Femtosecond X-Ray Diffraction from Nanolayered Oxides

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Abstract

Femtosecond X-ray scattering offers the opportunity to investigate reversible lattice dynamics with unprecedented accuracy. We show in a prototype experiment how strain propagation modifies the functionality of a ferroelectric system on its intrinsic time scale.

Keywords: Femtosecond X-ray diffraction; nanolayer oxides; superlattice; ferroelectricity

1. Introduction

‘If you want to understand function, study structure’, exhorted Francis Crick when he resolved the molecular structure of DNA. However, knowledge of a static structure is often only a first step towards unraveling how microscopic systems work. In particular, elementary processes in condensed matter are frequently governed by nuclear rearrangements, which take place on a femtosecond time scale, and are ultimately set by the translational, rotational or vibrational motions on an atomic length scale. Hence, function is intrinsically coupled to dynamic structure.

While ultrafast optical spectroscopy has become a well established tool to follow such microscopic processes in real time, the information on structural changes is, at most, indirect and changes in geometry triggered by elementary excitations and interactions have mostly remained elusive. X-ray scattering, on the other hand, gives direct access to structure in condensed media. Since the wavelength of X-ray photons is comparable to interatomic distances, diffraction patterns determine atomic positions with high precision. During the last decade great progress has been made to combine the temporal resolution of ultrafast technologies with the spatial resolution of X-rays, that

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is, developing X-ray sources with ever shorter pulse durations [1]. Yet, ultrafast X-ray scattering is still a nascent field of science with not insignificant technical constraints, and only a limited number of successful femtosecond X-ray diffraction experiments have been carried out, e.g. reviews [2],[3].

In this conference contribution, we present time-resolved X-ray diffraction experiments on a perovskite metal-ferroelectric-metal nanolayer system and demonstrate how tailored strain patterns couple to electronic properties, i.e., to the macroscopic polarization on an ultrafast time-scale. Additionally, a superlattice structure consisting of metallic and dielectric nanolayers is investigated on a longer time scale. Here, the measured transient X-ray reflectivity and line shift allows following strain propagation and relaxation of the entire multilayer structure with high precision.

This contribution is organized as follows: first, we discuss the structural properties of superlattice samples and give a detailed explanation of the mapping of the measured X-ray reflectivity to the underlying strain patterns (section 2). We briefly mention the experimental techniques of femtosecond X-ray scattering (section 3), and present the experimental results of strain propagation (section 4) and its coupling to polarization dynamics in ferroelectric nanolayers (section 5). We conclude with section 6.

2. Nanolayered Structures

2.1. Structural Properties

Systems consisting of thin epitaxial layers of different materials which are repeated periodically along one direction are usually referred to as superlattices (SL). Recently, it has been shown that such artificial structures of high structural quality can be synthesized with perovskite materials and may exhibit tailored and new electronic properties [4][5].

In addition to the periodicity of the constituent crystal structures, described by the out-of-plane lattice constants c, superlattices exhibit a further periodicity along the growth direction, specified by the thickness of one layer pair, \(d_{SL}\). (cf. Fig. 1 (a)). The SL periodicity results in a modification of the phonon spectrum as well as of the X-ray diffraction pattern. For phonons with k-vectors along the SL stacking axis, the SL period defines a mini-Brillouin zone of width \(\pm \pi/d_{SL}\). The corresponding bulk phonon branches are folded back into this mini-zone and develop energy gaps at \(k=0\) and \(k=\pm \pi/d_{SL}\) as shown schematically for an acoustic phonon branch in Fig. 1 b). The phonon mode intersecting the k-axis at \(k=0\) (marked with a red dot in Fig. 1 c)) corresponds to the symmetric superlattice phonon mode, where the expansion of one layer is accompanied by a concomitant compression of the neighboring layer. This is equivalent to a standing strain wave, similar to non-propagating optical phonons.

