2D Materials

LETTER

Narrow photoluminescence and Raman peaks of epitaxial MoS₂ on graphene/Ir(1 1 1)

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Abstract

We report on the observation of photoluminescence (PL) with a narrow 18 meV peak width from molecular beam epitaxy grown MoS₂ on graphene/Ir(1 1 1). This observation is explained in terms of a weak graphene-MoS₂ interaction that prevents PL quenching expected for a metallic substrate. The weak interaction of MoS₂ with the graphene is highlighted by angle-resolved photoemission spectroscopy and temperature dependent Raman spectroscopy. These methods reveal that there is no hybridization between electronic states of graphene and MoS₂ as well as a different thermal expansion of both materials. Molecular beam epitaxy grown MoS₂ on graphene is therefore an important platform for optoelectronics which allows for large area growth with controlled properties.

1. Introduction

Following in the wake of graphene research, the optical properties of monolayer MoS₂ and related materials have stimulated intense research efforts over the last years [1–3]. The MoS₂ monolayer can take the form of 2H or 1T (1T’) crystal structures [4], with the 2H phase being a two-dimensional semiconductor with a direct band gap that exhibits photoluminescence [1]. Research has shown promise for applications of MoS₂ as field effect transistors, electroluminescent devices [5, 6] and in the area of spintronics [7]. However, most progress in our understanding of this material is still based on exfoliated layers, e.g. the recently observed record narrow luminescence of 5 meV [8]. Small flake size and the inherent inability of exfoliation for scale up impedes not only scientific research using methods where a large area film with a single orientation is needed. It also precludes the development of MoS₂ based electronics.

Thus, considerable efforts have been devoted to the synthesis of large area transition metal dichalcogenides (TMDGs) on metals and insulators [9–12]. The main difficulties which are common for TMDGs grown on a substrate are island growth and the nucleation of bilayer before saturation of a complete monolayer, the existence of mirror domains and the fact that some growth approaches rely on a metallic substrate. The latter not only quenches the luminescence but also demands transferring the TMD layer for electrical applications. For MoSe₂ grown on bilayer graphene, photoluminescence was observed [13]. However, for MoS₂, the prototypical TMD, no such observation has been shown. A clean and scalable approach to MoS₂ and other TMD synthesis is very low pressure chemical vapour deposition (CVD) using a catalytically active metallic substrate to support the decomposition of a sulphur containing precursor molecule. For example, simultaneous supply of Mo and H₂S molecules yields large islands and even single domain monolayer coverage of MoS₂ on Au(1 1 1) [14, 15]. However, the substantial interaction and hybridization with the metallic substrate modifies the properties of the layer substantially. This is a drawback specifically when considering potential applications in optics. Due to the low reactivity of van der Waals substrates like graphene or...
hexagonal boron nitride, neither phase pure layers nor a well defined epitaxial relation could be realized up to now with such sulphur containing precursor molecules [16]. Through molecular beam epitaxy (MBE) using elemental sulphur—supplied e.g. from a valved sulphur cracker cell or from a Knudsen cell releasing elemental sulphur out of a compound like FeS2—phase pure and epitaxial transition metal disulphide layers could be grown even on van der Waals substrates to which they are only weakly bonded [17, 18].

However, a complete spectroscopic characterization of such heterostructures is missing so far despite the fundamental interest in MoS2 on graphene (MoS2/Gr) e.g. as a photodetector [19]. Moreover, none of the above mentioned works on MBE grown MoS2 reported optical (photoluminescence or Raman) characterization of the material. This is surprising because optical methods are a main tool for the investigation of exfoliated MoS2 [3]. The lack of optical spectroscopy characterization for MBE grown MoS2 might be explained by the fact that these methods are less prevalent in the MBE community.

