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Patterned tungsten disulfide/graphene heterostructures for efficient multifunctional optoelectronic devices†

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One of the major issues in graphene-based optoelectronics is to scale-up high-performing devices. In this work, we report an original approach for the fabrication of efficient optoelectronic devices from scalable tungsten disulfide (WS₂)/graphene heterostructures. Our approach allows for the patterned growth of WS₂ on graphene and facilitates the realization of ohmic contacts. Photodetectors fabricated with WS₂ on epitaxial graphene on silicon carbide (SiC) present, when illuminated with red light, a maximum responsivity $R \sim 220 \text{ A W}^{-1}$, a detectivity $D^* \sim 2.0 \times 10^9$ Jones and a -3 dB bandwidth of 250 Hz. The retrieved detectivity is 3 orders of magnitude higher than that obtained with graphene-only devices at the same wavelength. For shorter illumination wavelengths we observe a persistent photocurrent with a nearly complete charge retention, which originates from deep trap levels in the SiC substrate. This work ultimately demonstrates that WS₂/graphene optoelectronic devices with promising performances can be obtained in a scalable manner. Furthermore, by combining wavelength-selective memory, enhanced responsivity and fast detection, this system is of interest for the implementation of 2d-based data storage devices.

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In the last decade van der Waals (vdW) materials have been in the spotlight of the scientific community, since their two-dimensional (2d) nature allows the direct exploration of electronically confined systems.¹ Graphene has been so far the most investigated 2d material and has proven to be a table top choice for fundamental research² and for applied science.³ However, its lack of bandgap has been a major issue in many applications in electronics and photonics. On the other hand, transition metal dichalcogenides (TMDs) exhibit electronic properties that are complementary to those of graphene, despite sharing the same vdW 2d nature.^{4,5} The combination in vertical heterostructures of 2d layers has paved the way for a novel device concepts.⁶ Among TMDs, one of the most interesting is tungsten disulfide (WS₂). In its monolayer form, it

shows a direct bandgap of 2.1 eV at the two non-equivalent K-points of the Brillouin zone.⁷ In the vicinity of those points it shows a remarkable splitting of the valence band due to spin-orbit coupling.^{8,9} Because of symmetry selection rules, spin polarized carriers can be promoted in the conduction band using polarized light.^{7,10,11} Its optical properties can be used for photodetection to enhance the response of graphene. Indeed, when placed in vertical heterostacks,¹² the charge transfer between WS₂ and graphene under optical pumping¹³ was reported to be fast and efficient. Recently, much effort has been devoted to create efficient hybrid TMD/graphene photodetectors.^{12,14,15} Room temperature photoresponsivities as high as $R \sim 5 \times 10^8 \text{ A W}^{-1}$ ⁶ and very fast response times (down to $\tau = 130 \text{ }\mu\text{s}$)¹⁷ have been demonstrated. Yet, one major issue that still has to be efficiently addressed is that of device scalability. Indeed, hybrid photodetectors are generally fabricated using exfoliated TMD/graphene heterostructures. Very recently, photodetectors obtained by combining one layer produced by chemical vapor deposition (CVD) with exfoliated flakes have been reported,¹⁷ but although performing well they lack in scalability. Devices fabricated with heterostacks obtained only with CVD grown materials have also been recently proposed.^{18–20} In De Fazio *et al.*, MoS₂ and graphene were separately synthesized *via* CVD and then transferred on top of each other.²⁰ This approach presents advantages such as the

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possibility to transfer the heterostack on a selected substrate – either flexible or rigid – and a high photoresponsivity up to hundreds of A W^{-1} .²⁰ However, despite being a large-scale approach, its extension to wafer-scale is complicated by the transfer step.

