

Deterministic transfer of two-dimensional materials by all-dry viscoelastic stamping

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ABSTRACT

Deterministic transfer of two-dimensional crystals constitutes a crucial step towards the fabrication of heterostructures based on artificial stacking of two-dimensional materials. Moreover, control on the positioning of two-dimensional crystals facilitates their integration in complex devices, which enables the exploration of novel applications and the discovery of new phenomena in these materials. Up to date, deterministic transfer methods rely on the use of sacrificial polymer layers and wet chemistry to some extent. Here, we develop an all-dry transfer method that relies on viscoelastic stamps and does not employ any wet chemistry step. This is found very advantageous to freely suspend these materials as there are no capillary forces involved in the process. Moreover, the whole fabrication process is quick, efficient, clean, and it can be performed with high yield.

Since its isolation in 2004¹, graphene has raised a huge interest in the scientific community². This breakthrough also constitutes the origin of a new research topic devoted to the study of two dimensional atomic crystals³. One of the keys for the success of graphene research was the development of the micromechanical exfoliation method (so called Scotch tape method). Despite the simplicity of this method it can provide extremely high quality samples⁴. Nevertheless, the exfoliation method produces flakes with different sizes and thicknesses randomly distributed over the sample substrate, and only a small fraction of these flakes are atomically thin. The introduction of the optical identification method to find atomically thin crystals from the crowd of thicker bulky flakes constitutes the second key to guarantee the success of the graphene related research as it provides a fast, reliable and non-destructive way of locating the flakes⁵⁻⁷. The combination of mechanical exfoliation and optical identification, however, cannot provide a reliable way to fabricate more complex systems such as heterostructures formed by artificial stacking different 2D crystals⁸⁻¹⁴. The probability of creating these heterostructures by randomly depositing different 2D crystals onto the substrate is too small. To fabricate such systems new experimental approaches are needed to place the 2D crystals at a specific location^{15, 16}. Three of these deterministic transfer methods are rather extended nowadays: the wedging method¹⁷, the polyvinylalcohol (PVA) method¹⁸ and the Evalcite method¹⁹.

In the wedging transfer method water is used to lift off a hydrophobic polymer layer spin-coated onto a hydrophilic substrate. If the hydrophilic substrate was covered by flakes, they can be lifted off with the hydrophobic polymer layer and transferred to another substrate using water as the transfer-active component. After the transfer, the hydrophilic polymer layer has to be removed with solvents. In the PVA transfer method, the flakes are transferred onto a polymer sacrificial layer (spin-coated on a substrate previously treated with a water solvable PVA polymer layer). The substrate is floated on the surface of a deionized water bath and once the water-soluble polymer had dissolved, the substrate sank to the bottom of the bath and the polymer layer is scooped and subsequently dried. The polymer layer is then mounted in a micromanipulator to transfer the flakes to an arbitrary substrate. After transfer, the

polymer sacrificial layer is dissolved with solvents. Finally, in the Evalcite method, the flakes are transferred onto a glass slide which has been spin-coated with a low glass temperature polymer (Evalcite). The glass slide is mounted in a micromanipulator and the acceptor substrate is heated up to 75 °C – 100 °C. When the polymer touches the substrate it melts and adheres strongly to the surface, facilitating the transfer from the glass slide to the surface. After the transfer, the polymer layer has to be removed with solvents as in the previous methods.

All these transfer methods thus rely on sacrificial polymer layers and require wet process at some stage of the fabrication process. This characteristic may hamper their usability as the acceptor surface may contain structures sensitive to the chemicals employed or to the capillary forces involved in the process. For instance, fabrication of freely suspended structures by conventional wet transfer methods remains challenging as they tend to collapse by the capillary forces. An all-dry alternative transfer method is therefore necessary to widen the range of applications of the deterministic transfer methods and to avoid contamination of the fabricated structures. In this article we present an all-dry transfer method that relies on viscoelastic stamps. Two-dimensional crystals are transferred with this method without employing any wet chemistry step. This is found very advantageous to freely suspend these materials as there are no capillary forces involved in the process. Fabrication of artificial heterostructures and freely suspended atomically thin layers and the transfer of 2D crystals onto arbitrary substrates are demonstrated.

The experimental setup employed to transfer two-dimensional crystals comprises an optical microscope (Olympus BX 51 supplemented with an Olympus DP25 digital camera) supplemented with large working distance optical objectives and a three axis micrometer stage to accurately position the stamp (see Figure 1(a)), very similar to the setups employed in other transfer methods¹⁷⁻¹⁹. We have also developed a dedicated setup to carry out the transfer process which shows even better performance than the modified optical microscope with a much lower price (see Supporting Information for more details of this dedicated transfer setup).

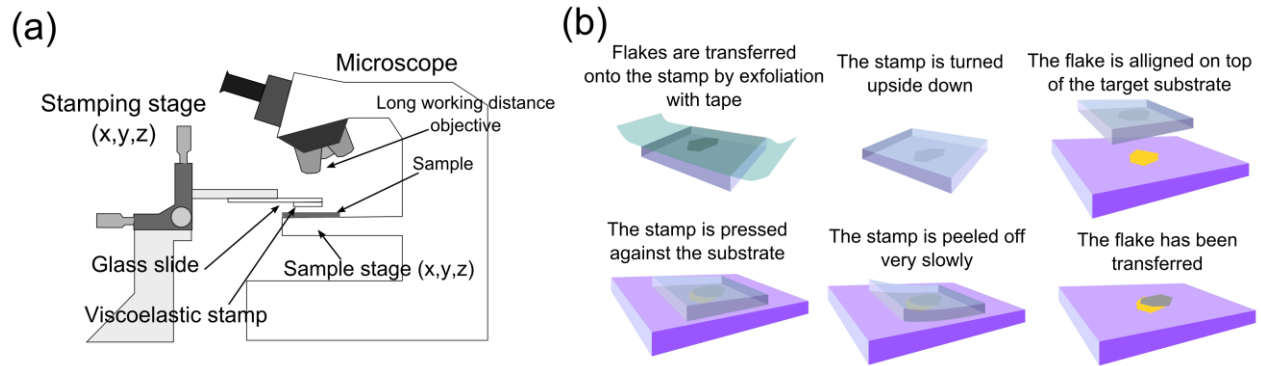


Figure 1. Deterministic transfer setup and process. (a) Schematic diagram of the experimental setup employed for the all-dry transfer process. Diagram of the steps involved in the preparation of the viscoelastic stamp and the deterministic transfer of an atomically thin flake onto a user-defined location (for instance another atomically thin flake).

The stamp is a thin layer of commercially available viscoelastic material (Gelfilm from Gelpak) which is adhered to a glass slide to facilitate its handling. The two-dimensional crystals to be transferred are deposited onto the viscoelastic layer by mechanical exfoliation of the bulk layered crystal with Nitto tape (Figure 1(b)). The surface of the stamp is inspected under the optical microscope to select the thinner flakes due to their faint contrast under normal illumination. As the stamp is transparent, transmission mode can be used to determine the number of layers. Raman spectroscopy can be also carried out on the surface of the stamp to confirm the thickness of the flake^{20, 21}. Once a thin flake has been identified, the acceptor substrate is fixed on the sample XYZ stage using double side tape. The stamp is then attached to the three axis manipulator with the flakes facing against the sample. As the stamp is transparent, one can see the sample through it and thus it is possible to align the desired flake on the acceptor surface where one wants to transfer the flake with sub-micrometer resolution. A step-by-step guide of the transfer process can be found in the Supporting Information.

In order to transfer the flake to the acceptor surface, the stamp is pressed against the surface and it is peeled off very slowly. The working principle of the transfer is based on the viscoelasticity: the stamp behaves as an elastic solid at short timescales while it can slowly flow at long timescales²². Flakes are adhered to its surface because the viscoelastic material gets an intimate contact with the flakes. By

slowly peeling off the stamp from the surface, the viscoelastic material flows out releasing the flakes that adhere preferentially to the acceptor surface.

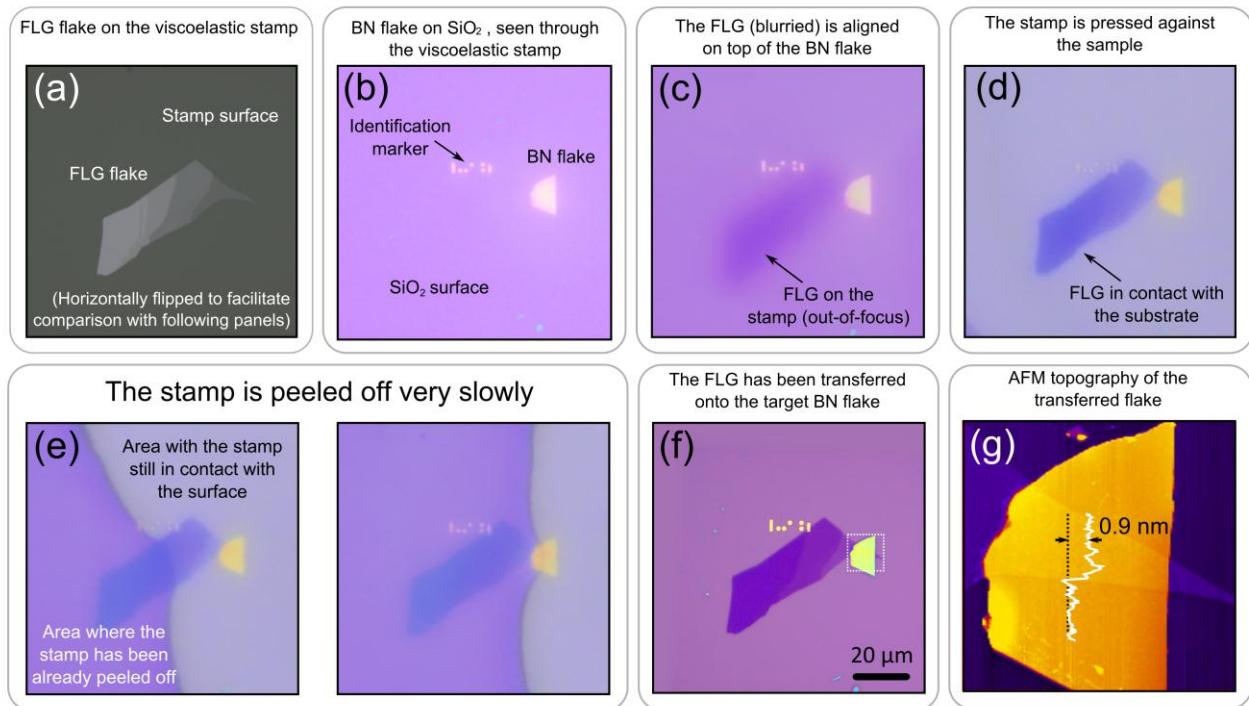


Figure 2. Placing a few-layer graphene flake onto a hexagonal boron nitride flake. (a) to (f) Optical micrographs acquired during the transfer process. (a) A few-layers graphene flake has been identified on the surface of the viscoelastic stamp. (b) A boron nitride flake has been selected on the acceptor surface. (c) the few-layers graphene flake is aligned on top of the boron nitride with a three axis micrometer positioner and looking through the transparent stamp during the handling. (d) once the flake is aligned, the stamp is brought into contact with the sample. During this process the few-layer graphene flake becomes more and more focused. (e) The viscoelastic stamp is peeled off very slowly until the few-layer graphene flake is fully transferred. (f) Resulting heterostructure of few-layer graphene onto a boron nitride flake. (g) AFM topography of the transferred FLG flake (acquired on the area highlighted with a dashed square in (f)). A topographic line profile has been included as an inset.

