Tip-Based Nanomachining on Thin Films: A Mini Review

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Abstract

As one of the most widely used nanofabrication methods, the atomic force microscopy (AFM) tip-based nanomachining technique offers important advantages, including nanoscale manipulation accuracy, low maintenance cost, and flexible experimental operation. This technique has been applied to one-, two-, and even three-dimensional nanomachining patterns on thin films made of polymers, metals, and two-dimensional materials. These structures are widely used in the fields of nanooptics, nanoelectronics, data storage, super lubrication, and so forth. Moreover, they are believed to have a wide application in other fields, and their possible industrialization may be realized in the future. In this work, the current state of the research into the use of the AFM tip-based nanomachining method in thin-film machining is presented. First, the state of the structures machined on thin films is reviewed according to the type of thin-film materials (i.e., polymers, metals, and two-dimensional materials). Second, the related applications of tip-based nanomachining to film machining are presented. Finally, the current situation of this area and its potential development direction are discussed. This review is expected to enrich the understanding of the research status of the use of the tip-based nanomachining method in thin-film machining and ultimately broaden its application.

Keywords Atomic force microscopy · Tip-based nanomachining · Thin films · Nanostructure · Application

1 Introduction

Nanostructures have shown an increasing potential in the field of nanooptics [1], nanoelectronics [2], and nanofluidics [3]. Methods such as ion-beam lithography [4], electron-beam lithography [5], and nanoindentation lithography [1] have been used to fabricate nanostructures. Atomic force microscopy (AFM) tip-based nanomachining (TBN), in particular, offers several advantages, including nanoscale manipulation accuracy [6], atmospheric requirement operating environment [7], and low-cost maintenance. Different from bulk samples, thin-film materials exhibit special physical and chemical properties that are affected by size; such materials have been widely used as etch masks [8], data storage media [9], sacrificial layers for lift-off [2], and so

forth. TBN shows a high degree of applicability in machining nanopatterns on various types of thin films, including polymers [8], metals [10], and two-dimensional materials (2DMs) [11, 12].

Severe tip damage occurs during direct machining on hard substrates, such as silicon (Si) or silicon dioxide (SiO₂). Therefore, machining on soft polymer films that are spin-coated on the surface of hard substrates first and subsequently transferred to the target hard substrates via etching may be a good approach to reducing tip wear. Nanopatterns of varying dimensions, including nanopits/dots [9, 13], nanogrooves/lines [14, 15], and bundles [16], have been achieved on polymer films via TBN and have been applied to data storage [17], etch masks [18], sacrificial layers for lift-off [19], and so on. As for machining on metal films, numerous TBN methods have been employed, and they include constant force mode [20], dynamic plowing lithography (DPL) [21], phase mode nanofabrication [22], vibration-assisted nanomachining [23], AFM electric lithography [24], and coupling AFM lithography [25]. Reports have shown that 2DMs demonstrate immense potential in the fabrication of nanobiosensors [26] and nanoelectronic sensors [2]. However, only a few studies have utilized TBN for

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direct machining on 2DMs in contact mode. Most scholars have used AFM tips for sliding on 2DMs to investigate their frictional behavior [27–30] and their possible application to the reduction of friction and wear [31, 32]. Much effort is needed to realize the industrialization of 2DMs.

In the present work, the current status of the application of the TBN method to machine on thin-film materials is reviewed. The thin-film materials include polymers, metal and metal-based thin films, and 2DMs. Nanostructures fabricated on films by using heated AFM tip-based thermomechanical lithography are also presented. At the end of the article, a summary of the current study and possible future directions are discussed.

2 Machining on Polymer Thin Films

Polymer thin films are widely used as an anti-etching resist because of their stable machining characteristics, low costs, and good light transmittance. They are usually obtained by spin coating. Moreover, the structures machined on polymer thin films can be easily transferred to other substrates. Traditional polymers include polymethyl methacrylate (PMMA), polystyrene, and polycarbonate (PC). To date, nanodots/pits, nanogrooves/lines, and even three-dimensional (3D) complex structures have been achieved on these films by using the TBN method. Various types of nanomachining methods based on tips involving static scratch [33–35], DPL [9, 13, 14, 36, 37], and vibration-assisted approach [22, 38–46], especially the ultrasonic vibration-assisted (UV-assisted) method, have been used to machine nanopatterns on polymer films (Table 1). Heated tips have been found to offer important advantages in machining polymer film materials. They also

lead to different results when the material properties are changed. Specifically, the heat from the tip can soften the sample surface to induce material deformation or thermal decomposition.

Tip wear may be caused when the tip is used to machine structures on hard materials, such as Si and SiO₂. Therefore, machining patterns first on a soft resist (e.g., polymers) and subsequently transferring them to the target substrate may be a good solution. As an excellent etch mask, nanopatterns on polymer films can be transferred to other materials via etching and lift-off and can be applied to the field of nanooptics. Recently, Kim et al. fabricated plasmonic nanostructures, such as nanodisks and nanotriangle arrays, on a glass substrate by combining nanotip indentation lithography (NTIL) and wet etching [1].

As shown in Fig. 1a, a two-layer polymer film was spin-coated on the substrate; the top one is polymer B that acted as the etch mask, while the bottom layer is polymer A that served as the sacrificial layer. They indented polymer B by using the AFM tip with a conical shape or pyramidal shape to form the corresponding shape of a nanohole. Then, the sample was soaked into AZ 300 MIF Developer to etch the sacrificial layer. Thereafter, a layer of Au measuring around dozens of nanometers was deposited on the sample surface. The bilayer of the polymer film was removed via lift-off, and the plasmonic nanostructures were transferred to the glass substrate successfully, as shown in Fig. 1b–e. These Au nanostructures exhibited excellent plasmonic properties (Fig. 1f–h) and thus presented immense potential in the field of nanooptics. Although the operation of this method is relatively complex, it can guarantee nanopatterns with highly precise dimensions and shape controllability and reproducibility; it can also adequately reduce tip wear. Thus, this

Table 1 Use of AFM tip-based nanomachining methods for polymer films

Nanostructures	Mechanism	Methods	References
Nanodot arrays	Nanoindentation		
	Overlapping of nanogrooves in different directions	DPL	[13, 36]
Nanopits	Nanoindentation	DPL/NTIL/ t-SPL	[1, 9, 37, 47, 48]
	Single-scratch	t-SPL	[6]
Nanogroove/channel	Force control scratch	DPL	[14, 36]
		Static scratch	[33–35]
	Thermomechanical lithography	t-SPL	[49]
	Vibration-assisted	UV-assisted	[22, 38–42]
		Others	[43]
Nanoline	Thermomechanical lithography	t-SPL	[50–52]
3D nanostructures	Vibration-assisted	UV-assisted	[38, 44–46]
	Thermomechanical lithography	t-SPL	[18, 52–55]
	Overlapping of nanogrooves in the same direction with interval	DPL	[13]

Fig. 1 Fabrication of plasmonic nanostructures on glass substrate through the combination of nanotip indentation lithography (NTIL) and wet etching: **a** the schematic of using NTIL to fabricate plasmonic nanostructures; **b** AFM and SEM images of nanodisk plasmonic nanostructures; **c** AFM and SEM images of nanotriangle plasmonic nanostructures; **d** bright field optical microscopy images of

eight nanodisk arrays and enlarged view of the selected areas; **e** diameters of the nanodisks (*top*) and their coefficient of variation (CV); **f** and **g** dark-field images of various nanodisk arrays prepared with composite materials of Ag (**f**) and Au (**g**); **h** the scattering spectrum obtained experimentally. Republished with permission from Ref. [1], Copyright 2021 RSC Pub

technique is expected to be used widely in the fabrication of structures on hard substrates, such as Si and glass.

On the surface of polymer films, nanodot arrays can be fabricated via tip nanoindentation directly or through the overlap of two machined nanogrooves by a single scratch performed twice in different directions [13, 36]; a third scratch may be employed to improve density [13]. Nanopits have been obtained using a tip that is pressed into a sample, similar to nanoindentation [1] or DPL based on tapping [9, 37]. Some scholars have found that heated tips can modify polymer surfaces by changing their properties by heating. Chang et al. recently proposed the use of thermomechanical lithography to regulate the formation of nanopatterns, such as nanowires, nanogrooves, and

nanopits, on PMMA films via single scratch [6]. Nanopits were machined on the basis of a stick-slip mechanism, as shown in Fig. 2a. They found that the formed nanopits resulting from the material used are softened by tip heating; meanwhile, a previous study reported that no nanopits are machined when samples are not heated [43]. As shown in Fig. 2b–d, nanopits with various dimensions can be achieved by adjusting the coupling of scratching velocity and heated temperature to change the heat transfer between the tip and the film. In addition, nanopit arrays can be machined in one single scratch with a velocity of several to dozens of microns per second. Therefore, this method is expected to be widely used to fabricate nanopits with high efficiency.

