Thermomechanical Nanostraining of Two-Dimensional Materials

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ABSTRACT: Local bandgap tuning in two-dimensional (2D) materials is of significant importance for electronic and optoelectronic devices but achieving controllable and reproducible strain engineering at the nanoscale remains a challenge. Here, we report on thermomechanical nanoindentation with a scanning probe to create strain nanopatterns in 2D transition metal dichalcogenides and graphene, enabling arbitrary patterns with a modulated bandgap at a spatial resolution down to 20 nm. The 2D material is in contact via van der Waals interactions with a thin polymer layer underneath that deforms due to the heat and indentation force from the heated probe. Specifically, we demonstrate that the local bandgap of molybdenum disulfide (MoS2) is spatially modulated up to 10% and is tunable up to 180 meV in magnitude at a linear rate of about −70 meV per percent of strain. The technique provides a versatile tool for investigating the localized strain engineering of 2D materials with nanometer-scale resolution.

KEYWORDS: 2D materials, strain nanopattern, molybdenum disulfide, local bandgap, thermal scanning probe lithography, tip-enhanced Raman spectroscopy

INTRODUCTION

Straining atomically thin 2D materials (2DMs) is a promising strategy to modify their electronic and optoelectronic properties, enabling high-performance device applications such as single-photon emitters, high-responsivity photodetectors, and flexible nanoelectronic systems. For the case of graphene, it has been computed that by applying a strain of about 12% along C—C bonds a bandgap of about 0.5 eV is obtained, which enables graphene to be used as a semiconductor. For the case of molybdenum disulfide (MoS2) and molybdenum ditelluride (MoTe2), their phase change between semiconducting and metallic phases can be modulated by biaxial and uniaxial strain. Additionally, it has also been demonstrated that the mechanical strain in transition metal dichalcogenides (TMDCs) increases the carrier mobility by almost 2 orders of magnitude and influences their local bandgap as well as their quantum emission properties. So far, methods to strain 2DMs include introducing strain during growth, stretching/bending the supporting substrate, or transferring the 2DM onto a topographically patterned substrate. These methods create a strain before or during the growth/deposition of the 2DM and generally induce a global strain covering large surface areas.

To further improve strain engineering in 2DMs and to be able to integrate them into devices, a method is required that allows for two assets, namely to achieve spatial control of the strain pattern and to adjust its magnitude. Probe-based indentation techniques offer a convenient solution to these challenges because strain can be locally generated and the ability of indenting strain profiles makes it possible to control the strain distribution. In previous works, an atomic force microscopy (AFM) tip was used to temporarily induce strain in a suspended graphene membrane. In another approach, permanent local strain patterns in graphene on a SiO2 substrate were created by means of an AFM tip at room temperature yielding an indentation depth below 2 nm resulting in a strain magnitude of only 0.1%. Though various types of strain engineering methods have been proposed for 2DMs, both the strain magnitude and spatial distribution are far from being controlled with the high resolution that is needed to fabricate integrated nanodevices. Thermal scanning probe lithography (t-SPL) is an advanced direct-write method that uses a heated nanotip for 2D and 3D subtractive/additive manufacturing.

Received: August 18, 2020
Revised: September 27, 2020
Published: October 8, 2020
By expanding from there, we demonstrate here that by applying a suitable combination of indentation force and tip temperature below the cutting threshold, we are able to induce a well-controlled and permanent local deformation of the 2DM. This permanent local deformation determines the local strain, which results finally in a local bandgap modification. By raster scanning the tip over the sample, arbitrary patterns, such as lines, squares, and ripples, can be written through consecutive indentations. A key benefit of our technique is that the indentation depth can be controlled by the indentation force of the tip, the strain in the 2DM being locally confined to the writing area due to van der Waals interactions. Forcing the tip out of contact results in fast cooling and resolidification that induces the formation of permanent ripples in a shape corresponding to the written pattern (Supporting Information Section 1). The ripples induce a permanent strain in the 2D layer at a resolution primarily given by the tip apex.