The potential of the presented technique is illustrated by transferring a few-layer graphene (FLG) flake onto h-BN. Figure 2(a) shows an example of a FLG flake deposited on the viscoelastic stamp. Figure 2(b) shows the h-BN flake, previously deposited on a Si/SiO₂ substrate by mechanical exfoliation (see materials and methods section in the Supporting Information), as seen through the viscoelastic stamp when the separation between the sample and the stamp is still large. When the stamp is brought closer and closer to the sample, the FLG flake appears more clearly as it gets more and more focused (Figure

2(c)). At this stage, it is still possible to align the flake to the h-BN flake using the XY knobs of the stamp stage. Once both flakes are aligned, the stamp is brought into contact with the acceptor surface, which can be clearly seen by a sudden change in color (Figure 2d). Once in contact, the stamp is not pressed further against the sample and it is peeled off very slowly (Figure 2e). Figure 2f shows the optical image of the transferred FLG flake after removing the stamp. The topography of the transferred flake is shown in Figure 2g, demonstrating that the FLG flake lays flat on the h-BN surface without bubbles or wrinkles. The whole transfer process can be accomplished in less than 15 minutes (see the Supporting Information for a real time video of a stamping process).

The method can be applied to any kind of exfoliable layered crystals, allowing for almost infinite combinations of materials. We found that, with the dry transfer process, one can achieve a yield close to 100% when transferring onto atomically flat materials (to fabricate heterostructures, for instance). When rougher substrates are employed (such as samples with evaporated metals or with abrupt changes in their topography) the yield can be lower due to the reduced adhesion forces between the 2D material and the substrate. Figure 3 shows some examples of atomically thin heterostructures fabricated by stacking other two-dimensional materials employing this transfer technique. In Figure 3c, the transfer process has been repeated to fabricate a ‘sandwiched’ MoS₂ bilayer in between two h-BN flakes (see Supp. Info.). Dashed lines have been used to highlight the different materials in the optical microscopy images (cartoons of the fabricated heterostructures are depicted above the optical images). The topography of the samples has been characterized by atomic force microscopy (AFM), which are shown above the optical microscopy images. Line profiles are included in the AFM images as insets to determine the thickness and the roughness of the transferred flakes. Note that although the fabricated heterostructures have not been subjected to any post-fabrication annealing step, their surfaces are clean of contaminants (typically present on samples fabricated by wet-transfer procedures).

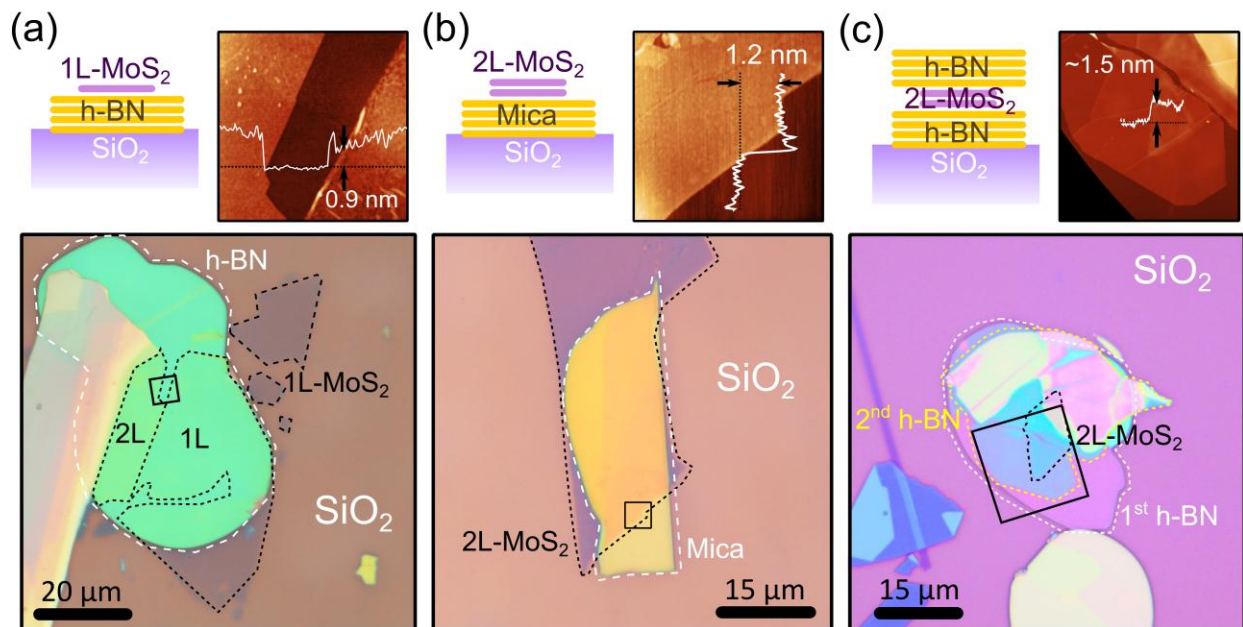


Figure 3. Artificial heterostructures. Optical and AFM images of some heterostructures fabricated by stacking different two-dimensional crystals (h-BN, MoS₂ and mica) with our all-dry transfer technique. A sketch of the fabricated heterostructure is shown below the optical images (at the left side). Atomic force microscopy images (acquired in the regions highlighted by a black square in the optical images) are also shown below the optical images (at the right side). (a) mono- and bilayer MoS₂ onto h-BN. (b) Bilayer MoS₂ onto a muscovite mica flake. (c) a bilayer MoS₂ flake ‘sandwiched’ between two h-BN flakes.

We found that an excessive pressure applied during the transfer process may deform the viscoelastic stamp material yielding a high density of bubbles after the peeling off because of the sudden release of strain, similar to what has been observed in Ref. ²³ (see Supporting Information). Nonetheless by carefully controlling the transfer pressure one can typically achieve large flat areas (as those shown in Figure 3) without wrinkles and bubbles, which is desirable for further fabrication of devices out of these heterostructures. The fabrication of heterostructures with large areas without bubbles and wrinkles can be achieved with yields of 30-40%. Some of the heterostructures fabricated by this technique have also been previously characterized by Raman spectroscopy and photoluminescence; these results can be found in Ref. ²⁴.

Another advantage of the all-dry transfer technique is that, due to the lack of capillary forces involved during the transfer procedure, fabricating freely suspended structures can be done straightforwardly.

Figure 4a shows an example of a single-layer MoS₂ crystal that has been transferred onto a SiO₂/Si substrate pre-patterned with holes of different diameters. The single-layer MoS₂ is freely suspended over the holes forming micro-drumheads. The mechanical properties of these single-layer MoS₂ mechanical resonators fabricated by the stamping technique have been recently reported in Ref. ²⁵. The stamping method can be also applied to transfer two-dimensional crystals onto pre-fabricated devices with trenches and electrodes (see Figure 4b). Our stamping transfer method has demonstrated to be very gentle, allowing the deposition of two-dimensional crystals even onto very fragile substrates. Figure 4c shows an example of a few-layer MoS₂ crystal transferred onto an AFM cantilever without damaging the cantilever. We have also successfully transfer two-dimensional materials onto silicon nitride membranes and holey carbon films, typically employed in transmission electron microscopy.

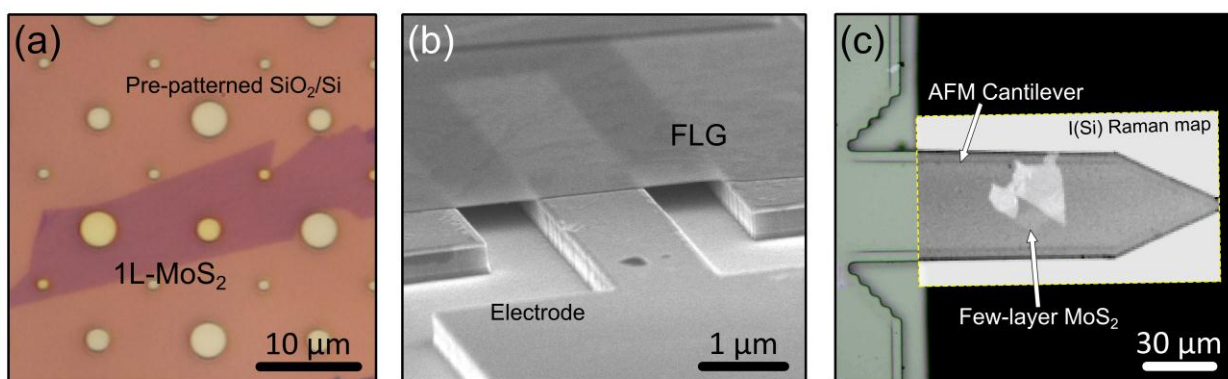


Figure 4. Transfer of atomically-thin crystals onto different substrates. (a) Single layer MoS₂ flake transferred onto a SiO₂/Si substrate pre-patterned with holes of 1, 2 and 3 μm in diameter. The MoS₂ flake covering the holes is freely suspended forming a micro drumhead. (b) Few-layer graphene (~ 10 layers) flake transferred onto a device, suspended between drain and source electrodes. (c) Few-layer MoS₂ flake (3 to 15 layers) transferred onto an freely overhanging AFM cantilever. A Raman map with the intensity of the silicon peak has been superimposed to the optical image of the cantilever to facilitate the identification of the transferred flake (region where the silicon peak has lower intensity due to the absorption of the MoS₂ flake) as it was almost invisible in the optical image.

