nature physics

Article

https://doi.org/10.1038/s41567-022-01848-w

Ultrafast X-ray imaging of the light-induced phase transition in VO_2

In the format provided by the authors and unedited

Supplementary discussion for: Ultrafast X-Ray imaging of the light-induced phase transition in VO_2

Supplementary Note 1: Fluence dependence of the phase transition and initial domain stability

For pump-probe experiments, it is vital that the initial state is stable to repeated exposures. In completely clean samples, nucleation of domains would be random, and would change each time the system is driven above T_c. Thus spatial dynamics would not be observable with pump-probe methods that average multiple shots. However, defects can pin the position of domains. We have found that the same domain structure forms with repeated temperature cycling in static conditions, which pointed to the feasibility of these measurements. In addition, prior to our time-resolved experiments at PAL, we performed imaging experiments where we compared the domain structure before and after optical excitation at the I06 beamline at the Diamond light source. It was found that while a single pulse could change the initial domain pattern, the changes only resulted from the first laser pulse and the new domain structure would be stable to further excitation **(Extended data figure 1)**. Additional changes to the domain structure only occurred when the pump fluence was increase. However, again, only the first pulse at the higher fluence generated any change in the sample.

This result was confirmed at PAL-XFEL as shown in **Extended data figure 2b**, where we constantly monitored the domain structure at negative time delays to ensure permanent changes were not being detected as time-resolved changes. Occasionally permanent changes were observed. These occurred normally when the laser fluence was changed significantly, but could also change during a run, which were attributed to a higher than average fluence X-ray shot[52]. We briefly note that these changes are not associated to damage, as measurements made of the thermal domain structure at the BOREAS beamline at the ALBA synchrotron following the experiment do not show these features (**Extended data figure 2c),** and as such we attribute them to features uniquely introduced by the rapid cooling following laser excitation.

In general, we believe that domain structures should be more reproducible to laser cycling than thermal cycling because optical excitation only heats a fraction of the total sample. The unpumped region will provide a “boundary condition” for the sample to nucleate in, which will favour the original structure. We also point out that domain structures we also suggested to be stable to photoexcitation in the manganites[18] and to thermal jumps in the cuprates[16], suggesting coherent imaging with averaging methods can be applied to a range of samples.

Supplementary Note 2: Effects of global changes in FTH images

Extended data figure 3 shows the effect of the beam block on images when recorded with Holography. **Extended data figure 3a** shows the actual transmission of the sample. In one case (orange, mixed), the sample consists of two states (insulator and metal). The insulating state has a higher transmission than the metallic state. The second case, (green, metal) is that of a homogenous state. If the mixed state is converted to a homogenous metallic phase, then the only negative changes should be seen in regions that were initially in the insulating phase. Regions that started off metallic remain metallic and thus no changes in transmission occur. As a result, the DC transmission of the sample has changed. When holographic

imaging is performed with a beam block, the central region of the scattering pattern is obscured, which acts as a high pass filter and enhances edge contrast. The result of this filter is shown in **Extended data figure 3c**, which shows the real part of the FTH image for the data shown in **Extended data figure 3a**. The high pass filter removes the DC component of the image, making homogenous samples look flat and enhancing the contrast at the edges. Importantly the domain structure can still be seen in the heterogeneous sample. When comparing the difference between the homogenous metal and the mixed phase, regions that were initial metallic now show a positive change, even though no real change occurred in order to compensate for a change in the DC level.