Fig. 2 Fabrication of nanopit array on PMMA film using thermo-mechanical nanolithography: **a** nanopit and its cross section in the direction of scratching; **b** nanopit array formed at 170 °C and 0.1–3.4 μm/s; **c** nanopit array machined at 200 °C and 0.1–3.4 μm/s; **d** nanopit array formed at 230 °C and 4.4–40 μm/s. Reprinted with permission from Ref. [6], Copyright 2021 Elsevier

Although various nanopatterns have been achieved on traditional polymer films, limitations such as poor dimension consistency, bad machining quality, elastic recovery, and pile-up have been observed. Therefore, scholars have been focused on identifying polymers with good machining quality. In 2010, Pires et al. realized patterns at a half-pitch down to 15 nm without proximity corrections on a type of molecular glass resist by using a heated AFM tip [52], the machining accuracy of which is comparable to that of electron beam lithography. The molecular glass resist was specifically tailored in the lab, and its hydrogen bonds were

broken down by heating at several microseconds and evaporated to the environment for complete removal. The research results were published in *Science* and have since attracted increasing attention from scholars. However, this material is difficult to synthesize; thus far, it has been replaced by polyphthalaldehyde (PPA), which can be purchased easily.

PPA is a type of thermal-induced depolymerization polymer, and the material of which can be removed during machining using a heated tip. As an etch mask, PPA performs well in acting as a resist for thermal scanning probe lithography (t-SPL). In this process, polymer chains are broken down into small molecules at high temperatures and evaporate into the environment to realize the removal of the sample material. This approach is thus a good solution for eliminating pile-up in machining on traditional polymers. Given these strengths of t-SPL, scholars have attempted to broaden its application by integrating it with other etching techniques. Nanopatterns are machined first on a PPA surface by using a heated AFM tip and are then transferred to the target substrate through etching. Aminzadeh et al. fabricated a 3D Fresnel zone plate on a PPA film that was spin-coated on a Si_3N_4 substrate first and then transferred to the underlying Si_3N_4 surface via reactive ion etching (RIE), as shown in Fig. 3a [18]. By using a heated tip, Rawlings et al. formed 30-nm-deep Gaussian-shaped twin microcavities on PPA, etched them into SiO_2 , and then embedded them in a distributed Bragg reflector stack (Fig. 3b) [53]. Photonic molecules were created by adjusting the distance between the twin microcavities. In addition, the combination of t-SPL and etching was found to have potential applications in data storage and recording. As shown in Fig. 3c, the archival data were first patterned on PPA and then transferred to a poly-Si- SiO_2 substrate through RIE to realize the permanent storage of data [47]. This study provided a simple method for storing data with high efficiency, and the method is expected to be widely used in the data recording field. Attempts have been made to fabricate electron microscopy phase masks by using focused (Ga^{+}) ion beam milling of films. However, ion implantation may influence the phase masks. To rise from the limitations, Hettler et al. proposed using t-SPL integrated with RIE to fabricate phase masks, as shown in Fig. 3d [54]. They achieved a highly accurate control of patterns and depths and thus predicted the wide use of the method in the future. Cheong et al. fabricated lines on a PPA film with a half-pitch of 27.5 nm and then transferred the pattern into a Si substrate with excellent accuracy via RIE (Fig. 3e) [50]. In the following studies, Cho et al. reduced the half-pitch of lines to sub-10 nm (Fig. 3f) and thus greatly improved the resolution of patterns fabricated by t-SPL [51].

Thus far, t-SPL has been utilized to fabricate extremely tiny structures with special properties because of its sub-10-nm resolution. Moreover, t-SPL integrated with etching has been utilized to prepare micro/nanoelectronic and optical

Fig. 3 Applications of PPA as an etch mask. **a** 3D Fresnel zone plate fabricated on PPA film and transferred to Si_3N_4 via reactive ion etching (RIE). Reprinted with permission from Ref. [18]. Copyright 2019, American Vacuum Society. **b** Gaussian-shaped twin micro-cavities machined on PPA and transferred on SiO_2 to create photonic molecules. Reprinted under CC BY 4.0 License from Ref. [53], Copyright 2017 Springer Nature. **c** Archival data patterned on PPA and transferred to poly-Si- SiO_2 substrate through RIE to realize the permanent storage of data. Reprinted from Ref. [47], with the permis-

sion of AIP Publishing. **d** Using thermal scanning probe lithography integrated with RIE to fabricate phase masks. Reprinted with permission from Ref. [54], Copyright 2019 Elsevier. **e** Dense lines written on PPA with a half-pitch of 27.5 nm and then transferred into Si with excellent accuracy via RIE. Reprinted with permission from Ref. [50]. Copyright 2013 American Chemical Society. **f** Fabrication of Si nanowire with a half-pitch of sub-10 nm. Reprinted with permission from Ref. [51]. Copyright 2017 American Chemical Society

devices, as introduced in the following section. Cheng et al. used an ultra-sharp heated tip with a radius of 2.5–3.5 nm

to create an indentation on a PPA film to generate an ultra-small sharp hole, which served as the mold for preparing Ag

electrodes for use in advanced memristor devices (Fig. 4) [48]. The sharp hole pattern was transferred to the underlying SiO_2 by RIE. After metal deposition, the Ag electrode embedded in SiO_2 was formed. The distance between the Ag electrode and the vertical Pt electrode was only 1 nm, which meets the requirement for reliable switching OFF/ON control even at voltages as low as 100 mV. This application of t-SPL machining may inspire the preparation of other similar electronic devices. Another typical example is the combined use of t-SPL and laser writing to write patterns on PPA that are then transferred to the SiO_2 surface via RIE to fabricate silicon point contact quantum-dot transistors [56]. This method takes full advantage of the 10-nm high resolution of t-SPL and the high efficiency of laser machining for large-area structures. It is expected to be applied broadly in the fabrication of large-scale nanodevices.

Nanostructures with a high aspect ratio were fabricated in a study by combining t-SPL and dry etching [49]. As shown in Fig. 5a, a nanogroove with a depth of 38 nm was first machined on 73-nm-thick PPA by t-SPL. The residual PPA layer was then etched through O_2 plasma to expose the underlying SiO_2 substrate. The pattern was transferred to Si via dry etching at a depth that was 4 μm and 100 times that on the PPA. The depth was thus greatly improved. Through dry etching, Lisunova et al. transferred a 3D nanostructure machined by t-SPL on PPA to Si at a depth of 45 nm (Fig. 5b) [55]. The nanopattern on Si reached 420–480 nm in depth. These examples demonstrate the combination of t-SPL and etching as a promising technique to fabricate structures with high aspect ratios. Moreover, they show that the use of a heated tip to machine high-resolution patterns on PPA resist has become a popular technique that is expected to be applied widely in the future.

3 Machining on Metal and Metal-Based Thin Films

Various AFM tip-based nanomachining methods have been used to fabricate nanostructures on metal films. These methods include scratching based on a constant force mode, DPL, phase mode nanofabrication, vibration-assisted nanomachining, AFM electric lithography, and coupling AFM lithography (Table 2). Thus, patterns are machined on metal films to mainly serve as a mask for etching. Meanwhile, machining on metal-based thin films mainly promotes these materials' wide applications according to their special physical characteristics.

When scratching based on the constant force mode, the machined depth is dependent on the force, therefore, the machined depth can be controlled with high precision by adjusting the normal load. In addition, the constant force

machining system does not require leveling, particularly, the machining accuracy on the curved surface can easily reach less than 100 nm. However, the machining system based on the constant force mode is complex and requires force feedback system to realize force control. Moreover, another disadvantage is that it is hard to machine structures with high aspect ratios on metal films using the constant force mode due to its lower stiffness. The tip wear may also be a point of concern due to the relatively large hardness of metal films.

However, DPL may be a good solution to reduce the tip wear to a certain degree when machining on the metal film. This is because DPL is based on the tapping mode, and cantilever vibrates at resonance frequency during machining to realize intermittent contact between tip and sample. Simultaneously, using the DPL method, the cantilever of the tip is driven to oscillate at several thousands of Hertz, which results in the tip interacting with the sample surface many times in a short period. Therefore, the DPL method can machine nanostructures on the metal film with high throughput. Moreover, structures with characteristic sizes ranging from a few nanometers to tens of nanometers on the metal film can be easily achieved via DPL method. When using the DPL method to machine on the metal film, it is hard to achieve patterns with larger depth due to the relatively large hardness of metal films and the relatively light force between the tip and sample. Therefore, this method is usually to be used to machine on the polymer film, while there are few reports on metal films.

In the phase mode nanomachining method, the phase feedback signal from cantilever was extracted by the lock-in amplifier, and then the feedback signal was sent to the PID controller to compare with the preset value. The phase response signal will be affected by the machined depth; therefore, the machined depth can be regulated by real-time monitoring of the phase feedback signal. Therefore, the machined depth can be monitored accurately to avoid the tip from penetrating the film completely and contacting the underlying hard substrate, which can protect the tip from wearing as enough as possible. Furthermore, based on the phase mode, the machining results are not affected by the debris and pile-up, which overcomes the limitation of constant force mode. However, this machining system requires phase response as feedback signal to achieve closed-loop control, the configuration of which may be a little complex.

