A key feature of the design of the silicon quantum well is the introduction of a large biaxial tensile strain to modify the band structure within the well. In nanodiffraction studies, this strain allows X-ray reflections from the silicon quantum well to be easily distinguished from the reflections arising from the silicon substrate. In addition, the silicon quantum well has smooth interfaces, which lead to rods of intensity in reciprocal space. Maps of the intensity and angular location of these rods as a function of the position of the X-ray nanobeam provide local information about the thickness and orientation of the silicon quantum well layer. The intensity of the rod extending from the 004 X-ray reflection of the Si quantum well (inset in **Figure 109**) exhibits variations at the 100 nm length scale that result from local differences in the thickness of the quantum well layer. The intensity exhibits local variations of several percent, a magnitude that is consistent with what would be expected due to unit-cell-scale variations in the thickness of the quantum well. In addition to these local differences in thickness, the local orientation of the atomic planes within the quantum well varies due to the randomness associated with the underpinning silicon-germanium layers of the heterostructure. These orientation variations lead to a lateral variation of the strain in the quantum well over distances of hundreds of nanometres to 1 µm, modifying the potential well confining electrons. Precise structural information allows theoretical studies of the effects of structural features on quantum electronic properties to be tested and will enable the creation of optimised devices.
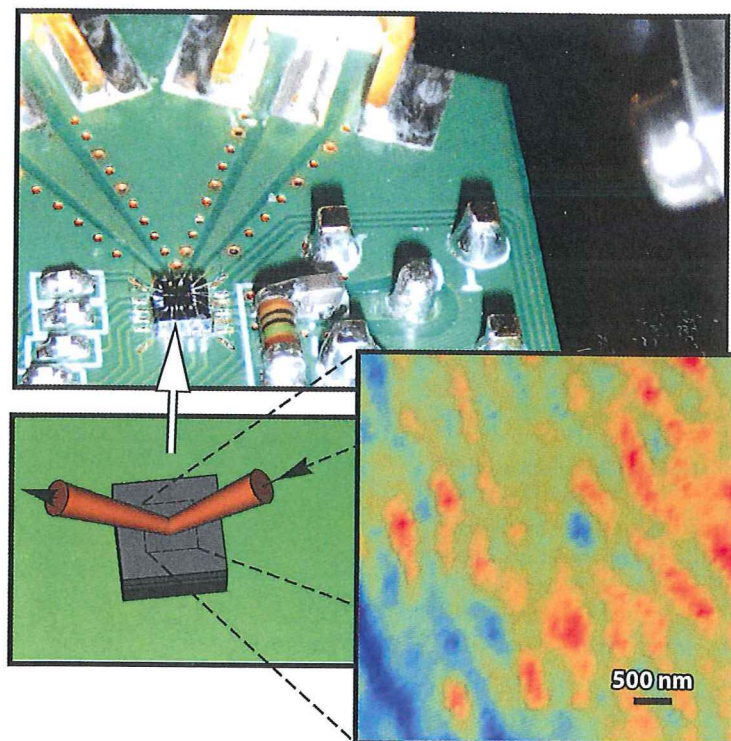

Fig. 109: X-ray nanodiffraction map of the waviness in a 10 nm-thick buried Si quantum well. Si quantum wells in a Si/SiGe heterostructure are characterised using a tightly-focused X-ray beam, without destructive sample preparation. Structural effects at the 100-nm length scale arising from local variations in the quantum well thickness are apparent in the total intensity of the 004 X-ray reflection of the quantum well.

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BaTiO$_3$ (001) (2x1): Relation between structure and magnetism

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BaTiO$_3$ (BTO) is an archetype ferroelectric whose physical properties have been well known for decades and have been thoroughly documented in solid state physics textbooks. Bulk BTO is a perovskite type ferroelectric (transition temperature T$_C$ = 408 K) insulator (bulk band gap = 3.2 eV). It is used in technological applications as a piezoceramic capacitor and in nonlinear optics. In contrast, nothing is known about the structure and physical properties of the surface of a BTO crystal, which has become a focus for research owing to possible applications in nanoscale oxide spintronic devices [1]. Although the (001) surfaces of STO and BTO are known to reconstruct to from a (2x1) and a (2x2) superstructure [2], a structure model exits only for STO [3]. We have carried out a combined surface X-ray diffraction (SXRD) and theoretical study of the atomic structure and the corresponding physical properties for BTO.

