Ultrafast control of exciton dynamics by optically-induced thermionic carrier injection in a metal-semiconductor heterojunction

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ABSTRACT

Interface effects in metals-semiconductors heterojunctions are subject of intense research due to the possibility to exploit the synergy between their electronic and optical properties in next-generation opto-electronic devices. In this framework, understanding the carrier dynamics at the metal-semiconductor interface, as well as achieving a coherent control of charge and energy transfer in metal-semiconductor heterostructures, are crucial and yet quite unexplored aspects. Here, we experimentally show that thermionically injected carriers from a gold substrate can drastically affect the dynamics of excited carriers in bulk WS_2. By employing a pump-push-probe scheme, where a push pulse excites direct transitions in the WS_2, and another delayed pump pulse induces thermionic injection of carriers from the gold substrate into the semiconductor, we can control both the formation and annihilation of excitons. Our findings might foster the development of novel opto-electronic approaches to control charge dynamics using light at ultrafast timescales.

Keywords: Exciton dynamics, Thermionic carrier injection, Metal-semiconductor heterojunction, Transition metal dichalcogenides, Ultrafast dynamics, Hot carriers, Pump-push-probe spectroscopy, van der Waals materials

1. INTRODUCTION

Light-driven electronics represents a great promise in overcoming the fundamental limits of standard electronics, since controlling electrons using light is at the same time less dissipative and much faster. Examples on how photonics, the science of light, can enable real life applications based on advanced materials and interfaces, has been reported in the past years, for instance for sensing[1–6], photocatalysis and spectroscopy[7–15], as well as data storage and processing[16] and quantum technologies[17]. In this context, it is fundamental to unveil and understand light-matter interactions in novel materials able to combine both electronic and optical properties and, consequently, to work at significantly higher speeds than electronics[18,19]. After the development of femtosecond lasers for the generation of ultrashort light pulses[20,21], it became clear that we can use such technology to drive ultrafast electronic processes at the nanoscale, including plasmonic excitations[22–28]. In this context, heterojunctions of metals and dielectric materials allow a lot of possibilities for the manipulation and exploitation of light-matter interactions, including ultrafast hot electrons dynamics, magneto-optical effects and nonlinear optical processes[18,29–38]. In particular, if the dielectric material is replaced by a semiconducting transition metal dichalcogenide (TMD), we can further boost the control of nanoscale optical excitations[39–42], including plasmonic-induced charge injection[43–48], as well as enhance charge dynamics in transistors[49] and photovoltaic devices[50].

Excited electrons and holes in TMDs exhibit enhanced Coulomb interactions in both monolayer and bulk (> 5 layers) forms[51], leading to room-temperature stable excitons, which dominate the optical and charge transport properties in these materials. Moreover, TMDs form clean and sharp interfaces with other materials[52], and this feature makes them ideal candidates for opto-electronic applications where high-quality interfaces are essential. Finally, TMDs offer a superior alternative to other semiconductors, as TMD/metal interfaces show weak Fermi-level pinning[53]. For these reasons, the

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exploitation of TMDs for opto-electronics is the subject of current intense research[54] where different degrees of freedom, such as manipulation of the dielectric environment[55] or exciton-plasmon interaction [47], have been studied so far. As well, the ultrafast charge dynamics in layered TMDs have been the focus of recent studies[56–58].

Here, we show a different perspective by studying the interplay between thermionic carrier injection and exciton dynamics at a van der Waals semiconductor/metal interface in view of future applications which exploits the ultrafast opto-electronic properties of TMDs. It has been shown theoretically that an excess of free electrons in the conduction band of TMDs compared to the density of free holes affects the probability to form neutral and charged excitons, i.e. trions[59]. Also, experiments showing that an excess of electrons in the conduction band due to n-doping modulate the excitonic absorption have been reported[60]. Furthermore, recent studies revealed that at WS_2/semimetal heterojunctions hot carriers injected from the semimetal into a TMD can affect the exciton formation dynamics by comparing the transient signal of pump-probe experiments for pumping above and below the optical bandgap of the TMD[61–63]. In our case, we designed an experiment to tune the effect of mutual interaction between injected and excited charge carriers on the transient signal in the absorption line of the exciton. We measure the ultrafast transient response of the heterojunction employing a three-pulse pump-push-probe (PPP) configuration, which enables us to disentangle the effect of thermionic carriers injection from the metallic substrate, from the direct excitations in the semiconductor, thus controlling the latter process through the former

