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Biaxial strain tuning of interlayer excitons in bilayer MoS$_2$

Felix Carrascoso $^1$, Der-Yuh Lin $^2$, Riccardo Frisenda $^{1,3}$$^*$ and Andres Castellanos-Gomez $^{1,3}$$^*$

$^1$ Materials Science Factory, Instituto de Ciencia de Materiales de Madrid (ICMM), Consejo Superior de Investigaciones Científicas (CSIC), Sor Juana Inés de la Cruz 3, E-28049 Madrid, Spain
$^2$ National Changhua University of Education, Bao-Shan Campus, No. 2, Shi-Da Rd, Changhua City 500, Taiwan, ROC
$^3$ Authors to whom any correspondence should be addressed.

$^*$E-mail: riccardo.frisenda@csic.es and andres.castellanos@csic.es

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Abstract

We show how the excitonic features of biaxial MoS$_2$ flakes are very sensitive to biaxial strain. We find a lower bound for the gauge factors of the A exciton and B exciton of ($-41 \pm 2$) meV/% and ($-45 \pm 2$) meV/% respectively, which are larger than those found for single-layer MoS$_2$. Interestingly, the interlayer exciton feature also shifts upon biaxial strain but with a gauge factor that is systematically larger than that found for the A exciton, ($-48 \pm 4$) meV/%. We attribute this larger gauge factor for the interlayer exciton to the strain tunable van der Waals interaction due to the Poisson effect (the interlayer distance changes upon biaxial strain).

The isolation of atomically thin MoS$_2$ by mechanical exfoliation in 2010 opened the door to study the intriguing optical properties of this 2D semiconductor material [1–3]. In fact, MoS$_2$ and other members of the transition metal dichalcogenide family show a rich plethora of excitonic phenomena, present even at room temperature. Mak et al and Splendiani et al observed a strong thickness dependent photoluminescence emission and a direct-to-indirect band gap transition [1, 2]. MoS$_2$ also has tightly bound negative trions, an exciton quasiparticle composed of two electrons and a hole [4, 5], and several groups in parallel reported the valley polarization, the selective population of one valley, by pumping with circularly polarized light [6–8]. Moreover, heterostructures built with these 2D systems have also attracted the interest of the scientific community because of the presence of interlayer excitons: excitons formed by electrons and holes that live in different layers [9–13]. Very recently, Gerber et al and Slobodeniuk et al demonstrated that naturally stacked bilayer MoS$_2$ (2H-polytype) also presents interlayer excitons, with high binding energy, that can be observed at room temperature [14, 15] and Niehues et al demonstrated that uniaxial strain could be used to tune the energy of the interlayer exciton [16].

In this work we employ biaxial strain to modify the band structure, and thus the excitonic resonances, in bilayer MoS$_2$ flakes. We observe that both the A and B excitons, as well as the interlayer exciton, substantially redshift upon biaxial tension. Interestingly, unlike to what has been reported for uniaxial strain, we found that the interlayer exciton is more effectively tuned upon straining than the A and B excitons. We attribute this effect to a modification of the interlayer interaction as an in-plane biaxial expansion of the bilayer MoS$_2$ is expected to come hand-by-hand of an out-of-plane compression due to the MoS$_2$ Poisson’s ratio.

MoS$_2$ flakes were prepared by mechanical exfoliation of bulk natural molybdenite (Moly Hill mine, QC, Canada) with Nitto tape (SPV 224). The cleaved MoS$_2$ flakes are then transferred to a Gel-Film (WF 4 × 6.0 ml Gel-Film from Gel-Pak®), Hayward, CA, USA). The flakes are optically identified, and their number of layers are determined from quantitative analysis of transmission mode optical microscopy images and micro-transmittance/reflectance spectroscopy [17–19]. Once a suitable bilayer MoS$_2$ flake is located it is transferred onto a polypropylene (PP) substrate by an all-dry deterministic transfer method [20, 21].

