23 Novel AFM Nanoprobes

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23.1 Introduction and Historic Developments

The atomic force microscope (AFM) is a member of the family of scanning probe microscopes, which makes use of specialized probes to scan a sample surface to produce maps of topography, conductivity or friction among many others. The resolution of the technique is highly dependent on the probe quality and sharpness. To appreciate this, let us start with some historic developments. Scanning probe microscopy started in 1981 with the discovery of the scanning tunneling microscope (STM) by Binnig and Rohrer, who were awarded the Nobel Prize in Physics in 1986 for this invention. The STM operates by keeping constant a tunneling current established between a sharp conductive probe and a conductive sample, while scanning the sample using a high-accuracy xyz piezoactuator. Although the first STMs had relative modest probe sharpness (approximately 1-µm tip radius), atomic resolution could be obtained with remarkable simplicity in view of the fact that the tunneling current was established between one or a few atoms of the probe tip and one or a few atoms of the substrate. To keep the tunneling current constant, a constant tunneling gap had to be maintained during the lateral motion of the probe. This was achieved through feedback by amplifying the tunneling current and coupling the signal to a z-motion actuator to which the probe was attached. While the feedback acts to keep the tunneling current constant, it provides a voltage signal proportional to the topographic height information on the scanned surface, which is recorded.

Soon after the invention of the STM, the challenge was to extend the technique to nonconductive samples. Experiments showed that whenever a probe tip was close enough to a sample to establish a tunneling current, there were also small but significant forces acting on the probe. With cantilevered probes, these forces could be used to retrieve the topographic information by monitoring the cantilever deflection. This latter task was accomplished by detecting the position of a laser beam reflected on the cantilever, forming a so-called *optical lever*. The signal provided by the light detector was coupled via an amplifier to the *z*-motion actuator of the probe relative to the substrate to achieve feedback control. This constituted the AFM, as invented in 1986 by Binnig and developed in the same year by Binnig, Quate, and Gerber (1986). Modern AFMs have a four-quadrant photodiode (Fig. 23.1) to detect both vertical and lateral displacements of the laser spot. The latter is used to record probe tilt, which is due to lateral forces (friction) and constitutes the basis for lateral force microscopy (LFM). Maps of the friction coefficient between the probe and sample



Fig. 23.1. Optical lever scheme of an atomic force microscope (AFM) and signal processing from a four-quadrant photodiode; the height signal is used as a feedback to keep the cantilever deflection constant, while the lateral force signal is processed for lateral force microscopy (LFM) measurements

can be obtained using this scheme. For a detailed history of the development of the AFM and other scanning probe techniques, we refer the reader to [1,2].

Over the years, many types of atomic force microscopy techniques were developed. Among them, we distinguish those operating with the probes in contact or noncontact mode, lateral force probes [3], vibrating probe techniques [4], AFMs operating in different environments (vacuum [5, 6], air, gas¹ or immersed in liquids [7,8]), probes sensitive to other type of forces (electrostatic [9], magnetic [10]) or signals (electrical [11,12], capacitive Kelvin probes [13–15], temperature [16,17], light [18], chemical [19]), and probes integrating electrostatic [20,21], piezo-, thermal or magnetic actuators for their *z*-motion or vibration [22, 23]. During the last decade, more complex probes integrating different types of sensors or even microfluidics were developed [24–28]. Novel AFM techniques were also developed in which the *z*-motion feedback is achieved with other types of sensors independently of the optical lever (e.g., piezoresistive [29], capacitive [30], complementary metal oxide superconductor, CMOS, integrated deflection sensors [31–33], interferential optical schemes, and membrane deflection [34]).

AFM-related techniques were further developed during the last decade for actively producing nanoscale changes on the sample surface. This latter research domain showed a strong development leading to specialized probes and techniques for various purposes especially in biochemistry and the life sciences. New tools were developed, along with methods and software. Ultimately, entire companies emerged, specializing in their production. The same probes may be capable of multitasking by combining different modes of operation and sensing [35, 36].

The methods for local surface modification with AFM probes range from simply mechanically scratching the surface [37–39] or nanomanipulation of nanoscale objects on surfaces for the purpose of building structures [40–42], to chemical

¹ Several companies produce environmental chambers for SPM. Some of them are EnviroView 1000, Nanonics product sheet, http://www.nanonics.co.il; EnviroScope atomic force microscope, Digital Instruments, Veeco product sheet, http://www.veeco.com/appnotes/ DS48_EScope_Compressed.pdf; Environmental control chamber, Molecular Imaging, product sheet, http://www.molec.com/products_options.html#env_ctrl



Plate 23.1. Comparison of different atomic force microscopy nanopatterning tools. (**a**) dip-pen nanolithography – DPN [50–54]; (**b**) nanopipettes [24]; (**c**) apertured probes [28]; (**d**) nanofountain probe – NFP [58]

or electrochemical-induced modifications, such as oxidation of surfaces [43–46], etching (e.g., Cr for mask repair [24]), local chemical vapor deposition (CVD) of metal nanowires [47,48] and electrodeposition [49]. A distinct class with a variety of direct deposition methods emerged from a technique first proposed in 1999 by Mirkin [50–54], dip-pen nanolithography (DPN). This uses AFM probes coated with certain molecular ink species to write patterns on substrates, as will be detailed in Sect. 23.2.

DPN techniques for writing with a large variety of inks on suited substrates were developed, but they all exhibit a common feature: DPN patterning, owing to its serial nature and diffusion-controlled mechanism, is slow (a few microns per second writing speed). Likewise, interruptions for reinking, changing molecular inks and realignment as well as for changing the probes owing to wear or particle contamination are customary. Several techniques and specialized probes were developed to alleviate these inconveniences. Among them are nanofountain probe (NFP) lithography (in which ink is delivered to the probe in liquid form) [24,55–59], electro-pen lithography (in which, additional to inking, a voltage is applied between the probe and the substrate, producing oxidation of the substrate and an increase in writing speed) [60], nanopipette writing [24], and quills-based techniques [26, 27] with applications mainly in biomolecular chemistry. In Plate 1, a comparison of these techniques is presented. Each of them has its advantages and disadvantages. DPN (a) is characterized by simplicity, high writing resolution (smaller than 100 nm) and a large amount of literature available, but is the slowest of the techniques; apertured probes (b, c) can store and dispense larger amounts of ink molecules, but writing speed is not increased substantially and the writing resolution (regular approximately 300 nm, best reported 70nm-diameter spots) is inferior to DPN. Moreover, because of the ink supply into the probe cavities, it cannot be easily handled and integrated. Pulled-glass nanopipettes (b) have continuous ink delivery, but lower resolution (approximately $1 \mu m$), and cannot be integrated by microfabrication into larger systems; NFP (d) have continuous ink delivery for a long-range writing capability, resolution close to that of DPN, and can be integrated in arrays and systems, although the probes and AFM systems become more complicated and costly. The electro-pen approach was not mentioned separately, since, although developed only for DPN, it may work with any of the other types of probes, provided they are made conductive and a voltage is applied.

The growing complexity of the probes makes them more laborious to manufacture and quite costly. AFM probes, even if complex, remain disposable laboratory accessories owing to inherent demands on avoiding cross-contamination and tip sharpness. However, it becomes more and more desirable to extend their lifetime for applications involving large area patterning or large-scale imaging. In these cases wear of the tip is one of the main limiting factors. Integration of low-wear materials such as diamond into the tips of the probes is one solution we will discuss in Sect. 23.3. Usage of conductive diamond also has advantages regarding the possibility of their use in electro-pen nanolithography (EPN) and other conductive probe AFM techniques while preserving tip sharpness. We will demonstrate this technology in the same section.