2. MATERIALS AND METHODS

The TMD employed in our study is tungsten disulfide (WS_2), a promising material for applications given its superior charge transport performance compared to other TMDs[64]. It is also worth noticing that it displays a single and very strong primary exciton feature which dominates the optical spectrum even in the bulk form and at room temperature. In bulk WS_2, the A-exciton exhibits a binding energy of about 50 meV, and an electronic band gap at the K-point of 2.1 eV[51,65]. We chose to work on bulk WS_2 instead of monolayer due to the higher absorption as well as lower contact resistance at the TMD/metal interface[55]. After optical excitation, the ultrafast dynamics in inorganic semiconductors are dominated by carrier-carrier (c-c) scattering, that involves electron-electron, electron-hole and hole-hole scattering, promoting exciton formation, which typically happens below one ps[58]. For the metal we employ gold, since it displays a large work function (WF) of 5.1 eV, thus leading to a lower Fermi level pinning effect and oxidation that otherwise would introduce additional resistance during the charge injection process we want to study[66]. Figure 1a shows the steady state spectra of WS_2/Au (red curve – 'pump blocked') in reflection and transmission. The dip at 618 nm (2.01 eV) corresponds to the absorption of the A-exciton. From the spectral position of the etalon mode at 730 nm (1.70 eV), due mainly to the presence of gold as substrate, we can determine the thickness of the WS_2 flake, which is about 20 nm[42]. In our experiments, we focus on the neutral A-exciton absorption spectral region, thus detecting the probe signal by using a band-pass filter centered at 610 nm (2.03 eV) with a spectral width of 10 nm. The WS_2 sample is directly exfoliated on Au (Figure 1b), leading to weak electronic coupling. This results in the formation of a Schottky junction[67] with distribution of metal electronic states and band bending in the WS_2[66] in proximity of the interface. In our case, an important parameter affecting the contact resistance is the so called Schottky barrier height (SBH), which is the potential barrier that the hot carriers need to overcome in order to be injected from the gold into the semiconductor. For the WS_2/Au junction the SBH is approximately 1 eV[66]. To ensure a flat surface of the gold back reflector rather than the rough surface of the evaporated Au, an epoxy-based peeling procedure was applied to the 100 nm-thick Au film evaporated on a clean polished Si wafer (parent wafer) using an e-beam evaporator (Kurt J. Lesker PVD 75). A piece of silicon wafer (transfer wafer) was glued to the Au film using a thin layer of thermal epoxy (Epo-Tek 375, Epoxy Technology) and then peeled upwards after the epoxy layer achieves its final hardness (curing), resulting in stripping of the Au film from the parent wafer. WS_2 was mechanically exfoliated from bulk crystal (HQ-graphene) using Scotch Tape and transferred onto the Au substrate.

In the PPP experiments (see Figure 2), we generated the second harmonic of a Yb:KGW amplified laser, operating at 50 kHz repetition rate, to produce pulses centered at 515 nm (2.4 eV), with a duration of 150 fs, as a push pulse, whose fluence was set to 200 $\mu J/cm^2$. This fluence excites an electron-hole density on the order of 10^{13} cm^{-2} on the surface layer of the WS_2 sample, which is two orders of magnitude higher than in other studies on ultrafast dynamics in TMDs[56–58]. Since the aim of this work is to study the effect of injected carriers on exciton dynamics, a large cross section between the injected and directly excited charge carriers can be realized with a high density of excited carriers. This excitation density has been chosen since it is below the regime where the excitons would be ionized due to band gap renormalization, where the transient vanishing of the excitonic resonance in the range of few hundreds of fs after