The present manuscript addresses these points and, besides structural investigation, investigates MBE-grown MoS2 spectroscopically using x-ray photoemission spectroscopy (XPS), angle-resolved photoemission spectroscopy (ARPES) and optical (Raman and luminescence) methods. For the monolayer islands of MoS2 epitaxially grown on a closed layer of graphene on Ir(1 1 1), as seen by scanning tunneling microscopy (STM) and low energy electron diffraction (LEED), the band structure measured by ARPES highlights the absence of any hybridization between MoS2 and graphene. Our results reveal that the photoluminescence (PL) of MoS2/Gr/Ir(1 1 1) is present despite the metallic substrate. We compare the optical bandgap obtained from PL measurements of the pristine MoS2/Gr/Ir(1 1 1) system to the energy separation between valence and conduction bands of the lithium (Li) doped system that we measured using ARPES. By

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careful analysis of this data and taking into account the doping induced band gap renormalization, we estimate an exciton binding energy of 480 meV. The temperature dependence of the bond lengths in graphene and MoS2 is probed using Raman spectroscopy. We find that the lattice expansion of graphene and MoS2 behave completely different. Graphene’s lattice expansion is dictated by the underlying Ir. The layer of MoS2, which is not in direct contact with the Ir(1 1 1), roughly follows the lattice expansion expected for freestanding MoS2. Our findings introduce MBE grown MoS2/Gr as a highly ordered, epitaxial heterostructure with a sharp optical emission that can be grown in large scale.

2. Experimental results

2.1. Structure and electronic properties
Prior to the analysis of the electronic and optical properties of the MoS2 layer, we present in figure 1 its microscopic, structural and chemical characterization. In (a), a large scale STM topograph of the MoS2 island layer is shown. The islands rest on the Gr/Ir(1 1 1) substrate, which has two monatomic step edges crossing the topograph horizontally. A large fraction of the substrate is covered by monolayer islands (green arrow in the inset), decorated with small bilayer islands (black arrow). On both, the monolayer and the bilayer, the metallic edge state [20] surrounding the islands can be observed (blue arrow), since the bias voltage lies in the band gap of the semiconductor MoS2. Bright lines, running across the MoS2 islands can be identified as (mirror) twin boundaries (white arrow) [21]. The MoS2 islands are extremely clean with a negligible density of defects. Subfigure (b) displays a LEED pattern of the sample, indicating the epitaxial relation between the substrate and the adlayer. Going from outside to inside, the first order Gr and Ir(1 1 1) spots and their associated moiré can be seen. Farthest inside, slightly rotationally broadened first order MoS2 diffraction spots indicate a lattice constant of (3.13 ± 0.03) Å, in line with the literature [22]. To probe the chemical properties, XPS was performed. Figure 1(c) compares the Mo 3d core level of elemental molybdenum in red (produced by evaporating molybdenum onto the Gr/Ir(1 1 1) surface without any source for sulphur) to the grown MoS2/Gr/Ir(1 1 1) structure in green. It can be seen that the Mo 3d core level is shifted to higher binding energy by 0.95 eV. This shift is in line with earlier observations of MoS2 grown on a gold substrate [10]. In these previous results, a splitting of the Mo 3d core level was observed into three components (low binding-energy, mid binding-energy and high binding-energy component) [10]. In comparison, our Mo 3d peak lacks the reported low binding-energy and mid binding-energy components which are attributed to metallic Mo and Mo on the edge of a flake. For the low binding-energy peak, we attribute this to the fact that all available Mo was used up in the reaction to form MoS2 and no elemental Mo is left over. The absence of the mid binding-energy component

