LOCALIZED AND CONFORMAL STRAIN ENGINEERING OF 2D MATERIALS FOR SCALABLE, FUNCTIONAL DEVICES

*Sarah O. Spector, Weikun Zhu, Alex Quach, Peter F. Satterthwaite, and Farnaz Niroui**
Massachusetts Institute of Technology, USA

ABSTRACT

We present a platform for localized and conformal strain engineering of two-dimensional (2D) materials with nanoscale control and compatible with wafer-scale processing. Unlike conventional approaches where strain is induced by 2D material transfer onto pre-fabricated topographical structures, our approach enables post-transfer, spontaneous formation of non-planar features to strain the 2D layer. As a result, straining can be achieved without the common formation of bubbles, wrinkles, or tears in the material. We show that such uniform straining can be used to engineer the 2D material band structure post-synthesis, tuning its optical and electronic characteristics. This platform opens up new device opportunities in sensors, transistors, and quantum light sources.

KEYWORDS

Two-dimensional (2D) materials, Strain engineering, Band gap engineering, Nonplanar nanofabrication, Interface engineering, Optoelectronics, Nanoelectromechanical devices

INTRODUCTION

Since the discovery of graphene, rapid advancements in two-dimensional (2D) materials have led to a diverse library of atomic building blocks for next-generation devices with improved and unique functionalities. For example, 2D materials have demonstrated promise for high-mobility transistors due to their intrinsic atomic thickness, avoiding the increased surface charge scattering experienced with conventional channel scaling [1]. They also enable sensors with enhanced response due to their large surface area-to-volume ratios [2], and flexible electronics due to their high mechanical compliance [3]. Exotic quantum and topological physics have also emerged in these materials, leading to applications in quantum information sciences [4].

The atomic structure of 2D materials makes them highly susceptible to lattice perturbations which, if intentionally induced, provides a strategy to actively engineer their optical and electronic properties. Strain engineering has long been used as an important approach to enhance semiconductor device performance; high-mobility transistors with strained SiGe channels are a prominent example [5]. Compared to bulk semiconductors, atomic 2D materials are even more sensitive to strain and can withstand larger deformations before rupture [3]. This makes strain engineering highly promising for the development of new 2D material device platforms including enhanced sensors, transistors, photodetectors and quantum light sources [6].

Despite the promise, controlled, localized straining of atomically-thin materials remains challenging. For localized straining in particular, present techniques largely rely on draping the 2D material over pre-textured substrates [3]. This involves lithographically fabricating topographical features on the substrate, onto which a 2D material layer is then transferred. During the transfer, however, the nanostructured surface prevents a conformal van der Waals contact with the 2D material, often resulting in trapped bubbles, wrinkles, and tears. These defects cause non-deterministic straining and hinder practical device implementations. Moreover, these passive surfaces offer no direct path towards active mechanical tuning without additional complex fabrication steps. Such mechanically-active straining could enable real-time electromechanical control of material properties.

To address these challenges, we present a platform where the features used to locally strain a 2D material are formed after transferring the 2D material, using a thermally-activated nonplanar substrate transformation based on spatially-controlled interface engineering of nanoscale thin-films. To this end, the 2D material can first be transferred onto a planar surface, allowing conformal adhesion to minimize the formation of bubbles, wrinkles and tears, and can subsequently be locally strained in a controlled and scalable approach. We demonstrate this technique for the example of straining a monolayer of molybdenum disulfide (MoS_2), a transition metal dichalcogenide 2D semiconductor, with engineered optical and electrical response.

POST-TRANSFER STRAINING PLATFORM

Our strain engineering approach is outlined in Figure 1a. First, a substrate is prepared which allows for thermally-induced formation of localized nonplanar features [7]. For this, the substrate is patterned with a self-assembled molecular monolayer (SAM) of (3-aminopropyl)triethoxysilane (APTES) to spatially engineer its surface adhesion. The SAM is patterned using a lithographically-defined oxide hard-mask followed by APTES vapor phase assembly