excitation is identified as a hallmark of this regime[68]. The pulse duration of the fundamental (pump pulse) at 1030 nm (1.2 eV) was 220 fs. In contrast to our previous study, where we were mainly interested in understanding the thermionic carriers injection effect on the exciton formation[19], in the present work this pulse is coming after the push pulse, since here we aim to understand effects of thermionic carriers injections on a system where the excitons are already formed. The first pulse arriving at the interface is the "push" pulse, and it is the previously mentioned second harmonic at 515 nm (2.4 eV) with a fluence of 200 mJ/cm^2. Thus, it has sufficient photon energy to excite an electron-hole plasma in the WS_2. The subsequent pulse, referred here as "pump", is the fundamental wavelength of the laser amplifier at 1030 nm (1.2 eV), with a fluence of 1.7 mJ/cm^2 and a temporal duration of 220 fs. The purpose of this pulse is to increase the electronic temperature of gold and promote the thermionic injection of electrons into the WS_2[19]. With a photon energy of 1.2 eV, this pulse cannot directly excite carriers in the semiconductor. Furthermore, we do not observe an ionization of the A-exciton due to thermionically injected electrons. Also, the contribution of two-photon absorption is negligible since the signal scales linearly with the fluence ranging from 0.8 mJ/cm^2 to 7.2 mJ/cm^2, as previously demonstrated[19].

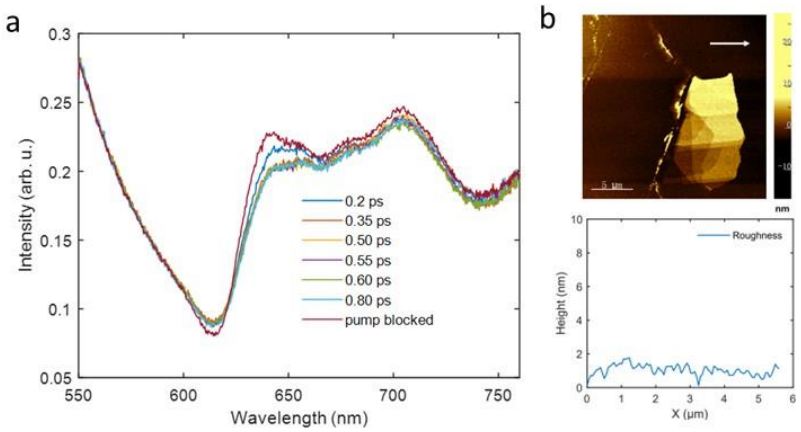

Figure 1 – (a) Absorption spectra of WS_2/Au in push-probe experiments (without pump pulse) at different push-probe delays. (b) AFM measurement of gold substrate: amplitude image (upper panel) and roughness (lower panel).

As a probe pulse we used visible white light generated by the fundamental laser pulses in a YAG crystal with a fluence of about 40 μJ/cm^2. Due to the narrowband detection, temporal compression of the probe pulse is not necessary. The temporal overlap between pump and probe $t_2 = 0$ is defined as the time when the normalized signal is equal to 0.5. The temporal overlap between pump and push $t_1 = 0$ was determined by generating a nonlinear optical signal between the two pulses. Modulation of the exciting pulse (515 nm) was achieved with a Pockels cell. The sensitivity of our setup allows to detect a variation of the transient signal given a root-mean-square of the noise floor on the order 10^{-4} to 10^{-5}.

