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Nanoporous Silicon-Assisted Patterning of Monolayer MoS$_2$ with Thermally Controlled Porosity: A Scalable Method for Diverse Applications

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Abstract

Nanoscale pore formation on chemical vapor deposition grown monolayer MoS$_2$ is achieved using oxygen plasma etching through a nanoporous silicon mask, creating round pores of ~70 nm in diameter. The microscale areas with high porosity were successfully patterned via the usage of silicon masks. Thermal annealing in air after the pore formation in the monolayers results in the gradual enlargement of the pores, providing an effective method of controlling edge-to-area ratio of MoS$_2$ crystals. The photoluminescence of the

nanoporous MoS$_2$ exhibits rapid increase and blue-shift due to facile p-doping during the thermal annealing process, compared to pristine MoS$_2$. This method of fabricating porous transition metal dichalcogenide layers with controlled edge densities presents opportunities in various applications that require atomically thin nano-materials with controlled pore density and edge sites, such as filtration, electrocatalysis, and sensing.

Keywords: Molybdenum disulfide, two-dimensional materials, nanoporous silicon, patterning, oxygen plasma, porosity, thermal annealing, catalysis

Two-dimensional (2D) nanoporous materials, due to their atomically thin structures and mechanical strength, are being explored as an alternative class of materials for many applications, including sensors,[1] catalysts,[2] filtration membranes,[3,4] and electronic devices.[5] In all of these cases, precise control over porosity, pore size, and pore location is crucial in order to obtain the desirable mechanical, thermal, electrical, and transport properties necessary to advance these devices in their respective fields.

The challenges of constructing precise nanopores or a narrow range of pore dimensions, particularly over large areas, make the application of 2D nanoporous materials for commercial use difficult, along with the complicated fabrication of large-scale defect-free monolayers. Generating selective nanoporous regions on 2D materials, which enables the localization of active area and protection of the rest of surface in sensors and other electronic devices, has been also challenging and time-consuming. Reported methods for nanopore generation range from ion bombardment and oxidation,[6] which rely on the naturally occurring defects, to precise drilling techniques involving focused ion beam[7] or electron beam[8] that require longer fabrication time

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and are limited to small-scale substrates. For larger-scale and more rapid nano-patterning, block copolymer (BCP) lithography has been conducted on graphene[9] and MoS$_2$,[10] showing the large-scale generation of the ordered arrays of nano-features including nanodots, nanorods, and hexagonal nanomesh of 15-20 nm dimensions. The nanomesh created by the BCP lithography can be a potential nanoporous membrane material that is generated by the simple and fast nano-patterning technique, despite the current state-of-the-art patterning capability restricted to a few micron scale due to the non-uniform BCP phase separation across the cm-size substrates[10] or limited by the micron scale substrate.[9]

While the optimization of the BCP lithography technique will enable the fabrication of uniform nanomeshes of TMD monolayers, alternative lithographic methods utilizing non-polymeric mask materials have also been explored, including nanoporous anodized aluminum oxide (AAO) which has been applied to graphene[11] and MoS$_2$[12] patterning. Such an approach offers advantages with regard to its highly controllable pore sizes, ordered structures, and physical and chemical durability during the etch process. There also exist drawbacks associated with the implementation of this mask material, however, namely the fragility and high cost of AAO which limit its scalability, and in general the lack of mask resolution at the sub-30 nm scale demonstrated to this point for any such approach. In order to further leverage the favorable properties of such nanoporous masks, the development of robust and finely tunable materials with improved feature sizes must be further advanced.

Here we explore the use of nanoporous silicon (NPSi) membranes as mask materials for the patterning of MoS$_2$ via oxygen plasma etching. NPSi is a widely studied material spanning multiple fields, but to the best of our knowledge has yet to be utilized as a mask for the

patterning of 2D materials. This is likely due to the lack of available processes which can produce sufficiently small (sub-30 nm) pores in silicon with aspect ratios greater than 10:1, in order to penetrate sufficiently thick freestanding films so as to provide mechanical stability over large areas. Previous ground-breaking work on the production of NPSi membranes by Fissell *et al*[13] and Gaborski *et al*[14] resulted in pore diameters below 30 nm, but is limited to membrane sizes on the order of mm^2 or less, which is a precluding factor for the large-area processing of 2D materials. By leveraging a novel approach for the production of porous silicon membranes, containing nanopores with aspect ratios greater than 1000:1 and diameters less than 20 nm, we demonstrate the direct applicability of NPSi as an etch mask for the patterning of MoS_2, and 2D materials in general over arbitrarily large areas. Particularly we demonstrate the patterning of areas with porosity, which is realized by the use of silicon masks where nanoporous areas are confined to micron scale. Upon the generation of nanoporous 2D monolayers, the pore size is further controlled by facile thermal annealing in air, which was monitored by optical spectroscopy and electron microscopy.

Results and Discussion

Fabrication of nanoporous silicon (NPSi) masks and their morphology dependence on substrate thickness.

Robust large-area NPSi membrane masks were fabricated for the first time via a modified technique which was previously used for generating a partially nanoporous silicon substrate with high aspect ratio dead-end pores.[15] In brief, silver films of 1 angstrom nominal thickness were sputtered onto a (100) Si surface, resulting in the nucleation of hemispherical nanoislands. Samples were then submerged in a solution of hydrogen peroxide and hydrofluoric acid (HF) for

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varying amounts of time, facilitating the etching of nanopores via a process known as metal-assisted chemical etching (MACE),[16] whereby oxidation occurs locally at the silicon-catalyst interface, and oxide is subsequently consumed by HF. This electroless etching process is only limited by the presence of reactants in solution, and when performed over extended periods of time can produce pores of aspect ratio over 1000:1 which completely penetrate Si substrates many microns in thickness.

