

Vu Nguyen

Department of Mechanical Engineering,
University of California, Berkeley,
Berkeley, CA 94720

Hannah Gramling

Department of Mechanical Engineering,
University of California, Berkeley,
Berkeley, CA 94720

Clarissa Towle

Department of Materials Science and
Engineering,
University of California, Berkeley,
Berkeley, CA 94720;
Materials Sciences Division,
Lawrence Berkeley National Laboratories,
Berkeley, CA 94720

Wan Li

Department of Chemistry,
University of California, Berkeley,
Berkeley, CA 94720

Der-Hsien Lien

Department of Electrical Engineering and
Computer Sciences,
University of California, Berkeley,
Berkeley, CA 94720;
Materials Sciences Division,
Lawrence Berkeley National Laboratories,
Berkeley, CA 94720

Hyungjin Kim

Department of Electrical Engineering and
Computer Sciences,
University of California, Berkeley,
Berkeley, CA 94720;
Materials Sciences Division,
Lawrence Berkeley National Laboratories,
Berkeley, CA 94720

Daryl C. Chrzan

Department of Materials Science and Engineering,
University of California, Berkeley,
Berkeley, CA 94720;
Materials Sciences Division,
Lawrence Berkeley National Laboratories,
Berkeley, CA 94720

Ali Javey

Department of Electrical Engineering and
Computer Sciences,
University of California, Berkeley,
Berkeley, CA 94720;
Materials Sciences Division,
Lawrence Berkeley National Laboratories,
Berkeley, CA 94720

Ke Xu

Department of Chemistry,
University of California, Berkeley,
Berkeley, CA 94720

Deterministic Assembly of Arrays of Lithographically Defined WS₂ and MoS₂ Monolayer Features Directly From Multilayer Sources Into Van Der Waals Heterostructures

One of the major challenges in the van der Waals (vdW) integration of two-dimensional (2D) materials is achieving high-yield and high-throughput assembly of predefined sequences of monolayers into heterostructure arrays. Mechanical exfoliation has recently been studied as a promising technique to transfer monolayers from a multilayer source synthesized by other techniques, allowing the deposition of a wide variety of 2D materials without exposing the target substrate to harsh synthesis conditions. Although a variety of processes have been developed to exfoliate the 2D materials mechanically from the source and place them deterministically onto a target substrate, they can typically transfer only either a wafer-scale blanket or one small flake at a time with uncontrolled size and shape. Here, we present a method to assemble arrays of lithographically defined monolayer WS₂ and MoS₂ features from multilayer sources and directly transfer them in a deterministic manner onto target substrates. This exfoliate-align-release process—without the need of an intermediate carrier substrate—is enabled by combining a patterned, gold-mediated exfoliation technique with a new optically transparent, heat-releasable adhesive. WS₂/MoS₂ vdW heterostructure arrays produced by this method show the expected interlayer exciton between the monolayers. Light-emitting devices using WS₂ monolayers were also demonstrated, proving the functionality of the fabricated materials. Our work demonstrates a significant step toward developing mechanical exfoliation as a scalable dry transfer technique for the manufacturing of functional, atomically thin materials. [DOI: 10.1115/1.4045259]

Keywords: nanomanufacturing, van der Waals integration, exfoliation, 2D materials, optoelectronic, WS₂, MoS₂

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Joel Ager

Department of Materials Science and Engineering,
University of California, Berkeley,
Berkeley, CA 94720;
Materials Sciences Division,
Lawrence Berkeley National Laboratories,
Berkeley, CA 94720

Hayden Taylor

Department of Mechanical Engineering,
University of California, Berkeley,
Berkeley, CA 94720
e-mail: hkt@berkeley.edu

1 Introduction

The ability to produce monolayers of transition metal dichalcogenides (TMDCs), which form a class of one-molecule-thick sheets with useful mechanical [1], electronic [2,3], and optoelectronic [3–5] properties, has motivated intense research in their applications through van der Waals (vdW) integration with other two-dimensional (2D) materials as well as with traditional semiconductor technologies [6,7]. vdW integration [8,9], the process of assembling dissimilar materials together using the universal vdW force, promises artificial structures with controlled chemical composition, atomically sharp interfaces without the lattice matching requirement, and advanced material properties for applications such as tunneling transistors [10], light-emitting devices [11,12], photodetectors [13,14], and silicon photonic integrated circuits [15]. The current state-of-the-art of vdW integration of 2D materials can produce either microscale heterostructures composed of as many as 29 layers [16], or continuous blanket heterostructures as large as 2-in.-wafer-scale [17,18]. The techniques currently used for deterministically transferring microscale monolayer features, however, largely rely on features obtained from laborious and probabilistic “Scotch-tape” exfoliation, and are limited to transferring individual features, which requires impractical repetitive placement to scale to large-area arrays [16,19]. The most studied deterministic transfer technique for arrays of microfeatures so far is microtransfer printing, which uses an elastomeric polydimethylsiloxane stamp as the transfer medium with a controlled peeling rate to tune between pick-up (faster) and release (slower) modes [20,21]. However, fully implementing such a technique requires a sophisticated and dedicated mechanical system and complex stamp design [22,23]. Although polydimethylsiloxane stamps have been adopted in the transfer of 2D materials of many kinds [24–27], they still rely on an initial probabilistic exfoliation step, meaning that the size, shape, and thickness of exfoliated layers are variable.

