Temperature dependent valley polarization in WS$_2$ heterostructures

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Abstract

The absence of degeneracy in the valley indices of transition metal dichalcogenide monolayers serves as a pivotal property for the development of future valleytronic devices in which both spin and charge are used to transport and store information. One essential criterion for the realization of such a device is to attain high values of polarization degree at room temperature. Here, we examine different cases of vertical WS$_2$ heterostructures and we show that the material type used to form the heterostructure significantly influences the degree of valley polarization of WS$_2$. Our results show the interaction between WS$_2$ and graphene has a strong effect on the temperature dependent depolarization, with polarization degrees reaching 24% at room temperature under near-resonant excitation. This contrasts with hBN-encapsulated WS$_2$, which exhibits a room temperature polarization degree of only 11%. The observed low depolarization rate in WS$_2$/Graphene heterostructure is attributed to a) rapid charge and energy transfer processes of the scattered excitons via near-field interactions, b) absence of thermal dissociation of trions and thermally assisted dark-to-bright state transitions and c) partial suppression of the temperature dependent band-gap renormalization. Significant variations in the degree of polarization are also observed at 4K between the different heterostructure configurations. Intervalley hole scattering in the valence band proximity between the K and Γ points of WS$_2$ is sensitive to the immediate environment, leading to the observed variations. These findings will be useful towards understanding fundamental spin relaxation phenomena in 2D heterostructures and engineering of specialized electronic devices based on WS$_2$ and other TMD monolayers.
1. Introduction

Transition metal dichalcogenide (TMD) monolayers are semiconductors with a direct transition at the K-point of the Brillouin zone. The band structure of these materials has unique features that makes them ideal candidates for valleytronics, a field where the valley index is a potential new state variable.\(^1\)\(^-\)\(^6\) The low-dimensional hexagonal lattice structure of TMDs, combined with strong orbital hybridization and time reversal symmetry result in two inequivalent, high symmetry points, K and K’, with coupled spin and valley indices and unique optical selection rules. An imbalance in the carrier population between the K and K’ valleys, referred to as a valley polarization or the degree of polarization, can therefore be created under excitation with circularly polarized light, enabling the independent initialization and addressing of the valley index. Also in these materials, the relatively strong spin-orbit (SO) interaction, which originates from the d-orbitals of the transition metal atoms, splits the conduction (CB) and valence (VB) bands by tens and hundreds of meV, respectively.\(^7\)\(^,\)\(^8\) This SO splitting in the CB and VB has a profound influence on the valley polarization.

Research on a more fundamental understanding of all the parameters affecting the valley polarization is ongoing. Some of the parameters that can affect the polarization by enabling depolarization processes include excitation energy,\(^4\)\(^,\)\(^9\) temperature,\(^9\) electron-hole exchange interactions,\(^10\) and electron-phonon coupling.\(^4\)\(^,\)\(^11\) Although there are several reports on the effect of the surrounding background on the electronic properties of TMDs,\(^12\)\(^-\)\(^22\) only a few examine the effect of temperature, excitation energy and environment on the valley polarization.\(^23\)\(^,\)\(^24\) Further investigation is expected to provide additional insight into the physics of spin relaxation of TMDs in different surrounding environments. This is a crucial consideration since the supporting layer is an important factor in thin optoelectronic systems and future valleytronic devices.

In this work, we investigate the temperature dependent valley polarization properties of chemical vapor deposition (CVD) synthesized WS\(_2\) monolayers and their heterostructures with different materials. In particular, temperature dependent (4K-300K) valley polarization phenomena and the related scattering mechanisms of neutral (X\(^0\)) excitons are examined in near-resonant and off-resonant conditions for WS\(_2\) on graphene (WS\(_2\)/Gr) and hBN/WS\(_2\)/hBN heterostructures. Because of the absence of charged excitons in the WS\(_2\)/Gr system, in this study we only focus on the properties of neutral excitons in order to compare the exact same PL recombination channel in different systems (the properties of charged excitons (X\(^-\)) are briefly discussed). Interestingly, significant differences are observed in the low temperature valley polarization degree, \(P(4K)\), as well as in the rate the polarization drops as a function of temperature in the systems studied. In addition, a surprising nearly temperature independent valley polarization close to 30% in the WS\(_2\)/Gr system was observed under near-resonant pumping conditions. These differences are investigated through changes in the band structure between WS\(_2\)/Gr and hBN/WS\(_2\)/hBN, doping effects, charge and energy transfer, and thermal dissociation of trions to neutral excitons. In addition, screening provided by the environment influences both electron-phonon (e-ph) coupling and Coulomb interactions. This study is expected to offer an insight into fundamental spin relaxation phenomena of 2D TMD monolayers towards the development of future fast, low cost, environmentally sustainable valleytronic devices.
2. Results

The current study will focus on WS₂/Gr and hBN/WS₂/hBN heterostructures. Comparison with standard WS₂/SiO₂ samples and WS₂/hBN (non-encapsulated) heterostructures will be also provided when needed, however we note that WS₂/Gr and hBN/WS₂/hBN have superior stability and spatial uniformity with respect to WS₂/SiO₂ and WS₂/hBN. Fig. 1a presents, from bottom to top, optical images of 3 different structures: 1) WS₂/SiO₂, 2) WS₂/Gr and 3) hBN/WS₂/hBN. A portion of the WS₂ triangle in the hBN/WS₂/hBN sample is not encapsulated giving us access to a WS₂/hBN sample.

