Multi-scale time-resolved electron diffraction enabled by high repetition rate, high dynamic range direct electron detection

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(Dated: June 20, 2022)
Abstract

Ultrafast-optical-pump — structural-probe measurements, including ultrafast electron and x-ray scattering, provide direct experimental access to the fundamental timescales of atomic motion, and are thus foundational techniques for studying matter out of equilibrium. High-performance detectors are needed in scattering experiments to obtain maximum scientific value from every probe particle. We present the first ultrafast electron diffraction experiments to deploy a hybrid pixel array direct electron detector, and we show that its single-particle sensitivity, high dynamic range and 1 kHz frame rate enable new probe modalities in electron-based structural dynamics. Specifically, we perform measurements on a WSe$_2$/MoSe$_2$ 2D heterobilayer that resolve the weak features of diffuse scattering and moiré superlattice structure without saturating the zero order peak. Enabled by the detector’s high frame rate, we show that a lock-in technique provides diffraction difference images with signal-to-noise at the shot noise limit. Finally, we demonstrate that a fast detector frame rate coupled with a high repetition rate probe can provide continuous time resolution from femtoseconds to seconds, enabling us to perform a scanning ultrafast electron diffraction experiment that maps thermal transport in WSe$_2$/MoSe$_2$ and resolves distinct diffusion mechanisms in space and time.

Ultrafast x-ray and electron scattering experiments are essential tools in the materials-by-design thrust of modern condensed matter physics and engineering [1–6]. In particular, breakthroughs in the study of atomically thin 2D materials, including twisted bilayers and monolayer heterostructures [7–13], demand advances in instrument sensitivity in space and time, both real and reciprocal [14, 15]. A challenge when characterising 2D materials from information-rich diffraction measurements is that diffraction features are separated by many orders of magnitude in intensity, descending from the (0,0,0) peak, to Bragg scattering, to weaker satellite peaks caused by longer wavelength periodic lattice distortions (PLD), to yet weaker thermal diffuse scattering (TDS). In pump-probe ultrafast electron diffraction (UED), the separation of scales becomes more extreme, and important details of electron-phonon coupling can be found in parts per thousand modulation of scattering signals that in static diffraction are already at the 10$^{-4}$ level of total beam current. Moiré materials exemplify this challenge, and could plausibly present correlated signatures of interlayer interactions in Bragg, PLD and TDS scattering, with tunable superstructure periodicity that
can extend to tens of nm [8].

Investigating correlated but intensity-scale-separated features in the same scattering data requires single-particle detection with high dynamic range. Direct-conversion, single-electron-sensitive CCDs have poor dynamic range, no more than a single decade. Indirect detectors function by detecting light generated in a scintillator. The broad angular distribution of the emitted scintillation light, the finite aperture, and inevitable scatter off the optical surfaces of the light-guiding optics, limits the dynamic range, spatial resolution, and sensitivity of indirect detectors [16–19].

Among devices that aim to overcome these limitations [20], integrating direct detectors with several decades of dynamic range and kHz frame rates are now an established tool at x-ray user facilities [21–23], and enable computational imaging with state-of-the-art resolution in non-time-resolved electron microscopy [24, 25]. Even if probe particles arrive close to simultaneously — as happens especially when the illumination source is a high intensity, high repetition rate pulsed beam of sub-ps duration — integrating detectors accurately report the total probe-particle energy incident on a pixel, a distinct advantage over high-resolution fast-frame-rate counting detectors [26].

Here we deploy a leading example of integrating detector technology — the Electron Microscope Pixel Array Detector (EMPAD) — to study the multiscale out-of-equilibrium dynamics of a WSe$_2$/MoSe$_2$ moiré bilayer [27–30]. For the first time in UED, we resolve the 10 nm periodicity of the moiré superlattice. We integrate the superlattice signal without saturating the more intense Bragg peaks caused by angstrom scale interatomic spacing. We demonstrate that the 1 kHz detector frame rate enables a fast lock-in technique that drastically improves signal-to-noise in measurements of the sample response to ultrafast pumping. We show that lock-in data acquisition yields signal-to-noise at the Poisson limit imposed by the total number of probe particles incident on the sample.

The fast 1 kHz detector frame rate also enables a novel pulse-picking technique, which extends the range of timescales accessible in ultrafast pump-probe experiments beyond $\mu$s with fs precision. Implementations of pump-probe delays at the $\mu$s scale typically rely on electrically triggering, eg., a laser diode with picosecond pulse duration or longer. Femtosecond pulses, by increasing the peak laser field strength for the same deposited energy, have the potential to unlock interesting metastable behaviour [31], and our method could resolve, e.g., THz frequency modulations $\mu$s after excitation. We demonstrate our pulse-
picking technique with a microdiffraction probe and map the diffusion of heat in our sample in space and time from initial fs ultrafast excitation, out to ms thermal relaxation, with μm spatial resolution. Experimental access to 100 μs timescales allows us to extract from our space-and-time-resolved data the thermal diffusivity of our moiré sample.

Our beamline setup is summarized in the Supplemental Material and described in detail elsewhere [28]. To take best advantage of the detector frame rate, we independently gate pump and probe pulse trains obtained from a seed laser pulsing at 125 kHz. A schematic of our timing system is shown in Fig. 1. The EMPAD registers electron counts with a per-pixel signal-to-noise of $10^2$. The pump wavelength in the experiments reported here is 515 nm.

