

# Fast Pump-Probe Microscopy Imaging with Asynchronous Optical Sampling

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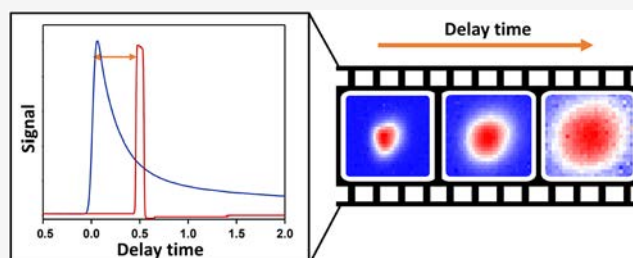


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**ABSTRACT:** Asynchronous optical sampling (ASOPS) allows rapid collection of transient absorption/reflection data over wide time scales with a high dynamic range in both time and signal magnitude. In this paper, a method for recording transient images using ASOPS is presented based on time-gated integration of the transient signal. This technique allows diffraction-limited pump-probe microscopy images to be rapidly collected at precise, user-specified time delays, with approximately 15 picoseconds time resolution. Results are presented for the excited-state dynamics in multilayered WSe<sub>2</sub> flakes, charge-carrier diffusion in a silicon wafer, and images of Au nanoparticle arrays that demonstrate the spatial/temporal resolution and sensitivity of the technique. Potential applications and the ultimate time resolution that can be achieved are also discussed.



## 1. INTRODUCTION

Pump-probe microscopy is a widely used technique for interrogating and visualizing excited-state processes in nanomaterials.<sup>1–5</sup> These experiments allow studies of how excited-state dynamics vary within and between different structures, providing unique information about the heterogeneous nature of nanomaterials and the spatial distribution of excitons and charge carriers as a function of time.<sup>1–5</sup> In a standard transient absorption/reflection experiment, the dynamics are measured by exciting the sample with a pump laser pulse and varying the time delay between the pump and probe laser pulses with a mechanical delay line.<sup>1–5</sup> In these experiments, there is typically a trade-off between time resolution (as determined by the step size used for the delay line) and the total time window of the transient absorption/reflection trace. This mechanical dependency fundamentally limits the speed for acquiring kinetic traces on long time scales. This problem can be overcome using asynchronous optical sampling (ASOPS).<sup>6–11</sup>

In ASOPS two separate mode-locked lasers (acting as dual-frequency combs) operate at slightly different and precisely controlled repetition rates,  $f_r$  and  $f_r + \Delta f$ . Due to the frequency mismatch ( $\Delta f$ ), the temporal delay between the pump and probe continuously changes with each laser cycle. This automatically sweeps one set of pulses across the other at a constant rate, eliminating the need for moving delay stages.<sup>6–11</sup> The temporal scanning window of ASOPS is inversely proportional to the lasers' repetition rate ( $1/f_r$ ): a standard 100 MHz system provides a 10 ns measurement window,

which is sufficient for many studies.<sup>1–5</sup> The transient absorption/reflection traces are averaged at  $\Delta f$ , which is typically in the kHz range. Thus, thousands of full time-sweeps can be averaged per second, yielding high sensitivity. ASOPS has been extensively used in picosecond acoustics experiments, especially those implemented in a microscopy system, where maintaining alignment while scanning a mechanical delay line over a long range is challenging.<sup>12–17</sup>

An important application in pump-probe microscopy is to record images at different time delays to map excited-state dynamics.<sup>1–5</sup> There are two basic modalities for transient imaging. First, transient absorption/reflection images can be collected by either scanning the sample through the focus of the pump and probe lasers or by scanning the pump and probe beams over the sample. Examples of these two approaches for imaging graphene are described in refs 18 and 19, respectively. These types of experiments can provide information about spatial heterogeneity in materials.<sup>1–5,18,19</sup> In the second imaging modality, the pump laser beam is held at a fixed position and the probe is scanned over the sample,<sup>20–22</sup> or widefield images of a defocused probe beam are recorded with a camera.<sup>23</sup> This allows the motion of charge carriers and

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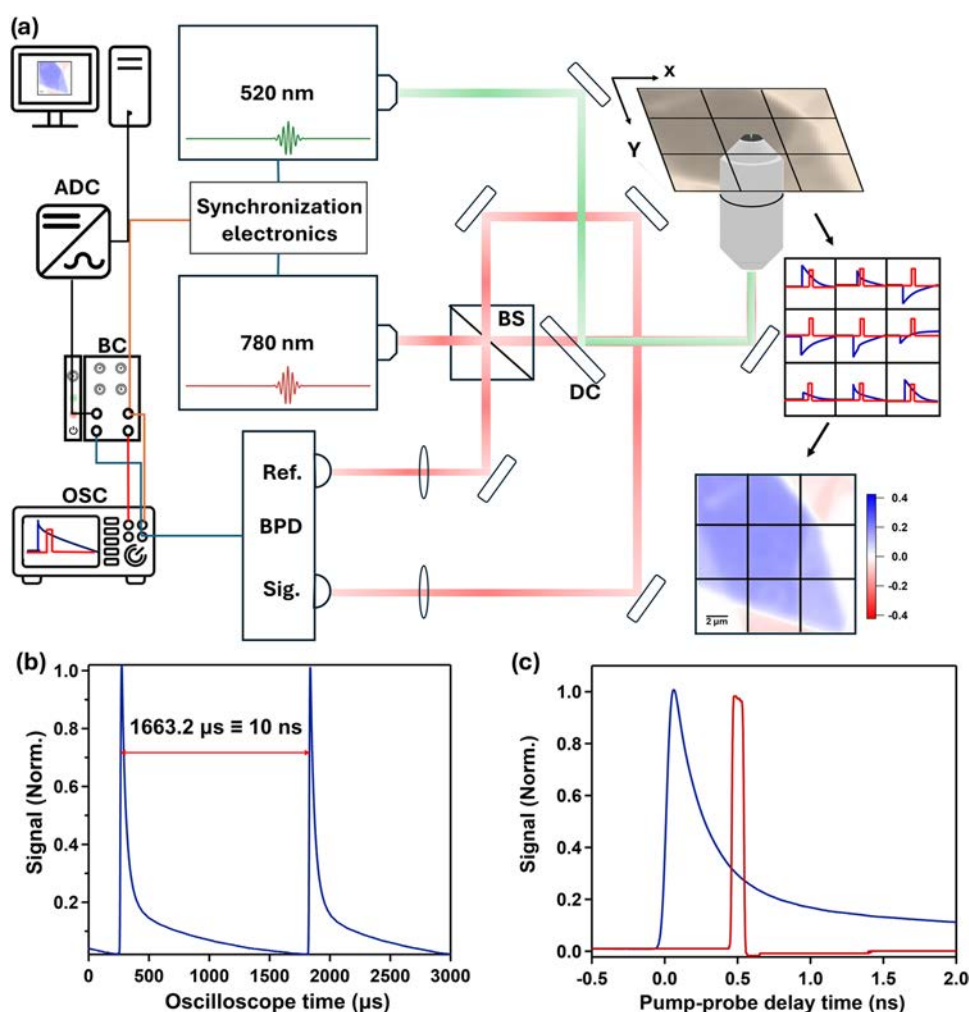