The degree of circular polarization will be extracted from helicity-resolved photoluminescence (PL) spectra; therefore, it is important to first examine the different emission features (excitonic complexes) in each system. In Fig.1b we compare the micro-PL emission spectra of the different cases when excited with a 543nm (2.283 eV) laser source at low temperature (4K). Two distinct features are present in the WS₂/SiO₂ system, located at 2.083eV and 2.046eV (Table I). We assign these features to the neutral (X₀) and negatively charged excitons (trions, X⁻), respectively. In the case of WS₂/Gr, there is only one emission peak (2.042 eV) in the PL spectrum. This feature is due to X₀ emission and is red shifted 41meV compared to the WS₂/SiO₂. The assignment of this peak as X₀ is established with differential reflectivity measurements (Fig. 1c). The energy difference between the B-exciton and A-exciton is preserved, as both are red shifted equally, compared to the SiO₂ substrate (Supplementary Fig.S1). The observed shift is attributed to the presence of the underlying graphene which screens the electric field between the electrons and holes and leads to a strong reduction in the bandgap and more modest reduction of the exciton binding energy of the monolayer (ML) WS₂.

|            | EX₀ (eV) | EX⁻ (eV) | P(X₀) (%) | P(X⁻) (%) |
|------------|----------|----------|-----------|-----------|
| WS₂/SiO₂   | 2.083    | 2.046    | 25%       | 20%       |
| WS₂/Gr     | 2.042    | -        | 19%       | -         |
| WS₂/hBN    | 2.08     | 2.041    | 34%       | 34%       |
| hBN/WS₂/hBN| 2.065    | 2.021    | 41%       | 42%       |

Table I | Neutral and charged (intravalley) exciton peak energy at 4K for each sample, as well as the valley polarization degree with 543 nm (2.283 eV) excitation at 4K.
(Supplementary Fig.S2) is a result of nonradiative recombination processes such as photogenerated charge carrier transfer to graphene due to strong interlayer electronic coupling.\textsuperscript{26}

We will now focus on the case of the hBN encapsulated WS\textsubscript{2}. The suppression of disorder effects by the crystalline, wide band-gap hBN substrate leads to a reduction of the excitonic emission linewidths, compared to the WS\textsubscript{2}/SiO\textsubscript{2} case, and facilitates the identification of additional peaks.\textsuperscript{17,21,22} Multiple features in the top panel of Fig. 1b include X\textsuperscript{0}, X\textsuperscript{−} and a biexciton (XX). For the hBN/WS\textsubscript{2}/hBN system, X\textsuperscript{0} is centred at 2.065eV, and XX at 2.002eV.\textsuperscript{27} For the trion peak that is asymmetric up to 80K and cannot be fitted well by a single function, two pseudo-Voigt functions are superimposed with an energy difference of 10meV (Supplementary Fig. S3a). The lower energy feature corresponds to intravalley trions (X\textsubscript{intra} - 2.021eV, one hole and two electrons in the same valley) while the higher energy one to intervalley trions (X\textsubscript{inter} - 2.031eV, the two electrons originate from different valleys, i.e. K and K').\textsuperscript{28,29} Similar effects are observed in the trion emission of the WS\textsubscript{2}/hBN system (Supplementary, Fig. S3b), where the positions of the X\textsubscript{intra} (2.041eV) and X\textsubscript{inter} (2.049eV) result in an energy difference of 8meV. Since X\textsubscript{inter} is temperature sensitive and observable only up to 80K, in Table I only the energy position and the polarization values for the X\textsubscript{intra} are reported. The intensity of X\textsuperscript{0} in the hBN/WS\textsubscript{2}/hBN system is also considerably suppressed compared to the WS\textsubscript{2}/hBN. This can be attributed to cavity effects\textsuperscript{30}, as well as the n-type character of WS\textsubscript{2}. It has been shown that exposure to air can deplete excess electrons in WS\textsubscript{2} and enhance the X\textsuperscript{0} emission (e.g. physisorbed O\textsubscript{2} and H\textsubscript{2}O).\textsuperscript{31,32} Finally, the intensity of XX is reduced by \textasciitilde50\%, and X\textsuperscript{0}, X\textsubscript{intra} and X\textsubscript{inter} are red shifted by 15meV to 20meV in hBN/WS\textsubscript{2}/hBN compared to WS\textsubscript{2}/hBN. These changes can be explained by taking into account the reduction in the strength of the Coulomb interaction when additional hBN layers are added on top of WS\textsubscript{2} which leads to a further decrease in both the exciton binding energy and the bandgap.\textsuperscript{16} A summary of the emission energies of the different exciton complexes is presented in Table I.

The SO splitting in the valence band plays a crucial role in the valley polarization phenomena. For this reason, reflectance contrast spectra, \(\Delta R/R = (R_{\text{substrate}} - R_{\text{sample}})/R_{\text{substrate}}\), were collected at 4K (Fig. 1c) to examine possible variations in the energy difference between the A and B ground state \((n=1)\) excitonic resonances due to changes in the dielectric environment. In all cases, the SO splitting is of the same order (400meV – see Supplementary Fig.S1) with negligible variations indicating similar behaviour of the A- and B-excitonic state and ruling out effects that could arise from shifts in the energy splitting at the K-points. More detailed fitting of the reflectance contrast spectra (Fig.S1) as well as Raman measurements (Fig.S4a) and a discussion of strain effects in the system are presented in the supplementary information (section D).

