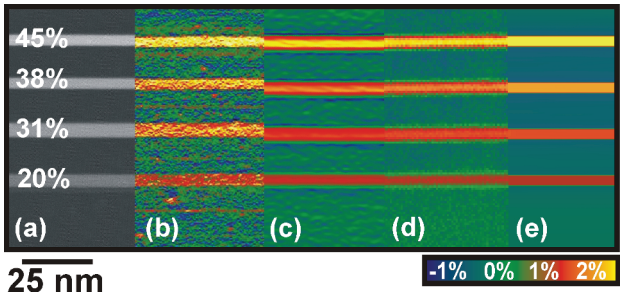

Figure 1. HAADF STEM image of the calibration specimens with deformation maps acquired by HAADF STEM, dark holography, precession diffraction and finite element simulations.

Keywords: Strain Mapping, TEM, Semiconductors.

MS27-O2 Electron diffraction and imaging of 3D nanocrystals of pharmaceuticals, peptides and proteins

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High-energy electrons provide 1000 times more information per Gray (absorbed energy, i.e. radiation damage), compared to X-rays. Hence electrons outperform X-rays for structure determination when radiation damage is the limiting factor. Unlike X-rays, electrons can not only be diffracted, but also imaged. However, when imaging transparent samples, the *total number* of quanta per unit area determines the signal-to-noise ratio. When diffracting transparent samples, the *number of interacting* quanta per unit area determines the signal-to-noise ratio. Measuring electron diffraction accurately has only recently become possible with the advent of quantum area detectors. One of the challenges is that an electron microscope is flooded with photon radiation resulting from Bremsstrahlung generated by the high-energy electrons. Only an area detector that can discriminate between photon noise and electron signal is insensitive to this noise.

This difference in signal-to-noise ratio was demonstrated in practice for electrons using a Timepix quantum area detector. When imaging a 100 nm thick lysozyme protein crystal with electrons, typically one to two images of the same location could be measured with significant details up to 3.5 Å resolution. Subsequent images had suffered too much from radiation damage to show such detail. When diffracting similar crystals, hundreds of electron diffraction patterns with Bragg spots beyond 3 Å resolution could be measured from the same location. However, there is no such thing as a free lunch. Diffraction comes at a price: the structure factor phases are lost. They can only be retrieved using additional (prior) information, for instance obtained from (a few) electron images. We demonstrated this strategy by phasing the 3D structure factors of a nano-crystalline amyloidic peptide.

Keywords: electron diffraction, phasing, detectors