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Free-Standing Two-Dimensional Gold Membranes Produced by Extreme Mechanical Thinning

Qi Zhu,[†] Youran Hong,[†] Guang Cao,[†] Yin Zhang, Xiaohan Zhang, Kui Du, Ze Zhang, Ting Zhu,* and Jiangwei Wang*



ABSTRACT: Two-dimensional (2D) materials exhibit exceptional physical and chemical properties owing to their atomically thin structures. However, it remains challenging to produce 2D materials consisting of pure monoelemental metallic atoms. Here free-standing 2D gold (Au) membranes were prepared *via in situ* transmission electron microscopy straining of Au films. The applied in-plane tensile strain induces an extensive amount of out-of-plane thinning deformation in a local region of an Au thin film, resulting in the nucleation and growth of a free-standing 2D Au membrane surrounded by its film matrix. This 2D membrane is shown to be one atom thick with a simple-hexagonal lattice, which forms an atomically sharp interface with the face-centered cubic lattice of the film



matrix. Diffusive transport of surface atoms, in conjunction with the dynamic evolution of interface dislocations, plays important roles in the formation of 2D Au membranes during the mechanical thinning process. These results demonstrate a top-down approach to produce free-standing 2D membranes and provide a general understanding on extreme mechanical thinning of metallic films down to the single-atom-thick limit.

KEYWORDS: 2D gold membrane, mechanical thinning, defect, diffusion, in situ transmission electron microscopy

wo-dimensional (2D) materials possess unusual physical and mechanical properties compared with their bulk counterparts.¹⁻⁴ They have been widely used for advanced electronic and optoelectronic devices, electrocatalysts, solid lubricants, and energy dissipation.8,9 Beyond the first 2D material of graphene,¹⁰ preparation of other 2D materials via either a bottom-up or top-down approach has seen rapid progress in the past decade, 11,12 notably for 2D hexagonal boron-nitride¹³ and transition metal dichalcogenides/selenides (TMD/TMS).14-16 Mechanical cleavage has been used to prepare graphene by taking advantage of weak van der Waals bonding in between atomic carbon layers in bulk graphite.¹⁷ However, this method can hardly be applied to produce other monoelemental equivalents to graphene (e.g., silicene, germanene, and borophene) $^{18-20}$ and superconductive metallic films (e.g., Pb and In),^{21,22} because of their strong covalent or metallic bonding and the lack of weak interlayer bonding in bulk counterparts. Instead, monoelemental 2D materials are produced primarily by either epitaxial growth or electron beam deposition on a substrate,¹¹ which can strongly influence the stability and properties of these 2D materials.^{21,23} Recent studies have demonstrated a new approach of electron beam irradiation to prepare freestanding single-atom-thick Fe, Cr, and Au, which were suspended either in graphene pores^{24–26} or in Au–Ag alloys,²⁷ opening opportunities for the top-down fabrication of monoelemental 2D membranes. However, the production and support of these 2D materials involve the use of multiple chemical compounds or bulk alloys other than the monoelement itself. It is, therefore, desired to produce free-standing monoelemental 2D membranes directly from bulk counterparts, so as to enable further investigation of their intrinsic properties without interference of impure elements.

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Figure 1. In situ preparation of a free-standing 2D Au membrane by mechanical thinning of a bicrystal Au thin film. (a-d) Time series of HRTEM images showing the nucleation and growth of a free-standing 2D Au membrane at the GB under in-plane tensile load. (a) An as-fabricated Au bicrystal thin film containing a general GB, as delineated by the yellow dashed line. An in-plane tensile load was applied to the bottom grain (G2), as indicated by the white arrow. (b) Nucleation of an embryonic 2D membrane (delineated by the red loop), resulting from extensive local thinning of the film at the curved GB under tensile normal stress σ . (c) Initial growth of the 2D membrane, as shown by the increased area compared to b. (d) Rapid growth of the 2D membrane, as indicated by the red arrows. (e) Crack initiated from the right surface of the Au matrix and propagated toward the 2D membrane, as indicated by the yellow arrow. (f) A void was left after fracture of the 2D membrane. (g-j) Magnified images showing the atomic-scale growth process of 2D membrane at the interface. (g, h) Disappearance of a nanoisland consisting of five atom columns at the interface, which should result from diffusive removal of atoms from the interface. (i, j) Lateral migration of an atomic step along the interface. The nanoisland and atomic step at the interface are indicated by the yellow and purple arrows, respectively. (k) Schematic illustration of the production of a 2D membrane in a bicrystal thin film via mechanical thinning and surface diffusion. Scale bars: (a) 5 nm; (g) 2 nm.