A possible solution to the abovementioned hurdles has been recently reported in our previous work through the demonstration of the direct scalable synthesis *via* CVD of continuous mono-bilayer WS_2 on epitaxial graphene (EG) on silicon carbide (SiC).¹¹ The WS_2 layer synthesized in this way is azimuthally aligned with the underlying EG.⁹ The precise band alignment and the atomically sharp interfaces of this heterostack are crucial to control the optoelectronic properties of the full structure. In this work, we demonstrate an entirely scalable hybrid WS_2/EG photodetector with a maximum photoresponsivity $R \sim 220 \text{ A W}^{-1}$ under continuous-wave illumination and a -3 dB bandwidth of 250 Hz . The photodetectors also display wavelength-dependent persistent photoconductivity (PPC). The devices were realized with a novel approach for the patterned growth of WS_2 on EG, so that WS_2 is present only in the active areas for photodetection and the underneath graphene is accessible to metal deposition of ohmic contacts.

Indeed, contacting the WS_2 directly would generate a Schottky barrier.²¹ This approach allows minimizing the contact resistance and thus improving the photodetection efficiency.^{12,15,22}

Methods

Synthesis and patterned masking of graphene

EG was grown on nominally on-axis high purity semi-insulating (HPSI) 4H-SiC(0001) substrates (CREE, Inc.) by adapting the approach reported by Emtsev and coworkers²³ in an Aixtron HT-BM reaction chamber.²⁴ Before proceeding with WS_2 growth, the areas of graphene where contacts shall be subsequently deposited were masked by evaporating 100 nm of gold (Au) (Fig. 1(a)). Au is a highly suitable mask material, because it can sustain high temperatures and it is inert to sulfur (S) atmosphere,²⁵ therefore remaining unaffected during the growth process. The Au mask was obtained using a standard procedure: graphene coating with poly(methyl methacrylate) (PMMA) resist, followed by electron beam lithography (EBL), thermal evaporation of Au and lift-off. It is important to mention that the same results, also in terms of graphene/con-