**Figure 1.** (a) Schematic of the experimental system for ASOPS imaging. BPD = balanced photodetector; ADC = analog-to-digital converter; BS = 50:50 beam splitter; DC = dichroic mirror; OSC = oscilloscope; BC = boxcar integrator. The oscilloscope monitors the boxcar gate and the signal from the BPD, and the integrated signal from the boxcar is digitized by the ADC. (b) ASOPS traces recorded with an oscilloscope time base of 200  $\mu\text{s}/\text{division}$ . The time between pulses in this trace calibrates the laboratory/oscilloscope time with the pump and probe delay time. (c) Transient reflection trace (blue line) from panel (b), overlaid with the boxcar gate (red line). The time scale has been converted to the time between the pump and probe pulses using the data in panel (b).

excitons in semiconductor materials,<sup>1,3,4,18,22–24</sup> electrons in metals,<sup>25</sup> or plasmons in metallic nanostructures<sup>26,27</sup> to be visualized and quantified. However, the inherent nature of ASOPS, where the probe pulse continuously sweeps across the entire temporal window, limits its application in pump-probe microscopy imaging.

In this contribution, a simple scheme for recording pump-probe microscopy images with ASOPS is presented based on time-gating the transient signal with a boxcar integrator triggered by the ASOPS synchronization electronics. To demonstrate the utility of this method, spatially resolved images of the ultrafast dynamics within twisted  $\text{WSe}_2$  bilayers, multilayered  $\text{WSe}_2$  flakes, and a silicon wafer are presented, as well as images of Au nanoparticle arrays. Note that imaging measurements with ASOPS have previously been demonstrated, where a full ASOPS trace is taken at each position in the sample.<sup>28,29</sup> This technique has been applied to thin-film characterization and can yield detailed information about the spatial variation of mechanical properties.<sup>29</sup> However, these experiments are much more time-consuming than the

measurements described here, and the extra temporal detail they contain is not needed for many applications.

## 2. EXPERIMENTAL SECTION

A diagram of the experimental setup is presented in Figure 1(a). The laser system used was a Menlo Systems ASOPS DUAL COLOR 520/780 system. The visible 520 nm laser (Orange SYNC Yb:doped fiber oscillator, repetition rate  $f_r = 100$  MHz) served as the pump, and a near-IR 780 nm laser (C-Fiber SYNC 780 high power Er:doped fiber, repetition rate  $f_r + \Delta f$ ) was the probe. The difference in repetition rates between the two lasers  $\Delta f$  was controlled by the Menlo Systems EM100 synchronization electronics. Both beams were aligned and focused onto the sample using an Olympus 60 $\times$  MPlan APO 0.9 NA objective, and the change in reflectivity of the probe induced by the pump was monitored by a balanced photodetector (Newport 2107-FS-M). To collect transient reflection traces, the output of the detector was AC coupled and digitized by a Tektronix TBS 2000B series digital oscilloscope, which was triggered at the difference frequency  $\Delta f$ . The signal was averaged both with the oscilloscope and

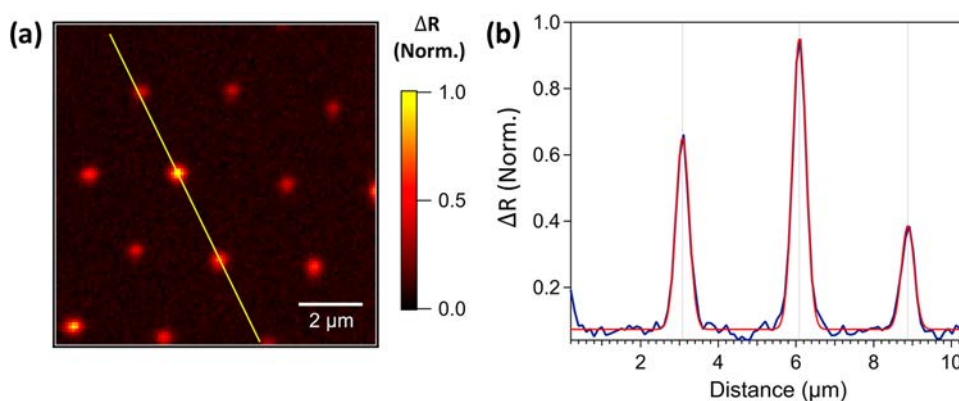


**Figure 2.** (a) Transient reflection image from a hexagonal array of 100 nm diameter gold hemispheres recorded with the boxcar gate set to the maximum of the signal. (b) Line profile extracted from the image. The blue line is the experimental data, and the red line is a fit using a series of Gaussian functions.

through a custom LabVIEW program.<sup>15,16</sup> The time resolution for the transient reflection traces (as measured by the rise time of the signal, see [Supporting Information](#)) is ca. 15 ps. This is longer than expected from the bandwidth of the detection electronics and is limited by the jitter in triggering the oscilloscope.<sup>10</sup>

For transient reflection imaging the output of the detector was sent to a boxcar integrator (Stanford Research Systems, SR250) that was also triggered at  $\Delta f$ . The width and position of the boxcar gate were adjusted to give the desired time resolution and time delay for the measurement using the analog front-panel controls on the boxcar integrator. The boxcar integrates the output of the detector over the time defined by the gate. This signal was typically averaged for 30 samples, and the averaged output was sent to an Analog-to-Digital Converter (ADC, National Instruments USB 6009) and further averaged and recorded by a custom LabVIEW program. Images were obtained by raster-scanning the sample through the laser focus using a piezo stage (P-527.3CL, Physik Instruments) that was also controlled in LabVIEW, or by scanning the pump laser over the sample with a galvo-mirror system (Thorlabs, GVS012 Galvo Mirror Assembly and Driver Boards) while holding the probe beam fixed. The typical step size for the piezo scanning experiments was 0.2  $\mu\text{m}$  per point, with a settling time between steps of 300 ms. For the galvo-mirror scanning experiments, the step size was also 0.2  $\mu\text{m}$ , with the same 300 ms time per point. The data presented in this paper was collected with  $\Delta f = 600$  Hz. As will be discussed below, the value of  $\Delta f$  is an important consideration for the time resolution of these measurements. Reflected laser light images were recorded by DC coupling the output of the balanced detector, digitizing with the ADC, and averaging in LabVIEW. The pump beam was blocked in these experiments. Incoherent reflected light images of the WSe<sub>2</sub> nanoflakes were recorded with a white LED source and a CMOS camera (Thorlabs, DCC3260).