The vibration is introduced to achieve larger depth even under a relatively small force, and increase the material removal efficiency. Another strength of vibration-assisted nanomachining method is that the width of structure can be controlled by adjusting the vibration amplitude in the x - y plane. Similar to DPL, the z -axis high-frequency vibration machining method makes the probe in intermittent contact with the sample surface, which can reduce

the tip wear and increase the material removal efficiency as well.

Compared to traditional AFM mechanical machining, AFM electric lithography shows potential in improving material removal efficiency and the quality of machining structure on the metal film owing to the existence of both bias voltage effect and the force effect. However, it is difficult to precisely control the machined depth due to the complex coupling effect of bias voltage and force.

The coupling AFM lithography is developed to machine the structures with deeper area through applying both force and bias voltage simultaneously. It has been demonstrated that under the same machining condition, the patterns machined by the coupling AFM lithography are much deeper and with lower roughness than that of the AFM mechanical lithography and the AFM electric lithography. However, the weakness of this method is that the consistency and stability of machined structure still need to be further improved.

The metal film is a good mask for etching because of its excellent etching resistance, and the nanopatterns can be easily transferred to other substrates for fabricating structures with high aspect ratios [38]. Metal thin films are usually prepared by electron beam deposition and magnetron sputtering. The adhesion between films and various substrates tends to differ, and the differences greatly affect the machining results when TBN is used. In addition, considerable silicon tip wear can be observed when scratching on metal films because of the materials' high hardness. Therefore, a diamond tip is usually employed by scholars for direct machining. Peng et al. scratched distributed submicron grooves with good machining quality on an Al film by using a diamond tip; these patterns can be transferred to Si to fabricate structures with high aspect ratios [57]. Scholars have recently found that local stress exerts an obvious effect on the polarization of ferroelectric materials [59] and that it may promote the application of such materials to data storage. Zhang et al. fabricated a nanocapacitor array with individually addressable ferroelectric elements on a BiFeO₃-Cr-Au film [60] and reported its possible use in the field of storage data in the future. Another work described the machining of The University College Dublin's harp logo, a 100-nm nanoisland array comprising circles with a diameter of 2.5 μm and parallel lines, on ferroelectric films [60].

However, the size of patterns machined using a diamond tip may be too large to meet the demand of small structures in some specific applications. A possible solution for this is to use DPL to machine ultra-small patterns on metal films. DPL is based on the tapping mode. In the process, the cantilever vibrates at a resonance frequency during machining to realize intermittent contact between the tip and the sample and thereby reduce tip wear to a certain degree. Thus, this method can realize high-resolution nanomachining. Schumacher et al. employed DPL to machine 5.4-nm-deep holes

and 50-nm-wide grooves on a Pt/Co/Pt trilayer [21]. These patterns served as mesoscopic defects to modulate the propagation of domain walls in a magnetic memory prototype, as well as adjust and optimize domain shapes during the reversal of magnetization. This research laid the foundation for the use of TBN to control the reversal of magnetization at the microscopic scale.

As a type of novel and advantageous nanomachining method, nanomilling reaches great depths even under a relatively small force, and the material removal efficiency can be increased. Moreover, the width of a structure can be controlled by adjusting the vibration amplitude in the x - y plane. Similar to DPL, the z -axis high-frequency vibration machining method makes the probe come into contact with the sample surface intermittently, so as to reduce the tip wear and increase the material removal efficiency. Zhang et al. introduced ultrasonic vibration to assist nanomachining on Al films [39]. They fixed an Al film on the surface of a nanovibrator, which vibrated in the z -axis at 3 MHz to regulate the machined depth; in the x - y plane, it vibrated at 4 kHz, which was set to adjust the width of the machined patterns. They found that the normal and lateral forces during UV-assisted nanomachining are significantly lower than those of the traditional setpoint-force control. Hence, the method shows great potential in reducing tip wear. In addition, a greater reduction in tip wear has been observed when using the UV-assisted nanomachining method to fabricate patterns on PMMA films than when using the traditional setpoint force control. The mechanism of tip wear reduction can be explained as follows: only a certain amount of the material determined by the feed is removed at one vibration period in the x - y plane; this condition reduces the contact force between the tip and the sample dramatically. Furthermore, this method can yield structures in the nanometer scale that are much smaller than those machined using a diamond tip. It is also able to meet the requirement of small-sized patterns. Therefore, the UV-assisted nanomachining method is expected to be widely used in the machining of nanostructures on metal films. Following the study of Zhang et al. [39], Park et al. employed a vibration-assisted nanomachining method to fabricate nanogrooves on an Au film by using a diamond tip [23]. As shown in Fig. 6a, they fixed the vibration stages on top of the AFM device to realize the excitation of the sample in the x , y , and z directions. The groove depth was controlled by regulating the amplitude in the direction of the z -axis. Figure 6b illustrates the motion of the tip when machining. Comparing Figs. 6c and d indicate that the vibration-assisted nanomachining method, relative to the approach without vibration, can increase the machining depth while reducing the interaction force. Moreover, the vibration-assisted nanomachining approach is a good solution for fabricating patterns on metal films, as it can balance the size of the structure and tip wear.

Fig. 4 Application of PPA as an etch mask in fabricating extremely tiny structures: employing heated tip to indent an ultra-small sharp hole with a radius of 2.5–3.5 nm on PPA that serves as a mold for

preparing Ag electrodes of advanced memristor devices. Reprinted under CC BY 4.0 License from Ref. [48]. Copyright 2019 Springer Nature

In addition, multiple furrows [20] have been machined on Al films, and vector scan method-based scratching has been applied to Ni–Fe films to fabricate nanoconstriction [58]. However, in using the aforementioned force control method, one cannot easily determine whether the film is cut through or not. Moreover, the direct contact between the tip and the substrate leads to severe tip wear and undesired machining results. To address this limitation, a previous study proposed the phase method and obtained nanogrooves with desirable depths on Au thin films [22]. In the study, a control loop based on phase mode was built for machining on the sample (Fig. 7a). The phase feedback signal from the cantilever was extracted by a lock-in amplifier, and the feedback signal was sent to the PID controller to be compared with the preset value. The phase response signal was found to be affected by the machined depth; therefore, the machined depth was regulated by performing a real-time monitoring of the phase feedback signal. Figure 7b shows that the machined depth

on the Au film matched the theoretical model well and that the machining depth was accurately controlled. The results also indicated the feasibility of using this method to predict machined depths without imaging. The phase mode nanomachining approach exhibits great potential in predicting machined depths and may thus be widely used as a type of nanomachining method for metal films with minimal tip wear.

In addition to using an AFM tip to machine directly on metal films, other types of energy, such as electric field, have been introduced to facilitate nanomachining. In an existing study, square and “V” patterns were machined on a Cu film under the effect of force and bias voltage via AFM electric lithography [24]. Moreover, 2.5D square patterns, which showed a larger depth and lower surface roughness than those machined by AFM mechanical lithography, on Pt and Cu films were obtained using the

Fig. 5 Application of PPA as an etch mask in fabricating nanostructures with high aspect ratios. **a** Depth of groove on Si amplified to more than 100 times that on PPA via the combination of etching and t-SPL. Reprinted with permission from Ref. [49], Copyright 2017

Elsevier. **b** Depth of 3D structure amplified through etching to around ten times that of the structure originally machined on PPA by thermal scanning probe lithography. Reprinted with permission from Ref. [55], Copyright 2018 Elsevier

Table 2 TBN methods for machining on metal films

Methods	Mechanism	Structures	References
Force mode machining	Maintaining force constant	Submicron grooves	[57]
		Multiple furrows	[20]
		Nanogrooves	[58]
DPL	Tip vibrates at high frequency to remove the material	Nanometer-deep holes	[21]
		Nanogrooves	[21]
Phase mode machining	The phase response of the cantilever is used to modulate the machining force to achieve the desired machined depth	Nanogrooves	[22]
Vibration-assisted nanomachining	External vibration actuates the work piece in elliptical motions	Nanogrooves	[23, 39]
AFM electric lithography	Applying bias voltage and force to realize patterning	“V” word patterns	[24]
Coupling AFM lithography	Material is removed by the coupling effects of mechanical force and electric field	2.5D square patterns	[25]

coupling AFM lithography, which applies force load and bias voltage simultaneously [25].

4 Machining on 2DMs

Since the first successful separation of graphene in 2004 [61], 2DMs such as graphene have become a research hotspot owing to their unique properties in electricity, magnetism, heat, force, and light [62, 63]. AFM is widely used to investigate the friction and wear characteristics

of 2DMs or cut them into desired patterns on the basis of mechanical lithography because of its nanoscale machining accuracy. Heat [64–66] and pressure [67] have been integrated into the AFM tip to actuate a chemical reaction on 2DMs and thereby realize patterning. The relevant research status is summarized in Table 3.