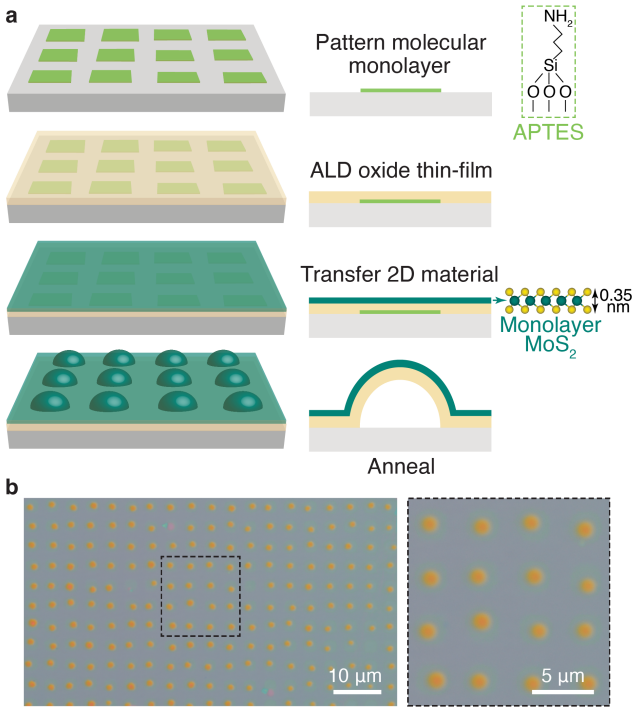

Figure 1: Post-transfer strain engineering platform. (a) Substrate is patterned with a self-assembled molecular monolayer, APTES. Next, an oxide thin-film is deposited using atomic layer deposition. A 2D material such as MoS_2 is transferred onto the substrate while it remains flat. Finally, an anneal step induces oxide delamination at molecule-functionalized regions where surface-adhesion is low, straining the 2D material. (b) Microscope image of a periodically-strained MoS_2 monolayer (left), and a zoomed-in view (right).

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in a vacuum desiccator for 12 hours. Once the assembly is completed, the sample is rinsed in ethanol and the hard-mask is etched to reveal a spatially patterned SAM on the surface. The shape, size, and spatial arrangement of the lithographically-defined functionalized regions will determine the position, size and distribution of the 2D material strained sites later in the process.

Next, an oxide thin-film, here 10 nm of aluminum oxide (Al_2O_3), is deposited onto the patterned SAM using atomic layer deposition (ALD) at 200°C, a temperature sufficiently low to avoid SAM degradation. Careful coordination between the SAM termination group and the ALD chemistry allows us to locally control the interaction between the deposited oxide film and the molecule-functionalized substrate. In the case of APTES and ALD Al_2O_3, the oxide is expected to nucleate on the APTES amine termination group rather than directly growing on the underlying substrate, such that the oxide-substrate adhesion is controlled by the interfacial SAM [8].

Crucially, at this point, the sample surface remains flat, enabling pristine and conformal transfer of the 2D material. We use a gold-mediated transfer technique which allows for large-area exfoliation of an MoS_2 monolayer from its bulk natural crystal source [9-10]. Specifically, our transfer process begins with 80 nm of gold evaporated onto a silicon carrier wafer with no adhesion layer. Poly(methyl methacrylate) (PMMA) is spin-coated onto the gold to act as a sacrificial release layer. Thermal release tape is used to template-strip the gold-PMMA stack, peeling it off of the silicon carrier substrate to reveal an atomically smooth gold underside. This ultrasmooth gold-tape stack is then brought into conformal contact with the MoS_2 crystal, where the uniformly large Au-MoS_2 van der Waals interactions experienced lead to large-area exfoliation of a monolayer. The transfer stack is then placed onto our engineered APTES-Al_2O_3 receiving substrate. The thermal tape is released by heating it to 130°C. Once PMMA residues and the gold film are removed using N-methylpyrrolidone and gold etchant (potassium iodide), respectively, an MoS_2 monolayer remains on the substrate.

The final step is thermal transformation of our planar substrate into nonplanar features. For this, we anneal the sample at > 400°C for 5 minutes, activating the local delamination of the oxide layer at the APTES-functionalized sites where adhesion to the substrate is low. The anneal is performed in forming gas to prevent 2D material oxidation, thus maintaining the material's intrinsic optoelectronic properties. As thermal stress builds in the Al_2O_3 film due to its mismatched thermal expansion coefficient with the silicon substrate, the APTES molecules begin to thermally degrade, leading to local release of the oxide adhesion and providing preferential sites for the Al_2O_3 to buckle. At these locations, the oxide forms dome-shaped blisters, with size determined by the dimensions of the APTES-functionalized site in combination with the anneal temperature and oxide thickness [7]. The 2D material, conformal and well-adhered to the oxide via van der Waals forces, is deformed along with the oxide, inducing biaxial tensile strain. An example of a strained MoS_2 monolayer is shown in Figure 1b.

The strain (ϵ) induced in the 2D material at the apex of the dome can be determined using Hencky's model for a circular, clamped membrane [11]:

$$\epsilon = \left(\frac{h}{r}\right)^2 f(\nu) \qquad (1)$$

where h is the dome's maximum height, r is its radius, and $f(\nu)$ depends on the material's Poisson's ratio, ν. In the case of MoS_2, $f(\nu) = 0.721$ [11].