The samples investigated were arrays of Au nanoparticles, twisted bilayers of WSe<sub>2</sub>, multilayered nanoflakes of WSe<sub>2</sub> prepared by mechanical exfoliation of the bulk crystal, and a bulk silicon wafer (University Wafer, Inc.). For the Au nanoparticle arrays, substrate-supported Au seeds were fabricated according to the procedure reported previously by Panda et al.<sup>30</sup> Briefly, C-plane sapphire substrates were coated with a bilayer PMGI/SPR700 resist system to facilitate high-quality lift-off. The desired seed pattern was defined by direct-

write maskless photolithography (Heidelberg MLA150) by using 700 nm circular openings arranged in the required array geometry. Following resist development, sequential Sb and Au thin films were deposited by ion-beam sputtering without breaking the vacuum. Lift-off removed the excess metal, leaving periodic arrays of Sb/Au nanodisks on the SiO<sub>2</sub>/sapphire surface. The patterned substrates were then thermally processed under flowing Ar by using a programmed high-temperature annealing cycle. During annealing, Sb sublimated while promoting the formation of isolated, epitaxial Au seeds that remained immobilized on the sapphire substrate. These Au seeds served as the starting templates for all of the subsequent crystal growth. Complete fabrication details, including resist processing, lithographic conditions, deposition parameters, lift-off, and thermal processing, are described in ref 30.

Multilayer WSe<sub>2</sub> nanoflakes (up to  $\sim 100$  nm thickness) were prepared by mechanical exfoliation of bulk WSe<sub>2</sub> crystals (HQ Graphene, Netherlands) using a Polydimethylsiloxane (PDMS) stamping method.<sup>31</sup> These samples were deposited onto glass coverslips for microscopy experiments.<sup>31</sup> Twisted bilayers of WSe<sub>2</sub> are fabricated using ‘tear and stack’ and sequential ‘dry transfer’ technique reported in ref 32. Briefly, monolayer WSe<sub>2</sub> and multilayer hexagonal boron nitride (hBN) flakes were initially exfoliated onto SiO<sub>2</sub>/Si substrates using a standard mechanical tape exfoliation process and subsequently identified based on their optical contrast under a microscope. Monolayer WSe<sub>2</sub> flakes were then mechanically cut into two distinct segments using the cantilever tip of an atomic force microscope (AFM). Following that, a thin ( $\sim 10$   $\mu\text{m}$ ) hBN flake was picked up using a polycarbonate (PC)/polydimethylsiloxane (PDMS) stamp at 120  $^{\circ}\text{C}$ . The hBN flake was subsequently brought into contact with one half of the WSe<sub>2</sub> monolayer and used to pick up that segment. The rotation stage was then set to the desired twist angle ( $\theta$ ), after which the stamp was brought into contact with the second half of the WSe<sub>2</sub> flake to complete the twisted heterostructure. The entire hBN/WSe<sub>2</sub> pick-up process was performed at 120  $^{\circ}\text{C}$ . The resulting twisted heterostructure was subsequently released onto a cleaned SiO<sub>2</sub>/Si substrate at 180  $^{\circ}\text{C}$ . Following the transfer, residual PC polymer was thoroughly removed by rinsing the sample with chloroform, followed by O<sub>2</sub> plasma cleaning.

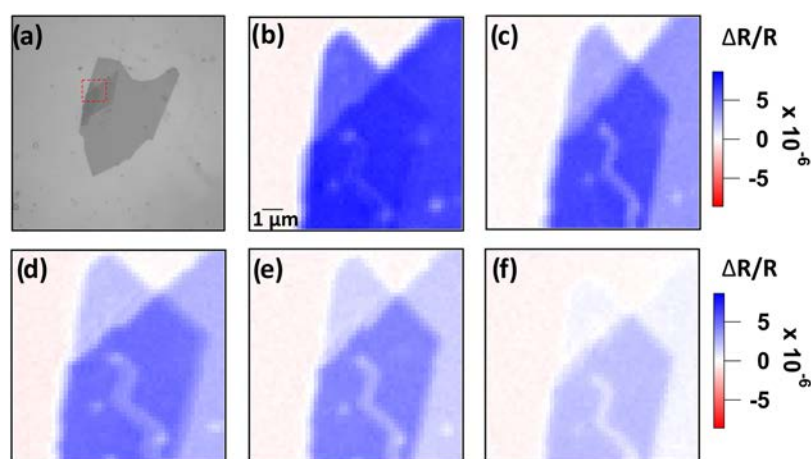


**Figure 3.** Steady state and transient reflection microscopy measurements on hBN capped 45° twisted WSe<sub>2</sub> bilayer deposited on a Si/SiO<sub>2</sub> substrate. (a) Reflected light image recorded with an incoherent white light LED source. (b–f) Transient reflection images for the selected area in panel (a) taken at delay times of 0 ps, 18 ps, 34, 50, and 134 ps. The gate width for these experiments was 15 ps.

### 3. RESULTS AND DISCUSSION

Figure 1(b) shows a typical ASOPS trace from a WSe<sub>2</sub> nanoflake recorded at  $\Delta f = 600$  Hz. For this value of  $\Delta f$  successive laser pulses are separated by 1663.2  $\mu$ s on the oscilloscope (the laboratory time), which allows us to calibrate the pump-probe delay time for the experiment. Figure 1(c) shows the transient reflection signal as a function of time delay between the pump and probe pulses, along with the gate from the boxcar integrator. The gate width presented in Figure 1(c) is 13.9  $\mu$ s on the oscilloscope, which corresponds to a width of 84 ps in the ASOPS trace. The boxcar integrates the transient reflection signal over the gate. Thus, for Figure 1(c), the averaged boxcar output would represent the transient reflection signal at a pump-probe delay time of  $0.50 \pm 0.04$  ns. The transient signal at different time delays can be determined by simply changing the gate delay for the boxcar. In the following experiments the gate width setting for the boxcar integrator was adjusted to give the minimum width without decreasing the gate amplitude and, therefore, decreasing the sensitivity of the measurement. For  $\Delta f = 600$  Hz, this corresponds to a near Gaussian gate with a full-width-at-half-maximum of 15 ps, which defines the time resolution in the experiments and is, coincidentally, the same as the rise time for the transient reflection traces (see Supporting Information).

