Strain, Doping, and Electronic Transport of Large Area Monolayer MoS$_2$ Exfoliated on Gold and Transferred to an Insulating Substrate

Salvatore Ethan Panasci, Emanuela Schiliro, Giuseppe Greco, Marco Cannas, Franco M. Gelardi, Simonpietro Agnello, Fabrizio Roccaforte, and Filippo Giannazzo*

Cite This: ACS Appl. Mater. Interfaces 2021, 13, 31248–31259

ABSTRACT: Gold-assisted mechanical exfoliation currently represents a promising method to separate ultralarge (centimeter scale) transition metal dichalcogenide (TMD) monolayers (1L) with excellent electronic and optical properties from the parent van der Waals (vdW) crystals. The strong interaction between Au and chalcogen atoms is key to achieving this nearly perfect 1L exfoliation yield. On the other hand, it may significantly affect the doping and strain of 1L TMDs in contact with Au. In this paper, we systematically investigated the morphology, strain, doping, and electrical properties of large area 1L MoS$_2$ exfoliated on ultraflat Au films (0.16–0.21 nm roughness) and finally transferred to an insulating Al$_2$O$_3$ substrate. Raman mapping and correlative analysis of the E$_1$ and A$_1$ peak positions revealed a moderate tensile strain ($\epsilon \approx 0.2\%$) and p-type doping ($n \approx -0.25 \times 10^{13}$ cm$^{-2}$) of 1L MoS$_2$ in contact with Au. Nanoscale resolution current mapping and current–voltage ($I$–$V$) measurements by conductive atomic force microscopy (C-AFM) showed direct tunneling across the 1L MoS$_2$ on Au, with a broad distribution of tunneling barrier values ($\Phi_{t}$ from 0.7 to 1.7 eV) consistent with p-type doping of MoS$_2$. After the final transfer of 1L MoS$_2$ on Al$_2$O$_3$/Si, the strain was converted to compressive strain ($\epsilon \approx -0.25\%$). Furthermore, an n-type doping ($n \approx 0.5 \times 10^{13}$ cm$^{-2}$) was deduced by Raman mapping and confirmed by electrical measurements of an Al$_2$O$_3$/Si back-gated 1L MoS$_2$ transistor. These results provide a deeper understanding of the Au-assisted exfoliation mechanism and can contribute to its widespread application for the realization of novel devices and artificial vdW heterostructures.

KEYWORDS: MoS$_2$, gold-assisted exfoliation, Raman, photoluminescence, conductive atomic force microscopy, doping, strain

1. INTRODUCTION

Semiconducting transition metal dichalcogenides (TMDs) are a class of two-dimensional (2D) layered materials with the general chemical formula MX$_2$, where M is a transition metal (Mo, W, ...) and X is a chalcogen (S, Se, ...), which are characterized by strong (covalent) in-plane bonds and weak van der Waals (vdW) interactions between the layers. In particular, due to its abundance in nature and good stability under ambient conditions, molybdenum disulfide (MoS$_2$) has been the most widely investigated TMD for potential applications in electronics, optoelectronics, photodetection, and sensing. In its bulk form, MoS$_2$ shows an indirect band gap of 1.2 eV, whereas the monolayer counterpart exhibits a direct band gap of $\sim 1.8$ eV. Many of the MoS$_2$ device prototypes demonstrated so far have been fabricated using monolayer flakes or few-layer flakes obtained by mechanical exfoliation from bulk molybdenite. In spite of the reported progress in the scalable exfoliation (lithiation/sonication, electrochemical exfoliation, etc.) and large area deposition of TMDs (chemical vapor deposition, molecular beam epitaxy, etc.), mechanical exfoliation still remains a method of choice for investigating basic physical phenomena and demonstrating new device concepts, due to the superior quality of the material produced by this approach.2,3

To overcome the limitations represented by the small (micrometer) size of the exfoliated flakes and the lack of reproducibility in the thickness, appropriate strategies allowing increase of the exfoliated monolayer area have been recently
In particular, the so-called “gold-assisted” mechanical exfoliation approach showed the possibility of separating large area (cm²) monolayer MoS₂ (1L MoS₂) from a bulk crystal stamp by exploiting the strong affinity between a gold film and the topmost sulfur atoms of MoS₂.²⁶⁻²⁹ The exfoliation process from the bulk stamp can be repeated many times, producing flakes with reproducible geometry at each exfoliation step, with a size limited only by the dimensions of currently available bulk samples. The Au/1L MoS₂ stack can be also transferred to insulating substrates, and after Au removal by chemical etching, the large area MoS₂ film exhibits electronic properties fully comparable with those of the semiconducting MoS₂ flakes obtained by conventional Scotch tape exfoliation.²⁷,³⁰ The gold-assisted exfoliation approach has been shown to be effective also with other common TMDs (such as MoSe₂, WS₂, WSe₂, MoTe₂, WTe₂, and GaSe)²⁶,²⁸,³¹,³² as well as with other 2D crystals, including metal monochalcogenides (e.g., GaS), black phosphorus, black arsenic, metal trichlorides (e.g., RuCl₃), and magnetic compounds (e.g., Fe₃GeTe₂).³² Furthermore, it has been recently proposed as a general approach to produce large area heterostructures of different TMDs with outstanding electronic quality by sequentially stacking the exfoliated monolayers.³¹ The 1L MoS₂/Au system is also currently the object of

Figure 1. (a) Optical images at two different magnifications of exfoliated MoS₂ on Au/Ni/SiO₂. (b) AFM image of ultrathin MoS₂ film with a fracture. The ~0.7 nm step height in the height profile along the red line demonstrates the 1L thickness of MoS₂ on Au. (c) Schematic illustration of the three steps for Au-assisted exfoliation of 1L MoS₂ and transfer to Al₂O₃/Si substrate. (d) Optical image and (e) AFM morphology of transferred 1L MoS₂ membrane on Al₂O₃/Si substrate and height line scan along the red line.
increasing interest for technological applications. As an example, the Au/1L MoS$_2$/Au heterojunctions hold great promise for nonvolatile switching memory applications.\textsuperscript{33,34} After the first “atomristor” demonstration using a CVD grown monolayer MoS$_2$ sandwiched between two inert Au contacts,\textsuperscript{33} the possibility to implement such a system using high quality and large area 1L MoS$_2$ mechanically exfoliated on Au has been also recently explored.\textsuperscript{34}

In the past few years, several morphological and spectroscopic investigations have been reported on the Au/MoS$_2$ system, with the aim of deeply understanding the mechanisms of the Au-assisted exfoliation and to maximize the monolayer fraction and the lateral size of the obtained MoS$_2$ films. In particular, the 1L exfoliation yield was shown to be strongly influenced by the gold surface morphology and its exposure to the air before exfoliation.\textsuperscript{26} Due to the strong vdW interaction at the MoS$_2$/Au interface, the Au morphology may significantly affect also the doping and strain in 1L MoS$_2$ as shown by Raman analyses.\textsuperscript{29} An increase of the density of states (DOS) at the Fermi energy (i.e., a metallic character) was predicted by ab initio simulations of the MoS$_2$/Au heterostructure as compared to semiconducting freestanding MoS$_2$.\textsuperscript{26} Such an increased DOS in 1L MoS$_2$ associated with the heterostructure as compared to semiconducting freestanding MoS$_2$.\textsuperscript{26} Recent investigations have been also reported on the evolution of the electronic properties of 1L MoS$_2$ and other TMDs (MoSe$_2$, MoTe$_2$) exfoliated on Au surfaces during thermal annealing processes at temperatures up to 500 °C.\textsuperscript{55,56} These studies revealed the occurrence of a phase transition from the 2H semiconductor to the 1T conductive phase of MoS$_2$ after the annealing, as a result of the interplay of charge transfer and strain induced by the Au substrate and defects in the MoS$_2$ layer.