Here, we develop a top-down approach to prepare freestanding single-atom-thick Au membranes via in situ mechanical straining of Au thin films inside a transmission electron microscope (TEM). The applied in-plane tension induces an extensive out-of-plane thinning deformation in a defective region of an Au thin film, leading to the nucleation and growth of a free-standing 2D Au membrane surrounded by its film matrix. In situ atomic-resolution TEM observations reveal the simple-hexagonal (SH) lattice in the 2D Au monolayer, which forms an atomically sharp interface with the face-centered cubic (FCC) film matrix. The nucleation and growth of 2D Au membranes during mechanical thinning are facilitated by the diffusion of surface atoms as well as dynamic evolution of dislocations. These results demonstrate an effective top-down strategy to prepare free-standing monoelemental 2D metallic membranes and reveal a general formation mechanism of 2D metallic monolayers via mechanical means at room temperature.

RESULTS AND DISCUSSION

We first prepared a bicrystal Au thin film inside TEM via in situ welding of two nanosized Au single crystals (Figure 1a, see Methods). A general grain boundary (GB) formed in the middle of the film. We then conducted the in situ tensile straining experiment of this thin film sample inside TEM (Figure 1a and Movie S1). Initially, a uniform tensile deformation occurred within the entire film. As the applied load increased, an extensive plastic deformation was induced in a local region near the GB by the tensile normal stress σ , where the plastic resistance is relatively low because of defective structures at the GB.²⁸ Plastic deformation tends to conserve the crystal volume. Hence, a large in-plane tensile elongation can yield an approximately equal amount of out-of-plane thinning deformation in the same local region, as a negligible in-plane lateral contraction was observed. This mechanical thinning process produced a long-leaf-shaped ultrathin region

(referred to as an embryonic 2D membrane), which was surrounded by the Au film matrix. The 2D membrane region was readily recognized during TEM imaging, because of its lighter contrast relative to the surrounding film matrix (Figure 1b). This difference in image contrast arises due to the thickness and structure differences between the 2D Au membrane with an SH lattice and the film matrix with a FCC lattice. The atomic structure of the 2D Au membrane will be discussed in detail later. With increasing normal stress σ_i the 2D Au membrane grew continuously (Figure 1c, d) and reached an area of approximately 100 nm² before the onset of fracture (Figure 1d). The fracture process began with the formation of a crack in the Au film matrix that propagated rapidly towards the 2D Au membrane (Figure 1e). Once the crack entered the 2D membrane, the whole 2D membrane ruptured abruptly, leaving a large void in the Au thin film (Figure 1f).

The 2D Au membrane was produced via mechanical thinning of the Au film at room temperature. During the initial thinning process, the displacive dislocation slip can operate as an effective deformation mechanism, producing inplane elongation accompanied by out-of-plane thinning of the Au film. The dislocation-mediated thinning deformation in metallic films has been reported by both experiment and simulation in the literature.^{29,30} Our *in situ* high-resolution TEM (HRTEM) imaging is focused on the final thinning process (i.e., formation of a 2D membrane), which features the diffusive removal of Au atoms at the membrane/matrix interface. That is, Au atoms on the FCC matrix side of the interface were removed continuously, such that the 2D SH membrane grew via migration of the membrane/matrix interface. For example, Figure 1g shows a nanoisland consisting of five atom columns in the FCC matrix. This nanoisland subsequently disappeared, causing the local growth of the 2D membrane (Figure 1h). Likewise, Figure 1i shows an atomic step at the membrane/matrix interface (marked by a purple