Recent advances in the chemical vapor deposition (CVD) of TMDC 2D crystals have provided large-area uniform sources, and the exfoliation-based transfer of wafer-scale continuous blankets of 2D materials could therefore be realized [17,18]. However, large blanket transfer may easily trap contaminants, requires subsequent patterning steps which in turn potentially impose high etch-selectivity requirements on the fabrication of multiplexed heterostructures and limits the complexity of the resultant heterostructures. Adoption of existing transfer techniques developed for predefined arrays of three-dimensional materials—such as coating the arrays to be transferred with a carrier polymer layer—is a potential approach [28,29], but in those cases a monolayer source is still required to yield monolayer exfoliation, which is key to achieving composition-controlled assembly of heterostructures. Although a recent exfoliation technique has achieved monolayer selectivity from multilayer CVD sources, it was only demonstrated for wafer-scale blanket layers [18].

In an effort to meet the need for a scalable technique to transfer pre-patterned monolayer arrays, we have recently developed a thin-film-mediated process to transfer arrays of TMDC monolayer features with predefined geometry directly from multilayer sources [30,31]. A key advantage of this process is that it incorporates the use of an evaporated gold film which bonds to and strains the topmost monolayer of the TMDC source crystal, providing monolayer selectivity [32–34] and thus easing the layer-controlled requirement of the source. Therefore, millimeter-scale arrays of monolayer microfeatures could be obtained in just one single exfoliation from multilayer source crystals of MoS₂ and WS₂ that are widely available in the general market. Nevertheless, although that process succeeded in predefining the *relative* positions of the microfeatures being transferred, it did not control their *absolute* location on the target substrate. Moreover, the process used commercially available thermal release tape, which is opaque and is unsuitable for scaling down the transferred feature size because it contains heat-expandable microspheres. Thermal release tape also contains a proprietary adhesive polymer that is challenging to remove completely from the surfaces it touches [35]. Material residues were implicated in limiting the process’s release yield and monolayer cleanliness, while the opacity of the tape inhibited accurate positioning on the substrate.

Here, we present a deterministic assembly process compatible with existing semiconductor manufacturing equipment that can achieve fully position-controlled transfer of arrays of lithographically defined WS₂ and MoS₂ monolayer features from multilayer sources, thereby enabling straightforward stacking of optoelectronically functional vdW heterostructure arrays. We dub the new process covalent-bond exfoliate-align-release (CoBEARs). The process is enabled by the use of a transparent thermal release adhesive layer, which is fabricated from readily available materials using spin-coating to achieve uniform sample coverage. Positioning can be achieved with standard alignment equipment such as mask aligners and wafer bonders. The CoBEARs process is able to achieve monolayer selectivity in the exfoliation step thanks to the use of an evaporated Au film on the multilayer source. The maximum processing temperature required during monolayer deposition is only about 90 °C, which is needed to achieve the release of the microfeatures onto the target substrate. Such a temperature is low enough to enable integration with heat-susceptible substrates such as thermoplastic polymers. The release yield of the exfoliated microfeature arrays from the adhesive to the target substrate is reliably close to 100%. The overall monolayer yield of the whole process is currently about 50%, which is mainly limited by the quality of the multilayer sources. Inspection of the obtained monolayers by optical microscopy, atomic force microscopy (AFM), photoluminescence (PL), and electroluminescence (EL) shows that they are clean and without polymeric residues and provide functional material for light-emitting devices. The process was then repeated to produce WS₂/MoS₂ heterostructure arrays that show coupled excitonic emission. Our work