4.1 Machining Based on Traditional AFM Tip

This section mainly introduces a probe that is applied directly to the film surface. On the one hand, 2DMs were cut into preset shapes via mechanical machining. On the

Fig. 6 Nanomachining based on vibration-assisted method: **a** schematic of machining equipment; **b** schematic of tip motion; **c** machining results with no vibration; **d** machining results with vibration in

the x – y plane at 265 Hz and in the z -axis at 10 kHz. Reprinted with permission from Ref. [23], Copyright 2014 Elsevier

other hand, an AFM tip was used for sliding on the 2DMs to reveal their friction and wear characteristics.

4.1.1 Mechanical Cutting of 2DMs

Graphene has shown huge potential in nanosensors [68–70], field-effect transistors [71], solar cells [72], and

others. However, the lack of a bandgap in graphene limits its application in the preparation of traditional semiconductor devices. Therefore, breaking the bandgap of graphene is important in extending its application. The electrical characteristics of graphene are related to its configurations. If the graphene can be cut into a desired shape, then it exhibits semiconducting properties. Zhang

Fig. 7 Nanomachining based on phase mode: **a** schematic of machining; **b** machined depth on Au and PS. Reprinted with permission from Ref. [22], Copyright 2017 Elsevier

Table 3 Using TBN for machining on 2DM films

Methods	Research details	Mechanism	Classification	References
AFM tip-based nanomachining	Mechanical cutting of 2DMs	Cutting 2DMs into desired shapes under force	Monolayer graphene	[11]
			MoS ₂	[12]
	Study of friction and wear characteristics	Using AFM tip for sliding on 2DMs	Interplanar sliding friction between 2DMs and nonlayered materials	[32]
			Influence of fold deformation on real contact area and friction	[29, 30, 76, 81–83]
			Tribological properties of graphene in liquid	[27, 28]
			Effect of surface functional group modification on the friction properties of graphene	[84–87]
			Effect of substrate on the friction of graphene	[88–90]
			Study on wear properties of graphene	[91–94]
Heated AFM tip-based nanomachining	Thermo-induced material denaturation	The heat field was introduced to drive the occurrence of chemical reactions on the surface of 2DMs	Conversion of GO to rGO	[65, 66]
			Conversion of GF to rGF	[64]

et al. conducted a cutting experiment on monolayer graphene using an AFM diamond tip with scan angles of 60° and 90° to investigate the relationship between the cutting force and the lattice orientations of graphene. They cut the monolayer graphene into nanopatterns of various shapes, including circles, squares, and ribbons [11]. Li et al. compared the fabrication results of nanogrooves on molybdenum disulfide (MoS₂) by using the phase and force modes (Fig. 8). They verified the effectiveness of the phase mode-based fabrication technique in layer control and debris avoidance [12].

As for its application, graphene has been employed to prepare nanoelectronic devices because of its excellent electrical conductivity. Graphene interdigitated electrodes have been achieved by using AFM to cut graphene according to the designed machining paths; the method provides a flexible approach to preparing single-walled carbon nanotube-graphene field-effect transistors [73–75]. Although the AFM tip for machining on 2DMs has been used in certain applications, its industrialization will take time.

Fig. 8 Fabrication of nano-grooves on MoS₂ using phase mode and force mode: **a** and **b** phase-mode fabrication; **c** and **d** force-mode fabrication. Reprinted with permission from Ref. [12], Copyright 2018 Elsevier

4.1.2 Friction and Wear Characteristics

In 2010, Lee et al. first characterized the friction properties of 2DMs, such as graphene, MoS₂, and hexagonal boron nitride (h-BN) [76]. Their experimental results showed that although these 2DMs are only a few atomic layers thick, they have the same friction reduction effect as bulk lubricated materials. The excellent mechanical and tribological properties of 2DMs require further study. Meanwhile, a series of unique frictional behaviors and mechanisms of 2DMs have been successively discovered and reported [77–80]. For example, an AFM tip was used to study the friction and wear properties of 2DMs, such as graphene, in nanoscale. Herein, six aspects of the existing research about the friction and wear properties of 2DMs related to the use of AFM tips are introduced: the interplanar sliding friction between 2DMs and nonlayered materials, the influence of fold deformation on the real contact area and friction, tribological properties of graphene in liquid, the effect of surface functional group modification on the friction properties of graphene, the effect of substrates on the friction of graphene, and wear properties of graphene.

The interplanar sliding friction phenomenon between 2DMs and nonlayered materials has been studied. The experimental study of Kawai et al. showed that the superlubrication properties between layers of non-commensurate graphene could also be extended to other crystalline materials. They prepared a regular graphene nanoribbon on the surface of Au (111) and anchored the ends of the graphene nanoribbon using the AFM tip in a low-temperature and ultra-high-vacuum environment. Then, the graphene

nanoribbon was dragged to reciprocate the motion on the surface of Au (111) by the probe (Fig. 9a). Through the real-time measurement of the tangential force of the probe, they found that the static friction and dynamic friction between the nanoribbon and Au (111) were less than 100 pN (Fig. 9b). The stick-slip phenomenon in the solid-solid connection of the quasi-transmission system was also observed during the sliding process (Fig. 9c) [32].

As 2DMs are only a few nanometers thick, their out-of-plane bending stiffness is very low. When the AFM tip slides on the 2DM surface, it can easily be sucked up to generate puckering under the action of van der Waals force. Lee et al. used AFM to characterize the frictional properties of several mechanically stripped 2DMs, such as graphene, h-BN, and MoS₂ (Fig. 10) [76]. Their experimental results revealed for the first time that the surface friction of 2DMs on weakly adhered substrates is strongly dependent on the number of molecular layers. That is, the greater the number of layers is, the thicker the sample and the smaller the surface friction resistance will be. When the number of molecular layers is greater than four, the surface friction properties tend to be similar to those of bulk materials (Fig. 10d). This trend is independent of the applied pressure load, scanning speed, and probe material [76]. Following the study of Lee et al., Deng et al. employed AFM to measure the friction properties of graphene on a SiO₂ substrate, and their experimental results also reproduced the trend of friction reduction with the increase of graphene layers [81]. Paolicelli et al. characterized the friction of graphene in the atmosphere, dry nitrogen, and vacuum, and their results showed that the variation trends of the graphene surface friction with the number of

Fig. 9 Using AFM tip to study the interplanar sliding friction between two-dimensional materials and nonlayered materials: **a** graphene nanoribbon sliding on Au (111) surface; **b** relationship between static friction and length of graphene nanoribbon; **c** fre-

quency variation of graphene nanoribbon when reciprocating sliding at different pull-off heights. From Ref. [32]. Reprinted with permission from AAAS

layers were similar in different atmospheres [82]. In addition to causing the friction of graphene surface to vary with the number of sample layers, the out-of-plane folds in graphene contact sliding also provide its surface friction a unique anisotropy. The correlation between the friction and wrinkles on the surface of graphene has been revealed using AFM tips [30]. Choi et al. developed a method for quickly determining the orientation of the wrinkles on the graphene surface by using the longitudinal force scanning model of AFM, thereby providing a new idea to study the deformation behavior of graphene wrinkles [29].

Although humidity exerts a significant effect on frictional behavior at the macroscale, its effect on the frictional behavior of 2DMs at the nanoscale remains unknown. To address this problem, Ye et al. used an AFM tip in their study of the friction of submerged graphene and found that nanoscale friction exhibits hysteresis in the process of normal load loading and unloading (Fig. 11a) [27]. They also reported that as long as water molecules exist, the hysteresis of friction occurs; the degree of hysteresis depends on whether the graphene surface is hydrophilic or hydrophobic (Fig. 11b), i.e., the contact angle of the surface (Fig. 11c). The authors

Fig. 10 Relationship between friction and number of layers of layered two-dimensional material (2DM): **a** optical microscope images; **b** AFM topography; **c** friction images; **d** friction varying with the number of 2DM layers. From Ref. [76]. Reprinted with permission from AAAS

also systematically analyzed the influence mechanism of humidity in combination with molecular dynamics. Vilhena et al. used an AFM tip to slide on graphene that was fully immersed in water to study the effect of humidity on its friction properties [28]. The subaqueous atomic-scale stick-slip curve was achieved in water, and the result showed a high agreement with that measured under ultra-high vacuum conditions (Fig. 11d). Hence, friction force microscopy in water may serve as an alternative to ultra-high vacuum measurement. The results demonstrated that water plays a purely stochastic role in the friction production process. In sum, humidity does not seem to have a significant effect on the friction of 2DMs at the nanometer scale.

