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Contact morphology and revisited photocurrent dynamics in monolayer MoS₂Eric Parzinger^{1,2}, Martin Hetzl^{1,2}, Ursula Wurstbauer^{1,2} and Alexander W. Holleitner^{1,2}

Two-dimensional (2D) layered transition metal dichalcogenides (TMDs) have emerged as promising materials for electronic, optoelectronic, and valleytronic applications. Recent work suggests drastic changes of the band gap and exciton binding energies of photo-excited TMDs with ultrafast non-radiative relaxation processes effectively heating the crystal lattice. Such phenomena have not been considered in the context of optoelectronic devices yet. We resolve corresponding ultrafast photoconductance dynamics within monolayer MoS₂. The data suggest that a bolometric contribution as well as a defect-related conductance dominate the overall photoconductance. We further reveal that a focused laser illumination, as is used in many standard optoelectronic measurements of MoS₂, can modify and anneal the morphology of metal contacts. We show that a junction evolves with lateral built-in electric fields, although Raman spectra and photoluminescence spectra indicate no significant changes, such as a crystal phase transition. We highlight how such optimized devices can drive ultrafast electromagnetic signals in on-chip high-frequency and THz circuits.

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INTRODUCTION

Future applications of transition metal dichalcogenides (TMDs) rely on the fabrication of good and well-defined contacts.^{1–24} Although a lot of progress has been made in the fabrication of metal contacts with reduced contact resistance,^{3,6,7,10,25,26} the corresponding impact on optoelectronic phenomena in TMDs is not yet fully understood.^{4,6} In fact, low resistant contacts remain still the key bottleneck for the realization of a high device performance, and they are especially interesting for optoelectronic devices to avoid depletion regions at the contacts. In general, a combination of top and edge contact is used to describe the morphology of contacts to TMDs.⁶ The top contact is formed either by a van der Waals gap between metal and the TMD-crystal or by the creation of covalent bonds to the two-dimensional semiconductor, leading to Fermi level pinning^{7,25} or the metallization^{6,25} of the TMD in the contact region. As for pure edge contacts, the fabrication turns out to be rather difficult for obvious reasons and so far, has only been reported for graphene.²⁷ Thus, understanding the interfacial properties of the metal-TMD interface, dominating for most contact geometries, is a key aspect. Considerable efforts have been made by investigating different contact metals by means of density functional theory calculations^{25,26} as well as the realization of field effect transistors (FETs) with different metals.^{3,4,7,10} These studies conclude that for monolayer MoS₂, Ti/Au contacts exhibit the least contact resistance, and they deduce a contact barrier height of ~200 meV,^{3,7,25} which is consistent with transistor curves on multi-layer MoS₂ annealed by laser irradiation.²⁸ However, the influence of the metal contact on the underlying MoS₂ remains unclear. This holds in particular, if one considers the presence of defects, such as sulfur vacancies at the basal plane of the two-dimensional (2D) material. Defects may not only cause Fermi level shifts of up to 1

eV over tens of nanometers,⁴ they also open the possibility for the formation of covalent bonds between the contact metal and the TMDs.^{6,25} Whereas covalent bonds may reduce the interface resistance, a significant impact on the Fermi level in the 2D material is expected. Recent reports show by evaluating the transfer curves of field effect transistors, that the work function of the contact metal has very weak influence on the Fermi level pinning in MoS₂.⁷ Noteworthy, the best contacts so far have been achieved by inducing a metallic phase transition within the 2D semiconductors, e.g., via a phase transition from 2H to 1T in MoS₂ FETs.⁵

The Coulomb screening in monolayer TMDs can be significantly altered by the presence of a large density of photo-generated charge carriers.^{15,29–33} In turn, it has been demonstrated that both the quasi-particle band gap and the excitonic binding energies are renormalized after a pulsed photo-excitation of the TMDs. The renormalization effects are based upon an interplay of excitation-induced dephasing, phase-space filling and the mentioned screening of Coulomb interaction in combination with ultrafast non-radiative relaxation and recombination processes.^{15,29–33} Particularly, the latter give rise to a transfer of the photo-induced excess energy to the phonon bath.^{33,34} In turn, the lattice heats up to several tens of Kelvin, and the corresponding cooling process can last for hundreds of picoseconds depending on the interfacial thermal conductance to the substrate and to the metal contacts of the TMDs.^{33,35} Generally, there have been several reports on photocurrent and photoconductance phenomena in TMDs.^{2,8,10,12,13,16,17,21} They mainly discuss the observed phenomena in terms of photo-thermoelectric and photovoltaic effects. However, the above-mentioned, drastic photo-induced ultrafast dynamics of the energy scales and local temperatures have not