To test the spatial resolution of the measurements, experiments were performed on a lithographically patterned array of gold hemispheres arranged in a hexagonal lattice. These structures have a “dome” shape with a diameter of  $100 \pm 3$  nm and a center-to-center pitch of 3  $\mu$ m.<sup>30</sup> Figure 2(a) displays a transient reflection image recorded with the boxcar gate positioned at the maximum of the signal. The spatial intensity pattern in the image replicates the pattern of the array. The differences in the intensities of the features in the images are attributed to slight differences in the size and shape of the particles, which change the wavelength and intensity of their localized surface plasmon resonance. The point spread function (PSF) for the transient reflection system was evaluated by analyzing a line profile extracted from the image (Figure 2(b)). Fitting the features in this profile to Gaussian functions yields a FWHM of 240 nm for the PSF, which is close to the expected spatial resolution for the pump

laser ( $\lambda_{\text{pump}}/2\text{NA} \approx 290$  nm). This is consistent with the understanding that a transient reflection signal is only generated when the pump beam is spatially overlapped with the nanoparticle.<sup>33</sup>

To demonstrate the potential of our technique to interrogate heterogeneous samples, transient reflection microscopy experiments were performed on hBN capped twisted bilayers of WSe<sub>2</sub>. Figure 3(a) shows a reflected light image of a hBN capped twisted bilayer. The large uniform layer showing high optical contrast against the substrate corresponds to the hBN flake. Positioned beneath the left edge of this layer are two WSe<sub>2</sub> monolayers stacked at a 45° angle. Their overlapping region forms a bilayer, which exhibits a clear optical contrast change compared to the individual monolayers. Transient decay traces collected from both the monolayer and bilayer regions are shown in Figure S2. Figure 3(b–f) shows the temporal evolution of the transient reflection signal within the region highlighted in Figure 3(a). The transient reflectivity images effectively map out the monolayer and bilayer regions, showing the spatial heterogeneity of the dynamics of these samples. Specifically, the bilayer region exhibits a longer lifetime than the constituent monolayers. This is attributed to the formation of interlayer excitons.<sup>34–37</sup> Interlayer excitons are formed by electrons and holes localized in two different constituent monolayers. This spatial separation reduces the electron-hole wave function overlap, thereby increasing the lifetime.<sup>34–37</sup> The weak, negative background signal observed in the images originates from the underlying silicon substrate. Because hexagonal boron nitride (hBN) is a wide-bandgap insulator ( $E_g \sim 6$  eV), it is not photoexcited by our pump laser and consequently produces no detectable transient signal. Corresponding transient decay traces and reflection images for a second WSe<sub>2</sub> bilayer structure, featuring a 4.5° twist, are shown in Figures S2 and S3 respectively. The transient reflectivity images also show defects in the bilayer region, presumably created during the cutting and/or lift-off steps during fabrication, that accelerate exciton recombination. These results demonstrated the sensitivity of the technique: the transient dynamics of monolayer and bilayer WSe<sub>2</sub>, with reflectivity changes on the order of  $\Delta R/R \approx 5 \times 10^{-6}$  can be detected with high signal-to-noise.

Unlike monolayer and bilayer WSe<sub>2</sub>, multilayered WSe<sub>2</sub> flakes exhibit interesting transient dynamics that extend into

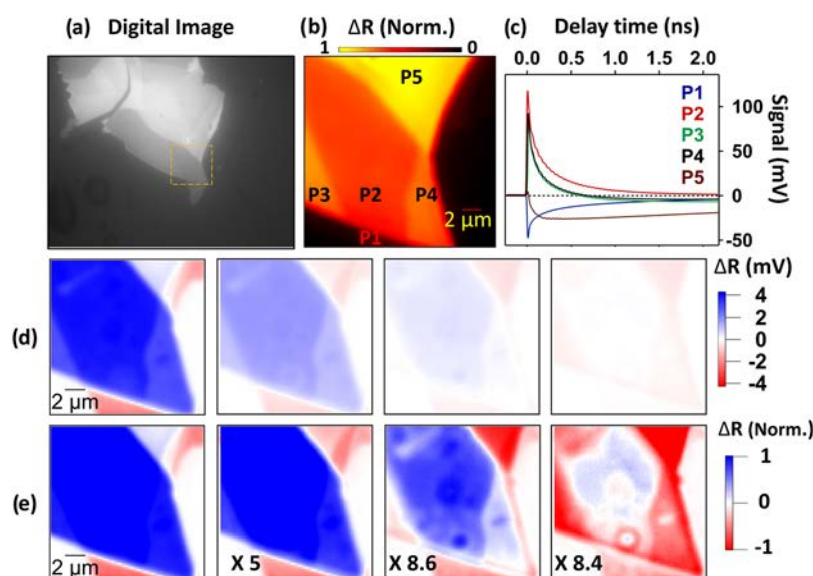


**Figure 4.** (a) Reflected light image of a WSe<sub>2</sub> nanoflake on a glass coverslip recorded with an incoherent white light LED source. (b) Reflected 780 nm laser light images from the selected area of the nanoflake in panel (a), recorded by scanning the sample through the focus of the laser. (c) ASOPS traces obtained from different points in the image in panel (b). (d) Transient reflection images of the WSe<sub>2</sub> nanoflake in panel (b) recorded at 15 ps, 135, 203, and 270 ps time delay. (e) Normalized versions of the images in panel (d). The numbers in panel (e) give the multiplicative factor used to normalize the images. The time resolution in these experiments (determined by the boxcar gate width) was 15 ps.

the nanosecond regime.<sup>17,31</sup> A standard 100 MHz ASOPS system provides an inherent 10 ns delay time window ( $1/f_r$ ), which is ideal for probing the long-lived dynamics in multilayered flakes without requiring any modifications to the optical setup. Figure 4(a) shows a reflected light image of a WSe<sub>2</sub> nanoflake on a glass coverslip recorded with a white light LED source. Due to their high refractive index and large thickness, the multilayered WSe<sub>2</sub> flakes reflect significantly more light than the mono/bilayers, so a Si/SiO<sub>2</sub> substrate is not needed to visualize the sample.<sup>38–40</sup> A reflected laser light image of a selected area of the flake, obtained by monitoring the probe laser with the balanced detector and raster-scanning the sample through the laser focus via the piezo stage, is presented in Figure 4(b). The differences in contrast in Figure 4(a,b) are attributed to differences in the overall nanoflake thickness.<sup>17,38–41</sup>

Figure 4(c) shows transient absorption traces from different points in the nanoflake. There are several important features to be noted in the traces. First, transient absorption measurements for WSe<sub>2</sub> typically shows a fast picosecond time scale decay that is not resolved in our experiments.<sup>42–44</sup> Second, almost all of the traces in Figure 4(c) show modulations. These can arise from either acoustic vibrations in the WSe<sub>2</sub> nanoflakes or Brillouin oscillations in the substrate.<sup>17,31,41</sup> For the data in Figure 4(c), the oscillation frequencies are all close to the expected Brillouin frequency in glass of 21.7 GHz and, thus, are attributed to Brillouin oscillations rather than acoustic vibrations.<sup>31</sup> Second, both the sign and the magnitude of the transient reflection signal change across the nanoflake, and in some cases, the signal changes sign during the trace (points P3 and P4 in Figure 4(c)).