In this context, a systematic study on the evolution of the structural and electronic properties of 1L MoS$_2$ in the different stages of the Au-assisted exfoliation process, i.e., after adhesion with gold and after final transfer to an insulating substrate, is still missing in the literature, and it would be highly desirable, considering the interest in this material system. In our work, we investigated the morphology, strain, doping, and electrical properties of 1L MoS$_2$ exfoliated on ultraflat Au films and finally transferred to an Al$_2$O$_3$/Si substrate. To this purpose, micro-Raman and microphotoluminescence mapping experiments have been carefully executed and a method for the evaluation of doping and strain status has been applied in an original way. The correlative analysis of the E’ and A$_1$ Raman peak positions in spatial mapping revealed a moderate tensile strain (~0.2%) and p-type doping ($0.25 \times 10^{13}$ cm$^{-2}$) of 1L MoS$_2$ in contact with Au. Nanoscale resolution current mapping and current–voltage (I–V) measurements by conductive atomic force microscopy (C-AFM) showed direct tunneling across the 1L MoS$_2$ on Au, with a broad distribution of tunneling barrier values ($\Phi_b$ from 0.7 to 1.7 eV) indicating wide point-to-point variations of MoS$_2$ p-type doping. After the final transfer of 1L MoS$_2$ on Al$_2$O$_3$/Si and complete removal of the Au film, the strain was converted to compressive (~0.25%) and an n-type doping of $\sim 0.5 \times 10^{13}$ cm$^{-2}$ was observed by Raman spectroscopy and confirmed by electrical measurements on an Al$_2$O$_3$/Si back-gated 1L MoS$_2$ transistor.

2. RESULTS AND DISCUSSION

The lateral extension and thickness uniformity of MoS$_2$ monolayers exfoliated on a smooth gold surface were initially assessed. To this aim, a 15 nm thick Au film was deposited onto a SiO$_2$/Si substrate by DC magnetron sputtering (as schematically reported in Figure S1 of the Supporting Information). Prior to Au deposition, a 10 nm thick Ni film was sputtered to improve the adhesion onto the SiO$_2$. Beside ensuring an optimal adhesion to the SiO$_2$ surface, the Ni interlayer was beneficial for achieving a very smooth surface of the Au overlayer, with a low root-mean-square (RMS) roughness of 0.16 nm, as deduced from the tapping mode atomic force microscopy (AFM) image reported in Figure S2 of the Supporting Information. Mechanical exfoliation of MoS$_2$ was carried out on the fresh Au surface, i.e., immediately after the deposition, in order to avoid its contamination with adventitious carbon, which is known to reduce the interaction strength between S atoms and Au.\textsuperscript{26} By this procedure, very large area MoS$_2$ films, mostly composed of a monolayer, were separated from the bulk crystal.

Figure 1a shows two optical images at different magnifications (10× and 100×, respectively) of the exfoliated MoS$_2$ on the Au surface. The presence of an ultrathin MoS$_2$ film extending for several hundred micrometers can be deduced from the color contrast in the lower magnification image, which also shows the presence of thicker MoS$_2$ areas of smaller size and fractures of the MoS$_2$ membrane (i.e., bare Au regions) due to the exfoliation process. The optical contrast difference between the uniform ultrathin MoS$_2$ membrane and one of these fractures can be better visualized in the higher magnification image in the inset of Figure 1a. Furthermore, a typical tapping mode AFM image of a fracture of the MoS$_2$ film is reported in Figure 1b. The ~0.7 nm step height measured by the line profile in the inset is a direct confirmation of the 1L thickness of the MoS$_2$ membrane. Furthermore, a higher resolution AFM image of 1L MoS$_2$ partially covering the Au surface is reported in Figure S3 of the Supporting Information. The histogram of the height distribution extracted from this image shows very similar RMS values for the MoS$_2$/Au (~0.25 nm) and bare Au areas (~0.28 nm), indicating a very conformal coverage by the MoS$_2$ membrane.

After assessing the thickness uniformity of 1L MoS$_2$ films exfoliated on gold, we investigated the transfer of these films to an insulating substrate, which is a mandatory requirement for most electronic applications. More specifically, a Si substrate covered by a 100 nm Al$_2$O$_3$ film was employed in this experiment, although the transfer procedure can be easily extended to other semiconductors or dielectric materials. Following the approach recently demonstrated by Liu et al.,\textsuperscript{31} the transfer procedure consisted of three different steps, schematically illustrated in Figure 1c. The first step was the fabrication of an ultraflat “gold tape”, consisting of a gold film on a polymer substrate. To this aim, a ~100 nm thick Au layer was deposited by DC magnetron sputtering on an accurately precleaned silicon sample. Afterward, the Au surface was spin-coated by a protective PMMA layer and attached to a thermal release tape (TRT). By exploitation of the poor adhesion between Au and Si, the TRT/PMMA/Au stack was easily peeled from the silicon surface, and thus the desired “gold tape” was obtained. The surface of Au films prepared by this method is typically very flat,\textsuperscript{37,38} and it has already been demonstrated to be suitable for the exfoliation of large area
monolayers of MoS₂ and other TMDs. In particular a RMS roughness of 0.21 nm was evaluated with AFM on the peeled Au films on PMMA in our experiments (see Figure S4 of the Supporting Information), which is comparable with that of the Au/Ni film on SiO₂. The TRT/PMMA/Au stamp with a fresh Au surface, i.e., immediately after peeling from Si, was used to exfoliate 1L MoS₂ from a MoS₂ bulk sample. The final step of the process was the transfer of 1L MoS₂ on the target Al₂O₃/Si surface. This was achieved by pressing the TRT/PMMA/Au/1L MoS₂ stack onto the Al₂O₃/Si substrate while heating at 120 °C to promote the TRT release, followed by PMMA removal and final chemical etching of the Au film (with KI/I₂ solution). Figure 1d reports a typical optical microscopic image of the transferred MoS₂ membrane on the Al₂O₃ surface. As compared to the case of 1L MoS₂ exfoliated on gold (Figure 1a), a much sharper color contrast can be observed between

Figure 2. (a) Representative Raman spectra for 1L MoS₂ on Au (black line) and on Al₂O₃/Si (red line). Color maps of E‘ peak frequency values (ω_E‘) for 1L MoS₂ on Au (b) and on Al₂O₃ (c) and corresponding histograms (d). Color maps of A₁‘ peak frequency values (ω_A₁‘) for 1L MoS₂ on Au (e) and on Al₂O₃ (f) and corresponding histograms (g). Color maps of peak frequency difference (Δω = ω_A₁‘ – ω_E‘) for 1L MoS₂ on Au (h) and on Al₂O₃ (i) and corresponding histograms (j).
the regions coated by the extended 1L MoS2 membrane (blue) and bare Al2O3 regions (violet), due to the favorable optical interference with the 100 nm Al2O3/Si substrate. Furthermore, the small regions coated by few-layer or multilayer MoS2 can be easily identified by the azure or bright color, respectively. Hence, the optical image provides useful information on the thickness uniformity of the transferred MoS2 film on a large area. Furthermore, a morphological AFM image of a sample region partially covered by the 1L MoS2 membrane is shown in Figure 1e.