Fig.2 presents the effect of the different heterostructures on the degree of valley polarization. To measure the polarization, the system is excited with right-handed circularly polarized light \((\sigma_+\) and then the resultant photoluminescence is analysed for co-polarized \((\sigma_+\) and cross-polarized/lefthanded circularly polarized light \((\sigma_-\). The degree of valley polarization is related to the circularly polarized emission \((P_{circ}^\pm)\), where
\[ P_{circ} = (I_+ - I_-)/(I_+ + I_-), \]
and \(I_+ (I_-)\) is the intensity of the \(\sigma_+ (\sigma_-)\) helicity PL component. In Figs. 2a and 2c the temperature-dependent, helicity-resolved PL spectra of hBN/WS\textsubscript{2}/hBN and WS\textsubscript{2}/Gr are shown for non- and near-resonant excitation conditions using the 543nm (2.283eV) and 594nm (2.087eV) laser sources, respectively. The degree of circular polarization for only the neutral exciton (X\textsuperscript{0}) is plotted in Figs. 2b and 2d in order to compare the exact same PL recombination channel in both systems. Slight variations in \(P_{circ}^\pm\) across different areas of the same monolayer are observed, likely related to spatial non-uniformities in the electron density of the sample.\textsuperscript{33,34} For this reason statistical analysis over several points has been applied and the mean values together with their standard deviations are presented.
For non-resonant excitation, $P_{\text{circ}}$ of the neutral exciton emission at room temperature is nearly zero for both hBN/WS$_2$/hBN and WS$_2$/Gr (Fig 2a, b). Both systems exhibit a monotonic increase in the degree of polarization with decreasing temperature (Fig 2b). However, the final polarizations reached at cryogenic temperatures are distinctly different for the two systems, with $P_{\text{circ}}=41\%$ for hBN/WS$_2$/hBN and $P_{\text{circ}}=19\%$ for WS$_2$/Gr at 4K. This will be addressed more in the discussion.

Excitation energy is a significant parameter when studying valley polarization phenomena since phonon assisted intra and intervalley scattering can be enabled as a function of excess energy, $\Delta E = E_{\text{excitation}} - E_{\text{emission}}$.$^{4,9}$ To evaluate this effect, we have performed experiments using a 594nm (2.087eV) laser source, which is very close to the excitonic emission of WS$_2$, to reduce the excess energy introduced into our systems. In Fig. 2c, $\sigma_+$ and $\sigma_-$ PL spectra are presented from 100K up to 300K, and the corresponding $P_{\text{circ}}$ is plotted in Fig. 2d. As might be expected, overall the values of $P_{\text{circ}}$ acquired at these temperatures are higher compared to those measured with the non-resonant 543nm excitation because of the suppression of the excess energy which would otherwise introduce additional intervalley scattering effects. More surprisingly however, $P_{\text{circ}}$ of X$_0$ from the WS$_2$/Gr system is nearly temperature independent exhibiting a valley polarization close to 30% in excellent agreement with previous reports using Mueller polarimetry analysis and in MoS$_2$.23,24 This results in a rather robust $P_{\text{circ}}$ of 24% in WS$_2$/Gr even at 300K. Note that experimental issues, related to a strong contribution from Raman scattering make determining the degree of polarization below 100K unreliable. This point is discussed in more detail in the supplementary information (section E).
3. Discussion

To exploit the valley index as a controllable degree of freedom, it is important to create a high degree of polarization in the electronic valleys. WS\textsubscript{2} is expected to exhibit stable valley polarization because of its strong spin-orbit splitting of the valence band at K and K’ which suppresses intervalley scattering (i.e. valley depolarization). It is also well-established that there is a \( \sim 55 \) meV splitting between the bright and dark state of WS\textsubscript{2} with the latter being in lower energy.\textsuperscript{35-37} The carrier populations in the K and K’ valleys, i.e. \( N \) and \( N’ \) can be described by:

\[
\frac{dN}{dt} = g - \frac{N}{\tau_r} - \frac{N - N’}{\tau_p}, \quad (1)
\]

\[
\frac{dN’}{dt} = g’ - \frac{N’}{\tau_r} - \frac{N’ - N}{\tau_v}, \quad (2)
\]

where \( g \) and \( g’ \) are the generation rates of the K and K’ valleys, respectively. If we define \( P_{\text{circ}} = \frac{(N - N’)/(N + N’)}{P_0} \) and \( P_0 = (g - g’)/(g + g’) \), then for steady-state conditions the measured polarization will be:

\[
P_{\text{circ}} = \frac{P_0}{1 + 2\tau_r/\tau_p}, \quad (3)
\]

where \( \tau_p \), is the overall intervalley scattering time (or valley relaxation time) and \( \tau_r \), is the effective exciton lifetime (including both radiative and non-radiative decay channels). Here \( P_0 \) is the initial polarization of the system which is considered to be equal to 1. It is clear from Fig.2b that the circular polarization of the \( X^0 \) does not exceed 50% at 0K, even in the case of hBN/WS\textsubscript{2}/hBN where we observe the highest degree of polarization.

The monotonic temperature dependence of the degree of polarization is mostly expected based on Eq. (3), and we can model this behavior by considering screening effects due to carrier doping as has been done elsewhere.\textsuperscript{38,39} This analysis together with the fitting of the experimental points of Fig.2 is presented in the supplementary information (section F). Yet, it should be noted that the excitation energy strongly affects the temperature dependence and this model is not sufficient to fit the experimental results under near-resonant conditions. In addition, we should comment that taking into account similar doping densities in WS\textsubscript{2} when it is encapsulated in hBN or on top of graphene is not a realistic scenario since graphene will certainly affect the electron density of WS\textsubscript{2}. On the other hand, if we change the electron density in the Thomas-Fermi wave vector equation, we do not get a reliable fit. A reason for this could be the competition between screening due to electrons and other effects, such as the dielectric screening from hBN or graphene, the activation of dark-to-bright exciton path at elevated temperatures, the electron-phonon coupling and the energy difference between the excitation and emission which affects the relaxation mechanisms.