In summary, we have introduced an all-dry transfer method that allows one to place two-dimensional crystals on a position desired by the user with sub-micron precision. As the process does not require any wet chemical steps, it can be reliably used to fabricate freely suspended structures and it significantly reduces the contamination in the fabricated samples. The potential of the proposed method has been illustrated by fabricating heterostructures formed by stacking different two-dimensional materials. The

whole fabrication process can be accomplished in less than 15 minutes with a success yield close to 100%. Moreover, we find that about 30-40% of the fabricated heterostructures present large areas free of bubbles and wrinkles. The transfer method also offers the possibility to place two-dimensional crystals directly onto pre-fabricated circuit devices and micromechanical systems. Our all-dry transfer method has the potential to become a widely employed in nanotechnology, as it offers important advantages over alternative methods involving wet-chemical steps.

ACKNOWLEDGMENT

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REFERENCES

1. Novoselov, K. S.; Geim, A. K.; Morozov, S.; Jiang, D.; Zhang, Y.; Dubonos, S.; Grigorieva, I.; Firsov, A. *Science* **2004**, 306, (5696), 666-669.
2. Geim, A. K.; Novoselov, K. S. *Nature materials* **2007**, 6, (3), 183-191.
3. Novoselov, K.; Jiang, D.; Schedin, F.; Booth, T.; Khotkevich, V.; Morozov, S.; Geim, A. *Proceedings of the National Academy of Sciences of the United States of America* **2005**, 102, (30), 10451-10453.
4. Novoselov, K. S.; Jiang, Z.; Zhang, Y.; Morozov, S.; Stormer, H.; Zeitler, U.; Maan, J.; Boebinger, G.; Kim, P.; Geim, A. *Science* **2007**, 315, (5817), 1379-1379.
5. Blake, P.; Hill, E.; Neto, A. C.; Novoselov, K.; Jiang, D.; Yang, R.; Booth, T.; Geim, A. *Applied Physics Letters* **2007**, 91, 063124.
6. Roddaro, S.; Pingue, P.; Piazza, V.; Pellegrini, V.; Beltram, F. *Nano letters* **2007**, 7, (9), 2707-2710.
7. Castellanos-Gomez, A.; Agraït, N.; Rubio-Bollinger, G. *Applied Physics Letters* **2010**, 96, (21), 213116-213116-3.
8. Novoselov, K.; Neto, A. C. *Physica Scripta* **2012**, 2012, (T146), 014006.
9. Dean, C.; Young, A.; Wang, L.; Meric, I.; Lee, G.-H.; Watanabe, K.; Taniguchi, T.; Shepard, K.; Kim, P.; Hone, J. *Solid State Communications* **2012**, 152, (15), 1275-1282.
10. Grigorieva, A. G. I. *Nature* **2013**, 499, (7459), 419-425.
11. Britnell, L.; Ribeiro, R.; Eckmann, A.; Jalil, R.; Belle, B.; Mishchenko, A.; Kim, Y.-J.; Gorbachev, R.; Georgiou, T.; Morozov, S. *Science* **2013**, 340, (6138), 1311-1314.
12. Britnell, L.; Gorbachev, R.; Jalil, R.; Belle, B.; Schedin, F.; Mishchenko, A.; Georgiou, T.; Katsnelson, M.; Eaves, L.; Morozov, S. *Science* **2012**, 335, (6071), 947-950.
13. Yu, W. J.; Li, Z.; Zhou, H.; Chen, Y.; Wang, Y.; Huang, Y.; Duan, X. *Nature materials* **2012**, 12, (3), 246-252.

14. Georgiou, T.; Jalil, R.; Belle, B. D.; Britnell, L.; Gorbachev, R. V.; Morozov, S. V.; Kim, Y.-J.; Gholinia, A.; Haigh, S. J.; Makarovskiy, O. *Nature nanotechnology* **2012**, 8, (2), 100-103.
15. Bonaccorso, F.; Lombardo, A.; Hasan, T.; Sun, Z.; Colombo, L.; Ferrari, A. C. *Materials Today* **2012**, 15, (12), 564-589.
16. Song, X.; Oksanen, M.; Sillanpää, M. A.; Craighead, H.; Parpia, J.; Hakonen, P. J. *Nano letters* **2011**, 12, (1), 198-202.
17. Schneider, G. F.; Calado, V. E.; Zandbergen, H.; Vandersypen, L. M.; Dekker, C. *Nano letters* **2010**, 10, (5), 1912-1916.
18. Dean, C.; Young, A.; Meric, I.; Lee, C.; Wang, L.; Sorgenfrei, S.; Watanabe, K.; Taniguchi, T.; Kim, P.; Shepard, K. *Nature nanotechnology* **2010**, 5, (10), 722-726.
19. Zomer, P.; Dash, S.; Tombros, N.; van Wees, B. *Applied Physics Letters* **2011**, 99, (23), 232104-232104-3.
20. Ferrari, A. C.; Basko, D. M. *Nature nanotechnology* **2013**, 8, (4), 235-246.
21. Lee, C.; Yan, H.; Brus, L. E.; Heinz, T. F.; Hone, J.; Ryu, S. *Acs Nano* **2010**, 4, (5), 2695-2700.
22. Meitl, M. A.; Zhu, Z.-T.; Kumar, V.; Lee, K. J.; Feng, X.; Huang, Y. Y.; Adesida, I.; Nuzzo, R. G.; Rogers, J. A. *Nature materials* **2005**, 5, (1), 33-38.
23. Goler, S.; Piazza, V.; Roddaro, S.; Pellegrini, V.; Beltram, F.; Pingue, P. *Journal of Applied Physics* **2011**, 110, (6), 064308-064308-6.
24. Buscema, M.; Steele, G. A.; van der Zant, H. S. J.; Castellanos-Gomez, A. *arXiv:1311.3869* **2013**.
25. Castellanos-Gomez, A.; van Leeuwen, R.; Buscema, M.; van der Zant, H. S. J.; Steele, G. A.; Venstra, W. J. *Advanced Materials* **2013**.

Supporting Information:

Deterministic transfer of two-dimensional materials by all-dry viscoelastic stamping

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Content

- **Materials and methods**
- **Step-by-step guide for transfer**
- **Real time video of the stamping process**
- **Sequential transfer: sandwiched structures**
- **More examples of heterostructures**
- **Strain induced bubbles**

1. Materials and methods

For our stamping method we employed commercially available elastomeric films as stamps. The films (Gel-Fim® WF ×4 6.0mil) were supplied by Gel-Pak. The Gel-Pak polymer is a polysiloxane based material similar to poly-dimethyl siloxane. In fact, we have characterized both Gel-Films® and home-made poly-dimethyl siloxane samples (made by curing Sylgard 184 elastomeric kit purchased from Dow Corning) by Raman spectroscopy finding that their spectra is very similar. This indicates that both polymers are very similar in structure. Moreover, we employed home-made poly-dimethyl siloxane stamps in an early stage finding similar results. Nevertheless, we found that the surface of the Gel-Films® is flatter than that of home-made poly-dimethyl siloxane sheets fabricated by casting Sylgard 184 elastomer onto a Petri dish.

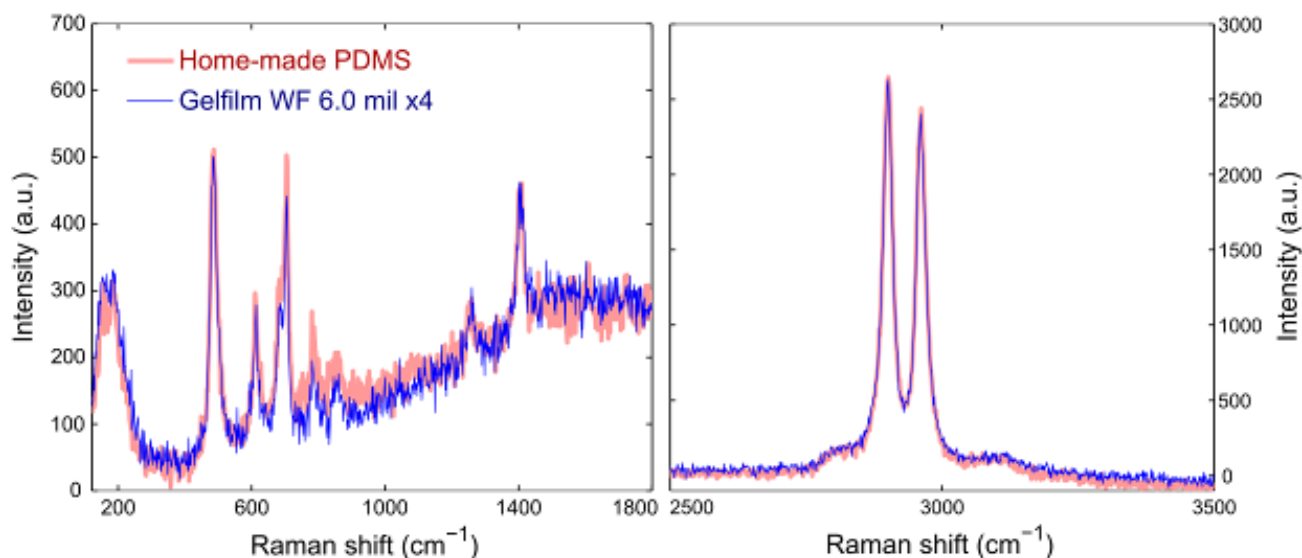


Figure S1. Characterization of the elastomeric substrates. Raman spectra acquired for an in-house fabricated poly-dimethyl siloxane substrate and for a commercially available Gel-Film® substrate.

The two-dimensional crystals are deposited onto the stamp surface by direct mechanical exfoliation of bulk layered materials (Graphite, MoS₂, h-BN and muscovite mica) with blue Nitto tape (Nitto Denko Co., SPV 224P). The employed bulk layered materials are: natural graphite flakes, natural MoS₂ (SPI Supplies, 429ML-AB), h-BN powder (Momentive, Polartherm grade PT110) and synthetic muscovite

mica (grade V1). We located the atomically thin sheets under an optical microscope (Olympus BX 51 supplemented with an Canon EOS 600D digital camera) and estimated the number of layers by their opacity in transmission mode.

