Strain propagation in nanolayered perovskites probed by ultrafast x-ray diffraction

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Strain propagation in a perovskite heterostructure grown on a SrTiO$_3$ (STO) substrate is studied by ultrafast x-ray diffraction. Femtosecond displacive phonon excitation in a PbZr$_{0.2}$Ti$_{0.8}$O$_3$/SrRuO$_3$ (PZT/SRO) film launches acoustic strain waves propagating into the STO substrate. We demonstrate a two-step time evolution of diffraeted x-ray intensity which originates from different interfering contributions to the (004) Bragg peak of the STO substrate. Analysis by dynamical x-ray diffraction theory gives the absolute strain $\Delta a/a_0 = 2 \times 10^{-5}$ is determined in this way.

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Transition metal oxides with a perovskite crystalline structure display a variety of interesting physical properties, e.g., high-$T_c$ superconductivity and ferroelectricity which are not fully understood. Thin ferroelectric perovskite films of high structural quality have been grown by different epitaxial techniques and their electronic properties have been studied over a wide range of carrier concentrations, in external electric and magnetic fields as well as under photoexcitation. Static mechanical strain, induced by mismatching the lattice constants of film and substrate, can lead to an enhancement of the remanant polarization and to an increase of the trans-constant of film and substrate, can lead to an enhancement of the remanent polarization and to an increase of the trans-

As strain propagates at the speed of sound ($v_{ph} \approx 8000$ m/s), the relevant time scale of strain transients in nanostructured perovskites (thickness $d \leq 100$ nm) is on the order of tens of picoseconds. Ultrafast time-resolved x-ray diffraction provides direct insight into the generation and propagation of strain by monitoring atomic motions via changes of the Bragg diffraction pattern. This technique has been applied for studying transient phonon-related phenomena in bulk metals and semiconductors$^{3-7}$ and nanolayered semiconductors.$^{7-10}$ In contrast, ferroelectric systems have remained unexplored.

In this Brief Report, we report the quantitative measurement of photoinduced transient strain in a perovskite thin film heterostructure. In ultrafast x-ray diffraction experiments, we identify a peculiar two-step time evolution of diffracted x-ray intensity which originates from the interference of x rays diffracted from strained and unstrained parts of the sample. An analysis of such behavior by dynamical diffraction theory allows for an absolute calibration of strain in a range down to $\Delta a/a_0 = 2 \times 10^{-5}$. The x-ray interference effect occurs generally in crystals of good crystalline quality, when the average amplitude of the acoustic strain waves reaches an amplitude of $\Delta a/a_0 = a_0/(l-D)$, where $D$ is the thickness of the compressive or tensile strain wave and $a_0/l$ is the lattice spacing of the x-ray reflection, i.e., $a_0$ is the lattice constant and $l$ is the index of the Bragg reflection $(0,0,l)$.

The heterostructure was fabricated by pulsed-laser deposition, employing a KrF excimer laser ($\lambda = 248$ nm). The SrRuO$_3$ (SRO) layer was deposited on single crystalline SrTiO$_3$ (100) (STO) substrates (miscut angle 0.25°) at a temperature of $T=980$ K in a background atmosphere of 100 mTorr oxygen. The subsequent PbZr$_{0.2}$Ti$_{0.8}$O$_3$ (PZT) layer was grown at $T=850$ K in 200 mTorr oxygen, and the ratio of Zr vs Ti ions was chosen to match the in-plane lattice constant of PZT with SrRuO$_3$. Macroscopic ferroelectric hysteresis curves, dielectric measurements, and local piezoresponse scanning force microscopy investigations confirmed the ferroelectric behavior of the PZT film, including a remanant polarization of the order of $P_r = 80 \mu C/cm^2$. TEM and electron diffraction investigations performed on a thinned$^{15}$ cross-section sample revealed the entire heterostructure to be epitaxial and the interfaces to be plane and sharp. The films contain ferroelectric domain boundaries of 90° $a-c$ type [Fig. 1(c)]. The layer thicknesses of 100 nm for the SRO and 250 nm for the PZT layer are read from the TEM image.

In our experiments [Fig. 1(a)], electrons in the PZT and SRO layers of the sample are excited by a 400 nm pump pulse of an energy up to 100 $\mu J$ and a duration of 50 fs. The spot size on the sample is 6 mm$^2$. Electronic excitation creates strain in the excited layers which is probed by diffracting hard x-ray pulses (200 fs) of variable delay from the excited sample. Visible pump and Cu $K_\alpha$ probe pulses ($E_{a1} = 8.045$ keV, $E_{a2} = 8.026$ keV) are derived from the output of a Ti:sapphire laser system working at a 1 kHz repetition rate. The hard x-ray flux has a value of up to 6.8 $\times 10^{10}$ photons s$^{-1}$. The x rays diffracted from the sample are detected by a CCD camera (Roper Scientific) as shown in Fig. 1(b) for the (004) reflection of STO. For each value of
the pump-probe delay, the diffracted signal is accumulated for 120 seconds and at least two scans in the temporal forward and backward direction are averaged. The influence of x-ray intensity fluctuations on the signal is minimized by normalizing to the reflection unaffected by the pump light [cf. Fig. 1(b)]. To monitor unwanted effects like thermally induced angular misalignment of the crystal, every fourth measurement point is taken at negative delay, i.e., before the pump pulse excites the sample.