A magnetic quadrupole lens triplet controls the angular magnification of the diffraction pattern on the detector. Lens settings are summarized by camera length: the hypothetical drift distance to the detector plane that would result in equivalent diffraction data. Figure 2(a) shows a static diffraction pattern obtained from the WSe$_2$/MoSe$_2$ sample at short camera length. The logarithmic scale color bar includes over four orders of magnitude of contrast from the (0,0,0) peak to thermal diffuse scattering. The six-fold symmetry of the short-camera-length data arises from the underlying symmetry of the WSe$_2$/MoSe$_2$ lattices.

The inset to Fig. 2(a) shows a long-camera-length diffraction difference pattern isolating a single pair of Bragg peaks (1210), aligned vertically in the image, with two additional satellite peaks visible, aligned horizontally. The difference pattern is formed by subtracting pumped exposures from unpumped at a delay of 4 ps. The more intense of the two highlighted Bragg peaks results from scattering off the WSe$_2$ monolayer, the other from the MoSe$_2$ monolayer. The interlayer twist angle controls the separation in reciprocal space between the two Bragg peaks, measured here to be 2°. The sixfold symmetry of the real-space moiré pattern entails that scattering from the moiré superlattice forms a hexagon dressing each Bragg peak. The satellites observable in the inset to Fig. 2(a) lie at scattering vectors where monolayer contributions overlap. Static selected area electron diffraction (SAED) from twisted bilayer graphene performed by others shows that the intensity of moiré satellite peaks decays exponentially with twist angle between 0.5°–2° [8]. These results, and static SAED data from 1° twisted WSe$_2$/MoS$_2$ [32], are consistent with our observation of two satellites along the midline of a (1210) Bragg pair. A future work will present time-series data showing the detailed dynamics of the moiré superstructure.

We benchmark our experimental uncertainty with pump-probe time-series data, summa-
rized in Fig. 2(b)-(c). To analyze the dependence of experimental uncertainty on chopping rate, we divide time-series data into \( n \) integration time-bins of duration \( W \) equal to the chopping period. We evenly split each time-bin into *hot* exposures, when pump and probe pulses are coincident on the sample, and *cold* exposures, when only the probe is incident. The number of hot (*\( N_{\text{hot}} \)*) and cold (*\( N_{\text{cold}} \)*) electrons counted is a random variable with statistics we can estimate by taking averages with the respect to our ensemble of \( n \) time-bins. We compute a variance-to-mean ratio (VMR) over \( W \):

\[
\text{VMR}(W) := \frac{\text{Var}_W(N_{\text{hot}} - N_{\text{cold}})}{E_W[N_{\text{hot}} + N_{\text{cold}}]},
\]

where \( \text{Var}_W(X) \) denotes the variance of \( X \) over duration-\( W \) time-bins and \( E_W[X] \) the mean. The VMR defined in Eq. (1) can be interpreted as the square of the experimental uncertainty in estimating the effect of pumping the sample, normalized by the shot-noise limit. If \( N_{\text{hot}}, N_{\text{cold}} \) are drawn from independent Poisson distributions then the VMR must equal one. The VMR rises above one with the introduction of fluctuations in the mean of the Poisson distribution, due, e.g., to fluctuating laser power on the photocathode, and flicker noise in the steering magnets and accelerating voltage.

Figure 2(b) plots \( \sqrt{\text{VMR}} \) (as defined in Eq. (1)) against lock-in frequency and compares two different scattering rates. The lower rate is typical for our microdiffraction experiments. We change the scattering rate by increasing the diameter of the probe-defining aperture from 10 to 70 \( \mu \)m. The two data sets are fit to power law trend lines. Both data-sets are at the shot-noise floor when chopped at 500 Hz. The data reveals that the higher the scattering rate, the higher the lock-in frequency required to hit the shot-noise floor (holding fixed the total integration time). At the higher scattering rate, the VMR is appreciably greater than unity at lock-in frequencies below 100 Hz, while at the lower scattering rate, the VMR begins to rise above shot noise only below 10 Hz. The explanation is that more counts for fixed acquisition time reduces the Poisson contribution to the noise in any given frequency band, increasing the experimental sensitivity to correlated noise in the same band.

Demonstrating the advantage of the lock-in technique for pump-probe experiments, Figure 2(c) shows the measurement of the ultrafast response at two lock-in frequencies with the small probe beam. The trend is an exponential decay convolved with the instrument response [33]. The non-zero sample response at delay times earlier than the pump arrival is due to 1 kHz thermal cycling, investigated below. Each data point is acquired with a
two-minute integration time. The spread in the data at the slow chopping rate (one minute hot, followed by one minute cold) is comparable to the size of the ultra-fast effect. In stark contrast, the data acquired at the 500 Hz lock-in frequency follows the fitted trend closely.

The ability to isolate and compare the response to fs excitation at µs and ms delays is critical to understanding microscopic heat transport and potentially the formation of metastable phases [34]. The pulse-picking method illustrated in Fig. 1 allows us to perform multi-dimensional, multi-scale thermometry on WSe₂/MoSe₂ via the Debye Waller effect. The detector frame rate sets the effective repetition rate of the pulse-picked probe, so that the kHz frame rate reduces the time required to perform the experiment from weeks with a conventional CCD to eight hours with the EMPAD.