Figure 2. Atomic structure of the simple-hexagonal lattice in a 2D Au membrane. (a) A free-standing 2D Au membrane suspended in the Au bicrystal film during the mechanical thinning process. The inset shows two sets of fast Fourier transform (FFT) patterns across the Au membrane/matrix interface, which correspond to conventional face-centered cubic (FCC) matrix and simple-hexagonal (SH) 2D membrane, respectively. The image was rotated clockwise to horizontally align the parallel planes in the matrix and 2D membrane. (b) Inverse fast Fourier transform (IFFT) image showing the atomically sharp membrane/matrix interface, corresponding to the interface segment in the white rectangle in a. The light blue and yellow lines delineate the characteristic lattice planes in the matrix and 2D membrane, respectively. Two interface dislocations are marked by the symbols of " \perp ". (c) Fourier-filtered image showing the SH lattice of the Au membrane. (d-f) Atomic structure models showing the {111}-projection of (d) trilayer, (e) double-layer and (f) single-layer of an FCC membrane embedded in the {110} FCC matrix. The atomic structure in (f) is equivalent to that of an SH monolayer. A triangle of the same size is superimposed on the projected lattice to highlight the different atomic structures in d-f. Scale bars: (a, b) 2 nm, (c) 1 nm.

arrow). This step migrated laterally along the interface (Figure 1j), leading to the growth of the 2D membrane as well. During these interfacial processes, atoms at the nanoisland or step were removed, so as to reduce the thickness of the local film matrix down to that of the 2D membrane. Hence, the final thinning process was likely completed by the diffusion of Au atoms along the film surface as well as the local displacive transformation from the FCC to the SH lattice. The surface diffusion should be favored because of the higher surface diffusivity than the bulk diffusivity of atoms in FCC lattices.³¹ The majority of the removed atoms is deemed to be relocated to the film matrix instead of joining the 2D membrane. Otherwise, a number of new lattice sites should have been created to accommodate those atoms at the membrane/matrix interface; such nonconservative lattice processes, if occurred, would be readily identified during our in situ HRTEM observations. However, some of the removed atoms could be sunk into the core of dislocations at the membrane/matrix interface to facilitate the diffusive growth of the 2D membrane, as will be discussed in detail later. During these processes, the mechanical stress can increase the rates of atom diffusion,^{32,33} interface dislocation climb, and displacive lattice transformation, thus promoting the growth of 2D Au membranes. We also note that in general, an ultrathin Au film would become unstable and trigger an immediate local fracture to limit the size of the resulting monolayer Au membrane. However, the fracture was suppressed (or much delayed) in the present Au bicrystal film, thus making possible the production of a stable 2D membrane surrounded by the film matrix. On the basis of the above in situ TEM observations, Figure 1k presents a schematic illustration of the formation and growth of a 2D Au membrane during the mechanical thinning of the Au bicrystal film.

Using the mechanical-thinning approach, we produced a number of 2D Au membranes in Au nanostructures containing GBs, twin boundaries or triple junctions of GBs, which acted as the preferred sites of nucleation of 2D Au membranes (Figures S1 and S2 and Movie S2). As a result, the Au membranes grew in accordance with the local geometry of these boundaries, adopting a long-leaf shape along the GB or TB, as well as a triangular shape at the triple junction of GBs. Incidentally, a similar process of deformation-induced formation of 2D metallic membranes (as demonstrated in Figure 1) can occur during the final stage of fracture in both bulk³⁴ and nanosized metals (see the Pt film generated at a crack tip in Figure S3),³⁵ particularly when GBs are present near the crack path (Figures 1 and 2).