To demonstrate this approach, we first wrote a pattern consisting of horizontal and vertical lines to create arrays of designed ripples on a monolayer (1L) MoS2 flake (Supporting Information Section 2). Figure 1c shows the topography of the written MoS2 ripple nanostructures. The probe was scanned at a velocity of 0.5 mm/s and the total writing and imaging time for a 1.5 × 1.2 μm² area (Figure 1c) was 38 s. Surface imaging with a conventional AFM confirms the topography measured with the t-SPL tool (Supporting Information Section 3). The three-dimensional (3D) topography demonstrates how accurately the strain nanopatterns in the MoS2 layer can be written (Figure 1d). Figure 1e shows the cross-section profile of the selected area in Figure 1c with nanoripples consisting of 4 nm deep valleys and 1.5 nm high pileups. We notice by detailed evaluation of the surface topography that the integrated volume of the valleys is larger than that of the pileups. This volume loss can be attributed to the local densification of the PPA polymer, an interpretation that is consistent with a similar nanoscale densification observed in earlier thermal scanning probe studies for nanolithography on PPA and data storage using cross-linked polymers. Here, in addition, because the 2DM layer is impermeable, the locally created monomers cannot outgas but rather diffuse into the polymer matrix, occupy free-volume sites of the polymer, and thereby cause further densification.

Versatility of the Strain Nanopatterning of 2DMs. To further investigate the capabilities of this approach, we designed additional patterns with the width ranging from 2 to 100 nm. Using monolayer MoS2, this results in measurable van der Waals interactions. Forcing the tip out of contact results in fast cooling and resolidification that induces the formation of permanent ripples in a shape corresponding to the written pattern (Supporting Information Section 1). The ripples induce a permanent strain in the 2D layer at a resolution primarily given by the tip apex.

RESULTS AND DISCUSSION

The Creation of Strain Nanopatterns in MoS2. The concept of thermomechanical strain nanopatterning is illustrated in Figure 1a. A monolayer of 2DM, such as TMDC or graphene, is transferred onto a 50 nm thick polyphthalldehyde (PPA) polymer layer that serves as thermosensitive deformable material. With the combination of heat and indentation force from the t-SPL nanotip, the 2DM and the underlying polymer are locally deformed as shown in Figure 1b. The deformation in the polymer is due to a combination of thermoplastic indentation and sublimation of PPA at a temperature of about 150 °C, where PPA decomposes into monomers. At this temperature, the 2DM layer stays physically and chemically intact and remains in conformal contact with the entrapped polymer, linked through van der Waals interactions.
indents with a feature size down to 20 nm, which is mainly limited by the size of the tip apex (Figure 2a). We also successfully demonstrate a resolution of 20 nm over larger areas (5 μm × 3.5 μm) in the same material (Supporting Information Section 4). The depth for each indent can be quantitatively tuned by the combination of temperature and force of the tip during the t-SPL writing (Supporting Information Section 5). The temperature of the tip−sample contact increases monotonically with the heater temperature but due to the high and hardly measurable effective thermal resistance of the tip it is difficult to quantify accurately. The actual temperature of the tip in contact with the sample is approximately 40−70% of the heater temperature as discussed also in previous works. We performed experiments with a linear increase of the heater temperature from 200 to 1200 °C and corresponding depth profile under the voltage of 7.5 V. The designed width is 20 nm. The writing direction is starting from bottom left to upper right. (c) Topography of 2L MoTe₂ nanoripples. (d) Topography of 1L graphene nanowells array. (e) Topography of 1L MoSe₂ nanopattern with arbitrary strain distribution (the EPFL logo is given as an example). Logo is used with permission. The writing direction in panels c, d, and e is starting from bottom right to upper left.

Figure 2. Versatility of the method and application to other 2D materials. (a) AFM topography of an array of nanostripes in 1L MoS₂ with designed width in the range from 2 to 100 nm and corresponding depth profile using the voltage of 7.5 V and the temperature of 950 °C. The writing direction is starting from upper right to bottom left. (b) AFM topography of nanopatterns produced with a heater temperature from 200 to 1200 °C and corresponding depth profile under the voltage of 7.5 V. The designed width is 20 nm. The writing direction is starting from bottom left to upper right. (c) Topography of 2L MoTe₂ nanoripples. (d) Topography of 1L graphene nanowells array. (e) Topography of 1L MoSe₂ nanopattern with arbitrary strain distribution (the EPFL logo is given as an example). Logo is used with permission. The writing direction in panels c, d, and e is starting from bottom right to upper left.