Figure 2. (a) ARPES spectra of MoS2/Gr/Ir(1 1 1) taken with p-polarized light at hν = 31 eV and T = 20 K. The inset shows the region around the MoS2 K point in high-resolution. An energy distribution curve (EDC) cut of that data at the K point of MoS2 (labelled by KMoS2) is depicted in (b). The extracted spin–orbit splitting is 144 meV. (c) Fermi–surface map of graphene. The blue dot in the Fermi surface map denotes the position of the K point of graphene and is labelled by KGr in (a). We extract a hole density of 1.484 × 10^{13} cm^{−2}. (d) ARPES scan of Li-doped MoS2/Gr/Ir(1 1 1). (e) High resolution scan close to the Fermi level around the K point of doped MoS2 shows the conduction band shifting below the Fermi level upon Li evaporation. As a guide to the eye we have inserted a parabola shown in red. EDC cuts through the data are shown to the right of the ARPES scans in blue. A fit to the data is shown in black.
can be explained by the large island size achieved in this work. This increases the ‘bulk’ versus the edge contribution to a point where the edge contribution is negligible. The sulphur 2p peak is shown in figure 1(d). Our analysis confirms the growth of crystalline MoS\(_2\) and the absence of amorphous MoS\(_3\) [23]. Results of MoS\(_2\) grown on gold show an asymmetry in the S 2p peak compared to the present work. This can be explained by the influence of the gold substrate on the lower sulphur layer. This asymmetry is not visible for MoS\(_2\)/Gr/Ir(1 1 1) substrate on the lower sulphide layer and thus a weak interaction of the substrate with the grown MoS\(_2\) islands. As we will discuss later, this weak interaction is key to observing PL. The C 1s peak of the graphene layer is shown in figure 1(e).

Figure 2 shows angle-resolved photoemission spectroscopy (ARPES) results of the same system. An overview scan depicting the bands of graphene, MoS\(_2\) and the Ir substrate is shown in figure 2(a). The K point of graphene is at \(-1.7 \text{ Å}^{-1}\) and the K point of MoS\(_2\) at \(-1.3 \text{ Å}^{-1}\), both are indicated at the top x-axis. The valence band (VB) maximum of MoS\(_2\) appears at the K-point consistent with monolayer MoS\(_2\). For comparison, bilayer MoS\(_2\) (shown in the supporting information) has the VB maximum at the Γ point.

By taking the distance between the VB maximum of MoS\(_2\) at the K-point to the Fermi level (approximately 1.5 eV), it suggests that the Fermi level is closer to the conduction band (CB) than to the valence band of MoS\(_2\) as the measured electronic bandgap is typically below 2.6 eV [3]. The splitting of the VB at the MoS\(_2\) K-point due to spin–orbit interaction is clearly seen in the high resolution scan shown in the inset to figure 2(a). The fit to the energy distribution curve from a cut through the MoS\(_2\) K-point is shown in figure 2(b) and reveals a band splitting due to spin–orbit coupling of 144 meV. Interestingly, graphene is more hole doped than it was before MoS\(_2\) growth, the Dirac-point binding energy is evaluated to be \(E_{\text{Dirac}} = -0.25 \text{ eV}\) compared to \(E_{\text{Dirac}} = -0.1 \text{ eV}\) in the pristine case [24]. The hole doping can be seen from the ARPES scans and the map shown in figures 2(a) and (c). The fact that hole doping increases after performing the MoS\(_2\) growth on Gr/Ir(1 1 1) is also evident from a comparison to other works on Gr/Ir(1 1 1) [25, 26]. Analysis of the Fermi surface yields a hole concentration of 1.48 × 10\(^{13}\) cm\(^{-2}\). As we will see later, this hole doping is also responsible for the shift of the Raman active G band of Gr. Regarding the origin of the hole doping, we believe that sulphur intercalation under graphene can be excluded because we performed a test experiment where we exposed Gr/Ir to an equal amount of sulphur vapor and did not observe an increase in the hole concentration in graphene. Notably, ARPES does not show any hybridization between MoS\(_2\) and graphene bands which supports the idea that MoS\(_2\) is weakly interacting with Gr.