At this point, we will focus on the observed low depolarization gradient of the WS\textsubscript{2}/Gr heterostructure compared to the hBN/WS\textsubscript{2}/hBN, under both non-resonant excitation (543nm) and more importantly near-resonant excitation (594nm), shown in Fig. 2b and 2d respectively. Several mechanisms could be responsible for the temperature insensitive valley-polarization of WS\textsubscript{2}/Gr which we discuss in the following paragraphs.

First, the presence of the linear dispersion of graphene close to the K point of WS\textsubscript{2}, gives rise to rapid charge and energy transfer processes via near-field interactions.\textsuperscript{40,41} The fingerprint of these processes is a 14.7meV broadening in the excitonic absorption due to the initiation of a new decay channel for WS\textsubscript{2} excitons (Fig.1c).\textsuperscript{40} The fitting analysis of the reflectivity spectra is included in section A of the Supplementary material (Fig. S1). As
a result, following the generation of e-h pairs in the K-valley, a portion of the population that will be subjected to intervalley scattering processes will rapidly recombine and transfer the photoexcited energy to graphene non-radiatively, preserving the valley-polarization degree.\textsuperscript{23,24} However, a critical parameter we should take into consideration is the temperature dependent intervalley scattering rate under resonant and non-resonant excitation for WS\textsubscript{2}/Gr and hBN/WS\textsubscript{2}/hBN. Considering the electron-phonon coupling in these two heterostructures, we have calculated the scattering rates a) from the bottom of the conduction band at the K point to all available states near the K’ point, b) for intermediate initial state energies enough to excite an optical phonon in WS\textsubscript{2} or SiO\textsubscript{2} and c) at excitation energies large enough to scatter an optical phonon in hBN which has a stronger electron-phonon scattering (Fig. S8). Details in the calculations can be found in Section H of the Supplementary material. The results indicate that intervalley scattering rate is not strongly affected by temperature because of the large phonon energy, therefore the main contribution to the observed valley polarization curve comes from changes in the radiative lifetime. It should be noted that a strong correlation between the exciton radiative rate and the thickness of the hBN encapsulation was recently revealed as a consequence of the Purcell effect, therefore the valley polarization degree can be further tailored.\textsuperscript{42}

Second, in Fig. 3a, the PL intensity of X\textsuperscript{0} after 543nm excitation is plotted as a function of temperature and normalized at 4K. From this figure significant variations are observed between the two cases. While there is a clear enhancement of X\textsuperscript{0} starting at ~40K in hBN/WS\textsubscript{2}/hBN, for WS\textsubscript{2}/Gr the intensity remains almost constant until ~170K. These intensity variations are a consequence of thermal dissociation of X\textsuperscript{−} and thermally assisted dark-to-bright state transitions. Thermal dissociation of X\textsuperscript{−} will increase the population of X\textsuperscript{0} in hBN/WS\textsubscript{2}/hBN and this pathway could further introduce intervalley scattering effects. On the contrary, in WS\textsubscript{2}/Gr where X\textsuperscript{−} is not formed (Fig.1b), this effect is minimized. Note that transitions from the dark to bright state are also expected to enhance the X\textsuperscript{0} PL intensity at elevated temperatures\textsuperscript{43}, surprisingly though in the WS\textsubscript{2}/Gr this effect is negligible, possibly because of energy transfer from the dark state to graphene (Fig. 3a). Therefore, intravalley scattering does not seem to have a significant contribution in the latter case.

A final note regarding the thermally stable valley-polarization of WS\textsubscript{2}/Gr is related to the observed temperature dependent X\textsuperscript{0} emission energy. In Fig. 3b, we compare the measured X\textsuperscript{0} energy between hBN/WS\textsubscript{2}/hBN and WS\textsubscript{2}/Gr, normalized at 4K. Interestingly, the temperature dependent band-gap renormalization in WS\textsubscript{2}/Gr is partially suppressed, resulting in a ~20meV energy difference at 300K compared to hBN/WS\textsubscript{2}/hBN. Therefore, the temperature dependent excess energy, $\Delta E$, has a weaker contribution to the depolarization rate in WS\textsubscript{2}/Gr which further assists the robust room temperature valley-polarization. To investigate the origin of the reduced thermal effect to the band-gap renormalization in WS\textsubscript{2}/Gr we have performed additional calculations, shown in Fig.S9; the temperature dependent bandgap renormalization appears much weaker than what is observed in the experiment, however two reasons could be responsible for this discrepancy: a) only Fröhlich coupling to phonons was considered in our calculations, whereas there are also other phonons such as interband (virtual valence to
conduction transitions), which we could not take into account and b) the temperature dependence of the screening could also modify the energy of the excitons.