The applied indentation force \( F_{\text{ind}} \) at which the heated t-SPL tip presses against the surface can be estimated as follows: \( F_{\text{ind}} = F_{V,T} - F_k \), where \( F_{V,T} \) is the applied force due to heating and electrostatic bending, and \( F_k \) is the cantilever’s spring force (detailed in Supporting Information Section 6). In the experiments performed here, the indentation force is estimated to be ~280 nN for a heater temperature of 950 °C and an indentation tip−sample voltage of 7.5 V (see Supporting Information Section 6). To determine the local pressure exerted on the 2DM during the process, one has to consider the contact area. If we assume a tip diameter of 15 ± 5 nm, we obtain a local pressure in the range from 1 to 4 GPa.

Besides MoS₂, we demonstrate here the use of nanoprobe based strain engineering also on other single and multilayer 2DMs of interest, such as MoTe₂, MoSe₂, and graphene. To show the versatility of the method we patterned nanoripples in 2L MoTe₂ (Figure 2c), nanowells in 1L graphene (Figure 2d), and arbitrary design patterns, such as the EPFL logo in 1L MoSe₂ (Figure 2e). So far, the underlying thermosensitive polymer used was PPA, which under the effect of heat and force breaks into monomers. To elucidate the importance of the decomposing polymer, we also performed nanoindentation experiments with the identical parameters described in Figure 2a on thermoplastic poly(methyl methacrylate) (PMMA) polymer that has a glass transition temperature \( T_g \) of about 105 °C and a much higher thermal decomposition temperature of 325−500 °C. Therefore, in the case of PMMA, the indent causes only a thermoplastic deformation and no sublimation, thus pushing some material into the site of and around the preceding indent. Similar to the case of PPA, the PMMA as supporting polymer layer deforms, which results in local strain in the 1L MoS₂ layer; however, the pattern formation is, as
expected, less uniform due to the higher thermal decomposition temperature (Supporting Information Section 7).

**Scanning Raman Spectroscopy of Nanopatterned 1L MoS$_2$.** The spatially varying strain distribution over the nanopatterned monolayer MoS$_2$ is verified by micro-Raman spectroscopy. Figure 3a shows the topography of a representative deep nanopatterned 1L MoS$_2$ created by the t-SPL at a heater temperature of 900 °C and an indentation voltage of 8.5 V. The valley depth and pileup height of the strained area is about 8 and 5 nm, respectively. There are two columns of strained ripples with a valley width of 60 ± 3 nm. The Raman spectrum of the patterned MoS$_2$ shows significant redshifts of the E$_{2g}$ and A$_{1g}$ peaks as compared to pristine MoS$_2$ (Figure 3b) as a result of the induced strain. The E$_{2g}$ mode is assigned to the in-plane vibration of the two S atoms with respect to the Mo atom, and the A$_{1g}$ mode is assigned to the out-of-plane vibration of the two S atoms (Figure 3b). The typical Raman spectrum of pristine 1L MoS$_2$ presents two dominant peaks at 385.7 cm$^{-1}$ (E$_{2g}$) and 405.3 cm$^{-1}$ (A$_{1g}$).$^{37}$ No oxidation of the nanopatterned MoS$_2$ is observed in wide-range Raman spectra (Supporting Information Section 8).

Figure 3c,d shows the scanning Raman spectroscopic maps of the E$_{2g}$ and A$_{1g}$ peaks of the strained MoS$_2$, respectively, with the redshifts for the E$_{2g}$ peak position by 2.4 cm$^{-1}$ and the A$_{1g}$ peak position by 1 cm$^{-1}$. It should be noted that the micro-Raman spectrum is an optical average of the strained valleys and pileups due to the laser spot diameter (about 0.5–1 μm). From an overall fit to the redshift magnitudes and the height profile, we estimate that an average strain of 1.3% is induced in the nanopatterned MoS$_2$ according to the theoretical calculation discussed in Supporting Information Section 9.

To corroborate our hypothesis that the strain is maximized by writing ripples, we performed another test and wrote a single square (without ripples) of the same size as the rippled area (1 μm × 1 μm) with the same indentation depth. As expected, we do not observe the Raman shift in the single square region (Supporting Information Section 10), which indicates that the strain is a result of the nanostructures written by t-SPL as illustrated in Figure 1a. In addition, the Raman spectra of the strained 2L MoTe$_2$ (Figure 2c) and 1L graphene (Figure 2d) also show significant redshifts of the Raman peaks as compared to unstrained MoTe$_2$ and unstrained graphene, respectively (Supporting Information Section 11).