In order to measure the CB edge using ARPES, we have performed Li doping which induces an electron transfer from Li to the MoS\(_2\) layer thereby populating its CB. Figures 2(d) and (e) show ARPES spectra of Li doped MoS\(_2\)/Gr heterostructures. The doping turns MoS\(_2\) into a metal which is corroborated from the ARPES observation of a CB at the K point of MoS\(_2\) (the CB is visible as a parabola crossing the Fermi level in figure 2(e)). Assuming a circular Fermi surface of Li-doped MoS\(_2\), we estimate an electron concentration on the MoS\(_2\) layer of 3.2 × 10\(^{13}\) electrons per cm\(^2\).

The VB shifts down in energy and broadens but is otherwise unchanged. A Li induced phase transition in MoS\(_2\) has been predicted theoretically [27, 28] and experimentally reported in Li intercalated quantum dots [29]. Interestingly, in the present system we do not observe a structural phase transition of MoS\(_2\) to a 1T (or 1T’) phase which would be visible as a different band structure in the ARPES measurements [28, 30].

An energy distribution curve (EDC) through the K point yields peaks for the VBs and the CBs. In order to fit these EDCs, we have constrained the VB spin–orbit coupling (SOC) to vary only within a ±10 meV window around 144 meV as observed for the pristine system. The resulting fits for the spin–orbit split VB maxima are shown in figure 2(d). Regarding the CB, we are unable to perform a fit with only one component. Using two components, we can obtain a good fit as shown in figure 2(d). However, the obtained splitting of 30 meV is probably not due to SOC but due to other effects such the appearance of an extra band or linewidth broadening induced by the disorder in the Li layer. Nevertheless, since the splitting is comparably small, we can use estimate the separation between VB and CB. Taking the peak at 75 meV (CB minimum) and 2.05 eV (upper VB maximum) we find a difference that is equal to 1.975 eV. This value is similar to what has been measured in potassium intercalated monolayer MoS\(_2\) on bulk MoS\(_2\) where 1.86 eV was found [31]. In the next section we compare the obtained VB-CB separation to the energy of the PL to estimate a lower bound of the exciton binding energy.

The EDC curve also depicts small peaks at about 1.0 eV and 1.7 eV that appear only after Li deposition. We speculate that these could be related to either mid-gap states, Li induced defect states or polaronic bands, similar to what has been shown already [32].

2.2. Luminescent properties

Samples prepared and characterized in this way have then been transferred without exposure to air to an ultrahigh-vacuum (UHV) PL/Raman system [33]. Despite the MoS\(_2\) islands are grown on a metallic substrate we were able to detect PL at low temperatures. Figure 3(a) shows the PL spectra as the sample temperature is lowered. Besides the peak that originates from the PL a second order 2D Raman peak from graphene is seen.
slightly above 1.98 eV. A shift towards higher energy and a narrowing of the linewidth can be observed with decreasing temperature for the PL related peak while the Raman peak of graphene is not shifting. Figure 3(b) shows the dependence of the area and FWHM of the PL peaks. The area under the PL is temperature independent suggesting that the peak becoming more prominent is due to the reduced FWHM at low temperatures. Figure 3(c) shows the PL spectrum recorded at 8 K with a maximum at $E = 1.945$ eV together with a lineshape analysis. The narrow width of 18 meV of the PL points towards a long excitonic lifetime at low temperatures. This value is smaller than the observed PL linewidth of 120 meV of CVD grown MoS$_2$ on graphene [9] but it is still above the record measured excitonic linewidth of 4.5 meV in hBN/MoS$_2$/hBN van der Waals heterostructures [8]. Despite ARPES was carried out at 20 K and PL at 8 K we believe that the spectra are comparable as the PL of MoS$_2$ for 10 K, 20 K and 40 K has been observed to be not discernible [34].

