Spectrally narrow exciton luminescence from monolayer MoS$_2$ exfoliated onto epitaxially grown hexagonal BN

E. Courtade$^1$, B. Han$^1$, S. Nakhaie$^2$, C. Robert$^1$, X. Marie$^1$, P. Renucci$^1$, T. Taniguchi$^3$, K. Watanabe$^3$, L. Geelhaar$^2$, J.M.J. Lopes$^2$, and B. Urbaszek$^1$

$^1$Université de Toulouse, INSA-CNRS-UPS, LPCNO, 135 Av. Rangueil, 31077 Toulouse, France
$^2$Paul-Drude-Institut für Festkörperlektronik, Leibniz-Institut im Forschungsverbund Berlin e.V., Hausvogteiplatz 5-7, 10117 Berlin, Germany
$^3$National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan

The strong light-matter interaction in transition metal dichalcogenides (TMDs) monolayers (MLs) is governed by robust excitons. Important progress has been made to control the dielectric environment surrounding the MLs, especially through hexagonal boron nitride (hBN) encapsulation, which drastically reduces the inhomogeneous contribution to the exciton linewidth. Most studies use exfoliated hBN from high quality flakes grown under high pressure. In this work, we show that hBN grown by molecular beam epitaxy (MBE) over a large surface area substrate has a similarly positive impact on the optical emission from TMD MLs. We deposit MoS$_2$ and MoSe$_2$ MLs on ultrathin hBN films (few MLs thick) grown on Ni/MgO(111) by MBE. Then we cover them with exfoliated hBN to finally obtain an encapsulated sample: exfoliated hBN/TMD ML/MBE hBN. We observe an improved optical quality of our samples compared to TMD MLs exfoliated directly on SiO$_2$ substrates. Our results suggest that hBN grown by MBE could be used as a flat and charge free substrate for fabricating TMD-based heterostructures on a larger scale.

Introduction.— Transition metal dichalcogenides (TMDs) are van der Waals crystals with the chemical formula MX$_2$, where M is a transition metal such as Mo or W and X is a chalcogen atom such as S, Se or Te. TMD monolayers (MLs) are direct semiconductors in the ML limit, as first shown for MoS$_2$ in 2010 [1, 2]. Their strong light-matter interaction is governed by robust excitons [3] with binding energies of the order of some hundreds of meV [4–10], making them potential candidates for optoelectronic applications over a wide range of temperatures [11]. Moreover, strong spin-orbit coupling and breaking of inversion symmetry allow to explore unique spin/valley properties in TMD MLs [12–20].

For preparing field effect devices [21], first studies focused on TMD MLs exfoliated on SiO$_2$/Si. However, this substrate is not ideal due to surface roughness and uncontrolled charge puddles [22, 23], responsible for very poor mobility [24]. The SiO$_2$ surface is also known to degrade the optical properties of TMD MLs. The most prominent example is ML MoS$_2$, for which photoluminescence (PL) at low temperature shows neutral exciton linewidth as broad as 50 meV [15, 16, 25–31] close to a charge exciton (trion) transition and an intense defect-related emission [27]. Broad emission spectra with strong inhomogeneous contributions do not allow to take full advantage of the strong light-matter interaction and the spin-valley properties of these materials.

Recently, TMD MLs have been encapsulated in hexagonal boron nitride (hBN) to solve this problem, similar to graphene encapsulation by hBN for transport [22, 23]. Compared to SiO$_2$, the hBN is a nearly charge free material with an atomically flat surface, the top hBN layer protects the TMD ML surface [32]. These van der Waals heterostructures [33] are usually prepared by mechanical exfoliation. Although this is a very convenient technique for scientific research, it seems difficult to envisage device fabrication on a large scale based on exfoliation only, using flakes with dimensions in

![FIG. 1: Investigated samples](image-url)
FIG. 2: Optical spectroscopy results for exfoliated-hBN/MoS$_2$ ML/MBE-hBN. (a) PL spectra with 5 $\mu$W excitation power taken at different positions to illustrate sample inhomogeneities. (b) Comparison between PL and reflectivity at the same sample position. The A exciton is visible on both spectra around 1.97 eV and the B exciton appears in reflectivity 150 meV above the A transition. (c) PL spectra with 20 $\mu$W excitation before (black curve) and after (red curve) exposure up to 50 $\mu$W. (d) PL spectra with increased excitation power from 1 $\mu$W to 50 $\mu$W.

the $\mu$m to tens of $\mu$m range. That is why we investigate here substrates of 1 cm$\times$1 cm surface area for which molecular beam epitaxy (MBE) has been used for hBN growth instead of mechanical exfoliation. Compared to TMD MLs directly deposited on SiO$_2$/Si substrates, our samples reveal an improved optical quality. We reach neutral exciton emission linewidth as low as 6 meV for ML MoS$_2$ and 2 meV for ML MoSe$_2$, a considerable improvement in terms of FWHM compared to the same transitions for MLs deposited on SiO$_2$. We are able to distinguish optical features stemming from the A-exciton and the B-exciton state.