![Fig.1 a) Schematic of a superlattice structure. b) Linear chain calculation of a SL phonon dispersion. The superlattice period \(d_{SL}\) defines the mini-Brillouin zone with \(k_{SL} = \pi/d_{SL}\). c) The symmetric SL phonon mode is marked with a red dot.](image-url)
The superlattice periodicity modifies the X-ray diffraction pattern resulting in equally spaced Bragg peaks separated by $2\pi/d_{SL}$. Their intensity is controlled by the diffraction pattern of a single layer pair. The position of these intensity envelopes are determined by the out-of-plane lattice constants and appear at $k=2\pi/c_A$ and $2\pi/c_B$ (and multiples), while their intensity is determined by the respective structure factors of the two constituent materials A and B (cf. Fig. 2). Compression (expansion) of the nano-layers will shift the envelope functions to larger (smaller) angles. This implies that the intensity of the SL peaks positioned at the slope of the envelope function will depend very sensitively on the value of the respective c-lattice constants, or equivalent, on strain.

Fig. 2: Static X-ray reflectivity measurement of the STO/SRO superlattice structure as a function of diffracting angle $\theta$ together with a calculation based on dynamic X-ray diffraction theory (red line). The envelope functions of the single layers STO and SRO are shown in as the green and blue line respectively. For the inset, see the text.

2.2. Characterization of Superlattice samples

2.2.1. Structure of SrTiO$_3$/SrRuO$_3$ superlattice

Two different samples have been investigated in this work: First, a sample consisting of alternating layers of metallic SrRuO$_3$ (SRO) and dielectric SrTiO$_3$ (STO) and, secondly, a sample consisting of alternating layers of metallic SrRuO$_3$ and ferroelectric PbZr$_{0.2}$Ti$_{0.8}$O$_3$ (PZT). These perovskite SL samples were fabricated by pulsed-laser deposition [6].

The SL SrRuO$_3$/SrTiO$_3$ consists of 10 double layers on top of a 50 nm thick SrRuO$_3$ buffer layer grown epitaxially on a SrTiO$_3$ substrate (miscut angle 0.1 degree). Fig. 2 shows a high resolution X-ray reflectivity measurement of the SL around the Bragg angle of the (002) diffraction peak of bulk SrTiO$_3$ at 23.3 degrees. In the $\omega/2\theta$ scan one can identify about 9 equidistant superlattice peaks, with intensities characteristic for the superlattice structure. Additionally, the envelope functions of the single layer STO (green line) and SRO (blue line) are shown. The most intense SL peak (0 0 116) at 23.15 degrees, between the peak of the SRO buffer layer and the STO substrate reflection, is investigated in the time-resolved experiments. The inset of Fig. 2 is a magnification of the buffer layer reflection where one can clearly see the (N-2) side-maxima, with $N=10$ being the number of double layers. A simulation based on dynamical X-ray diffraction theory (red line) yields the structural parameters averaged
over the whole structure as summarized in Table 1. We find excellent agreement between measurement and simulation.

Table 1. Equilibrium structural parameters of the STO/SRO SL

<table>
<thead>
<tr>
<th>parameters</th>
<th>value (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(d_{\text{SL}})</td>
<td>22.72</td>
</tr>
<tr>
<td>(d_{\text{STO}})</td>
<td>7.48</td>
</tr>
<tr>
<td>(d_{\text{SRO}})</td>
<td>15.24</td>
</tr>
<tr>
<td>(c_{\text{SRO}})</td>
<td>0.3938</td>
</tr>
<tr>
<td>(c_{\text{STO}})</td>
<td>0.3907</td>
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<tr>
<td>No of unit cells STO, (n_{\text{STO}})</td>
<td>39</td>
</tr>
<tr>
<td>No of unit cells SRO, (n_{\text{SRO}})</td>
<td>19</td>
</tr>
</tbody>
</table>

The structural parameters of the ferroelectric SL PZT/SRO are discussed in section 5.

2.2.2. Reflectivity-Strain Mapping

In the following the relation between the time-dependent X-ray reflectivity change of the superlattice peak \((0\ 0\ 116)\) and strain in the SRO layers is established. We will see that for early times \((t < 10\ \text{ps})\) this relation is linear and that only for long delay times, when the entire superlattice starts to expand, the link between reflectivity and strain becomes more complicated.