Our multi-dimensional, multi-scale thermometry data is shown in Fig. 3. The three data dimensions are probe delay and probe position (both plotted horizontally) and the relative change in diffraction intensity ∆I/I (plotted vertically). Colors indicate which spatial cuts in Fig. 3(b) correspond to the pump-probe delay shown in Fig. 3(c). Panel (b) i. shows the ultrafast response taken at a pump delay of 20 ps. The remaining data are taken by progressively extending the duration of the pump pulse train and probing the sample 8 µs after the final pulse in the pump pulse train. The 8 µs increment corresponds to the period between pulses at our 125 kHz repetition rate. The data in Fig. 3(b) ii.–v. clearly show the accumulation of energy through the duration of the pump pulse train, while panels vi.–viii. show the dissipation of energy to the sample boundaries after the pump-pulse train terminates.

In the limit that the relaxed sample temperature is well above zero and the temperature change ∆T is small, both compared to the sample Debye temperature, the fractional change in the Bragg scattering rate ∆I/I with scattering vector k is proportional to k²∆T. Hence, by scanning ∆I/I as a function of pump spatial position and pump delay, it is possible to map out thermal transport in the sample. We choose a low pump fluence of 2 mJ/cm² as a compromise between, on the one hand, maintaining linearity in the relationship between ∆I/I and T, and on the other, minimising Poisson noise in the diffraction difference.

To model the heat transport phenomenology, we fit to our diffraction signal ∆I/I ∝ T an analytic, approximate solution to the inhomogeneous 2D heat equation,

\[
\left[ \frac{\partial}{\partial t} - \alpha \nabla^2 \right] T(t, x; \alpha, A, \sigma_0) = f(t, x; A, \sigma_0).
\]
We parameterize the periodic solution \( T(t, x; \alpha, A, \sigma_0) \) with three time-independent scalars: the diffusion constant \( \alpha \), and the amplitude \( A \) and width \( \sigma_0 \) of the pump pulses. The forcing term \( f(t, x; A, \sigma_0) \) represents the pump periodically injecting energy into the system. The transverse diffusivity \( \alpha \) is a fit parameter and the model expressed in Eq. (2) makes no assumptions concerning the mechanism for heat transport. The diffraction intensity \( I \) is the sum of all contributions within the region of interest around the \((1 \bar{2}10)\) peaks highlighted in Fig. 2(a). Equation (2) is solvable by Fourier series, and the analytic approximation we make consists in simply truncating this series to finite order. A detailed derivation of the explicit expression for the fit function is provided in the Supplemental Material.

We find excellent agreement between our data and three-parameter phenomenological model. Solid lines in Fig. 3 (b) ii–viii show the spatial profile implied by the fitted model; the solid line in Fig. 3 (c) shows the fitted temperature envelope at the center of the sample square. The interpretation of Fig. 3 is that the extreme aspect ratio of the bilayer-substrate combination — 10 nm thick versus 250 \( \mu \)m wide — results in two relaxation timescales: a fast timescale, \( \tau_{\text{fast}} < 1 \) ns, and a slow timescale, \( \tau_{\text{slow}} > 1 \) ms. The fit implies a decay in the temperature of the bilayer following the arrival of the first pump pulse to 5\% of its peak value before the arrival of the second. This 5\% residue accumulates for the duration of the 440 \( \mu \)s pulse train and, following the end of the pulse train, relaxes exponentially at a rate set by the sample window size \( L \): \( \tau_{\text{slow}} = L^2/(\pi^2\alpha) \).

The fit in Fig. 3 gives the value \( \tau_{\text{slow}} = 6 \) ms. When, as in our experiment, the period between pump pulse trains is less than the relaxation time, the bilayer reaches a periodic state in which the minimum temperature of the pumped region during a cycle remains elevated above the temperature of the boundaries. The estimate of \( \tau_{\text{slow}} \) unambiguously defines the repetition rate that allows for the sample to fully relax before the arrival of each pump pulse in stroboscopic data acquisition. This relaxation time is sample and substrate dependent, as are the physical implications of pumping at a repetition rate faster than sample relaxation. Our method of extending the range of ultrafast pump-probe delays to \( \mu \)s–ms enables us to investigate these issues experimentally.

Pump-probe delays in the \( \mu \)s–ms range provide a technique to extract the transverse thermal conductivity of the bilayer. This intrinsic property cannot be inferred from sub-ns data alone, because the ultrafast relaxation we observe is dominated by the interfacial resistance between bilayer and SiN substrate, as heat is transferred across the nm dimension.
Whereas, on the slow timescale, the bilayer and SiN substrate provide parallel channels for conducting heat transversely over the $10^{-4}$ m distance to the Si wafer at the transverse boundary. The transverse diffusivity parameter $\alpha$ that we fit with our phenomenological 2D model (solid lines in Fig. 3(b)–(c)) does not discriminate between bilayer and substrate contributions. From the same data, finite-element simulations (see, e.g., [35]) can extract the intrinsic transverse diffusivity of the bilayer. Hypothetically, data obtained from a freestanding bilayer would be simpler to analyze: however, an implication of the data we collect is that pumping a freestanding bilayer with 2 mJ/cm$^2$ fluence at $10^2$ Hz or faster repetition rates would cause irreversible damage within a few pulses, without the SiN present to act as a heatsink.