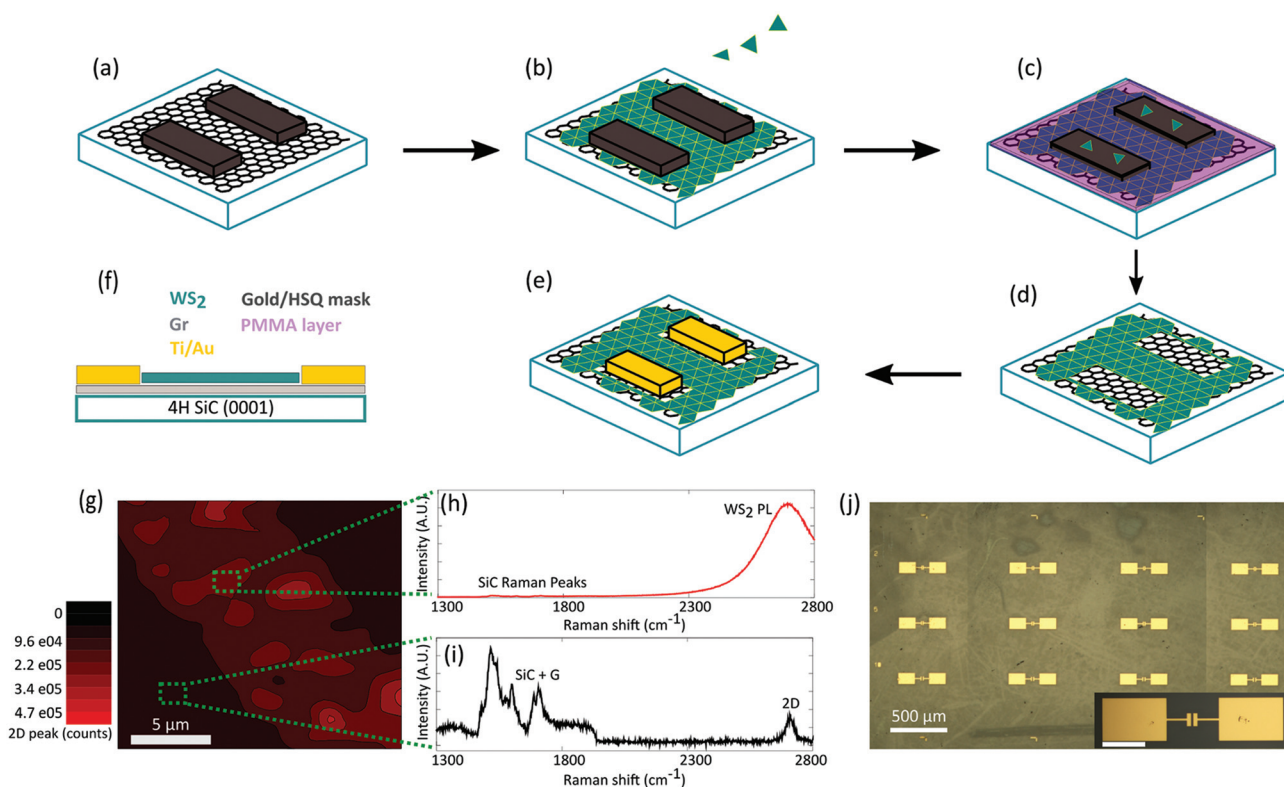


Fig. 1 (a) A mask, either Au or HSQ, is deposited on the graphene substrate to prevent the formation of WS_2 on selected areas, which allows to (b) obtain full coverage of WS_2 outside the mask by the deposition technique described in the text. (c) PMMA is spin coated and patterned to remove the WS_2 crystals on top of the mask. (d) The mask is removed either with KI, I₂ solution, for Au or HF solution for HSQ. This leaves a pattern behind, on which the contacts can be deposited (e). (f) Legend of the colors used in panels (a)–(e) and side-view of the geometry of the device. (g) Raman/PL map of the active channel with WS_2 and graphene and of the contact area with graphene only. The map shows the integrated intensity in the range 2600 cm^{-1} and 2800 cm^{-1} , in which both the PL of WS_2 and graphene 2D peak fall. (h–i) Representative $\text{WS}_2/\text{graphene}$ (h) and graphene only spectra (i). (j) Optical image of a set of devices. The optical contrast observable in the form of “scratches and patches” is due to the backside of the sample, being semi-insulating SiC transparent. Inset showing a zoom-in over device contacts (scale bar $100 \mu\text{m}$).



lysis and the electrical characteristics of the device suggest that our fabrication process results in a clean interface between the graphene and the metal contacts.

As the whole patterning and device fabrication processes can also be performed *via* mask-aligner optical lithography, the reported method can be readily extended to wafer-scale.

Fig. 2(a) reports the device photoresponsivity measured in DC (stars) and AC (diamonds) at 173 Hz for 638 nm illumination at different photoexcitation intensities. The photoresponsivity is calculated using $R = \frac{I_{pc}}{P_{opt}}$, where I_{pc} is the measured photocurrent, P_{opt} is the power incident over the active area. For the AC measurements an additional $\frac{\pi}{\sqrt{2}}$ factor is needed to take into account the lock-in amplifier contribution. The photoresponsivity reaches a maximum value of $R_{DC} \sim 220 \text{ A W}^{-1}$ in DC and $R_{AC} \sim 36 \text{ A W}^{-1}$ in AC (Fig. 2(a)). The observed difference between AC and DC results can be reasonably attributed to the presence of the $\text{EH}_{6/7}$ trap states within the SiC substrate which, lying at SiC midgap are readily excited with a 638 nm wavelength. Nevertheless, their optical activation occurs on the time scale of tens of seconds and their carrier trap cross section is quite low compared with other SiC trap states.³⁰ This prevents $\text{EH}_{6/7}$ states from affecting AC measurements. For the detectivity, calculated from $D^* = \frac{\sqrt{A} \cdot R}{S_i}$, where A is the active area and S_i is the noise spectral density calculated considering thermal noise from dark resistance and shot noise from dark current, we obtain a maximum value (in DC) of $D^* \sim 2.0 \times 10^9$ Jones. Such responsivity and detectivity values are promising,¹⁵ considering that they are obtained from a vertical heterostack entirely synthesized *via* CVD. The photoresponse of graphene-only devices is barely detectable at this wavelength (at best $R_{DC} \sim 0.04 \text{ A W}^{-1}$ ($D^* \sim 5.2 \times 10^5$ Jones), see ESI† for measurement details). Hence, the $\text{WS}_2/\text{graphene}$ device manifests an improvement