Recently, AFM techniques have been used in identifying mechanical properties of nano-objects, ranging from nanowires [61] and carbon nanotubes [62] to single molecules [63–65] (molecular pulling). For these techniques, the probes must be precisely calibrated regarding their spring constant (force spectroscopy) and vibration properties (dynamic force spectroscopy) [66]. For retrieving the properties of the objects investigated, the motion characteristics of the probes must be understood and analyzed coupled with the mechanical properties of the molecules investigated. In many cases, this involves molecular dynamics simulations.

As the ultimate force measuring tools at the nanoscale (down to piconewtons – picoforce meters), AFMs have been involved also in detecting the occurrence of

liquid–solid phase transitions at the nanoscale on surface-adsorbed water. The study revealed ice formation at room temperature if voltage in the range 5–10 V is applied between the probe and the substrate [67]. This is particularly interesting and relevant for electrically biased DPN techniques such as electrochemical DPN and EPN, in relation to the formation of a water meniscus between tips and substrates, wear mechanisms and molecular ink transport.

23.2 DPN and Fountain Pen Nanolithography

Tips integrated on microcantilevers may function as pens or quills, to locally deliver molecules previously present on the tip surface. The tip sharpness allows sub-100-nm patterning with various molecular species. The domain known as DPN is relevant for high-resolution patterning of limited areas, such as for life sciences applications (nanoassays). In most cases, the ink molecules produce a local reactive functionalization of the surfaces, such that specific biochemical adhesion experiments can be conducted at these length scales. In general, the deposited material and the substrate must be paired, such that a chemical reaction occurs upon delivery, or a surface self-assembled monolayer (SAM) is formed, such that a reading is possible using the same AFM technique. In some cases, this reaction or SAM formation is not needed; for example, in the case of simple patterning with fluorescent dyes in which the reading can be achieved optically.

In the DPN technique (Fig. 23.2), the ink molecule species are physisorbed on the tip surface, such that the tip geometry is not significantly altered. When the tip is placed in contact with a target surface, the molecules migrate from the tip onto the surface and the time of surface contact directly correlates with the amount of material transferred. A model of the DPN material transfer was elaborated by Jang et al. [68]. It supposes that the ink molecules form a monolayer spot on the substrate, developing from the area of probe contact. The probe acts as an infinite source of molecules, while the surface diffusion of ink molecules on the existent monolayer transports the molecules to the edge of the spot, where they stick to the surface, extending the spot diameter. The model equations lead to a dependence of spot diameter proportional to the square root of contact time, which is verified experimentally in most cases of practical interest, evidently before the ink exhaust on the tip. The diffusion-driven





writing process also explains the dynamics of line writing and is responsible for the low writing speed in DPN, typically below $1 \,\mu$ m/s. According to the model, the writing speed also depends on the reactivity of the ink with the substrate and the contact radius of the tip. This was confirmed experimentally, although a quantitative verification was not reported.

A water meniscus formed by capillary condensation was suggested as the mechanism of molecular transfer from a tip to the substrate in DPN, and the formation of such a meniscus was recently confirmed using an environmental scanning electron microscopy (SEM) technique (Fig. 23.3) [69]. The formation of this meniscus causes the ink delivery to depend on the humidity, temperature and air flow in the AFM chamber. Because of this, specialized equipment for DPN writing is usually placed in chambers with controlled environmental parameters. Typical values reported for successful writing are 10–100% humidity and 23–33 °C [70]. However, DPN in very dry environments and on carefully dried substrates was also reported [71], leading to a controversy. Our recent investigations on the aspect of ink-coated DPN probes showed that although ink is supplied from solutions in most DPN writing schemes, the ink species dries up during usage, forming a compact, quite irregular coating on the writing AFM probe.

Figure 23.4 presents a SEM view of a standard Si_3N_4 probe before and after dipping it into a 16-mercaptohexanoic acid (MHA) solution and drying. Even when a careful dip was performed using a micromachined ink well and the AFM head motion in order to achieve a controlled and partial coating [72] (Fig. 23.4c), the features of the coating suggest that writing performed with such probes is quite



Fig. 23.3. Sequence of images collected in an environmental scanning electron microscope (SEM) at various relative humidity levels, showing meniscus formation between an AFM tip and a substrate. All images were collected at 5 °C, 15.0-kV accelerating voltage, at \times 35,000. The humidity was varied by decreasing the pressure of the water vapor from 6.4 Torr down to 1 Torr: 40% relative humidity, 2 Torr; 60% relative humidity, 3.2 Torr; 99% relative humidity 6.4 Torr. (After [69])



Fig. 23.4. SEM images of a standard nitride AFM probe before (**a**) and after (**b**) dipping it in 16-mercaptohexadecanoic acid (MHA) solution and drying. (**c**) Probe dipped carefully, by using a micromachined ink well and the AFM motion for dipping

different from the simplified picture provided by the meniscus-driven model. Even if capillary condensation plays a strong role in the DPN patterning, these images suggest that writing can actually be performed at least in part like with a pencil, rather than with a quill. This may explain why DPN writing was also successfully accomplished in a dry nitrogen atmosphere and with very dry substrates [71] – ultimately, the transfer of molecules should also be possible by direct contact, without the aid of a meniscus. This writing mode continues to support the square-root-oftime dependence of the spot diameter, since the latter reflects only the behavior of ink diffusion to the substrate.

If environmental conditions and ink and substrate chemistry are optimized, patterning small feature sizes is critically dependent on the material and radius of curvature of the AFM probe tips. The most commonly used probes in the DPN technique are made of silicon nitride cantilevers with integrated pyramidal tips, which are typically fabricated using the pyramidal-pit molding technique [73]. For higher-resolution DPN writing, sharper tips produced by oxidation-sharpening [74] are usually employed. The dimensions of the cantilevers have been selected to meet the desired range of spring constants 0.03–0.3 N/m [50].

DPN was originally reported to pattern gold surfaces with a solution of alkanethiols [75]. Its applications have been subsequently extended to patterning surfaces with versatile types of materials such as biomolecules [51, 52, 76], polymers [77], small organic materials [78], sol precursors [79] and metal salts [46]. One of the advantages of the DPN technique is that biomolecules, such as DNAs or proteins, can be patterned both by direct write and indirect assembly [51, 52, 54, 80–82], which can be utilized to build nanoscale biomolecular sensor arrays with higher sensitivity and selectivity requiring much smaller sample volumes. For example, modified singlestrand DNAs with a thiol group at one end were patterned on a gold surface and used to capture complementary DNA sequences tagged with gold nanoparticles [51]. In this way, a pattern of gold particles could be assembled (*bottom up*) on the surface, in a completely different way than by thin film deposition and etching, or lift-off (traditional *top-down* techniques). Feature sizes ranging from a few micrometers to less than 100 nm were achieved.

Once a tip is coated with the molecules of interest, patterning is typically controlled by commercially available AFM instruments to precisely deposit desired amounts of molecules at controlled locations. DPN writing has been typically performed with a single probe; however, patterning large areas with a single tip, owing to its serial nature and the limited scan size of the AFM, is very inefficient. In an effort to improve the throughput of the DPN technique, the feasibility of parallel DPN patterning with a commercially available tip array was demonstrated in a commercially available AFM [50].

Furthermore, linear arrays of high-density probes with integrated tips for DPN were microfabricated [83, 84]. Two types of DPN probe arrays were developed using surface micromachining techniques. The first type, or type-1 probe array, was fabricated out of thin-film silicon nitride using the molding technique with a protruding tip, whereas the second type, or type-2 probe array was fabricated from heavily boron doped silicon (Fig. 23.5). The type-1 probe array consists of 32 straight probes in a 1D arrangement, with the space between consecutive probes being 100 μ m. The dimensions of an individual cantilever were 400- μ m long, 50- μ m



Fig. 23.5. SEM micrographs of DPN probe arrays with the type-1 (*left*) and type-2 (*right*) arrays [83]

wide and 0.6- μ m thick. The type-2 array had eight probes separated from each other by a spacing of 310 μ m, whereas each cantilever was in a multifold configuration. The dimensions were 1400, 15 and 10 μ m for the cantilever length, width and thickness, respectively.