Next, we consider the relation between the CB-VB separation from ARPES of doped MoS$_2$ (1.976 eV) and the PL peak (1.945 eV). Naively (assuming that the Li doping does not affect the band gap value) one might expect that the difference between these two values (30 meV) is equal to the exciton binding energy. However, considering that the bandgap is related to the dielectric function and that doping leads to better screening, we expect a decrease of the bandgap. This has been observed for carbon nanotubes [35, 36] and graphene nanoribbons [37] and theoretically calculated for TMDCs [38, 39]. According to quasiparticle calculations, the band gap renormalization due to doping is expected to be the dominant factor that needs to be considered for the determination of exciton binding energies out of such an experiment. For example, for the present carrier concentration of $3.2 \times 10^{13}$ cm$^{-2}$ (as estimated by ARPES) a band gap reduction by 450 meV is predicted [39]. Ignoring this effect would therefore only yield a lower bound of the exciton binding energy. However, if we include the calculated reduction of the ARPES band gap by doping (450 meV), we can estimate an exciton binding energy of about 480 meV. Indeed, this value is very similar to related experiments. Ugeda et al found an exciton binding energy of 550 meV for MoSe$_2$ on bilayer graphene on 6H-SiC(0001) by comparing PL and STS data [13]. A recent study combining ARPES and inverse photoemission of the MoS$_2$/Au system by Park et al found an exciton binding energy of 90 meV [40]. This value is considerably lower because of better screening on Au and highlights the important role of the dielectric environment. Furthermore, a decrease in the band gap upon photodoping has also been observed [41].

The appearance of PL is surprising because one would expect exciton quenching by the graphene or the metallic substrate by either Förster or Dexter transfer processes [19]. Electroluminescence of monolayer MoS$_2$ on a gold surface has been observed previously [42] by tunneling electrons directly into the MoS$_2$ via an STM tip. Experimentally it is known that the interaction between graphene and MoS$_2$ or semiconducting quantum dots results in luminescence quenching [19, 43, 44]. To the best of our knowledge there is no theoretical study of the mechanism of exciton quenching in the present system. However, a theoretical study of exciton quenching of luminescent molecules on graphene [45] suggests that both Förster and Dexter processes are relevant and graphene is an efficient energy sink. We speculate that the same is true for the present system.

The efficiency of luminescence quenching in exfoliated MoS$_2$/Gr heterostructures is reduced by the intercalation of adsorbates into the interface [19]. In the present case however, we can rule out such effects because we keep the sample always in either N$_2$ or high vacuum (samples were carried from the growth chamber to the UHV PL/Raman system in a vacuum suitcase or a vacuum tight N$_2$ container). The transferred samples still show a LEED pattern and the apparent height of the MoS$_2$ islands in STM is unchanged. Therefore, we believe that intercalation of adsorbates into the MoS$_2$/

![Figure 3.](image-url)
Gr interface is not responsible for the appearance of PL. Instead, we suspect that the key for PL observation is the relatively weak graphene-MoS$_2$ interaction as already discussed in the context of XPS and ARPES data analysis. To learn more about this interaction, we show temperature dependent Raman spectroscopy data taken inside UHV in the next section.

2.3. Vibrational properties and strain

Raman spectra have been taken in the same experimental setup as the PL measurements inside a vacuum better than 2 × 10$^{-10}$ mbar (see methods). Figure 4(a) shows an overview Raman spectrum taken at 4 K using a 442 nm excitation. The MoS$_2$ related phonons with $A_{1g}$ and $E_{2g}$ symmetry are strong in intensity compared to graphene (see inset of figure 4(a)) and have a splitting of 21 cm$^{-1}$.