of three orders of magnitude with respect to graphene-only devices. The response time of the devices has been investigated by studying the photoresponsivity signal dependence on the AC frequency, as reported in Fig. 2(b). Despite the non-perfect behavior as RC low-pass filter, the response time of the device can be estimated by using the -3 dB bandwidth figure of merit, *i.e.* the point at which the signal has dropped to 70% of its initial value.^{17,31}

The obtained value is $\tau_r = \frac{1}{2\pi f_c} \sim 0.6 \text{ ms}$ (corresponding to a bandwidth $f_c = 250 \text{ Hz}$ calculated with respect to the maximum value at 20 Hz). To the best of our knowledge, this response time is among the fastest obtained for TMD/graphene devices.¹⁵ It is worth of note that a significant signal can be detected also above 10 kHz, where the responsivity is $\sim 10\%$ of the maximum value. We believe that the clean ohmic contact obtained with our approach is at the basis of the fast response time of our devices. Furthermore the epitaxial relation in our heterostack⁹ could have a positive impact as well.

In Fig. 3 the wavelength-dependent behavior of the device is reported. Fig. 3(a) shows the $\text{WS}_2/\text{graphene}$ device responsivity in AC at 173 Hz, for three different illumination wavelengths. The responsivities, within the error bars, are generally unaffected by the change in wavelength and, overall, responsivity decreases with increasing light intensity.

Fig. 3(b) reports the temporal response of the photocurrent under DC illumination at different wavelengths for on/off cycles with period of 20 s. The three curves collected at different wavelength are offset on the vertical axis for sake of clarity. In this case, the response changes dramatically when we switch from blue (473 nm) to red (638 nm) light. With the excitation at 473 nm once the light is switched off, there is a PPC that remains even on a time scale of hours (see ESI Fig. S6(a)†). The PPC is observed (although to a lesser extent) also for the green illumination, while for excitation with the