There are several possibilities for the sign change in these experiments. First, the probe wavelength in the experiments is near the A-exciton of WSe<sub>2</sub>.<sup>45</sup> Visible excitation of WSe<sub>2</sub> promotes electrons to the conduction band, which bleaches the A-exciton transition and creates an induced absorption signal on the wings of the resonance.<sup>42–44</sup> Because the strength

and position of the exciton resonance depends on the nanoflake thickness,<sup>42,45</sup> the transient reflection signal recorded at 780 nm could appear as an absorption (decrease in  $\Delta R$ ) or a bleach (increase in  $\Delta R$ ) for different flakes, or different regions of a single flake.<sup>31</sup> Another possibility is contributions from lattice heating to the transient reflectivity signal. Specifically, recombination of the excited charge carriers created by the pump laser heats the WSe<sub>2</sub> lattice, thereby changing the refractive index. This changes the reflectivity of the sample,<sup>38–40</sup> which can lead to a negative signal in our transient reflectivity measurements. Figure S4(a) shows the calculated reflectivity as a function of thickness for WSe<sub>2</sub> on a glass substrate using the thin-film expressions given in ref.<sup>38–40</sup> and the refractive index data from ref. 46. Changes in reflectivity for different temperature rises are presented in Figure S4(b), where the temperature dependence of the refractive index was estimated from data for monolayer samples.<sup>47</sup> The calculations show that an increase in lattice temperature can cause either a positive or negative transient reflectivity, depending on the exact thickness of the nanoflakes. It is important to note that for thin flakes (<50 nm thickness), the thin-film reflectivity calculations predict a positive  $\Delta R$ —as observed in Figure 3.

Figure 4(d,e) shows the temporal evolution of the transient reflection images for the selected region of the flake in Figure 4(a). Both raw (un-normalized, Figure 4(d)) and normalized (Figure 4(e)) transient reflection images are presented. The images show a complicated spatial distribution of the sign and magnitude of the transient reflection signal that evolves on different time scales. Several regions of the image show a change in sign as time increases, with the signal evolving from a positive  $\Delta R$  (bleach) to a negative  $\Delta R$  (increased absorption or reduced reflection). Comparison to the reflectivity data (Figure 4(b)) shows that these regions correspond to thicker portions of the nanoflake. These observations can be explained as follows: the pump laser generates excitons that subsequently relax, leading to lattice heating. The excitons produce a

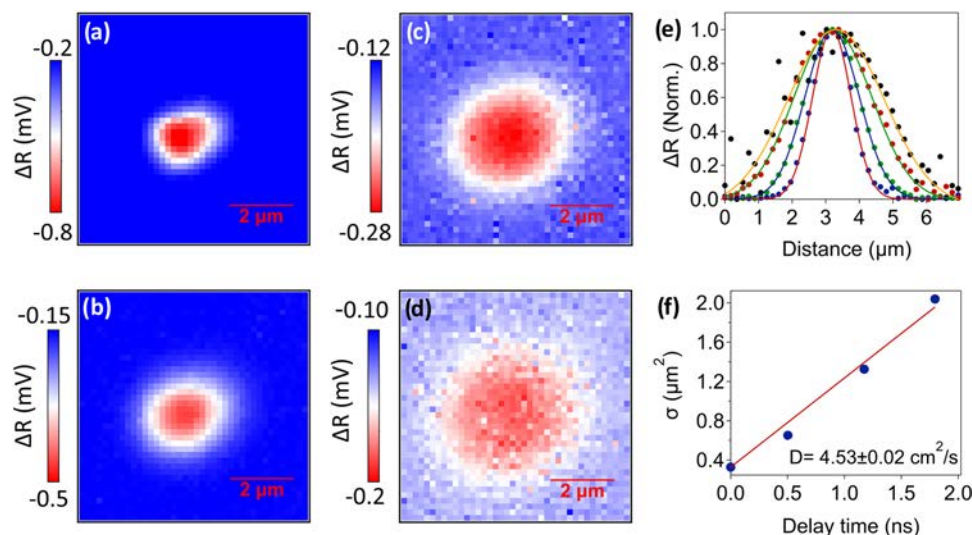


**Figure 5.** (a–d) Transient reflection microscopy images recorded with a fixed 780 nm probe beam, and a scanned 520 nm pump beam for a silicon wafer recorded at (a) 0 ns, (b) 0.5 ns, (c) 1.2 ns, and (d) 1.8 ns time delay between the pump and the probe. The time resolution in these experiments (determined by the boxcar gate width) was 15 ps. (e) Normalized plots of the transient reflection signal versus relative distance between the pump and probe beam extracted from a vertical line profile through the images in panels (a–d). (f) Plot of the variance versus time. The red line is a fit to the data using  $\sigma(t)^2 = \sigma_0^2 + 2Dt$ .

transient bleach (positive  $\Delta R$ ),<sup>42–44</sup> whereas lattice heating can create a positive or negative  $\Delta R$  depending on the nanoflake thickness. Because the time scales for the decay of the excitons and lattice temperature are different, the signal can change from a bleach to an absorption. Recording images that allow the correlation of the dynamics to structural features is essential for developing this assignment and demonstrates the advantages of imaging techniques for studying heterogeneous materials in general, and two-dimensional transition metal dichalcogenides in particular.<sup>3,4</sup>

The images in Figures 3 and 4, where the pump and probe beams are overlapped and are moved relative to the sample, provide information about the spatial heterogeneity of the dynamics in nanomaterials. Another important imaging modality in pump-probe microscopy is to scan one beam relative to the other.<sup>20–22</sup> This technique has been applied to study diffusion of excitons and charge carriers in semiconductor and metal nanostructures<sup>1,3,4,20,22–25</sup> and propagating plasmons in metal nanostructures.<sup>2,21,26,27</sup> These experiments are usually done by holding the pump beam fixed and scanning the probe. However, for materials that are homogeneous over a few micrometers range, scanning the pump beam while holding the probe fixed gives the same information: both scanned pump/fixed probe and scanned probe/fixed pump experiments yield images that represent how the transient absorption/reflection signal changes as a function of the relative distance between the two beams. For our experiments, where the probe is monitored by using a balanced detector, it is better to scan the pump and fix the probe. This is because even slight misalignments of the probe on the balanced detector can produce a large spurious signal.