Surface chemical modification and functionalization are important means to regulate the physical properties of 2DMs

[95–97]. The friction of graphene treated by perfluorination [84–86], hydrogenation [86, 87], and oxidation [86] has been investigated. 2DMs are generally prepared through mechanical exfoliation from flakes or via chemical vapor deposition, and they can be transferred to various types of substrates. The interaction between 2DMs and substrates can affect the continuous deformation of 2DMs and, subsequently, their frictional behavior. Many scholars have applied AFM to explore the influence of substrates on the friction characteristics of the graphene surface [88–90]. As a potential atomically thin solid lubricant, 2DMs have attracted much attention for their ability to resist wear during friction sliding. Therefore, the wear resistance test has been conducted via AFM tips on 2DM surfaces [91–94].

Fig. 11 Tribological properties of graphene in liquid. **a** Load-dependent hysteresis of friction in graphene. Reprinted with permission from Ref. [27]. Copyright 2016 American Chemical Society. **b** Simulation of load-dependent friction under various environments. Reprinted with permission from Ref. [27]. Copyright 2016 American Chemical

Society. **c** Simulation of contact angle under loading and unloading. Reprinted with permission from Ref. [27]. Copyright 2016 American Chemical Society. **d** Friction behavior of submerged graphene. Reprinted with permission from Ref. [28]. Copyright 2016 American Chemical Society

2DMs with a layered structure generally form a planar layer through strong 2D (or quasi-2D) chemical bonds, and their in-plane strength and surface chemical stability are generally high. Thus, the surface lubrication effect is obvious and exhibits huge potential in reducing friction. Zhang et al. utilized an AFM tip for sliding on mica and monolayer MoS_2 to investigate the friction behavior and found that the surface friction of monolayer MoS_2 can be reduced by about 30% relative to that of a mica substrate [86].

4.2 Surface Modification Based on Heated AFM Tip

The heat field has been introduced to drive the occurrence of chemical reactions on the surface of 2DMs and then change their electrical conductivity. A study used a heated tip to locally reduce the highly insulating graphene oxide (GO) to a conductive graphene-like material (reduced GO, rGO) [65, 66].

Wei et al. first used a heated AFM tip for scanning on a GO film. As shown in Fig. 12a, patterns such as crosses, squares, and zigzag-shaped nanoribbons were written at different temperatures [66]. During the scanning process, the lateral force of the tip was observed to decrease with an increase in temperature. They believed that this result might be due to GO being replaced by rGO, which has relatively low friction, as the temperature increased. The electrical properties on the rGO surface were characterized by conductive AFM and Kelvin probe force microscopy (KPFM),

and the results proved the reduction of the insulating GO to conductive rGO. Their results also demonstrated that rGO could serve as a substitute for graphene to address the electronic gaps in the preparation of flexible electronic devices. Following the study of Wei et al., Carroll et al. used a heated tip array for scanning on GO deposited on SiO_2 in a zigzag path [65]. The position on the surface of GO written by the heated tip was reduced to conductive rGO. The current sensing AFM image in Fig. 12b was used to measure the current between the tip and GO. The contact potential difference for the zigzag nanostructures in rGO was also characterized via KPFM (Fig. 12b). The change in the current and contact potential demonstrated the reduction of the insulating GO to the conductive rGO. Similarly, the highly insulating graphene fluoride (GF) was locally converted to the conductive reduced graphene fluoride (rGF) by Lee et al. [64]. As shown in Fig. 12c, an rGF nanoribbon with a width of 120 nm and depth of 0.65 nm was achieved. The friction of rGF was also studied through writing rectangles at temperatures in the range of 200–550 °C. The friction of the patterns on the rGF decreased with an increase in temperature; the result was also compared with that on rGO in the research of Wei et al. [66]. The resistance of graphene nanoribbons was also measured using a nanotip system. The study generated graphene nanoribbons via writing on the GF using a heated tip. The method is expected to be applicable to modulating devices.

Fig. 12 Surface modification of graphene derivatives by heated AFM tip. **a** Reduction of graphene oxide (GO) to reduced GO (rGO). From Ref. [66]. Reprinted with permission from AAAS. **b** Reduction of GO to rGO via tip array. Republished with permission from Ref. [65],

Copyright 2014 RSC Pub. **c** Local conversion of graphene fluoride to reduced graphene fluoride. Reprinted with permission from Ref. [64]. Copyright 2013 American Chemical Society

5 Conclusions

To date, the TBN method has been demonstrated as a powerful approach to fabricate nanopatterns on films, which include polymers, metals, and 2DMs. In this work, the current development status of this method for machining on such films and its applications were reviewed from the following aspects:

1. Mechanical nanomachining and thermomechanical lithography were conducted on polymer films. Various 1D, 2D, and even 3D structures were achieved. These structures can be transferred to other substrates easily via etching when polymer films serve as etch masks. Several machining methods, including force control mode, phase mode, vibration-assisted method, and heated AFM tip, were employed. The application of TBN to machining

on polymer films makes this material applicable as an etching mask and sacrificial layer for lift-off and useful in data storage and other applications.

2. As for machining on metal and metal-based thin films, various methods, including scratching based on constant force mode, DPL, phase mode nanofabrication, vibration-assisted nanomachining, AFM electric lithography, and coupling AFM lithography, were utilized. Nanodot arrays, nanowires, nanogrooves, and even 2.5D patterns were obtained. Further major advances may be focused on broadening the application of TBN to machining on metal films.
3. 2DMs have become a research hotspot because of their special physical and chemical properties. Scholars have conducted extensive friction and wear experiments by using AFM tips for sliding on graphene surfaces to investigate the frictional behavior. A few studies have

reported the direct mechanical cutting of 2DMs. In addition, the heat field has been introduced to drive the occurrence of chemical reactions on the surface of 2DMs and then change their electrical conductivity. The application of TBN to machining on 2DMs is mostly focused on its surface lubrication effect, which has been considered in reducing friction and wear. In addition, graphene has been employed to prepare nanoelectronic devices because of its excellent electrical conductivity. Much effort is needed to broaden the application of TBN to machining on 2DMs.

Although using the TBN method to machine on the film material has been developed for decades, there is still a long way to go to realize industrialization. Further study in this area is yet to be carried out and the possible development directions in the future can be given as follows:

1. Development of theoretical models. The existing depth prediction model based on the constant force mode is not suitable for machining on the polymer film due to its large elastic recovery. The existence of high viscoelasticity makes the machining on polymer films more complex. Therefore, more factors such as the adhesion force, the elastic recovery, the ploughing process, and so forth needed to be considered to establish the theoretical model for more machining conditions, such as the phase mode, DPL, vibration-assisted, t-SPL, and so forth.
2. Reduction of tip wear. In order to achieve higher machining accuracy and meet the requirement of structure with dozens of nanometers, the silicon tip is usually used to act as the machine tool. However, for machining on thin films, large tip wear will be caused when the tip completely penetrates the film and contacts directly with the underlying hard substrate. Poor machining results will be caused by the worn tip. Thus, some measures should be taken to protect the tip from wearing as enough as possible. One of them is to establish a more accurate depth prediction model to protect the tip from penetrating the film. Moreover, machining the film under liquid may be a possible development direction to reduce tip wear. This is because the existence of water may act as a lubricant for tip cutting and reducing the friction between tip and sample effectively. Although some methods involving employing the diamond tip, introducing vibration to assist machining, and so forth have been successfully studied, the tip wear mechanism and new method to reduce tip wear still need to be further studied.
3. Improvement of machining accuracy. It is difficult to achieve the structure with a transverse dimension of less than 100 nm via the existing AFM tip-based mechanical nanomachining methods, which limits its further appli-

cation in some area where there is a need for small-size patterns, such as nanooptics. To rise above the limitations, the multi-tip probe may be an important growth factor for future TBN methods. This is because the original tip with apex radius of several tens of nanometers can be divided into several tips with apex radius of more than a dozen nanometers through focused ion beam lithography. The multi-tip probe can achieve the nanostructure with a transverse characteristic size of dozens of nanometers, improving the precision of transverse machining greatly.

4. Promotion of wider applications. It can be found that the application of machining on the film materials has not been industrialized. Though machining on the polymer film has been applied in the field of nanooptics [1, 18], nanoelectronics [2, 48], data storage [47], and so forth, one point that needs to be noted is that in these works the polymer film is acting as the etching mask and only when other nanofabrication methods such as etching technique, lift-off process, ultra-violet lithograph, and so forth are integrated with the TBN method can these applications be achieved. However, machining on metal films and 2DMs has not obtained such a wide application like polymer film. In the future, machining on the metal film may be used as an etching mask to achieve patterns with high aspect ratio on the arbitrary substrate based on its stable machining characteristics and excellent etching resistance. In addition, preparing flexible wearable nanosensors may be an important development direction for machining on 2DMs.