This work has presented new, dramatic advantages of an integrating direct electron detector with high dynamic range and fast frame rate for structural dynamics data acquisition. We are able to resolve for the first time in UED the ultrafast response of a 10 nm periodic moiré superlattice, and to track the ms long thermal relaxation of the WSe$_2$/MoSe$_2$ bilayer following ultrafast excitation. Future experiments plan to apply this technique to investigate the effects of interlayer interactions on thermal transport in two ways: by measuring the dependence of transverse relaxation on bilayer twist angle [30], and by tuning pump photon energy to resonantly excite a specific monolayer in the heterostructure. A natural extension of our pulse-picking technique is to utilize a commercially available femtosecond GHz oscillator and fast pulse picker to achieve nanosecond pulse selection precision prior to the amplification stage. Such a system, when coupled with a delay stage to cover the range $<1$ ns, would provide seamless delay capability from femtoseconds to seconds with femtosecond resolution. The next generation EMPAD increases the frame rate to 10 kHz [36], which raises the maximum lock-in detection frequency. Our results suggest that lock-in frequencies above 1 kHz, while unnecessary for our system in micro-diffraction mode, have the potential to significantly improve signal-to-noise in experiments that involve large bunch charges of $10^5$ electrons or more, and in high-flux x-ray experiments with free electron laser sources. Measuring the transverse relaxation time of the bilayer, we are the first to demonstrate an experimental method for unambiguously defining the sample-dependent optimal repetition-rate for ultrafast stroboscopic data collection. Our results highlight the need for pump-probe modalities that can access multiple time and intensity scales when investigating the rich, multi-scale physics of 2D quantum materials.
This work was supported by the U.S Department of Energy, awards DE-SC0020144 and DE-SC0017631, and U.S. National Science Foundation Grant PHY-1549132, the Center for Bright Beams. D.L., A.S., and A.M.L. acknowledge support from the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division, under Contract DE-AC02-76SF00515.
FIG. 1. Schematic of the pump-probe technique in time; the 8 µs period between pump pulses is exaggerated here for clarity; the duration of the pump-pulse train is controlled by an acousto-optic modulator; an optical delay stage controls pump-probe delays from 100 fs to 1 ns and detector exposure timing (marked with grayscale ovals) controls pump-probe delays > 1 µs. The solid waveform represents the microsecond-scale temperature envelope predicted by Eq. (2). The dashed waveform indicates whether exposures are hot or cold (defined in the body text with reference to Eq. (1)).
FIG. 2. (a) Logarithmic scale diffraction pattern obtained from WSe$_2$/MoSe$_2$, demonstrating the EMPAD dynamic range. Inset, a long camera-length diffraction pattern showing a single, vertically aligned pair of moiré Bragg peaks: also visible, a pair of horizontally aligned satellite peaks, with 10 nm periodicity. Detector camera length is varied with a magnetic quadrupole lens triplet. (b) Measurement uncertainty as a function of lock-in frequency: referring to the variance-to-mean ratio (VMR) defined in Eq. (1), the vertical axis shows $\sqrt{\text{VMR}}$ and can be interpreted as the ratio of total uncertainty to the shot noise limit set by the total integration time. Two curves compare different rates of scattering into the solid angle highlighted in (a). (c) Measurement of the ultrafast Debye-Waller effect, comparing data quality with high and low lock-in frequencies, each data point integrated for two minutes.
FIG. 3. Multi-dimensional, multi-scale sample thermometry. (a) Spatial scanning technique showing i. detector, ii. WSe$_2$/MoSe$_2$ sample, iii. pump pulse moving over sample surface, iv. probe defining aperture, v. electron pulse. (b) i.–viii. change in diffraction intensity $\Delta I/I$ (vertical axis) versus the spatial displacement of pump and probe (horizontal axis), at pump-probe delays spanning eight orders of magnitude. The diffraction signal is the sum of all electron counts in the highlighted region around the (1 2 1 0) peak indicated in Fig. 2: both monolayers contribute. (b) i. The ultrafast response 20 ps after one pump pulse, with the solid line showing a Gaussian fit. (b) ii. The response 8 $\mu$s after a 200 $\mu$s pump-pulse train containing 25 pump pulses. (b) iii.–v. Extending the duration of the pump-pulse train to a maximum of 440 $\mu$s, the response 8 $\mu$s after the final pulse in the train: the method is illustrated in Fig. 1. (b) vi.–viii. Sample relaxation, holding the 440 $\mu$s pump-pulse train duration fixed. (c) $\Delta I/I$ (vertical axis), at 0 $\mu$m spatial displacement, versus pump-probe delay. All solid lines in (b) ii.–viii. and (c) are cross sections of the fitted, three-parameter diffusion model summarized in Eq. (2). The fitted transverse diffusivity $\alpha = 1.1 \pm 0.1$ mm$^2$/s. (d) Heat diffusion time-scales: the duration of pump excitation is $10^{-13}$ s, heat is transferred from bilayer to 10 nm thick substrate in $10^{-10}$ s, heat diffuses transversely to the sample boundaries over $10^{-3}$ s.
SUPPLEMENTAL MATERIAL:
MULTI-SCALE TIME-RESOLVED ELECTRON DIFFRACTION ENABLED BY HIGH REPETITION RATE, HIGH DYNAMIC RANGE DIRECT ELECTRON DETECTION

Materials and Methods

Experimental Setup

Our beamline is shown in Fig. S1(a). The probe electron beam is photoemitted with 650 nm laser pulses and accelerated to a primary energy of 140 keV, and the sample is pumped with 515 nm pulses obtained from the same 1030 nm source. Electron beam optics for magnifying the diffraction pattern are shown in Fig. S1(b). Our scanning ultrafast electron diffraction technique is illustrated in Fig. S2(a), with the sample and sample environment shown in Fig. S1(b). The spot size of the electron probe on the sample is defined by a laser-milled aperture 15 mm upstream. An in-vacuum lens focuses the 515 nm pump pulse to a 10 µm rms spot on the sample, and the pump spot is steered on the sample by an out-of-vacuum mirror. A virtual-sample camera placed out of vacuum monitors the location of the central peak of the pump laser to µm precision. The duty cycle of the acousto-optic-modulator that gates pump pulses is variable to single-pulse precision: we typically choose a duty-cycle to match the detector exposure, eliminating un-detected pulses and thus reducing the thermal load on the sample. We verify the reliability of the timing system by measuring the total pump-energy per exposure with the detector, and we see a sharp quantization of energy as a function of exposure length at intervals of the 8 µs laser repetition period. Pump and probe beams are aligned by performing knife-edge scans at the vertical and horizontal sample edges. For the data presented in main text Fig. 3, knife-edge scans give 6 µm rms probe size in the sample plane.