Two types of mask were explored in this work. The first is a 50 nm-thick (100) NPSi layer, etched for 1-2 min following catalyst deposition (Figure 1(a) to 1(c)), and the second is an approximately 15 μm-thick (100) NPSi layer, etched for 24 hours (Figure 1(d) to 1(f)). While the 50 nm-thick mask allows for pore diameters less than 10 nm after 1 min etching (Figure 1(c)) or ~15 nm upon 2 min etching, it is fragile, and therefore only available as a free-standing film in 100 μm by 100 μm windows. In contrast, the 15 μm-thick mask may be produced over many cm^2 of area, but has a larger average pore diameter of 13.5 nm as indicated by Brunauer–Emmett–Teller (BET) nitrogen desorption analysis (Figure S1). Part of the pore size increase in the thick mask as measured by BET can be attributed to the heavily roughened surface and the underlying few micrometers of highly perforated material (Figure 1(e)), though imaging of the smoother back surface in contact with the MoS_2 during patterning (Fiugre 1(f)) also reveals larger pore diameters than are present in the thin masks. For the 50 nm-thick masks, tranmission electron microscopy (TEM) imaging of thousands of pores suggests an areal porosity of approximately 2.8% (Figure 1(c)) at the surface where etching is initiated. In the case of the thin NPSi masks, it is reasonable to assume that the majority of pores penetrate through the film completely, given that etching is observed to proceed at a rate greater than 65 nm/min to depths greater than 4 μm in bulk Si, where etching would be expected to experience significant

retardation given the increased difficulty of reactant diffusion into the ultrahigh aspect ratio pores. These observations facilitate an estimate of 1-2% for areal porosity on the opposite side of the 50 nm-thick NPSi masks. In the context of masking materials, it is areal porosity which will play a dominant role in governing the extent to which the underlying material will be exposed to plasma etching, and specifically the areal porosity of the mask at the NPSi-MoS$_2$ interface.
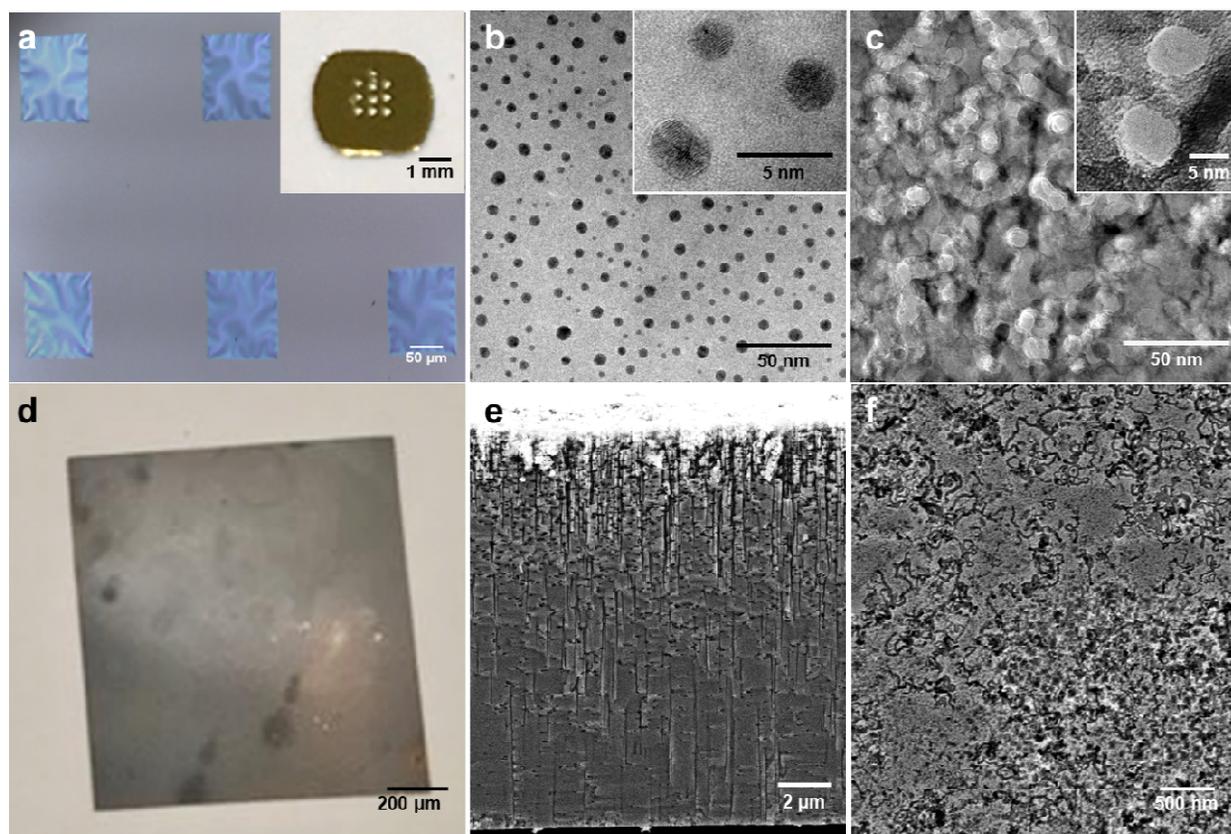
Figure 1. (a) Optical microscope image of five crystalline Si (c-Si) windows (100 μm by 100 μm) of 50 nm thickness on a single silicon mask chip (3 mm by 3 mm). The patterned mask defines the areas to be porous after etching. (inset: a photograph of an entire silicon mask chip containing ten 50 nm-thick c-Si windows). (b) TEM image of a 50 nm-thick c-Si window coated with Ag nanoisland catalysts via radio frequency (RF) sputtering. (c) TEM image of a porous 50

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nm-thick c-Si window following 1 min of MACE (inset: sub-10 nm pores in the NPSi layer

etched via the MACE process). (d) Photograph of a ~1 cm^2 NPSi mask of 15 μm thickness. (e)

SEM cross-sectional image of the 15 μm-thick NPSi mask in (d). Porosity is observed to

decrease with depth due to the lack of completely anisotropic etching in the MACE process. (f)

SEM image of the bottom surface of the NPSi mask in (e), which is the surface in contact with

the MoS$_2$ flakes during oxygen plasma exposure.

Patterning process of monolayer MoS$_2$ using NPSi masks.

A schematic illustration of the patterning process is shown in Figure 2(a). The chemical vapor

deposition (CVD)-grown MoS$_2$ domains (10–100 μm) on silicon wafer with a 300 nm silicon

oxide layer were spin-coated with poly(methyl methacrylate) (PMMA) and transferred onto a

NPSi substrate via KOH-assisted etching of the silicon oxide layer. The substrate was exposed to

O$_2$ plasma selectively on the opposite side of MoS$_2$/PMMA, in order to etch only the nanoscale

fractional areas of MoS$_2$ that are in contact with the nanopore areas of the NPSi mask. Then the

NPSi mask was removed by KOH-assisted etching, and the MoS$_2$/PMMA layer was transferred

to another silicon wafer. After the removal of PMMA coating by acetone, the nanoporous MoS$_2$

domains were examined by optical microscopy, scanning electron microscopy (SEM), and

photoluminescence (PL) and Raman spectroscopy. The initial porous structures were then further

modified by thermal annealing in air, while the structural changes were investigated by the

microscopy and spectroscopy tools.