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References

- Kim J, Lee JS, Kim JW, De Wolf P, Moon S, Kim DH, Song JH, Kim J, Kim T, Nam SH, Suh YD, Kim KH, Kim H, Shin C (2021) Fabrication of plasmonic arrays of nanodisks and nanotriangles by nanotip indentation lithography and their optical properties. *Nanoscale* 13:4475–4484. <https://doi.org/10.1039/d0nr08398d>
- Zheng XR, Calo A, Albisetti E, Liu XY, Alharbi ASM, Arefe G, Liu XC, Spieser M, Yoo WJ, Taniguchi T, Watanabe K, Aruta C, Ciarrocchi A, Kis A, Lee BS, Lipson M, Hone J, Shahrjerdi D, Riedo E (2019) Patterning metal contacts on monolayer MoS₂ with vanishing Schottky barriers using thermal nanolithography. *Nat Electron* 2:17–25. <https://doi.org/10.1038/s41928-018-0191-0>
- Skaug MJ, Schwemmer C, Fringes S, Rawlings CD, Knoll AW (2018) Nanofluidic rocking Brownian motors. *Science* 359:1505–1508. <https://doi.org/10.1126/science.aal3271>
- Erdmanis M, Sievila P, Shah A, Chekurov N, Ovchinnikov V, Tittonen I (2014) Focused ion beam lithography for fabrication of suspended nanostructures on highly corrugated surfaces. *Nanotechnology* 25:7. <https://doi.org/10.1088/0957-4484/25/33/335302>
- Hong Y, Zhao D, Wang JY, Lu JS, Yao GN, Liu DL, Luo H, Li Q, Qiu M (2020) Solvent-free nanofabrication based on ice-assisted electron-beam lithography. *Nano Lett* 20:8841–8846. <https://doi.org/10.1021/acs.nanolett.0c03809>
- Chang SY, Yan YD, Li B, Geng YQ (2021) Nanoscale manipulation of materials patterning through thermomechanical nanolithography using atomic force microscopy. *Mater Des* 202:9. <https://doi.org/10.1016/j.matdes.2021.109547>
- Naifar S, Bradai S, Viehweger C, Kanoun O, Choura S (2016) Investigation of the magnetostrictive effect in a terfenol-D plate under a non-uniform magnetic field by atomic force microscopy. *Mater Des* 97:147–154. <https://doi.org/10.1016/j.matdes.2016.02.065>
- Geng YQ, Yan YD, Wang JQ, Zhuang Y (2018) Fabrication of nanopatterns on silicon surface by combining AFM-based scratching and RIE methods. *Nanomanufacturing and Metrology* 1:225–235. <https://doi.org/10.1007/s41871-018-0024-9>
- He Y, Yan YD, Wang JQ, Geng YQ, Xue B, Zhao XS (2019) Study on the effects of the machining parameters on the fabrication of nanoscale pits using the dynamic plowing lithography approach. *IEEE Trans Nanotechnol* 18:351–357. <https://doi.org/10.1109/tnano.2019.2904336>
- Xue B, Geng Y, Wang D, Sun Y, Yan Y (2019) Improvement in surface quality of microchannel structures fabricated by revolving tip-based machining. *Nanomanufact Metrol* 2:26–35. <https://doi.org/10.1007/s41871-018-0032-9>
- Zhang Y, Gao Y, Liu LQ, Xi N, Wang YC, Ma LP, Dong ZL, Wejinya UC (2012) Cutting forces related with lattice orientations of graphene using an atomic force microscopy-based nanorobot. *Appl Phys Lett* 101:3. <https://doi.org/10.1063/1.4767230>
- Li M, Shi JL, Xi N, Wang YC, Liu LQ (2018) Layer-controllable nanofabrication of two-dimensional materials with phase-mode AFM. *Mater Lett* 232:43–46. <https://doi.org/10.1016/j.matlet.2018.08.030>
- He Y, Yan YD, Geng YQ, Brousseau E (2018) Fabrication of periodic nanostructures using dynamic plowing lithography with the tip of an atomic force microscope. *Appl Surf Sci* 427:1076–1083. <https://doi.org/10.1016/j.apsusc.2017.08.134>
- Yan YD, He Y, Geng YQ, Hu ZJ, Zhao XS (2016) Characterization study on machining PMMA thin-film using AFM tip-based dynamic plowing lithography. *Scanning* 38:612–618. <https://doi.org/10.1002/sca.21308>
- Bae JH, Ono T, Esashi M (2003) Scanning probe with an integrated diamond heater element for nanolithography. *Appl Phys Lett* 82:814–816. <https://doi.org/10.1063/1.1541949>
- Gnecco E, Riedo E, King WP, Marder SR, Szoszkiewicz R (2009) Linear ripples and traveling circular ripples produced on polymers by thermal AFM probes. *Phys Rev B* 79:7. <https://doi.org/10.1103/PhysRevB.79.235421>
- Binnig G, Despont M, Drechsler U, Haberle W, Lutwyche M, Vettiger P, Mamin HJ, Chui BW, Kenny TW (1999) Ultrahigh-density atomic force microscopy data storage with erase capability. *Appl Phys Lett* 74:1329–1331. <https://doi.org/10.1063/1.123540>
- Aminzadeh A, Bose M, Smith D, Uddin MH, Peele AG, van Riessen G (2019) Investigation and optimization of reactive ion etching of Si₃N₄ and polyphthalaldehyde for two-step gray scale fabrication of diffractive optics. *J Vac Sci Technol B*. <https://doi.org/10.1116/1.5121760>
- Liu LQ, Shi JL, Li M, Yu P, Yang T, Li GY (2018) Fabrication of sub-micrometer-sized MoS₂ thin-film transistor by phase mode AFM lithography. *Small* 14:6. <https://doi.org/10.1002/sml.201803273>
- Fang TH, Chang WJ (2003) Effects of AFM-based nanomachining process on aluminum surface. *J Phys Chem Solids* 64:913–918. [https://doi.org/10.1016/s0022-3697\(02\)00436-5](https://doi.org/10.1016/s0022-3697(02)00436-5)
- Schumacher HW, Ravelosona D, Cayssol F, Wunderlich J, Chappert C, Mathet V, Thiaville A, Jamet JP, Ferre J, Haug RJ (2002) Control of the magnetic domain wall propagation in Pt/Co/Pt ultra thin films using direct mechanical AFM lithography. *J Magn Magn Mater* 240:53–56. [https://doi.org/10.1016/s0304-8853\(01\)00727-2](https://doi.org/10.1016/s0304-8853(01)00727-2)
- Shi JL, Liu LQ, Yu P, Li GY (2017) Phase mode nanomachining on ultra-thin films with atomic force microscopy. *Mater Lett* 209:437–440. <https://doi.org/10.1016/j.matlet.2017.08.071>
- Park SS, Mostafa MG, Park CI, Mehrpouya M, Kim S (2014) Vibration-assisted nano mechanical machining using AFM probe. *CIRP Ann-Manuf Technol* 63:537–540. <https://doi.org/10.1016/j.cirp.2014.03.138>
- Yang Y, Lin J (2016) Comparison of the bias voltage effect and the force effect during the nanoscale AFM electric lithography on the copper thin film surface. *Scanning* 38:412–420. <https://doi.org/10.1002/sca.21287>
- Yang Y, Zhao WS (2019) Fabrication of nanoscale to microscale 2.5D square patterns on metallic films by the coupling AFM lithography. *J Manuf Process* 46:129–138. <https://doi.org/10.1016/j.jmapro.2019.08.032>