We now move to another significant observation, that is the 2-fold enhancement of the hBN/WS₂/hBN valley polarization compared to WS₂/Gr at 4K under non-resonant excitation (Fig.2b). This is a non-trivial result considering the shorter recombination lifetime of WS₂/Gr. To understand this, we first consider the emission and absorption energy of the neutral exciton. X₀ in the WS₂/Gr system is red-shifted by >20meV compared to the X₀ of hBN/WS₂/hBN, an effect we attribute to dielectric screening effects (Fig.1b, 1c). Therefore, under the same excitation energy, WS₂/Gr will always have additional excess energy in the system that can contribute to intervalley scattering relaxation mechanisms. While excess energy could be part of the answer, this explanation may be insufficient to explain the full difference between $P_{\text{circ}} = 41\%$ (hBN/WS₂/hBN) and $P_{\text{circ}} = 19\%$ (WS₂/Gr) at 4K. Changes in the band structure of WS₂ in the proximity of hBN or graphene will also affect hole scattering mechanisms during relaxation. It has been proposed that spin degeneracy in the Γ valley can enable incoherent two-step transitions and therefore holes can relax from K to K’ through scattering via the Γ valley. We have performed band structure calculations (details in supplementary – Section G) and we find there is a considerable shift in the valence band at the Γ-point in WS₂ on graphene compared to the corresponding band structure at hBN/WS₂/hBN (Fig.4a, 4b). For hBN/WS₂/hBN, the energy difference between the valence bands at the K and Γ points of the Brillouin zone is 590meV, whereas in WS₂/Gr it is only 261meV. The relative proximity of the Γ-band to the top of the valence band at K/K’ could affect the low temperature polarization, $P_{\text{circ}}(4K)$, when the structure is excited under non-resonant conditions (2.283eV excitation) and should be considered during intervalley scattering events. To model the observed differences in the low temperature circular polarization, $P_{\text{circ}}(4K)$, we introduce a simplified model that takes into account the photo-generated holes scattered to Γ valence bands (Fig. 4c). The Γ- valley holes are then re-scattered back to the K and K’ valleys (to reduce their energy) on a time scale $\tau^*$ during the electron relaxation process. Therefore, in the presence of Γ valence bands in close proximity to K and K’, the rate equations (1) and (2) are modified as follows:

$$\frac{dN}{dt} = g - \frac{N}{\tau_c} - \frac{N}{\tau_v} + \frac{N'}{\tau_v} + \frac{N}{\tau^ \star} - \frac{N}{\tau^ \star}, \quad (4)$$
\[
\frac{dN'}{dt} = g' - \frac{N'}{\tau_r} - \frac{N'}{\tau_v} + \frac{\alpha \cdot N}{\tau^*},
\]

considering that \(\alpha\) is a percentage of holes at \(\Gamma\) with respect to \(K\): \(N_1 = \alpha \cdot N\).

In steady state, \(\frac{dN}{dt} = 0\) and \(\frac{dN'}{dt} = 0\). Assuming \(g = 1\) and \(g' = 0\),

\[
\frac{N'}{N} = \frac{1}{\frac{1}{\tau_r} + \frac{1}{\tau_v} + \alpha \cdot \frac{1}{\tau^*}}.
\]

Figure 4 | Band structure calculations of a) WS\(_2\)/6layer hBN and b) WS\(_2\)/Gr. c) Schematic representation of the hole-phonon intervalley scattering effects in the proximity of \(\Gamma\) band close to \(K\), that the proposed model considers.

\[
P_r = \frac{N - N'}{N + N'} = \left( \frac{1}{1 + \frac{2}{\tau_r} + \alpha \cdot \frac{1}{\tau^*}} \right) - \frac{\alpha \cdot \frac{1}{\tau_v} + \frac{1}{\tau^*}}{1 + \frac{2}{\tau_r} + \alpha \cdot \frac{1}{\tau^*}},
\]

where it is apparent that, as the energy of \(\Gamma\) approaches \(K\) and \(K'\), there will be a reduction of the polarization. Hole scattering effects should be suppressed under near-resonant excitation, since the relaxation of the hole through the \(\Gamma\) valence band is not energetically favorable.

4. Conclusions

We have demonstrated temperature dependent valley polarization measurements in a) ML WS\(_2\) encapsulated in hBN and b) ML WS\(_2\) on top of graphene excited with two different photon energies (i.e. off-resonant and near-resonant excitation). The results reveal a surprisingly low depolarization rate as a function of temperature that is attributed to a) rapid charge and energy transfer processes of the scattered excitons in the \(K'\) valley of WS\(_2\) to graphene via near-field interactions, b) absence of thermal dissociation of trions and thermally assisted dark-to-
bright state transitions in WS2/Gr and c) partial suppression of the temperature dependent band-gap renormalization in WS2/Gr. Consequently, WS2/Gr displays a robust valley polarization degree at room temperature (24%) under near-resonant excitation. Notable differences are also presented in the low temperature polarization $P_{\text{circ}}$ (4K) under non-resonant excitation, with hBN/WS2/hBN showing a strong value of 42% whereas WS2/Gr only 19%. To explain this observation, a model that considers the effect of the proximity of $\Gamma$ to $K$-$K'$ valence bands of WS2 is introduced and indicates that in WS2/Gr, holes can be scattered to $K$-$K'$ via the $\Gamma$, resulting in a reduction of the valley polarization degree, $P_{\text{circ}}$ (4K), whereas in hBN/WS2/hBN the energy difference is large enough (590meV) to suppress this effect and demonstrate 42% valley polarization. We believe that our observations will contribute towards understanding fundamental spin relaxation phenomena in 2D heterostructures for future valleytronic devices.

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A. Reflectance contrast spectra

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hBN/WS₂/hBN
A-T = 34 meV

hBN/WS₂/hBN
B-A = 395 meV

WS₂/graphene
B-A = 392 meV

WS₂/SiO₂
B-A = 403 meV

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Peak 1 – Trion
A = 0.0108
E₀ = 2.0257 eV
Δ = 17.6 meV

Peak 2 – A-exciton
A = 0.1066
E₀ = 2.0596 eV
Δ = 15.3 meV

Peak 3 – B-exciton
A = 0.0046
E₀ = 2.4508 eV
Δ = 27.8 meV

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Common fit parameters:
Fano parameter = 2.5
Linear slope = 0.3381
Background = 0.2888
Fig. S1: Differential reflectivity analysis of hBN/WS₂/hBN (a,b), WS₂/Gr (c,d) and WS₂/SiO₂ (e,f). The energy difference between A and B exciton is indicated in each case. The fitting equation for the A and B exciton is \( f(x) = A \left( \frac{m^2 - x^2}{\Delta m^2} \right)^2 + kx + b \), where \( A \) is the amplitude, \( q \) is the Fano parameter which represents the ration of resonant scattering to the background scattering, \( m \) is the width of the line shape, \( k \) is the linear slope and \( b \) is the intercept. The corresponding energies and linewidths of A and B excitons are presented after fitting (orange lines) of the experimental data (blue lines), for the case of g) hBN/WS₂/hBN, h) WS₂/graphene and i) WS₂/SiO₂.
**B. WS₂/graphene – a 6-fold suppression of the X⁰ PL intensity**

![Graph showing PL intensity comparison between WS₂/SiO₂ and WS₂/graphene](image)

Fig. S2: Comparison of the PL emission between WS₂/SiO₂ and WS₂/graphene under 543nm excitation at 300K. A 6-fold decrease in the case of WS₂/graphene is observed.