The large area 1L MoS2 membranes exfoliated on Au and transferred onto Al2O3/Si were extensively investigated by micro-Raman mapping and photoluminescence (PL) spectroscopy, in order to evaluate the impact of the different substrates on relevant parameters, such as the doping and strain distributions. Figure 2a shows the comparison between two representative Raman spectra for 1L MoS2 on Au (black line) and on Al2O3/Si (red line), which indicated the characteristic $E_s'$ and $A_{1s}'$ peaks associated with the in-plane and out-of-plane MoS2 vibrational modes, respectively. It is worth noting that a peak frequency difference of $\Delta \omega = 18 \text{ cm}^{-1}$ is measured for our large area 1L MoS2 produced by Au-assisted exfoliation and transferred onto Al2O3, a value very similar to those reported for mechanically exfoliated or CVD-grown 1L MoS2 on common insulating substrates (such as SiO2).25,39 On the other hand, for the Au-supported 1L MoS2, the $E_s'$ peak

| $\omega_{E_s'}$ (cm$^{-1}$) | $\omega_{A_{1s}'}$ (cm$^{-1}$) | $\Delta \omega$ (cm$^{-1}$) | $\varepsilon$ (%) | $n$ (10$^{13}$ cm$^{-2}$) |
|---------------------------|-----------------------------|---------------------------|-----------------|-------------------------|
| 1L MoS2 on Au | 383.9 ± 0.3 | 405.1 ± 0.1 | 21.2 ± 0.3 | 0.21 ± 0.06 | −0.25 ± 0.06 |
| 1L MoS2 on Al2O3 | 386.2 ± 0.1 | 404.2 ± 0.1 | 18.1 ± 0.2 | −0.25 ± 0.01 | 0.5 ± 0.09 |

Figure 3. (a) Correlative plot of $A_{1s}'$ and $E_s'$ peak frequencies to evaluate biaxial strain and charge doping distributions in 1L MoS2 on Au (black circles) and on Al2O3 (blue triangles). The red (black) lines represent the strain (doping) lines for ideally undoped (unstrained) 1L MoS2, while the green square indicates the $\omega_{E_s'}^0 = 385 \text{ cm}^{-1}$ and $\omega_{A_{1s}'}^0 = 405 \text{ cm}^{-1}$ frequencies for freestanding 1L MoS2, taken as zero reference. The dashed red (black) lines parallel to the strain (doping) lines serve as guides to quantify the doping and strain values, respectively. Color maps of strain for 1L MoS2 on Au (b) and 1L MoS2 on Al2O3 (c) samples and histograms of the strain values (d). Color maps of doping for 1L MoS2 on Au (e) and 1L MoS2 on Al2O3 (f) and histograms of the doping values (g).
exhibits a red shift and the \( A'_1 \) peak exhibits a blue shift, resulting in a significantly larger value of \( \Delta \omega = 21 \text{ cm}^{-1} \). It is well-known that \( E' \) and \( A'_1 \) spectral features are highly sensitive to strain and doping of 1L MoS\(_2\).\(^{40,41}\) In particular, a red shift of the \( E' \) peak is typically observed with increasing tensile strain,\(^{42,43}\) followed by a peak splitting for large strain values.\(^{29,44}\) On the other hand, the \( A'_1 \) peak is known to be sensitive to doping, and a blue (red) shift of its position is typically reported for p-type (n-type) doping of 1L MoS\(_2\).\(^{45}\)

Hence, the increase in \( \Delta \omega \) for 1L MoS\(_2\) on Au/Ni/SiO\(_2\)/Si can be ascribed to a change both in the strain and doping of the 2D membrane.

In order to extract relevant statistical information on the doping and strain uniformity of the 1L MoS\(_2\) membranes exfoliated on Au and transferred to the Al\(_2\)O\(_3\)/Si substrate, Raman mapping was carried out on both samples by collecting arrays of 6 \( \times \) 6 spectra on a 5 \( \times \) 5 \( \mu \text{m}^2 \) area. Parts b and c of Figure 2 show the color maps of the \( E' \) peak frequency (\( \omega_{E'} \)) in the scanned areas for 1L MoS\(_2\) on Au and Al\(_2\)O\(_3\), respectively, while the comparison between the histograms of the \( \omega_{E'} \) values in the two maps is shown in Figure 2d. Similarly, the color maps of the \( A'_1 \) peak frequency (\( \omega_{A'_1} \)) and corresponding histograms are reported in Figure 2e–g. Besides the individual peak positions, also their difference \( \Delta \omega = \omega_{A'_1} - \omega_{E'} \) was calculated for all the collected Raman spectra. The color maps of the \( \Delta \omega \) values for 1L MoS\(_2\) on Au and Al\(_2\)O\(_3\) are shown in Figure 2h,i, and the histograms of the \( \Delta \omega \) values are reported in Figure 2j.

The comparison between the color maps allows visualization of the spatial distribution of the \( \omega_{E'} \), \( \omega_{A'_1} \), and \( \Delta \omega \) spectral features in the two different samples. As an example, it can be clearly deduced that the maxima of \( \Delta \omega \) for the Au-supported 1L MoS\(_2\) sample (Figure 2h) are correlated to the minima of the \( \omega_{E'} \) map (Figure 2b), where the \( E' \) peak is more red shifted. On the other hand, for the 1L MoS\(_2\) on Al\(_2\)O\(_3\), the \( \Delta \omega \) map exhibits an almost uniform contrast, and the spatial variations are clearly correlated with those of the \( A'_1 \) peak. The histograms in Figure 2d,g confirm on a large set of data the red shift of the \( E' \) peak and the blue shift of the \( A'_1 \) peak for 1L MoS\(_2\) on Au with respect to 1L MoS\(_2\) on Al\(_2\)O\(_3\). It is also interesting to observe a significantly narrower spread of \( E' \) values for the 1L MoS\(_2\) transferred to Al\(_2\)O\(_3\) which can be ascribed to a more uniform strain distribution. By Gaussian fitting of the histograms, the average values and standard deviations of the peak frequencies and their difference have been obtained and are reported in Table 1.

In the following, the spatial distributions of strain \( \varepsilon \) (%) and doping \( n \) (cm\(^{-2}\)) for 1L MoS\(_2\) on Au and on Al\(_2\)O\(_3\) will be quantitatively evaluated from a correlative plot of the \( A'_1 \) vs \( E' \) peak frequencies for all Raman spectra in the maps of Figure 2. A similar approach, based on the correlative plot of the characteristic 2D and G peaks, has been widely employed for strain and doping quantification of monolayer graphene on different substrates.\(^{46–50}\) More recently such a method has been adopted by some authors also for 1L MoS\(_2\).\(^{30,41,51}\)

In Figure 3a, the black open circles represent the \( A'_1 \) vs \( E' \) pairs for all the Raman spectra collected on 1L MoS\(_2\) on Au, while the blue open triangles represent the data pairs for 1L MoS\(_2\) on Al\(_2\)O\(_3\). The red and black lines represent the theoretical relations between the frequencies of the two vibrational modes at a laser wavelength of 532 nm in the ideal cases of a purely strained (strain line) and of a purely doped (doping line) 1L MoS\(_2\).\(^{43,45}\) The strain and doping lines cross in a point, corresponding to the \( \omega_{E'} \) and \( \omega_{A'_1} \) frequencies for ideally unstrained and undoped 1L MoS\(_2\). In the following, the literature values of the peak frequencies for a suspended MoS\(_2\) membrane (\( \omega_{E'} = 385 \text{ cm}^{-1} \) and \( \omega_{A'_1} = 405 \text{ cm}^{-1} \))\(^{43}\) have been kept as the best approximation to these ideal values, as substrate effects are excluded in this case. Starting from this reference point, the directions of increasing tensile strain and n-type doping are also indicated by the arrows along the two lines.