**AFM-TERS Measurement of the Nanopatterned 1L MoS$_2$.** To identify the strain with nanoscale resolution below the optical diffraction limit, we performed an AFM-based tip-enhanced Raman spectroscopy (AFM-TERS) investigation over the nanopatterned 1L MoS$_2$ as illustrated in Figure 4a,b. The AFM-TERS combines Raman spectroscopy with scanning probe microscopy.$^{38}$ Upon illumination, the electric field strength at the tip apex (Supporting Information Section 12) strongly increases thanks to localized surface plasmon resonance.$^{39,40}$ Therefore, the Raman signal of the probed material is enhanced in the vicinity of the tip. Figure 4c shows an AFM topography of the nanopatterned 1L MoS$_2$, acquired prior to the AFM-TERS study. A small rectangular area of 30 nm × 200 nm in Figure 4d includes two valleys and one pileup, where AFM-TERS signals are acquired with a resolution of 3 × 20 pixels. Each pixel represents a 10 nm × 10 nm area, which is small enough to resolve the strain differences present within the nanopatterned 1L MoS$_2$. At each pixel, tip-enhanced near-field Raman signals are collected using tapping mode AFM feedback at ambient conditions. During TERS measurements,
the laser power and signal acquisition time are optimized to minimize far-field Raman signals.

The two first-order Raman active vibrational modes of MoS$_2$, E$_{12g}$ and A$_{1g}$ modes, are selected for screening the nanoscale vibrational changes in the strained 1L MoS$_2$. All spectra are background corrected for enhancement fluctuations by normalization to the local enhancement. Figure 4e shows that the tip-enhanced Raman spectroscopic map of the A$_{1g}$ peak corresponds to the height map in Figure 4d. The TERS map of the E$_{12g}$ peak is also consistent with the height map as shown in Supporting Information Section 13. The patterned MoS$_2$ shows the most redshifts for both E$_{12g}$ and A$_{1g}$ peaks: 4.7 and 2.1 cm$^{-1}$ for the valley regions and 2.7 and 1.5 cm$^{-1}$ for the pileup region (Figure 4f). This indicates that the strain has been successfully created in the entire nanoripples including valleys and pileups. The redshift value of the strained MoS$_2$ in the valleys is about two times of that measured using micro-Raman spectroscopy. The most strain in the valleys is estimated to be 2.6% and the most strain in the pileup is 1.5%. Figure 4g plots the average E$_{12g}$ and A$_{1g}$ peak shift within the strained region, which is consistent with that measured in the micro-Raman spectroscopy.

Bandgap Modulation of Nanostrained 1L MoS$_2$. The bandgap modulation of the strained MoS$_2$ crystal is examined by scanning photoluminescence (PL) spectroscopy. Figure 5a,b shows the A-exciton and B-exciton peak maps of the PL spectra of the same sample studied in micro-Raman characterization (Figure 3), respectively. The PL measurement is also optically averaged over the laser spot diameter (about 0.5–1 μm). The PL intensity peak of the strained area is consistently observed at lower PL energy (blue color). The unstrained MoS$_2$ shows the typical PL spectrum of monolayer MoS$_2$ with a principal peak at 1.9 eV (A exciton). However, the strained MoS$_2$ clearly exhibits redshift of the A-exciton peak, indicating a strain-induced bandgap reduction. Figure 5c compares the representative PL spectra of the strained MoS$_2$ and the unstrained MoS$_2$, where the strong PL peaks arise from the direct bandgap emissions in monolayer MoS$_2$. The A-exciton peak intensity is more than doubled in the strained MoS$_2$. The enhanced PL intensity has been observed in strained MoS$_2$ nanocones$^{32}$ and semiconductor nanowires. As suggested by other works, this might be due to 2D exciton funnel effect,$^{32}$ exciton drifting, and concentrating.$^{43}$ By varying the indentation depth and hence the average strain, the bandgap...
for 5 s and then 6000 rpm for 60 s). MoS_2 exfoliated from a MoS_2 bulk crystal onto polydimethylsiloxane (PDMS) stamps and then were transferred on the PPA substrate. The MoTe_2, MoSe_2, and graphene flakes were obtained and processed with the same procedure. The layer number of the flakes is identified by Raman spectroscopy (Supporting Information Section 2). MoTe_2, MoS_2, MoSe_2, and graphene crystals were purchased from HQ Graphene.