Figure 5(a–d) shows fixed probe/scanned pump images recorded at different time delays for a silicon wafer.<sup>48</sup> The signal is assigned to transient absorption from charge carriers created by pump laser excitation. At early times (Figure 5(a)), the excited charge carriers are tightly confined within the focal spot of the pump beam, and a signal is only observed when the pump and probe are spatially overlapped. The size of the

feature in the transient reflection images increase as time progresses due to carrier diffusion. Figure 5(e) shows plots of the normalized intensity versus distance taken from a vertical line profile through the images. Fitting these line profiles with a Gaussian function gives the time dependent variance  $\sigma(t)^2 = \sigma_0^2 + 2Dt$ , where  $\sigma_0^2$  is the initial variance of the spatial distribution of charge carriers created by the pump, and  $D$  is the diffusion constant of the excited species.<sup>3,4,49,50</sup>  $\sigma(t)^2$  is plotted versus time in Figure 5(f), and fitting this data gives a diffusion constant of  $D = 4.53 \pm 0.02 \text{ cm}^2/\text{s}$ . This value is smaller than that recently reported for electrons in p-doped Si ( $D = 35 \text{ cm}^2/\text{s}$ ),<sup>50</sup> but within the range reported for ambipolar diffusion in silicon, especially at medium to high carrier densities where carrier–carrier interactions reduce carrier mobility.<sup>51–53</sup>

The images and analysis in Figures 3–5 show the utility of our time-gated ASOPS technique for measuring dynamics in pump-probe microscopy experiments on a tens-of-picoseconds to nanoseconds time scale. In principle, the boxcar gate width and, thus, the temporal resolution can be improved by decreasing the difference frequency ( $\Delta f$ ) used in the ASOPS system. Decreasing  $\Delta f$  stretches the ASOPS trace out in laboratory time, which means that the effective gate width of the boxcar is decreased. However, the potential improvement in time resolution comes with a reduction in the data collection speed, which is one of the main attributes of ASOPS.<sup>6,7</sup> A reasonable compromise for our current system would be to use  $\Delta f = 100 \text{ Hz}$ , which implies a time resolution of 2.5 ps.

#### 4. SUMMARY AND CONCLUSIONS

A simple scheme for recording pump-probe microscopy images in an ASOPS system has been presented. This technique will allow transient absorption/reflection imaging to be extended to longer time scales than delay line measurements, filling the gap between ultrafast sub-ps delay-line-based experiments,<sup>1–4,18,19,22–25,54</sup> and longer time scale fluorescence detection or “stroboSCAT” measurements.<sup>48–50</sup> This is an

important capability for studies of “relaxed” excited-state systems, that is, excitons or charge carriers that have relaxed to the bottom of the conduction band.<sup>3,4</sup> These time scales are also relevant to studies of thermal diffusion.<sup>48,50</sup> A significant limitation is that current ASOPS systems typically operate at repetition rates in the 80–100 MHz region, which means that the system being studied should return to the ground state within 10 ns to avoid overexciting the sample. This is a problem for many semiconductor materials, but not a significant limitation for studies of heat dissipation in nanoscale materials,<sup>55</sup> or exciton lifetimes in many two-dimensional materials, such as the WSe<sub>2</sub> nanoflakes examined above.<sup>42,43</sup> Importantly, the technique also extends the utility of ASOPS systems to imaging applications.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpca.6c04871>.

Details of the time resolution for ASOPS traces and transient reflection images; additional WSe<sub>2</sub> bilayer measurements; correlation between the sign of the WSe<sub>2</sub> transient reflection signal and the sample thickness; calculated changes in sample reflectivity versus thickness (PDF)

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## Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) Grumstrup, E. M.; Gabriel, M. M.; Cating, E. E. M.; Van Goethem, E. M.; Papanikolas, J. M. Pump-probe microscopy: Visualization and spectroscopy of ultrafast dynamics at the nanoscale. *Chem. Phys.* **2015**, *458*, 30–40.
- (2) Beane, G.; Devkota, T.; Brown, B. S.; Hartland, G. V. Ultrafast measurements of the dynamics of single nanostructures: a review. *Rep. Prog. Phys.* **2019**, *82*, No. 016401.
- (3) Zhu, T.; Snider, J. M.; Yuan, L.; Huang, L. Ultrafast Dynamic Microscopy of Carrier and Exciton Transport. *Annu. Rev. Phys. Chem.* **2019**, *70*, 219–244.
- (4) Deng, S. B.; Blach, D. D.; Jin, L. R.; Huang, L. B. Imaging Carrier Dynamics and Transport in Hybrid Perovskites with Transient Absorption Microscopy. *Adv. Energy Mater.* **2020**, *10*, No. 1903781.
- (5) Gross, N.; Kuhs, C. T.; Ostovar, B.; Chiang, W.-Y.; Wilson, K. S.; Volek, T. S.; Faltz, Z. M.; Carlin, C. C.; Dionne, J. A.; Zanni, M. T.; Gruebele, M.; Roberts, S. T.; Link, S.; Landes, C. F. Progress and Prospects in Optical Ultrafast Microscopy in the Visible Spectral Region: Transient Absorption and Two-Dimensional Microscopy. *J. Phys. Chem. C* **2023**, *127*, 14557–14586.
- (6) Bartels, A.; Cerna, R.; Kistner, C.; Thoma, A.; Hudert, F.; Janke, C.; Dekorsy, T. Ultrafast time-domain spectroscopy based on high-speed asynchronous optical sampling. *Rev. Sci. Instrum.* **2007**, *78*, No. 035107.
- (7) Gebis, R.; Klatt, G.; Janke, C.; Dekorsy, T.; Bartels, A. High-speed asynchronous optical sampling with sub-50fs time resolution. *Opt. Express* **2010**, *18*, 5974–5983.
- (8) Li, C.; Gusev, V.; Dekorsy, T.; Hettich, M. All optical control of comb-like coherent acoustic phonons in multiple quantum well structures through double-pump-pulse pump-probe experiments. *Opt. Express* **2019**, *27*, 18706–18730.
- (9) Asahara, A.; Arai, Y.; Saito, T.; Ishi-Hayase, J.; Akahane, K.; Minoshima, K. Dual-comb-based asynchronous pump-probe measurement with an ultrawide temporal dynamic range for characterization of photo-excited InAs quantum dots. *Appl. Phys. Exp.* **2020**, *13*, No. 062003.
- (10) Zhang, Y.; Wu, R.; Shahjahan, M.; Yang, C.; Pyeon, D.; Harel, E. Nanoscopic acoustic vibrational dynamics of a single virus captured

by ultrafast spectroscopy. *Proc. Natl. Acad. Sci. U.S.A.* **2025**, *122*, No. e2420428122.

(11) Han, G. R.; Jang, H.; Yoon, T. H.; Cho, M. Asynchronous and Interferometric Nonlinear Spectroscopy (AI-NS): Expanding Temporal and Spectral Horizons. *J. Phys. Chem. B* **2025**, *129*, 1891–1903.

(12) Hettich, M.; Jacob, K.; Ristow, O.; Schubert, M.; Bruchhausen, A.; Gusev, V.; Dekorsy, T. Viscoelastic properties and efficient acoustic damping in confined polymer nano-layers at GHz frequencies. *Sci. Rep.* **2016**, *6*, No. 33471.

(13) Gusev, V. E.; Ruello, P. Advances in applications of time-domain Brillouin scattering for nanoscale imaging. *Appl. Phys. Rev.* **2018**, *5*, No. 031101.