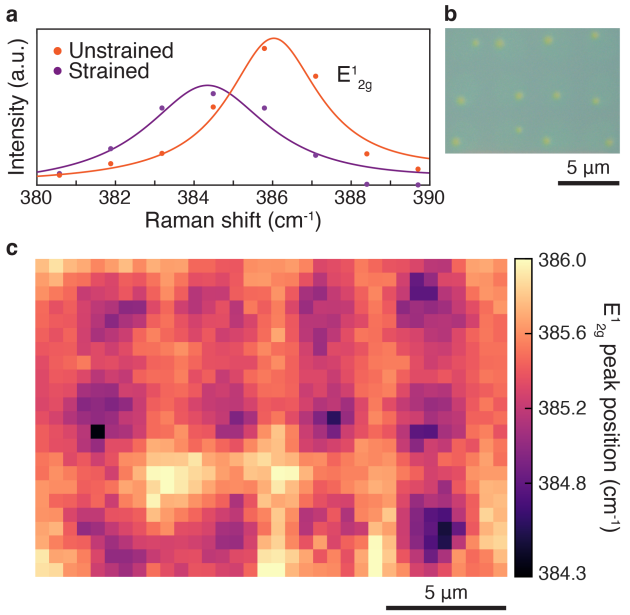

Figure 2: Verifying 2D material straining using Raman spectroscopy. (a) Measured Raman spectra and corresponding fits showing the E^1_{2g} peak for an unstrained and strained monolayer MoS_2. A red-shift of this peak indicates in-plane tensile strain. (b) Optical image and (c) corresponding Raman map of a periodically-strained monolayer of MoS_2, showing the position of the E^1_{2g} peak. At each dome-site, a ~ 2 cm^{-1} shift of the E^1_{2g} peak is observed.

CONTROLLED, LOCALIZED, AND SCALABLE

Successful straining of our sample is evident through the experimentally measured red-shift in the E^1_{2g} Raman peak of MoS_2 (Figure 2a), as is expected with an applied in-plane tensile strain [12]. Figure 2c shows the position of the E^1_{2g} peak over the array of strained features pictured in Figure 2b; a consistent red-shift of ~ 2 cm^{-1} is observed at each dome-site, suggesting controlled and localized MoS_2 straining.

In addition to enabling controlled, localized straining, notably, our approach helps avoid damage such as formation of bubbles, wrinkles and tears. These defects, which can degrade the material's intrinsic properties and introduce undesired variabilities, are nevertheless common in the conventional platforms where a 2D material is draped over a nanostructure. We demonstrate this advantage in Figure 3, where our approach is compared against a sample fabricated with conventional draping. Here, both samples are prepared in parallel to keep all fabrication steps consistent. The only difference is the step at which the nonplanar features are formed. In Figure 3a (our approach), the thermal annealing is performed post-MoS_2 transfer. In Figure 3b (conventional), the annealing forms the nonplanar features prior to transferring the MoS_2.

The atomic force microscope (AFM) images of the resulting samples clearly show uniform and damage-free straining with our approach, while bubbles and wrinkles are observed in the conventional sample. Our platform succeeds because 2D material transfer onto a planar substrate allows for conformal adhesion between the material and the receiving surface, whereas this is not possible when transferring onto a pre-textured surface with topographical features. Our platform is uniquely not limited to transferred 2D materials. Using chemical vapor deposition, 2D materials can be directly grown [13] on our engineered substrates, and strained through post-synthesis substrate transformation. To this end, our approach can be compatible with wafer-scale processing.

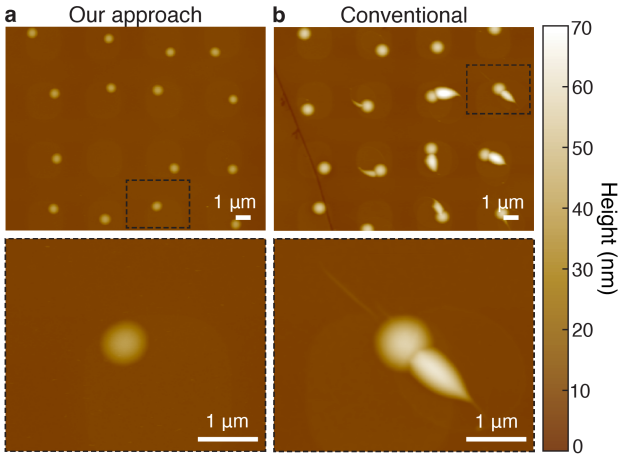

Figure 3: Comparing 2D material straining between our approach and conventional draping. (a) AFM topography of MoS_2 strained using our conformal technique, where the 2D material is applied before texturing the substrate. Wrinkles, bubbles, and tears are absent. (b) AFM topography of identical material strained using the conventional draping technique, where the 2D material is applied to an already textured substrate. Undesired wrinkles, bubbles, and tears are inevitable.