Imaging of the MoS$_2$ domains following oxygen plasma exposure through the NPSi mask

reveals the introduction of significant porosity in the material. This is exemplified via

comparison between pristine MoS$_2$ domains (Figure 2(b) and 2(c)) and those patterned by

selective etching through a thin (50 nm) NPSi mask (Figure 2(d) to 2(g)), where the latter

possesses an average porosity of 8.5%, with a pore diameter of 65.9 ± 13.3 nm. The measured

porosity of 8.5% in the MoS_2 is nearly an order of magnitude greater than the estimated mask

porosity of 1-2% at the $NPSi-MoS_2$ interface, which is not unexpected given that the O2 plasma

is capable of etching laterally once an initial defect is produced in the MoS_2 domains.

In addition to MoS_2, a large family of 2D materials stand to benefit from the ability to

induce large-scale nanoporosity across initially pristine domains. The relevance of the developed

approach is evaluated by extension to the nano-patterning of tungsten disulfide (WS_2). Figure

2(h) shows a WS_2 domain patterned with a 15 μm-thick NPSi mask (1 cm by 1 cm) over 4-5 μm

continuous area, and the magnified images (Figure 2(i) and 2(j)) indicate the morphology of the

nanoporous domain resembling that of the 15 μm-thick NPSi mask. The density and size of

pores generated by the large-scale free-standing mask is comparable to those observed in Figure

2(d) to 2(g), which indicates the scalability of this patterning method over a range of Si mask

thickness and lateral dimension. Given the successful patterning of WS_2 domains, we expect the

application of the etching technique to be extended to general sets of 2D materials including

graphene, *h*-BN, and other TMDs.

We note that the O_2 plasma etching through NPSi masks completed in different time

scales depending on the thickness of the masks. The plasma treatment of 2 min was required to

pattern TMD domains through 50 nm-thick Si masks with sub-10 nm pores, while 30 sec

exposure to plasma through 15 μm-thick Si masks was sufficient to generate similar scale pores

on the domains. The shorter plasma treatments in each case resulted in the nanoporous domains

with smaller pores which were difficult to distinguish from naturally occurring defects under

SEM.
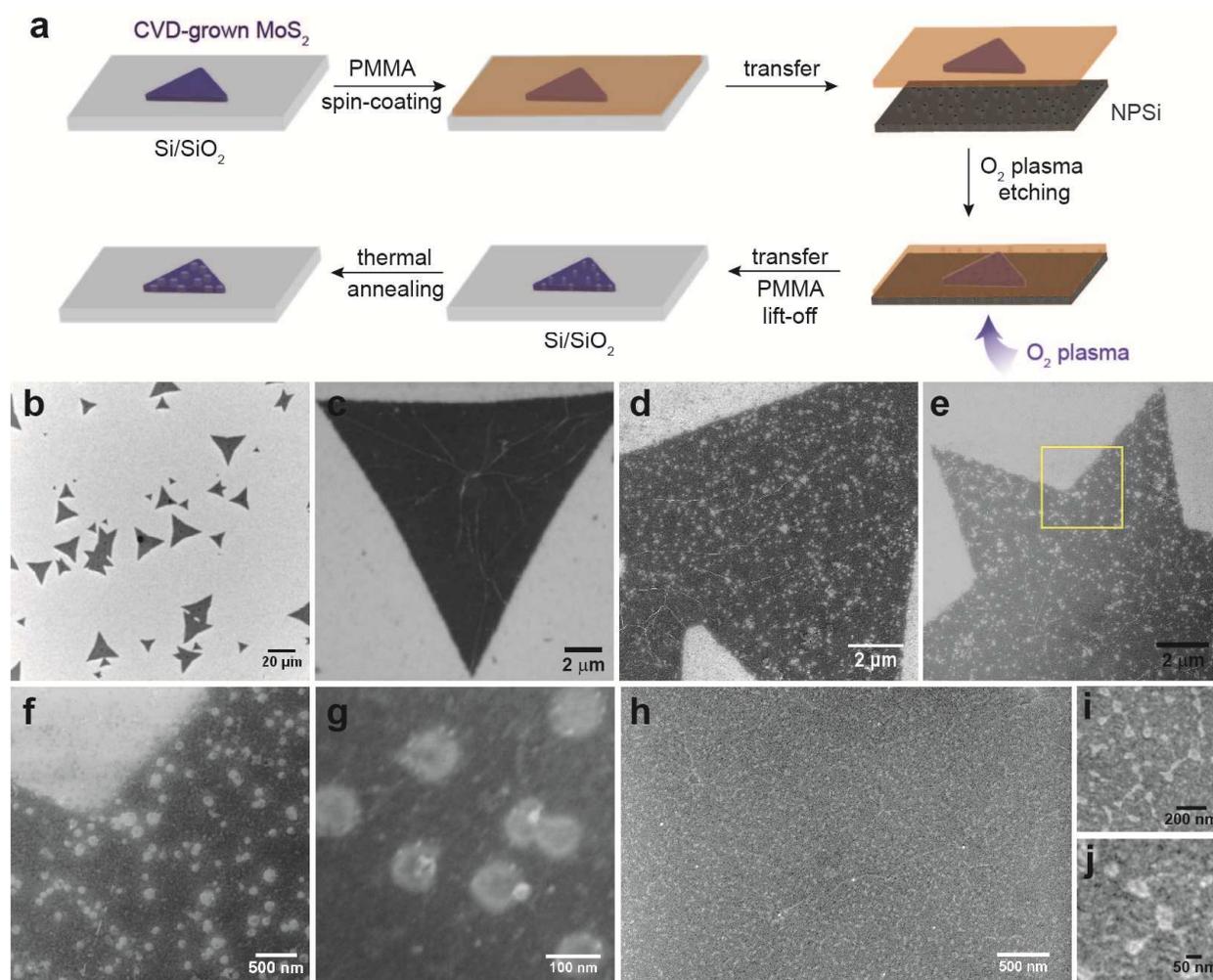
Figure 2. (a) Schematic illustration of the NPSi-assisted patterning process for nanoporous

monolayer TMDs and the subsequent thermal annealing process to control the porosity. (b) SEM

image of pristine MoS_2 domains on a Si/SiO_2 substrate. (c) SEM image of a single triangular

MoS_2 domain that underwent the patterning process without being exposed to O_2 plasma as

covered by the silicon mask chip. (d) SEM image of a nanoporous MoS_2 domain produced via

selective etching through a thin (50 nm) NPSi mask for 2 min. (e) SEM image of a star-shaped

nanoporous MoS_2 domain that is found on the identical substrate as (d). (f) Magnified view of the region indicated with the yellow box in (e) showing the nanoscale pores with a range of diameters. (g) High magnification SEM image of a nanoporous MoS_2 domain. (h) SEM image of a nanoporous WS_2 domain following 30 sec of O_2 plasma etching using a 1 cm^2 NPSi mask of 15 µm thickness. (i) Magnified view of the sample in (h) showing less round and connected morphology of nanopores on WS_2 domains. (j) Magnified view of the sample in (h) showing the comparable size of pores to those in (g).