The topography of the transferred flakes has been characterized by atomic force microscopy and high-angle scanning electron microscopy. A Digital Instruments D3100 AFM (with standard cantilevers with spring constant of 40 N/m and tip curvature <10 nm) operated in the amplitude modulation mode has been used.

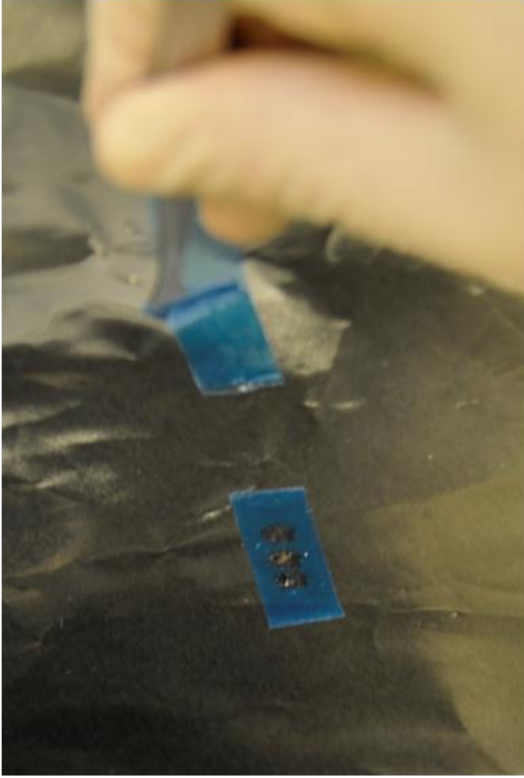
2. Step-by-step guide for transfer

A. Exfoliation

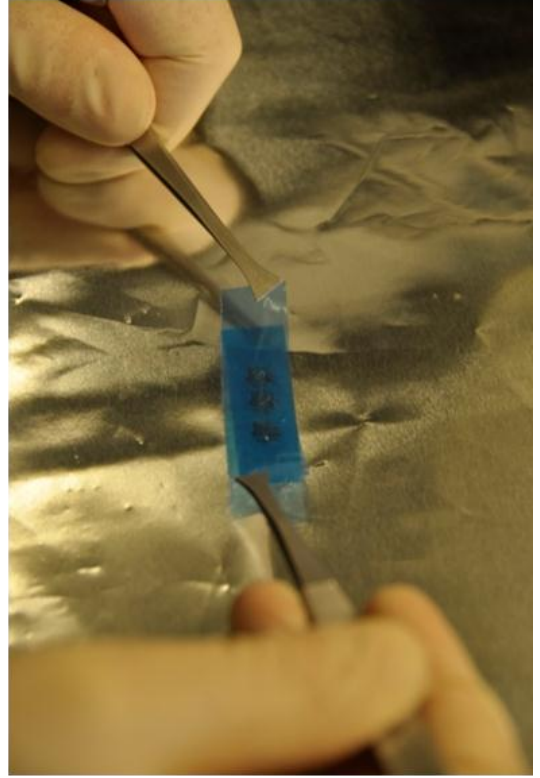
We start by mechanically exfoliating the layered material:

- Preparation of the empty tape and the tape with material
- Bringing the two pieces of tape into contact
- Apply slight pressure uniformly with a cotton swab
- Mechanical cleaving the crystal by pulling the pieces of tape away from each other

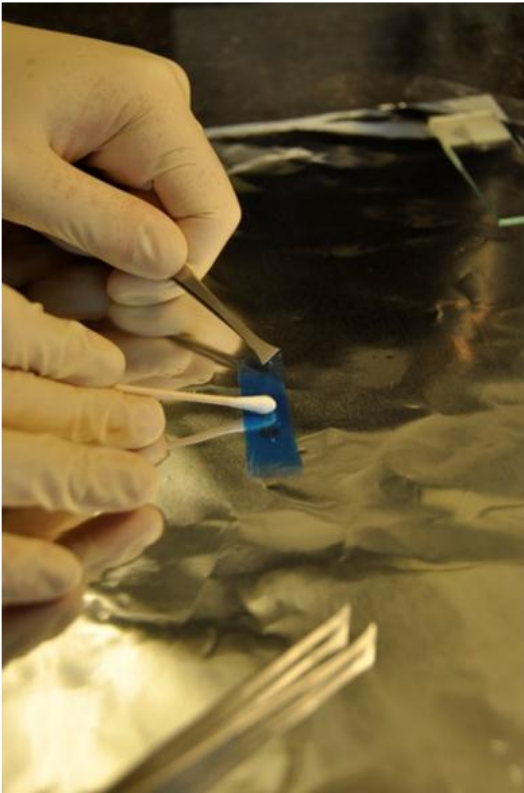
1



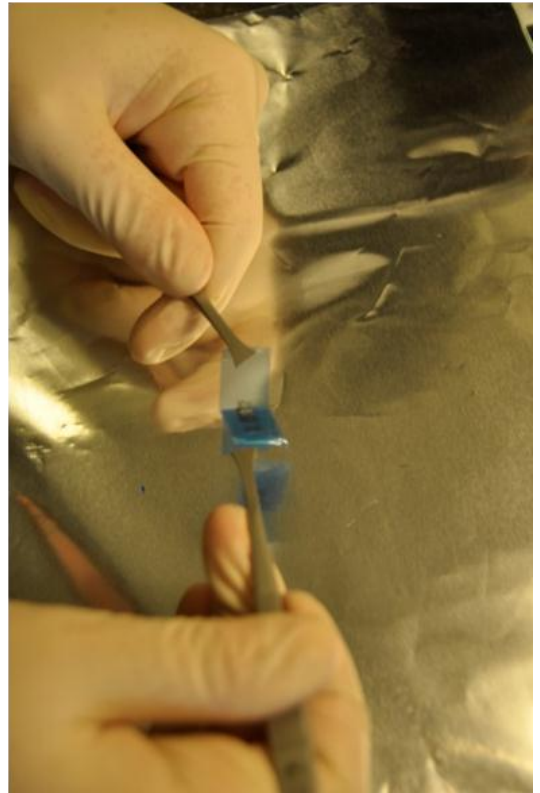
2



3



4



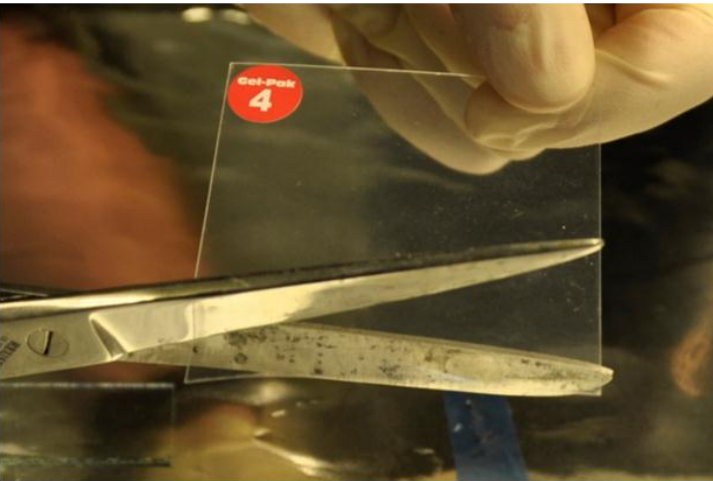
B. Preparation of the viscoelastic stamp (1)

1



We start by taking a sheet of a commercial PDMS-based gel:
Supplier: Gel-Pak®
Part n: PF-3-X4
The gel is sandwiched between two protective polymeric layers

2



We proceed by cutting a piece out of the PDMS sheet

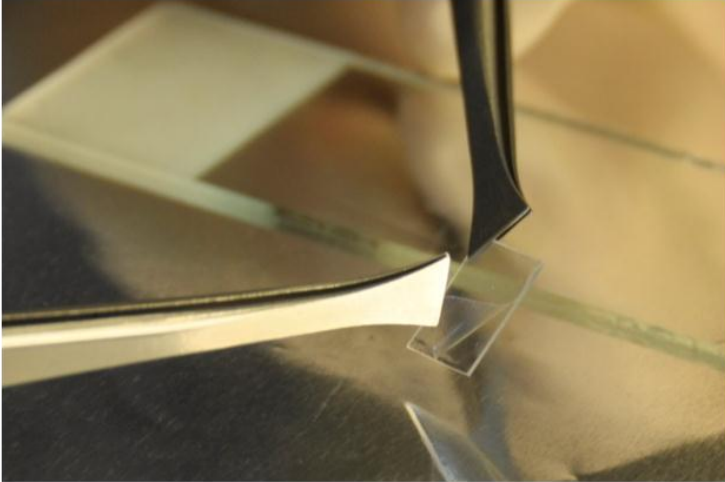
3



Detail of the cutout part

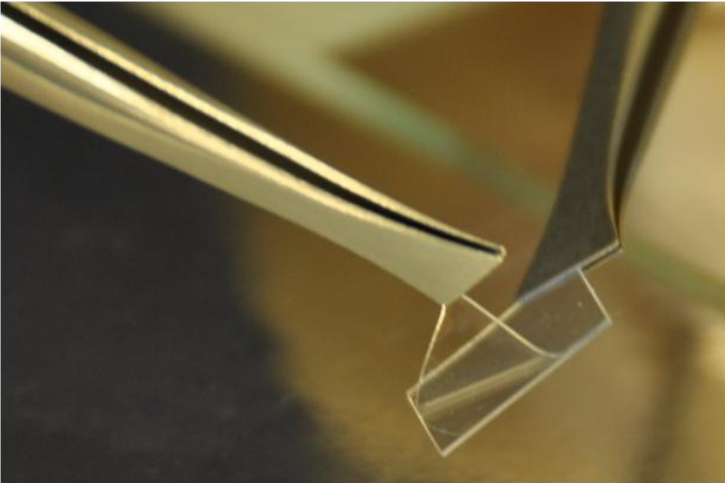
C. Preparation of the viscoelastic stamp (2)