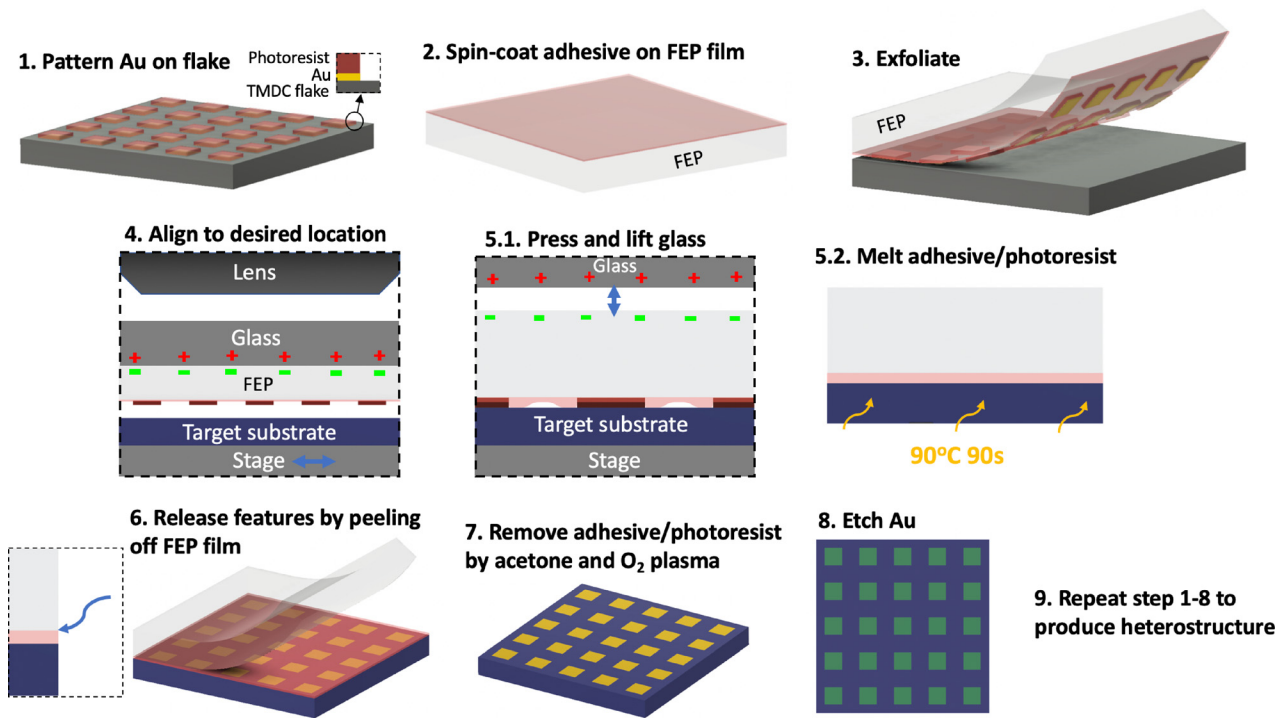


Fig. 1 Schematic of the CoBEARs process. In this work, the prototypical adhesive used in step 2 is the same photoresist material (AZ P4620) used to pattern the features in step 1. The electrostatic charges in step 4 were produced by gently rubbing a bare FEP film against the glass, and then, the adhesive film with exfoliated features was placed on the rubbed location. Step 5.2 could also be done before the glass is lifted in step 5.1 if the alignment tool also has heating capability. The green regions in step 8 represent monolayer exposed after the Au etch. The substrate after step 8 could be returned to step 4 repeatedly to produce arrays of heterostructures. (1) Pattern Au on flake; (2) spin-coat adhesive on FEP film; (3) exfoliate; (4) align to desired location; (5.1) press and lift glass; (5.2) melt adhesive/photoresist; (6) release features by peeling off FEP film; (7) remove adhesive/photoresist by acetone and O₂ plasma; (8) etch Au; and (9) repeat step 1–8 to produce heterostructure.

therefore represents significant progress in the assembly of mechanically exfoliated 2D material arrays for manufacturing functional, atomically thin materials.

2 Materials and Fabrication Process

A schematic of the CoBEARs process is shown in Fig. 1. The WS₂ multilayer sources were obtained as crystals synthesized through chemical vapor transport (HQ Graphene, Groningen, Netherlands), while the MoS₂ sources were naturally occurring crystals (Crystal Age, Bristol, UK). The as-received source crystals were prepared for exfoliation by applying patterned Au and photoresist handles using the procedure described in our previous work [30], which is summarized as follows. A 100-nm Au film was thermally evaporated on top of the TMDC crystal to provide monolayer exfoliation selectivity and also to protect the monolayer in subsequent processing steps. A 15- μ m-thick photoresist handle (AZ P4620, MicroChemicals GmbH) was then spun on and patterned. This photoresist served both to mask the subsequent etching steps that would define the size and shape of the microfeatures (100 μ m \times 100 μ m squares in this work), and then to offset the adhesive from the surface of the bulk crystal to prevent uncontrolled contact and exfoliation of thick TMDC layers. The etching consisted of two steps: a KI/I₂ wet etch to pattern the gold, followed by SF₆ plasma etching of the bulk 2D crystal (20 sccm, 200 W, 60 s, Plasma Equipment Technical Services, Inc., Brentwood, CA). The plasma etch was found to enhance the yield of exfoliation and is thought to create crack initiation sites at the edges of the microfeatures. Crucially, the plasma etch step does *not* need to be atomically precise, although we found that its duration could be optimized for monolayer exfoliation (see Fig. S1¹).

¹Supplementary figures are available at: <https://doi.org/10.6078/D16T1S>

Immediately before the exfoliation step, the heat-releasable adhesive was fabricated by spin-coating a layer of low-crosslinked viscoelastic polymer (AZ P4620 photoresist, \sim 7 μ m thick, unbaked) onto a fluorinated ethylene propylene (FEP) film (127- μ m-thick film for Wanhao Duplicator, Amazon; Fig. 1, step 2). Details of the spin-coating parameters are provided in the Supplemental Material.¹ FEP film was selected for its optical transparency, its high tendency to gain electrostatic charge [36] to enable temporary mounting onto a micromanipulator, and its low surface energy for effective release of the viscoelastic polymer layer. Despite the nonsticky nature of the FEP film, the viscoelastic polymer was successfully coated over its entire 25 mm \times 25 mm area thanks to a high-acceleration spin recipe (1600 rpm/s ramp from rest to 2200 rpm, 2200 rpm for 1 min, and then 1000 rpm for 20 s; see Fig. S2¹). The FEP film spin-coated with the unbaked photoresist was used as an adhesive to exfoliate material from the bulk 2D crystal (Fig. 1, step 3). The exfoliation was typically done within 3 min of spin-coating, while the wet photoresist was still sufficiently tacky. It is worth reiterating that the Au layer and the patterned photoresist handle enabled an array of monolayer features to be obtained after one single exfoliation, instead of after repetitive exfoliations as are needed in the conventional Scotch-tape technique.