In Fig. 2, the transient change of the angle-integrated reflectivity \( \Delta R/R_0 \) of the (004) reflection of the STO substrate is plotted as a function of the delay time between 400 nm pump and x-ray probe pulses (circles, \( R, R_0 \); reflectivity with and without excitation). The transients measured with pump fluences of (a) 1.6 mJ/cm\(^2\), (b) 0.74 mJ/cm\(^2\), and (c) 0.43 mJ/cm\(^2\) display an increase of reflectivity which occurs in the picosecond time domain, i.e., much slower than our time resolution. The time evolution changes significantly with pump fluence. For the strongest excitation [Fig. 2(a)], the signal clearly grows in two steps, whereas only one step is found for weaker excitation. Moreover, the maximum reflectivity change \( \Delta R/R_0 \) does not scale linearly with the excitation fluence.

We now discuss the origin of the x-ray reflectivity changes and—in particular—their change with pump fluence. The pulses centered at 400 nm are exclusively absorbed in the PZT and SRO layers, as the STO substrate is transparent at this wavelength.\(^{14,15} \) The pump pulses change the electronic configuration of the absorbing material, resulting in a change of vibrational potentials in the PZT and SRO layers. A shift of the potential minima leads to the displaceable excitation of coherent phonons (DECP), i.e., the creation of phonon wave packets which represent a coherent nonstationary superposition of phonon states. Acoustic phonon wave packets propagate in the different material layers with the respective sound velocity and correspond to propagating strain fronts,\(^{16} \) which modify the separation of lattice planes. Such transient changes of lattice geometry give rise to changes in the x-ray diffraction pattern.

For an analysis of the experimental data, three different strain fronts are relevant, one generated at the air-PZT interface and two at the SRO/STO interface.\(^{17} \) At \( t=0 \), an expansion front with an amplitude \( 2\Delta a/a_0 \) starts from the sample surface entering the STO substrate after \( \Delta t=d_{\text{PZT}}/v_{\text{PZT}}+d_{\text{SRO}}/v_{\text{SRO}} \approx 100 \) ps. At the SRO/STO interface, two strain fronts of amplitude \( \Delta a/a_0 \) start at \( t=0 \), a compressive one into the optically unexcited STO substrate and an expansive one into the SRO and PZT layers. The latter strain front is reflected at \( \Delta t \) from the sample surface and converted into a compression front which enters the STO substrate at \( 2\Delta t \).

In our high-quality STO crystal, the x-ray penetration depth at Bragg peaks is determined by extinction, i.e., by the constructive interference of all waves scattered from lattice planes that scatter in phase. For the (004) peak of the STO substrate studied here, the x-ray extinction length depends strongly on the diffraction angle \( \Theta \) [Fig. 4(b)]. As a result, dynamical x-ray diffraction theory must be applied to account correctly for the angle-integrated transients of Fig. 2.\(^{18,19} \) For this, we use the Darwin formalism in combination with the fast matrix transfer method\(^{20,21} \) including all complex atomic scattering factors. The x-rays are scattered by each individual lattice plane in forward and diffracted direction and the scattering of all planes adds up coherently. The strain wave changes the lattice-plane distances which determine the phase shift of the x-ray waves scattered from each lattice plane. Figure 4(a) shows the calculated (004) reflection of STO, both for the unstrained sample (black line) and for the situation where the strain wave has completely entered the STO (red dotted). The dashed lines are convolu-
strain amplitudes as indicated. For grows in two steps of the experimentally accessible strain amplitudes

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FIG. 3. (Color online) (a) Schematic of the strain wave in the STO substrate for three time delays after impulsive excitation of stress in the PZT/SRO layers. (b) Calculated reflectivity change $\Delta R/R_0$ of the (004) reflection of STO normalized to the strain amplitude $\Delta a/a_0$ as a function of the position of the strain wave [leading edges of the wave in (a) indicated by dashed lines] for different strain amplitudes as indicated. For $\Delta a/a_0=1.25 \times 10^{-4}$ the signal grows in two steps (thick red line). (c), (d) Schematic of lattice planes in the unstrained and strained STO crystal. (d) shows an accumulated lattice displacement of one full lattice-plane distance, i.e., 1/4 of the lattice constant $a_0$. 

FIG. 4. (Color online) (a) Reflectivity of the (004) reflection of the STO substrate as a function of the diffraction angle $\Theta$ calculated without (solid black) and with (red dotted) a strain wave. A convolution with the angular resolution of the experiment results in the dashed lines. (b) Calculated extinction length of the (004) reflection as a function of $\Theta$. 