The \( \varepsilon \) and \( n \) values for each experimental point in Figure 3a can be evaluated from the combination of the linear relationships between the biaxial strain/charge doping and Raman shifts of the vibrational modes:

\[
\omega_{E'} = \omega_{E'}^0 - 2\gamma_{E'} \omega_{E'}^0 + k_{E'} n \quad (1a)
\]

\[
\omega_{A'_1} = \omega_{A'_1}^0 - 2\gamma_{A'_1} \omega_{A'_1}^0 + k_{A'_1} n \quad (1b)
\]

Here, \( \gamma_{E'} = 0.68 \) and \( \gamma_{A'_1} = 0.21 \) are the Grüneneisen parameters for the two vibrational modes of 1L MoS\(_2\).\(^{43,52,53}\) The \( \omega_{E'} = -0.33 \times 10^{13} \) cm and \( \omega_{A'_1} = -2.2 \times 10^{13} \) cm coefficients are the shift rates of Raman peaks as a function of the electron concentration \( n \) (in \( \text{cm}^{-2} \)) in 1L MoS\(_2\) obtained by Raman characterization of electrochemically top-gated MoS\(_2\) transistors.\(^{45}\)

In particular, the relation for the strain line can be obtained by solving the system of eqs 1a and 1b in the case of \( n = 0 \):

\[
\omega_{A'_1} = \omega_{A'_1}^0 + \frac{\gamma_{A'_1}}{\gamma_{E'}} (\omega_{E'} - \omega_{E'}^0) \quad (2)
\]

whereas the doping line equation is obtained by the same procedure for \( \varepsilon = 0 \):

\[
\omega_{A'_1} = \omega_{A'_1}^0 + \frac{k_{A'_1}}{\gamma_{E'}} (\omega_{E'} - \omega_{E'}^0) \quad (3)
\]

Hence, \( \frac{\gamma_{A'_1}}{\gamma_{E'}} = 0.32 \) and \( \frac{k_{A'_1}}{\gamma_{E'}} = 6.67 \) are the slopes for the strain and doping lines, respectively. The dashed red lines parallel to the strain line \( (n = 0) \) and the dashed black lines parallel to the doping line \( (\varepsilon = 0) \) serve as guides to quantify the doping and strain values, respectively. They correspond to \( \pm 0.1 \% \) variations for the strain and \( \pm 0.1 \times 10^{13} \) \text{ cm}^{-2} variations for the doping. Since \( \omega_{E'} \) is more sensitive to biaxial strain,\(^{43}\) the spacing between the dashed black lines parallel to the doping line is calculated from the \( E' \) mode strain rate, \( 2\gamma_{E'} \omega_{E'}^0 = 5.2 \text{ cm}^{-2}/\% \). On the other hand, since the \( A'_1 \) mode results are mainly influenced by charge doping,\(^{43}\) the spacing between the dashed red lines parallel to the strain line is calculated from the \( A'_1 \) mode doping rate, \( k_{A'_1} \).

The plot in Figure 3a shows that all the experimental data points for 1L MoS\(_2\) on Au are located above the strain line and in the left side with respect to the doping line. Hence, as compared to the reference case of a freestanding (suspended) 1L MoS\(_2\), our gold-supported 1L MoS\(_2\) films exhibit a tensile strain in the range from \( \sim 0.1 \) to \( \sim 0.3 \%) \) and a p-type doping in the range from \( \sim 0.1 \times 10^{13} \) to \( \sim 0.4 \times 10^{13} \) \text{ cm}^{-2}. The average values of the strain (\( \sim 0.21 \% \)) and doping (\( \sim 0.25 \times 10^{13} \) \text{ cm}^{-2} \)) are indicated by the black square in Figure 3a. A tensile biaxial strain, originating from the lattice mismatch between MoS\(_2\),
Figure 4. (a) Typical micro-PL spectra collected under excitation at 532 nm on 1L MoS₂ on Au (with the intensity multiplied by a factor of 10) and 1L MoS₂ transferred to Al₂O₃. Correlative plots of the PL peak energy with the strain (b) and doping values (c) deduced by PL and Raman mapping on the same sample area.

and Au,⁵⁴,⁵⁵ has been recently observed in the case of 1L MoS₂ exfoliated on Au also by other authors,²⁹ who reported very large ε values up to 1.2%. The smaller tensile strain obtained in our samples is probably due to the very smooth surface of the gold films. The observed p-type doping of MoS₂ in contact with Au is consistent with several recent reports of a p-type behavior induced by MoS₂ functionalization with gold nanoparticles, adsorbates, or Au-based chemicals.⁵⁶–⁵⁸

On the other hand, the cloud of data for 1L MoS₂ on Al₂O₃ is located in a region of the n–p plane corresponding to a compressively strained and n-type doped film, with the strain values comprised in a narrow range around ~−0.25% and the electron density ranging from ~0.4 × 10¹⁴ to ~0.7 × 10¹⁴ cm⁻². The compressive strain can be plausibly related to the transfer procedure and the adhesion properties of 1L-MoS₂ with the Al₂O₃ surface. The observed n-type doping is consistent with the unintentional doping typically observed for MoS₂ layers on insulating substrates and can be ascribed, in part, to charge transfer by adsorbed or interface trapped charges under ambient conditions, as well as to native defects of MoS₂.

The Raman mapping experiments reported so far provided information on the dopant uniformity of 1L MoS₂ based on the correlation between characteristic vibrational peaks and the carrier type and density. In the following, electrical measurements will be also employed to get further insight into the electronic transport in the 1L MoS₂/Au system and after transfer to the insulating substrate. Recently, other groups used electrical and spectroscopic probe methods on TMDs transferred onto noble metal contacts to characterize the semi-conductor/vdW interface.⁶¹,⁶² Here, we carried out a nanoscale resolution electrical characterization of the Au-supported 1L MoS₂ membrane by C-AFM measurements⁶³ to get further information on the doping uniformity in this

Photoluminescence analyses were also performed using the 532 nm laser probe of the Raman equipment as the excitation source. Figure 4a shows the comparison between two representative PL spectra collected on two different samples under the same illumination conditions. It is worth noting that the large 1L MoS₂ membrane produced by gold-assisted exfoliation and finally transferred onto Al₂O₃ exhibits a prominent peak at 1.83 eV, very similar to that observed for monolayer MoS₂ obtained by the traditional mechanical exfoliation or deposition by CVD. On the other hand, a strongly reduced PL intensity is observed when the exfoliated 1L MoS₂ membrane is still in contact with Au, together with a red shift of the main PL peak to 1.79 eV. The strong reduction of the PL intensity is consistent with the emission quenching reported by other authors for 1L MoS₂ exfoliated on Au²⁶ and for MoS₂ functionalized with Au nanoparticles.⁵⁹ This PL quenching can be explained in terms of a preferential transfer of photoexcited charges from MoS₂ to Au. In addition, the tensile strain of the MoS₂ layer in contact with Au can also play a role in the reduction of the PL yield.⁴³ In order to obtain statistically relevant information, arrays of PL spectra have been collected on the two samples in the same areas previously probed by Raman mapping. The obtained color maps of the PL peak energy for 1L MoS₂ on Au and after transfer on Al₂O₃ are reported in Figure S5 of the Supporting Information. Furthermore, Figure 4b,c shows the correlational plots of the PL peak energy with the strain and doping values deduced from Raman maps. These plots show a narrow distribution of the PL peak energies for both 1L MoS₂/Au and 1L MoS₂/Al₂O₃ samples. In particular, in Figure 4b the observed peak energy variations observed within each sample and the difference between the average values of the data points collected on the two different substrates are compatible with the PL peak shift rate as a function of the strain (~100 meV/%) reported in the literature.⁶⁰

Through the solving of eqs 1a and 1b for all the data points of the ωEk and ωAn maps, the corresponding color maps of the strain (Figure 3b,c) and doping (Figure 3e,f) for the two samples were obtained. The corresponding histograms of the strain and doping values are reported in parts d and g, respectively, of Figure 3. From the comparison of the strain and doping maps on 1L MoS₂/Au, a correlation between the regions with higher tensile strain and those with higher p-type doping can be noticed. This suggests that both strain and p-type doping originate from a locally stronger interaction with Au. On the other hand, the compressive strain distribution appears very uniform in the 1L MoS₂ membrane transferred onto Al₂O₃, without any clear correlation with the doping distribution. The average values and standard deviation of the strain and doping for the two different samples have been extracted by Gaussian fitting of the histograms in Figure 3d,g and the obtained values have been reported in the Table 1. Obviously, the spatial resolution in these maps is limited by the laser spot size (~1 μm). Furthermore, the concentration sensitivity (on the order of 10¹² cm⁻²) is limited by the shift rate of the A₁g peak with doping concentration. Higher spatial resolution and sensitivity information on the doping distribution in the Au-supported 1L MoS₂ will be deduced from conductive atomic force microscopy analyses reported later in this paper.