**C. hBN/WS₂/hBN and WS₂/hBN heterostructures – PL analysis**

![Voigt fitting of the PL emission](image)

Fig. S3: Voigt fitting of the PL emission at 4K under 543nm excitation in the cases of a) hBN/WS₂/hBN and b) WS₂/hBN.
D. Raman measurements

Strain is a parameter that could affect the band structure of WS$_2$, therefore we utilized Raman spectroscopy to characterize WS$_2$ to identify possible strain effects in the different cases studied. A possible source of strain is the lattice constant mismatch of WS$_2$ with graphene and hBN. Room temperature Raman spectra of the two main vibrational modes of WS$_2$ (i.e. in-plane mode E’ and out-of-plane mode A$_1$’) are presented in Fig. S4a. Compared to the SiO$_2$ substrate, a systematic red shift of the E’ mode and a blue shift of the A$_1$’ mode is observed due to an increase of the weak interaction with atoms from neighbouring layers (graphene and hBN) and a raise in the

Figure S4: Raman spectra of (a) WS$_2$/SiO$_2$, WS$_2$/Gr, WS$_2$/hBN, and hBN/WS$_2$/hBN structures, b) CVD graphene and c) hBN acquired with a 473nm laser.
effective screening of the Coulomb potential.\textsuperscript{2} In addition, a clear decrease in the linewidth of the vibrational modes is observed on hBN and graphene compared to the SiO\textsubscript{2} substrate. Due to the larger lattice constant of WS\textsubscript{2} (3.15 Å)\textsuperscript{3} compared to graphene (2.46 Å)\textsuperscript{4} and hBN (2.5 Å)\textsuperscript{5}, we would expect that contraction should occur, accompanied by a blue shift of the E’ mode. However, the ~1.7 cm\textsuperscript{-1} red shift of the E’ in the WS\textsubscript{2}/graphene and hBN/WS\textsubscript{2}/hBN samples suggests that the effective screening of the Coulomb potential dominates any effect due to lattice mismatch. Such an effect was seen in MoS\textsubscript{2} and attributed specifically to the dielectric screening of the long-range components of the Coulomb forces. In Fig. S4b and Fig.S4c we present Raman spectra from the underlying CVD graphene and hBN respectively. The position and the linewidth of the G and 2D peaks, as well as the intensity ratio (I\textsubscript{2D}/I\textsubscript{G}) confirm a p-type graphene in our heterostructures.\textsuperscript{6}

**E. Raman contribution to PL spectra**

![Raman spectra](image)

*Figure S5:* Raman contribution in the PL emission at low temperatures under resonant excitation in the cases of a) WS\textsubscript{2}/SiO\textsubscript{2}, b) hBN/WS\textsubscript{2}/hBN, c) WS\textsubscript{2}/graphene and d) WS\textsubscript{2}/hBN.

Helicity resolved PL spectra measured below 100 K under 594nm excitation (Fig.2c and 2d in the main text) are not included in our analysis because the contribution of the active Raman modes in the photoluminescence spectra and their strong effect in the $\sigma_+$ and $\sigma_-$ emission make the extraction of the degree of polarization unreliable. In Fig. S5a we present photoluminescence spectra of hBN/WS\textsubscript{2}/hBN and WS\textsubscript{2}/Graphene excited with a 594 nm laser at 4 K. In the same plot we have included Raman spectra acquired with a 473 nm laser to demonstrate the pure Raman signal. It is apparent that the strong underlying vibrational modes have a significant contribution in the PL emission when the excitation is near-resonant. In addition, the cross-polarized helicity of the Raman modes (due
to mirror backscattering effects) affect strongly the PL polarization analysis. Therefore, we only present the degree of polarization above 100 K.

**F. Screening effects due to carrier doping**

To model the monotonic temperature dependence of the degree of polarization, we consider screening effects due to carrier doping. WS$_2$ is in general an n-type semiconductor and we confirm this character in our monolayers by extracting the binding energy of the X on WS$_2$/SiO$_2$ (~38meV). Theoretical calculations$^7$ have considered the effect of doping on the valley relaxation by using a statically screened Coulomb potential with finite Thomas-Fermi wave vector ($k_{TF}$), which is related to the carrier density of $n$ by

$$k_{TF} \equiv k_{TF}^0 \left[1 - e^{-\frac{\pi \hbar^2}{g_s g_v m^* k_B T}}\right] \quad (S1)$$

where $k_{TF}^0 = g_s g_v m^* e^2/(4\pi \varepsilon \hbar^2)$ is the zero-temperature Thomas-Fermi wave vector, $g_s$ ($g_v$) is the degeneracy number for spins (valleys), $m^*$ is the carrier effective mass, and $\varepsilon$ is the dielectric constant which is different for the 4 cases studied in this work.