The measured transients display an increase of angle-integrated reflectivity, similar to studies of strained semiconductors.\textsuperscript{5,22} According to Bragg’s law, the compressed part of the sound wave reflects at larger angle $\Theta$, while the expansion wave reflects at smaller $\Theta$. In addition, the x-ray penetration depth at the center of the Bragg peak increases. In the angle-resolved pattern [Fig. 4(a)], strain-induced sidebands occur around the central peak which is slightly reduced in intensity by absorption over the enhanced penetration depth. In the angle-integrated signal, the additional intensity of the sidebands overcompensates the loss in the center, resulting in an overall increase of diffracted intensity.

In Fig. 3(b), the calculated angle-integrated reflectivity change (normalized to the strain amplitude $\Delta a/a_0$) is plotted as a function of the propagation distance of the strain wave into the STO substrate for different strain amplitudes. The shape of the curves changes above a certain threshold (for $\Delta a/a_0 < 5 \times 10^{-6}$ the shape remains constant), indicating a nonlinear dependence of the integrated x-ray reflectivity on the strain amplitude. While for extremely low strain amplitudes the reflectivity change $\Delta R/R_0$ shows a pronounced maximum within the first micron of penetration, the curves of the experimentally accessible strain amplitudes $\Delta a/a_0 > 2 \times 10^{-3}$ show a single, steplike reflectivity increase up to a plateau extending over several microns of penetration depth. In the time-resolved experiment, different propagation depths of the strain front are probed at different time delays as the strain front propagates with the finite sound velocity\textsuperscript{23} in STO of $v_{\text{STO}}=7876$ m/s.

For $\Delta a/a_0=1.25 \times 10^{-4}$ [thick red curve in Fig. 3(b)] the reflectivity change $\Delta R/R_0$ grows in two distinct steps as a function of the penetration depth as observed in our time-resolved experiment shown in Fig. 2(a). This feature occurs when the accumulated lattice displacement on both the STO compression and expansion waves approaches 1/4 of the lattice constant $a_0$ [c.f. Figs. 3(c) and 3(d)]. For the (004) x-ray reflection this condition implies, pictorially speaking, a $\pi$ phase shift between waves reflected from the central parts of the compression and expansion wave with respect to the unstrained parts of the lattice, i.e., destructive interference and a saturation of the time-dependent reflectivity. In fact, the destructive interference interrupts the monotonous increase due to the buildup of sidebands, observed for weaker strain amplitudes.

The two-step relation between $\Delta R/R_0$ and $\Delta a/a_0$ which is observed here, is only observed in a narrow range of strain amplitudes in the simulation around $\Delta a/a_0=1.25 \times 10^{-4}$ [cf. red line in Fig. 3(b)]. This allows for an absolute calibration of the strain amplitudes underlying the measured transients. The double-step measured with a pump fluence of 1.6 mJ/cm$^2$ [Fig. 2(a)] is in excellent agreement with the calculated signal for a strain amplitude $\Delta a/a_0=1.25 \times 10^{-4}$ [cf. red line in Fig. 3(b)]. The absolute value of the reflectivity change depends on the crystalline perfection of the sample, and the amplitude of the double-step curve is used to set the (small) degree of disorder in the calculation.\textsuperscript{21} The reflectivity changes observed with lower pump fluences [Figs. 2(b) and 2(c)] are in good agreement with simulated
traces. This allows for deriving the strain amplitude as a function of fluence, as shown in Fig. 2(d) together with a linear fit to the data. The evaluation shows that within the experimental accuracy, the response is linear and the smallest measured amplitude of the strain wave has a value of only $\Delta a/a_0=2 \times 10^{-5}$. We derived values for the simple strain profiles shown in Fig. 3(a), however, the interference effect is only sensitive to the accumulated strain and not to the exact strain profile. The results obtained here can be compared to experiments in Ge on Si, where the strain transients in the Si substrate were determined from the observed line shift. In these experiments a much larger peak strain of 5 $\times 10^{-5}$ induced by the weakest pulses (15 mJ/cm$^2$) was detected via the line shift of 3 arc s. Our weakest excitation is 30 times smaller and leads to a correspondingly smaller peak strain.

In conclusion, femtosecond time-resolved x-ray diffraction gives direct insight into strain propagation in ferroelectric nanostructures. The intensity of the (004) Bragg peak of the STO substrate displays a time evolution strongly depending on the strain-inducing optical pump fluence. For a narrow range of strain amplitudes, interference of different diffracted x-ray components results in a characteristic two-step increase of Bragg intensity with time. This behavior is fully reproduced by a dynamical theory of x-ray diffraction and allows for an absolute calibration of strain amplitudes. Our results demonstrate the potential of ultrafast x-ray diffraction for a nondestructive analysis of short-lived strain phenomena down to $\Delta a=2 \times 10^{-5} \times a_0 \approx 10$ femtometer in technologically relevant perovskite nanostructures.

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17We neglect the strain wave originating from the small discontinuity at the PZT/SRO interface.


21The used dynamical x-ray diffraction formalism allows us to vary gradually the degree of imperfection (i.e., mosaicity) from a perfect to an ideally imperfect STO crystal.