Figure 2a shows the HRTEM image of a large-area Au 2D membrane surrounded by its Au film matrix. This image was taken from the same *in situ* straining experiment as in Figure 1. Inset in Figure 2a presents the fast Fourier transform (FFT) pattern across the membrane/matrix interface. The two different sets of FFT patterns correspond to the (110)oriented FCC lattice of the Au matrix (with 3-fold symmetry) and the (0001)-oriented SH lattice of the Au membrane (with 6-fold symmetry), respectively. The Fourier-filtered HRTEM image in Figure 2b clearly shows the projected {0001} lattice of the SH membrane that forms an atomically sharp interface with the projected {110} lattice of the FCC matrix. It should be noted that in the HRTEM image, a hexagonal lattice may correspond to either the {0001} plane of an SH Au membrane or the projected {111} plane of an FCC Au crystal. However, the distance between the nearest edge-on atomic planes in the former is 2.38 Å (Figure 2c), which is much greater than that of ~1.48 Å in the latter (see Figure S4). Moreover, this characteristic interplanar spacing in the Au membrane is

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Figure 3. Dislocation-mediated nucleation and growth of a 2D membrane. (a-d) Time series of HRTEM images showing the stress-induced nucleation (a, b) and growth (c, d) of an Au SH membrane from a pre-existing incoherent twin boundary (ITB) in the Au film. The ITB and coherent twin boundary (CTB) are marked by the dotted and solid lines, respectively, and the red dotted loop delineates the membrane/matrix interface. (e, f) Magnified images showing the dislocation-mediated membrane nucleation. (e) Small embryonic 2D membrane with a local lattice misorientation of 6° with respect to the matrix. Four dislocations (marked by the symbol of " \perp ") are identified near the interface based on the extra half atomic plane at each dislocation core. (f) Slight growth of the 2D membrane induced by glide and climb of interface dislocations. (g-i) Rapid growth of the 2D membrane through glide and climb of multiple interface dislocations. (g) Fully formed 2D membrane growth. Some new interface dislocations nucleate during this process. (i) Further growth of the membrane via diffusive climb of interface dislocations. The white dashed-line loops in (h, i) highlight the original size of the 2D membrane in g. (j) IFFT image showing the atomic structure near the interface between the SH membrane and FCC matrix. This image corresponds to the boxed region in d. The (111) and (002) planes of the Au matrix are misaligned by 10 and 5° with the respective $\{10\overline{10}\}$ planes of the monolayer. Scale bars: (a) 5 nm, (e, g) 1 nm.

quantitatively consistent with both the experimental result from a free-standing single-atom-thick Au nanoribbon suspended in the graphene pore²⁶ and the first-principles calculation result.³⁶ To further prove the formation of a monolayer of the SH lattice in this 2D membrane, we compare the projected lattice structure of the FCC membrane containing triple, double, or single $\{111\}$ layer(s) of atoms, each of which is surrounded by the {110} lattice of the FCC matrix (Figure 2d-f). These structure models respectively exhibit (i) a projected {111} lattice of FCC Au crystals with each atom having six nearest neighbors and a relatively small interatomic distance between nearest neighbors (Figure 2d); (ii) a projected honeycomb lattice with each atom having three nearest neighbors while maintaining the same interatomic distance (Figure 2e); and (iii) a projected SH lattice with each atom having six nearest neighbors and a relatively large interatomic distance (Figure 2f). Clearly, the lattice geometry of the monolayer SH model (Figure 2f) closely matches that of the 2D Au membrane observed in the HRTEM image (Figure 2b). Our molecular dynamics (MD) simulations further exclude the possibility of A-A stacking of the SH lattice (see Supplementary Method). This is because two SH layers with A-A stacking are unstable and spontaneously transform into A-B stacking during structural relaxation by energy minimization (Figure S5), yielding a projected lattice that is similar to Figure 2e but distinct from our experimental observation shown in Figure 2c. These results provide strong evidence for the production of one-atom-thick Au membranes with the SH lattice in this work.