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Fig. 1 Laser processing of MoS₂-on-titanium contacts. **a** Optical microscopy image (100×) of an exfoliated monolayer-flake (1 L), trilayer-flake (3 L) and bulk MoS₂-flake stamped on top of a 20-nm-thick titanium (Ti) contact. **b** Schematic side view of the Ti-contact with the MoS₂-flake on top with a focused laser beam. The laser-induced change of the work function ΔE of a monolayer MoS₂ on top of 10-nm shows a Gaussian shape with maximum of $\Delta E = -0.16$ eV. The total laser dose is 0.74 GJ cm^{-2} at $E_{\text{photon}} = 2.54 \text{ eV}$. **c** Similar laser dose pattern applied to the black dashed area in Fig. 1a at power of $\sim 1.5 \text{ mW}$. Each dot in **c** represents a laser spot position where the laser energy is applied for a certain dwell time amounting to 0.4 kJ cm^{-2} per dot. Moreover, the shaded area highlights an increased laser dose ranging from $\sim 10^4$ to $\sim 5 \times 10^4 \text{ J cm}^{-2}$. **d** Atomic force microscope (AFM) image of the dashed area in Fig. 1a after laser patterning. **e** Corresponding Kelvin probe force microscope (KPFM) image after laser patterning. The lettering pattern with an increased laser dose can be clearly recognized as an area with a lowered work function. In Fig. **c**, **d** and **e**, the solid blue (green) lines mark the 1 L (3 L) part of the MoS₂-flake on top of the Ti-contact

been considered in the discussion of photoconductance phenomena in TMDs yet.

RESULTS AND DISCUSSION

Our study is based on several tens of different monolayer MoS₂-flakes, which are micromechanically exfoliated from bulk crystals and then transferred by an all-dry viscoelastic stamping technique (cf. methods).³⁶ We utilize either Si/SiO₂ or sapphire-substrates for the different spectroscopy methods (cf. methods). Figure 1a depicts an optical image of a MoS₂-flake with varying layer thickness (monolayer-1 L, trilayer-3 L, up to bulk) which is placed on top of a 20-nm-thick Ti contact. To demonstrate the laser annealing effect (cf. Fig. 1b and methods), we focus a laser with varying dwell times onto the flake (cf. dot pattern and black lettering in Fig. 1c). Then, we perform atomic force microscopy (AFM) and Kelvin probe force microscopy (KPFM) to characterize the morphology and the work function change within the same flakes (cf. Fig. 1d, e, and methods). The impact of the laser-annealing on the work function of monolayer MoS₂ is found to be as large as $\Delta E \sim -0.16 \text{ eV}$ (lower panel of Fig. 1b, and black lettering in Fig. 1e). A comparative study on thermally annealed monolayers suggests values even up to -0.4 eV (Fig. 2a–d, and methods). By utilizing Raman and photoluminescence (PL) measurements during the laser-annealing process, we can exclude metallization or the creation of a phase transition from the 2H to the 1T or 1T' phase⁵ for monolayer MoS₂ in contact with Ti or Au as possible explanations (cf. Supplementary Fig. S1 and methods). However, we can observe an energy difference of the A_{1g} Raman

mode of contacted and non-contacted monolayer MoS₂, indicating a reduction of the electron density³⁷ under the contact region in the order of $\Delta n \approx -2.8 \cdot 10^{12} \text{ cm}^{-2}$ (cf. Supplementary Fig. S2), which is consistent with a shift of the Fermi energy of $\Delta E \approx -0.16 \text{ eV}$ assuming parabolic bands with an effective electron mass of $0.5 m_e$. Noteworthy, we find that the work function adjustment by the laser-annealing is a persistent effect. It can be observed by performing the KPFM measurements in ambient conditions one week after the actual laser-annealing. This clearly distinguishes the effect from volatile doping effects, such as the previously observed photogating³⁷ or work function modulation³⁸ of monolayer MoS₂, which are reversible processes related to adsorbed species and ambient gases. Moreover, we do not observe the work function shift for MoS₂-flakes positioned directly on Si/SiO₂ or sapphire as substrates, i.e., without metals involved (data not shown). In our understanding, the laser-annealing reduces the van der Waals gap between the contacting metal and the MoS₂ (cf. Fig. 1b), resulting in an apparent work function adjustment. We note, however, that this gap alteration must be smaller than about $\sim 1 \text{ \AA}$, because it cannot be resolved in our AFM measurements (cf. Fig. 1d).

Figure 3a summarizes the measured work function of MoS₂ before and after the annealing steps, as it is determined relative to the value of Ti in air.^{39,40} By the impact of a focused laser, we find that the work function of MoS₂ can have a local gradient of $\sim 0.16 \text{ eV}$ on $\sim 0.5 \mu\text{m}$ (cf. lower panel in Fig. 1b). This suggests that after an annealing step, horizontal Ti/MoS₂–MoS₂ junctions do not necessarily consist of a Schottky barrier.^{7,9,17,18,25,28,41} Instead, they rather comprise an effective junction with built-in electric fields