![Fig.3](image-url)  
**Fig.3**  
(a) Calculated reflectivity change of the \((0\ 0\ 116)\) SL peak as a function of the c-lattice constants of SRO and STO. The magenta colored dot marks the equilibrium structure at room temperature.  
(b) Calculated change of the superlattice periodicity \(\Delta d_{\text{SL}}/d_{\text{SL}}\) as a function of the c-lattice constants of SRO and STO. The arrow points along the direction of expansive strain in SRO and corresponding compressive strain in STO, corresponding to the symmetric SL-phonon.  
(c) Calculated normalized reflectivity change as a function of SRO strain for constant \(\Delta d_{\text{SL}}\).
The contour plot in Fig. 3 a) shows the calculated reflectivity change of the (0 0 116) SL peak as a function of the c-axis lattice parameters of STO \( c_{\text{STO}} \) and SRO \( c_{\text{SRO}} \), normalized to the reflectivity for the known c-axis parameters at room temperature. In the upper left hand corner the contour lines are equidistant and run diagonally along increasing lattice constants of STO and SRO. Starting from the equilibrium values (pink dot in Fig. 3 a), for smaller values of \( c_{\text{STO}} \) and larger values of \( c_{\text{SRO}} \) the reflectivity change decreases. Contour plot 3 b) shows the relative change of the superlattice periodicity \( \Delta d_{\text{SL}}/d_{\text{SL}}^0 \) as a function of \( c_{\text{STO}} \) and \( c_{\text{SRO}} \). Apparently, \( d_{\text{SL}}^0 = n_{\text{SRO}} c_{\text{SRO}} + n_{\text{STO}} c_{\text{STO}} \), where \( d_{\text{SL}}^0 \) is the SL periodicity at equilibrium. The black arrow along the green contour line corresponds to the symmetric SL phonon, where an expansion of SRO is exactly compensated by a compression of STO, i.e., \( \Delta d_{\text{SL}}/d_{\text{SL}}^0 = 1 \). Fig. 3 c) shows a linear dependence of the reflectivity change of the (0 0 116) SL peak as a function of strain in SRO for constant \( d_{\text{SL}} \). An expansion of the SRO layers by 0.5% will result in a reduced reflectivity of -30%.

Excitation of the symmetric superlattice phonon mode corresponds to an expansion of the SRO layers and a concomitant compression of the STO layers, leaving the superlattice period \( d_{\text{SL}} \) constant. In the contour plot 3 b) these structural changes of oscillating layer thickness run along the diagonal contour lines, marked with a black arrow. The slope of the arrow is determined by the relative thicknesses of the two layers.

Measurements of the line shift of the superlattice peaks are proportional to the superlattice periodicity

\[
\frac{\Delta d_{\text{SL}}}{d_{\text{SL}}^0} = -\frac{\theta_0}{\tan\theta_0} \Delta \theta. \tag{1}
\]

Hence, simultaneous time-resolved measurements of the line shift, \( \Delta \theta/\theta_0 \), and of the reflectivity change, \( \Delta R/R_0 \), determine the intersection of the quasi-perpendicular contour lines of plots 3 a) and b) and allow to identify the time dependent c-axis of STO, \( c_{\text{STO}} \), and of SRO, \( c_{\text{SRO}} \), individually.

3. Experimental Techniques

The experiments are based on a pump-probe scheme where a 50 fs optical pump pulse induces the ultrafast lattice dynamics and a delayed hard x-ray probe pulse is diffracted off the excited sample. Changes of the angular position and intensity of Bragg peaks are measured as a function of pump-probe delay using an X-ray CCD camera. The experimental setup is based on a Ti:sapphire laser system, providing amplified femtosecond pulses that drive a Cu Kα plasma source at a 1 kHz repetition rate. Details of the X-ray source developed at the Max-Born-Institute have been reported elsewhere [7]. Driven by 50 fs pulses of up to 5 mJ energy, the source provides a total Kα (wavelength 0.154 nm) of up to \( 6 \times 10^{10} \) photons/s. The X-ray pulse duration is estimated to be less than 200 fs. The pulse-to-pulse intensity fluctuations of the X-ray output are of the order of 10 percent. The X-ray emission originates from a point-like area of 10 μm diameter only, facilitating the imaging of the X-ray output by X-ray optics [8]. In the experiments reported here, the X-ray pulses were focused onto the sample with a multilayer X-ray mirror (Montel optics), resulting in a spot size on the sample of approximately 150 μm and an X-ray flux of \( 10^6 \) photons/s.