The SXRD experiments were carried out at beamline **ID03** using a bulk crystal, which

after mild Ar+ sputtering and annealing up to about 1000°C exhibits a (2x1) reconstruction with no traces of a (2x2) reconstruction.

Fig. 110: Model of the BaTiO₃(001)-(2x1) structure in perspective side view. Two TiO₂ layers (atoms #1-8) are located above the bulk-like BaO layer (primed labels correspond to symmetrically equivalent atoms).
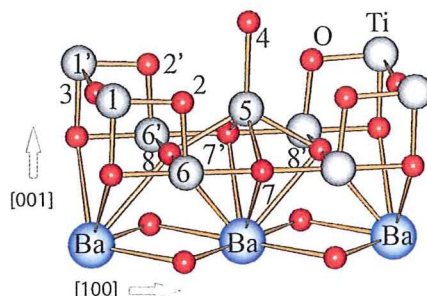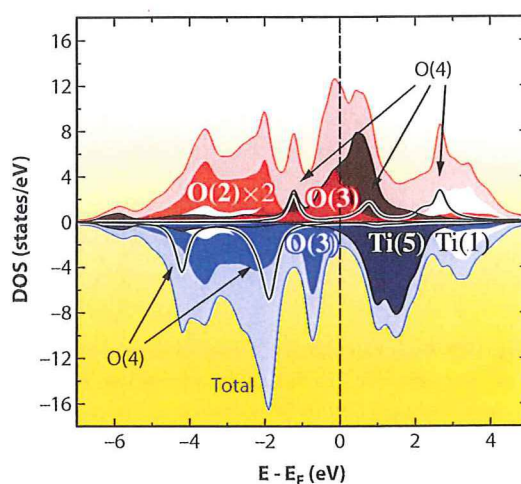

Fig. 111: Spin resolved DOS of BTO(001)-(2x1). The contributions of the different atoms are indicated. Dark colour (red, blue) corresponds to Ti (5). The light (red) and blue profiles correspond to the total DOS.

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The structure model is shown in **Figure 110** in perspective side view. The BTO crystal is terminated by two stoichiometric TiO₂ layers, similar to the STO(001) surface [3], but significant differences exist with respect to the position of the top layer structure. Here, the most important characteristic is that one titanium atom (5) resides in a fivefold coordination to oxygen atoms (7, 7', 8, 8' and 4) in the centre of a pyramid. In this way, the titanium atom (5) shifts inward thereby binding to oxygen atom (4) and to the second layer oxygen atoms at a distance of 2.30 ± 0.15 Å.

Based on this structure model the electronic and magnetic properties of the (2x1) BTO surface were calculated within the density functional theory (DFT) in the local density approximation using a Korringa-Kohn-Rostoker Green-function method, which is specially designed for semi-infinite layered systems. According to the DFT calculations, the BTO(001)-(2x1) surface is metallic and magnetic. **Figure 111** shows the density of states (DOS) for spin up ($\uparrow$) in red which is different from the spin down DOS ($\downarrow$) shown in blue.

The DOS is large at the Fermi level (E_F), this is related to the ($\uparrow$) contribution of titanium atom (5) and oxygen atom (3). The filling of the titanium 3d states is mainly a consequence of the charge transfer from oxygen to titanium. Moreover, due to the low coordination and reduced symmetry, the different DOS contributions are narrow and involve partially unsaturated 2p states in the case the oxygen atoms (3) and (4). In turn this leads to high local magnetic moments up to 1.3 μ_B and -2.0 μ_B for the titanium atom (5) and oxygen atom (4), respectively.

In summary, our X-ray diffraction analysis of the BTO(001)-(2x1) reconstruction has identified an atomic arrangement that had not been considered before for (001) oriented perovskite surfaces. The most remarkable unit is a titanium atom in the centre of a tetragonal pyramid. This unique motif causes symmetry breaking, localisation of the electronic states, and charge transfer to the central titanium atom from surrounding oxygen atoms. This leads to metallisation and magnetisation which is now identified as an intrinsic property of the surface. We infer that this metallisation might also contribute to the stabilisation of the reconstruction related to the depolarisation of the surface.

Reversible formation of a PdC$_x$ phase in Pd nanoparticles upon CO and O$_2$ exposure

Palladium nanoparticles are usually assumed to be in a purely metallic state during a CO oxidation reaction when CO is in excess. In this work, we tested this hypothesis studying the behaviour of Pd nanoparticles under reaction conditions. A combination of X-ray diffraction and X-ray photoelectron spectroscopy was used for pressures ranging from UHV to 10 mbar and from room temperature to a