1



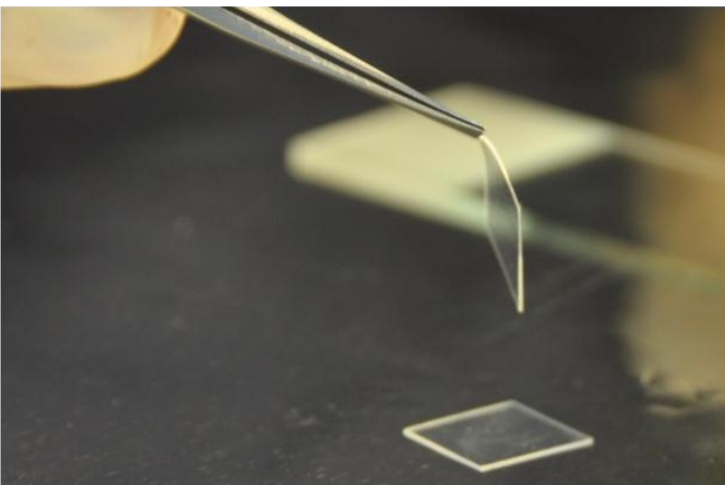
The first protective layer is removed

2



The PDMS gel is then slowly removed from the second protective layer

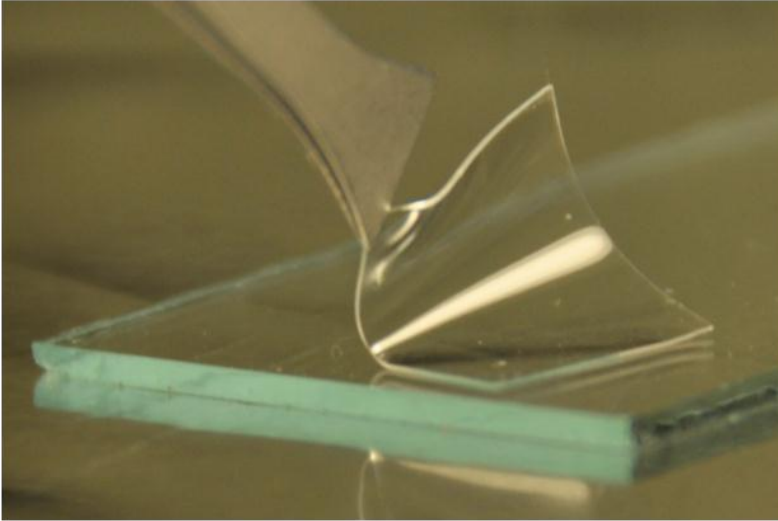
3



The PDMS gel is now freestanding and can be handled with tweezers

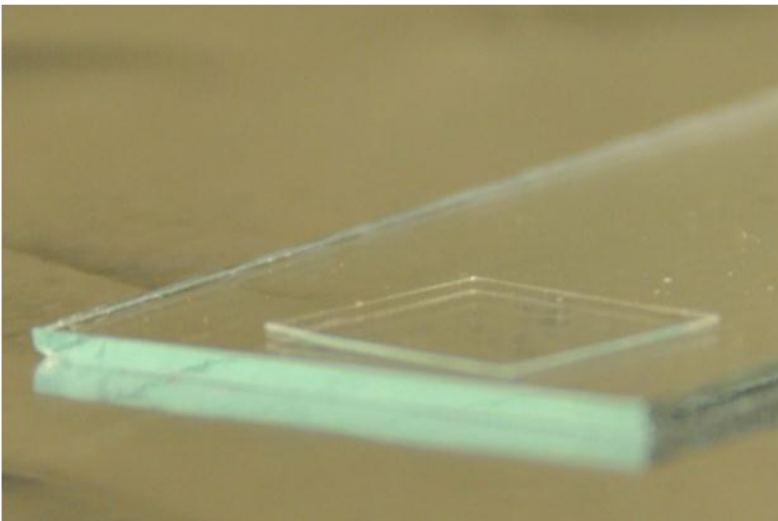
D. Preparation of the viscoelastic stamp (3)

1



The PDMS gel is carefully brought in contact with the glass slide.

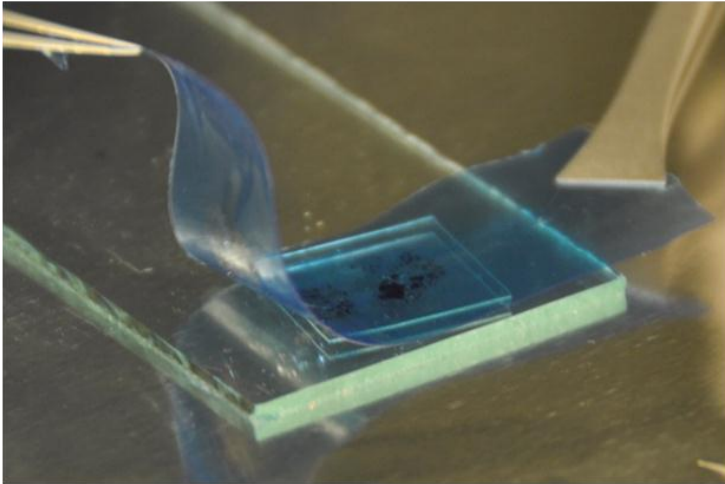
2



The PDMS gel adheres on the glass slide with no apparent wrinkles or bubbles.

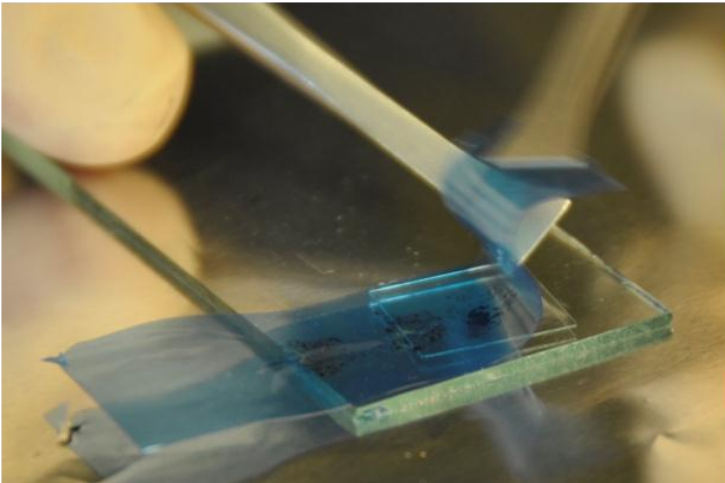
E. Transfer of flakes to the stamp

1



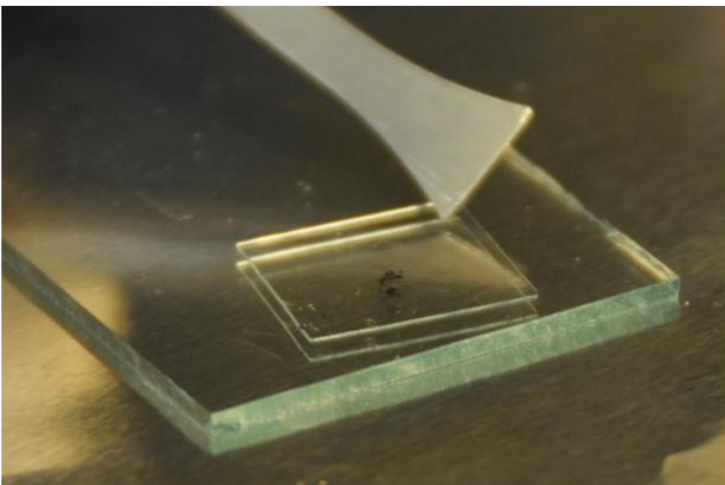
The blue/scotch tape previously prepared is brought in contact with the PDMS stamp surface.

2



While keeping the slide and the PDMS stamp into place, the blue tape with flakes is rapidly detached from the surface of the PDMS stamp.

3



After the removal of the tape, it is possible to see the transfer of some material. The stamp is now ready for optical inspection

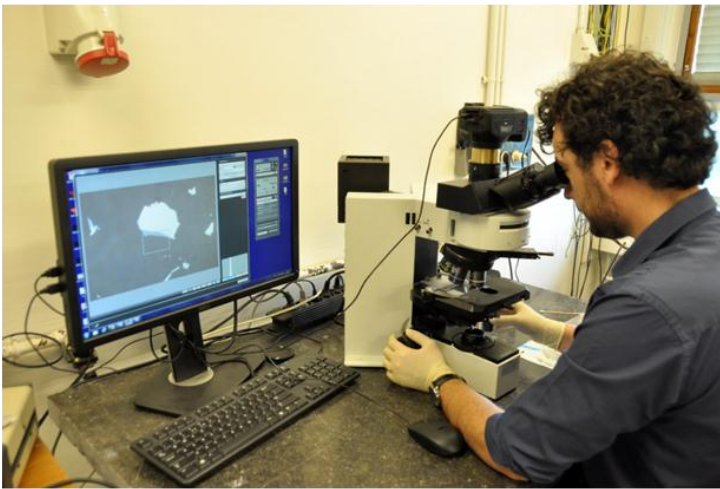
F. Optical identification

1



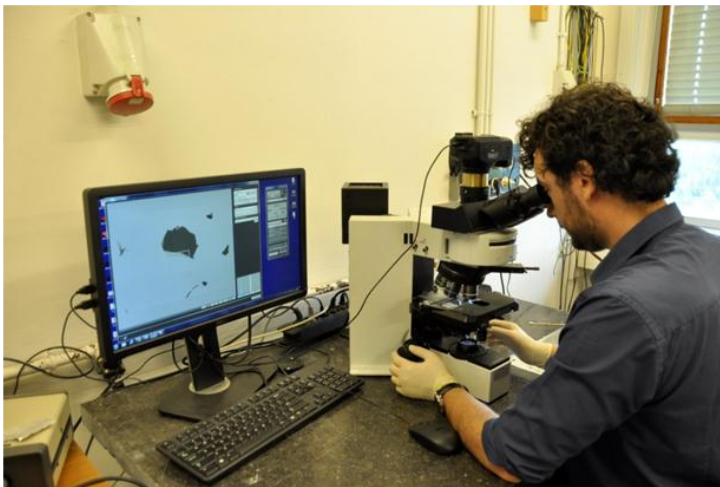
The stamp is transferred to an optical microscope that can be operated in both backscattering and transmission mode.