Fig. 2 Work function mapping for temperature-treated MoS₂-metal contacts and comparison to laser processing. **a** AFM image of a monolayer MoS₂-flake (marked by dotted red lines) on top of a 10-nm-thick Ti-contact (left) and a 15-nm-thick Au-contact (right). The adhesion of Au is promoted by 5 nm Ti. In the central overlap region (bright), Ti is on top of Au. The image area is 5 × 5 μm². **b** Work function profile of the MoS₂-flake along the dashed line (1) in Fig. 2a with a clear decrease of the work function after thermal annealing at 200 °C for 45 min in a vacuum of 1 mbar. Arrows indicate the downshift of the respective work function due to annealing. **c** Equivalent work function profile for the Ti-contacts and Au-contacts along the dotted line (2) in Fig. 2a with an upshift (downshift) for Ti (Au) after annealing. For initialization, the work function of Ti in air is defined to be −4.33 eV (cf. methods). **d** Laser-induced change of work function ΔE of a monolayer MoS₂ on top of 20-nm Ti-contact

due to the different doping levels (Fig. 3b–d). In this respect, 1 L MoS₂ covered by the contact metal yields a shifted and pinned Fermi-level position, while MoS₂ away from the contact is intrinsically *n*-doped,^{1,4,8} forming an effective junction with built-in electric fields close to the contact's edge.

We point out that all of our investigated optoelectronic metal/MoS₂-monolayer/metal devices (about 20 optoelectronic devices in the course of 3 years) finally turned into having a contact morphology as sketched in Fig. 3. We explain this observation by the long exposure times to a laser as is necessary for optoelectronic experiments. In other words, scanning photocurrent experiments with a focused laser spot can anneal the contacts of metal/MoS₂-monolayer/metal devices, and this annealing gives rise to a permanent renormalization of the contact energy landscape. In Fig. 1c, e, the dose depicted as “gray” in the capitalized lettering gives a threshold for the contact modification within the given experimental error. It corresponds to a laser dose of 1×10^4 kJ cm^{−2}. In other words, we observe that for the given photon energy and contact morphology, a focused illumination for ~67 s can anneal the contacts at a laser power of 1.5 mW. This dose compares well to earlier work on laser annealing on multi-layer MoS₂ transistors.²⁸ In standard scanning photocurrent experiments, certainly lower laser powers are used, although much longer exposure times are common, such that

similar doses can be reached. However, it is apparent that the annealing efficiency and threshold dose depends on the specific morphology and thickness of the contacting metal and the interface to the MoS₂ monolayer.

To resolve the impact of the annealed contacts on the optoelectronic dynamics, we present time-integrated data as well as time-resolved photocurrent data on the same 1 L MoS₂ (cf. Figs. 4, 5, and Supplementary Fig. S3). We utilize photon energies E_{photon} exceeding the ones of the so-called A-exciton and B-exciton in the MoS₂ with absorbance energies of $E_{\text{A-exciton}} = 1.89$ eV and $E_{\text{B-exciton}} = 2.03$ eV in our devices.⁴² With an absorbance of ~0.03 at $E_{\text{photon}} = 2.25$ eV (for the time-resolved data in Fig. 5) and a maximum laser fluence of 210 μJ cm^{−2}, we can estimate the initial maximum photogenerated electron-hole pair density to be in the order of $\sim 1.75 \times 10^{13}$ cm^{−2}. This charge carrier density is below the so-called Mott-threshold of an exciton-dissociation,¹⁵ but in a regime where a renormalization of both the quasi-particle band gap and the exciton binding energy occurs. The renormalizations happen on timescales as fast as femtoseconds and prevail up to several hundreds of picoseconds after the photo-excitation.^{15,29–33}

Generally, we observe that the time-resolved photocurrent signal I_{sampling} as in Fig. 5 can be separated into four components: I_1 , I_2 , I_3 , and the offset with different characteristic timescales. The

Fig. 3 Sketch of the effective band structure of a laser processed MoS₂-metal contact. **a**, Experimentally determined work functions of monolayer MoS₂ in the pristine case and after a thermal or a laser annealing step with respect to the value of Ti in air. **b**, The contact comprises Au and Ti on top of MoS₂-monolayers on a sapphire-substrate (alternatively SiO₂/Si-substrates). **c**, Band structure sketched across the contact region with E_c (E_v) the energy of the conduction (valence) band of the MoS₂-flake and E_f the Fermi energy. The laser processing downshifts E_f at the position of the metal contact. As a result, an effective junction with adjacent areas of differing Fermi levels evolves. **d**, Sketch of the resulting built-in electric field E_x at the interface between the laser-annealed contact region and pristine MoS₂

initial photocurrent response I_1 (blue in Fig. 5) has a temporal Gaussian shape with a FWHM of ~ 3 ps, which exceeds the experimental resolution of ~ 1 ps of the utilized THz-time-domain circuit.^{43,44} One possible explanation of this first contribution is the so-called photovoltaic effect, as it is termed in standard time-averaged photocurrent experiments.^{2,8,10,12,13,16,17,21} On ultrafast timescales as in Fig. 5, this photovoltaic effect translates to both, the so-called transient displacement current j_D and the lifetime-limited current $j_{lifetime}$. The former is typically written as⁴⁵