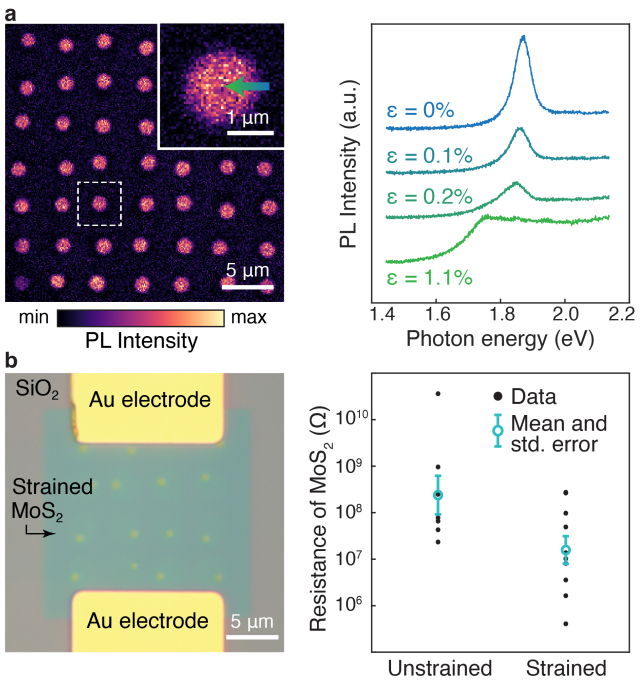

Figure 4: Strain engineering optical and electrical properties for device applications. (a) PL intensity map of strained MoS_2 (left). Right plot shows A exciton PL peak shift along the strain profile indicated by the arrow. Peak position is correlated to strain (ε) based on [12]. (b) Microscope image of a strained MoS_2 electrical device with gold electrodes (left). The average resistance of the device decreases 75-fold with strain, indicating a strain-induced piezoresistive effect (right).

STRAIN ENGINEERING OF PROPERTIES

Since strain alters the band structure of 2D materials, we can use our technique to engineer their optical and electrical properties for diverse device applications. Specifically, with tensile strain, monolayer MoS_2 experiences a decrease in the band gap and funneling of the photogenerated excitons towards regions of higher strain [14]. In Figure 4a, we have measured the photoluminescence (PL) intensity map of a 7×7 array of strained MoS_2 features (left). Here, the map shows the integrated emission intensity across 1.2 eV to 2.8 eV under optical excitation with a 405 nm pulsed laser. The PL spectra collected across the dome (right) shows a continuous decrease in the emission energy of the principal A exciton peak from 1.87 eV in the unstrained, flat region to 1.75 eV at the point of highest strain. This red-shift corresponds to an estimated strain of 1.1% [12]. With the height-to-radius ratio (h/r) of 0.133 experimentally measured for our samples using AFM, a maximum strain of 1.27% is theoretically expected for this dome design based on Equation 1.

The strain-induced decrease in the band gap also yields a piezoresistive effect in MoS_2, where a decrease in the electrical resistance is observed with increasing tensile strain. To probe this effect, we fabricated 2-terminal electrical devices as shown in Figure 4b (left). First, using the process in Figure 1a, we prepared periodically-strained monolayer MoS_2. Next, electrical contacts were added using a lift-off process and gold electron-beam evaporation. Lastly, the MoS_2 device channel was defined using a lithographic mask and oxygen plasma etching of the excess MoS_2. Strained devices were designed to include 16 dome structures in the channel, in a 4×4 configuration, with 4 µm spacing. To avoid the influence of inter-substrate variabilities in MoS_2 properties, the unstrained, control samples were prepared on the same substrate, just without the patterned APTES regions that produce the domes. When comparing 17 devices (10 strained and 7 unstrained) in a current-voltage sweep experiment, an average 75-fold decrease in the MoS_2 resistance is observed with strain ($p = 0.03$ from a two-sample t-test), as shown in Figure 4b (right).

CONCLUSION

We have developed a technique for controlled, localized and scalable straining of 2D materials without inducing defects such as bubbles, wrinkles and tears. Our approach enables this by straining a 2D material only after its transfer onto a planar substrate. Such post-transfer strain engineering is achieved through site-selective thermally-induced formation of nonplanar features. We note that our platform can further be extended to 2D materials directly grown on our engineered substrate. We demonstrate our platform using an MoS_2 monolayer, showing that strain can modulate the MoS_2 band gap, leading to a shift in the PL emission wavelength and change in the material resistance. Such strain-induced band gap engineering significantly extends the scope of 2D material applications, leading to new opportunities including in sensors, photodetectors, transistors, and light-emitting devices. Moreover, if the extent of the applied strain could be actively controlled, dynamically tunable devices can be realized. Our technique, which applies strain using an ultrathin suspended membrane, can provide a robust platform for actively tunable 2D devices integrated with nanoelectromechanical systems.

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CONTACT

*F. Niroui, tel: +1-617-324-7415; fniroui@mit.edu