23.2.1 NFP Chip Design – 1D and 2D Arrays

As mentioned, a major limitation of the DPN approach is the slowness in writing. There are several causes for the this: the diffusion-driven ink dispersion on the surface; the necessity to reink and reposition the probes if the species delivered are exhausted: the limited response time of the electromechanical scanning systems: and the necessity to scan large areas with a single probe in a serial type of writing. To speed up the process, parallel writing with probe arrays, continuous ink delivery to avoid reinking and realigning interruptions, and speeding up of the ink transfer as much as possible are needed. Parallel writing with probe arrays involves large-scale fabrication processes using microelectromechanical systems (MEMS) techniques, which eliminates the use of pulled-glass nanopipette types of probes; continuous ink delivery means integration of microfluidics into probes - which replaces dip-and-write techniques with fountain-pen-type writing; attempts to speed up the ink transfer can be addressed by optimization of ink solutions, by using electrical biasing of probes, like in EPN. Hidden in the parallel writing requirement lies the necessity of individual control on the positions of the probes in the vertical direction, with independent actuation and independent position readout and, eventually, feedback. Since the primary task for such probes is to write, the optimization of writing is the first to be solved, which leads to a gradual approach for increasing the probe's complexity: first individual probes with fountain-pen-type ink delivery, then arrays of fountain probes, then integration of independent actuation and independent sensing have to be pursued. For the time being, individual fountain probes [57, 58] and arrays of fountain probes have been fabricated, while independent actuation and sensing are being tested separately and can benefit from the experience accumulated from other parallel AFM techniques, such as imaging or data storage/readout [85,86]. In the following, we present some developments in these directions.

23.2.1.1 Writing Mechanisms with Direct Feeding of Ink

Feeding fluid ink to the AFM probe for writing brings into question if the writing mechanism is or is not the same as in DPN. The answer to this question is rather complex, and requires a deeper insight into the phenomena at the tip-to-substrate transfer of molecular species. Figure 23.6 presents a schematic comparison between writing mechanism of DPN, nanopipettes, apertured AFM probes and NFP.

The "standard" mechanism of DPN starts from an infinite source of ink molecules adsorbed on the probe, which are transferred with the aid of a water meniscus to the substrate surface, where they form a SAM and continue their ride from the tip to the boundary of this layer, as previously discussed. The water meniscus, if present, is formed between the tip and the substrate owing to capillary condensation from the environment, but also by gathering water molecules already existing on the surface itself, as an adsorbed or prewetting layer. The role of this water meniscus (shown also in Fig. 23.3) could be to ease the molecule transfer, but, eventually, the meniscus could be very limited or even missing, while molecules still transfer by direct contact. The ink molecules are usually species with very low solubility in water (MHA, octadecanethiol, ODT, nanoparticles) and, if amphiphilic, as is mostly the case, are supposed to have a preferential orientation on the surface of water, with the hydrophilic end facing the water and the hydrophobic end facing out. The low solubility and supersaturation regime (due to the heavy evaporation of solvent) is favorable for the micellar transition, which means that the amphiphilic molecules will try to connect by the hydrophobic ends through van der Waals forces to form colloidal groups. However, the limited size of the meniscus suggests that the volume properties of solutions at equilibrium, such as concentration and micellation (as well as density, temperature and pressure), cannot describe properly what is happening at this scale, the more suggestive picture being probably a succession of fluctuations with some statistical tendencies. The physical properties of adsorbate layers, especially the coadsorption and codiffusion properties, are also not well known. DPN experiments performed with MHA molecules as ink, with coating of the tips by dipping into solutions of different solvents (ethanol, acetonitrile, dimethylformamide, etc.), and different concentrations, showed different writing dynamics. This suggests that, although not much solvent is left on the tips after drying, it still alters the surface diffusion in the coadsorbed layer.



Fig. 23.6. Writing mechanism of DPN (**a**), nanopipettes and apertured probes (**b**) and nanofountain probes (NFP) (**c**)

In case of probes such as nanopipettes [24] and apertured tips [28] (Fig. 23.6b) liquid ink solution is touching the substrate and, owing to capillary action, has the tendency to form an exterior meniscus. The presence of sufficient solution allows this meniscus to grow close to the equilibrium shape, dictated by the pressure balance at the ends of the capillary channel; thus, it is not the inner diameter of the aperture, but the outer diameter of this meniscus that determines the ultimate writing resolution. The best resolution reported with such probes is in the 1- μ m range, although capillary probes with outer diameters as small as 20 nm were used. Open channel microspotters [87] essentially share the same meniscus-controlled writing mechanism. Table 23.1 shows a comparison of performances of DPN, NFP and various other types of microfluidic probes.

NFP (Fig. 23.6c) combine both the tip-transfer of ink, similar to DPN, and the presence of liquid ink in close proximity of the tip. One early problem is the transport of the fluid ink through the microchannels, from a reservoir to a special type of tip, with a volcano structure. While in nanopipettes the capillary lumen is large $(20-50 \,\mu\text{m})$ and shrinks to a few nanometers (best reported 5 nm [24]) only at the end of the probe, transport by capillary action is very similar to that predicted by classical theory. In the case of NFP, channels with cross sections as small as $0.3-0.5 \,\mu\text{m} \times 4-10 \,\mu\text{m}$ are customary, stretching over approximately 1 mm lengths. The surface-to-volume ratio of the liquid is much increased in this case, possibly allowing the formation of an ink concentration gradient along the channel; this is likely to be the case for low-solubility ink molecules which try to occupy the liquid-solid interfaces. The phenomenon is similar to prewetting effects in separation columns, known to work even for mixtures containing highly soluble components. The preferential evaporation of solvent at the tip end creates another source of concentration gradient, this time with higher concentration in the downstream (tip) end of the microchannel. This concentration increase, if not balanced by a continuous supply of solvent by diffusion, may lead to the supersaturation and precipitation of ink molecules, clogging the channel.

Microfluidic simulations performed for the NFP's volcano-shaped tips show different possible scenarios of meniscus formation depending on the contact angles of the materials used for the tips and the shell material (Fig. 23.7). For contact angles, $C_t = 20^\circ$ and $C_s = 65^\circ$, for a tip made of SiO₂ and a shell made of Si₃N₄, a stable fluid–air interface develops. In the case of small contact angles,

	Dip-pen nano- lithography [75]	Nano- pipette [24]	Microspotters SPT (Surface Patt- erning Tool) [87]	Apertured tip [28]	Nanofountain probe [58]
Resolution	< 100 nm; best 15-nm lines/ 5-nm spaces	$\sim 1\mu m$	2–3 μm	$\sim 1 \mu\text{m};$ best 300 nm	< 100 nm; best 40-nm lines
Micro- fabrication Continuous delivery	Commercial tips No	No Yes	Developed steps Yes	Developed steps Yes, very limited volume	Developed steps Yes

Table 23.1. Comparison of different types of micropatterning and nanopatterning probes



Fig. 23.7. Finite-element simulations (CFD-ACE+) of capillary motion of water through microchannels and a volcano tip, stopping in the final equilibrium position for the meniscus. The contact angles with the tip and shell are, respectively, $C_t = 20^\circ$ and $C_s = 65^\circ$, SiO₂ tip and Si₃N₄ shell (*left*), $C_t = C_s = 65^\circ$, tip and shell both Si₃N₄ (*middle*) and $C_t = C_s = 20^\circ$, tip and shell both SiO₂ (*right*)