**Nanostrain Engineering.** The strain nanopatterning of 2D materials was performed using a commercial t-SPL (NanoFrazor, Heidelberg Instruments, Switzerland). The cantilever is made of n-doped silicon. The spring constant of the cantilever is around 0.9 N/m. The apex diameter is 15 ± 5 nm. During the writing process, the tip was heated at a temperature in the range of 200–1200 °C. This operation was performed under N_2 atmosphere to minimize the likelihood of oxidation. The indentation tip–sample voltage was in the range of 4.5–9.5 V. One layer MoS_2, 2L MoTe_2, 1L MoSe_2, and 1L graphene samples were patterned at nanoscale.

**Material and Structure Characterizations.** AFM was conducted to collect the topographies of the nanostrained 2D materials. AFM was also used to verify the thickness of the nanofilm. Images were collected using Bruker’s Dimension FastScan AFM system. The FastScan AFM scanner mode (contact mode) was used. Raman spectroscopy was performed to confirm the monolayer nature of all the exfoliated MoTe_2 flakes and to characterize the properties of the patterned nanostructures. Raman spectra and PL spectra were collected using a confocal Raman microscope system (nVia Qntor, Renishaw) coupled with an Olympus inverted optical microscope and using a laser source with an excitation wavelength of 532 nm. The laser power (84 μW) was adjusted to avoid sample damage. Raman spectra were acquired in the range from 61 to 1850 cm\(^{-1}\) with a 15 s exposure time and an average of three measurements. Gratings of 3000 and 1800 gr/mm were used for Raman mapping and wide-range Raman measurements, respectively. The PL spectra were acquired in the range from 1.6 to 2.1 eV with a 10 s exposure time and an average of three measurements. A grating of 300 gr/mm was used for PL mapping. The peak at 520.5 cm\(^{-1}\) from the silicon substrate was used as a reference.

**Tip-Enhanced Raman Spectroscopy (TERS).** AFM-based TERS measurements were performed using an integrated atomic force microscope, and Raman spectrometer system (NT-MDT, NTegra, Russia) in the top-illumination configuration, equipped with a 0.7 NA 100× objective (Mitutoyo, Japan). To prepare probes for AFM-TERS measurements, commercially available monolithic silicon-based ATEC-NC AFM probes (Nanosensors AG, Switzerland) were coated with an adhesion layer of 10 nm Cr followed by 50 nm Au using an e-beam evaporator (Evatec, model: BAKS01 LL). After preparation of TERS probes, the probes were either directly used for TERS measurements or stored under N_2 flow in a chamber. A 561 nm Nd:YAG laser was used as excitation source. The incident laser power on the sample was in the range from 0.5 to 1.5 mW, depending on the spectral quality and to avoid damage in samples. The scattered light from the sample was detected by an electron multiplying charge coupled device (EMCCD, Newton 971 UVB, Andor) thermoelectrically cooled to around −85 °C. The acquisition time of the spectral signal at each pixel was 10 s. Before recording the high-resolution AFM-TER spectra and/or maps, the thermal drift was minimized by prerunning the instrument and pseudo scanning the nearby sample areas with laser illumination.

***CONCLUSIONS***

In this work, we demonstrate strain nanopatterning of 2DMs in ambient conditions on a thermosensitive polymer by using thermal scanning probe lithography. A strain pattern resolution down to 20 nm is achieved on 1–2L TMDCs and 1L graphene. By adjusting the indentation force and heater temperature, the bandgap of the strained 2DMs can be precisely modulated locally at the nanoscale. The bandgap is linearly proportional to the indentation depth, making the strain tunable and exhibits advantages in the nanoscale resolution and controllability of strain distribution.

***EXPERIMENTAL METHODS***

**Material Preparation.** PPA (polyphthalaldehyde, Allresist) solution (3 wt % in anisole) was spin coated on SiO_2 (200 nm thick)/Si (500 μm thick) substrate (conditions, 100 rpm for 5 s and then 6000 rpm for 60 s). MoS_2 flakes were exfoliated from a MoS_2 bulk crystal onto polydimethylsiloxane (PDMS) stamps and then were transferred on the PPA substrate.
The authors would like to acknowledge the operations team of the Binnig and Rohrer Nanotechnology Center (BRNC) at the IBM Zurich Lab for their support during the tip preparation and AFM-TERS measurement.

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