$$j_D = \epsilon_r \epsilon_0 \frac{\partial E}{\partial t} \quad (1)$$

with ϵ_r (ϵ_0) the relative (vacuum) permittivity and $\partial E/\partial t$ the ultrafast change of the local electric field E , when the laser pulse impinges on the sample. In principle, this change includes the photogeneration of charge carriers as well as the renormalization of the quasi-particle band gap and the exciton binding energy. Importantly, j_D allows to map-out the polarity of electric fields present in the investigated samples. For a positive (negative) bias voltage U_{sd} , we observe that the sign of I_1 is negative (positive) in the center of the sample (cf. top panel of Fig. 5e). Since I_1 has an opposite sign at the two contacts, this ultrafast contribution corroborates the existence of built-in electric fields at the annealed metal contacts. The “temporal duration” of j_D is given

by the dielectric response ϵ_r of the overall circuit, which is fundamentally limited by a phonon-excitation in the underlying sapphire substrate at ~ 12 THz;⁴⁴ i.e., significantly faster than the observed constant FWHM of ~ 3 ps across the whole device. This consideration brings the lifetime-limited current $j_{lifetime}$ into play⁴⁵

$$j_{lifetime} = \sigma_{eff} \cdot e^{-t/\tau_1} \cdot E \quad (2)$$

with σ_{eff} the effective conductivity of the locally photo-excited electron bath and τ_1 a corresponding lifetime. From Equation (2), we find the same sign for the built-in electric fields at the laser-annealed contacts as in the case of j_D , as it is consistent with the sketch in Fig. 3d. The notation of σ_{eff} implies that the locally excited electron bath is thermalized, as it can be assumed to occur at ~ 100 fs of femtoseconds.³³ At the utilized laser fluences of $\sim 100 \mu\text{J cm}^{-2}$ and beyond, it has been demonstrated that the non-radiative relaxation and recombination lifetimes are only a few picoseconds.³³ In turn, there is not a clear timescale separation between j_D and $j_{lifetime}$, and we interpret the observed timescale of ~ 3 ps with the non-radiative relaxation and recombination times^{33,46} and fast capture mechanisms by traps via Auger processes⁴⁷ or surface defects.⁴⁸ Consistent with this interpretation, we observe that the FWHM of I_1 increases with a lower laser fluence (data not shown).³³ Furthermore, we can neglect a photo-thermoelectric current for this first contribution I_1 , as we do not detect it for a laser excitation below the band gap of MoS₂ (cf. Supplementary Fig. S4). In other words, within the given experimental noise, I_1 seems to comprise all ultrafast non-radiative processes involving the non-equilibrium dynamics and energetics of charge carriers, which are photogenerated above band gap.

The second contribution I_2 shows a fast rise followed by an exponential decay $\propto e^{-\Delta t/\tau_2}$ with $\tau_2 \sim 100$ ps (cf. orange contribution in Fig. 5), pointing towards a lifetime-limited current as in Equation (2). Since I_2 is most pronounced at the contact regions (second panel in Fig. 5e), it also points towards the presence of electric fields as discussed for I_1 . In this respect, we associate I_2 to photoexcited carriers having an extended lifetime τ_2 . This interpretation agrees well with the timescale of an energy transfer between the electron bath and the phonon bath,³³ but also with carriers captured by defects via Auger processes and slow trap states⁴⁸ or photo-injected charge carriers in indirect-gap side valleys.⁴⁹ We note, however, that I_2 can be detected for a laser excitation below band gap as well (cf. Supplementary Fig. S4). Then, the signal is ~ 10 -fold reduced but with an equivalent timescale. In this respect, I_2 comprises a thermo-electric contribution, which is consistent with the fact that the heated electron bath can drive corresponding thermoelectric currents at the contacts’ interfaces.¹³

The third component I_3 (green in Fig. 5), differs from the previous two contributions by the clearly visible rise time τ_3^{rise} followed by a very slow decay time τ_3^{decay} . Moreover, I_3 can be observed both at the contact region ($\blacktriangleleft$) as well as in the center ($\blacklozenge$) of the monolayer MoS₂ flakes. We attribute I_3 to a bolometric effect, which is driven by a heated phonon bath. As demonstrated in Supplementary Fig. S5, the annealed samples exhibit a positive bolometric coefficient $a_{annealed}$ even for small temperature changes. Taking $a_{annealed}$ (cf. Supplementary Fig. S5) and the amplitude of I_{photo} (cf. Fig. 4), we can estimate a maximum temperature increase of the overall device to be $\Delta T \sim 60$ K. To estimate the maximum temperature increase ΔT of just the crystal lattice, we consider the specific heat capacitance of monolayer MoS₂ c_{MoS_2} and compute $\Delta T = aF/c_{MoS_2}$, where a is the absorption coefficient. For our experimental conditions, $F = 210 \mu\text{J cm}^{-2}$, $E_{photon} = 2.25$ eV, $a = 0.03$ ⁵⁰ and $c_{MoS_2} = 4.25 \cdot 10^{-8} \text{ J cm}^{-2} \text{ K}^{-1}$,⁵¹ we calculate $\Delta T \sim 150$ K. The in-plane thermal conductance of monolayer MoS₂ is rather poor and can therefore be neglected.^{51,52} Thus, we can estimate the cooling time by

