Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

WS_2-Induced Enhanced Optical Absorption and Efficiency in Graphene/Silicon Heterojunction Photovoltaic Cells

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1. Raman spectra showing the G and 2D bands for graphene on n-Si with and without WS_2.

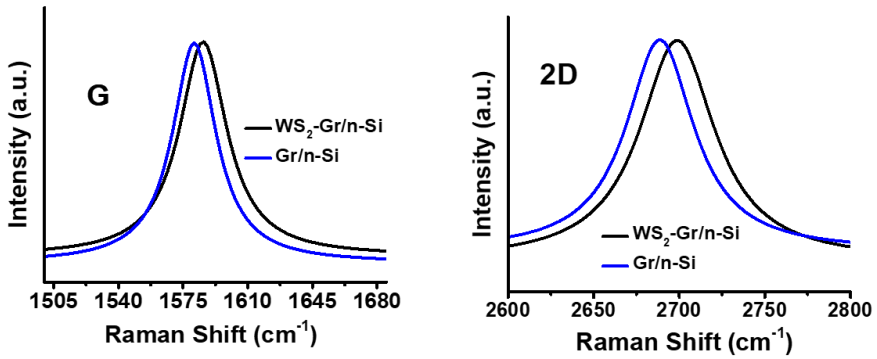

Fig. 1 Raman spectra showing the G and 2D phonon vibrational modes for graphene/n-Si and WS_2-graphene/n-Si structures.

2. Current density vs. voltage (J-V) characteristic under illumination for a second graphene/n-Si and WS_2-graphene/n-Si device.

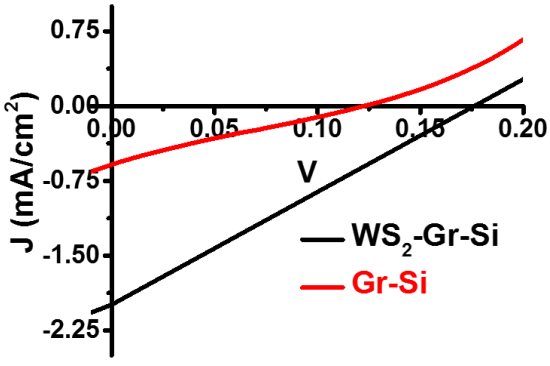

Fig. 2 J-V characteristic under illumination for a second graphene/n-Si and WS_2-graphene/n-Si device.

3. Transmission Electron Microscopy Characterization for WS_2-Graphene Film.

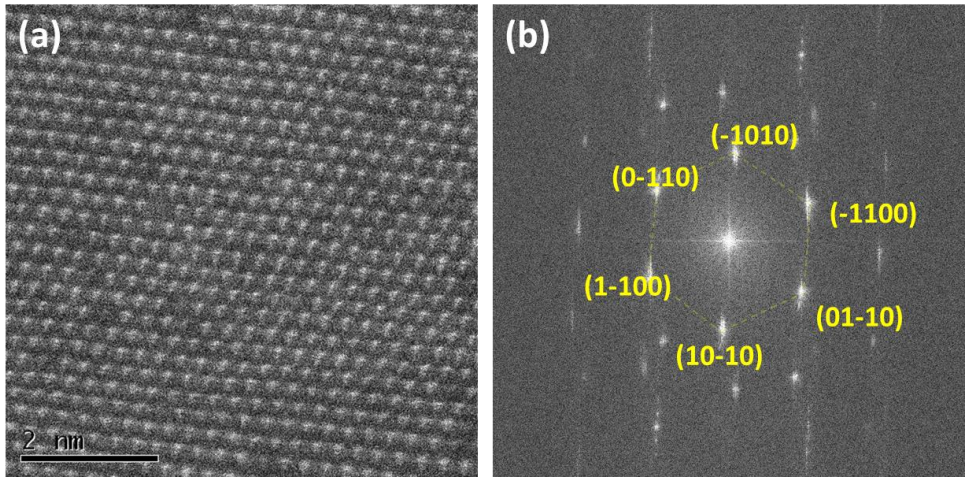

Fig. 3 (a) TEM image of WS_2-graphene film. (b) Selected area electron diffraction (SAED) pattern of WS_2-graphene film.

4. Doping Levels of Graphene in WS_2-Graphene/n-Si Heterostructure.

The doping level for the graphene sheet has been calculated from the shift in the graphene G peak position. The upshifts in the peak positions of both the G and 2D peak positions point to the electron (n) doping of the underlying graphene after the deposition of WS_2 layers *via* chemical vapor deposition.[1] The table below shows the peak positions (also shown in the Raman spectra in the above Figure 1).

	Graphene/n-Si	WS_2-Graphene/n-Si
G peak position (cm^{-1})	1581	1586
2D peak position (cm^{-1})	2688	2699

At room temperature (298 K) the G peak position for undoped graphene is 1579 cm^{-1}.[2] The total shift in the G peak position can be modelled as:

$$\Delta\omega = \Delta\omega_A + \Delta\omega_{NA}$$

where $\Delta\omega_A$ and $\Delta\omega_{NA}$ represent shifts due to adiabatic and non-adiabatic contributions.[3] The adiabatic contribution[4] is given by the formula:

$$\Delta\omega_A = -2.13n - 0.036n^2 - 0.00329n^3 - 0.226|n|^{3/2}$$

where $\Delta\omega_A$ is the shift in cm^{-1} and n is the charge carrier concentration in graphene (10^{13} cm^{-2}). The non-adiabatic contribution is given by:

$$\Delta\omega_{NA} = \frac{2\pi\alpha P}{h}\int_{-\infty}^{\infty}\frac{[f(E-E_F)-f(E)]E^2 sgn(E)}{E^2-\left(\frac{h\omega_o}{4\pi}\right)^2}dE$$

where $\Delta\omega_{NA}$ is the shift in cm^{-1}, α=4.39x10^{-3} is a constant, P is the principal part, h is the Planck constant, f is the Fermi-Dirac distribution, E_F is the Fermi energy, and ω_o is the G mode frequency of the undoped graphene.[5] For $|E_F| < 1\ eV$ the adiabatic contribution to the total peak shift can be ignored:

$$\Delta\omega \approx \Delta\omega_{NA}$$

The non-adiabatic shift exhibits asymptotic behavior when $|E_F| \gg h\omega_o/4\pi$ and the total shift exhibits a linear relationship with the Fermi energy. For $E_F \geq 100\ meV$ (electron doping), the linear relationship between the G peak shift and the Fermi energy is given by:

$$E_F = 21\Delta\omega + 75$$

where E_F is in meV and $\Delta\omega$ is in cm^{-1}. The Fermi energy can be further related to the carrier concentration by the formula:

$$E_F = \frac{sgn(n)\sqrt{n\pi}hv_F}{2\pi}$$

where n is the carrier concentration and v_F is the Fermi velocity ($v_F = 1.1 \times 10^6\ m/s$). The calculated Fermi energy and doping levels are shown in the table below.

	Graphene/n-Si	WS_2-Graphene/n-Si
$\Delta\omega\ (cm^{-1})$	2	7
$E_F(meV)$	117	222
$n\ (cm^{-2})$	8.28x10^{11}	2.98x10^{12}

The doping levels of the graphene exhibited an increase of 260% on the deposition of WS_2 layers.

References

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(3) Froehlicher, G.; Berciaud, S. *Phys. Rev. B - Condens. Matter Mater. Phys.* **2015**.

(4) Lazzeri, M.; Mauri, F. *Phys. Rev. Lett.* **2006**.

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