 $C_{\rm t} = C_{\rm s} = 20^{\circ}$, for a tip and shell both made of SiO₂, the meniscus can surround the shell and lead to unstable flow, potentially affecting the local diffusion processes (Fig. 23.7). While the simulations in Fig. 23.7 were performed for pure SiO_2 and Si₃N₄, crossover or different values for the contact angles can be easily reached by surface oxidation of the nitride, by etching processes, contamination or targeted chemical functionalization. The presence of ink outside the volcano tip is confirmed by SEM images of probes after the ink solution had dried and solidified (Fig. 23.8). However, ink can be present even on quite remote points on the probes, for which meniscus reshaping is a poor hypothesis. A typical case is the ink climbing from the base on long whiskerlike probes, such as those grown on volcano probes by electronbeam-assisted W deposition (Fig. 23.9). Such W nanowires show ink clusters and also performed writing, confirming once again the presence of molecular ink. One possible explanation is that ink molecules are coevaporated with solvent molecules and can recondense on solid surfaces such as the tip and substrate, contributing to the transport of ink by mechanisms other than in the case of DPN. This actually adds to the complexity of the phenomena, since the ink solvent, as viewed from the size scale



Fig. 23.8. Image of a NFP before (**a**) and after (**b**) ink delivery through the channel. The image corresponds to a first-generation NFP, with the gold sealing layer apparently forming a second volcano shell, although no gap is in reality present between the gold and the nitride



Fig. 23.9. Volcano-shaped probe with a W nanowire. Empty volcano cavity prior to ink supply (*above the line*); volcano filled with molecules after ink supply (*below the line*). Two images are combined for comparison purposes. A nanowire grown by electron-beam-enhanced deposition of W is shown at the center of the volcano. The *inset* and *right image* show the W nanowire with clusters of MHA molecules coating its surface [57]

of the tip, is subjected to heavy evaporation and recondensation. Such phenomena are expected to play an even stronger role in the case of microspotters and open channel devices [85], where they can lead to cross-contamination of probes.

Returning to the microfluidic transport model (Fig. 23.7), another degree of complexity observed in NFP writing is the relative motion of the core tip within the shell. In such architectures, the core tip and shell form a highly compliant micromechanical structure, which could be evidenced during observation of volcano tips with SEM. Owing to charging or possible unhomogeneous heating and thermal expansion, core tips can be seen (live) to move from their nominal center position (Fig. 23.15b). Similar motion is expected to occur when the volcano is filled with liquid. The capillary force on a center pillar in a ring surrounded by a meniscus increases with the off-center displacement of the pillar, leading to mechanical instability. The force opposing this instability is the elastic deformation, which renders the central position of the tip metastable. Thus, during writing, the volcano tip is likely to have an off-center position, touching the shell. The high elastic compliance of the volcano core also allows its vertical motion relative to the shell, resembling a rapidograph writing mechanism. While the vertical motion of the core is favorable (allows rewetting of the tip, "calligraphy" by changing of writing features with the contact force in the AFM cantilever, and can be used as a declogging means), the lateral motion is less desirable, leading to misalignment and decreased position accuracy. This allows the development of different classes of probes: more rigid for high position accuracy, less rigid for calligraphy, etc.

23.2.1.2 1D Fountain Probe Array

The design of a first microfluidic nanoprobe with integrated microfluidics is presented in [58] and was driven by the functionality requirements discussed earlier. A first constraint in the design was imposed by the desire to preserve the highresolution DPN writing mode. For this reason, the ultimate ink delivery system required an AFM tip, rather than a tube or simple aperture. However, the supply of ink had to be continuous to avoid interruptions for the replenishing of molecules. Since distances along the chip and cantilevers are in the millimeter range, a liquid source was supposed to be the only one providing good molecular transport. In this scenario, the ink molecules must be soluble in the ink solvent (at least to some degree), and the liquid must be delivered through capillary channels close to the tip apex. However, the meniscus must end prior to reaching the apex of the AFM probe to avoid the formation of an outer meniscus as in nanopipette-type devices, which have poor resolution (approximately 1 μ m) [24]. To avoid the rapid evaporation of the ink solvent and cross-contamination through coevaporation and remote condensation of the ink species, the channels were preferred to be closed along the path from the reservoir to the dispensing tip. A schematic representation of this design is presented in (Fig. 23.10).

Other constrains on the cantilevers were imposed by the requirement to keep their stiffness low (0.03-0.3 N/m), to achieve both normal (for writing) and LFM (for reading) high resolutions, while the tip material had to be hard and sufficiently hydrophilic to facilitate molecular transport. For instance, silicon nitride was proven to give good results in most DPN experiments. The minimization of processing steps



Fig.23.10. General view of microfluidic nanoprobe: (a) cross-sectional view showing microfluidic components, from reservoir to tip; (b) 3D schematic view of the cantilever, showing 1 laser beam from the AFM position sensor, 2 piezoactuator, 3 electrode for applying pressure pulses and 4 microfluidic volcano tip. Note that 2 and 3 are in development stages and are discussed here only from a design viewpoint

and the use of common fabrication techniques and materials available in standard microfabrication laboratories were also sought. A versatile design was adopted to permit easy addition of upgrades, such as variation in tip shapes, cantilever stiffness, integration of independent actuation and large-scale arraying capabilities for both the micromechanical parts and the electrical and microfluidic circuitry.

A first exploratory device of this kind, used for testing the writing capability of NFP with ink fed through microchannels as long as 1.35 mm, is presented in Figs. 23.10 and 23.11. The NFP chips had a single on-chip reservoir and five cantilever probes of different lengths, with volcano-shaped ink delivery tips. The chips were designed to use only one probe at a time.

The fabrication of the device used surface micromachining for producing the microfluidic structure, comprising a sacrificial SiO_2 layer for forming the lumen of the microchannels, sandwiched between two low-stress Si_3N_4 layers – the structural material of the cantilevers. The channels were sealed by a bird's beak oxidation to bring the two edges of the nitride together, followed by the deposition of an additional sealing Si_3N_4 layer. The on-chip reservoirs were formed and chips were released by KOH etching.

The first generation of microfabricated NFP chip was capable of writing with sub-100-nm resolution, down to 45-nm line widths, but also revealed fabrication difficulties and possible failure modes. Among them were quite large tip radii in the range 300–500 nm, channel sealing difficulties resulting sometimes in leaking of the channels, easy clogging of the microchannels owing to their small lumen size in some critical portions (0.1–0.4 × 5 μ m² cross section), a too low cantilever torsional



Fig. 23.11. First-generation NFP with on-chip reservoir, microchannels incorporated into cantilevers and volcano-shaped dispensing tips. The *inset* shows a detail of the volcano-shaped tip, at the free end of the cantilever. The dimensions are 2.66 mm \times 3.27 mm (chip excluding cantilevers), 810 µm \times 891 µm (reservoir) and 400–600 µm (cantilevers). The chip is designed for individual probe writing

stiffness and too small reflective area leading to poor signals in the AFM optical lever detectors, difficulties in achieving the connections between the channels and volcano tips, a large fracture rate of the reservoir membranes during the fabrication owing to the composite nature of the membranes and their different residual stresses, and a quite loose management of wafer real estate owing to the KOH release of the chips.

The decrease of tip radius for this first-generation device was made possible by growing W nanowires through electron-beam-assisted deposition [57]. The deposition of the W nanowire was accomplished when the electron beam was focused at one spot on the tip and a W precursor gas was injected in the SEM chamber (Zeiss 1540XB Crossbeam). For these experiments, configurations with poor volcano-shaped tip geometry were chosen, usually obtained close to the edges of the wafers. SEM observations after ink feeding revealed that transport of molecular inks along the W nanowire is in fact achieved (Fig. 23.9). Molecular precipitation was observed as an increase in nanowire surface roughness.