Fig. 4 Time-averaged optoelectronic response in MoS₂-devices with laser processed contacts. **a** Optical microscope image (100 $\times$) of a monolayer MoS₂-flake (encompassed by solid lines) and two Ti/Au-contacts (10/300 nm) forming striplines on a sapphire substrate. **b** Reflectivity map of the investigated central area of the device with solid lines highlighting the area of the MoS₂-flake. Scale bars, 5 μm . **c** Concurrently measured map of the time-averaged photocurrent I_{photo} at $E_{\text{photon}} = 2.25$ eV, when the laser is swept across the same area as in Fig. 4b for a bias voltage of $U_{\text{sd}} = -5$ V. **d** Equivalent photocurrent map for $U_{\text{sd}} = +5$ V. **e** Time-integrated photocurrent I_{photo} for $U_{\text{sd}} = +5$ V and -5 V vs. the x -direction (perpendicular to the striplines) along the dotted-dashed lines in Fig. 4b-d. On the bottom of the figure, the reflectivity signal is shown (not to scale). Gray areas mark the position of the striplines

$\tau_c = c_{\text{MoS}_2}/G$, where G is the interfacial Kapitza conductance. However, the value for G at a van der Waals interface varies strongly between ~ 0.1 and several tens of $\text{MW m}^{-2} \text{K}^{-1}$,³³ which results in timescales ranging from ~ 10 ps to several nanoseconds. In this interpretation, τ_3^{decay} corresponds to the time it takes for the monolayer MoS₂ on top of sapphire to dissipate the heat introduced by the laser pulse. We performed a fluence dependence of the components I_3 and the offset (cf. Supplementary Fig. S6). Both I_3 and the offset increase with the laser fluence. In first approximation, both increments can be understood by an increased temperature of the phonon bath and a corresponding heat transfer to the underlying substrate. In this respect, a cooling timescale in the order of the laser repetition time ($76^{-1} \text{ MHz}^{-1} \sim 13.2$ ns) gives rise to a bolometric fraction of the offset. However, we further observe that the ratio of I_3 vs. offset also increases with the laser fluence (cf. Supplementary Fig. S6), which suggests that a significant part of the offset seems to have an additional origin with a less steep dependence on the laser fluence than I_3 . A possible explanation are optically excited, but trapped charges. Depending on the laser fluence, this charge carrier density can exceed the density of trapped charges without laser excitation in thermal equilibrium. Furthermore, upon detrapping, these charges may contribute to the current on long timescales until they eventually recombine. In this interpretation, the optically excited and trapped charge carriers are neither free carriers nor are they initially thermally generated. However, the lattice heating following the laser pulse can drive the detrapping. The latter process may produce similarities in the conductivity and the longer timescale conductivity induced by the laser versus temperature (cf. Supplementary Fig. S5 and Fig. 5e). We further note that a heated phonon bath can also contribute by a temperature-induced change of the quasi-particle band gap.³⁴ Notably, Fig. 5 demonstrates that I_3 and the offset are the dominating

optoelectronic contributions long after the initial laser pulse, and that their lateral dependences largely agree with the one of the time-integrated photocurrent signal (cf. two lower panels of Fig. 5e and Fig. 4e).

The combined observations let us conclude that scanning photocurrent experiments with a focused laser spot can anneal the contacts of metal/MoS₂-monolayer/metal devices, and this annealing gives rise to more transparent contacts which favor a bolometric response in combination with defect-related conductance effects to dominate the optoelectronic signal. The built-in electric fields at the annealed contacts additionally give rise to photovoltaic currents (I_1 and majority of I_2), which enhance the overall optoelectronic response close to the contacts. Our results are relevant to a large class of experiments on MoS₂ and 2D materials, since a focused laser spot is standard in state-of-the-art optoelectronic characterization techniques.^{2,8–14,16–18,20–22,41} Moreover, our work demonstrates how such devices can be implemented into on-chip high-frequency and THz circuits.

