IL NUOVO CIMENTO **46 C** (2023) 114
DOI 10.1393/ncc/i2023-23114-x

COMMUNICATIONS: SIF Congress 2022

Studying ultrafast carrier diffusion in spatially heterogeneous samples with transient holographic microscopy

F. VISENTIN([1])([*]), M. HÖRMANN([1]), G. CERULLO([1])([2]) and F. V. A. CAMARGO([2])

([1]) *Dipartimento di Fisica, Politecnico di Milano - Milano, Italy*
([2]) *Istituto di Fotonica e Nanotecnologie, CNR - Milano, Italy*

received 1 February 2023

Summary. — Transient absorption microscopy enables the observation of ultrafast excited-state dynamics with spatial resolution. Conventional implementations are technologically limited to small fields of view around a single diffraction-limited spot, offering no statistical information on the photophysics of the sample. We recently used off-axis holography to demonstrate an all-optical lock-in camera enabling widefield transient imaging at arbitrary repetition rate. Here, we use a structured excitation pattern comprised of hundreds of diffraction-limited spots as an effective way to study diffusion of carriers in semiconductors, whilst probing the sample's heterogeneity over an area of ($\approx 60\,\mu\text{m}^2$), more than 100 times larger than current techniques. We envision that this technique can be used to provide a much more complete picture of photophysical processes in heterogeneous samples.

1. – Introduction

Offering femtosecond temporal resolution and sub-μm spatial resolution, ultrafast transient absorption (TA) microscopy is as a key tool to study charge carrier transport properties in organic and inorganic semiconductors [1]. Typically, a tightly focused pump photoexcites a diffraction-limited spot on the sample, while a scanning or widefield probe monitors the response of the sample around that spot. However, due to the limited frame rates of large camera sensors, most TA microscopes use confocal designs with single-pixel detectors and raster scanning [2]. Widefield cameras have been used, but acquisition of several laser shots in each frame inevitably compromises the signal-to-noise ratio [3,4]. As a consequence, conventional TA microsopy techniques are limited to sample areas of a few squared micrometres, hampering the study of large-scale heterogeneities of the sample in a single transient image. Recently, we introduced ultrafast holographic transient (UHT)

([*]) E-mail: federico.visentin@polimi.it

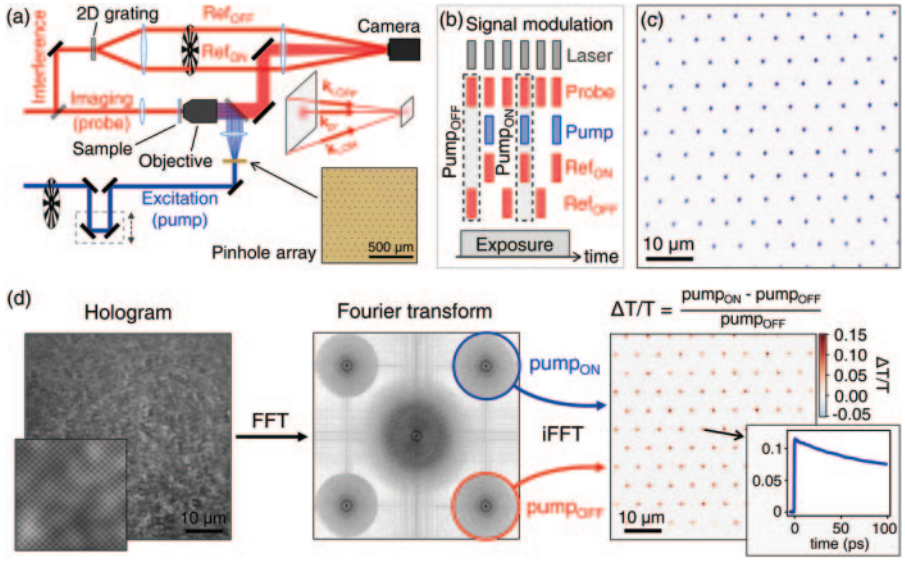

Fig. 1. – Holographic recording and image processing. (a) Experimental setup. (b) Signal modulation. (c) Pump excitation pattern measured placing a mirror at the sample position. (d) Signal demodulation through Fourier filtering in k-space.