2



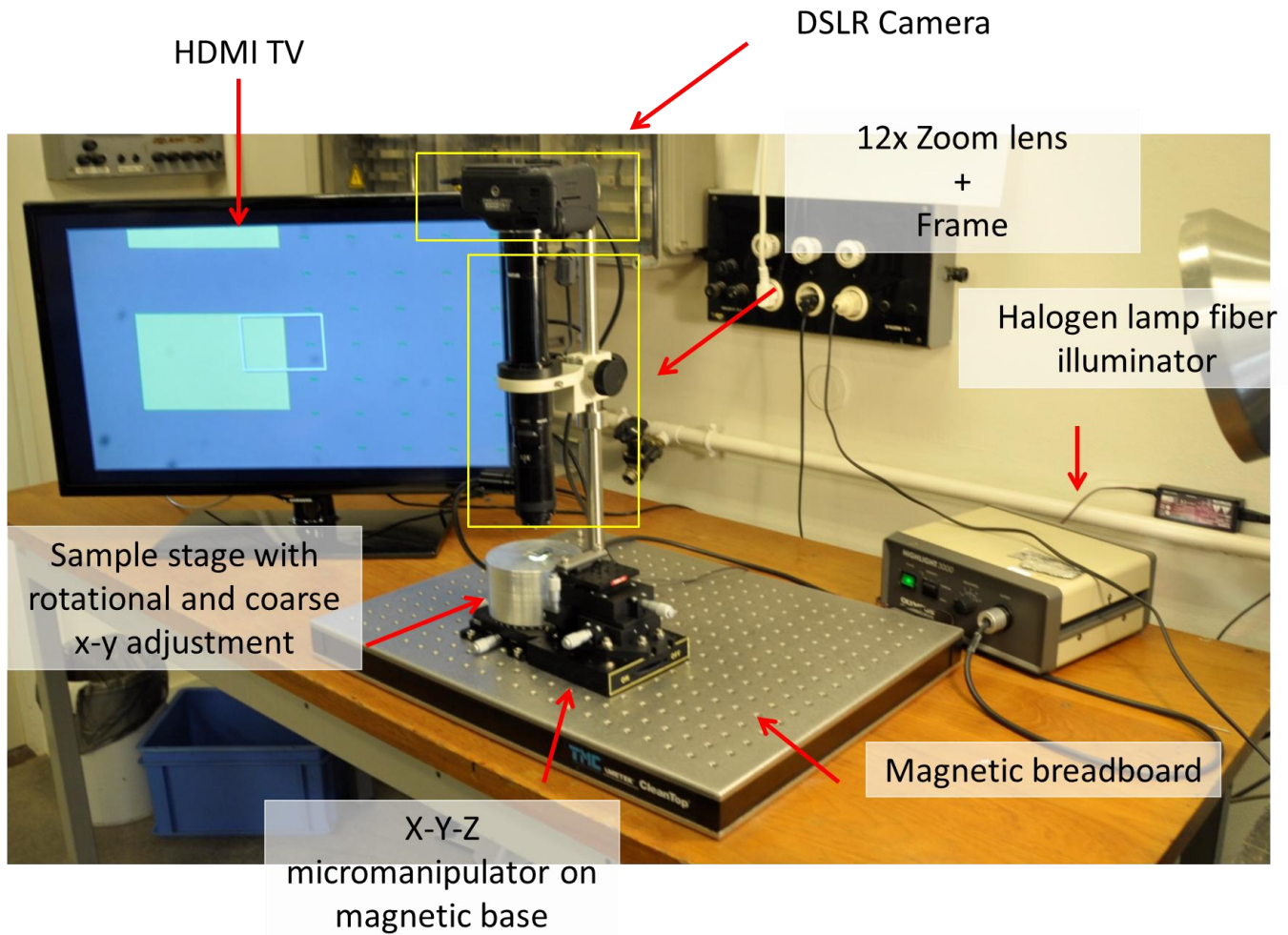
Typical appearance of a flake in backscattering (2) and transmission (3) optical microscopy

3



Once the desired flake is identified, the stamp can be used in the stamping setup

G. Dedicated stamping setup



| Description | Part number | Price (€) | Supplier |
|--------------------------------|-------------|-------------|---------------|
| Optical breadboard | #55-227 | 854.05 | Edmund Optics |
| Magnetic clamp | #62-272 | 369.55 | Edmund Optics |
| Table clamp | #54-262 | 75.05 | Edmund Optics |
| Steel bar | #39-353 | 52.25 | Edmund Optics |
| Rack and pinion | #03-609 | 237.5 | Edmund Optics |
| Extension Tube for Zoom lenses | MVL20FA | 542.88 | Thorlabs |
| Coaxially focusable Zoom lens | MVL12X3Z | 1887.9 | Thorlabs |
| Magnification lens | MVL12X20L | 281.88 | Thorlabs |
| XYZ micrometer stage | RB13M/M | 1152.72 | Thorlabs |
| Top plate for micrometer stage | RB13P1/M | 42.11 | Thorlabs |
| XY(theta) stage | XYR1/M | 494.16 | Thorlabs |
| Canon EOS600D | | 495 | |
| AC Charger (Canon EOS600D) | | 76.99 | |
| 16 GB SD card | | 29 | |
| Canon to F-mount adapter | | 8-20 | eBay |
| 32" TV Screen + HDMI adaptor | | 310 | |
| Total | | 6916 | |

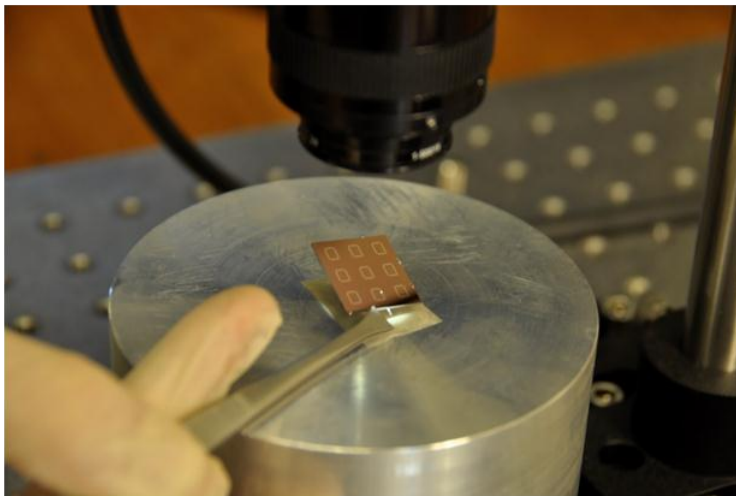
H. Stamping the desired flake (1)

1



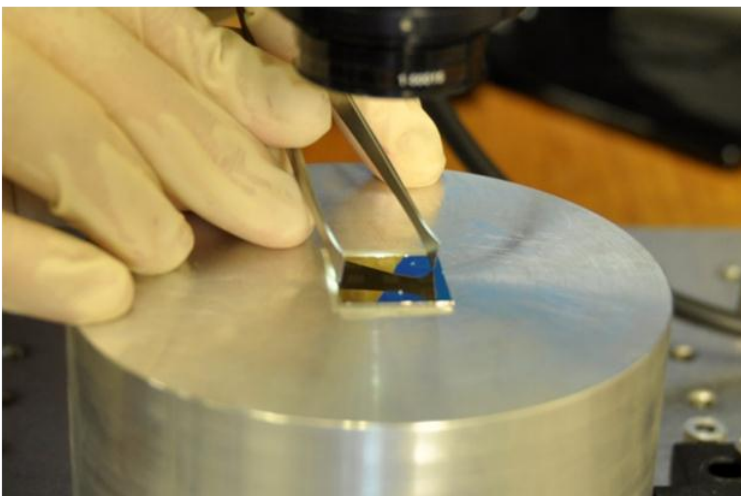
Double sided tape is placed on the sample stage

2



A patterned sample is placed on the sample stage

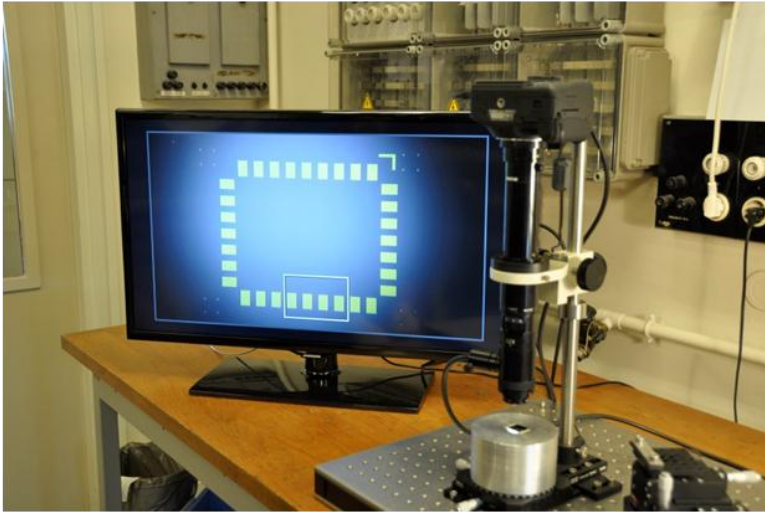
3



The sample is pressed on two corners to ensure flatness

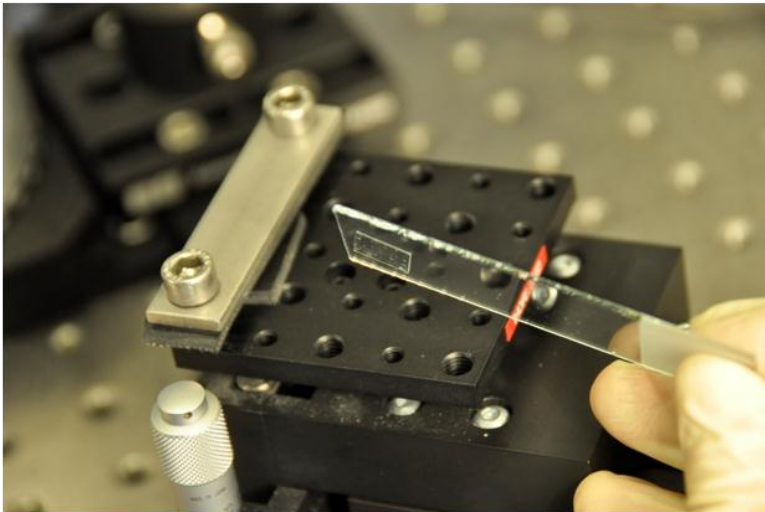
I. Stamping the desired flake (2)