4. Coherent Superlattice Phonon Motion

4.1. Symmetric Superlattice Phonon Mode

Fig. 4 displays the X-ray reflectivity change of the (0 0 116) peak as a function of time delay between the excitation pump pulse (\( \lambda = 800 \) nm, fluence of 7.5 mJ/cm²) and the X-ray probe pulse. It shows oscillatory signal
changes around a decreased reflectivity of approximately 20%. The oscillation period is $T=3$ ps. For later time delays one observes smaller amplitudes and after 30 ps the reflectivity has dropped by 40%.

The blue line in Fig. 4 shows the time dependent line shift of the (0 0 116) SL peak. For early times the line shift remains approximately constant and experiences its largest shift to smaller angles after 40 ps.

The 800 nm and near infrared pump pulses exclusively interact with the metallic SRO layers and cause a uniaxial stress with the superlattice periodicity. Phonon driven stress is generated on a time scale, which is short compared to the vibrational period $T = 3$ ps of the SL phonon mode and thus launches a coherent superposition of acoustic phonon states corresponding to a standing wave in the SL [9]. The period of 3 ps is given by the layer thicknesses and the respective velocity of sounds for SRO and STO. For a constant thickness of the entire SL structure (for times $t < 10$ ps, compare Fig. 4 b)), this implies an expansion of the SRO layer and a concomitant compression of the adjacent STO layers, equivalent to a change in their respective lattice constants. In agreement with the presented discussion of the X-ray pattern of a SL structure (compare section 2) the induced changes of the respective lattice constants result in a shift of the envelope functions, which in turn modulate the intensity of the SL peaks and cause the observed time-dependent reflectivity changes.

Fig. 4 a) X-ray reflectivity change and b) line shift as a function of time delay for an excitation fluence of 7 mJ/cm².

The expansion of the entire SL structure originates from strain fronts starting from the interfaces of the SL to air and to the substrate, where the stress is not balanced [10]. The shift of the Bragg peak positions occur on a timescale $T = N \cdot d_{SL}/v_{ph} = 40$ ps, where N is the number of SL layers and $v_{ph} = 6$ nm/ps is the approximate phonon group velocity.

While the measured line shift only yields the expansion of the whole superlattice structure, the additionally measured intensity change allows us to calculate the strain for the two layers individually. The result for the reflectivity curve shown in Fig. 4 and its corresponding line shift is displayed in Fig. 5. One clearly sees the oscillatory expansion of the SRO layers and the simultaneous compression of the STO layers. Their relative amplitude is determined by their respective thicknesses and amounts to approximately 2:1. After 40 ps the
expansion of the SRO layers reaches a maximum of about 1%. Here the STO layers have already relaxed to their original thickness. For delay times of 200 ps the amplitude of the thickness variation for SRO has dropped to about 50% of its first maximum at \( t = 2 \) ps. Finally, one observes a slight expansion of the STO layers at 200 ps. The same temporal behavior is visualized in Fig. 5 b) as a trajectory in \( c_{\text{SRO}} - c_{\text{STO}} \) space.

![Fig. 5](image_url)

Fig. 5 a) Change of the layer thickness of \( \Delta d_{\text{SRO}}/d_{\text{SRO}} \) (red line) and \( \Delta d_{\text{STO}}/d_{\text{STO}} \) (black line) as a function of time delay for an excitation fluence of 7.5 mJ/cm\(^2\). b) Time dependent trajectory in \( c_{\text{SRO}} - c_{\text{STO}} \) space. This trajectory is also shown in Fig. 3 a).