Under non-resonant excitation conditions, the temperature dependence of the polarization degree (Fig. 2b) was fitted using equation $S3$, derived by considering the steady state of a rate equation model. Both characteristic times, the exciton radiative lifetime $\tau_r$ and the spin-valley relaxation time $\tau_v$, depend on temperature. Whereas the former is just proportional to the temperature, if there are no dark states, whereas it shows a non-monotonic behavior in the presence of dark states, the latter has a nontrivial dependence through the Thomas-Fermi wave vector and the homogeneous broadening$^7$

$$\tau_v \sim k_{TF}^2 \tau_r \quad (S2)$$

According to Eq. (3) of the main text the polarization rate should follow:

$$P_{circ} = \frac{P_0}{1 + \frac{A}{\left(1 - e^{-0.8n/T}\right)}}, \quad (S3)$$

where $A$ is a fit parameter fixed at 0.0005. We also fixed the carrier density at $4 \times 10^{12} cm^{-2}$ in the two cases and varied the low temperature polarization $P(4K)$ in the hBN/WS2/hBN sample we used $P(4K)=40.84$ whereas in the WS2/Gr, $P(4K)=18.62$. For carrier densities of the order of $10^{12} cm^{-2}$ an almost linear dependence of the intervalley scattering time as a function of temperature is observed and our experimental results are well fitted with this model (Fig. F1). Nevertheless, we should comment that taking into account similar doping densities in WS$_2$ when it is encapsulated in hBN or on top of graphene is not a realistic scenario since graphene will certainly affect the electron density of WS$_2$. On the other hand, if we change the electron density in the Thomas-Fermi wave vector equation, we do not get a reliable fit. A reason for this could be the competition of the screening due...
to electrons with other effects, such as the dielectric screening from hBN or graphene, the activation of dark-to-bright exciton path at elevated temperatures, the electron-phonon coupling and the energy difference between the excitation and emission which affects the relaxation mechanisms. For instance, it is obvious that the temperature dependent spin-valley polarization under near-resonant excitation shown in Fig. 2d cannot be fitted with the same equation, i.e. taking into consideration only screening effects that will affect the valley lifetime. Therefore, this becomes a complicated problem and a single model cannot explain the observations.

G. The band-proximity effect

Band structures are obtained within the frame work of plane-wave density function theory using the open source code Quantum Espresso.\(^8\) Fully relativistic norm-conserving pseudopotential is used to include spin-orbit coupling. The cutoff energy is set to 60 Ry and Brillouin zone samplings is approximated by 16×16×1 k-points. Crystal structures of WS\(_2\) heterostructures are shown in fig. (S6).

![Figure S6: Crystal structures of (a) 2×2 WS\(_2\) on √7×√7 hBN and (b) 2×2 WS\(_2\) on √7×√7 graphene. Lattice constants of WS\(_2\), hBN and graphene of 3.18 Å, 2.5 Å, and 2.46 Å, respectively, correspond to the strains in hBN and graphene of −4.14% and −2.35%, correspondingly.](image)
**H. Phonon limited scattering rate**

The schematic structure of heterostructures is depicted in Fig. S7. Atomically thin materials 1 and 2 are bounded between two semi-infinite substrate materials 3 and 4, characterized by their dielectric function. The thickness of materials 1 and 2 are $t_1$ and $t_2$, respectively. $\varepsilon_n$ the dielectric functions of the mediums $n$, where $n = 1,2,3,4$:

$$\varepsilon_n(\omega) = \varepsilon_n(\infty) \frac{\omega^2 - \omega_{LO,n}^2}{\omega^2 - \omega_{TO,n}^2} \quad (S4)$$

![Figure S7: Schematic structure of heterostructures.](image)

We look for the solution of Maxwell equations in the form of:

$$\phi(q,z) = \sum_q \Phi(q,z) e^{i q \cdot \rho}, \quad (S5)$$

Where

$$\phi(q,z) = \begin{cases} 
A e^{-q(z-t_2)} & t_1 < z \\
B e^{q(z-t_1)} + C e^{-qz} & 0 < z \leq t_1 \\
D e^{qz} + E e^{-q(z+t_2)} & -t_2 < z \leq 0 \\
F e^{q(z+t_2)} & z \leq -t_2 
\end{cases} \quad (S6)$$

Continuity of the potentials, $\phi_n$, and displacement fields, $\varepsilon_n \frac{\partial \phi_n(z)}{\partial z}$ at the boundaries are used to express coefficients $A, B, D$ and $F$ in eq. (S6) in term of $C = \phi_0$ and the frequencies from the secular equation:

$$\frac{(\varepsilon_1+\varepsilon_4)}{[(\varepsilon_1+\varepsilon_2)(\varepsilon_2-\varepsilon_3)\exp(-2qt_2)+(\varepsilon_2+\varepsilon_3)]\exp(-qt_1)} + \frac{(\varepsilon_2-\varepsilon_3)\exp(-qt_1)}{(\varepsilon_2-\varepsilon_3)(\varepsilon_1-\varepsilon_2)\exp(-2qt_2)+(\varepsilon_1+\varepsilon_2)(\varepsilon_2+\varepsilon_3)} = 0 \quad (S7)$$
\[
\phi(q, z) = \phi_0 \begin{cases} 
(\alpha_1 + 1)e^{-qz} & t_1 < z \\
\alpha_2 e^{q(z - 2t_1)} + e^{-qz} & 0 < z \leq t_1 \\
(1 + \alpha_1 e^{-2qt_1})(1 - \alpha_2 e^{-qt_1})e^{qt_1} + \alpha_2 e^{-qt_1} & -t_2 < z \leq 0 \\
(\alpha_2(1 - e^{-2qt_1}) + e^{-qt_1})(1 + \alpha_1 e^{-2qt_1})e^{qt_1} & z \leq -t_2 
\end{cases}
\]

(S8)

Where \( \alpha_1 = \frac{e_1 - e_4}{e_1 + e_4} \) and \( \alpha_2 = \frac{(e_2 - e_3) \exp(-qz_2)}{e_2 + e_3 + (e_2 - e_3) \exp(-2qz_2)} \).