The adhesive, loaded with the exfoliated array of microfeatures, was then mounted on a blank glass plate in a photomask aligner (OAI Series 200 Aligner) by electrostatic force. Glass and FEP lie at the two opposite ends of the empirical triboelectric series [36,37], and thus tend to gain positive and negative charges, respectively, when brought into contact. Using this well-known effect, a bare FEP piece was gently rubbed against the glass plate to produce a certain amount of electrostatic charge, before the adhesive-coated FEP was placed on the rubbed location of the glass plate. Thanks to the transparency of the glass plate and the adhesive, the location of the array on the target substrate could be

controlled using the microscope and manipulator setup of the mask aligner (Fig. 1, step 4). After the desired location had been determined, the adhesive was firmly pressed against the target substrate using the manual Z-adjustment knob of the aligner, until the unbaked photoresist adhesive no longer visually deformed with further pressing, corresponding to the photoresist handle contacting the FEP backing (Fig. 1, step 5.1). The bonding between the adhesive and the target substrate was strong enough to defeat the weak electrostatic force when the glass plate was lifted, keeping the exfoliated array at the desired location and separating the FEP from the glass. The substrate could now be taken out of the mask aligner and placed on a hotplate at 90 °C for 90 s to melt the photoresist adhesive completely, which formed an encapsulation over the exfoliated array and clamped it to the target substrate. Alternatively, steps 5.1 and 5.2 in Fig. 1 could be combined into one step if the mask aligner has a heating capability. We were also able to perform this transfer procedure in a wafer bonder (AML AWB-08) in 5×10^{-6} Torr vacuum, where the 90 °C heating could be applied immediately after pressing, followed by lifting the glass plate (a dummy glass wafer). The ability to perform the transfer in a wafer bonder chamber, under vacuum, offers additional control of environmental conditions during the process. Nevertheless, all samples shown in this work were made in ambient cleanroom conditions.

After melting the adhesive, the FEP film could be easily peeled off the target substrate (Fig. 1, step 6), leaving the exfoliated array encapsulated with the melted viscoelastic polymer on the target substrate. Due to the low-crosslinked nature of the now slightly baked photoresist, it could be visibly removed in acetone in 10 min (Fig. 1, step 7). An additional gentle O₂ plasma cleaning (15 W, 15 s, 300 mTorr, Plasma Equipment Technical Services, Inc.) was applied to clean all polymer residues completely from

the substrate. Finally, the Au layer was etched away in KI/I₂ solution (Transene Gold Etchant Type TFA) for 2 min, followed by rinsing in DI water (step 8 in Fig. 1).

3 Results and Discussion

The array of microfeatures was monitored by optical microscopy at each stage of the process (Fig. 2(a)), from exfoliation until after the last Au-etching step when the exposed monolayer was obtained. Using optical images, we can define three yield metrics that characterize the degree of success in the transfer of microfeatures after important steps, as well as the final amount of monolayer area obtained. We term these metrics: *feature exfoliation yield*, *feature release yield*, and *monolayer yield*.

The *feature exfoliation yield* is defined as the ratio of the number of successfully exfoliated features on the adhesive (immediately after step 3 in Fig. 1) to the number of features brought into contact with the adhesive during that step. Sites where features had touched the adhesive but not successfully remained adhered to it, leading to failed exfoliation, could be readily recognized in optical images from indentations made by the photoresist handle into the wet photoresist adhesive (Fig. 2(a)). Successfully exfoliated material, in contrast, was visible as reflective gold squares on the adhesive. Both the numerator and the denominator of the feature exfoliation yield calculation were counted over the entire area of the adhesive piece used (low-magnification images of the whole exfoliated array on one sample are shown in Fig. S3¹).

The *feature release yield* is defined as the ratio of the number of features successfully released from the adhesive onto the target substrate (immediately after step 7 in Fig. 1) to the number of successfully exfoliated features on the adhesive (immediately after