Porosity of monolayer MoS_2 controlled by post-patterning thermal annealing process.

Following initial O_2 plasma treatment of 2 min which generates round pores as determined by the shape of the NPSi structures, an effective strategy to control the pore size of monolayer MoS_2 domains was demonstrated via thermal treatment at 300 °C in air. Defect sites of MoS_2 flakes are prone to oxidative etching under high temperature conditions,[17,18] so we expect to control the size of nanopores by gradual thermal annealing. The nanopore size and density increases with heating time, indicating mass loss occurs from the edge of existing nanopores, most likely in the form of S depletion. The enlargement of these holes results in an increased edge to area ratio in the MoS_2 sample. The increase of edge sites, which have implications in the optical and catalytic properties, can be effectively modified by the simple heating process without the need of a furnace or inert conditions. Depending on the application, the optimal edge-to-area ratio can be selected, and diverse nanoscale patterns can be achieved.

Until 30 min annealing, the oxidation does not lead to any visible change on the morphology of the nano-pattern under SEM. Figures 3(a) to 3(h) display the effect of annealing

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(30, 60, and 100 min), which is the expansion of pores and their convergence due to the

oxidation of the edge sites of patterned MoS_2. The product of oxidation, MoO_3 particles,[19] is

visible in the magnified images as bright dots (Figure 3(h)). Figure 3(i) summarizes the effect of

thermal annealing on the edge density and porosity of the MoS_2 domains following plasma

treatment, where edge density is calculated via SEM image analysis in ImageJ (Figure S2).

Unsurprisingly, porosity increases monotonically with annealing time, gradually over the first 30

min, then more aggressively, reaching $87.3 \pm 2.6\%$ after 100 min at 300°C. Less intuitive is the

effect of annealing time on edge density, a relationship for which a rigorous understanding could

prove beneficial in catalytic and sensing-focused applications. Perhaps counterintuitively, edge

density is observed to remain statistically similar after 30 min of annealing time. This can be

explained by the convergence of pores as they expand, resulting in the decrease in edge-to-area

ratio within the porous MoS_2 domain. This balancing effect is observed to dissipate however by

60 min of annealing, primarily due to drastically increased pore intercalation corresponding with

a significantly greater porosity of $55.2 \pm 10.1\%$, resulting in a near doubling of edge density

from 0.00827 ± 0.00170 nm^{-1} after 30 min to 0.0145 ± 0.00106 nm^{-1}. Further annealing is

observed to have a negative impact on edge density, as an increase in porosity to $87.3 \pm 2.61\%$

after 100 min corresponds to a drop in edge density to 0.0107 ± 0.00135 nm^{-1}, as connectivity

between remaining MoS_2 regions is diminished. This result provides valuable insight for

optimizing edge densities in MoS_2 and other 2D materials via nano-patterning and thermal

annealing.

Figure 3(j) demonstrates the efficacy of the developed process, where half of a MoS_2

domain resting over a 50 nm thick NPSi porous mask region is nearly effectively patterned

following O_2 plasma exposure, while the other half located on a non-porous region remains in a

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pristine state. This shows the seamless attachment of MoS_2 domains on the mask across the boundary of the 50 nm-thick NPSi window and the supporting silicon chip, enabled by the PMMA-assisted transfer and mild drying process at 100 ^{o}C. The SEM image showing the half-patterned MoS_2 domain after 60 min of thermal annealing also confirms that the oxidation occurs more extensively on the nanoporous side rather than on the pristine area under identical annealing conditions. Figure 3(k) displays the formation of nanopores smaller than 50 nm in diameter on a pristine MoS_2 domain after 100 min of thermal annealing in air, as previously seen as triangular pits created by prolonged thermal annealing.[19] These pores formed in a lower density than that of O_2 plasma etched pores are expected to grow via the preferential oxidation of defect sites on the basal plane of MoS_2 and more severely around the domain edges and the present cracks, as observed in SEM images (Figure S3).

The understanding of the gradual morphology changes induced by thermal annealing gives valuable insight for the optimization of porosity, which is essential for developing porosity-dependent applications such as nanoporous filtration and edge-site-specific applications including sensing and electrocatalysis.
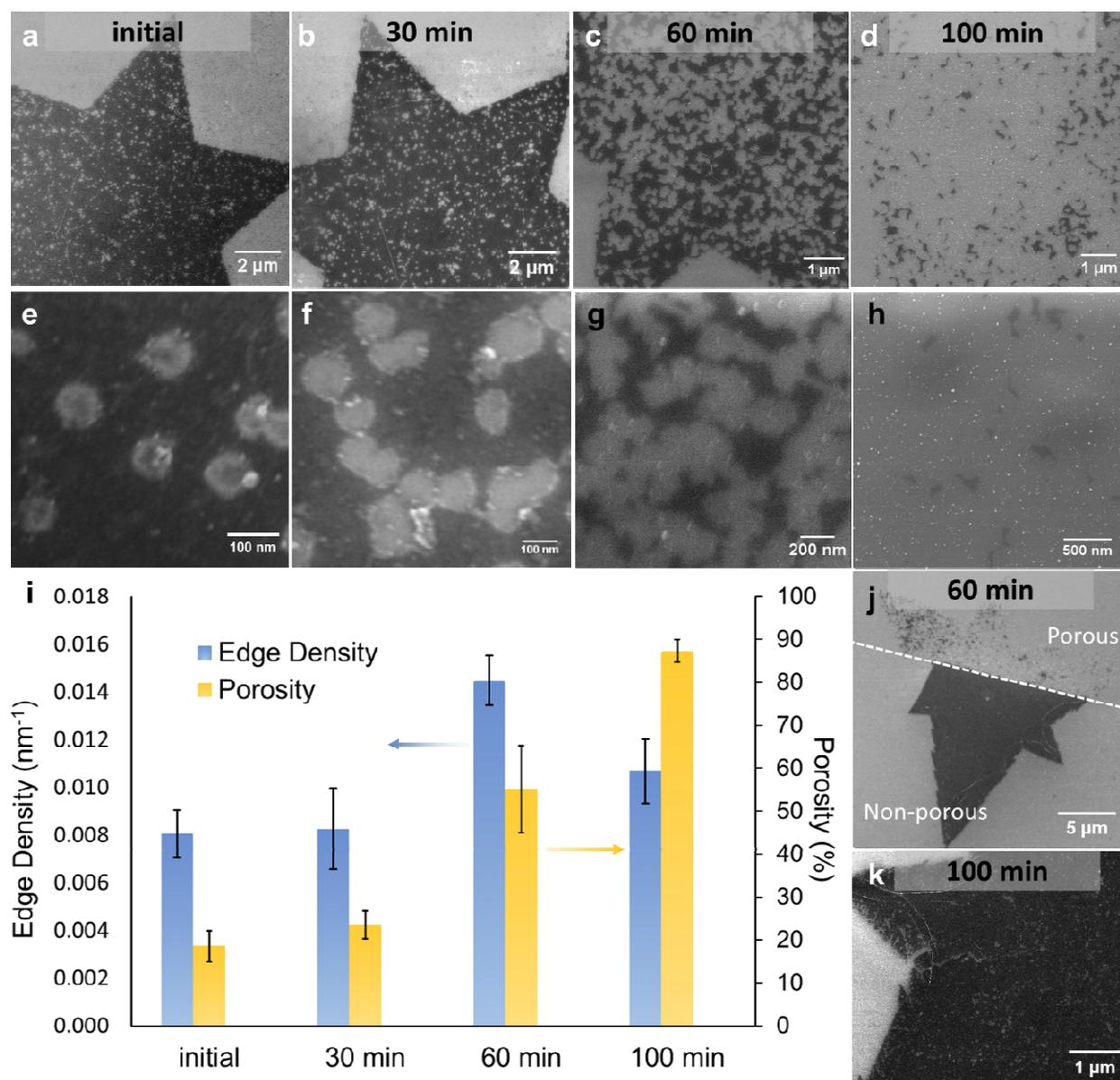
Figure 3. Effect of thermal annealing on the morphology of nanoporous MoS_2. (a) SEM image of a MoS_2 domain after initial 2 min O_2 plasma treatment through a 50 nm-thick NPSi mask. (b) SEM image of the MoS_2 domain in (a) after 30 min of thermal annealing in air. (c) SEM image of a MoS_2 domain from an identical sample after 60 min of annealing. (d) SEM image of a MoS_2 domain from an identical sample after 100 min of annealing. (e) Magnified view of the sample in (a) showing individual pores with diameter ~70 nm. (f) Magnified view of the sample in (b)