Our *in situ* HRTEM imaging also revealed dislocations at the interfaces between the free-standing 2D Au membrane and the film matrix. As shown in Figure 2b, these dislocations can be readily identified from a standard procedure of finding an extra or a missing half atomic plane at the interface between the

projected SH {0001} lattice and FCC {110} lattice. These interface dislocations are geometrically necessary and serve to accommodate the lattice misfit and misorientation between the 2D membrane and the matrix (Figure 2b). In addition, the edge-on "atomic planes" (i.e., atom arrays in a 2D film) in the projected {0001} lattice of the SH Au membrane are misaligned with those in the projected {110} lattice of the FCC Au matrix (see the relative crystallographic orientation in Figure 2b). Specifically, the edge-on (111) and (002) planes of the FCC film matrix have the misalignment angles of 10.4 and 5.5° with respect to the two equivalent edge-on $\{10\overline{10}\}$ planes of the SH Au membrane, respectively. These misalignment angles were measured by aligning the edge-on $(11\overline{1})$ plane in the Au matrix with the third edge-on $\{10\overline{1}0\}$ plane in the SH Au membrane (Figure 2b). Such misalignments underscore the small, but necessary displacive transformation from the {110} lattice of the FCC Au matrix to the {0001} lattice of the SH Au monolayer. In addition, we note that minor deviations of Au atom positions from the corresponding perfect lattice sites occurred in the 2D membrane (Figure S6). These "fluctuations" probably stem from the out-of-plane relaxation or knock-on effect of electron beam, and they became more noticeable in the 2D membranes than bulk samples because of less constraints from neighboring atoms in the former. However, the stable structures of 2D Au membranes observed in our experiments indicate little effect of these fluctuations on the overall structural stability of Au membranes, because of the strong bonding and high in-plane stiffness as predicted by firstprinciples calculations.

The nucleation and growth of 2D Au membranes are facilitated by a variety of dynamic dislocation processes as well, as shown in Figure 3. Before the nucleation of an embryonic 2D Au membrane, a dislocation pre-existed near an incoherent twin boundary (Figure 3a). We found that the dislocation in



Figure 4. Electron beam irradiation assisted fabrication of a 2D Au membrane. (a) Free-standing SH 2D membrane surrounded by the $(1\overline{10})$ matrix. The black and blue lines delineate the lattices of the membrane and matrix, respectively. Three dislocations are identified at junctions of the neighboring "facets" of the membrane/matrix interface. Each yellow dotted circle marks a vacancy in the film. (b, c) Slow growth of the 2D membrane accompanied by the limited glide and climb of interface dislocations (shown by the red arrows). (b) Formation of a divacancy in the thin film. (c) Dynamic evolution of the divacancy via short-range diffusion. (d) Fracture of the 2D membrane left a void in the matrix. (e) Intensity profile along an array of atoms enclosed by the white box in b. The lower peaks (1 and 2) confirm the existence of a divacancy in the 2D membrane. (f, g) SH Lattices and the corresponding horizontal strain (ε_{xx}) maps acquired from geometric phase analysis before and after the formation of a divacancy in the 2D membrane. Localized tensile strain (indicated by the yellow arrow) was induced by the formation of divacancy, whereas slight compressive strain was retained among the 2D membrane. Scale bar: 1 nm.

the Au thin film can facilitate the heterogeneous nucleation of an embryonic 2D membrane at the incoherent twin boundary (Figure 3b), which is usually recognized as a fast diffusion path.³⁷ In addition, we observed the dislocation-mediated growth of this embryonic 2D membrane with increased load (Figure 3c), leading to disappearance of an adjacent nanotwin on the left (Figure 3d). The magnified HRTEM images in Figure 3e-i reveal a series of dynamic dislocation processes. In Figure 3e, a few dislocations were identified at the membrane/ matrix interface after the initial nucleation of an embryonic 2D membrane, and they served to accommodate a local lattice misorientation of about 6° between the embryonic membrane and surrounding matrix. Subsequently, the embryonic membrane grew in concert with the glide and climb of interface dislocations (indicated by arrows in Figure 3f), yielding a fully transformed SH structure (indicated by a perfect hexagon in blue). We also observed that climb of interface dislocations played an important role in the subsequent growth of the 2D membrane (Figure 3g-i), which accommodated lattice misfit and misorientation across the membrane/matrix interface. The increase in interface dislocations involved the insertion of atoms at the membrane/ matrix interface, further driving the growth of the 2D membrane. New interface dislocations often nucleated (Figure 3h, i) and thus facilitated the sinking of Au atoms via climb of these interface dislocations, thereby expanding the 2D membrane. Meanwhile, the dynamic exchange of atoms and resultant local lattice adjustment occurred frequently at the