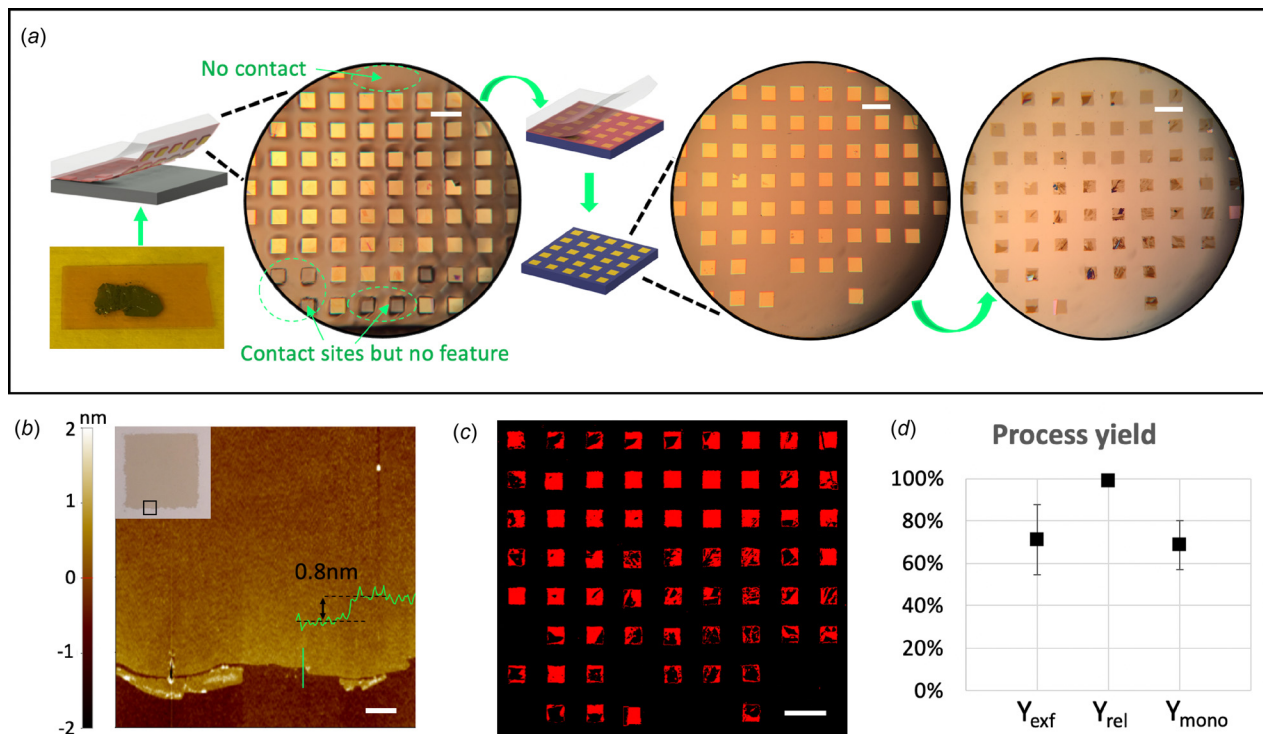


Fig. 2 Yield metrics of the process. (a) Optical-microscopy images of the array of WS₂ microfeatures after critical steps. The target substrate is 50 nm SiO₂/Si. The monolayer array is obtained after one single exfoliation. Scale bars are 200 μm. (b) AFM topography scan at the edge of a monolayer feature in (a), showing a smooth surface with a step height consistent with monolayer. Scale bar is 1 μm. (c) false color mapping of the monolayer region in (a), which is determined by comparing the contrast under 532 nm illumination (Fig. S3¹) with the theoretical contrast calculated with a thin-film interference model [38,39]. The areas where measured contrast agrees with calculated monolayer contrast are marked as red and black otherwise. Scale bars are 200 μm. (d) Summary of the yields calculated after the three steps in (a): feature exfoliation yield Y_{exf}, feature release yield Y_{rel}, and monolayer yield, Y_{mono}. Error bars are ±1 sample standard deviation with N = 8 samples.

step 3 in Fig. 1). The number of successfully exfoliated features is the same number that serves as the numerator in the calculation of feature exfoliation yield above.

The third yield metric, the *monolayer yield*, is defined as the ratio of the total monolayer area finally present on the target substrate to the total, ideal area of all features present on the target substrate. The monolayer regions were identified and confirmed using three independent methods: AFM (Fig. 2(b)), interpretation of the material's optical reflectance spectrum based on thin-film optical interference calculations [38,39] and mapping (Fig. 2(c) and Fig. S4¹), and determination of the material's characteristic PL peak (Fig. S4¹).

A summary of the three yield metrics is shown in Fig. 2(d), with the overall process yield of monolayer material being the product of all three numbers, and equaling, on average, 49% for WS₂ ($N=8$ samples) and 51% for MoS₂ ($N=4$ samples) (Fig. S5¹). Although these yield values are certainly not yet comparable with the production standards of the semiconductor manufacturing industry, the process that we have demonstrated has the potential to accelerate the development of new types of optoelectronic devices based on exfoliated 2D materials. Importantly, the method deposits regions of material in *predictable* locations so that arrays of devices can be readily created on a target substrate. As we will see below, the deterministic placement also allows effective formation of 2D heterostructures.

The high feature release yield, typically 100%, was achieved mainly thanks to the nonsticky surface of the FEP film, which was easily and cleanly peeled off the lightly baked photoresist layer encapsulating the array on the substrate. Feature release yield was also promoted by the strong vdW adhesion of the monolayer to the clean SiO₂ surface, which was able to withstand the liquid acetone cleaning of the excess photoresist. It is important to note that although the microfeature array was encapsulated in a layer of polymer during the release step, this polymer, the lightly baked AZ P4620 photoresist, is only slightly crosslinked thanks to the low-temperature process, and thus can be completely removed with acetone and gentle O₂ plasma. The smoothness of the AFM topography scan in Fig. 2(b) indicates that excess polymer was effectively cleaned. The ability to release microfeatures reliably and cleanly with this encapsulation approach promises to address the weaknesses of the widely used commercial thermal release tape, which employs heat-expandable microspheres that limit the scaling down of transferred feature size [35], and leaves behind

residue that requires an extended and high-power O₂ plasma-cleaning recipe [30].

The moderate monolayer yield—about 69% of the total feature area deposited on the target substrate—is apparently due to the inclusion of multilayer areas and the undesired removal of the monolayer areas. The inclusion of multilayer areas in the transferred material could be due to the gold film contacting multiple layers where the TMDC surface lacks atomic flatness, although further experimentation is needed to confirm this effect. The undesired removal of monolayer areas is found to be correlated to the O₂ plasma cleaning in step 7 of Fig. 1. The effectiveness of the protection provided by the 100-nm-thick Au layer for the monolayer underneath in this cleaning step appeared to depend on how energetic the plasma-cleaning recipe was, as shown in Fig. 3. For WS₂, a mild and short O₂ plasma recipe (with about 15 W power for 15 s) produced monolayer features with smoother surfaces, larger areas, and more sharply defined edges than a more energetic and extended recipe (either 120 W power for 15 s or 15 W for 60 s). A similar effect was also observed for MoS₂, although in this case the sharpness of edge definition was less dependent on plasma parameters (Fig. S6¹). Rough surfaces resembling nanoparticles scattered on the material have also been observed previously on monolayer features that had undergone energetic and extended O₂ plasma cleaning before the Au etch [30]. In that case, X-ray photoelectron spectroscopy suggested that some Au remained on the surface after cleaning [30]. As an alternative to the solution of using a mild and short O₂ plasma recipe, a thicker metal protection layer or a nonplasma-based recipe, such as atomic hydrogen cleaning [40], could be considered to remove polymer residue with minimal effect on the monolayer.

In this work, we report the results of transfer onto SiO₂/Si substrates, although we have also tested our transfer process on other substrates such as Si, sapphire, and glass with comparable results. Using polymeric substrates, meanwhile, might conceivably affect yield or placement accuracy due to their higher thermal expansion coefficients, surface roughness, and greater mechanical compliance, although any such effects could likely be mitigated by lamination onto more rigid substrates.