26. Liu SH, Fu Y, Xiong C, Liu ZK, Zheng L, Yan F (2018) Detection of bisphenol A using DNA-functionalized graphene field effect transistors integrated in microfluidic systems. *ACS Appl Mater Interfaces* 10:23522–23528. <https://doi.org/10.1021/acsami.8b04260>
27. Ye ZJ, Egberts P, Han GH, Johnson ATC, Carpick RW, Martini A (2016) Load-dependent friction hysteresis on graphene. *ACS Nano* 10:5161–5168. <https://doi.org/10.1021/acsnano.6b00639>
28. Vilhena JG, Pimentel C, Pedraz P, Luo F, Serena PA, Pina CM, Gnecco E, Perez R (2016) Atomic-scale sliding friction on graphene in water. *ACS Nano* 10:4288–4293. <https://doi.org/10.1021/acsnano.5b07825>
29. Choi JS, Chang YJ, Woo S, Son YW, Park Y, Lee MJ, Byun IS, Kim JS, Choi CG, Bostwick A, Rotenberg E, Park BH (2014) Correlation between micrometer-scale ripple alignment and atomic-scale crystallographic orientation of monolayer graphene. *Sci Rep* 4:5. <https://doi.org/10.1038/srep07263>
30. Choi JS, Kim JS, Byun IS, Lee DH, Lee MJ, Park BH, Lee C, Yoon D, Cheong H, Lee KH, Son YW, Park JY, Salmeron M (2011) Friction anisotropy-driven domain imaging on exfoliated monolayer graphene. *Science* 333:607–610. <https://doi.org/10.1126/science.1207110>
31. Feng XF, Kwon S, Park JY, Salmeron M (2013) Superlubric sliding of graphene nanoflakes on graphene. *ACS Nano* 7:1718–1724. <https://doi.org/10.1021/nn305722d>
32. Kawai S, Benassi A, Gnecco E, Sode H, Pawlak R, Feng XL, Mullen K, Passerone D, Pignedoli CA, Ruffieux P, Fasel R, Meyer E (2016) Superlubricity of graphene nanoribbons on gold surfaces. *Science* 351:957–961. <https://doi.org/10.1126/science.aad3569>
33. Fang T-H, Wu C-D, Kang S-H (2011) Thermomechanical properties of polymer nanolithography using atomic force microscopy. *Micron* 42:492–497. <https://doi.org/10.1016/j.micron.2011.01.010>
34. Yan Y, Zhuang Y, Geng Y, Cheng L, Li J (2014) In: Ye T, Poleshchuk AG, Hu S (eds) 7th international symposium on advanced optical manufacturing and testing technologies: design, manufacturing, and testing of micro- and nano-optical devices and systems
35. Sun Y, Yan YD, Liang YC, Hu ZJ, Zhao XS, Sun T, Dong S (2013) Effect of the molecular weight on deformation states of the polystyrene film by AFM single scanning. *Scanning* 35:308–315. <https://doi.org/10.1002/sca.21069>
36. He Y, Yan YD, Geng YQ, Hu ZJ (2017) Fabrication of none-ridge nanogrooves with large-radius probe on PMMA thin-film using AFM tip-based dynamic plowing lithography approach. *J Manuf Process* 29:204–210. <https://doi.org/10.1016/j.jmapro.2017.07.016>
37. He Y, Geng YQ, Yan YD, Luo XC (2017) Fabrication of nanoscale pits with high throughput on polymer thin film using AFM tip-based dynamic plowing lithography. *Nanoscale Res Lett* 12:11. <https://doi.org/10.1186/s11671-017-2319-y>
38. Zhang L, Dong JY (2012) High-rate tunable ultrasonic force regulated nanomachining lithography with an atomic force microscope. *Nanotechnology* 23:9. <https://doi.org/10.1088/0957-4484/23/8/085303>
39. Zhang L, Dong JY, Cohen PH (2013) Material-insensitive feature depth control and machining force reduction by ultrasonic vibration in AFM-based nanomachining. *IEEE Trans Nanotechnol* 12:743–750. <https://doi.org/10.1109/tnano.2013.2273272>
40. Shi JL, Liu LQ (2015) Interface sensing and cutting of ultra-thin film based on UV-assisted AFM. *IEEE, New York*
41. Shi JL, Liu LQ, Zhou PL, Wang FF, Wang YC (2015) Subnanomachining by ultrasonic-vibration-assisted atomic force microscopy. *IEEE Trans Nanotechnol* 14:735–741. <https://doi.org/10.1109/tnano.2015.2439311>
42. Shi J, Liu L, Yu P, Cong Y, Li G (2017) Phase shifting-based debris effect detection in USV-assisted AFM nanomachining. *Appl Surf Sci* 413:317–326. <https://doi.org/10.1016/j.apsusc.2017.03.218>
43. Geng YQ, Yan YD, Zhuang Y, Hu ZJ (2015) Effects of AFM tip-based direct and vibration-assisted scratching methods on nanogrooves fabrication on a polymer resist. *Appl Surf Sci* 356:348–354. <https://doi.org/10.1016/j.apsusc.2015.08.068>
44. Deng J, Dong J, Cohen P (2016) In: Shih A, Wang L (eds) 44th North American manufacturing research conference, NAMRC 44, pp 1283–1294
45. Deng J, Zhang L, Dong J Y, Cohen P H (2015) In: Shih AJ, Wang LH (eds) 43rd north American manufacturing research conference, NAMRC 43, Elsevier Science Bv, Amsterdam, pp 584–592
46. Deng J, Dong JY, Cohen PH (2018) Development and characterization of ultrasonic vibration-assisted nanomachining process for three-dimensional nanofabrication. *IEEE Trans Nanotechnol* 17:559–566. <https://doi.org/10.1109/tnano.2018.2826841>
47. Holzner F, Paul P, Drechsler U, Despont M, Knoll AW, Duerig U (2011) High density multi-level recording for archival data preservation. *Phys Lett Appl*. <https://doi.org/10.1063/1.3610490>
48. Cheng BJ, Emboras A, Salamin Y, Ducry F, Ma P, Fedoryshyn Y, Andermatt S, Luisier M, Leuthold J (2019) Ultra compact electrochemical metallization cells offering reproducible atomic scale memristive switching. *Commun Phys* 2:9. <https://doi.org/10.1038/s42005-019-0125-9>
49. Lisunova Y, Spieser M, Juttin RDD, Holzner F, Brugger J (2017) High-aspect ratio nanopatterning via combined thermal scanning probe lithography and dry etching. *Microelectron Eng* 180:20–24. <https://doi.org/10.1016/j.mee.2017.04.006>
50. Cheong LL, Paul P, Holzner F, Despont M, Coady DJ, Hedrick JL, Allen R, Knoll AW, Duerig U (2013) Thermal probe maskless lithography for 27.5 nm half-pitch SI technology. *Nano Lett* 13:4485–4491. <https://doi.org/10.1021/nl4024066>
51. Cho YKR, Rawlings CD, Wolf H, Spieser M, Bisig S, Reidt S, Sousa M, Khanal SR, Jacobs TDB, Knoll AW (2017) Sub-10 nanometer feature size in silicon using thermal scanning probe lithography. *ACS Nano* 11:11890–11897. <https://doi.org/10.1021/acsnano.7b06307>
52. Pires D, Hedrick JL, De Silva A, Frommer J, Gotsmann B, Wolf H, Despont M, Duerig U, Knoll AW (2010) Nanoscale three-dimensional patterning of molecular resists by scanning probes. *Science* 328:732–735. <https://doi.org/10.1126/science.1187851>
53. Rawlings CD, Zientek M, Spieser M, Urbonas D, Stoferle T, Mahrt RF, Lisunova Y, Brugger J, Duerig U, Knoll AW (2017) Control of the interaction strength of photonic molecules by nanometer precise 3D fabrication. *Sci Rep* 7:9. <https://doi.org/10.1038/s41598-017-16496-x>
54. Hettler S, Radtke L, Grunewald L, Lisunova Y, Peric O, Brugger J, Bonanni S (2019) Phase masks for electron microscopy fabricated by thermal scanning probe lithography. *Micron* 127:5. <https://doi.org/10.1016/j.micron.2019.102753>
55. Lisunova Y, Brugger J (2018) Combination of thermal scanning probe lithography and ion etching to fabricate 3D silicon nanopatterns with extremely smooth surface. *Microelectron Eng* 193:23–27. <https://doi.org/10.1016/j.mee.2018.02.012>
56. Rawlings C, Ryu YK, Ruegg M, Lassaline N, Schwemmer C, Duerig U, Knoll AW, Durrani Z, Wang C, Liu DX, Jones ME (2018) Fast turnaround fabrication of silicon point-contact quantum-dot transistors using combined thermal scanning probe lithography and laser writing. *Nanotechnology* 29:11. <https://doi.org/10.1088/1361-6528/aae3df>
57. Peng P, Shi TL, Liao GL, Tang ZR, Liu C (2009) 4th IEEE international conference on nano/micro engineered and molecular systems, vols 1 and 2, IEEE, New York, pp 983–986
58. Tseng AA, Shirakashi JI, Nishimura S, Miyashita K, Notargiacomo A (2009) Scratching properties of nickel-iron thin film