A comparison of G band Raman spectra for 442 nm and 532 nm excitation is shown in figure 4(b). A shoulder at ∼1650 cm$^{-1}$ can be identified which is attributed to the $D'$ band because its intensity is changing with laser energy [52, 53], as one can see from figure 4(b). The appearance of the $D'$ Raman band is ascribed to translational symmetry breaking by the MoS$_2$ islands (see the STM image in figure 1(a)) which act as scattering centers for graphene electrons. Importantly, the graphene G band prior to MoS$_2$ synthesis is not visible by 442 nm and 532 nm excitation [54]. However, it can be detected using UV excitation (325 nm). The comparison of UV Raman spectra for Gr/Ir(1 1 1) and the MoS$_2$/Gr/Ir(1 1 1) heterostructure are shown in figure 4(c). A shift of G band position from 1593 cm$^{-1}$ (Gr/Ir) to 1613 cm$^{-1}$ (MoS$_2$/Gr/Ir) is observed. The frequency upshift by 20 cm$^{-1}$ can be explained by two effects that take place after growth of MoS$_2$. First, graphene becomes p-doped (that we have analyzed by ARPES). The G band frequency upshift upon p-doping has been reported in the literature [54–57]. For the observed hole concentration of 1.48 × 10$^{13}$ cm$^{-2}$ an upshift from the position of charge neutral graphene by ∼18 cm$^{-1}$ is predicted [56]. Neglecting the small initial p-doping of Gr/Ir(1 1 1), this is in very good agreement to the observed 20 cm$^{-1}$ upshift. Notably, the precise value of the upshift depends also on the substrate and other works report values in the range of ∼5–10 cm$^{-1}$ [54, 55, 57]. Second, we believe that after MoS$_2$ growth, Gr on Ir(1 1 1) becomes flatter which leads to compressive strain in Gr. This is corroborated by the fact that the Gr/Ir(1 1 1) moiré spots in the LEED pattern become weaker after MoS$_2$ growth. The wavyness of the moiré can help to relax some of the strain in the Gr/Ir(1 1 1) system. However, after MoS$_2$ growth, as Gr becomes flatter, it also acquires compressive strain which is known to cause an upshift in the G band frequency [55, 58].

Let us now move to the investigation of temperature induced strain in the heterostructure. Raman spectroscopy is a well suited tool to investigate the change of bond length due to strain via the frequency change of Raman active vibrations. The behavior of the frequency change versus temperature yields information on how strongly bonded graphene and MoS$_2$ are to each other and to the substrate. For example, if both layers would follow the thermal expansion of the Ir substrate, we can assume that they are strongly bonded to each other. For graphene which is in direct contact to the Ir surface and fully covering it, one might expect that the C–C bond length follows the thermal expansion of the bulk Ir. However, the situation of MoS$_2$ is less obvious because it is not in direct contact to the Ir and not a complete monolayer which can make it
Table 1. The frequency of the $E_{2g}$ and $A_{1g}$ is denoted by $\omega$, $\gamma$ denotes the change of phonon frequency with temperature and $\gamma$ the Grüneisen parameter.

| Mode   | $\omega$ (cm$^{-1}$) | $\gamma$ (cm$^{-1}$ K$^{-1}$) | $\gamma$ (ML) | $\gamma$ (bulk) |
|--------|---------------------|-------------------------------|--------------|----------------|
| $A_{1g}$ | 405.1, 403.0, 402.4, 408.4, 405.0 | $-0.013$, $-0.0123$, $-0.0143$ | 0.21 | 0.21 |
| $E_{2g}$ | 384.1, 384.3, 383.3, 382.6, 385.0 | $-0.011$, $-0.0132$, $-0.0179$ | 0.65 | 0.42 |

* This work MoS$_2$/Gr/Ir(1 1 1) measured at RT.
* Lee et al exfoliated MoS$_2$ on SiO$_2$ [46].
* Rice et al [47] have determined $\omega$ on a polymer and $\gamma$ from four point bending.
* Sahoo et al [48] have determined $\omega$ on SiO$_2$ and $\gamma$ between 80 K $-$ 473 K.
* Najmaei et al [49] have determined $\gamma$ in the range 300 K $-$ 500 K.
* Yan et al [50] have performed measurements of $\gamma$ for suspended monolayers and found that $\gamma$ for sapphire supported monolayer is similar.
* Sugai et al [51].