microscopy, using off-axis holography to create an all-optical lock-in camera capable of widefield transient imaging at arbitrary repetition rates [5]. Here, we combine the large field of view enabled by the UHT microscope with a structured illumination pump scheme to create a photoexcitation pattern of regularly spaced diffraction-limited pump spots at the sample. We collect transient data in metal-organic perovskites at and around over 100 excitation spots covering a field of view of $(\approx 60\,\mu\text{m})^2$, one hundred times bigger than most current techniques.

2. – Ultrafast holographic transient microscopy

2˙1. *All-optical digital lock-in camera.* – Figure 1(a) shows a sketch of the UHT microscope, which has been described in detail before [5,6]. Briefly, it can be divided into three sections: excitation, imaging and interference. The imaging part consists of a standard widefield microscope using the probe pulses for illumination. To recover the TA signal, the pump (excitation) beam is modulated at half the repetition rate of the probe beam by a mechanical chopper. Due to the limited frame rate of large camera sensors, this imaging section is not sufficient to perform widefield transient imaging at high (>10 kHz) laser repetition rates. The UHT microscope overcomes this limit by exploiting multiplexed off-axis holography: two reference pulses are generated by diffracting a fraction of the probe intensity with a 2D diffraction grating and selecting two of the first orders of diffraction. These are then relay-imaged onto the camera where the interference with the probe beam takes place to generate the hologram. Due to the off-axis geometry, the two reference waves have different wavevectors, which results in a shift of the interference terms in k-space. The reference beams are modulated according to the scheme of fig. 1(b) such that one is present only when the pump illuminates the sample, while the other is present only when the pump is blocked. In this way, the information on pumped and

unpumped sample is encoded in two distinct regions of the spatial frequency domain, and the widefield transient images are then accessible through Fourier filtering in k-space, as shown in fig. 1(d). The simultaneous acquisition of pump-on and pump-off images allows the choice of arbitrary demodulation frequencies and signal integration times, with only the latter being dependent on the camera frame rate. Thus, the UHT microscope acts as an all-optical widefield digital lock-in camera, with the advantage of allowing a direct demodulation of the entire 2D image in a single exposure. Moreover, since any non-shot noise source is the same for both pump-on and pump-off images, the resulting transient images show signal fluctuations close to the shot noise limit [5]. Further, the holographic nature of the technique recovers both amplitude and phase of the signal, which allows digital post-acquisition processing of the image, such as computational focusing, making this a quasi-3D technique both for transient and static signals [6].

2˙2. *Experimental setup.* – Spectrally tunable probe pulses are generated by a home-built noncollinear optical parametric amplifier (NOPA), pumped by a 2 kHz, 100 fs amplified Ti:Sapphire laser system (Libra 2, Coherent), as described in ref. [7]. The 400 nm pump-pulse is directly obtained by frequency doubling the laser output and modulated at 1 kHz with a mechanical chopper. To study carrier diffusion over a wide sample area, the pump beam is passed through a pinhole array made of a thin film of gold with 10-μm holes arranged according to a hexagonal lattice of spacing 80 μm, and imaged onto the sample with a demagnification of 13.9 to obtain the excitation pattern of fig. 1(c). The probe is focused onto the sample to cover the whole field of view. A microscope objective (NA = 0.8; UPLXAPO20X, Olympus) images the sample onto a CMOS camera (Basler ace acA720–520 um, Basler AG) with a nominal magnification of 67, recording 540×540 pixel holograms. The two reference pulses are obtained by passing a fraction of the probe beam through a 2D diffraction grating. Two of the first diffraction orders are spatially selected and modulated at 1 kHz with a second mechanical chopper to achieve the modulation described in fig. 1(b).