Although the reinking time could be spared with these devices, the writing remained slow since single-probe patterning is slow as a result of the diffusiondriven and sequential nature of process. This drawback can be solved in part by arraying and parallel writing.

The principle of the first 1D array of NFP fed by two on-chip reservoirs is presented in Fig. 23.12. In the first stage, the 1D array chip should be designed to fit into commercially available AFMs to exploit their scanning and optical lever schemes. By arranging multiple on-chip reservoirs, we should be able to achieve patterning surfaces with different types of inks.

The difficulties of the first generation of NFP were analyzed and overcome by enhancements implemented in a newly designed device and fabrication sequence. The new-generation NFP chip contains a linear array of 12 cantilever probes, with microfluidic channels connecting two on-chip reservoirs to volcano-shaped ink delivering tips. The 12 probes can be used to write in parallel, thus helping to speed



Fig. 23.12. The operation of the 1D array of a NFP with two ink reservoirs. PZT lead zirconate titanate

up the process, but can be also fed with two different inks. A similar array of probes and reservoirs is placed on both sides of the chip to increase the success rate and usage of each chip, which was not possible with the old version of the NFP.

A general view of the microfabricated second-generation NFP device can be seen in Fig. 23.13. The chip has an overall size of 1.8 mm \times 3.2 mm (excluding the cantilever lengths), to fit easily into commercial AFM equipment. The cantilever lengths are 630 and 520 μ m, respectively, on the two sides of the chip. The different lengths account for a longitudinal bending stiffness of 0.175 and 0.312 N/m, respectively, to provide a choice for different applications. Otherwise, the chip has a fourfold symmetry, and uniform and repetitive architecture, to help in reducing the burden of optimizing the fabrication processes. The reservoirs feed six microchannels each. The microchannels are in part embedded in the silicon chip body and are in part embedded along the length of the silicon nitride cantilevers. The total lengths of the microchannels are 1110 (1000), 1175 (1055) and 1310 (1200) μ m, respectively, for the three types of channels surrounding symmetrically the reservoir and the two sides of the chip. Figure 23.14 shows a zoom-in view of a quarter of the chip, where the different components can be identified.

The cross section of the channels is rectangular, with a height of $0.5 \,\mu\text{m}$ and a width of $12 \,\mu\text{m}$. The reservoirs consist of a double silicon nitride membrane and a cylindrical well of 160- μ m diameter, which is etched from the backside of the chip, to reach this membrane. This cylindrical well gives the volume of the on-



Fig. 23.13. Overview of a second-generation NFP chip: (a) front-side view; (b) backside view. The chip is shown attached to the Si wafer by a pair of Si bridges with notches at their base, for controlled breaking. The long cantilever strips attached to the Si bridges are Si_3N_4 dummy structures introduced for better control of etching and mechanical tests chip reservoir, which is approximately 60 nl. The well opens at the backside of the chip into a trapezoidal trench of 40- μ m depth and 220- μ m width (at the wafer surface), extending from the reservoir to the margin of the chip over a total length of 965 μ m. This trench is designed to host a 100- μ m-diameter capillary which can be used to connect the on-chip reservoir to an even larger, remote reservoir (Figs. 23.13b and 23.14). In this case, the capillary needs to be glued and capped with a thin counterplate to cover the whole backside of the chip. The other side of the



Fig. 23.14. Zoom-in view on a quarter of the NFP chip in combined reflected and transmitted light optical microscopy: (a) top view with more reflected light; (b) top view with more transmitted light, showing the reservoir well. *1* Reservoir membrane, 2 microchannels, 3 tip, 4 stabilization beam, 5 central spacing post, 6 reservoir well



Fig. 23.15. Volcano ink dispensing tips: perspective on the cantilever end (**a**) and tip details (**b**),(**c**). The radius of the tips varies between the thickness of the lower thin nitride film (250 nm) molded around the convex Si precursor (**b**), to tens of nanometers (**c**). The latter was achieved by a sharpening process that occurred with prolonged CF₄ reactive ion etching (RIE) after removal of the top nitride. The off-center position of the core tip is an effect of reversible deformation of the structures that has been regularly observed live during the charging process and may lead to a mechanism similar to that of the rapidograph writing nibs

microchannels opens into a volcano-shaped dispensing tip with a height of 7–8.5 μ m at the end of the cantilever (Fig. 23.15). The front side of the chip is provided with a central rectangular post of 9–10 μ m thickness, to prevent the damaging of the reservoir membranes when mounting the chip under the spring clamps of AFM heads. In case electrodes are present on the chip, as planned for future applications such as EPN or actuated probes, this prevents also their shortcut.

The fabrication of the novel, second-generation NFP chip is presented in Sect. 23.2.2. Various tests performed with NFP chips to test their functioning and performances are presented and discussed in Sect. 23.2.4, where we give also an outlook to the future applications and device developments. The quest for integrating piezoactuators on these types of cantilevers is presented in Sect. 23.2.3.

23.2.2 Microfabrication of the NFP

The fabrication of the device in Fig. 23.16 starts with the formation of silicon tips on top of a silicon wafer, by underetching SiO₂ precursor caps in KOH to form {114}-faceted pyramids. These are further etched by a hydrofluoric acid–nitric acid– acetic acid isotropic etchant for detaching the caps and sharpening. This process is identical to the one used and optimized for the first-generation NFP [58]. The etching for the formation of the tips also produces the central mesa structure used as a spacer in the AFM mount, and recesses the active chip surface about 9 μ m below the wafer surface, which prevents damage of the tips in the later lithographic processes and wafer handling. This necessitated the performance of all subsequent optical lithography processes using relatively thick photoresist (7–12 μ m of Shipley SPR 220-7), with special care for high aspect ratio structures and side wall profiles.

A first layer of low-stress Si₃N₄ (low-pressure CVD, LPCVD) of 300–350-nm thickness is then deposited and patterned on the backside of the wafer, to form the rectangular windows for etching the trapezoidal trenches for the attachment of the capillaries (trenches can be seen in Fig. 23.13). The process flow in a cross section of the reservoir area can be followed in Fig. 23.16. A KOH etching of these trenches is subsequently performed for a depth of approximately 40 µm. The front-side nitride is then patterned (CF₄ reactive ion etching, RIE) outlining the cantilevers and the interchip. The pattern also contains an array of 3-µm-diameter holes at the place of the reservoir, forming a sieve to later connect the microchannels with the reservoir wells. This bottom nitride layer makes a conformal covering of the Si pyramids and forms the tip material. A SiO₂ layer is then deposited (500 nm, low-temperature plasma-enhanced, PECVD, at 200 °C) and patterned, to form the microchannel core sacrificial layer. Besides the path of the microchannel lumen and reservoir, the SiO_2 pattern contains lateral beams all along the microchannels (details visible in Fig. 23.17). These beams have a twofold role: on one hand, they provide the place from where the sacrificial material will later be contacted and removed while minimizing the sealing perimeter; on the other hand, they stiffen the cantilevers for lateral bending or torsion, while keeping the longitudinal bending stiffness low. This solution was adopted to improve upon the former-generation NFP, while keeping the cantilever stiffness in the desired range. The reflective area of the cantilevers was also increased, to provide a stronger reflected light signal for the optical lever.