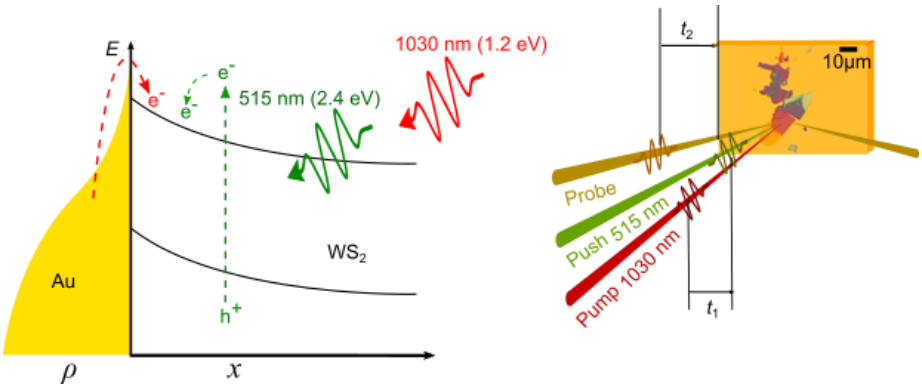

Figure 2 – Left panel: sketch of the experimental approach used in our work. A first push pulse excites electrons from the valence band in WS_2 to the conduction band, and exciton (electron-hole pairs) are formed. After this first pulse, a second (pump) pulse (red color) comes and start a process in gold where hot carriers are injected into the semiconductor. Right panel: sketch of the real experiment with an optical microscopy image of the sample measured. The flake lateral dimension is around 10 μm.

3. RESULTS AND DISCUSSION

The measured spectra of our WS_2/Au samples for push-probe delays (t_2) in the range of 0.2 ps to 0.8 ps (Figure 1a) show that the absorption associated with the A-exciton does not disappear for a fluence of 200 μJ/cm^2, which implies that the transition from an excitonic to a fully plasma dominated regime does not take place in our case. In case of strong interaction between the injected carriers from Au and the excited carriers in WS_2, it is reasonable to expect a significant change in the excited carrier dynamics especially when the ratio between the density of injected and excited carriers is varied. As shown theoretically in Ref. [59], the probability to form excitons in TMDs is modulated as a result of varying the density ratio between electrons in the conduction band and holes in the valence band. Therefore, we expect a modulation of the ultrafast dynamics in the absorption line of the A-exciton by varying this carrier ratio.