To further investigate the impact of the substrate/MoS₂ interaction on the electronic properties of 1L MoS₂, micro-
ultrathin layer. To this aim, the current injection at the interface between the Au substrate and 1L MoS$_2$ was probed at the nanoscale by a Pt coated Si tip, according to the configuration schematically illustrated in Figure 5a. The surface morphology in a sample region partially covered by 1L MoS$_2$ is reported in Figure 5b, showing how the 1L MoS$_2$ surface morphology in a sample region partially covered by a Pt coated Si tip, according to the configuration schematically illustrated in Figure 5a. The surface morphology in a sample region partially covered by 1L MoS$_2$ is reported in Figure 5b, showing how the 1L MoS$_2$ membrane conformally follows the smooth Au morphology. Furthermore, Figure 5c shows the simultaneously measured current map, collected by applying a DC bias $V_{tip} = 50\text{ mV}$ between the Pt tip and the Au electrode (substrate). For this low bias value, the current level measured on the bare Au region reaches the current amplifier saturation limit, whereas appreciable lateral variations of the injected current through the 1L MoS$_2$ membrane can be observed.

Such local variations of the injected current through the atomically thin membrane can be ascribed to the lateral inhomogeneities of MoS$_2$ electronic properties. In this respect, it is worth noting that, since C-AFM analyses were performed in ambient conditions, an ultrathin water layer is adsorbed on the MoS$_2$ surface and, consequently, the effective contact area is determined by the size of the water meniscus around the tip. As a matter of fact, the meniscus size is determined by the tip radius, the applied force, and the surface roughness. Hence, the smooth MoS$_2$ surfaces of our samples and the application of a constant force during measurements result in a nearly constant effective contact area. To further investigate the current transport mechanisms, a set of local current–voltage ($I$–$V_{tip}$) characteristics where acquired both on the bare Au surface and at different positions on the MoS$_2$ film, as reported in Figure 5d. The $I$–$V_{tip}$ curves measured by the Pt tip in contact with Au (see the red curve in Figure 5d) are very reproducible and exhibit an ohmic behavior with a very steep slope and current saturation at a few millivolts positive and negative biases (as shown in the right inset of Figure 5d). On the other hand, $I$–$V_{tip}$ curves measured on MoS$_2$ show significant variations at different positions. A possible reason for such variability can be the presence of nanoscale areas where 1L MoS$_2$ is locally in contact with Au and areas where it is locally suspended between the Au grains, as recently reported by Velicky et al. However, this scenario would imply a splitting of the A$_1'$ peak in the Raman spectra, due to the very different substrate-related doping for the Au-supported and suspended 1L MoS$_2$. Since such splitting is not observed in our Raman spectra, we excluded this effect in our 1L MoS$_2$/Au samples.

In the following, the Pt tip in contact with 1L MoS$_2$/Au is described as a metal/semiconductor/metal heterojunction, and the local $I$–$V_{tip}$ curves in Figure 5d have been fitted with relevant current transport mechanisms across the ultrathin MoS$_2$ barrier.

In Figure 5d all the curves measured on MoS$_2$ show a linear behavior at low $V_{tip}$ values, followed by a deviation from linearity at larger bias values. Furthermore, the slight asymmetry between positive and negative polarizations at larger biases can be ascribed to the different work functions of Pt and Au metals.

The linear behavior of the $I$–$V_{tip}$ characteristics indicates direct tunneling (DT) as the most appropriate mechanism ruling current transport at low bias values. In particular, the tunneling current can be expressed as

$$I_{DT} = B V_{tip} P(\Phi_{B, d}) = B \Phi_{B} \exp \left( \frac{-4\pi \sqrt{2m_{eff} \Phi_{B} d}}{\hbar} \right)$$

(4)

where $B$ is a prefactor (proportional to the tip contact area) and $P(\Phi_{B, d})$ is the direct tunneling probability, which is a function of the tunneling barrier thickness $d$ (i.e., the MoS$_2$ thickness) and its height $\Phi_{B, d}$ corresponding to the energy difference between the MoS$_2$ conduction band and the Au Fermi level (see the schematic in the left inset of Figure 5d).

Here $m_{eff} \approx 0.35 m_0$ is the electron effective mass in the transversal direction for 1L MoS$_2$ and $\hbar$ is Planck’s constant.

As a matter of fact, the thickness-dependent tunneling probability becomes unity when the MoS$_2$ layer is absent ($d$.
illustrated in the inset of Figure 6a. The output characteristics of MoS2 conduction band, as schematically illustrated in the left inset of Figure 5e. It is worth noting that this value is very close to the ideal barrier height between Au and charge-neutral MoS2, given by $\Phi_d = W - \chi$, where $W \approx 5.1$ eV is the gold work function and $\chi \approx 4.2$ eV is the electron affinity of 1L MoS2. This charge-neutral region can be ascribed to nanoscale areas where the p-type doping induced by the Au substrate is compensated by the presence of n-type doping impurities/adsorbates on the surface of MoS2. Due to the limited sensitivity of the Raman peak’s shift to doping concentration values of $10^{12}$ cm$^{-2}$, such low doping areas could not be detected in Raman maps. On the other hand, the component at larger $\Phi_B$ values in the distribution of Figure 5e can be ascribed to higher p-type doping of 1L MoS2, which was detected also by Raman spectroscopy. Such local p-type doping due to the Au substrate induces an upward bending of the conduction and valence bands of MoS2 (schematically illustrated in the right inset of Figure 5e), which extends over a distance of the order of a few nanometers, defined by the Debye length in the 2D semiconductor.

In addition to DT, trap-assisted-tunneling (TAT) is also expected to significantly contribute to the measured current by the C-AFM tip, due to the presence of a large density of native defects, such as sulfur vacancies, in exfoliated 1L MoS2 on Au. In particular, we have found that this transport mechanism is able to describe well the behavior of local $I$–$V$ curves in Figure 5d at higher bias values. Figure S6 of the Supporting Information shows the curves fitting with the TAT equation

$$I_{\text{TAT}} \approx \exp \left( -\frac{8\pi^2 p_m e \alpha}{3hE_t} E_t^{3/2} \right)$$

where $E$ is the electric field across 1L MoS2 and $E_t$ is the trap energy below the conduction band edge. The resulting distribution of $E_t$ values exhibits a peak at $\sim 0.8$ eV, consistent with the results of other recent reports.