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showing nano-patterns of enlarged pores produced in the monolayer MoS$_2$. (g) Magnified view of the sample in (c) showing further expanded and converged pores. (h) Magnified view of the sample in (d) showing MoS$_2$ flakes and oxidized MoS$_2$ particles. (i) Plot of MoS$_2$ edge density and porosity with respect to thermal annealing time for O$_2$ plasma etched samples. N=3 for all data. (j) SEM image of a MoS$_2$ domain located half on a 50 nm thick NPSi etch mask and half on non-porous silicon after O$_2$ plasma treatment and 60 min of thermal annealing. (k) SEM image of a pristine MoS$_2$ domain after 100 min of thermal annealing in air.

Optical properties of nanoporous MoS$_2$ with varied edge density.

The visual changes of the domain morphology corroborate the optical property changes measured by PL and Raman spectroscopy on the pristine and nanoporous MoS$_2$ (Figure 4). Optical properties of MoS$_2$ samples were first measured by PL spectroscopy on the selected spots of ~1 μm size within MoS$_2$ domains. Pristine MoS$_2$ domains before thermal annealing exhibit PL spectra with a peak at 683 nm upon excitation at 514.5 nm (Figure 4(a)). As thermally annealed at 300 °C, the PL increases and the peaks blue-shift to 680 nm after 40 min, 675 nm after 60 min, and 660 nm after 100 min of heating. Prior work on block copolymer (BCP)-assisted nano-patterned MoS$_2$ domains showed that increasing edge density causes PL quenching,[10] which is different than the observations in this work. This is due to the differences in edge density formation, where nanodots, nanorods, and nanomeshes in the prior work are not subjected to oxidation at high temperature and were shown by ADF-STEM to have non-reconstructed edges.

More remarkable PL increase and blue-shift are observed in the case of the nanoporous MoS_2

sample (Figure 4(b) and 4(c)). The O_2-plasma etched domains exhibit PL spectra with a peak at

677 nm which blue-shifts to 664 nm after 20 min of thermal annealing at 300 ^{o}C. After the peak

shift, the PL intensity increases as the domains are heated up to 70 min, then further annealing

results in the quenching of PL due to severe degradation of the material. The PL change seen in

the nanoporous MoS_2 sample follows the trend of edge/area ratio (Figure 3(i)) as previously

determined by analyzing SEM images. It has been reported that laser induced chemisorbed

oxidation of CVD-grown pristine MoS_2 causes PL increase due to the reduction in n-doping

followed by PL decrease after continued oxidation,[20] and that heating exfoliated MoS_2 in air also

causes rapid PL enhancements.[21] Another report illustrates that defect areas or cracks on MoS_2

layers exhibit a huge PL enhancement upon thermal annealing compared to pristine area due to

stronger binding to O_2, which leads to more prominent p-doping, and less non-radiative

recombination around the defective sites.[22] A similar effect is seen in the nanoporous MoS_2

samples as in Figure 4. The NPSi mask etched sample has more rapid PL increase compared to

the pristine MoS_2, which is associated with the higher edge density and defectiveness in the

nanoporous domains as seen in Figures 2 and 3. For the MoS_2 sample that is not etched, only a

slight PL increase is observed within the same time frame of high temperature heating. The

immediate PL change of nanoporous MoS_2 upon brief thermal annealing is likely caused by

initial reduction of the n-doping level of MoS_2 through the physisorption of oxygen molecules.

The degradation of edge sites and the pore opening require further annealing (which may activate

chemisorption and molecular conversion) and are accelerated as the edge-to-area ratio increases.

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Decoupling the contributions of exciton and trion emission to the PL spectra was performed by multiple peak fitting in order to explain the overall blue-shift and PL changes as a function of thermal annealing time. For pristine MoS_2, which was not etched but transferred multiple times during the nanopore fabrication process on the same substrate (Figure 2(a)), the PL mostly consists of strong trion emission at ~1.83 eV, and the continued thermal annealing induces exciton emission at ~1.87 eV. After 100 min annealing, the exciton/trion ratio was calculated to be 0.3. The nanoporous MoS_2 exhibits similar behavior, as the exciton contribution increases and dominates after thermal annealing. The trion emission observed at ~1.83 eV and exciton at ~1.87 eV both grow rapidly following thermal oxidation, and the exciton/trion ratio increases from 0.53 after 20 min to 1.07 after 50 min, 1.19 after 60 min, 1.32 after 70 min, and 1.43 after 80 min annealing (Figure S4). The exciton/trion ratio then drops to 0.77 after 100 min thermal treatment. This analysis indicates that both nanoporous and non-porous samples are heavily n-doped before thermal annealing as revealed by the initially dominating trion contribution.[23] Both samples have a similar degree of surface residue, and the comparison of the PL from both the etched and protected areas before the high temperature treatments shows similar spectra (Figure S5) indicating that the doping and defect densities are similar in both cases.