(14) Vialla, F.; Del Fatti, N. Time-Domain Investigations of Coherent Phonons in van der Waals Thin Films. *Nanomaterials* **2020**, *10*, No. 2543.

(15) Wright, C.; Hartland, G. V. Mode specific dynamics for the acoustic vibrations of a gold nanoplate. *Photoacoustics* **2023**, *30*, No. 100476.

(16) Wright, C.; Hartland, G. V. Vibrational Anharmonicity and Energy Relaxation in Nanoscale Acoustic Resonators. *Nano Lett.* **2023**, *23*, 11161–11166.

(17) Carr, A. D.; Ruppert, C.; Samusev, A. K.; Magnabosco, G.; Vogel, N.; Linnik, T. L.; Rushforth, A. W.; Bayer, M.; Scherbakov, A. V.; Akimov, A. V. Enhanced Photon–Phonon Interaction in WSe<sub>2</sub> Acoustic Nanocavities. *ACS Photonics* **2024**, *11*, 1147–1155.

(18) Huang, L. B.; Hartland, G. V.; Chu, L. Q.; Luxmi; Feenstra, R. M.; Lian, C. X.; Tahy, K.; Xing, H. L. Ultrafast Transient Absorption Microscopy Studies of Carrier Dynamics in Epitaxial Graphene. *Nano Lett.* **2010**, *10*, 1308–1313.

(19) Huang, K.-C.; McCall, J.; Wang, P.; Liao, C.-S.; Eakins, G.; Cheng, J.-X.; Yang, C. High-Speed Spectroscopic Transient Absorption Imaging of Defects in Graphene. *Nano Lett.* **2018**, *18*, 1489–1497.

(20) Kumar, N.; He, J. Q.; He, D. W.; Wang, Y. S.; Zhao, H. Charge carrier dynamics in bulk MoS<sub>2</sub> crystal studied by transient absorption microscopy. *J. Appl. Phys.* **2013**, *113*, No. 133702.

(21) Lo, S. S.; Shi, H. Y.; Huang, L. B.; Hartland, G. V. Imaging the extent of plasmon excitation in Au nanowires using pump-probe microscopy. *Opt. Lett.* **2013**, *38*, 1265–1267.

(22) Mehl, B. P.; Kirschbrown, J. R.; Gabriel, M. M.; House, R. L.; Papanikolas, J. M. Pump-Probe Microscopy: Spatially Resolved Carrier Dynamics in ZnO Rods and the Influence of Optical Cavity Resonator Modes. *J. Phys. Chem. B* **2013**, *117*, 4390–4398.

(23) Sung, J. Y.; Schnedermann, C.; Ni, L. M.; Sadhanala, A.; Chen, R. Y. S.; Cho, C.; Priest, L.; Lim, J. M.; Kim, H. K.; Monserrat, B.; Kukura, P.; Rao, A. H. Long-range ballistic propagation of carriers in methylammonium lead iodide perovskite thin films. *Nat. Phys.* **2020**, *16*, 171–176.

(24) Gabriel, M. M.; Grumstrup, E. M.; Kirschbrown, J. R.; Pinion, C. W.; Christesen, J. D.; Zigler, D. F.; Cating, E. E. M.; Cahoon, J. F.; Papanikolas, J. M. Imaging Charge Separation and Carrier Recombination in Nanowire p-i-n Junctions Using Ultrafast Microscopy. *Nano Lett.* **2014**, *14*, 3079–3087.

(25) Block, A.; Liebel, M.; Yu, R.; Spector, M.; Sivan, Y.; de Abajo, F. J. G.; van Hulst, N. F. Tracking ultrafast hot-electron diffusion in space and time by ultrafast thermomodulation microscopy. *Sci. Adv.* **2019**, *5*, No. eaav8965.

(26) Yu, K.; Devadas, M. S.; Major, T. A.; Lo, S. S.; Hartland, G. V. Surface Plasmon Polariton Propagation and Coupling in Gold Nanostructures. *J. Phys. Chem. C* **2014**, *118*, 8603–8609.

(27) Beane, G.; Yu, K.; Devkota, T.; Johns, P.; Brown, B.; Wang, G. P.; Hartland, G. Surface Plasmon Polariton Interference in Gold Nanoplates. *J. Phys. Chem. Lett.* **2017**, *8*, 4935–4941.

(28) Abbas, A.; Guillet, Y.; Rampnoux, J. M.; Rigail, P.; Mottay, E.; Audoin, B.; Dilhaire, S. Picosecond time resolved opto-acoustic imaging with 48 MHz frequency resolution. *Opt. Express* **2014**, *22*, 7831–7843.

(29) Théard, T.; Savi, E. D.; Avanesyan, S.; Chigarev, N.; Hua, Z. L.; Tournat, V.; Gusev, V. E.; Hurley, D. H.; Raetz, S. Photoacoustic 3-D

imaging of polycrystalline microstructure improved with transverse acoustic waves. *Photoacoustics* **2021**, *23*, No. 100286.

(30) Panda, D.; Nizam, M. R.; Tuff, W. J.; Wyant, C. C.; Zhukovskiy, M.; Rosenberger, M. R.; Santa, B.; Kinzel, E. C.; Hughes, R. A.; Neretina, S. Template-Confined Synthesis of Shape-Engineered Single-Crystal Gold Microplates in Lithographically-Defined Polymeric Patterns. *Adv. Funct. Mater.* **2026**, *36*, No. e76188.

(31) Trepalin, V.; Ross, N.; Shingote, A.; Ejike-Ilechukwu, K.; Ghosh, B.; Bhandari, J.; Subhra Guria, S.; Stepanov, P.; Hartland, G. V. Energy Dissipation in WSe<sub>2</sub> Opto-Acoustic Resonators. *J. Phys. Chem. Lett.* **2026**, *17*, 7079–7085.

(32) Xia, Y.; Han, Z.; Watanabe, K.; Taniguchi, T.; Shan, J.; Mak, K. F. Superconductivity in twisted bilayer WSe<sub>2</sub>. *Nature* **2025**, *637*, 833–838.

(33) Brown, B. S.; Hartland, G. V. Influence of Thermal Diffusion on the Spatial Resolution in Photothermal Microscopy. *J. Phys. Chem. C* **2022**, *126*, 3560–3568.

(34) Palummo, M.; Bernardi, M.; Grossman, J. C. Exciton Radiative Lifetimes in Two-Dimensional Transition Metal Dichalcogenides. *Nano Lett.* **2015**, *15*, 2794–2800.

(35) Rivera, P.; Schaibley, J. R.; Jones, A. M.; Ross, J. S.; Wu, S. F.; Aivazian, G.; Klement, P.; Seyler, K.; Clark, G.; Ghimire, N. J.; Yan, J. Q.; Mandrus, D. G.; Yao, W.; Xu, X. D. Observation of long-lived interlayer excitons in monolayer MoSe<sub>2</sub>-WSe<sub>2</sub> heterostructures. *Nat. Commun.* **2015**, *6*, No. 6242.