Finally, the electronic transport in 1L MoS2 membrane transferred onto the Al2O3 dielectric surface has been investigated by electrical characterization of a field effect transistor (FET) with the Al2O3 (100 nm)/Si back gate and Au source and drain contacts (channel length $L = 10 \mu$m), as illustrated in the inset of Figure 6a. The output characteristics (drain current vs drain bias, $I_D$–$V_D$) of the device for different gate bias values ranging from $V_G = -20$ V to $V_G = 10$ V are shown in Figure 6a. At low drain bias ($V_D < 3$ V) injection in the MoS2 channel is limited by the high Schottky barrier at Au/MoS2 contacts, whereas a linear behavior of the $I_D$–$V_D$ characteristics is observed at intermediate $V_D$ values (from 3 to 10 V), followed by current saturation at higher voltages. The transfer characteristic ($I_D$–$V_G$) at a drain bias of $V_D = 5$ V (i.e., in the linear region of $I_D$–$V_D$ curves) is reported in Figure 6b (black line). The monotonic increase of $I_D$ with $V_G$ is the typically observed behavior for a transistor with an n-type MoS2 channel. A negative threshold voltage of $V_{th} \approx -8$ V was evaluated by linear fitting of the $I_D$–$V_G$ curve and taking the intercept with the voltage axis, as indicated by the arrow in Figure 6b. Since $V_{th}$ represents the bias necessary to deplete the n-type MoS2 channel, the electron density can be estimated as $n = C_{ox}V_{th}/q$, where $C_{ox} = \varepsilon_0\varepsilon_{ox}/t$ is the Al2O3 capacitance per unit area, with $\varepsilon_0$ the vacuum permittivity and $\varepsilon_{ox} = 8$ is the relative dielectric constant of the Al2O3 dielectric. The obtained carrier density $n \approx 3.1 \times 10^{12}$ cm$^{-2}$ is in reasonably good agreement with the carrier density values obtained by Raman mapping. Furthermore, the channel electron mobility ($\mu = 2.3 \pm 0.1$ cm$^2$/V$^{-1}$s$^{-1}$) has been properly evaluated excluding the effect of the contact resistance, as illustrated in Figure S7 of the Supporting Information.

This value is similar to the ones reported for back-gated monolayer MoS2 transistors without high-k encapsulation, where the mobility is limited by Coulomb scattering due to charged impurities. In the present case, part of these impurities may originate from the KI/I2 etching of gold involved in the transfer procedure. In this respect, appropriate strategies should be further elaborated to detach the exfoliated 1L MoS2 from the Au substrate without the use of chemical etching. These may include electrolytic delamination by hydrogen bubbling, used in the past to separate CVD graphene from copper and more recently to separate CVD TMDs from Au foils. Furthermore, a number of potential applications (such as memristor devices) are currently emerging, where the large area 1L MoS2 on gold can be directly employed without any need for transfer. In these cases, the exfoliated MoS2 membrane retains its excellent crystal quality.

### 3. Conclusion

In summary, large area (cm$^2$) 1L MoS2 membranes have been exfoliated on very flat gold films and transferred to an insulating Al2O3/Si substrate. For 1L MoS2 in contact with Au, Raman mapping revealed a spatially inhomogeneous distribution of tensile strain (in the range from $-0.1$ to $-0.3\%$) and p-
type doping (from ~0.1 × 10^{13} to ~0.4 × 10^{13} cm^{-2}), with a correlation between regions showing higher strain and doping. The electrical properties of Au-supported MoS_2 were probed at the nanoscale by C-AFM, showing direct tunneling across the ultrathin 1L MoS_2 with a broad distribution of tunneling barrier values (Φ_{bar} from 0.7 to 1.7 eV) consistent with an inhomogeneous p-type doping of MoS_2. After the final transfer of 1L MoS_2 on Al_2O_3/Si, the strain was converted to compressive (ε ≈ −0.25%) with a very uniform distribution. Furthermore, an n-type doping (n ≈ 0.5 × 10^{13} cm^{-2}) was deduced by Raman mapping and confirmed by electrical measurements of an Al_2O_3/Si back-gated 1L MoS_2 transistor. These results provide a deeper understanding of the properties of large area 1L MoS_2 produced by Au-assisted exfoliation, and they will contribute to the widespread application of this outstanding quality material in the demonstration of novel device concepts and synthetic van der Waals heterostructures.

4. MATERIALS AND METHODS

4.1. Sample Preparation. The deposition of Ni (10 nm)/Au (15 nm) on a SiO_2 (900 nm)/Si sample was carried out by DC magnetron sputtering using Qorcom equipment. The base vacuum in the chamber was ~10^{-3} mbar, while during the deposition process the pressure was about 10^{-4} to 10^{-5} mbar. The same equipment was employed to deposit 100 nm of Au on a Si sample for the preparation of the gold tape with the peeling technique (see Figure 2). PMMA (200 K, 0.5 μm) was spin-coated on Au and at 150 °C. A Nittro Denko thermal release tape (with 180 °C release temperature) was used for the handling of the PMMA/Au gold tape. The 100 nm Al_2O_3 insulator on Si (used as a final substrate for 1L MoS_2 transfer) was deposited by DC-pulsed RF reactive sputtering.

4.2. AFM and C-AFM Analyses. Morphological analyses of the Au/Ni substrates and of the exfoliated MoS_2 films were carried out by tapping mode atomic force microscopy (AFM) using DI3100 equipment by Bruker with Nanoscope V electronics. Sharp silicon tips with a curvature radius of 5 nm were used for these measurements. C-AFM measurements were carried out with the same AFM system equipped with the TUNA module and using Pt coated Si tips. All the AFM and C-AFM analyses were carried out at room temperature and under ambient atmosphere.

4.3. Micro-Raman Spectroscopy and Photoluminescence. Raman spectroscopy and PL measurements were carried out by using a Horiba HR-Evolution micro-Raman system with a confocal microscope (100x objective) and a laser excitation wavelength of 522 nm. The laser power used for these analyses was filtered with a neutral density filter at 1% ensuring no sample degradation. A grating of 1800 lines/mm was employed to acquire Raman spectra in a range from 100 to 650 cm^{-1}, while a grating of 600 lines/mm was used to acquire photoluminescence spectra in a range from 100 to 5500 cm^{-1}. All the spectra were calibrated with respect to the silicon peak at 520.7 cm^{-1}.

4.4. Field Effect Transistor Preparation and Characterization. A back-gated 1L MoS_2 field effect transistor was fabricated with the Au-exfoliated film transferred onto Al_2O_3 (100 nm)/Si by sputtering Au source/drain contacts with a shadow mask. The contact spacing, i.e., the channel length, was L = 10 μm. The output and transfer characteristics of the transistor were measured in dark conditions by using a Cascade Microtech probe station with an Agilent 4156b parameter analyzer.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c05185.

Schematic illustration of procedure for 1L MoS_2 exfoliation on Au/Ni/SiO_2: AFM images and histograms of height distribution for Au/Ni/SiO_2 substrate, peeled Au on PMMA, and 1L MoS_2 partially covering the Au/Ni/SiO_2 substrate; maps of PL peak energy from spectra collected on 1L MoS_2 exfoliated on Au and after transfer on Al_2O_3; fit of local I−V_{th} curves by the trap-assisted-tunneling (TAT) mechanism; evaluation of the contact resistance and field-effect mobility of the back-gated MoS_2 field effect transistor (PDF).

AUTHOR INFORMATION

Corresponding Author

Filippo Giannonzo — CNR-IMM, 95121 Catania, Italy; orcid.org/0000-0002-0074-0469; Email: filippo.giannonzo@imm.cnr.it

Authors

Salvatore Ethan Panasci — CNR-IMM, 95121 Catania, Italy; Department of Physics and Astronomy, University of Catania, 95123 Catania, Italy
Emanuela Schildì — CNR-IMM, 95121 Catania, Italy
Giuseppe Greco — CNR-IMM, 95121 Catania, Italy; orcid.org/0000-0001-9423-1413
Marco Canas — Department of Physics and Chemistry Emilio Segrè, University of Palermo, 90123 Palermo, Italy
Franco M. Gelardi — Department of Physics and Chemistry Emilio Segrè, University of Palermo, 90123 Palermo, Italy
Simone Pietro Agnello — Department of Physics and Chemistry Emilio Segrè, University of Palermo, 90123 Palermo, Italy; CNR-IMM, 95121 Catania, Italy; ATeN Center, Università degli Studi di Palermo, 90128 Palermo, Italy; orcid.org/0000-0002-0346-8333
Fabrizio Roccasforte — CNR-IMM, 95121 Catania, Italy; orcid.org/0000-0001-8632-0870

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acsami.1c05185

Notes

The authors declare no competing financial interest.