After optical excitation of SRO the excited electron gas quickly thermalizes and couples to the phonon system (<500 fs [9]). The build-up of a non-equilibrated optical phonon population produces stress and for an estimated temperature rise of the SRO layers of 110 K the expansion of the SRO layers can be satisfactorily described by anharmonic phonon-phonon interaction. The somewhat puzzling result that no energy transfer into the neighboring STO layers takes place within the first 200 ps may be due to the superlattice dispersion relation, which makes the back folded acoustic modes essentially non-propagating along the stacking direction. Note that this is not true in the in-plane-directions. An energy transfer via the superlattice phonon mode is negligible. We estimate the optical induced stress to amount to 1 GPa for the highest excitation fluence, such that the ratio between the total deposited energy (1GJ/m\(^3\)) and the energy of the superlattice phonon is roughly 1/100.

5. Ultrafast Dynamics in Ferroelectric Nanolayers

In this section we present an ultrafast time resolved X-ray structure analysis to directly measure the polarization dynamics of PZT in a PZT/SRO superlattice, which is triggered by optically induced uniaxial stress in the metallic SRO layers [12].

5.1. Displacive Ferroelectricity in Perovskite Materials

In ferroelectric materials the lattice energy displays a double-minimum potential along the soft-mode distortion, i.e., the relative displacement of anions and cations, \( \xi \), within the unit cell. This goes along with a tetragonal distortion \( \eta \) in the ferroelectric phase [11], where \( \eta \) is defined as the ratio of the out-of- and in-plane lattice constants \( c/a \). These two lattice coordinates are anharmonically coupled through a third-order term in the crystal Hamiltonian proportional to \( \eta \xi^2 \). As a result, changes of the tetragonal distortion \( \eta \) affect the ferroelectric
polarization $P$ directly. This mechanism allows for switching the electric properties by transiently elongating the lattice along $\eta$, i.e., by exciting the symmetric superlattice phonon mode.

5.2. Coupled Lattice and Polarization Dynamics

The ferroelectric superlattice sample consists of 15 double layers of ferroelectric PZT (thickness 4 nm) and metallic SRO (thickness 6 nm) epitaxially grown on a relaxed SRO buffer layer. The exact equilibrium structural parameters have been determined by static X-ray reflectivity measurements and modeling by dynamical X-ray diffraction theory, along the same lines as described in section 2. The time-dependent reflectivity change of two SL diffraction peaks is measured. The (0 0 56) reflection is situated on the steepest slope of the two envelope functions of the constituent materials PZT and SRO and, hence, is most sensitive on the tetragonal distortion of the respective unit-cells. The (0 0 55) reflection is located at the maximum of the PZT envelope function and its intensity is particularly sensitive to the ionic displacement $\xi$ within the PZT unit cell.

Analogous to the experiment described in section 4, optical excitation of the SRO layers generates stress on an ultrafast time-scale and compresses the ferroelectric PZT layers, i.e., reduces the tetragonal distortion $\eta$.

Fig. 6. a) shows the first 4 ps of the oscillatory reflectivity change of the (0 0 56) reflection (blue squares) and (0 0 55) reflection (red dots) as a function of delay time. Our measurements for two different Bragg peaks allow for a quantitative analysis of the microscopic lattice dynamics, i.e., the time-dependent elongations along the two coordinates $\eta$ and $\xi$. The derived time-dependence of $\eta_{\text{PZT}}$ and $\xi_{\text{PZT}}$ is plotted in Fig. 6 b) and shows a slightly delayed reduction of the polarization with respect to the ultrafast compression of $\eta_{\text{PZT}}$. The polarization is reduced by 50% after 2 ps. For the highest excitation fluence of 15 mJ/cm$^2$ we measured a maximal $\Delta R_{\text{max}}/R_0=3$ of the (0 0 56) peak, which corresponds to a peak strain $\Delta \eta/\eta_0=2\%$ and a complete switch-off of the polarization $P$.
6. Conclusion

We demonstrated that reversible transient strain in perovskite nanolayers can be precisely determined by measuring the time-dependent reflectivity and angular position of a superlattice Bragg peak. This approach allows for the first time to study the ultrafast structure-function relationship in oxide thin films, a class of materials which has emerged as fertile ground for new physical phenomena and devices.

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