METHODS

Sample fabrication

For KPFM, Raman-measurements, and PL-measurements, the samples are fabricated on a 525- μm -thick p -type Si substrate with 285-nm SiO₂ layer. On top, Ti contacts with a thickness of 10 nm or Ti/Au contacts with thickness of 5 nm/15 nm are defined by standard photolithography. In a final step, the MoS₂-flakes are placed on top of the metal layer. This inverted geometry allows us to directly access the physical properties of the MoS₂-flakes by the mentioned KPFM, Raman-methodologies or PL-methodologies. The samples for temperature-dependent current-voltage (IV) traces are based on a 525- μm -thick sapphire substrate. Here, monolayers of MoS₂ are first transferred and subsequently contacted via Ti/Au contacts with a thickness of 5 nm/20 nm. For the photocurrent characterization, we utilize a 430- μm -thick sapphire substrate covered with

Fig. 5 Ultrafast optoelectronic response in two-terminal MoS₂-devices with laser processed contacts. **a** Time-resolved photocurrent $I_{\text{sampling}}(\Delta t)$ of the monolayer MoS₂-device as in Fig. 4 on a picosecond timescale at $E_{\text{photon}} = 2.25 \text{ eV}$. The laser excitation occurs at the drain contact (at position $x = 2.6 \mu\text{m}$ in Fig. 5e) with a laser spot with FWHM $\sim 2.5 \mu\text{m}$ and $U_{\text{sd}} = +5 \text{ V}$. **b** Same measurement for a timescale up to 1600 ps. **c, d** Equivalent measurements at the center of the channel ($x = 7.8 \mu\text{m}$ as in Fig. 5e). The fits to the three distinct contributions I_1 (blue), I_2 (orange) and I_3 (green) are highlighted in color. **e** The integrated area of the three contributions I_1 , I_2 , I_3 and the initial offset to the photocurrent signal vs. the position for a bias voltage of $+5 \text{ V}$ (open circles) and -5 V (filled circles). Scale bars denote the corresponding integrated amplitudes in $\text{pA}\cdot\text{ps}$. Gray areas mark the position of metal contacts

a 300-nm-thin layer of ion-implanted Si. In a first optical lithography step, an Auston-switch⁴⁵ geometry is formed via HNO₃/HF etching (cf. Supplementary Fig. S3). The remaining silicon strip serves as an on-chip photodetector (Auston-switch) as we use for ultrafast photocurrent measurements.^{43,44,53} In a second optical lithography step, we evaporate 10 nm/300 nm Ti/Au to define the contacts in form of two coplanar striplines. The striplines contact the monolayer MoS₂ and the read-out of the Auston-switch. Each individual stripline has a width of $5 \mu\text{m}$ and a distance of $10 \mu\text{m}$ in-between two coplanar ones. The MoS₂-flakes are placed at a distance of about $400 \mu\text{m}$ from the Auston-switch. The striplines have a total length exceeding 58 mm. The geometry allows for both time-integrated and time-resolved photocurrent measurements on individual MoS₂-flakes. A list of all contact thicknesses and geometries is listed in the Supplementary Table T1.

Optical microscopy

All samples are characterized by optical microscopy to investigate the layer-thickness and morphology of the individual MoS₂-flakes. Figure 1a depicts such an optical image of a MoS₂-flake with varying layer thickness placed on top of a 10-nm-thick Ti contact (on a 525- μm -thick *p*-type Si substrate with 285-nm SiO₂ layer). The monolayer, trilayer, and bulk areas have different contrast and they are marked as 1L, 3L and bulk, respectively.

Laser-annealing

We perform laser-annealing by continuously illuminating individual spots on the samples to locally introduce heat to the MoS₂-flakes on Ti (Fig. 1b). For the presented results, we use a Kr/Ar-laser with a wavelength of 488 nm, which is focused with a 100x objective onto the sample stored at $\sim 10^{-3}$ mbar. However, we note that we achieve similar results with a Ti: Sapphire laser at 780 nm. In both cases, the laser spot is scanned across the samples by the help of a x-y-z-piezo scanner (PI) with a specific dose per laser spot position. Figure 1c introduces a corresponding dose pattern as is applied to the MoS₂-flake shown in Fig. 1a. At each of the depicted positions (gray dots in Fig. 1c), the laser is focused at a dose of 0.4 kJ cm^{-2} forming a uniform grid with $1 \mu\text{m}$ spacing. Moreover, a dose gradient is superimposed to the pattern in the shape of a 'T-U-M' logo (shaded dark area in Fig. 1c). There, the dose ranges from $\sim 10^4$ to $\sim 5 \times 10^4 \text{ J cm}^{-2}$. We adjust the laser dose by varying the dwell time of each spot illuminated with a power of $\sim 1.5 \text{ mW}$. Figure 2d illustrates the measured work function shift induced by laser-annealing as a function of the overall applied laser doses. The doses are again adjusted by varying the dwell time with a laser wavelength of 488 nm, a laser power of 1.5 mW, and a spot diameter of $\sim 1 \mu\text{m}$. The corresponding KPFM traces are extracted across a laser-annealed spot and fitted by a single Gaussian (cf. Fig. 1b). In Fig. 2d, the amplitude of

the Gaussian is plotted as a measure for the maximum shift. We find that the work function shift seems to saturate at $\sim -0.2 \text{ eV}$ (red line in Fig. 2d).