Fig. 23.16. Fabrication sequence of the NFP chip after the formation of the Si tips – the reservoir area. (**a**) Si₃N₄ deposition, backside lithography, and backside KOH trench formation; (**b**) front-side lithography for cantilever and connection holes delineation; (**c**) plasma-enhanced chemical vapor deposition (PECVD) of SiO₂ and patterning for channel core and reservoir delineation; (**d**) low-pressure chemical vapor deposition of low-stress nitride and patterning; resist deposition on front side and etching of protruding tips (not shown); (**e**) etching of SiO₂ sacrificial layer; (**f**) PECVD of SiO₂ sealing layer on the front side and thick resist lithography on the backside of the wafer; (**g**) formation of reservoir wells and chips by deep RIE of Si

The deposition of the top Si₃N₄ layer (500 nm, low-stress LPCVD) continues with the lithographic patterning to enclose the formerly delineated cantilevers, and the SiO₂ pattern. Small openings ($2 \mu m \times 3 \mu m$) are provided across the base of the earlier-mentioned SiO₂ beams, and an array of 3-µm-diameter holes is also formed in the reservoir area, symmetrically intercalated with the similar holes made in the first nitride layer. Etching of these features in the top Si₃N₄ layer was done by CF₄ RIE through a thick (10-µm) photoresist mask, preventing the attack upon the tips. This photoresist was removed and replaced by a 5-µm-thick photoresist, through which the tips were this time protruding for about 2–3 µm. A CF₄ + O₂ RIE was performed to remove the nitride from the top part of the tips, exposing



Fig. 23.17. Snapshots of a movie showing the motion of water (*darker tint*) inside the sealed microchannels. *Arrows* point to sealing points and lateral channels. One can notice there is no penetration of water from the central channel into the lateral channel, a sign of a correct sealing. After snapshot 3, the sample was moved such that the meniscus was still observable; the *upper-left channel* in images 1-3 becomes the *lower-left channel* in images 4-8. The time spacing between the frames is approximately 1 s

the SiO₂ layer. In variations of this process, leading to sharp tip geometries such as in Fig. 23.15c, the etching was prolonged until the complete penetration of the SiO₂ layer at the tips, and continued for a slight etching of the bottom nitride layer. After these processes, the photoresist was removed and a buffered oxide etch (BOE 10:1) was performed for about 400 min, to completely remove the sacrificial SiO₂ layer. During this process, although not clearly measured, a slight attack on the Si₃N₄ is believed to have occurred, leading to thinning of the nitride especially in the portions where the material was exposed on both sides and for longer time, such as the channels and the tips. This may have contributed to an additional sharpening of the tips. To prevent the collapse of the double nitride membrane in the reservoir region, and the channels in general, supercritical CO₂ drying was used after every wet process following from this step.

The fabrication continued by depositing a SiO₂ layer (approximately 1.5 μ m, low-temperature PECVD) to completely seal the holes through which the channels and the reservoirs were cleared from the sacrificial material. Since minimal deposition conformity was desired to ensure that the channel lumen would not be reduced, the temperature in the PECVD process was reduced as low as 150 °C, which produced a material with residual stress similar to that of low-stress silicon nitride (approximately 180 MPa tensile), thus causing the cantilevers to remain reasonably straight after release. The sealing film was patterned lithographically by wet etching (BOE), to remove it from certain areas, including the tip region, such that a complete sealing along the channels and reservoirs was preserved while making the tip orifice communicate with the channels. At this step, the tip–channel–reservoir communication could be proven by watching the water motion and evaporation under the microscope, as shown in Fig. 23.17 and explained later.

The next step was the deep RIE (DRIE, Bosch process) of the backside of the wafer, through a 9-µm-thick photoresist layer patterned with the reservoir wells

and the chip delineation pattern. For this process, the photoresist was UV-hardened and baked for 9 h at 80 °C, to prevent the reflow, especially critical in the well region, since the wells are in the deeply recessed area of the trapezoidal trenches for the capillary connections. This fact imposed an optimization of the lithographic process. Since the etching rate in the DRIE process is highly sensitive to the area of the features, simultaneous opening of the reservoir well with reaching the cantilevers from the backside in the interchip required special attention. A preliminary study with dummy wafers showed that, if starting from a flat surface, the interchip complete opening was reached while the reservoir well remained with about 40 μ m to be etched. This result obviously depended on the particular wafer size (in this case 3-in. wafers of 380–425- μ m thickness), the exposed-to-unexposed area ratio, the relative positioning of features, the equipment used (Unaxis SLR 770), etc. The 40- μ m "handicap" for the large area proved reasonable for the thickness variation of wafers in our case.

For the etching, the 3-in. wafers were glued on handling 4-in. wafers using a ZnO-containing Dow Corning 340 silicone heat sink compound, which was applied manually on the front side of the NFP wafer, mainly on the Si frame area and especially avoiding the reservoir areas. This mounting also prevented the stopping of the process at the first punch-through events on the NFP wafer. The DRIE process was carried on in sequentially decreasing steps, by carefully measuring the initial thickness for each individual wafer and the etching depths achieved at each step. The rigorous control was needed since the Si₃N₄, although is has a lower etching rate than silicon in the Bosch process, is not an effective etch stop material and could have led to damages at the rear side of the cantilever channels. The DRIE process was stopped when the reservoir well reached the double Si₃N₄ membrane. Fine removal of Si for clearing completely the backside of the cantilevers was possible in some cases using XeF₂ etching, but for a limited time, since after approximately 30 min of etching, damages on the Si₃N₄ could be noticed. However, in most cases, this process was not necessary.

The choice of DRIE over KOH etching for the chip release and reservoir formation was motivated by the small amount of space available in the chip to fit two reservoirs, given the fact that the NFP chip should be of standard size for conventional AFM heads. Another advantage of DRIE is the increase in the number of chips fabricated per wafer, owing to the elimination of tilted walls and convex corner compensation beams in the interchip, required by the KOH release process [58].

After completing the etching, the NFP wafers were detached from the handling wafers in hot Nanostrip solution (Cyantek) by careful lateral sliding and were kept in solution until complete removal of the silicon heat sink compound was achieved. Deionized water and methanol rinsing followed and supercritical CO_2 drying completed the process. At this step, the NFP chips remained attached to a Si frame for easy handling, as shown in Fig. 23.13. The NFP wafers later underwent a gold sputtering (approximately 20 nm) on the backside, to enhance the reflectivity of the cantilevers (not shown in Fig. 23.13).

The connectivity between the reservoir, channels and volcano dispensing tips could be checked, after etching the sacrificial oxide layer and performing the sealing step, by imaging the chip under an optical microscope. In this experiment, a water was fed into the channels by placing a droplet onto a volcano tip using a micropipette. The motion of the water meniscus, due to capillarity and evaporation, could then be clearly observed and recorded (Fig. 23.17). After releasing the chips, the connectivity between the reservoir and microchannels was also tested by feeding water with a micropipette into the reservoir well. Proper sealing could also be tested in this manner, by observing the color change and meniscus motion, not proceeding beyond the sealing points and into the lateral channels. The connectivity from the reservoir up to the dispensing tips could also be substantiated from writing tests performed with various inks.

Figure 23.18a shows a SEM image of a volcano-shaped tip after feeding the reservoir with DNA and buffer solution. The image shows evidence of unstable flow with molecular ink around the tip and the volcano outside wall. As discussed in the context of Fig. 23.7c, depending on the wetting angles, which in turn are a function of the buffer chemistry for a given microchannel material, unstable flow may result. In this case it is clear that such unstable flow took place in agreement with the numerical predictions. The experiment was conducted to demonstrate the capability of the NFP to deliver copious amounts of ink if desired.

Evidence of fluid ink persistence in the reservoir and channels during sufficient periods of time, such as those required for performing writing tests, was also obtained. Simple timing measurements performed under a stereomicroscope revealed that solutions of water and alcohol persisted in liquid form for 10–30 minutes in the well even in the absence of capping. It was observed that the capillarity dynamics keeps the channels filled with liquid during all this time and that the channels are the last to dry out.