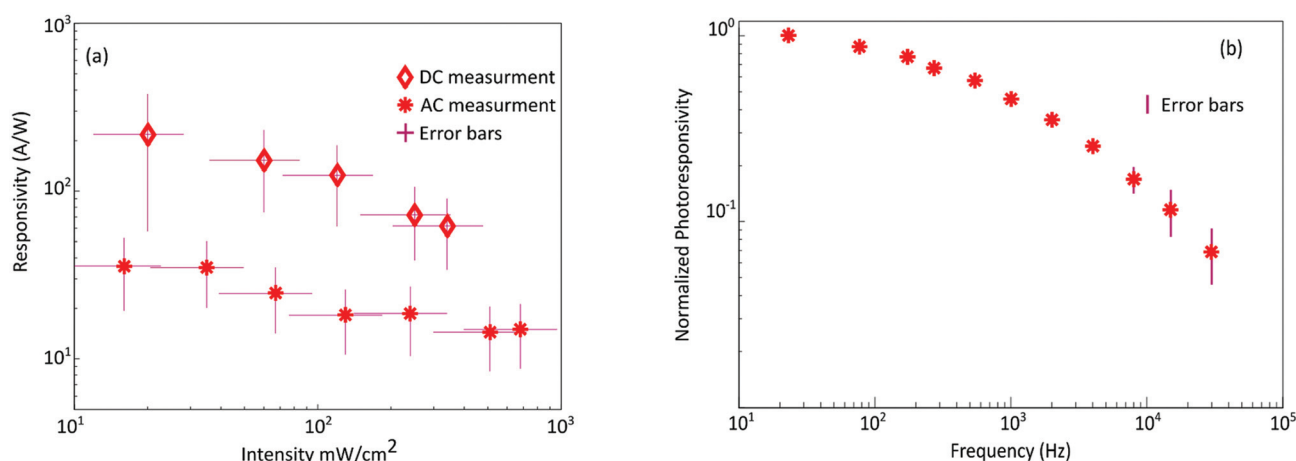


Fig. 2 (a) Comparison between photoresponsivity recorded with red light in AC (at 173 Hz) and DC measurements. (b) Normalized photoresponsivity in AC measurement as a function of the frequency, where the light was modulated by a chopper. Measurements were taken at bias voltage of $V_B = 1.8 \text{ V}$.



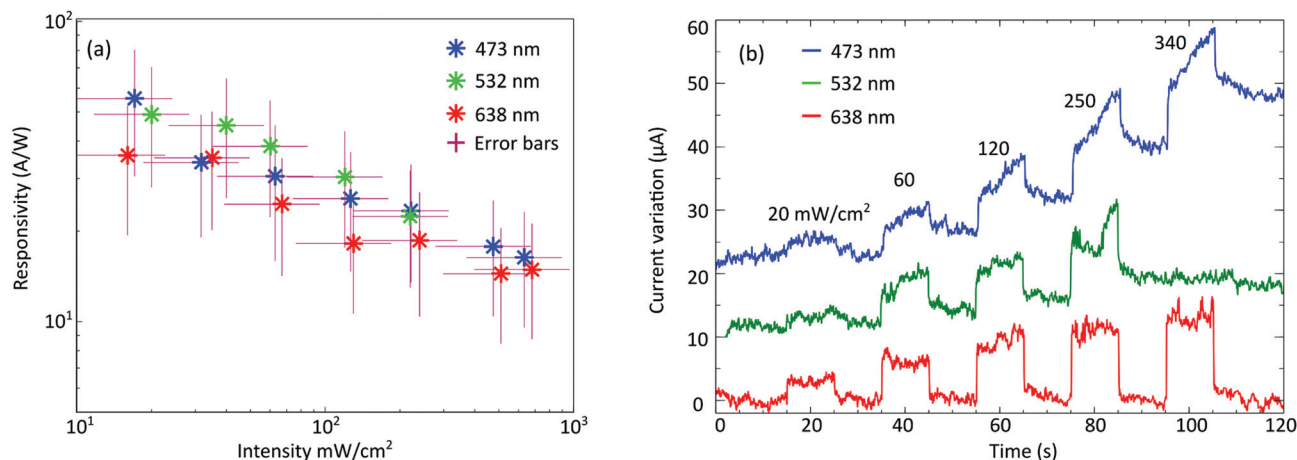


Fig. 3 (a) Responsivity vs. power intensity taken at different wavelengths in AC measurements (at 173 Hz). (b) DC measurements of photocurrent at different wavelength as a function of time. PPC progressively disappears with longer wavelength of the excitation light. With each light on/off cycle the light intensity was increased, as indicated by the values above the blue curve. Measurements recorded at a bias voltage $V_B = 1.8$ V.

red laser at 638 nm no PPC is recorded. The incident power dependence has been addressed by increasing the power at each on/off cycle. Although the photocurrent (the number of carriers) increases for all three wavelengths, the dark status is immediately restored for the red one only, even under the highest illumination intensity. This suggests the presence of a slow mechanism that retains the exceeding carriers, which keep accumulating when increasing the power at each cycle. Photocurrent measurements with a smaller illuminating spot (1 μm diameter) on devices with channels of 10 μm width were also carried out and allowed us to exclude the contribution of the contacts to the observed behavior (see ESI, Fig. S7†).