Figure 1(a) shows a reflection mode optical microscopy image of a MoS$_2$ flake transferred onto PP. Figure 1(b) shows differential reflectance spectra acquired on a mono-, bi- and tri-layer MoS$_2$ flake with a homemade micro-reflectance microscope. We direct the reader to [22] for technical details about the experimental
setup. To obtain the differential reflectance spectra we first collect the light reflected from the substrate \((R_s)\) by means of a fiber-coupled compact CCD spectrometer (see Materials and methods section). Then we collect the light reflected by the desired MoS\(_2\) flake \((R_f)\) and we calculate the differential reflectance as: \(\Delta R/R = 1 - R_s/R_f\) [19, 23]. All the spectra displayed in figure 1(b) show two strong transitions in all of them assigned to the A and B excitons (\(\sim 1.9\) eV and \(\sim 2.05\) eV respectively) originated from direct band gap transitions at the K point of the Brillouin zone [1, 2]. Interestingly, in bilayer MoS\(_2\) one can see another prominent peak between the A and B excitons. That peak can be also observed in trilayer and even multilayer MoS\(_2\) but it cannot be as easily resolved as in the case of bilayer MoS\(_2\). This feature in the reflectance spectra have been recently demonstrated (through temperature dependent optical spectroscopy studies, magneto-optical measurements and density functional theory calculations) to be originated by the generation of interlayer (IL) excitons [14, 15, 24]. These excitons are, similarly to the A and B excitons, due to direct transitions at the K point but unlike them the electron and hole are spatially separated in the different MoS\(_2\) layers (see the cartoon in figure 1(b)).

Uniaxial and biaxial strain have been proven to be effective methods to modify the optical properties of 2D semiconductors [25–28]. Here, in order to biaxially strain the MoS\(_2\) bilayers we exploit the large thermal expansion mismatch between the PP substrate \((\sim 130 \times 10^{-6}\) K\(^{-1}\)) and MoS\(_2\) \((1.9 \times 10^{-6}\) K\(^{-1}\)) [29]. PP has also a relatively high Young’s modulus \((1.5–2\) GPa) for a polymer, which is essential to guarantee an optimal strain transfer from substrate to flake. One can then biaxially stretch (or compress) the flakes by warming up (or cooling down) the substrate [30–32]. We used a Peltier element to control the temperature of the substrate around room temperature \((27\) °C–28°C) that allows us to cool down to 17°C (\(-0.13\)%) and to warm up to 95°C (+0.87%). The substrate temperature can be translated to biaxial expansion/compression through the thermal expansion coefficient of PP (see the supporting information available online at stacks.iop.org/JPMATER/3/015003/mediia).

Figure 2(a) shows the differential reflectance spectra acquired at different substrate temperatures from 19°C to 91°C. The spectra redshift upon temperature increase above room temperature and blueshift when the substrate is cooled down below room temperature. The spectra can be fitted to a sum of three Gaussian peaks in order to extract the energy position of the A, B and IL excitons. The summary of the exciton energy positions is shown in figure 2(b). From this figure one can extract the spectral shift per °C for the different excitons: \((-0.93 \pm 0.03)\) meV °C\(^{-1}\) for the A exciton and \((-0.97 \pm 0.03)\) meV °C\(^{-1}\) for the B exciton. In order to disentangle the intrinsic spectral shift expected for MoS\(_2\) upon temperature change from that originated from the biaxial strain we fabricated a MoS\(_2\) sample on a Si substrate with 50 nm of SiO\(_2\) which is expected to have a negligible thermal expansion, and we probe the exciton position as a function of temperature. We found that for single-, bi- and tri-layer MoS\(_2\) all the excitons shift by \(-0.4\) meV °C\(^{-1}\). By subtracting this intrinsic thermal shift value to the values measured in samples fabricated on PP we can determine the spectral shift induced by biaxial strain. And we can determine the gauge factor, the spectral shift per % of biaxial strain, by calculating the substrate biaxial expansion (or compression) upon temperature change (see the supporting information for

Figure 1. (a) Reflection mode optical microscopy image of a MoS\(_2\) flake with single- and bi-layer regions (highlighted with 1L and 2L respectively) transferred onto the surface of a polypropylene (PP) substrate. (b) Differential reflectance spectra acquired on single-, bi- and tri-layer MoS\(_2\) flakes on PP. The A and B excitons are clearly visible for all these thicknesses while the interlayer (IL) exciton, present in multilayer MoS\(_2\), is more clearly visible for the bilayer flake.
details about the thermal expansion calibration of the PP substrates. The resulting gauge factors for the A and B excitons are \((-41 \pm 2)\) meV/% and \((-45 \pm 2)\) meV/%. Note that these gauge factor values should be considered as a lower bound as we are assuming that all the biaxial expansion of the substrate can be effectively translated to biaxial strain to the MoS2 flake. Due to the Young’s modulus mismatch between the PP substrate and the MoS2, the strain transfer efficiency could be lower (and thus we would be underestimating the gauge factor values) [30, 33]. The fact that all the spectra shows a clear IL peak indicates that both MoS2 layers are equally strained (maintaining the 2H- stacking during the whole straining cycle) as the presence of IL exciton peaks is extremely sensitive to the relative atomic arrangement between the layers [14]. We also direct the reader to the supporting information section S6 for a finite element simulation used to estimate the strain transfer along the thickness of thick multilayered MoS2 flakes.