Raman spectroscopy of both samples (Figure 4(d) and 4(e)) exhibit an unchanging A_{1g} mode and decreasing E^1_{2g} mode with thermally annealing. The increasing A_{1g}/E^1_{2g} ratio indicates doping level changes[24] occurring to the monolayer MoS_2 flakes upon thermal annealing, consistent with the PL spectra changes. The negligible softening of the E^1_{2g} mode suggests insignificant changes in strain within the MoS_2 monolayers. Analysis of the time dependence of the heating process (Figure 4(f)) shows an initial stage where minimal PL increase is observed,

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which is likely due to a cleaning of surface residue, then a rapid onset of PL increase at 30-40

min (porous sample). The time scale of the rapid onset of PL is similar to prior studies on

exfoliated MoS_2 materials,[21] where approximately 25 min at 300 $^{\circ}$C causes the PL maxima to be

reached, followed by a rapid PL quench during the next 25 min. The PL increase of pristine

sample is much slower than that of nanoporous sample, which is associated with the larger

surface area of pristine MoS_2 covered with amorphous carbon protecting layers and with the less

available edge sites that are prone to oxidation process. The PL spectra were normalized to the

Raman A_{1g} peak, which normalizes the impact of different sample areas and materials quantity.[25]

Figure 4. Optical property changes of MoS_2 domains induced by nano-patterning and thermal

annealing. (a) Normalized photoluminescence (PL) spectra of pristine MoS_2 domains upon

thermal annealing. (b) Normalized PL spectra of nanoporous MoS_2 domains upon thermal

annealing up to 70 min. (c) Normalized PL spectra of nanoporous MoS_2 domains upon continued

thermal annealing. (d) Normalized Raman spectra of pristine MoS_2 domains upon thermal

annealing. (e) Normalized Raman spectra of nanoporous MoS_2 domains upon thermal annealing. (f) Relative maximum PL intensity change as a function of annealing time for nano-patterned and pristine MoS_2 domains. All spectra were normalized to the A_{1g} signal intensity for each sample.

Comparison to direct O_2 plasma exposure to MoS_2 without NPSi masks

The active selective masking behavior of the fabricated NPSi layers was confirmed via control experiments in which CVD-grown pristine MoS_2 domains were directly exposed to O_2 plasma for short (1 sec, 10 sec, and 30 sec) times with no masking. Drastically different results were achieved, helping to elucidate the crucial role of the NPSi masks in patterning. After only 1 sec of plasma exposure, the PL decreases and blue-shifts from 678 nm to 663 nm (Figure 5(a)), a phenomenon which was not observed in the plasma etching process through NPSi masks (Figure S5). Based on the Raman spectra in Figure 5(b), we can monitor the impact of p-doping on pristine MoS_2 upon the short plasma treatment. Any treatment longer than 1 sec destroys the material, resulting in the absence of PL or Raman signal from the samples.

The morphology changes upon the direct plasma treatment were investigated by SEM (Figure 5 (c) to 5(h)). After 1 sec exposure to O_2 plasma, the domains exhibit homogeneous cracking across the materials without significant changes of nanoscale morphology such as pore formation or defect enlargement. The longer treatment generates domains with lighter contrast and bright needle-shaped materials of tens and hundreds of nm in length. The conversion of MoS_2 to the oxidation product is responsible for the annihilated PL and Raman signals. The detailed progress of cracking by the direct O_2 plasma treatment was investigated previously,

which describes the initially isolated crack appearance on intrinsic defects of MoS_2 basal plane.

These initial cracks then propagate to form interconnected cracks which possess angle of around

120° between them. STEM images showed both Mo and S terminated exposed edges of cracks

with angle of around 120°.[2] The control experiment demonstrates the unique capability of NPSi

masks in the selective formation of nanopores on 2D materials that exhibit bright PL even after

the nano-patterning and extensive etching, allowing for the preservation of morphological and

optoelectronic properties, while increasing edge density as desired. The localized nanoscale

pores are believed to possess interesting atomic structures of edge sites, and the investigation on

the atomic resolution imaging of the nanoporous MoS_2 and on the impact of thermal annealing

will be explored in future work.

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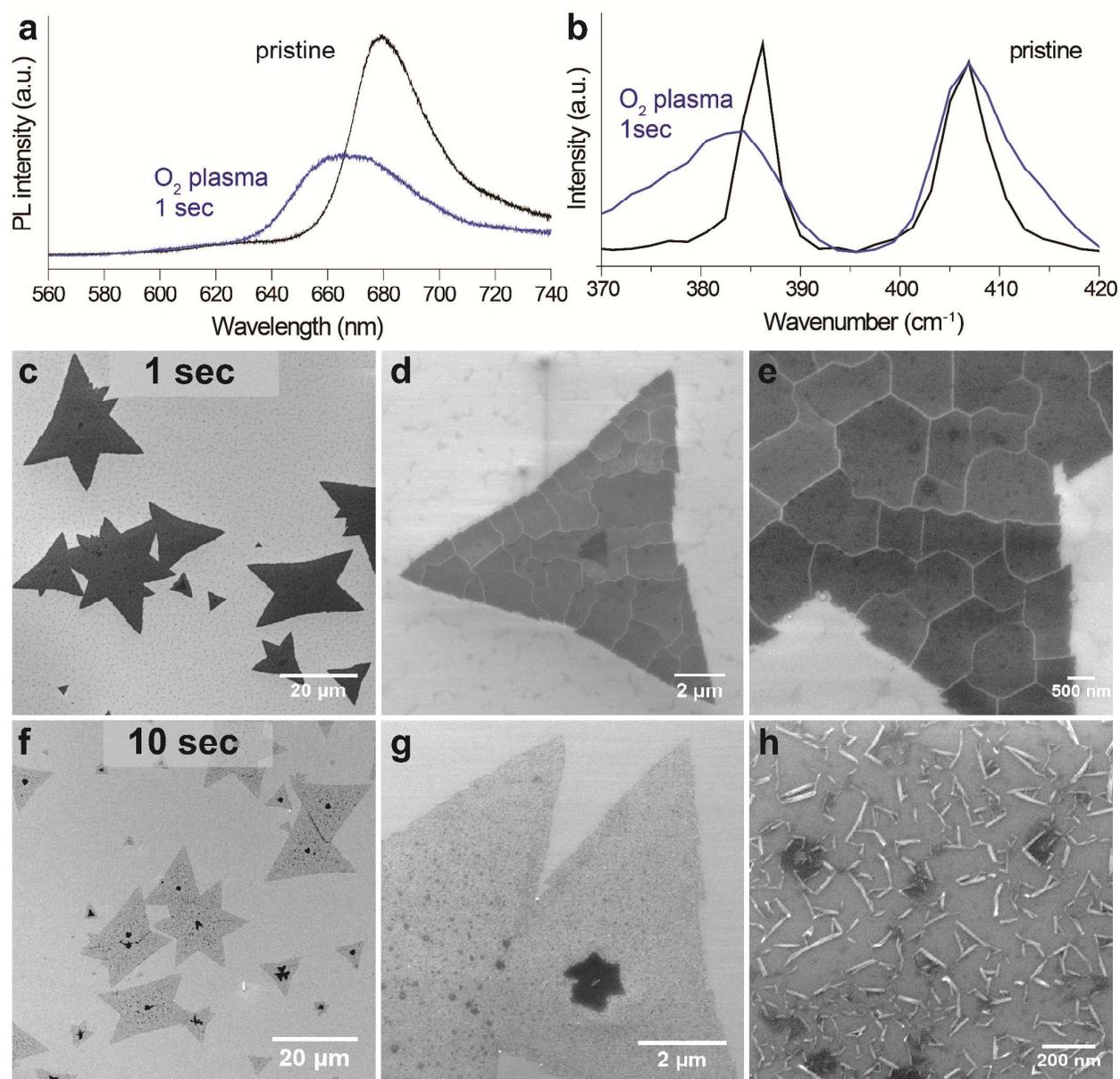
Figure 5. Optical property and morphology changes of MoS$_2$ domains induced by direct O$_2$ plasma exposure. (a) Normalized PL spectra of pristine MoS$_2$ domains before and after 1 sec direct O$_2$ plasma treatment. (b) Normalized Raman spectra of pristine MoS$_2$ domains before and after 1 sec direct O$_2$ plasma treatment. (c-e) SEM image of pristine MoS$_2$ domains after 1 sec direct O$_2$ plasma treatment with varied magnification. (f-h) SEM image of pristine MoS$_2$ domains after 10 sec direct O$_2$ plasma treatment with varied magnification.