ACKNOWLEDMENTS

The authors acknowledge S. Di Franco (CNR-IMM) for assistance in the sample preparation and P. Fiorenza and R. Lo Nigro (CNR-IMM) for useful discussions. The paper has been supported, in part, by MUR in the framework of the FlagERA-JTC 2019 project “ETMOS”. E.S. acknowledges the PON project EleGaNTe (ARS01_01007) for financial support. Part of the experiments have been carried out using the facilities of the Italian Infrastructure Beyond Nano.

REFERENCES

(1) Wang, Q. H.; Kalantar-Zadeh, K.; Kis, A.; Coleman, J. N.; Strano, M. S. Electronics and Optoelectronics of Two-dimensional Transition Metal Dichalcogenides. Nat. Nanotechnol. 2012, 7, 699.
(2) Radisavljevic, B.; Whitwick, M. B.; Kis, A. Integrated Circuits and Logic Operations Based on Single-Layer MoS_2. ACS Nano 2011, 5, 9934—9938.
(3) Lopez-Sanchez, O.; Lembek, D.; Kayci, M.; Radenovic, A.; Kis, A. Ultrasensitive Photodetectors Based on Monolayer MoS_2. Nat. Nanotechnol. 2013, 8 (7), 497—501.
(4) Yin, Z.; Li, H.; Li, H.; Jiang, L.; Shi, Y.; Sun, Y.; Lu, G.; Zhang, Q.; Chen, X.; Zhang, H. Single-Layer MoS_2 Phototransistors. ACS Nano 2012, 6 (1), 74—80.
(5) Li, H.; Yin, Z.; He, Q.; Li, H.; Huang, X.; Lu, G.; Fan, D. W. H.; Tok, A. L.Y.; Zhang, Q.; Zhang, H. Fabrication of Single- and Multilayer
MoS₂ Film-Based Field-Effect Transistors for Sensing NO at Room Temperature. Small 2012, 8 (1), 63–67.

(6) Kuc, A.; Zibouche, N.; Heine, T. Influence of Quantum Confinement on the Electronic Structure of the Transition Metal Sulfide TS₂. Phys. Rev. B: Condens. Matter Mater. Phys. 2011, 83 (24), 245213.

(7) Wilson, J. A.; Yoffe, A. D. The Transition Metal Dichalcogenides Discussion and Interpretation of the Observed Optical, Electrical and Structural Properties. Adv. Phys. 1969, 18 (73), 193–335.

(8) Mak, K. F.; Lee, C.; Hone, J.; Shan, J.; Heinz, T. F. Atomically Thin MoS₂: a New Direct-Gap Semiconductor. Phys. Rev. Lett. 2010, 105 (13), 136805.

(9) Velický, M.; Toth, P. S. From Two-Dimensional Materials to their Heterostructures: An Electrochemist’s Perspective. Applied Materials & Interfaces 2017, 8, 68–103.

(10) Splendiani, A.; Sun, L.; Zhang, Y.; Li, T.; Kim, J.; Chim, C.-Y.; Galli, G.; Wang, F. Emerging Photoluminescence in Monolayer MoS₂. Nano Lett. 2010, 10, 1271–1275.

(11) Ayari, A.; Cobas, E.; Ogundadebe, O.; Fuhrer, M. S. Realization and Electrical Characterization of Ultrathin Crystals of Layered Transition-Metal Dichalcogenides. J. Appl. Phys. 2007, 101, 014507.

(12) Yoon, Y.; Ganapathi, K.; Salahuddin, S. How Good Can Monolayer MoS₂ Transistors Be? Nano Lett. 2011, 11, 3768–3773.

(13) Radisavljevic, B.; Radenovic, A.; Brivio, J.; Giacometti, V.; Kis, A. Single-Layer MoS₂ Transistors. Nat. Nanotechnol. 2011, 6 (3), 147–150.

(14) Tosun, M.; Fu, D.; Desai, S. B.; Ko, C.; Kang, J. S.; Lien, D.-H.; Najmae, M.; Tongay, S.; Wu, J.; Javey, A. MoS₂ Heterojunctions by Thickness Modulation. Sci. Rep. 2015, 5, 10990.

(15) Conley, H. J.; Wang, B.; Ziegler, J. L.; Haglund, R. F., Jr.; Pantelides, S. T.; Bolotin, K. I. Bandgap Engineering of Strained Monolayer and Bilayer MoS₂. Nano Lett. 2013, 13 (8), 3626–3630.

(16) Giannazzo, F. Engineering 2D Heterojunctions with Dielecric. Nat. Electron. 2019, 2, 54–55.

(17) Giannazzo, F.; Greco, G.; Roccaporte, F.; Sonde, S. S. Vertical Transistors Based on 2D Materials: Status and Prospects. Crystals 2018, 8, 70.

(18) Fan, X.; Xu, P.; Zhou, D.; Sun, Y.; Li, Y. C.; Nguyen, M. A. T.; Terrones, M.; Mallouk, T. E. Fast and Efficient Preparation of Exfoliated 2H MoS₂ Nanosheets by Sonication-Assisted Lithium Intercalation and Infrared Laser-Induced 1T to 2H Phase Reversion. Nano Lett. 2015, 15, 5956–5960.

(19) Das, S.; Bera, M. K.; Tong, S.; Narayanan, B.; Kamath, G.; Man, A.; Paulikas, A. P.; Antonio, M. R.; Sarkaranarayanan, S. K. R. S.; Roelofs, A. K. A Self-Limiting Electro-Ablation Technique for the Top-Down Synthesis of Large-Area Monolayer Flakes of 2D Materials. Sci. Rep. 2016, 6, 28195.

(20) Lee, Y. H.; Zhang, X.-Q.; Zhang, W.; Chang, M.-T.; Lin, C.-T.; Chang, K.-D.; Yu, Y.-C.; Wang, J.T.-W.; Chang, C.-S.; Li, L.-J.; Lin, T.-W. Synthesis of Large-Area MoS₂ Atomic Layers with Chemical Vapor Deposition. Adv. Mater. 2012, 24, 2320–2325.

(21) Zhan, Y.; Liu, Z.; Najmaei, S.; Ajayan, P. M.; Lou, J. Large-Area Vapor-Phase Growth and Characterization of MoS₂ Atomic Layers on a SiO₂ Substrate. Small 2012, 8, 966–971.

(22) Fu, D.; Zhao, X.; Zhang, Y.-Y.; Li, L.; Xu, H.; Jang, A.-R.; Yoon, S. I.; Song, P.; Poh, S. M.; Ren, T.; Ding, Z.; Fu, W.; Shin, T. J.; Shin, H. S.; Pantelides, S. T.; Zhou, W.; Loh, K. P. Molecular Beam Epitaxy of Highly Crystalline Monolayer MoS₂ on H-Bonded Surfaces from Template-stripping Procedures. J. Phys. Chem. C 2017, 121, 13992–14000.

(23) Ho, Y.-T.; Ma, C.-H.; Luong, T.-T.; Wei, L.-L.; Wen, Y.-C.; Hsu, W.-T.; Chang, W.-H.; Chu, Y.-C.; Tu, Y.-Y.; Pande, K. W.; Chang, E. Y. Layered MoS₂ Grown on sapphire by Pulsed Laser Deposition. Phys. Status Solidi RRL 2015, 9, 187–191.