While yield of the deposited arrays was studied by optical-microscopy-based characterization, their optoelectronic properties were revealed through PL spectra. The transferred TMDC

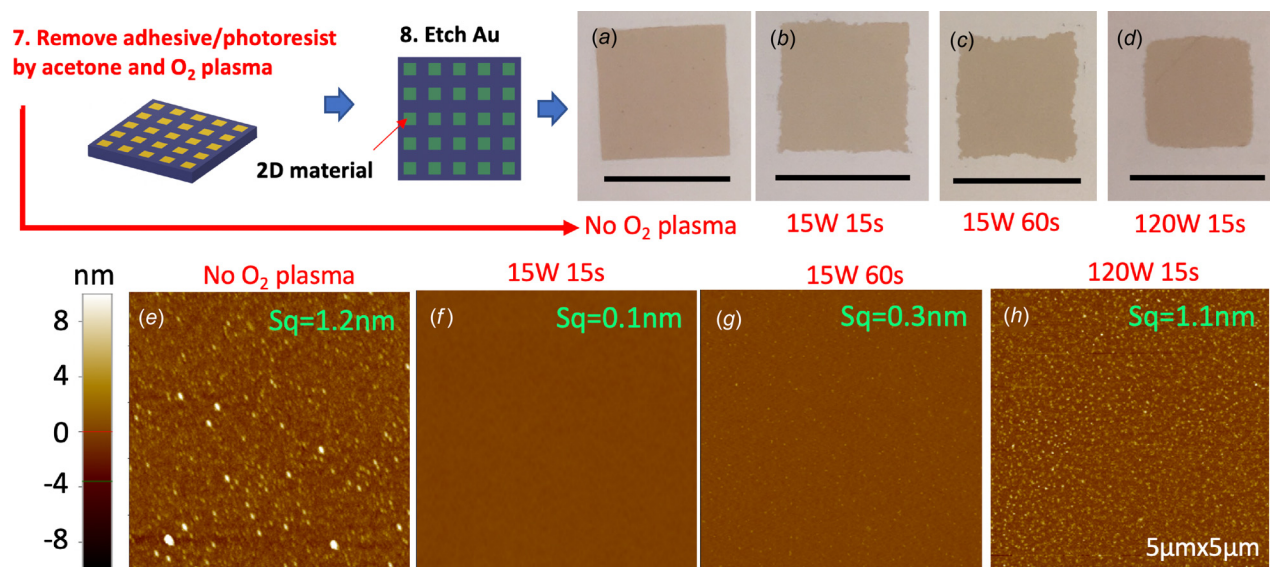


Fig. 3 Effect of O₂ plasma cleaning on the surface roughness and edge definition of WS₂ features. (a)–(d) Optical-microscope images of monolayers obtained following various cleaning recipes performed in step 7 of Fig. 1. All scale bars are 100 µm. Images shown are after etching of the gold, as in step 8 of Fig. 1. (e)–(h) AFM topography scans of features in (a)–(d), respectively. “Sq” denotes the root-mean-square surface roughness of the scanned area. All AFM scans shown are of a 5-µm-square region.