It is interesting to note that all the bilayer MoS2 flakes studied here have A and B exciton gauge factors that are substantially larger than those found for single-layer flakes which are in the \((-10–25)\) meV/% range [30], in agreement with density functional theory calculations [34]. We point the reader to the supporting information for a summary of the measured datasets in 2 single-layer flakes, other 5 bilayers and one trilayer flake.

For the interlayer exciton we find a gauge factor of \((-48 \pm 4)\) meV/% which is substantially larger than that found for the A exciton. We direct the reader to the supporting information for datasets acquired on other five bilayer MoS2 flakes (with gauge factor up to \(-55\) meV/%) and one trilayer flake that also have a substantially larger gauge factor for the interlayer exciton \((-23\) meV/%) than for the A exciton \((-11\) meV/%) similarly to the bilayer case. This contrasts with what has been recently reported for uniaxially strained bilayer MoS2 flakes by Niehues et al where the gauge factor of the interlayer exciton was slightly lower than that of the A exciton. We attribute the larger gauge factor observed in our experiment to a reduction (or increase) of the bilayer interlayer spacing upon biaxial tension (or compression) as expected from the Poisson effect: as the out-of-plane Poisson’s ratio of MoS2 is \(\nu_o \sim 0.2\) a biaxial tension of 1% would yield a reduction of 0.2% in the interlayer distance [35]. A similar tunability of the interlayer van der Waals interaction upon biaxial strain has been recently reported in black phosphorus by Huang and co-workers [36]. The strain tunable interlayer distance could explain the large gauge factor observed for bilayer MoS2 upon biaxial strain as Deilmann and Thygesen demonstrated through density functional theory calculations that the interlayer exciton position strongly depends on the interlayer...
distance [24]. In previous uniaxial strain works, on the other hand, because of the Poisson’s ratio of the polycarbonate substrate ($\nu = 0.37$) when the flake is uniaxially stretched in one direction it is compressed in the perpendicular direction (within the basal plane) [37] counteracting most of the Poisson’s effect induced upon uniaxial tension [16].

In figure 3 we test the reproducibility of the biaxial strain tuning exploiting the thermal expansion of the substrate. We modulated the temperature of the substrate between $\sim 30^\circ$C and $\sim 40^\circ$C (see the registered temperature versus time in the top panel of figure 3). The color map in the bottom panel shows the time evolution of the differential reflectance spectra and the extracted position of the A, IL and B excitons, extracted from fits similarly to figure 2(a), are displayed with the black lines. This illustrates the power of this method to tune the van der Waals interlayer interaction and thus the interlayer excitons in biaxial MoS$_2$.

**Conclusions**

In summary, we have exploited the large thermal expansion of polypropylene substrates to subject biaxial MoS$_2$ flakes to biaxial strain. We find that the excitons redshift upon biaxial tension with gauge factors that are larger than those reported for monolayer MoS$_2$. Interestingly, the interlayer exciton gauge factor is systematically larger than that of the A and B excitons (contrasting the results reported for uniaxially strained bilayer MoS$_2$). We attribute this larger gauge factor of the interlayer exciton to the strain tuning of the van der Waals interaction upon biaxial in-plane straining due to the Poisson effect.

**Materials and methods**

Optical microscopy images have been acquired with a Motic BA MET310-T upright metallurgical microscope equipped with an AM Scope MU1803 camera with 18 megapixels. The trinocular of the microscope has been modified to connect it to a fiber-coupled Thorlabs spectrometer (part number: CCS200/M) to perform the differential reflection spectroscopy measurements [19].

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**ORCID iDs**

Riccardo Frisenda @ https://orcid.org/0000-0003-1728-7354
Andres Castellanos-Gomez @ https://orcid.org/0000-0002-3384-3405

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