3. – Discussion

We performed widefield transient imaging of methylammonium lead bromide perovskite ($MAPbBr_3$) thin films, photoexcited above bandgap at 400 nm and probed at the band edge at 525 nm. Because of the low exciton binding energy in these materials, we are essentially probing free charges [8]. Despite the uniformity of the excitation pattern of fig. 1(c), we observed a vast heterogeneity in the transient response between different spots, as shown in fig. 2. These differences are associated to kinetic traces that are different not only between different spots, but also within the same spot (fig. 2(a)), suggesting that the underlying crystalline structure of the sample could play a relevant role in determining the photophysics. Inspection of the spots revealed that single-pixel kinetics can be grouped in 7 classes according to their behaviour in the first 2 ps (fig. 2(b)). To each class, a different colour is assigned: red-orange, decay; yellow, flat; green-blue: rise. Ultrafast diffusion of hot carriers is known in these materials [2,3], indeed figs. 2(c)–(f) show that a diffusion-like pattern is always present within a spot around the regions where a fast decay (red-orange) is observed. Moreover, the shape of the regions with the same class of kinetic features is different from spot to spot, highlighting the heterogeneity of the sample. Given that faster decays do not necessarily correspond to stronger transient signals, this should be related to the underlying crystalline structure of the material, namely defects and grain boundaries.

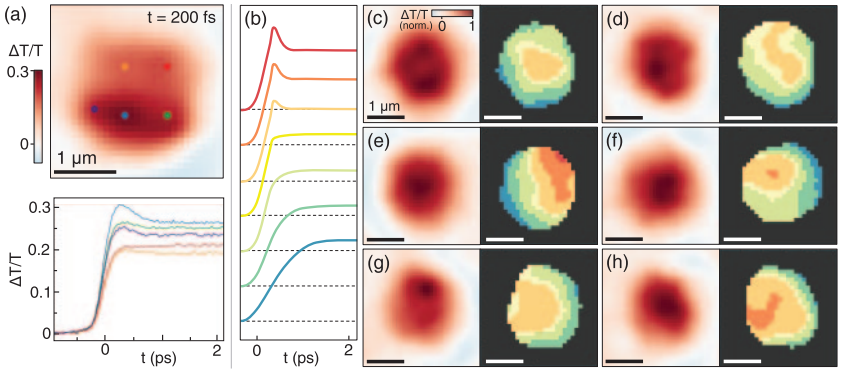

Fig. 2. – Sample heterogeneity visualised through TA kinetic traces in the first 2 ps. (a) Top: a single excited spot showing differences in signal intensity and in shape of the TA kinetics. Bottom: kinetics of five selected pixels of the top image. (b) TA kinetic traces are divided in 7 classes based on their behaviour in the first 2 ps. (c)–(h) Some representative spots with their correspondent kinetics classification.

4. – Conclusions

We have highlighted the capabilities of the UHT microscope to study ultrafast carrier diffusion around a hundred spots over a sample area 100 times larger than what is possible with current TA microscopy techniques, assessing the spatial heterogeneity of the sample within a single measurement. Expanding the UHT microscope to Fourier-transform hyperspectral imaging [9] will enable to decouple spectral and spatial diffusion processes, providing a complete picture of the material heterogeneity. Moreover, the large number of spots could be used to perform a statistical analysis of the diffusion properties, or the spots could be averaged to significantly improve the signal-to-noise ratio and reduce measurement times. This paves the way to a systematic application of the technique to study carrier and exciton diffusion in several new opto-electronic materials.

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The authors thank A. Zanetta and G. Grancini for preparing the samples, J. Osmond for making the pinhole array, and M. Liebel and N. F. van Hulst for the useful discussions. FV and GC acknowledge funding from HORIZON-EIC-2021-PATHFINDEROPEN-01 project "TROPHY" (Grant agreement No. 101047137). MH and GC acknowledge funding from the Marie Skłodowska-Curie project 812992 "MUSIQ".

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