(36) Miller, B.; Steinhoff, A.; Pano, B.; Klein, J.; Jahnke, F.; Holleitner, A.; Wurstbauer, U. Long-Lived Direct and Indirect Interlayer Excitons in van der Waals Heterostructures. *Nano Lett.* **2017**, *17*, 5229–5237.

(37) Mueller, T.; Malic, E. Exciton physics and device application of two-dimensional transition metal dichalcogenide semiconductors. *npj 2D Mater. Appl.* **2018**, *2*, No. 29.

(38) Blake, P.; Hill, E. W.; Castro Neto, A. H.; Novoselov, K. S.; Jiang, D.; Yang, R.; Booth, T. J.; Geim, A. K. Making graphene visible. *Appl. Phys. Lett.* **2007**, *91*, No. 063124.

(39) Jung, I.; Pelton, M.; Piner, R.; Dikin, D. A.; Stankovich, S.; Watcharotone, S.; Hausner, M.; Ruoff, R. S. Simple Approach for High-Contrast Optical Imaging and Characterization of Graphene-Based Sheets. *Nano Lett.* **2007**, *7*, 3569–3575.

(40) Ni, Z. H.; Wang, H. M.; Kasim, J.; Fan, H. M.; Yu, T.; Wu, Y. H.; Feng, Y. P.; Shen, Z. X. Graphene Thickness Determination Using Reflection and Contrast Spectroscopy. *Nano Lett.* **2007**, *7*, 2758–2763.

(41) Jeong, T. Y.; Jin, B. M.; Rhim, S. H.; Debbichi, L.; Park, J.; Jang, Y. D.; Lee, H. R.; Chae, D.-H.; Lee, D.; Kim, Y.-H.; Jung, S.; Yee, K. J. Coherent Lattice Vibrations in Mono- and Few-Layer WSe<sub>2</sub>. *ACS Nano* **2016**, *10*, 5560–5566.

(42) Chen, X.; Wang, L.; Wang, H.-Y.; Wang, X.-P.; Luo, Y.; Sun, H.-B. Electronic structure evolution and exciton energy shifting dynamics in WSe<sub>2</sub>: from monolayer to bulk. *J. Phys. D: Appl. Phys.* **2021**, *54*, No. 354002.

(43) Ezgi Eroglu, Z.; Contreras, D.; Bahrami, P.; Azam, N.; Mahjouri-Samani, M.; Boulesbaa, A. Filling Exciton Trap-States in Two-Dimensional Tungsten Disulfide (WS<sub>2</sub>) and Diselenide (WSe<sub>2</sub>) Monolayers. *Nanomaterials* **2021**, *11*, No. 770.

(44) Rieland, L.; Wagner, J.; Bernhardt, R.; Wang, T.; Abdul-Aziz, O.; Stein, P.; Pogna, E. A. A.; Dal Conte, S.; Cerullo, G.; Hedayat, H.; van Loosdrecht, P. H. M. Ultrafast Optical Control of Exciton Diffusion in WSe<sub>2</sub>/Graphene Heterostructures Revealed by Heterodyne Transient Grating Spectroscopy. *Nano Lett.* **2024**, *24*, 9824–9831.

(45) Gu, H.; Song, B.; Fang, M.; Hong, Y.; Chen, X.; Jiang, H.; Ren, W.; Liu, S. Layer-dependent dielectric and optical properties of centimeter-scale 2D WSe<sub>2</sub>: evolution from a single layer to few layers. *Nanoscale* **2019**, *11*, 22762–22771.

(46) Munkhbat, B.; Wróbel, P.; Antosiewicz, T. J.; Shegai, T. O. Optical Constants of Several Multilayer Transition Metal Dichalcogenides Measured by Spectroscopic Ellipsometry in the 300–1700

nm Range: High Index, Anisotropy, and Hyperbolicity. *ACS Photonics* **2022**, *9*, 2398–2407.

(47) Liu, H.-L.; Yang, T.; Chen, J.-H.; Chen, H.-W.; Guo, H.; Saito, R.; Li, M.-Y.; Li, L.-J. Temperature-dependent optical constants of monolayer MoS<sub>2</sub>, MoSe<sub>2</sub>, WS<sub>2</sub>, and WSe<sub>2</sub>: spectroscopic ellipsometry and first-principles calculations. *Sci. Rep.* **2020**, *10*, No. 15282.

(48) Weaver, H. L.; Went, C. M.; Wong, J.; Jasrasaria, D.; Rabani, E.; Atwater, H. A.; Ginsberg, N. S. Detecting, Distinguishing, and Spatiotemporally Tracking Photogenerated Charge and Heat at the Nanoscale. *ACS Nano* **2023**, *17*, 19011–19021.

(49) Ginsberg, N. S.; Tisdale, W. A. Spatially Resolved Photo-generated Exciton and Charge Transport in Emerging Semiconductors. *Annu. Rev. Phys. Chem.* **2020**, *71*, 1–30.

(50) Delor, M.; Weaver, H. L.; Yu, Q.; Ginsberg, N. S. Imaging material functionality through three-dimensional nanoscale tracking of energy flow. *Nat. Mater.* **2020**, *19*, 56–62.

(51) Eichler, H. J.; Massmann, F.; Biselli, E.; Richter, K.; Glotz, M.; Konetzke, L.; Yang, X. Laser-induced free-carrier and temperature gratings in silicon. *Phys. Rev. B* **1987**, *36*, 3247–3253.

(52) Rosling, M.; Bleichner, H.; Jonsson, P.; Nordlander, E. The ambipolar diffusion coefficient in silicon: Dependence on excess-carrier concentration and temperature. *J. Appl. Phys.* **1994**, *76*, 2855–2859.

(53) Mouskeftaras, A.; Chanal, M.; Chambonneau, M.; Clady, R.; Utéza, O.; Grojo, D. Direct measurement of ambipolar diffusion in bulk silicon by ultrafast infrared imaging of laser-induced microplasmas. *Appl. Phys. Lett.* **2016**, *108*, No. 041107.

(54) Yu, K.; Devadas, M. S.; Major, T. A.; Lo, S. S.; Hartland, G. V. Surface Plasmon Polariton Propagation and Coupling in Gold Nanostructures. *J. Phys. Chem. C* **2014**, *118*, 8603–8609.

(55) Panais, C.; Rouxel, R.; Lascoux, N.; Marguet, S.; Maioli, P.; Banfi, F.; Vallée, F.; Del Fatti, N.; Crut, A. Cooling Dynamics of Individual Gold Nanodisks Deposited on Thick Substrates and Nanometric Membranes. *J. Phys. Chem. Lett.* **2023**, *14*, 5343–5352.