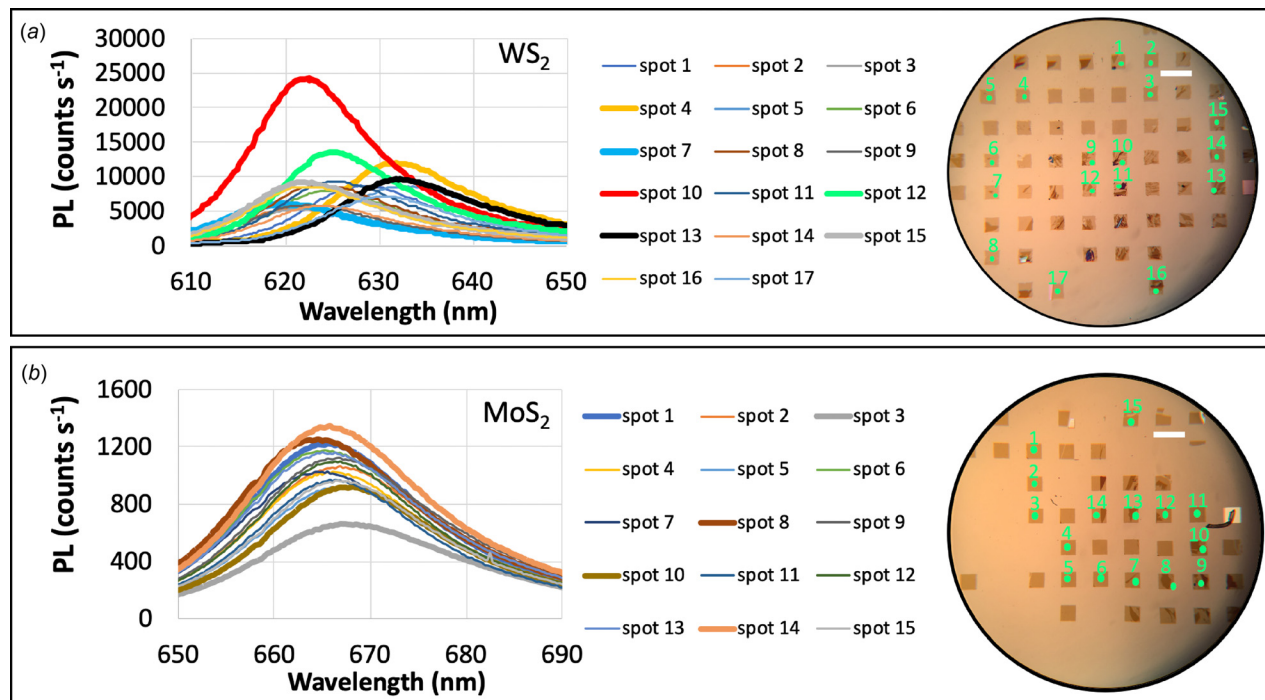


Fig. 4 Optoelectronic characterization. PL spectra of a randomly selected sample of spots in (a) the WS_2 sample and (b) the MoS_2 sample obtained through CoBEARs. All scale bars are $200\ \mu\text{m}$. PL peak wavelengths were $625 \pm 13\ \text{nm}$ for WS_2 and $666 \pm 3\ \text{nm}$ for MoS_2 (± 3 sample standard deviations in each case).

monolayer arrays are inherently direct-bandgap semiconductors, so they exhibit a strong PL peak at a characteristic wavelength corresponding to the energy of the bandgap. The PL spectra of a randomly selected sample of monolayer spots in WS_2 and MoS_2 arrays are plotted in Figs. 4(a) and 4(b), respectively. The average PL peak position in one representative WS_2 sample lies at $625 \pm 13\ \text{nm}$ (mean $\pm 3\sigma$, $N = 17$). The slight variation of the peak position could be due to native defects in the monolayer, substrate defects, or residual monolayer strain caused by the process. The presence of native defects seems the most likely explanation, considering the much more consistent PL peak position of the MoS_2 monolayer array ($666 \pm 3\ \text{nm}$: mean $\pm 3\sigma$, $N = 15$), which went through the same process but was made from a different material source. The higher variation in PL peak position of the WS_2 samples than that of the MoS_2 samples was also recorded in our previous work [30], which used similar material sources. Potential optoelectronic application of the obtained monolayer material was demonstrated in a transient-mode two-terminal EL device [12], which is shown in Fig. S7¹. We achieved tunable emission intensity of the EL device by varying both amplitude and frequency of the applied voltage, thus demonstrating the potential for light-emitting applications of monolayer material exfoliated using the process described in this work.

In addition to monolayer arrays, the CoBEARs process is also capable of producing heterostructure arrays by repeating the monolayer deposition steps (steps 1–8 in Fig. 1). In the example shown in this work (Fig. 5), a second monolayer array of WS_2 was overlaid onto a previously transferred MoS_2 monolayer array. Because the O_2 plasma cleaning in step 7 removes any exposed monolayer material from the substrate, the resulting heterostructure regions are confined to the Au area of the most recent deposition. The two arrays were purposefully offset in the horizontal direction so that about half of the area of each square feature is a heterostructure, and the other half is monolayer WS_2 for reference, as demonstrated in the high-magnification image in Fig. 5(a). The transparency of the transfer medium allowed the deposition location of the WS_2 array to be controlled to within about $\pm 5\ \mu\text{m}$ of its intended position relative to the MoS_2 , as

determined by visual inspection of the alignment between the horizontal edges of the square features in Fig. 5(a), and by the absence of any discernible relative rotation between the two material arrays. This level of alignment was achieved by simple visual feedback through the microscope objective of the mask aligner. It is expected that even tighter alignment tolerances could be achieved with the introduction of dedicated alignment marks to the exfoliation masks of the two materials.

The exposed parts of the first, MoS_2 , monolayer array were etched away in the cleaning step (step 7) of the WS_2 deposition cycle, leaving $100\ \mu\text{m} \times 100\ \mu\text{m}$ square areas of WS_2 monolayer and rectangular WS_2 -on- MoS_2 heterostructures where the two arrays overlapped. Raman spectroscopy, shown in Fig. 5(b), confirmed the presence of WS_2 monolayers and WS_2 -on- MoS_2 heterostructures. WS_2/MoS_2 has been demonstrated to constitute a type II heterostructure that is promising for charge-separating devices such as photodetectors and photovoltaics [6,13,41]. Insights into the electrical properties of this type of heterostructure can be gained through simple PL measurements. The spatial separation of electron–hole pairs in this type of heterostructure—with holes (electrons) generated in the MoS_2 (WS_2) layer being swept to the WS_2 (MoS_2) layer—is evident from the quenching of the PL peaks of both individual monolayers due to inefficient recombination [41–43]. We studied this PL quenching effect in our fabricated WS_2 -on- MoS_2 heterostructures before and after a short annealing (200°C for 5 min in air), as shown in Fig. 5(c). Before annealing, the heterostructures still exhibited two PL peaks, resembling the superposition of two independent monolayers, but with reduced intensities and a slight shift in peak positions compared to the individual monolayers. These pre-annealing spectra indicate that charge transfer had occurred, and the electronic band structure of each monolayer had been influenced by the other layer. After annealing, the PL peaks corresponding to individual monolayers disappeared, and a single peak at a new longer wavelength than those of the monolayers emerged. The complete suppression of the PL peaks of individual monolayers suggests efficient photoexcited charge separation, and the new and relatively weak PL peak can be attributed to the less efficient