Graphene-only devices displayed the same PPC observed for the WS₂/graphene devices (see ESI Fig. S6(b)†). Hence, the observed PPC – differently from what reported in ref. 16 – is not an intrinsic property of the hybrid heterostack. In order to understand the mechanism behind the PPC, the temporal response has been measured when illuminating the WS₂/graphene 2 μm device with a spot diameter larger than the channel length, but smaller than the channel width (diameter 15 μm , 532 nm laser). The illumination was switched off only when approaching current saturation. As can be seen in Fig. 4(a), the device shows a slowly decaying “off” current, but after several minutes the dark condition of the device is restored. The observed finite decay is attributed to the smaller illuminated area of the device. Before discussing in detail the measured temporal response of the photocurrent, we analyze the band alignment of our structure, *i.e.* of the WS₂ on epitaxial graphene on 4H-SiC, which we have directly measured *via* angle-resolved photoemission spectroscopy (ARPES).⁹ The properties reported in ref. 9 are valid for the case investigated in this work, since the doping level of the epitaxial graphene on hexagonal SiC(0001) is not influenced by the polytype (*i.e.*, 4H or 6H).³² Furthermore, assuming that the HPSI 4H-SiC used as a substrate has the chemical potential at midgap, the total

band alignment is the one sketched in Fig. 4(b). The energy band diagram of 4H-SiC is reported on the left, while the graphene cone, schematized in the center, presents the Dirac point 0.4 eV below the Fermi level, a hallmark for EG.^{33,34} On the right-hand side of panel (b), WS₂ bands are reported with the conduction band lying about 260 meV above the Fermi level, as reported for the WS₂/EG system.⁹ HPSI 4H-SiC displays several deep levels (sketched in panel b) with activation energies ranging between 0.7 eV and 0.9 eV below the SiC conduction band,³⁵ which are known to play a fundamental role in the semi insulating behavior of 4H-SiC. These intrinsic deep levels are either acceptor-like levels or negative-U centers generated from C-vacancy complexes (*e.g.*, $Z_{1/2}$ levels), and act as recombination centers and life-time killers in charge transport experiment.^{36–38} These defects in the 4H-SiC substrate are responsible for the photogating mechanism in our devices, preventing the decay of the photocurrent. As depicted in Fig. 4(c), if the impinging light has enough energy (*i.e.* larger than ~ 2.2 eV corresponding to a wavelength shorter than 563 nm), it is not only responsible for photocurrent in the WS₂/graphene heterostructure, but it also promotes electrons into the aforementioned 4H-SiC deep levels. By acting as recombination centres, such levels capture and neutralize electrons and leave charged holes behind. The accumulated holes generate an electric field that leads to a chemical potential shift in graphene, increasing the number of carriers (Fig. 4(d)). Since the trapping lifetime of these defects is extremely long,³⁹ PPC is observed. Nevertheless, eventually they recombine (Fig. 4(e)), thus the related gate voltage decays and the initial position of the chemical potential is restored. The presence of defect levels with different activation energies is responsible for the distinct behavior observed for blue and green light, *e.g.* when $Z_{1/2}$ deep levels are involved, a PPC lasting for several hours is obtained. Red light does not induce any long-lifetime deep level transition,⁴⁰ and therefore no photogating and no