Supplementary Note 3: PCA analysis

Principal component analysis decomposes a signal into a series of linear functions which are linearly uncorrelated and when summed describe the total dynamics. Individual PCs are not necessarily directly physically meaningful; however in our case we find a single component that describes all dynamics. We first analyze the noise in our data by examining the PCs of ten repeated measurements at -10 ps over a period of 6 hours. All PCs showed only random fluctuations with laboratory time, while all meaningful structural information was contained in the 0^{th} PC component (PC0). Thus we define our noise floor as the amplitude of the second largest PC (PC1). In analyzing the pump-probe time traces, we discard all PCs below this noise threshold, as shown in **Extended data figure 4a**. For the short time trace this leaves only two significant PCs. The first (PC0) shows only random fluctuations with pump-probe delay and is again attributed to the instability of the free electron laser intensity, while the second (PC1) exhibits the dynamics discussed in the main text. When including longer time delays a third PC (PC2), is comparable to the noise floor indicating that more spatial components are needed for longer dynamics. This is further supported by explicit examination of the spatial modes **(Extended data figure 4b-e)**, where for short times PC2 already resembles noise while including long times results in PC2 showing strong structure.

We verify that all short-time dynamics are captured in PC0 and PC1 by plotting the difference between the full pump-probe trace and one constructed from only the two most significant PCs. The result is plotted in **Extended data figure 5**, and shows no significant spatial structure at any time delay, justifying the approach.

Supplementary Note 4: Analysis of the time dependent data

The time dependent data were obtained from analysing two experimental runs. One with high time-resolution data over the first picosecond and a second with picosecond data over 20 ps. Between measurements, the initial pre-time-zero domain structure changed. As a result, the two runs could not be directly combined and the PCA amplitude as a function of time needs to be scaled in order to compare the data sets. To this end, a global fit was used to simultaneously fit the dynamics of both data sets. The long-time data, measured out to 20 ps, is shown in **Extended data figure 6**.

Supplementary Note 5: In and out of plane strain propagation

To understand the slower timescale in our data (4.98 ps) we have simulated the effect of both thermal and acoustic propagation in our sample. For thermal effects we solve the 1D heat diffusion equation using the values tabulated in reference[53]. We neglect emissivity effects, which should be negligible on the timescales considered here, and focus on heat propagation into the bulk. We consider the situation where the deposited fluence is enough to partially switch the sample, and heat propagation into the insulating region can initiate further changes, leading to a time-dependent metallic fraction. **Extended data figure**

7a shows the temperature profile as a function of time. As heat propagates from the front surface to the back more of the sample heats to above T_c. The volume fraction above Tc is plotted in **Extended data figure 7b** and shows a slow increase over tens of picoseconds, in disagreement with our observed timescales. We assumed no thermal transmission into the weakly absorbing silicon nitride substrate. Including this factor further reduces the heating rate.

The agreement with the acoustic propagation is far better. We solve the coupled acoustic wave equation in 1D according to the method described in references[39,40], but modified to include a discontinuous volume change at the phase transition in the source term of the stress tensor and damping of the propagating waves. The speed and damping rate of the acoustic waves in both phases are taken from Abreu *et al.*[10], while the volume discontinuity is taken from diffraction measurements[38]. The initial stress field for a homogenously switched sample is shown in **Extended data figure 7c**, and shows the overall stress field is dominated by the phase transition related volume expansion rather than the thermal effect. The stress immediately begins to relax by the volume expanding into the vacuum and silicon nitride substrate; the mean stress in the VO_2 is plotted in **Extended data figure 7d** and shows a rapid decrease over the first few-picoseconds, undergoing only a single notable reflection before damping away. We note here a perfect boundary is assumed; imperfect acoustic surfaces and sample inhomogeneity will both blur the perfect acoustic dynamics plotted here in real samples. If the sample is only partially switched more complex dynamics are observed due to the mixture of fast and slow propagation in the metallic and insulating volume fractions, respectively.

Note that both these simulations consider propagation in the bulk direction. In-plane, these dynamics are markedly slower due to the disparate length scales. For a pump spot size of 200 μm FWHM, the strain wave would take several nanoseconds to propagate from the edges of the photo-transformed region to the centre; these dynamics are furthermore much more sensitive to experimental geometry than the absorption length or film thickness limited out-of-plane dynamics. Defects could significantly reduce the transverse timescale by providing additional routes to strain relaxation, and may be important for spatially dependent dynamics observed at the 100s of picoseconds timescale. However, transverse thermal propagation will still be slow even in this case.