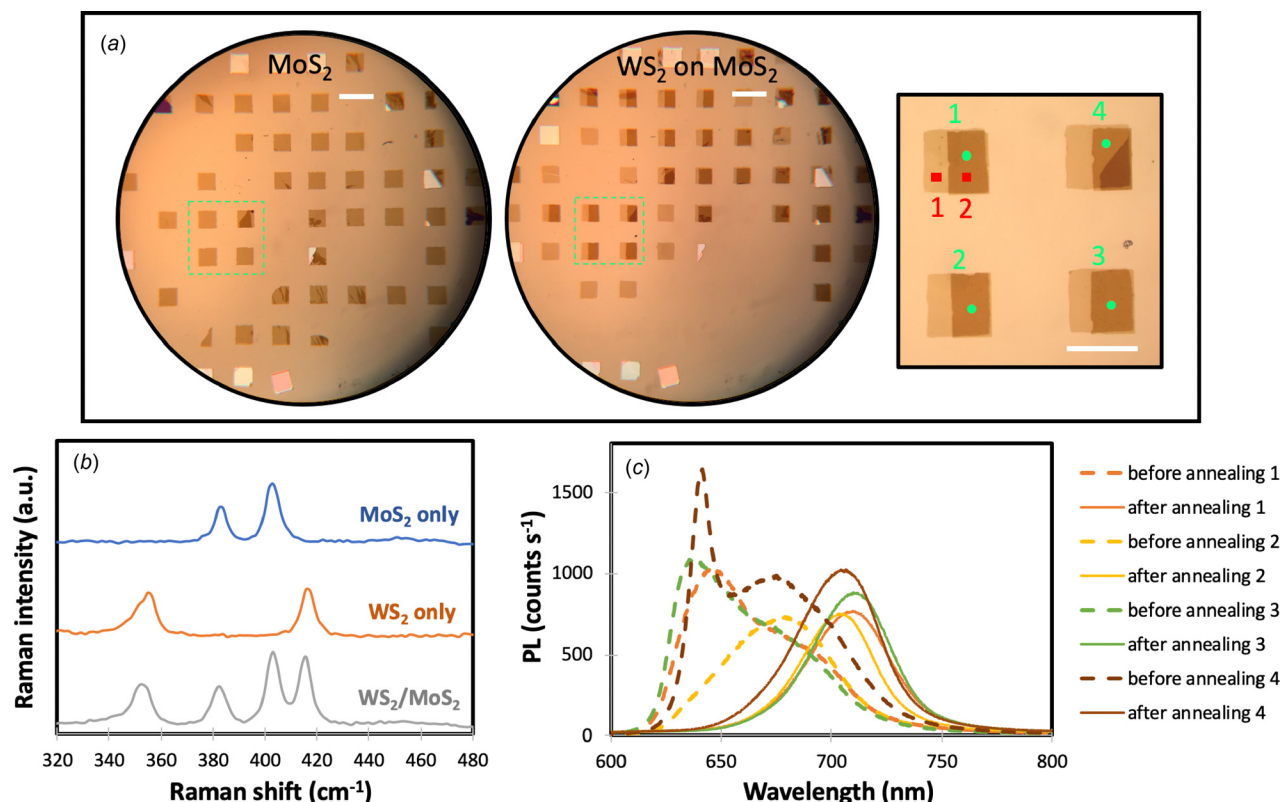


Fig. 5 Assembly and characterization of a heterostructure array. (a) WS₂/MoS₂ heterostructure array obtained by performing the steps in Fig. 1, with the first cycle depositing MoS₂ and the second cycle depositing WS₂. From left to right, scale bars are 200 μ m, 200 μ m, and 100 μ m. **(b)** Raman spectra of the samples in (a). The MoS₂-only spectrum was obtained before WS₂ deposition. The WS₂-only and WS₂/MoS₂ spectra, obtained after annealing, correspond to the two red spots numbered 1 and 2, respectively, in the high-magnification image of (a). **(c)** PL spectra showing the coupled exciton exhibited by the WS₂/MoS₂ heterostructure that emerges after annealing at 200 °C for 5 min. The four replicate PL spectra, 1–4 in both the before- and after-annealing states, correspond to the locations shown by numbered green dots in (a).

recombination of spatially separated charges [43]. Since the charge transfer dominates only for short interlayer distances [42,44], the annealing step could have driven the trapped species out of the heterojunction and brought the two layers into closer contact, thereby improving the charge separation.

4 Conclusion

We have developed a manufacturing process, CoBEARs, to transfer arrays of molecularly thin TMDC microfeatures directly and deterministically from multilayer sources to target substrates. CoBEARs augments an existing thin-film-mediated exfoliation technique with the use of an optically transparent thermal release adhesive that is compatible with standard semiconductor manufacturing equipment and processes, and specifically enables reliable multilayer alignment. The CoBEARs process has been shown to achieve almost 100% feature release yield on a target SiO₂/Si substrate, and an overall areal monolayer yield of about 50%. Although the present overall areal yield is not yet comparable to semiconductor industry standards, the process can already greatly accelerate research into new devices made from 2D materials, because it offers a way of defining monolayer material in predictable locations, allowing for straightforward alignment with other functional materials or electrodes.

Characterization by optical microscopy, AFM, PL, and EL showed that the obtained monolayers were smooth and without polymeric residues, had spatially consistent optoelectronic properties, and could serve as a functional light-emitting device. The WS₂/MoS₂ heterostructure array obtained by the process exhibited the interlayer exciton with completely quenched intralayer excitons, which is expected of a type II heterostructure and potentially enables the design of next-generation photodetectors. CoBEARs

therefore represents a significant step toward applying mechanical exfoliation as a transfer technique in the scalable manufacturing of multiplexed 2D material devices.

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Nomenclature

- Y_{exf} = feature exfoliation yield
 Y_{rel} = feature release yield
 Y_{mono} = monolayer yield
 σ = sample standard deviation

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