membrane/matrix interface. For example, a dislocation dipole was nucleated and subsequently annihilated at the interface (see the two dislocations at the top right corner in Figure 3h, i), which induced a temporary local reorientation of the membrane lattice. Eventually, a fully formed SH monolayer was produced (Figure 3i). Consistent with our earlier result of production of a 2D Au membrane near a GB (Figure 2b), the atomic structure at the 2D membrane/matrix interface in Figure 3j exhibits misalignments of the edge-on (111) and (002) planes in the FCC Au matrix by about 10° and 5° with respect to the respective edge-on $\{10\overline{10}\}$ planes in the SH monolayer. Altogether, these results underscore the important role of dynamic dislocation evolution in the formation and growth of 2D Au membranes.

During *in situ* TEM experiments, electron irradiation under low dose rates can still promote atomic diffusion by enhancing the mobility of vacancies and sometimes can even create vacancies by knocking off atoms from the lattice.^{38,39} These processes can facilitate diffusive transport of atoms during the nucleation and growth of 2D Au membranes. Nonetheless, the applied tensile normal stress acts as the main driving force of film thinning for production of 2D Au membranes, whereas the electron irradiation effect on the growth process warrants further in-depth study in the future. In this work, we further explored the fabrication of 2D Au membranes via direct electron beam irradiation under high dose rates without mechanical loading. This process enabled the well-controlled fabrication of 2D Au membranes by tuning the dose rate of the electron beam. Figure 4 shows an example of irradiationassisted fabrication of a 2D Au membrane surrounded by (110)-oriented FCC Au film matrix. It is worth noting that although the fabrication of the 2D membrane was realized by focused electron beam with a high dose rate on the Au matrix, our subsequent TEM observation was carried out under a low dose rate to minimize the potential damage from the electron beam (see Methods). A hexagonal-shaped membrane with interface facets formed after high dose beam irradiation for tens of seconds. This 2D Au membrane has the same SH lattice and sharp interface configurations as those prepared by mechanical thinning (Figures 1-3), while the size of the membrane is typically smaller. Moreover, the two equivalent edge-on {1010} planes of the 2D SH membrane are aligned approximately with the edge-on (002) and $(11\overline{1})$ planes of the FCC matrix (with a misorientation angle $<1^{\circ}$), respectively, while the third $\{10\overline{1}0\}$ plane deviates by $\sim 8^{\circ}$ from the edge-on (111) plane (Figure 4a). Also observed in Figure 4a are the dislocations near intersections between neighboring interface facets. These dislocations moved much smaller distances (indicated by arrows in Figure 4b, c) compared with those during mechanical thinning. As a result, the size of the 2D Au membrane prepared via electron beam irradiation did not change much throughout our observation. In addition, a divacancy formed in the 2D Au membrane, probably due to the knock-on effect of electron beam (Figure 4b). The formation of this divacancy in the 2D membrane was confirmed by the intensity profile along the atom array (Figure 4e), which induced an evident localized tensile strain, whereas the rest of the membrane lattice retained a slight compressive strain (see Figure 4f, g). The divacancy appeared to move randomly by a few atom columns in less than a second (Figure 4b, c), which indicates its high mobility in the 2D Au membrane. Further irradiation resulted in abrupt fracture of the 2D Au membrane, leaving a nanosized pore in the film matrix (Figure 4d).