\( \phi_0 \) can be found by relating energy of the excitation quanta \( \hbar \omega_q \) to the electromagnetic field energy\(^{10}\):

\[
\phi_0 = \sqrt{\frac{4\pi \hbar}{qA}} e^{e_1}(1 - e^{-2qt_1})(1 + \alpha_2 e^{-2qt_1}) + \frac{\partial e_2}{\partial \omega}(1 + \alpha_1 e^{-2qt_1})^2(1 - e^{-2qt_2})((1 - \alpha_2 e^{-qt_2})^2 + \alpha_2^2) + \frac{\partial e_3}{\partial \omega}(\alpha_2(1 - e^{-2qt_2}) + e^{-qt_2})^2(1 + \alpha_1 e^{-2qt_1})^2 + \frac{\partial e_4}{\partial \omega} (\alpha_1 + 1)^2 e^{-2qt_1} \right]^{1/2}
\]

(S9)

Where \( A \), area of the sample and \( h \) is reduces plank constant. The electron-phonon Hamiltonian can be written as\(^{10}\):

\[
H = \sum_q -e \phi(q, z) e^{iq\mathbf{\rho}} (a_q + a_{-q}^\dagger)
\]

(S10)

Where \( -e \phi(q, z) \) is known as an electron phonon coupling factor. \( a_q (a_{-q}^\dagger) \) is annihilation (creation) operator and \( e \) is the elementary charge. Scattering rate is calculated using Golden rule:

\[
\frac{1}{\tau_k(T)} = \frac{2\pi}{h} \sum_k |\Gamma(q, z)|^2 \times \left[ N(T) \delta(\epsilon_k - \epsilon_k - \hbar \omega) + (N(T) + 1) \delta(\epsilon_{k'} - \epsilon_k + \hbar \omega_q) \right]
\]

(S11)

Where \( q = |q| = |k - k'| \) is a momentum transfer. The energy dispersion \( \epsilon_k \) is approximated using parabola \( \epsilon_k = \frac{h^2 k^2}{2m} \) with an effective mass \( m = 0.34 m_e \). \( N(T) \) is Bose-Einstein distribution function and \( \omega_q \) is a solution of eq. (S7). By considering a homogenous electron distribution in the atomically thin \( WS_2 \), \( \Gamma(q, z) \) can be written as

\[
\Gamma(q, z) = -e \phi_0 \frac{1}{t_1} \int_0^{t_1} (\alpha_1 e^{q(z - 2t_1)} + e^{-qz}) dz
\]

(S12)
Dielectric function of graphene in layer 2, where applicable, is calculated using random-phase approximation

\[ \varepsilon_{Gr}(q, T) = 1 + \nu_c \Pi(q, T), \]  \hspace{1cm} (S13)

where \( \nu_c = \frac{2\pi e^2}{Kq} \), \( K \) is environment lattice dielectric constant. \( \Pi(q, T) \) is the polarization function.\(^{11}\)

The inter-valley scattering rates of electrons in WS\(_2\) hetero-structures are shown in Fig. S8, where the thickness of WS\(_2\) is assumed to be 6.14 Å.\(^{12}\) The Brillouin zone sampling for electronic states is 200 × 200 k-points. The corresponding parameters for the dielectric functions are listed in table S1.\(^{12-14}\)

|       | \( h\omega_{TO} \) [meV] | \( h\omega_{LO} \) [meV] | \( \varepsilon(0) \) | \( \varepsilon(\infty) \) |
|-------|--------------------------|--------------------------|-------------------|---------------------|
| WS\(_2\) | 42.9                     | 103                      | 13.7              | 13.6                |
| hBN   | 97.6                     | 5.1                      | 4.58              |                     |
| SiO\(_2\) | 55.7                 | 3.9                      | 3.36              |                     |

Table S1: Energies and dielectric constants of used materials.

Fig. S8a shows scattering rate from the bottom of the conduction band at the K point to all available states near the K’ point. As the temperature increases more phonons become available and the scattering rate grows as N(T) as shown in Fig. S8a. For intermediate initial state energies enough to excite optical phonon in WS\(_2\) or SiO\(_2\), scattering rate is finite even at the very low energies and it keeps increasing as more phonons become thermally populated as shown in Fig. S8b. This situation is applicable to the near resonant excitation conditions with the laser wavelength of 594 nm used in the experiment. As the excitation energy becomes large enough to scatter an optical phonon hBN at low temperatures the phonon inter-valley decay rate becomes much larger in hBN encapsulated sample due to the stronger electron-phonon scattering. This situation corresponds to the non-resonant excitation conditions with excitation laser wavelength of 543 nm and it is shown in Fig. S8c. Note that the exciton scattering rates are about twice as large since both an electron and a hole forming an exciton can scatter a phonon.
The bandgap energy shift due to electron-phonon coupling is calculated from the real part of the conduction band electron self-energy, similar to Ref. 15. The results are shown in Fig. S9, where the temperature dependence of the bandgap shift is much weaker than observed in the experiment. This suggests that other than just Fröhlich coupling to phonons and interband scattering (virtual valence to conduction transitions16) are responsible for the observed bandgap renormalization.

Figure S8: Inter-valley scattering rates of electrons in WS₂ heterostructures. (a) \( \epsilon_k = 0 \) meV, (b) \( \epsilon_k = 55 \) meV, and (c) \( \epsilon_k = 200 \) meV.
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