Conclusion

The newly developed nanoporous silicon membrane with a pore aspect ratio greater than 1000:1 and pore diameters less than 20 nm was used as an etch mask for 2D materials (MoS_2 and WS_2) nano-patterning. Application of the NPSi masks with lateral size ranging from 100 µm by 100 µm to 1 cm by 1 cm and thickness from 50 nm to 15 µm was demonstrated, which revealed the scalability of the patterning method for 2D materials. The optimized process generated nanopores with dimaters of ~70 nm within the selected area of sample, and the successful enlargement of the pores was conducted by a simple thermal annealing step in air. Gradual changes of the pore size, edge-to-area ratio, and connectivity between the nano-flakes are fully correlated to optical property changes that indicate an increase of p-doping and exciton contribution as the nanoporous materials are mildly oxidized. This study opens opportunities towards optimizing the porosity and edge site density of 2D materials for various applications such as water filtration, sensing, and electrocatalysis. In the catalysis case, it is expected specifically that the greatly increased edge density will improve catalytic performance for the HER, as demonstrated in existing work.[12] Further, such a versatile patterning method could be applied to a range of materials beyond TMDs for large-scale applications.

Methods.

Chemical vapor deposition growth of monolayer MoS_2.

Monolayer MoS_2 was grown by CVD utilizing a smaller inner tube (MoO_3) within a larger outer quartz tube (S).[26] This reduces the interaction between the S and MoO_3 precursor during the growth. Molybdenum trioxide (MoO_3, powder, ≥99.5%, Sigma-Aldrich) and sulphur (S, powder, ≥99.5%, Sigma-Aldrich) are used as the precursors. The MoO_3 (inner tube, 20 mg) and S (outer

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tube, 300 mg) were increased to ~180 and ~300 ^{0}C, respectively, while the 300 nm SiO$_2$/Si

substrate positioned downstream was at ~800 ^{0}C. This results in the CVD growth of MoS$_2$

monolayer domains that range from 10-100 μm. Sulphur vapour was flushed through the system

for 10 min before heating up the MoO$_3$. When the final temperature for growth was achieved, the

MoS$_2$ nucleates under a 150 sccm argon flow for 17 min, and then the flow rate is reduced to 10

sccm for a 23-min growth. Finally, the reaction is stopped by moving the sample from hot zone

of the furnace and this gives fast cooling.

Nanoporous silicon fabrication process.

NPSi masks were fabricated from 50 nm thick (100) crystalline Si films (SiMPore Inc.) and 15

μm thick (100) crystalline Si films, initially 300 μm thick (100) DSP wafers, resisitivity 1-10

Ω•cm, p-type (boron doped), which were thinned via potassium hydroxide in 30 wt.% aqueous

solution at 70°C, as described in previous work.[27] Both types of substrate were cleaned in

acetone, isopropanol, and DI water, and dried under nitrogen prior to catalyst deposition. The

hemispherical nanocatalysts were deposited via RF magnetron sputtering using an ATC 6-target

sputtering tool (AJA International). In all experiments, Ag was deposited to a nominal thickness

of 1 □ at an RF power of 30 W. Immediately after catalyst deposition, samples were submerged

in MACE solution containing 5.33 M HF and 0.12 M H$_2$O$_2$ for 1 min in the case of the 50 nm

thick masks and 24 hours for the 15 μm thick masks. Masks were rinsed extensively with DI

water upon completion of the etching and dried under nitrogen.

Nanoporous silicon masking and oxygen plasma etching process.

On the substrate with CVD-grown monolayer MoS_2, PMMA A7 solution was spin-coated (500 rpm for 5 sec, 2000 rpm for 10 sec, and 4500 rpm for 45 sec). The sample was annealed at 180 ^{o}C for 90 sec to evaporate anisole, and the Si/SiO_2 substrate was removed by dissolving in 1 M KOH solution overnight. The PMMA layer containing MoS_2 domains was then rinsed with DI water and transferred to NPSi substrate. The sample was dried at 150 ^{o}C for 10 min and turned upside-down to be selectively exposed to oxygen plasma. The oxygen plasma etching of MoS_2 through NPSi mask was conducted by using Harrick Scientific PDC-32G Plasma Cleaner (18 W, oxygen flow rate of 0.6 SCFH (standard cubic feet per hour)). The porous MoS_2 formed on PMMA layer was then transferred to a new Si/SiO_2 substrate via KOH etching of NPSi as described for the initial transfer process.

Measurements.

PL and Raman spectra were acquired using a Horiba LabRAM 800 HR spectrometer equipped with an Ar^+ (514.5 nm) excitation source and a Peltier-cooled CCD detector. The laser was focused on the sample using a 100x objective under reflected illumination and the PL measured under confocal conditions with a 400 nm hole. The laser spot on the sample was ~1 µm in diameter and had a power of ~4 mW at the sample surface. Scanning electron microscopy was performed using Zeiss Ultra Plus FESEM.