The Electron Microscope Pixel Array Detector (EMPAD) consists of a grid of 128 x 128 pixels each 150 µm x 150 µm in size. Each pixel has a 500 µm thick reverse-biased silicon diode bump bonded to its own read-out electronic circuit. The rms read noise (where the average is taken over all pixels) is equivalent to 0.011 electrons at 140 keV, a signal-to-noise of 100. The well of each pixel can record up to $10^6$ electron incidents per exposure, but the detector saturates at lower counts if the rate of incidents exceeds a threshold. Previous
measurements performed with continuous beam illumination (cw) estimated this threshold rate to be 22 electrons per pixel per microsecond at our 140 keV beam energy. Surprisingly, in our pulsed experiments we observe saturation at the significantly higher rate of 60 electrons per pixel per sub-picosecond pulse, a result likely analogous to effects studied in the context of x-ray free electron laser applications [37]. To explain this observation, the maximum charge that the EMPAD can remove per charge-removal cycle per pixel is equivalent to 11 incident electrons at 140 keV. The charge-removal circuitry cycles at 2 MHz. This maximum is set by protection diodes that limit the peak charging current of each pixel’s storage capacitor. In pulsed operation we measure saturation at 60 incident electrons per pixel per pulse. A plausible explanation of the observed saturation threshold is that the high charge density in pulsed operation results in the creation of an electron-hole plasma with microseconds lifetime. The long-lived plasma is removed over multiple charge-removal cycles [38]. The EMPAD design is under active development and the latest iteration (not deployed in our experiments) increases the cw saturation level to $10^3$ electrons per pixel per microsecond [36].

Sample Preparation

MoSe$_2$ and WSe$_2$ monolayers are exfoliated from bulk MoSe$_2$ and WSe$_2$ single crystals (HQ graphene) onto 285 nm SiO$_2$/Si substrate sequentially using a gold tape exfoliation technique [10], forming heterostructures with lateral dimensions of mm scale. The crystal orientations of the monolayers in the heterostructure are aligned with the crystal edges, and further confirmed in electron diffraction. The heterostructures are later transferred onto 10 nm thick, 250 $\mu$m x 250 $\mu$m Si$_3$N$_4$ windows on TEM grids (SiMPore), using a wedging transfer technique with cellulose acetate butyrate (CAB) polymer [39].

Diffusion Model

In this section we derive an explicit expression for the function used to fit the data in Fig. 3 of the main text.

Our model assumes: i. a square domain having side-length $L = 250 \mu$m, ii. that pump pulses strike the center of the square, and iii. that the boundaries of the square are held at
constant temperature. We experimentally verify i. With respect to assumption ii., in experiment, we hold the probe spot fixed at the center of the sample window and scan the pump, as shown in Fig. S2. Finally, assumption iii. is highly plausible given the overwhelming thermal mass of the Si wafer in which the SiN-supported sample window is embedded.

The fit function \( T(x, y, t; \alpha, A, \sigma_0) \) with fit parameters \( \alpha, A, \sigma_0 \) is a solution to the inhomogenous heat equation:

\[
\frac{\partial T}{\partial t} - \alpha \left[ \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right] = f(x, y, t; A, \sigma_0). \tag{S1}
\]

Equation (S1) is subject to the condition that \( T \equiv 0 \) on a square boundary of side length \( L \). The origin of the Cartesian coordinate system \( x, y \) lies at the center of the square. To avoid confusion, \( \alpha \) is a fit parameter and no assumption is made in the fit as to the mechanism for heat diffusion.

We model the forcing term \( f \) in Eq. (S1) as a sequence of delta-function impulses, each having the same Gaussian spatial profile centered at the origin, with amplitude \( A \) and r.m.s size \( \sigma_0 \). Pulses arrive in trains. Trains arrive at the rate \( \nu \) and, within each train, pulses arrive at the rate \( R \). Each train contains \( J \) pulses. The explicit expression for \( f \) is then,

\[
f(x, y, t; A, \sigma_0) = \frac{4A}{L^2} \sum_{q=-\infty}^{\infty} \sum_{j=0}^{J-1} \sum_{m=0}^{M-1} \sum_{n=0}^{N-1} \cos \left( (2m + 1) \frac{\pi x}{L} \right) \cos \left( (2n + 1) \frac{\pi y}{L} \right) \exp \left\{ -\frac{\sigma_0^2}{2} \left[ (2m + 1)^2 + (2n + 1)^2 \right] \frac{\pi^2}{L^2} \right\} \delta \left( t - \frac{j}{R} - \frac{q}{\nu} \right). \tag{S2}
\]

The sums in \( n, m \) are taken over Fourier modes that vanish at the boundary, truncated to orders \( M, N = 10 \).