Performing the same estimation for MoS$_2$ we try to obtain a value for the temperature dependent phonon energy shift. The Grüneisen parameters of monolayer MoS$_2$ are reported in the literature as $\gamma_{A_{1g}} = 0.21$ and $\gamma_{E_{2g}} = 0.65$ ([47]). If we now apply the above formula, assuming that $\epsilon$ is that of the strained Ir substrate, we find $\Delta \omega_{A_{1g}} = 0.11$ cm$^{-1}$ and $\Delta \omega_{E_{2g}} = 0.67$ cm$^{-1}$. This does not agree with experiment at all. Notably, also using the Grüneisen parameter of bulk MoS$_2$ ($\gamma_{A_{1g}} = 0.21$ and $\gamma_{E_{2g}} = 0.42$ from [51]) would not improve agreement. We thus conclude that MoS$_2$ does not follow the thermal expansion of Ir and its behaviour is better described by the expansion expected for a freestanding monolayer. Graphene, however, is stronger interacting with the Ir substrate and its Raman shift as a function of temperature can be fully understood by the thermal expansion of the substrate. The absence of strain in MoS$_2$ is also consistent with our previous STM and LEED investigations [18] that display an extremely weak interaction of the MoS$_2$ with the substrate: entire islands can be moved by the STM tip and depending on the growth conditions, MoS$_2$ islands can also be grown with a broad angular.
distribution on Gr/Ir(1 1 1) without any measurable change of lattice parameter. Therefore strain and stress in MoS$_2$ can be ruled out to very good approximation.

3. Conclusion and outlook

We have characterized the epitaxially grown MoS$_2$/Gr/Ir(1 1 1) system combining XPS, ARPES, Raman and PL measurements. STM, LEED and XPS confirm the good quality of our grown samples. We have observed a PL-signal with small FWHM suggesting a long excitonic lifetime. This surprising result is the first clear observation of photoluminescence of epitaxially grown MoS$_2$ on a metallic substrate. The absence of the expected quenching of the PL intensity on a metallic surface can potentially be explained by a weak interaction between the epitaxial MoS$_2$ and the substrate as is suggested by our XPS, ARPES and temperature dependent Raman measurements. Using Li deposition, we induced doping of MoS$_2$ into a degenerate semiconductor. From the analysis of ARPES data of Li doped MoS$_2$ we obtained the band gap. Using theoretical calculations on the band gap renormalization due to doping, we estimate an exciton binding energy of 480 meV. Our results suggest that the MoS$_2$-islands are only weakly interacting with the Gr/Ir surface which could explain the absence of quenching, but the microscopic mechanisms are still unclear. Theoretical calculations for the Dexter- and Förster-type energy transfer from the islands into the graphene substrate are thus needed to quantitatively explain the observed PL. With this background it would be interesting to grow MoS$_2$ on hexagonal boron nitride (h-BN) using the same method as used for this work and compare FWHM and intensity of the PL. Indeed, previous experiments on h-BN capped MoS$_2$ have shown an increase in the PL intensity upon h-BN encapsulation. Similarly, it was shown that chemical treatment of MoS$_2$ flakes via an organic superacid increased PL quantum yield to near unity, similar treatment of epitaxially grown MoS$_2$ monolayers might increase PL intensity even more. Regarding applications in valleytronics, it should be taken into account that the selection rules for optical absorption of circularly polarized light depend on the MoS$_2$ domain type regarding the inversion symmetry. Based on the MoS$_2$ unit cell there are two possible domain structures which are related to each other by 180° rotation. It has been shown previously that samples grown by a similar process than ours on Au exhibit preferentially one domain. In our STM figure, we observe domain boundaries corroborating the existence of both domains. A detail analysis of the ratio of the two domains by circular polarized PL or x-ray photoelectron diffraction is an interesting future work. The proposed growth method might also be useful for the fabrication of photodetectors based on MoS$_2$/Gr heterostructure. To that end, we suggest the synthesis of monolayer graphene which is then transferred to Si oxide. Such a sample can be used as a substrate for the growth of monolayer MoS$_2$ islands. After having electrically contacted graphene, light illumination with a photon energy, could efficiently excite electron-hole pairs in MoS$_2$. It has been shown that the proximity to graphene can lead to an efficient carrier transfer from MoS$_2$ to graphene. If a voltage is applied to graphene, the current measured depends on the illumination.