1



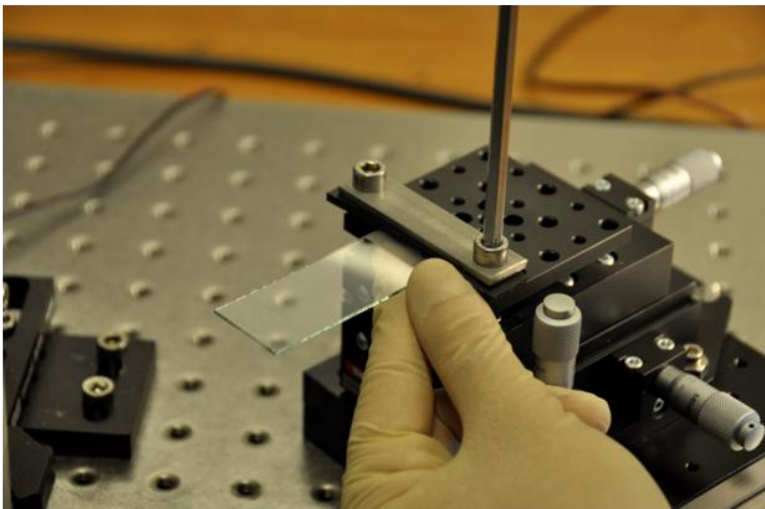
The pattern on the sample is imaged with the zoom lens

2



The stamp is rotated upside down

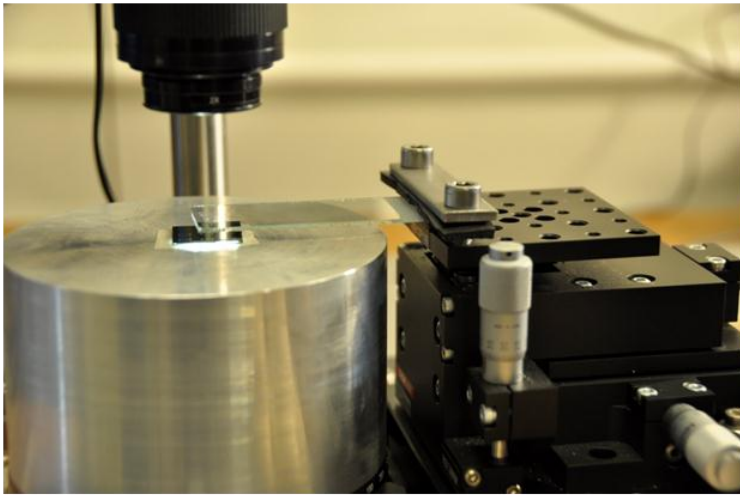
3



The stamp is mounted onto the micromanipulator

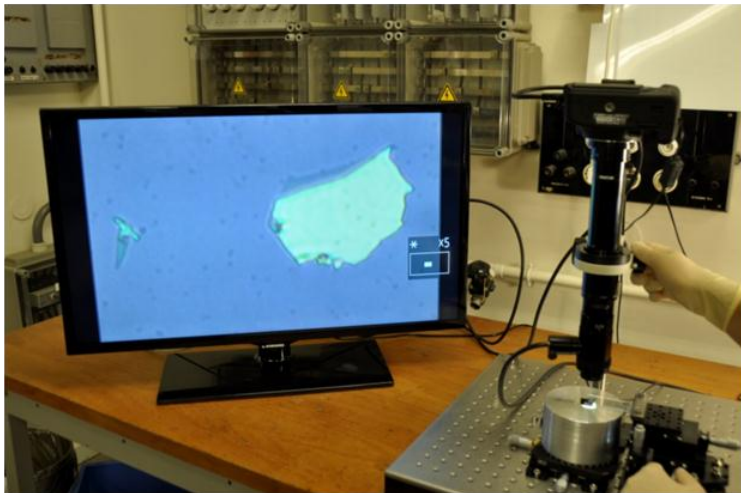
J. Stamping the desired flake (3)

1



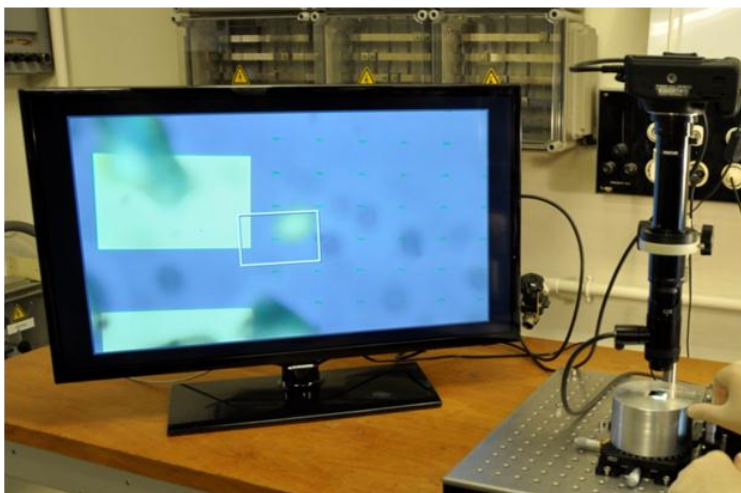
The stamp is coarsely positioned over the sample

2



The desired flake is brought in the field of view of the zoom lens/camera assembly

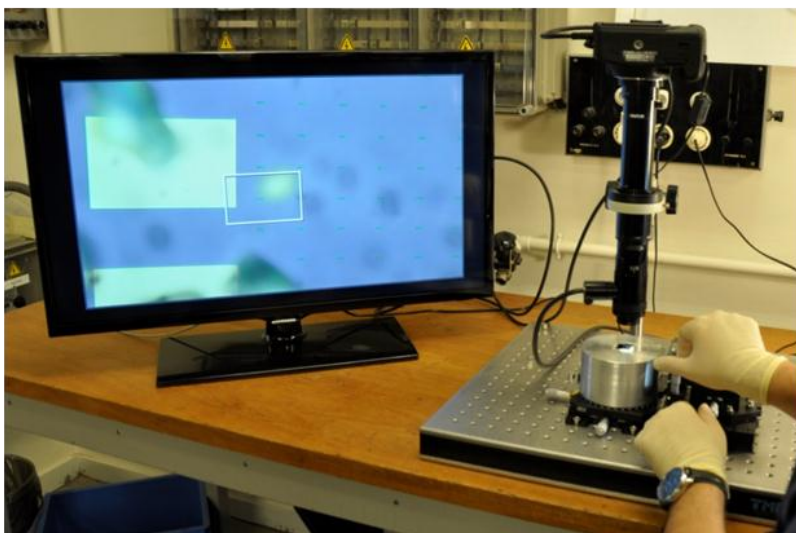
3



The desired pattern on the sample is brought into focus.

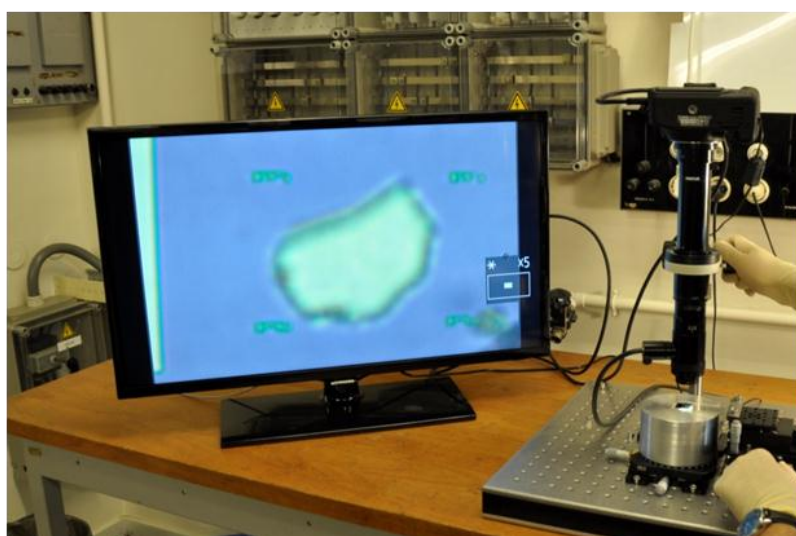
K. Stamping the desired flake (4)

1



The stamp is then carefully lowered and adjusted in x-y with the micromanipulator so that the desired flake is aligned with the desired pattern

2



When the stamp is almost touching the surface, its position is finely adjusted with the help of the digital zoom of the DSLR camera.

Now the stamp is ready to be brought into contact with the sample surface. Please refer to the video also included in the Supplementary Information (see also following section).

3. Real time video of the stamping process

In the Supporting Information of this manuscript it has been also included a real time video of the stamping process. A single layer MoS₂ flake is transferred over a pre-patterned gold structure with a 8 μm hole. Figure S2 shows 12 frames of this video.