Samples and Set-up.— Our substrates are completely covered with an ultrathin hBN film that were grown from the constituent elements B and N using MBE. As a template for the hBN synthesis, 300 nm thick Ni films deposited on MgO(111) were employed. More details about the hBN growth procedure as well as the Ni film preparation can be found elsewhere [34, 35]. Atomic force microscopy (AFM) reveals that the hBN film offers a smooth surface morphology with a root-mean-square roughness of about 0.3 nm for a 1 $\mu$m$^2$ surface area (see Fig.1a). The smooth nature of the surface is also illustrated in the AFM profile shown in the inset of Fig. 1a. The overall surface topology shown in the AFM image is dominated by the surface features of underlying Ni film such as step clusters. Also, the existence of wrinkles in the hBN can be observed, which form during cooling due to the unequal expansion coefficients of the hBN and Ni [35]. The average film thickness is 1 nm, i.e. around three MLs of hBN. Our growth technique results in crystalline hBN over the entire substrate surface. Crystalline domains are typically micrometers in diameter, as discussed in Nakhaie et al. [34].

Using the all-dry viscoelastic technique described in Castellanos-Gomez et al. [36], we exfoliate on the MBE grown hBN film MoS$_2$ and MoSe$_2$ monolayers. In a last step, the TMD MLs were covered with flakes exfoliated from high quality hBN grown under high pressure [37], used in our previous studies [32, 38] to obtain encapsulated TMD MLs. A schematic representation of the prepared samples is depicted in Fig.1b. The heterostructures were then investigated by performing PL and reflectivity measurements at low temperature (T=10 K) in a low vibration, closed cycle cryostat. The confocal set-up has a detection/excitation spot of about 1 $\mu$m diameter [39]. To observe PL, we excited MoS$_2$ with a cw laser at 532 nm and MoSe$_2$ with a laser at cw 633 nm, whereas we used polychromatic white light for reflectivity experiments.

Results and Discussion.— First we show results for an MoS$_2$ ML covered with exfoliated hBN on top
of MBE-hBN/Ni/MgO(111). By using an Attocube nano-positioner (nm step-size) we were able to choose precisely the position where we performed measurements on the encapsulated monolayer. As shown in Fig. 2a, we obtained similar, sharp PL spectra at different positions on the flake. Depending on the exact position of the detection spot on the MoS$_2$ ML flake the energy of the neutral excitonic transition (labelled $X_A$ on the spectra) can shift on average by an energy of about 10 meV, possibly due to topological imperfections of the underlying Ni layer or small wrinkles of the hBN layer grown by MBE. Our spectroscopy setup enabled us to take at the same position PL and reflectivity spectra to compare the two measurements. The overlap of the two spectra in Fig. 2b shows a negligible Stokes shift (i.e. negligible neutral exciton localization), thus revealing the good optical quality of our sample under the detection spot. In addition another feature appears in reflectivity about 3 meV below the neutral $X_A$. As illustrated in Fig. 3c, which shows the overlap of PL and reflectivity spectra taken with the same excitation intensity (see Fig. 2c), possibly a consequence of weak photodoping. We performed a power-dependence cycle going from 1 to 50 $\mu$W and coming back to 1 $\mu$W then we compared two spectra taken with the same excitation power (here 20 $\mu$W) during the two parts of the cycle. In Fig. 2c, we measure a reduction of the $X_A$ intensity of about 25%.

To study the impact of using MBE grown hBN substrates on another important TMD material in addition to MoS$_2$, we performed measurements for a MoSe$_2$ ML [43–46] deposited on an identical substrate of MBE-hBN/Ni/MgO(111) and covered afterwards with exfoliated hBN. In Fig. 3a the overlap of PL and reflectivity shows that the neutral A-exciton $X_A$ energy is identical for the two kinds of spectroscopic experiments. This negligible Stokes shift is a first indication of the good spectral quality of the sample. In reflectivity, the B-exciton $X_B$ appears 210 meV above $X_A$, in agreement with previous measurements [43, 47]. In PL another sharp transition commonly associated to the trion (T) [43, 48] is visible about 29 meV below $X_A$. As illustrated in Fig. 3b, the small FWHM of the transitions enables to clearly distinguish these two peaks. Depending on position, neutral exciton linewidths down to 2 meV were observed. As shown in Fig. 3c PL power-dependent measurements did not induce major changes of the spectral shape, but we noticed a slight hysteresis due to photodoping (Fig. 3b). The spectra reveal an increase of the PL intensity ratio $X_A/T$ from 0.48 to 0.63 after laser exposure.

In conclusion, we have shown narrow excitonic emission from MoS$_2$ and MoSe$_2$ MLs exfoliated on MBE grown hBN, suggesting that this substrate material is a suitable building block for high quality van der Waals heterostructures. In future experiments, the tunability of the hBN thickness on an ML level by MBE does allow...
in principle to see if hBN can act as a barrier material between the nickel film and the TMD to study proximity effects, similar to recent work on TMDs in contact with ferromagnetic materials [49, 50]. Our MBE-grown hBN can also be used in the future as a substrate material for MBE growth of transition metal dichalcogenides [51, 52].

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* Electronic address: lopes@pdi-berlin.de
† Electronic address: urbaszek@insa-toulouse.fr
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