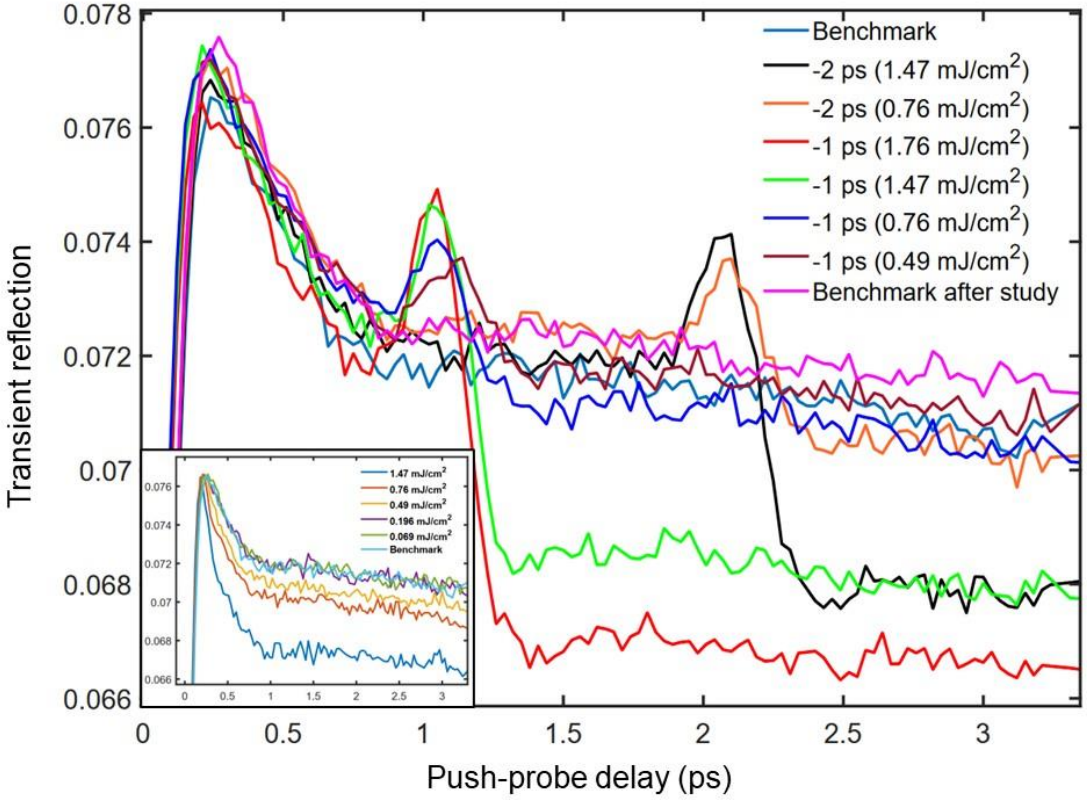

Figure 3 – PPP experiment displaying the transient reflection signal at different delays between pump and push pulses. The pump pulse arrives after the push pulse has excited carriers in the semiconductor, so after the excitons have been formed.

The introduction of an additional pump pulse with photon energy below the electronic bandgap of the WS_2 is essential as it injects excess charges in the WS_2. Furthermore, our PPP technique enables us to change the ratio between injected and excited charges by changing the fluence or by adding a temporal delay between the pump and push pulse (see for instance the inset in Figure 3, where we varied the pump fluence at t_1 = 0 ps, that is at the overlap between pump and push pulses). It is important to note that changes of this ratio imply that we can explore a different environment for c-c scattering in WS_2 which would affect the dynamics of processes occurring after exciton formation. In Figure 3 we show the transient reflection of our sample when the pump pulse excites the sample after 1 and 2 ps the arrival of the push pulse for different fluence values. As it can be inferred, after the push pulse has triggered the formation of excitons, hot carriers from gold start to trigger a process where the exciton population is reduced (compare the transient reflection signal for different fluences at a fixed pump-push delay time). This observation, in combination with the fact that exciton formation is accelerated at the overlap between pump and push pulses (see inset in Figure 3), confirms that optically pumped thermionic carrier injection represents a valid way to affect both excitons formation dynamics and their annihilation. A possible drawback of our approach is that the first push pulse might excite hot carriers also in gold, thus

in the first process is difficult to disentangle the effects of directly excited carriers in WS_2 and thermionically injected carriers, as proved by a simple pump-probe experiment on the same sample in comparison with a simple semiconductor-insulator system[19]. Nevertheless, electron dynamics due to gold is decaying very fast (within few hundreds of fs), so in the current experiment we can reasonably expect that the system, in particular at the metal-semiconductor interface, is mainly dominated by excitons population dynamics.

4. CONCLUSIONS

We used a pump-push-probe scheme to explore thermionic carrier injection effects at a metal-semiconductor interface by measuring the transient signal associated with the A-exciton relaxation dynamics in the semiconductor. Different dynamics are observed by varying the time delay between pump and push pulses, thus enabling to actively modulate the fast decay of the excitons population. The effect of optically excited carriers from gold induces a change in the rate of c-c scattering in WS_2 and consequently modifies the dielectric environment and the probability to form/destroy excitons and/or charged excitons (i.e., trions), intrinsically affecting the overall charge dynamics in the semiconductor. Interestingly, one effect that was observed in our experiments and that can be attributed solely to the effect of charge injection is a qualitative tendency for the rise time to decrease as the pump fluence increases, while the maximum transient signal amplitude remains unchanged. To the best of our knowledge this effect, which turns out to be independent of the ratio between injected and excited charges, has not been predicted by any theoretical model. Our findings introduce an alternative approach to couple opto-electronic properties at a metal-semiconductor interface by controlling and exciton dynamics through electron injection across the Schottky barrier induced by an optical pulse. We foresee a potential impact of our studies on research fields that target the exploitation of ultrafast opto-electronic processes.

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