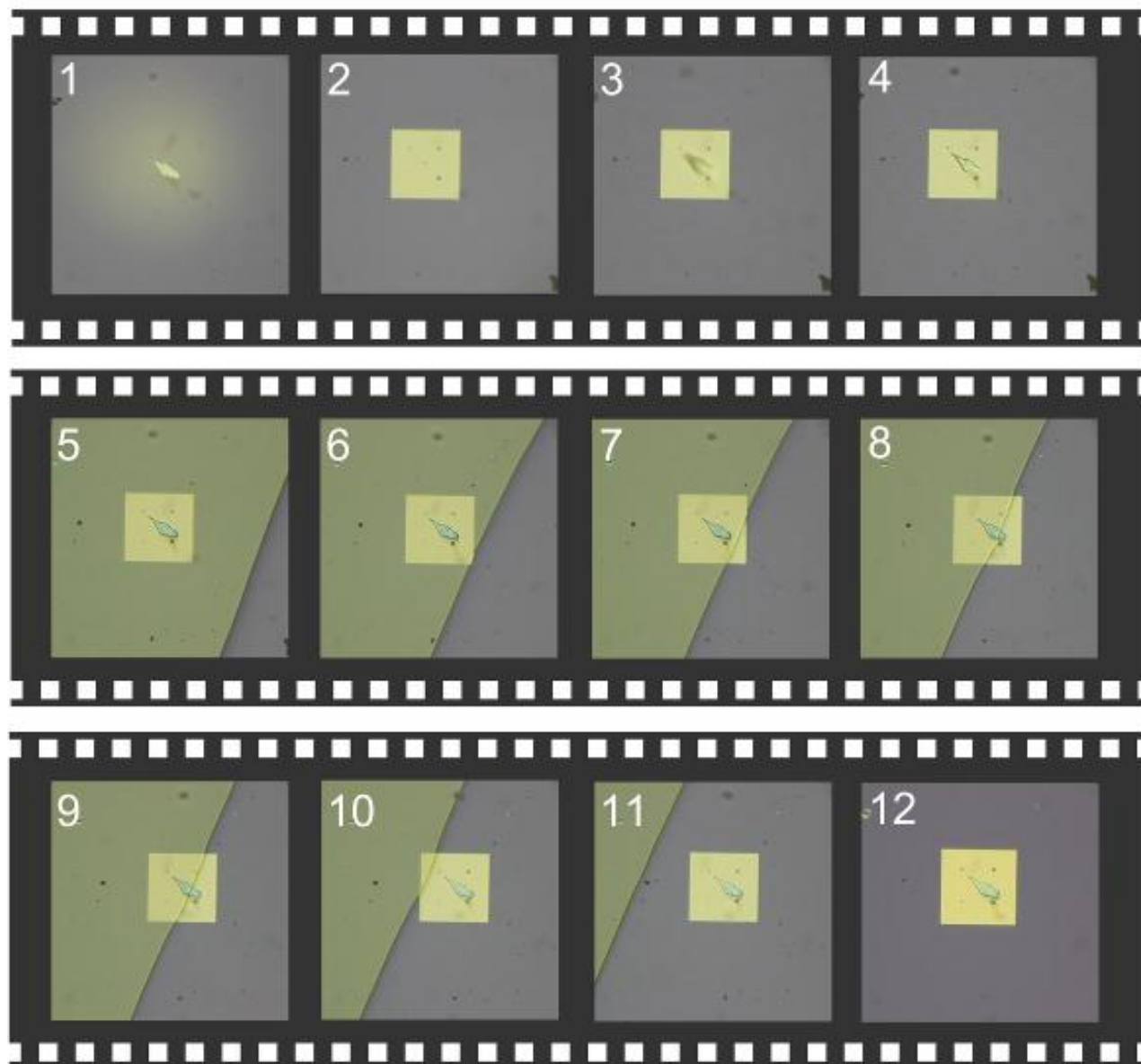


Figure S2. Frames of the real time video acquired during the stamping of a single-layer MoS₂ onto a pre-patterned substrate.

4. Sequential transfer: sandwiched structures

Figure S3 presents three optical images of the different steps in the fabrication of the ‘sandwiched’ MoS₂ structure shown in Figure 3d of the main text. A h-BN flake was first deposited onto a SiO₂(285 nm)/Si chip by mechanical exfoliation with Nitto tape (see Figure S3a). Then a bilayer MoS₂ flake was transferred onto the h-BN flake with the all-dry transfer technique (see Figure S3b). Finally, another h-

BN flake was transferred onto the h-BN/MoS₂ heterostructure by another stamping step (see Figure S3c).

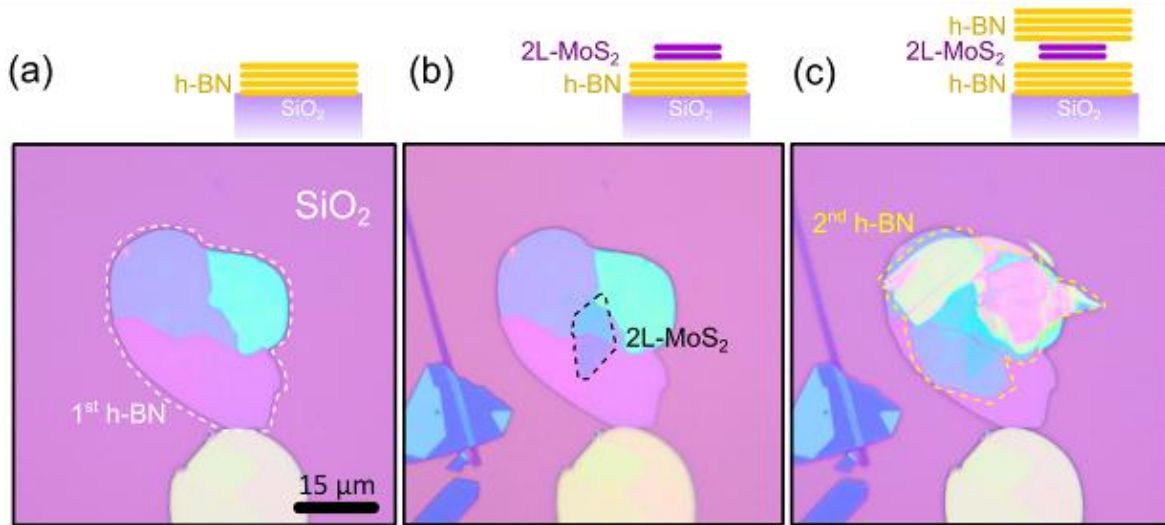


Figure S3. Sequence to fabricate a sandwiched structure. (a) Optical image of a h-BN flake transferred onto a SiO₂/Si chip by mechanical exfoliation. (b) Optical image of the same flake after transferring a bilayer MoS₂ flake. (c) Another h-BN flake is transferred onto the stack by employing another transfer step.

5. More examples of heterostructures

Figure S4 shows more examples of heterostructures, similar to those shown in Figure 3 of the main text.

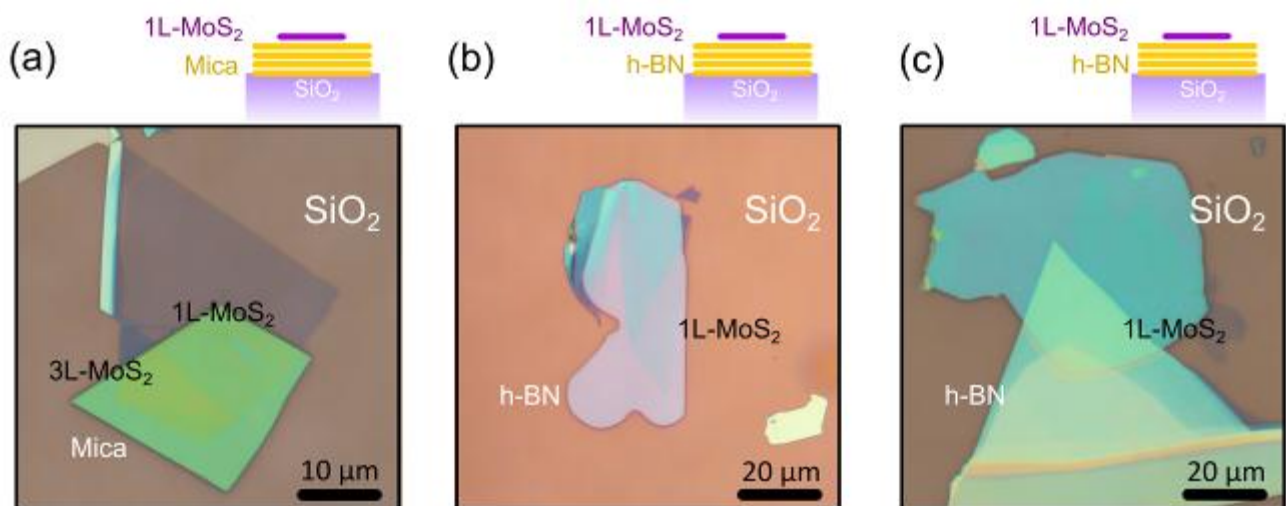


Figure S4. Artificial stacking of 2D materials. More examples of heterostructures fabricated with this technique. (a) Single-layer MoS₂ on mica. (b) and (c) Single-layer MoS₂ on h-BN.

6. Strain induced bubbles

During this work we have found that about 60%-70% of the fabricated heterostructures presented bubbles with diameters about 50 nm to 250 nm and height of 1 nm to 5 nm. These bubbles were present on the heterostructures fabricated by applying higher pressure to the stamp. We attribute the origin of these bubbles to the deformation of the viscoelastic stamp, which induces a large strain level on the transferred flake. Once the stamp is peeled off, this strain can be suddenly released forming these bubbles. A similar behaviour has been reported in Ref. ¹ for graphene flakes fabricated by mechanical exfoliation with PDMS layers. Figure S5 shows an example of a single-layer MoS₂ flake with bubbles induced by the deformation of the stamp during the transfer.

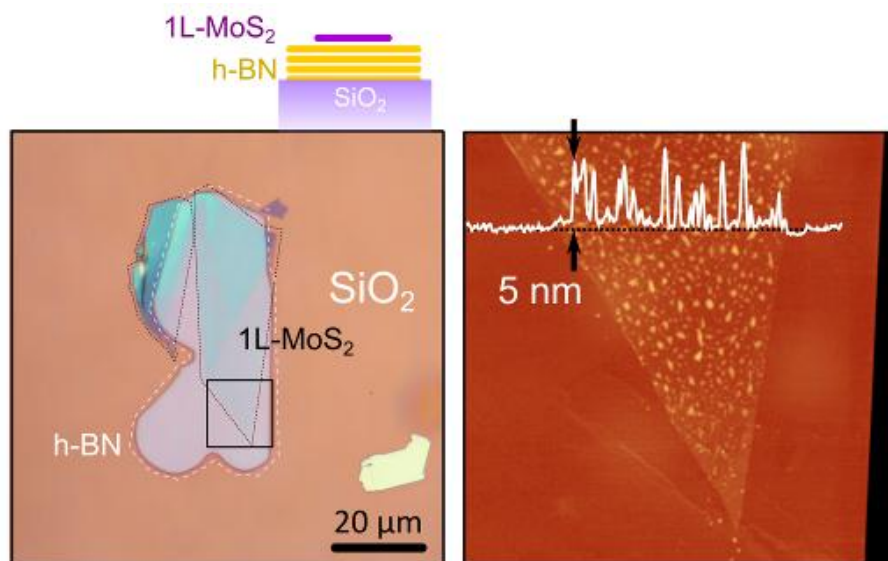


Figure S5. Strain induced bubbles. (Left) Optical image of a single-layer MoS₂ device transferred onto a h-BN flake. (Right) AFM image of the region highlighted in (a) with a black square. The MoS₂ layer presents bubbles about 5 nm height and 100 nm wide due to an excessive pressure during the transfer.

Supporting information references

1. Goler, S.; Piazza, V.; Roddaro, S.; Pellegrini, V.; Beltram, F.; Pingue, P. *Journal of Applied Physics* 2011, 110, (6), 064308-064308-6.