4. Appendix/supporting information

4.1. ARPES of bilayer MoS$_2$

Figure 5 depicts ARPES spectra of bilayer MoS$_2$ that has been grown by doubling the deposited amount of Mo. This resulted in 1.4 monolayers (ML) of MoS$_2$ but growth conditions were specifically tuned to induce bilayer growth via sulphur pressure in the chamber and cycled growth (see methods section). It is clear from ARPES that the VB maximum is not at the K point but at the Γ point (note the splitting of the band at Γ into two subbands, one with a higher binding energy of approximately 1.9 eV and one with a lower binding energy of approximately 1.3 eV).

5. Methods

5.1. X-ray photoemission spectroscopy

XPS was performed at the German–Russian beamline (RGBL) of the HZB BESSY II synchrotron in Berlin (Germany) with a beam energy of 650 eV and pass energy of 20 eV in a normal emission geometry. The MoS$_2$/Gr/Ir(1 1 1) samples were prepared in situ and measured in a vacuum better than 5 × 10$^{-10}$ mbar.

5.2. Angle-resolved photoemission spectroscopy

ARPES was performed at the BaDElPh beamline of the Elettra synchrotron in Trieste (Italy) with linear s- and p-polarisation at $h\nu = 31$ eV at temperatures of 20 K. The MoS$_2$/Gr/Ir(1 1 1) samples were prepared in situ and measured in a vacuum better than 5 × 10$^{-11}$ mbar. Li deposition was carried out in an ultra-high vacuum (UHV) chamber from SAES getters with the sample at 20 K. We performed stepwise evaporation of Li which we monitored by ARPES measurements of the band structure. Li evaporation was stopped after the desired doping level was reached.

5.3. Scanning tunneling spectroscopy and microscopy

Scanning tunneling microscopy was conducted in a home built variable temperature STM apparatus in Cologne at a base pressure below 8 × 10$^{-11}$ mbar. For image processing the software WSxM was used.

5.4. Growth

We employ molecular beam epitaxy via a two-step process: In the first step, with the sample held
at room temperature, Mo is evaporated at a rate of \(1.4 \times 10^{16}\) atoms m\(^{-2}\) s\(^{-1}\) into a S background pressure of \(p \approx 5 \times 10^{-9}\) mbar onto Gr/Ir(111). The elemental S background atmosphere is achieved by heating a pyrite (FeS\(_2\)) filled crucible to \(\approx 500\) K. During the second step, the sample is annealed for 300 s at \(T = 1050\) K in a S pressure of \(p \approx 2 \times 10^{-9}\) mbar. These two steps constitute one growth cycle.

To obtain a MoS\(_2\) layer with good orientation by epitaxy also for coverages beyond 0.4 ML the total coverage was deposited in subsequent growth cycles each yielding a coverage of \(\approx 0.35\) ML MoS\(_2\). Using this technique we realized two cycle MoS\(_2\) samples (nominal coverage 0.7 ML) and four cycle MoS\(_2\) samples (nominal coverage 1.4 ML).

5.5. Ultra-high vacuum Raman and photoluminescence spectroscopy

UHV Raman measurements were performed in the back-scattering geometry using commercial Raman systems (Renishaw) integrated in a homebuilt optical chamber [33], where the exciting and Raman scattered systems (Renishaw) integrated in a homebuilt optical back-scattering geometry using commercial Raman photoluminescence spectroscopy (nominal coverage 1.4 ML).

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