- and silicon using atomic force microscopy. *J Appl Phys* 106:8. <https://doi.org/10.1063/1.3197313>
59. Edwards D, Brewer S, Cao Y, Jesse S, Chen L-Q, Kalinin SV, Kumar A, Bassiri-Gharb N (2016) Local probing of ferroelectric and ferroelastic switching through stress-mediated piezoelectric spectroscopy. *Adv Mater Interfaces*. <https://doi.org/10.1002/admi.201500470>
 60. Zhang FY, Edwards D, Deng X, Wang YD, Kilpatrick JI, Bassiri-Gharb N, Kumar A, Chen DY, Gao XS, Rodriguez BJ (2020) Investigation of AFM-based machining of ferroelectric thin films at the nanoscale. *J Appl Phys* 127:10. <https://doi.org/10.1063/1.5133018>
 61. Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y, Dubonos SV, Grigorieva IV, Firsov AA (2004) Electric field effect in atomically thin carbon films. *Science* 306:666–669. <https://doi.org/10.1126/science.1102896>
 62. Geim AK, Novoselov KS (2007) The rise of graphene. *Nat Mater* 6:183–191. <https://doi.org/10.1038/nmat1849>
 63. Geim AK (2009) Graphene: status and prospects. *Science* 324:1530–1534. <https://doi.org/10.1126/science.1158877>
 64. Lee W-K, Haydel M, Robinson JT, Laracuate AR, Cimpoiasu E, King WP, Sheehan PE (2013) Nanoscale reduction of graphene fluoride via thermochemical nanolithography. *ACS Nano* 7:6219–6224. <https://doi.org/10.1021/nn4021746>
 65. Carroll KM, Lu X, Kim S, Gao Y, Kim H-J, Somnath S, Polloni L, Sordan R, King WP, Curtis JE, Riedo E (2014) Parallelization of thermochemical nanolithography. *Nanoscale* 6:1299–1304. <https://doi.org/10.1039/c3nr05696a>
 66. Wei ZQ, Wang DB, Kim S, Kim SY, Hu YK, Yakes MK, Laracuate AR, Dai ZT, Marder SR, Berger C, King WP, de Heer WA, Sheehan PE, Riedo E (2010) Nanoscale tunable reduction of graphene oxide for graphene electronics. *Science* 328:1373–1376. <https://doi.org/10.1126/science.1188119>
 67. Felts JR, Oyer AJ, Hernandez SC, Whitener KE, Robinson JT, Walton SG, Sheehan PE (2015) Direct mechanochemical cleavage of functional groups from graphene. *Nat Commun* 6:7. <https://doi.org/10.1038/ncomms7467>
 68. Schedin F, Geim AK, Morozov SV, Hill EW, Blake P, Katsnelson MI, Novoselov KS (2007) Detection of individual gas molecules adsorbed on graphene. *Nat Mater* 6:652–655. <https://doi.org/10.1038/nmat1967>
 69. Merchant CA, Healy K, Wanunu M, Ray V, Peterman N, Bartel J, Fischbein MD, Venta K, Luo ZT, Johnson ATC, Drndic M (2010) DNA translocation through graphene nanopores. *Nano Lett* 10:2915–2921. <https://doi.org/10.1021/nl101046t>
 70. Garaj S, Hubbard W, Reina A, Kong J, Branton D, Golovchenko JA (2010) Graphene as a subnanometre trans-electrode membrane. *Nature* 467:190–U73. <https://doi.org/10.1038/nature09379>
 71. Reddy D, Register LF, Carpenter GD, Banerjee SK (2011) Graphene field-effect transistors. *J Phys D-Appl Phys* 44:20. <https://doi.org/10.1088/0022-3727/44/31/313001>
 72. Wang X, Zhi LJ, Mullen K (2008) Transparent, conductive graphene electrodes for dye-sensitized solar cells. *Nano Lett* 8:323–7. <https://doi.org/10.1021/nl072838r>
 73. Xie SX, Jiao ND, Liu LQ, Tung S (2015) IEEE 10th international conference on nano/micro engineered and molecular systems. IEEE, New York, pp 314–317
 74. Xie SX, Jiao ND, Tung S, Liu LQ (2015) Fabrication of SWCNT-graphene field-effect transistors. *Micromachines* 6:1317–30. <https://doi.org/10.3390/mi6091317>
 75. Xie SX, Liu ZL, Jiao ND, Tung S, Liu LQ (2014) Fabrication and characteristic detection of graphene nanoelectrodes. *Sci China-Technol Sci* 57:1950–5. <https://doi.org/10.1007/s11431-014-5603-4>
 76. Lee C, Li QY, Kalb W, Liu XZ, Berger H, Carpick RW, Hone J (2010) Frictional characteristics of atomically thin sheets. *Science* 328:76–80. <https://doi.org/10.1126/science.1184167>
 77. Cao CH, Sun Y, Filleter T (2014) Characterizing mechanical behavior of atomically thin films: a review. *J Mater Res* 29:338–47. <https://doi.org/10.1557/jmr.2013.339>
 78. Penkov O, Kim HJ, Kim HJ, Kim DE (2014) Tribology of Graphene: a Review. *Int J Precis Eng Manuf* 15:577–85. <https://doi.org/10.1007/s12541-014-0373-2>
 79. Spear JC, Ewers BW, Batteas JD (2015) 2D-nanomaterials for controlling friction and wear at interfaces. *Nano Today* 10:301–14. <https://doi.org/10.1016/j.nantod.2015.04.003>
 80. Guo WL, Yin J, Qiu H, Guo YF, Wu HR, Xue MM (2014) Friction of low-dimensional nanomaterial systems. *Friction* 2:209–25. <https://doi.org/10.1007/s40544-014-0064-0>
 81. Deng Z, Klimov NN, Solares SD, Li T, Xu H, Cannara RJ (2013) Nanoscale interfacial friction and adhesion on supported versus suspended monolayer and multilayer graphene. *Langmuir* 29:235–43. <https://doi.org/10.1021/la304079a>
 82. Paolicelli G, Tripathi M, Corradini V, Candini A, Valeri S (2015) Nanoscale frictional behavior of graphene on SiO₂ and Ni(111) substrates. *Nanotechnology* 26:13. <https://doi.org/10.1088/0957-4484/26/5/055703>
 83. Choi JS, Kim JS, Byun IS, Lee DH, Hwang IR, Park BH, Choi T, Park JY, Salmeron M (2012) Facile characterization of ripple domains on exfoliated graphene. *Rev Sci Instrum* 83:7. <https://doi.org/10.1063/1.4737428>
 84. Kwon S, Ko JH, Jeon KJ, Kim YH, Park JY (2012) Enhanced nanoscale friction on fluorinated graphene. *Nano Lett* 12:6043–8. <https://doi.org/10.1021/nl204019k>
 85. Li QY, Liu XZ, Kim SP, Shenoy VB, Sheehan PE, Robinson JT, Carpick RW (2014) Fluorination of graphene enhances friction due to increased corrugation. *Nano Lett* 14:5212–7. <https://doi.org/10.1021/nl502147t>
 86. Zhang JN, Lu W, Tour JM, Lou J (2012) Nanoscale frictional characteristics of graphene nanoribbons. *Appl Phys Lett*. <https://doi.org/10.1063/1.4752724>
 87. Fessler G, Eren B, Gysin U, Glatzel T, Meyer E (2014) Friction force microscopy studies on SiO₂ supported pristine and hydrogenated graphene. *Appl Phys Lett*. <https://doi.org/10.1063/1.4863832>
 88. Zheng XH, Gao L, Yao QZ, Li QY, Zhang M, Xie XM, Qiao S, Wang G, Ma TB, Di ZF, Luo JB, Wang X (2016) Robust ultra-low-friction state of graphene via moiré superlattice confinement. *Nat Commun* 7:7. <https://doi.org/10.1038/ncomms13204>
 89. Quereda J, Castellanos-Gomez A, Agrait N, Rubio-Bollinger G (2014) Single-layer MoS₂ roughness and sliding friction quenching by interaction with atomically flat substrates. *Appl Phys Lett* 105:5. <https://doi.org/10.1063/1.4892650>
 90. Spear JC, Custer JP, Batteas JD (2015) The influence of nanoscale roughness and substrate chemistry on the frictional properties of single and few layer graphene. *Nanoscale* 7:10021–9. <https://doi.org/10.1039/c5nr01478f>
 91. Lin LY, Kim DE, Kim WK, Jun SC (2011) Friction and wear characteristics of multi-layer graphene films investigated by atomic force microscopy. *Surf Coat Technol* 205:4864–9. <https://doi.org/10.1016/j.surfcoat.2011.04.092>
 92. Vasic B, Zurutuza A, Gajic R (2016) Spatial variation of wear and electrical properties across wrinkles in chemical vapour deposition graphene. *Carbon* 102:304–10. <https://doi.org/10.1016/j.carbon.2016.02.066>
 93. Vasic B, Matkovic A, Gajic R, Stankovic I (2016) Wear properties of graphene edges probed by atomic force microscopy-based lateral manipulation. *Carbon* 107:723–32. <https://doi.org/10.1016/j.carbon.2016.06.073>

94. Qi YZ, Liu J, Zhang J, Dong YL, Li QY (2017) Wear resistance limited by step edge failure: the rise and fall of graphene as an atomically thin lubricating material. *ACS Appl Mater Interfaces* 9:1099–106. <https://doi.org/10.1021/acsami.6b12916>
95. Li XL, Wang XR, Zhang L, Lee SW, Dai HJ (2008) Chemically derived, ultrasmooth graphene nanoribbon semiconductors. *Science* 319:1229–32. <https://doi.org/10.1126/science.1150878>
96. Park S, Ruoff RS (2010) Chemical methods for the production of graphenes. *Nat Nanotechnol* 5:309. <https://doi.org/10.1038/nnano.2010.69>
97. Shao YY, Wang J, Wu H, Liu J, Aksay IA, Lin YH (2010) Graphene-based electrochemical sensors and biosensors: a review. *Electroanalysis* 22:1027–36. <https://doi.org/10.1002/elan.200900571>

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