Atomic force microscopy (AFM)

All AFM measurements are performed in ambient conditions using a Bruker MultiMode 8 atomic force microscope by means of PeakForce frequency-modulation with a SiN cantilever and a Si tip with a triangular shape.⁵⁴ Figure 1d depicts the AFM image of the MoS₂-flake on top of the Ti contact after laser-annealing. In the topography profile of the sample, there are no indications from the laser-annealing step. Only small protruding clusters are visible on the MoS₂-flake, which can be attributed to residual contaminations introduced by the viscoelastic stamping technique.³⁶

Kelvin probe force microscopy (KPFM)

KPFM measurements are carried out in ambient conditions using the same system as for AFM measurements in dual pass mode (lift height 50 nm).⁵⁴ Fig. 1e shows a KPFM map carried out simultaneously to the AFM results in Fig. 1d. Clearly, the 'T-U-M' pattern is visible in the KPFM signal of the MoS₂-flake placed on the thin Ti film. We detect that the work function is shifted by up to $\Delta E \approx -(0.1 - 0.2) \text{ eV}$ by the laser-annealing for the highest laser dose (Fig. 1e and lower panel in Fig. 1b). Noteworthy, we observe that the monolayer regions, which are not laser-annealed, show no difference in work function. This observation indicates that prior to laser-annealing, the van der Waals gap between the MoS₂-flake and the Ti contact is rather large, causing no significant Fermi level pinning.^{6,7} Given the fact that Ti is often used to promote the adhesion of Au contacts, the question arises if Ti or Au induces an additional work function shift of 1 L MoS₂. Therefore, we directly compare the Fermi level pinning of monolayer MoS₂ on Ti and Au before and after a thermal annealing step, as described in the next section.

Thermal annealing

Figure 2a depicts an AFM image of monolayer MoS₂ (encompassed by a red solid line) transferred on top of a 10-nm-thick Ti-contact (left) and a 15-nm-thick Au-contact (right) with a central overlap region ($\sim 1 \mu\text{m}$) of Ti on top of Au. For the Au-contact, a 5-nm-thick Ti is used below the Au, to promote the adhesion of the Au. In a second step, KPFM-traces of the monolayer MoS₂ and of the bare contact metals are extracted of the as-fabricated samples. The traces are taken along the dashed (1) and dotted (2) lines in Fig. 2a and depicted in Fig. 2b, c, respectively. For initialization of the KPFM traces, the work function of Ti in air is set to be -4.33 eV .³⁹ We are aware of possible changes due to oxidation of the Ti while exposed to ambient conditions, however, this can cause both negative and positive changes.⁴⁰ As we are focusing on the relative work function shifts, we neglect any offset of the absolute values caused by oxide formation. For

MoS₂ on Ti, we find then roughly -4.45 eV and on Au -4.25 eV, suggesting a change of the work function difference due to the different metals by ~ 0.2 eV. In average, these values agree well with the previously reported work function of monolayer MoS₂ on top of *p*-type Si by KPFM measurements also in ambient conditions.³⁸ In a third step, the sample is thermally annealed for 45 min at 200 °C and in a vacuum of ~ 1 mbar. Figure 2b, c show the corresponding KPFM traces after the thermal annealing step with the individual shift of the work functions indicated by red arrows. We find a significant difference in work function of the MoS₂-flake before and after the annealing (red arrows Fig. 2b). Within the overlap region, the 10-nm-thick Ti on top of the Au contact seems to define the work function of MoS₂. Figure 2c shows the KPFM traces of the bare metals (along the dotted line (2) in Fig. 2a). For Ti, the work function increases slightly, while for Au the work function slightly decreases (indicated by arrows). We interpret the small changes to stem from the removal of lithography residues during the thermal annealing.

Raman and PL spectroscopy

Raman and PL spectroscopy are powerful tools to probe a variety of fundamental properties of MoS₂ such as the number of layers,^{42,55} charge carrier density,³⁷ charge carrier lifetime,^{46,48,49} temperature,⁵² etc. We utilize Raman and PL spectroscopy to clearly identify the number of layers for the region of interest for all presented samples, and most importantly, we can exclude thermal degradation or an annealing induced phase transition (cf. Supplementary Fig. S1).⁵

Temperature-dependent transport spectroscopy

We take current-voltage (IV)-characteristics on annealed two-terminal metal-MoS₂-metal devices over a temperature range from 305 to 325 K (cf. Supplementary Fig. S5). In the devices, the Ti/Au-contacts (5/20 nm) cover the monolayer MoS₂-flake from the top on a sapphire-substrate (cf. Supplementary Figs. S2, S5). All IV-measurements are performed using an Oxford Instruments Optistat setup to control the temperature at a pressure of $\sim 10^{-5}$ mbar. The source-drain current is recorded utilizing a current voltage amplifier at a gain of 10^7 (cf. Supplementary Fig. S5).