For most transition metals, their monolayer structures are predicted to be unstable because of a significant increase in energy per bond (from 3D bulk crystals to 2D membranes).³⁶ However, theoretical studies have demonstrated a strong propensity for the planar structure of Au,⁴⁰ which is attributed to its close-packed hexa-coordinate lattice with the maximum number of in-plane chemical bonds³⁶ and predominant relativistic effect.⁴¹ Nevertheless, fabrication of free-standing 2D Au membranes remains a challenge. The commonly used synthesis methods, including epitaxial growth and electron beam deposition, need a substrate (*e.g.*, noble metal or Si) to support and stabilize 2D membranes.^{19,24,42} The recent selfassembly of 2D membranes in the graphene pore is applicable to a wide range of materials, ^{25,26,43} but the membrane size is limited. In contrast, the mechanical thinning through a series of plastic deformation processes of displacive dislocation slip, atomic diffusion, and displacive lattice transformation, as demonstrated in this work, provides an effective approach to fabricate large-area free-standing single-atom-thick 2D membranes directly from bulk crystals. In the future, the properties of 2D Au membranes could be further tuned by adsorption of small molecules and functional groups; and as-fabricated freestanding Au membranes could be rolled into single-wall nanotubes.36

In fact, suspended one-dimensional Au nanostructures have already been fabricated in previous *in situ* TEM straining experiments. For example, fabrication of single-atom nano-

bridges⁴⁴ and multi-atom nanorods⁴⁵ has been demonstrated, pointing to possibilities of harnessing the strong Au bonding for creating low-dimensional materials. However, these onedimensional metallic nanobridges (or atomic contacts) can hardly remain stable because of the high energy per atom⁴⁶ and a lack of in-plane anchor or underlying substrate. In contrast, the film matrix in our approach provides an effective support to the 2D Au membrane (Figure 2), which exhibits high stability throughout the mechanical straining process. Moreover, the Au film matrix, in contrast to the supporting substrate with multicomponent elements, 24,26 can serve as a pure-atom reservoir to supply Au atoms for the growth of a 2D Au membrane as well as to deposit Au atoms removed from the membrane/matrix interface (Figure 3). This growth mechanism takes the advantage of low energy barriers for Au atoms moving on the Au film surface and fast atom diffusion associated with climb of interface dislocations, which are greatly enhanced in the ultrathin film with large surface area and small film thickness.^{47,48} Hence, the mechanical thinning approach can realize the fabrication of extremely thin metallic membranes, as demonstrated by the production of large-area, free-standing 2D Au monolayers in this work. Nevertheless, a trade-off exists between the area of 2D membrane and the loading rate. Under the current loading rate of $\sim 1 \times 10^{-3} \text{ s}^{-1}$, a steady growth of the 2D membrane can proceed via the lateral movement of steps on the membrane/matrix interface as facilitated by surface diffusion of atoms. However, the diffusion-mediated uniform thinning may not be enough to accommodate the local plastic deformation under high loading rates, such that microcracks tend to form at weak GBs, prohibiting the formation of 2D membranes. Therefore, mechanical loading with a proper loading rate was required to realize the stable nucleation and growth of 2D membranes. In addition, we have also fabricated free-standing 2D Ag membrane using the same method of mechanical thinning, which shed light on a broad application of this top-down approach. For other transition metals with higher energy barrier of surface diffusion,⁴⁹ the quality and size of the mechanically fabricated 2D membrane may be limited. Therefore, future studies are needed to improve the controllability of mechanical thinning by tuning the loading rate and temperature, etc., toward its application in other metallic systems. Moreover, the mechanical thinning approach could be potentially explored to produce nonmonoelemental 2D membranes in the future.

CONCLUSIONS

In conclusion, we have developed a top-down approach to fabricate free-standing 2D metallic membranes. Single-atomthick Au membranes are produced by mechanical thinning through the combined displacive and diffusive deformation processes at room temperature. Our *in situ* HRTEM observations show that lattice defects, including grain boundaries, twin boundaries and dislocations, can act as preferred sites of nucleation of 2D membranes. Fast atom diffusion at both the film surface and the membrane/matrix interface can facilitate the continuous growth of 2D membranes. These findings shed light on fabricating freestanding 2D metallic membranes from bulk crystals, and may have broad implications for the top-down fabrication of other types of 2D materials through extreme mechanical thinning and defect engineering.