We solve the inhomogeneous problem Eq. (S1) by first solving for the response \( T_0(x, y, t; \alpha, A, \sigma_0) \) to a single forcing pulse, treated as a homogenous problem with the forcing term accounted for in the initial conditions. The linearity of Eq. (S1) then entails that,

\[
T(x, y, t; \alpha, A, \sigma_0) = \sum_{q=-\infty}^{\infty} \sum_{j=0}^{J-1} T_0 \left( x, y, t - \frac{j}{R} - \frac{q}{\nu}; \alpha, A, \sigma_0 \right). \tag{S3}
\]

It is well known that for a single spatial Fourier mode \( \hat{T}(k, t) \), the solution to the homogenous heat equation is,

\[
\hat{T}(k, t) = \hat{T}(k, 0) e^{-\alpha t k^2}. \tag{S4}
\]
For the first impulse we therefore obtain,

\[ T_0(x, y, t; \alpha, A, \sigma_0) = \]

\[ \frac{4A}{L^2} \sum_{m=0}^{M-1} \sum_{n=0}^{N-1} \cos \left( (2m + 1) \frac{\pi x}{L} \right) \cos \left( (2n + 1) \frac{\pi y}{L} \right) \exp \left\{ -\frac{1}{2} \left( \sigma_0^2 + 2\alpha t \right) \left[ (2m + 1)^2 + (2n + 1)^2 \right] \frac{\pi^2}{L^2} \right\}. \]  

(S5)

Having in hand the expression for \( T_0 \) on the right hand side of Eq. (S5), to compute the sums in Eq. (S3), we first approximate the sum inside each train as an integral. It is convenient to define three expressions that appear at intermediate steps in the computation,

\[ E_{mn}(t; \alpha) := \exp \left\{ -\alpha t \left[ (2m + 1)^2 + (2n + 1)^2 \right] \frac{\pi^2}{L^2} \right\}, \quad (S6) \]

\[ P_{mn}(t; \alpha) := E_{mn}(t; \alpha) * \sum_{j=0}^{J-1} \delta(t - j/R), \quad (S7) \]

and,

\[ \tilde{P}_{mn}(t; \alpha) := \sum_{q=-\infty}^{\infty} P_{mn}(t - q/\nu). \quad (S8) \]

The approximating integral is then performed piece-wise in time, first for \( t < J/R \), inside the pulse train,

\[ P_{mn}(t; \alpha) = R \int_0^t E_{mn}(\tau; \alpha) d\tau \]

\[ = \frac{L^2R}{\alpha \pi^2 [(2m + 1)^2 + (2n + 1)^2]} \left[ 1 - E_{mn}(t; \alpha) \right] \]

(S10)

Then, after the pulse train has ended, for \( t \geq J/R \):

\[ P_{mn}(t; \alpha) = \frac{L^2R}{\alpha \pi^2 [(2m + 1)^2 + (2n + 1)^2]} \left[ 1 - E_{mn}(J/R; \alpha) \right] E_{mn}(t - J/R). \]

(S11)

The remaining sum over all pulse trains can be be computed using the formula for a
geometric series to give, for $t < J/R$:

$$
\tilde{P}_{mn}(t; \alpha) = \frac{L^2R}{\alpha \pi^2 [(2m+1)^2 + (2n+1)^2]} \left\{ 1 - E_{mn}(t; \alpha) \\
+ [1 - E_{mn}(J/R; \alpha)] E_{mn}(t - J/R; \alpha) \sum_{j=1}^{\infty} \exp \left\{ - \frac{1}{2} \alpha j \left[ (2m+1)^2 + (2n+1)^2 \right] \frac{\pi^2}{fL^2} \right\} \right\}
$$

(S12)

$$
= \frac{L^2R}{\alpha \pi^2 [(2m+1)^2 + (2n+1)^2]} \left\{ 1 - E_{mn}(t; \alpha) \\
+ [1 - E_{mn}(J/R; \alpha)] \frac{E_{mn}(t - J/R; \alpha)}{E_{mn}(-1/\nu; \alpha)} \right\}
$$

(S13)

and for $t \geq J/R$,

$$
\tilde{P}_{mn}(t; \alpha) = \frac{L^2R}{\alpha \pi^2 [(2m+1)^2 + (2n+1)^2]} \left[ 1 - E_{mn}(J/R; \alpha) \right] \frac{E_{mn}(t - J/R; \alpha)}{1 - E_{mn}(1/\nu; \alpha)}.
$$

(S14)

The fit function expressed in terms of the $\tilde{P}_{mn}$ is therefore,

$$
T(x, y, t; \alpha, A, \sigma_0) = \frac{4A}{L^2} \sum_{m=0}^{M-1} \sum_{n=0}^{N-1} \cos \left( (2m+1) \frac{\pi x}{L} \right) \cos \left( (2n+1) \frac{\pi y}{L} \right) \tilde{P}_{mn}(t; \alpha) \exp \left\{ - \frac{1}{2} \sigma_0^2 \left[ (2m+1)^2 + (2n+1)^2 \right] \frac{\pi^2}{L^2} \right\}.
$$

(S15)
FIG. S1. (a) Schematic of the UED beamline, see reference [28] for details: a 1030 nm Yb-fiber laser drives an optical parametric amplifier that sends 650 nm light pulses to the photocathode. Photoemitted bunches are accelerated to 140 keV, compressed by an rf cavity, collimated by a probe-defining aperture, and are collected by the detector after scattering on the sample; the same 1030 nm pulses are split and frequency doubled to synchronously pump the sample. (b) Modification of the detector section of the beamline to accommodate a magnetic quadruple electron lens triplet. The lens triplet enables angular magnification of the scattering pattern. A diffraction feature is selected for magnification on the detector with a steering magnet upstream of the lens triplet.
FIG. S2. (a) Schematic of the spatial scanning technique used to collect the data plotted in the main text Fig. 3: a 10 µm aperture defines the size and position of the probe in the sample plane; pump pulses are scanned horizontally across the sample. (b) Optical microscope image of the sample, contrasting 10 nm thin windows hosting the heterobilayer on SiN substrate with Si holder-heat sink.
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[1] H. Ihee, V. A. Lobastov, U. M. Gomez, B. M. Goodson, R. Srinivasan, C.-Y. Ruan, and A. H. Zewail, Science 291, 458 (2001).