Despite these observations, there is also more direct evidence of fluid flow in the NFP system during writing. For instance, in tests performed with a solution containing fluorescein isothiocyanate labeled DNA there were instances in which a 10- μ m-diameter spot formed rapidly as a result of the unstable flow previously described (Fig. 23.18b). We found that by controlling the buffer chemistry, stable flow could be achieved. We will illustrate the NFP direct patterning of DNA molecules with a resolution of 200 nm in Sect. 23.2.4.



Fig. 23.18. Evidence of molecular ink coating and unstable flow during the writing process. (a) SEM micrograph showing unstable flow from a volcano tip, after feeding a solution of DNA and buffer into the reservoir. (b) A 10- μ m-diameter fluorescent dot of fluorescein isothiocyanate labeled DNA on a gold substrate formed as result of unstable flow (see also Fig. 23.7c and its discussion)

23.2.3 Independent Lead Zirconate Titanate Actuation

Independent actuation of probes and position/contact sensing are important aspects in the modern operation of AFMs. Normally, an AFM probe is moved in the zdirection by a piezocrystal mounted in the AFM head. The motion in the x-ydirections relative to the sample surface is achieved either by the x-y motion of the sample-holding stage, or by the x-y motion of the AFM head. In both cases, thermal or piezoactuation can be employed. In most modern AFM equipment, the x-y (scanning) motion of the AFM head is performed with a piezoelectric crystal of a special geometry, allowing the independent control of the z-motion and the x-yscanning. This is achieved at the expense of increasing the size of the AFM head (usually approximately 2-4 cm in diameter). The optical z-motion detector may also be included in this head. In the case of arrays of cantilevers as AFM probes, AFM heads can provide only one degree of freedom in the z-direction, i.e., a global motion of the entire probe chip. In the specific case of the "millipede" approach developed by IBM [86, 88], the z-motion of each cantilever in a 32×32 array is controlled by a thermal actuator. The device works in contact mode, such that a continuous contact is necessary during scanning. A global leveling scheme is used to keep the probe array parallel and in contact with a flat thermoplastic polymer surface. For this, four cantilevers at the corners of the 2D probe array are feedback-controlled to keep the probe array at approximately $1 \,\mu m$ from the substrate. Except for the four feedback-controlled cantilevers, all the others are moving without control. The method was previously used by Lutwyche et al. [89] to perform parallel imaging with a 5×5 array of AFM probes.

Multispot optical sensors for measuring the positions of several cantilevers at the same time (or sequentially, but at a fast rate) have not yet been developed. It is obvious then that independent actuation and control of probes in multitip AFM devices has to pursue a different path. Several methods for independent actuation were experimented.

Thermal actuation in the context of the DPN technique was pursued by Bullet et al. [90]. In this implementation, a general *z*-motion control for a linear array of probes is provided by the AFM head with feedback on one cantilever, while the others are independently actuated via bimorph thermal actuators with contact only assumed by the parallel placement of the probe array with regard to the substrate.

Piezoelectric actuation of AFM cantilevers was successfully pursued and is documented in the literature [91–93]. Two piezomaterials were employed: ZnO (single cantilevers with ZnO actuation are commercially available [94]) and lead zirconate titanate (PZT) [95, 96]. These materials can be used both for actuation (direct piezoelectric effect) and in sensing (inverse piezoelectric effect). Sensing can also be achieved on the basis of the piezoresistive effect in thin films or doped regions in silicon cantilevers. Complicated 3D structures for piezoresistive sensing both in the z-direction and in the lateral direction (y) were developed [97] and capacitive sensing was also reported [98]. The read-out circuitry, to measure sensor deflection, can be integrated on the chip, using a standard CMOS process [99], in which case the cantilever definition has to be a postprocessing step. The presence of an actuator on the AFM cantilever can be used also to control actively the Q factor of the cantilever, with benefits in increased scanning speed. For this, a force proportional to the deflection speed can be applied on the actuator, mimicking an increased damping factor.

The major difficulty in piezoelectric actuation is the integration of the piezoelectric material deposition, thermal curing and patterning in the general probe fabrication process. Piezoelectric materials are generally high thermal budget materials: they require high-temperature deposition or a thermal treatment for proper crystal formation. Adhesion is also a problem; hence, well-tailored electrodes are necessary such as Al with SiO₂ protection for ZnO [91] or a stack consisting of 0.25 µm Ti/Au, 3.5 µm ZnO, 0.25 µm Ti/Au [94]. PZT usually requires sputtered Pt thin films as electrodes and as adhesion layers, which also demand special attention in their patterning. Additionally, ZnO and PZT have a poor chemical resistance to most acids and bases used in the lithographic processing of the cantilevers, for which the piezomaterial needs to be protected during wet etching processes (such as KOH etching of Si or buffered HF for etching of SiO₂). RIE of ZnO or PZT is based on chlorine or fluorine chemistries, which also etch Si, Si₃N₄ and SiO₂. This low selectivity with regard to metals and Si-based materials makes it necessary to deposit additional protective layers (e.g., polyimide, wax, Teflon AF), while patterning of the top electrodes can be achieved only by lift-off processes [85] or by processes that etch both the metal and the piezomaterial [91]. While PZT has better piezoelectric properties than ZnO, it contains lead, which presents contamination problems. As a result, only postprocessing schemes or dedicated equipment can be used for patterning (such as RIE, DRIE, furnaces). Both ZnO and PZT are brittle materials and as such they raise challenges related to cracking, delaminating or bending induced by thermal mismatch or intrinsic stress. For DPN or NFP patterning, the desired cantilever stiffness is in the range 0.03 - 0.30 N/m; hence, the significant increase in stiffness resulting from the presence of a piezoelectric film is somewhat undesirable and needs to be taken into account in the cantilever design. Because of this and the inherent presence of electrode materials, low-stiffness AFM probes can be achieved only at the expense of increasing the cantilever lengths $(700-1000 \,\mu\text{m})$ [91]. Depending on the deposition method, the piezoelectric materials for cantilever actuators have thicknesses in the range $0.2-5 \,\mu\text{m}$. Although better piezoelectric properties are expected from thinner films [100], the necessary thickness of the material has to be determined from constraints in operating voltage and required cantilever end deflection. The calculation method is presented in [85]. Thickness and piezoelectric constants are dictated by the type of material (ZnO or PZT) and deposition method: 0.5-2 µm of ZnO films can be deposited by direct or reactive sputtering (sputtering from a Zn target in an O₂ atmosphere), while PZT can be deposited by metal organic CVD (MOCVD), sputtering [101], reactive RF sputtering [100] or sol-gel methods [102]. A thermal treatment at $650 \,^{\circ}$ C is usually necessary for sintering the PZT to form the perovskite phase, while a Pt film on the substrate (also used as the electrode) helps in texturing the grains with the *c*-axis (which presents the highest transversal piezoelectric effect) normal to the substrate. To exploit this orientation of the *c*-axis, the PZT has to be sandwiched between the electrodes (rather than forming interdigital electrodes with PZT on top).