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METHODS

In situ Fabrication of 2D Hexagonal Au Membrane. In situ nanofabrication of 2D Au membranes was carried out inside a Cscorrected FEI Titan G² 60-300 TEM operated at 300 kV, using a PicoFemto TEM electrical holder from Zeptools Co. Prior to the stress-mediated fabrication of 2D Au membranes, an Au bicrystal thin film consisting of a general GB was produced. First, two bulk Au rods (99.99 wt %, ordered from Alfa Aesar Inc.) with a diameter 0.25 mm were fractured by a ProsKit wire cutter to obtain clean fracture surfaces with numerous nanoscale tips. The two fractured rods were subsequently loaded onto the static and the probe sides of the TEM holder, respectively. Then, the Au rod on the probe side was moved by a built-in piezo-manipulator to contact with the rod on the static side of the holder. The two nanoscale tips were welded together in situ inside TEM by pre-applying a voltage of about -2 V on the nanoscale tip at the probe side. A bicrystal thin film with a general GB was formed due to misorientation between the nanoscale tips on the static and probe sides. During in situ straining, the Au rod on the probe side was controlled to move backward slowly to impose a tensile load at a constant velocity of ~ 0.005 nm s⁻¹, corresponding to a strain rate of $\sim 1 \times 10^{-3}$ s⁻¹. The weak GB region was largely deformed to accommodate the majority of the tensile strain applied on the thin film, such that it was continuously thinned down to a 2D membrane with an SH lattice structure. To minimize the irradiation damage on the Au thin film, a low beam intensity was used throughout the mechanical thinning process. In addition, the irradiation-mediated fabrication of 2D membranes without mechanical loading was carried out by converging the electron beam under the imaging mode and selecting an Au thin film with (110) zone axis on the static side of the holder. The irradiation dose $(1-2 \times 10^4 \text{ e}^-/\text{nm}^2 \text{ s})$ was carefully controlled based on sample thickness. The irradiated area was thinned rapidly by the intense knock-on electron beam, producing a 2D Au membrane embedded in an FCC Au matrix. After the formation of a thinned film, a low beam intensity was used to observe the structural evolution in the obtained products. The TEM video was recorded by a GATAN model 994 charge-coupled device (CCD) camera at a rate of ~0.3 s per frame.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.0c06697.

Stress-induced nucleation and growth of a 2D Au membrane at a triple junction of GBs; additional example showing the fabrication of a 2D Au membrane via mechanical thinning; nucleation and growth of a 2D Pt membrane at a crack tip; lattice structure comparison between the {0001} monolayer Au membrane and {111} FCC matrix; atomistic study of stacking sequence in free-standing double-layer Au membranes; in-plane fluctuation of Au atoms in the 2D membrane; Supplementary Method for atomistic modeling; Figures S1–S6 (PDF)

Movie S1, a large area of free-standing 2D SH Au membrane at a general GB in Au thin film produced by mechanical thinning; (MP4)

Movie S2, a free-standing 2D SH Au membrane at a triple junction in Au thin film produced by mechanical thinning (MP4)

AUTHOR INFORMATION

Corresponding Authors

Ting Zhu – Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States; Email: ting.zhu@me.gatech.edu Jiangwei Wang – Center of Electron Microscopy and State Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, P. R. China; orcid.org/0000-0003-1191-0782; Email: jiangwei wang@zju.edu.cn

Authors

- Qi Zhu Center of Electron Microscopy and State Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, P. R. China
- Youran Hong Center of Electron Microscopy and State Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, P. R. China
- **Guang Cao** Center of Electron Microscopy and State Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, P. R. China
- Yin Zhang Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States
- Xiaohan Zhang Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States
- Kui Du Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China; orcid.org/0000-0001-6698-3538
- Ze Zhang Center of Electron Microscopy and State Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, P. R. China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsnano.0c06697

Author Contributions

^TQ.Z., Y.H., and G.C. contributed equally to this work. J.W. designed the experiments and directed the project. Q.Z., Y.H., G.C. and J.W. conducted the experiments and analyzed the data. Y.Z., X.Z. and T.Z. conducted the modeling. Q.Z., J.W. and T.Z. wrote and revised the paper. K.D. and Z.Z. contributed to the data analysis and paper revision.

Notes

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