[2] A. Cavalleri, C. Tóth, C. W. Siders, J. A. Squier, F. Ráksi, P. Forget, and J. C. Kieffer, Phys. Rev. Lett. 87, 237401 (2001).

[3] B. J. Siwick, J. R. Dwyer, R. E. Jordan, and R. J. D. Miller, Science 302, 1382 (2003).

[4] N. Gedik, D.-S. Yang, G. Logvenov, I. Bozovic, and A. H. Zewail, Science 316, 425 (2007).

[5] L. Stojchevska, I. Vaskivskyi, T. Mertelj, P. Kusar, D. Svetin, S. Brazovskii, and D. Mihailovic, Science 344, 177 (2014).

[6] E. J. Sie, C. M. Nyby, C. D. Pemmaraju, S. J. Park, X. Shen, J. Yang, M. C. Hoffmann, B. K. Ofori-Okai, R. Li, A. H. Reid, S. Weathersby, E. Mannebach, N. Finney, D. Rhodes, D. Chenet, A. Antony, L. Balicas, J. Hone, T. P. Devereaux, T. F. Heinz, X. Wang, and A. M. Lindenber, Nature 565, 61 (2019).

[7] Y. Cao, V. Fatemi, S. Fang, K. Watanabe, T. Taniguchi, E. Kaxiras, and P. Jarillo-Herrero, Nature 556, 43 (2018).

[8] H. Yoo, R. Engelke, S. Carr, S. Fang, K. Zhang, P. Cazeaux, S. H. Sung, R. Hovden, A. W. Tsen, T. Taniguchi, K. Watanabe, G.-C. Yi, M. Kim, M. Luskin, E. B. Tadmor, E. Kaxiras, and P. Kim, Nat. Mater. 18, 448 (2019).

[9] M. Liao, Z. Wei, L. Du, Q. Wang, J. Tang, H. Yu, F. Wu, J. Zhao, X. Xu, B. Han, K. Liu, P. Gao, T. Polcar, Z. Sun, D. Shi, R. Yang, and G. Zhang, Nat. Commun. 11, 2153 (2020).

[10] F. Liu, W. Wu, Y. Bai, S. H. Chae, Q. Li, J. Wang, J. Hone, and X.-Y. Zhu, Science 367, 903 (2020).

[11] S. E. Kim, F. Mujid, A. Rai, F. Eriksson, J. Suh, P. Poddar, A. Ray, C. Park, E. Fransson, Y. Zhong, D. A. Muller, P. Erhart, D. G. Cahill, and J. Park, Nature 597, 660 (2021).

[12] B. Zhao, Z. Wan, Y. Liu, J. Xu, X. Yang, D. Shen, Z. Zhang, C. Guo, Q. Qian, J. Li, R. Wu, Z. Lin, X. Yan, B. Li, Z. Zhang, H. Ma, B. Li, X. Chen, Y. Qiao, I. Shakir, Z. Almutairi, F. Wei, Y. Zhang, X. Pan, Y. Huang, Y. Ping, X. Duan, and X. Duan, Nature 591, 385 (2021).

[13] A. C. Gadelha, D. A. A. Ohlberg, C. Rabelo, E. G. S. Neto, T. L. Vasconcelos, J. L. Campos,
J. S. Lemos, V. Ornelas, D. Miranda, R. Nadas, F. C. Santana, K. Watanabe, T. Taniguchi, B. van Troeye, M. Lamparski, V. Meunier, V.-H. Nguyen, D. Paszko, J.-C. Charlier, L. C. Campos, L. G. Cançado, G. Medeiros-Ribeiro, and A. Jorio, Nature 590, 405 (2021).

[14] C. Broholm, I. Fisher, J. Moore, M. Murnane, A. Moreo, J. Tranquada, D. Basov, J. Freericks, M. Aronson, A. MacDonald, E. Fradkin, A. Yacoby, N. Samarth, S. Stemmer, L. Horton, J. Horwitz, J. Davenport, M. Graf, J. Krause, M. Pechan, K. Perry, J. Rhyne, A. Schwartz, T. Thiyyagarajan, L. Yarris, and K. Runkles, USDOE Office of Science 10.2172/1616509 (2016).

[15] G. Carini, P. Denes, S. Gruener, and E. Lessner, USDOE Office of Science 10.2172/1287494 (2012).

[16] R. R. Meyer and A. Kirkland, Ultramicroscopy 75, 23 (1998).

[17] G. Y. Fan and M. H. Ellisman, J. Micros. 200, 1 (2000).

[18] J. M. Zuo, Micros. Res. Tech. 49, 245 (2000).

[19] S. M. Gruner, M. W. Tate, and E. F. Eikenberry, Rev. of Sci. Instrum. 73, 2815 (2002).

[20] T. Vecchione, P. Denes, R. K. Jobe, I. J. Johnson, J. M. Joseph, R. K. Li, A. Perazzo, X. Shen, X. J. Wang, S. P. Weathersby, J. Yang, and D. Zhang, Rev. Sci. Instrum. 88, 033702 (2017).