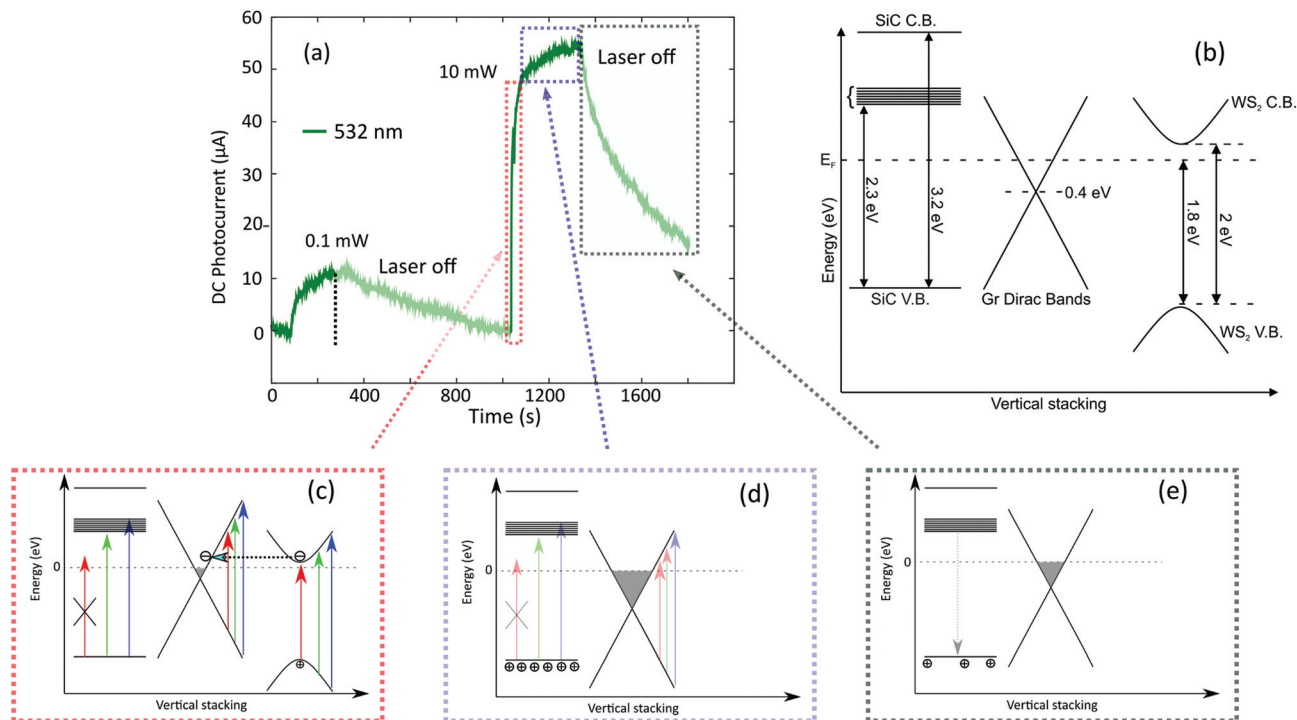


Fig. 4 DC photocurrent vs. time using 532 nm excitation wavelength. The curve is taken for two different incident light intensities, at a bias voltage of $V_B = 1$ V. Dimmed-colored areas are relative to “light-off” state. (b) Scheme of the band alignment of the system with the relative energies. (c) Scheme of the mechanism involved in the generation of photocurrent and photogating at different wavelengths in the rising part of the signal (red dashed box). (d) Gating effect on graphene from SiC substrate relative to the saturating part of the rising curve (blue dashed box). (e) Recombination in VB occurring with light off in falling curve (gray dashed box).

PPC occur. However, the energy of the red light is sufficient to excite the transition from VB to CB in WS_2 . Subsequently charge transfer from the active layer (WS_2) to graphene occurs, injecting carriers in the transport layer (graphene). Hence, the role of WS_2 is crucial to enhance the responsivity of the system making the device “active” in the visible range.

Conclusion

We reported a novel approach for the implementation of scalable WS_2 /graphene photoresponsive devices. The use of a mask during the growth is crucial to controllably deposit WS_2 just on the optical channel in order to create an effective ohmic contact to the graphene channel. The strength of this approach relies on its flexibility as it can be adopted on different systems, *e.g.* CVD graphene transferred on SiO_2 . The presented devices show – when illuminated with red light – a DC responsivity reaching 220 A W^{-1} and an AC response time of $\tau_r \sim 0.6$ ms. PPC is measured for shorter illumination wavelengths, and a nearly perfect charge retention is observed for blue light. Such PPC originates from deep levels in the SiC substrate. The combination of wavelength-selective memory effect, enhanced responsivity and fast detection is of interest for the fabrication of 2d based optical memories, which might be realized by exploiting a transparent top gate¹⁷ to reset the memory state and depopulate the traps.

Conflicts of interest

There are no conflicts to declare.

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