Data availability. The data that support the findings of this study are available from the corresponding author upon request.

Acknowledgements

Author contributions

G.G.D.H and B.D.S. conducted the patterning process of MoS_2 and characterized the morphology by SEM. G.G.D.H characterized optical properties of all samples. B.D.S. fabricated NPSi etch masks. W.X. provided CVD-grown MoS_2 samples. J.H.W. and J.C.G conceived and supervised the project. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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Supporting Information Available: Supporting information includes BET characterization of porosity in the 15 μm thick NPSi masks (Figure S1), details of image analysis for MoS$_2$ porosity characterization (Figure S2), characterization of porosity in pristine MoS$_2$ domains following annealing (Figure S3), optical characterization of nanoporous MoS$_2$ following annealing (Figure S4), and optical characterization of pristine and nanoporous MoS$_2$ prior to annealing (Figure S5).

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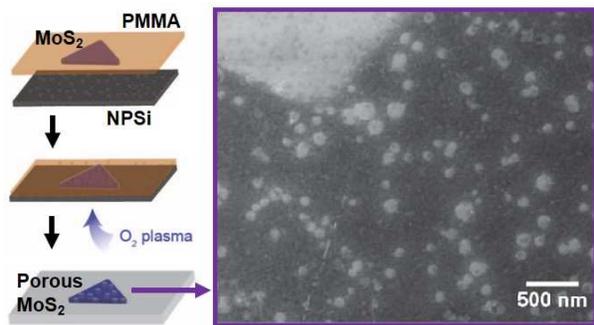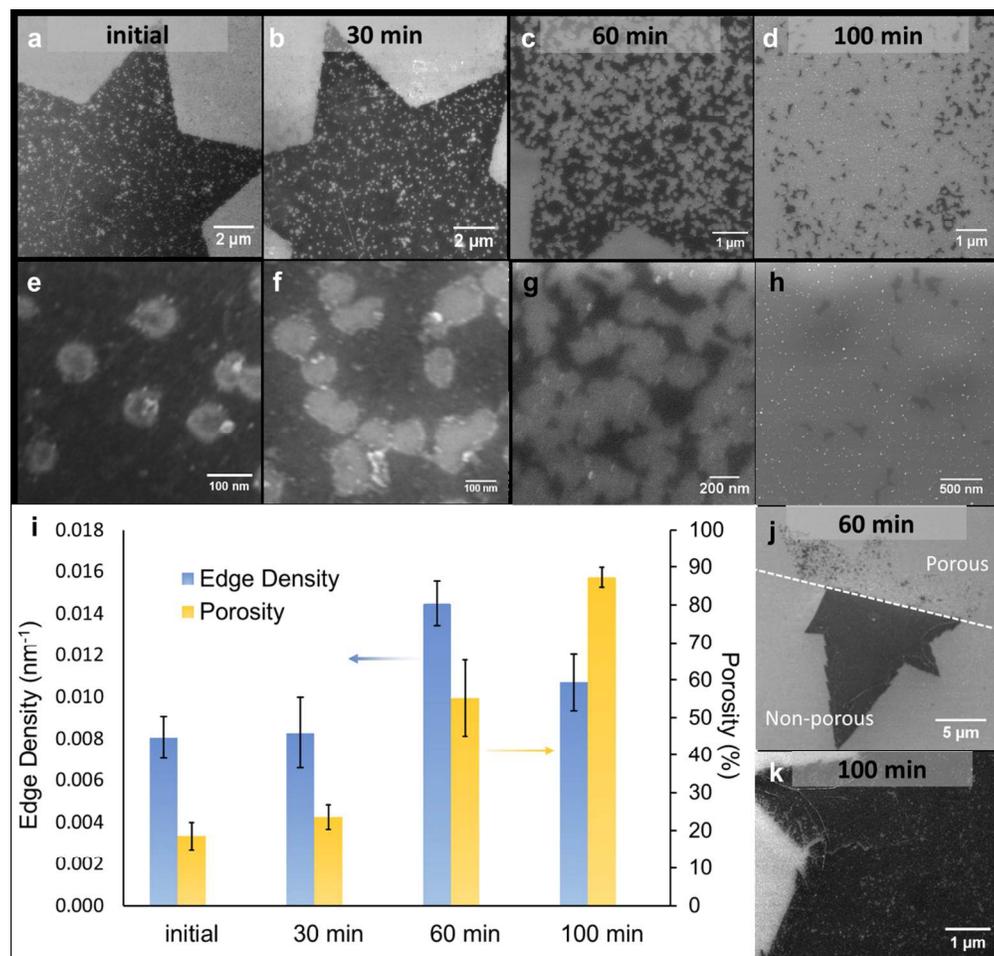
Effect of thermal annealing on the morphology of nanoporous MoS_2. (a) SEM image of a MoS_2 domain after initial 2 min O_2 plasma treatment through a 50 nm-thick NPSi mask. (b) SEM image of the MoS_2 domain in (a) after 30 min of thermal annealing in air. (c) SEM image of a MoS_2 domain from an identical sample after 60 min of annealing. (d) SEM image of a MoS_2 domain from an identical sample after 100 min of annealing. (e) Magnified view of the sample in (a) showing individual pores with diameter $\sim$70 nm. (f) Magnified view of the sample in (b) showing nano-patterns of enlarged pores produced in the monolayer MoS_2. (g) Magnified view of the sample in (c) showing further expanded and converged pores. (h) Magnified view of the sample in (d) showing MoS_2 flakes and oxidized MoS_2 particles. (i) Plot of MoS_2 edge density and porosity with respect to thermal annealing time for O_2 plasma etched samples. N=3 for all data. (j) SEM image of a MoS_2 domain located half on a 50 nm thick NPSi etch mask and half on non-porous silicon after O_2 plasma treatment and 60 min of thermal annealing. (k) SEM image of a pristine MoS_2 domain after 100 min of thermal annealing in air.

167x160mm (220 x 220 DPI)

Optical property changes of MoS$_2$ domains induced by nano-patterning and thermal annealing. (a) Normalized photoluminescence (PL) spectra of pristine MoS$_2$ domains upon thermal annealing. (b) Normalized PL spectra of nanoporous MoS$_2$ domains upon thermal annealing up to 70 min. (c) Normalized PL spectra of nanoporous MoS$_2$ domains upon continued thermal annealing. (d) Normalized Raman spectra of pristine MoS$_2$ domains upon thermal annealing. (e) Normalized Raman spectra of nanoporous MoS$_2$ domains upon thermal annealing. (f) Relative maximum PL intensity change as a function of annealing time for nano-patterned and pristine MoS$_2$ domains. All spectra were normalized to the A$_{1g}$ signal intensity for each sample.

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