[21] A. Allahgholi, J. Becker, A. Delfs, R. Dinapoli, P. Göttlicher, H. Graafsma, D. Greiffenberg, H. Hirsemann, S. Jack, A. Klyuev, H. Krüger, M. Kuhn, T. Laurus, A. Marras, D. Mezza, A. Mozzanica, J. Poehlsen, O. Shefer Shalev, I. Sheviakov, B. Schmitt, J. Schwandt, X. Shi, S. Smoljanin, U. Trunk, J. Zhang, and M. Zimmer, Nucl. Instrum. 942, 162324 (2019).

[22] F. Leonarski, S. Redford, A. Mozzanica, C. Lopez-Cuenca, E. Panepucci, K. Nass, D. Ozerov, L. Vera, V. Olieric, D. Buntschu, R. Schneider, G. Tinti, E. Froejdh, K. Diederichs, O. Bunk, B. Schmitt, and M. Wang, Nat. Methods 15, 799 (2018).

[23] M. W. Tate, D. Chamberlain, K. S. Green, H. T. Philipp, P. Purohit, C. Strohman, and S. M. Gruner, J. Phys. Conf. Ser. 425, 062004 (2013).

[24] Y. Jiang, Z. Chen, Y. Han, P. Deb, H. Gao, S. Xie, P. Purohit, M. W. Tate, J. Park, S. M. Gruner, V. Elser, and D. A. Muller, Nature 559, 343 (2018).

[25] Z. Chen, Y. Jiang, Y.-T. Shao, M. E. Holtz, M. Odstrčil, M. Guizar-Sicairos, I. Hanke, S. Ganschow, D. G. Schlom, and D. A. Muller, Science 372, 826 (2021).

[26] Y. M. Lee, Y. J. Kim, Y.-J. Kim, and O.-H. Kwon, Struct. Dyn. 4, 044023 (2017).

[27] M. W. Tate, P. Purohit, D. Chamberlain, K. X. Nguyen, R. Hovden, C. S. Chang, P. Deb, E. Turgut, J. T. Heron, D. G. Schlom, and et al., Microsc. Microanal. 22, 237–249 (2016).
[28] W. H. Li, C. J. R. Duncan, M. B. Andorf, A. C. Bartnik, E. Bianco, L. Cultrera, A. Galdi, M. Gordon, M. Kaemingk, C. A. Pennington, L. F. Kourkoutis, I. V. Bazarov, and J. M. Maxson, Struct. Dyn. 9, 024302 (2022).

[29] Y. Bai, L. Zhou, J. Wang, W. Wu, L. J. McGilly, D. Halbertal, C. F. B. Lo, F. Liu, J. Ardelean, P. Rivera, N. R. Finney, X.-C. Yang, D. N. Basov, W. Yao, X. Xu, J. Hone, A. N. Pasupathy, and X.-Y. Zhu, Nat. Mater. 19, 1068 (2020).

[30] J. Wang, Q. Shi, E.-M. Shih, L. Zhou, W. Wu, Y. Bai, D. Rhodes, K. Barmak, J. Hone, C. R. Dean, and X.-Y. Zhu, Phys. Rev. Lett. 126, 106804 (2021).

[31] A. S. Disa, M. Fechner, T. F. Nova, B. Liu, M. Först, D. Prabhakaran, P. G. Radaelli, and A. Cavalleri, Nat. Phys. 16, 937 (2020).

[32] J. Kim, E. Ko, J. Jo, M. Kim, H. Yoo, Y.-W. Son, and H. Cheong, Nat. Mater. 10.1038/s41563-022-01240-2 (2022).

[33] R. P. Chatelain, V. R. Morrison, B. L. M. Klarenaar, and B. J. Siwick, Phys. Rev. Lett. 113, 235502 (2014).

[34] D. Fausti, R. I. Tobey, N. Dean, S. Kaiser, A. Dienst, M. C. Hoffmann, S. Pyon, T. Takayama, H. Takagi, and A. Cavalleri, Science 331, 189 (2011).

[35] P. Zalden, F. Quirin, M. Schumacher, J. Siegel, S. Wei, A. Koc, M. Nicoul, M. Trigo, P. Andreasson, H. Enquist, M. J. Shu, T. Pardini, M. Chollet, D. Zhu, H. Lemke, I. Ronneberger, J. Larsson, A. M. Lindenberg, H. E. Fischer, S. Hau-Riege, D. A. Reis, R. Mazzarello, M. Wuttig, and K. Sokolowski-Tinten, Science 364, 1062 (2019).

[36] H. T. Philipp, M. W. Tate, K. S. Shanks, L. Mele, M. Peemen, P. Dona, R. Hartong, G. van Veen, Y.-T. Shao, Z. Chen, and et al., Microsc. Microanal. 28, 425–440 (2022).

[37] J. T. Weiss, K. S. Shanks, H. T. Philipp, J. Becker, D. Chamberlain, P. Purohit, M. W. Tate, and S. M. Gruner, IEEE Trans. Nucl. Sci, 64, 1101 (2017).

[38] J. T. Weiss, J. Becker, K. S. Shanks, H. T. Philipp, M. W. Tate, and S. M. Gruner, AIP Conf. Proc. 1741, 040038 (2016).

[39] G. F. Schneider, V. E. Calado, H. Zandbergen, L. M. K. Vandersypen, and C. Dekker, Nano Lett. 10, 1912 (2010).