Scanning photocurrent spectroscopy

Scanning photocurrent measurements are performed utilizing a Ti: Sapphire laser together with a non-linear optical fiber to photoexcite the MoS₂-flakes.^{2,8,10,12,13,16,17,21} The photon energy is set to be $E_{\text{photon}} = 2.25$ eV at a pump fluence $F = 210 \mu\text{J cm}^{-2}$, a repetition rate 76 MHz, and a pulse duration ~ 1 ps. The samples are kept at room temperature and vacuum conditions at a pressure of 10^{-5} mbar throughout the optoelectronic measurements. Before the presented photocurrent measurements, all samples are laser-annealed. We record the photocurrent signal by chopping the laser beam at a frequency of 1.7 kHz together with a lock-in detection. A current voltage amplifier is utilized to amplify the signal before lock-in detection. Figure 4a depicts an optical microscopy image of a monolayer MoS₂-flake contacted by two metal striplines. For better visibility, the MoS₂-flake is highlighted by solid white lines. For detecting photocurrent maps, the laser spot with diameter $\sim 2.5 \mu\text{m}$ is scanned across the sample while the photocurrent response as well as the reflectivity are simultaneously recorded for each spot. Figure 4b shows such a reflectivity map of the MoS₂-flake, while Fig. 4c, d show the corresponding photocurrent maps for $U_{\text{sd}} = -5$ V and $+5$ V. In the figures, the solid blue lines indicate the position of the MoS₂-flake, while the dashed gray lines highlight the positions of the contacting metal striplines. In the electronic circuitry, the right stripline represents the source contact, while the left stripline is the drain contact connected to ground. For negative (positive) bias, we observe a pronounced negative (positive) photocurrent signal close to the right (left) metal stripline (cf. Fig. 4c, d). For better visualization, Fig. 4e shows a cross-section of the photocurrent signal I_{photo} for both $U_{\text{sd}} = -5$ V and $+5$ V (along the dashed-dotted line illustrated in Fig. 4b–d). The cross-section of the reflectivity is also shown with a maximum reflectivity at the striplines (gray lines). We clearly observe that the time-integrated photocurrent is mainly generated at the contact regions but there are also finite smaller contributions in the center region. Noteworthy, for zero bias $U_{\text{sd}} = 0$ V, we observe a photocurrent response at both contacts with equal amplitude but opposite sign (data not shown). All time-averaged data are consistent with recent reports on the photoconductance and photocurrent phenomena of TMDs.^{2,8,10,12,13,16,17,21}

Ultrafast photocurrent spectroscopy

For measuring the ultrafast optoelectronic dynamics of the monolayer MoS₂-flakes, we use an on-chip THz-time domain photocurrent detection scheme based on coplanar striplines^{35,43,44,53,56,57} (cf. Supplementary Fig. S3). A short laser pulse with $E_{\text{photon}} = 2.25$ eV at a pump fluence $F = 210 \mu\text{J cm}^{-2}$, a repetition rate 76 MHz, and a pulse duration of < 1 ps is used to excite charge carriers in the MoS₂. The corresponding photocurrent response in the MoS₂-flake gives rise to electromagnetic transients in the striplines, which propagate along the striplines. We utilize a time-delayed laser pulse in combination with an Auston-switch⁴⁵ as an on-chip read-out of the electromagnetic transients. The probe laser pulse has a photon energy of 1.59 eV and a temporal width of 100 fs. The current I_{sampling} across the Auston-switch samples the electromagnetic transients on the striplines as a function of the time-delay Δt between the two laser pulses. It is directly proportional to the ultrafast photocurrents in MoS₂. Hereby, the photocurrents in MoS₂ can be measured with a (sub) picosecond time-resolution.⁴⁴ Figure 5 depicts the time-resolved photocurrent $I_{\text{sampling}}(\Delta t)$ of the monolayer MoS₂ excited at the drain contact (Fig. 5a, b) and at the center of the channel (Fig. 5c, d) on short (0–250 ps) and long (0–1600 ps) timescales. We can consistently fit the time-resolved data I_{sampling} with four components: an initial ultrafast response I_1 with a Gaussian lineshape and a FWHM ~ 3 ps (blue in Fig. 5), a second response I_2 as a Gaussian convoluted decay-function with a decay time τ_2 (orange in Fig. 5), a third comparably long lasting response I_3 with a rise time τ_3^{rise} and a decay time τ_3^{decay} (green in Fig. 5) and an offset. The offset is particularly observable for $\Delta t < 0$; shortly before the pump laser hits the MoS₂-flake in the repetitive scheme with a repetition time of $76 \text{ MHz}^{-1} \sim 13.2$ ns. Figure 5e depicts the integrated area of the fitting functions for all four contributions as a function of position along the MoS₂-flake for $U_{\text{sd}} = +5$ V (open symbols) and for $U_{\text{sd}} = -5$ V (filled symbols).

Data availability

The authors declare that [the/all other] data supporting the findings of this study are available within the paper [and its supplementary information]. Any additional data that support the findings of this study are available from the corresponding author upon reasonable request.

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AUTHOR CONTRIBUTIONS

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. E.P., U.W., and A.W.H. designed the experiments, E.P., and M.H. performed the experiments.

ADDITIONAL INFORMATION

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