(24) Novoselov, K. S.; Jiang, D.; Schedin, F.; Booth, T. J.; Khotkevich, V. V.; Morozov, S. V.; Geim, A. K. Two-Dimensional Atomic Crystals. Proc. Natl. Acad. Sci. U. S. A. 2005, 102, 10451–10453.
(42) McCrea, A.; Ghosh, R.; Amani, M.; Wang, J.; Duerloo, K. A. N.; Sharma, A.; Jarvis, K.; Reed, E. J.; Dongare, A. M.; Banerjee, S. K.; Terrones, M.; Nambrum, R. R.; Dubey, M. Effects of Uniaxial and Biaxial Strain on Few-Layered Terrace Structures of MoS2 Grown by Vapor Transport. ACS Nano 2016, 10, 3186–3197.

(43) Lloyd, D.; Liu, X.; Christopher, J. W.; Cantley, L.; Wadehra, A.; Kim, B. L.; Goldberg, B. B.; Swan, A. K.; Bunch, J. S. Band Gap Engineering with Ultralarge Biaxial Strains in Suspended Monolayer MoS2. Nano Lett. 2016, 16, 5836–5841.

(44) Melnikova-Kominkova, Z.; Jurkova, K.; Vales, V.; Drosgowski-Horná, K.; Frank, O.; Kalbáč, M. Strong and Efficient Doping of Monolayer MoS2 by a Graphene Electrode. Phys. Chem. Chem. Phys. 2019, 21, 25700–25706.

(45) Chakraborty, B.; Bera, A.; Muthu, D. V. S.; Bhowmick, S.; Waghmare, U. V.; Sood, A. K. Symmetry-Dependent Phonon Renormalization in Monolayer MoS2 Transistor. Phys. Rev. B: Condens. Matter Phys. 2012, 85, 161403.

(46) Lee, J. E.; Ahn, G.; Shim, J.; Lee, Y. S.; Ryu, S. Optical Separation of Mechanical Strain From Charge Doping in Graphene. Nat. Commun. 2012, 3, 1024.

(47) Armano, A.; Buscarino, G.; Cannas, M.; Gelardi, F. M.; Giannazzo, F.; Schilirò, E.; Agnello, S. Monolayer Graphene Doping and Strain Dynamics Induced by Thermal Treatments in Controlled Atmosphere. Carbon 2018, 127, 270–279.

(48) Mohiuddin, T. M. G.; Lombardo, A.; Nair, R. R.; Bonetti, A.; Savini, G.; Jallil, R.; Bonini, N.; Basko, D. M.; Galitois, C.; Maran, N.; Novoselov, K. S.; Geim, A. K.; Ferrari, A. C. Uniaxial strain in graphene by Raman spectroscopy: G peak splitting, Grünenein parameters, and sample orientation. Phys. Rev. B: Condens. Matter Phys. 2009, 79, 205433.

(49) Androlidakis, Ch.; Tsoukleri, G.; Koutroumanis, N.; Gkikas, G.; Pappas, P.; Parthenios, J.; Papageorgiou, K.; Galíotis, C. Experimentally Derived Axial Stress–Strain Relations for Two-Dimensional Materials such as Monolayer Graphene. Carbon 2015, 81, 322–328.

(50) Schilirò, E.; Lo Nigro, R.; Panasci, S. E.; Gelardi, F. M.; Agnello, S.; Yakimova, R.; Roccaforte, F.; Giannazzo, F. Aluminum Oxide Nucleation in the Early Stages of Atomic Layer Deposition on Epitaxial Graphene. Carbon 2020, 169, 172–181.

(51) Rao, R.; Islam, A. E.; Singh, S.; Berry, R.; Kawakami, R. K.; Maruyama, B.; Katach, J. Spectroscopic Evaluation of Charge-Transfer Doping and Strain in Graphene/MoS2 Heterostructures. Phys. Rev. B: Condens. Matter Mater. Phys. 2019, 99, 195401.

(52) Jorio, A.; Dresselhaus, M. S.; Saitoh, R.; Dresselhaus, G. Raman Spectroscopy in Graphene Related Systems: John Wiley & Sons: 2011.

(53) Ferralis, N. Probing Mechanical Properties of Graphene with Raman Spectroscopy. J. Mater. Sci. 2010, 45, 5135–5149.

(54) Gong, C.; Huang, C.; Miller, J.; Cheng, L.; Hao, Y.; Cobden, D.; Kim, J.; Ruoff, R. S.; Wallace, R. M.; Cho, K.; Xu, X.; Chabal, Y. J. Metal Contacts on Physical Vapor Deposited Monolayer MoS2. ACS Nano 2013, 7, 11350–11357.

(55) Sörensen, S. G.; Füchtbauer, H. G.; Tuxen, A. K.; Walton, A. S.; Lauritsen, J. V. Structure and Electronic Properties of In Situ Synthesized Single-Layer MoS2 on a Gold Surface. ACS Nano 2014, 8, 6788–6796.

(56) Singh, A. K.; Pandey, R. K.; Prakash, R.; Eom, J. Tailoring the Charge Carrier in Few Layers MoS2 Field-Effect Transistors by Au Metal Adsorbate. Appl. Surf. Sci. 2018, 437, 70–74.

(57) Liu, H.; Grasseschi, D.; Dodda, A.; Fujisawa, K.; Olson, D.; Kahn, E.; Zhang, F.; Zhang, T.; Lei, Y.; Branco, R. B. N.; Elias, A. L.; Silva, R. C.; Yeh, Y.-T.; Maroneze, C. M.; Seixas, L.; Hopkins, P.; Das, S.; de Matos, C. J. S.; Terrones, M. Spontaneous Chemical Functionalization Via Coordination of Au Single Atoms on Monolayer MoS2. Science Advances 2020, 6, eab9308.

(58) Liu, X.; Qu, D.; Ryu, J.; Ahmed, F.; Yang, Z.; Lee, D.; Yoo, W. J. P-Type Polar Transition of Chemically Doped Multilayer MoS2 Transistor. Adv. Mater. 2016, 28, 2345–2351.

(59) Bhanu, U.; Islam, M. R.; Tetard, L.; Khondaker, S. I. Photoluminescence Quenching in Gold-MoS2 Hybrid Nanoflakes. Sci. Rep. 2015, 4, 5575.

(60) Lloyd, D.; Liu, X.; Christopher, J. W.; Cantley, L.; Wadehra, A.; Kim, B. L.; Goldberg, B. B.; Swan, A. K.; Bunch, J. S. Band gap engineering with ultralarge biaxial strains in suspended monolayer MoS2. Nano Lett. 2016, 16, 5836–5841.

(61) Lee, H.; Deshmukh, S.; Weo, J.; Costa, V. Z.; Schuder, J. S.; Sanchez, M.; Ichimura, A. S.; Pop, E.; Wang, B.; Newaz, A. K. M. Layer-Dependent Interfacial Transport and Optoelectrical Properties of MoS2 on Ultraflat Metals. ACS Appl. Mater. Interfaces 2019, 11, 31543–31550.

(62) Kraye, A.; Bailey, C. S.; Jo, K.; Wang, S.; Singh, A.; Darlington, T.; Liu, G.-Y.; Gradecek, S.; Schuck, P. J.; Pop, E.; Jariwala, D. Dry Transfer of van der Waals Crystals to Noble Metal Surfaces To Enable Characterization of Buried Interfaces. ACS Appl. Mater. Interfaces 2019, 11, 38218–38225.

(63) Giannazzo, F.; Schilirò, E.; Greco, G.; Roccaforte, F. Conductive Atomic Force Microscopy of Semiconducting Transition Metal Dichalcogenides and Heterostructures. Nanomaterials 2020, 10, 803.