The integration of ZnO and PZT films on special AFM cantilevers of the type used in the NFP chip was experimented. The PZT material proved superior in terms of

general process compatibility and thickness requirements to achieve the same bending effect. The PZT deposition and patterning processes (Fig. 23.19) were studied and optimized to avoid destructive interferences in the fabrication processes. Successful cantilever array actuation was achieved by depositing a 250-nm-thick PZT



Fig. 23.19. Fabrication scheme (**a**) and optical image of cantilevers with PZT actuators and electrodes prior to release (images were taken portion by portion owing to the limited magnification of the microscope used, and were subsequently combined). Cantilevers were released afterwards by XeF_2 etching and were successfully actuated by applying square waves through the electrodes



Fig. 23.20. (a) Optical micrograph showing released cantilevers of the first-generation NFP with PZT actuation, with the lower cantilever actuated (raised) and the three upper cantilevers unactuated (down); actuation movie available at [103]. (b) Phase-shift interferometric microscopy image for actuation studies. (c) *Curves* showing the cantilever longitudinal profile upon applying actuation voltages from 0 to 5 V

layer by MOCVD on patterned Pt electrodes (lift-off). After sintering at 650 °C, a Pt top electrode was patterned on the top of the PZT material by lift-off. The Pt electrode was also used as a masking layer to etch the PZT in a CH₂FCl RIE plasma (100 standard cm³/min, 50 mTorr, 200 W). The cantilevers were released by XeF₂ etching of the underlying Si, a process that did not interfere much with the NFP cantilever structures (although a slight attack on the Si₃N₄ is known to result during long exposure times). Released cantilevers are shown in Fig. 23.20a. Employment of a phase-shift interferometric microscope allowed independent actuation of the cantilever to be assessed (Fig. 23.20b,c) [103]. The bending effect resulted in a total cantilever end displacement of 4 μ m for a 500- μ m-long cantilever at an applied voltage of 5 V. Repeated bending by application of a 5-V peak-to-peak square wave with a frequency of 100 Hz for 10 h showed no change in the electromechanical response.

23.2.4 Applications

23.2.4.1 Molecular Ink Writing with Continuous Ink Feeding

Several types of inks were tested with the NFP devices. To take advantage of the experience accumulated from DPN, ODT and MHA inks in conjunction with gold substrates were first tested. Patterns with line widths as small as 40 nm have been successfully written using "normal" volcano tips (without a W nanowire). In these experiments, an ink – a solution of MHA in ethanol at a concentration of 1 mM – was supplied via the on-chip reservoir to the dispensing tip by capillary action. After the tip had been brought into contact with a gold substrate, the molecules were transported to the substrate, creating the desired pattern as the tip was laterally



Fig. 23.21. Lateral force AFM image of MHA deposited in the shape of the letter N [57] (**a**) and text (**b**) [58] onto a gold substrate by the volcano tip with first-generation NFP. Both writing and imaging were performed by the same tip

moved along a preprogrammed path (Fig. 23.21). The pattern was obtained with a sweeping rate of $0.05 \,\mu\text{m/s}$, at room temperature and a relative humidity of 60%. The writing process was as repeatable as the DPN writing mode.

Taking into consideration that the microfabricated tip radius is about 3 times the patterned line width, we find that the resolution is somewhat surprising. We attributed this feature to the tip roughness, resulting from the RIE step during its microfabrication, which leads to a much smaller contact area than the one that would occur if the tip were perfectly smooth.

For a given protocol, writing with MHA produced repeatable and uniform line patterns (Figs. 23.21b and 23.22). The reported writing tests were generally performed 5-10 min after feeding the ink into the reservoir. Observation of the ink drying process in the reservoir of unmounted chips showed that the ink remains in the liquid state for about 12 min. Tips with longer delaying times before writing also performed well (dried ink).

Several writing protocols using thiol-based inks in conjunction with gold substrates and acetonitrile as solvent were performed with the second-generation NFP with similar results. More interestingly, the device was able to achieve parallel and dual ink writing. Simultaneous patterning with two types of inks was performed using solutions of different thiolates. MHA and 1H, 1H, 2H, 2H-perfluorododecane-1-thiol (PFT) were selected for testing since PFT produces dark contrast in AFM friction images while MHA gives bright contrast. We prepared saturated solutions in acetonitrile of both materials. One reservoir was filled with a droplet of MHA solution using a micropipette. Subsequently, with the micropipette tip replaced, the other reservoir was filled with the PFT solution. This feeding process was performed under a stereomicroscope to confirm that the droplets of both solutions did not cross-contaminate. Following the feeding procedure, the chip was mounted in an AFM instrument (Thermomicroscopes CP). Since only four cantilevers could be

Σ μm

Fig. 23.22. Lateral force image of arrays of lines written with MHA on gold, using the second-generation NFP device. The line widths in this picture are approximately 150 nm, but lines as fine as 40 nm were obtained [57]

seen by the CCD camera of the AFM, the viewing field was adjusted to capture the four cantilevers from the middle of the 12-cantilever array. While the deflection of only one of the four cantilevers was monitored by the AFM optical lever, the others were passively operated and supposed to touch the substrate roughly in the same way as the monitored one. Once the tips had been brought into contact with a gold surface, customized software was used to move the tips along the surface to pattern dot arrays. For characterization purposes and to avoid distortion of the dot patterns by depositing new ink, the patterns formed were examined with a different probe, a commercially available silicon nitride imaging tip. With a reference mark on the surface, the imaging tip was located first on an area where a MHA-fed tip was operated. The surface was scanned to obtain a LFM map (Fig. 23.23a). Subsequently, the tip was moved to an area where PFT was patterned, followed by imaging the area (Fig. 23.23b). Similar patterns were recorded for arrays of dots written with different probes of the array. The two molecular inks were chosen on purpose to have similar writing dynamic. For instance, independent tests demonstrated the writing capability of the NFP with both MHA-acetonitrile and ODT-ethanol solutions; however, the much lower writing speed of ODT made the simultaneous writing impractical.

In separate experiments, NFP chips were tested for patterning lines, using MHA solution in acetonitrile as the ink at various scanning speeds. Writing proved reliable up to a writing speed of about $15 \,\mu$ m/min. The minimum line width obtained was approximately 78 nm. (Fig. 23.24).



Fig. 23.23. Dot calligraphy test with the NFP for simultaneous writing with two different inks. LFM images of areas $(15 \,\mu\text{m} \times 15 \,\mu\text{m})$ patterned with MHA (**a**) and 1H, 1H, 2H, 2H-perfluorododecane-1-thiol (**b**). The difference in the sizes of the dots is deliberate: contact times were 6, 4 and 2 s for alternating rows, respectively. Relative humidity was maintained at $70\% \pm 5$



Fig. 23.24. Line patterns written with the NFP on a gold substrate with MHA ink. The LFM image was used for section analysis. The sweep rates for the unit set of lines (A, B, C and D) were 3.2, 6.4, 12.8 and 25.6 μ m/s, respectively

The patterning capabilities of NFP were also tested with other type of inks, such as ODT, hexamethyldisilazane, diamond nanoparticles, DNA and proteins. The last two are of particular significance for making the NFP a specialized tool for biopatterning, as presented in the next section.

23.2.4.2 DNA and Protein Arrays

Precise placement and control of biological materials down to a few molecules per surface spot is crucial in developing bioassays and novel biomolecular recognition techniques, such as sequencing, protein identification and combinatorial drug testing. Reducing the size of the active assay area is essential for maximizing the probability of interaction between molecular species, when they randomly diffuse over a nanoarray area, especially when the number of molecules to be identified is limited. While decreasing the number of reacting molecules, there is, however, an increase in the relative weight of fluctuation in the number of occurrences per spot, which makes an assay significant statistically only if the experiment involves a high number of spots. Thus, arrays of high density of spots are needed and are highly desirable in biomolecular applications.

Since the introduction of DNA or protein microarrays, which consist of a dot matrix of such molecules, developments in the life sciences have been expedited. Such controlled deposition is the key leading to the development of many surface patterning and advanced cantilever-based patterning tools [24,27,28,57,87,104,105]. A few micron-diameter arrays of dots are currently produced with microspotters, but the challenge is to produce submicron dot arrays, with sub-100-nm diameters, for which DPN and NFP are a sensible technical solutions.

DPN was used to pattern modified oligonucleotides on surfaces of gold and modified silicon oxide [51]. In typical DNA patterning by the DPN technique, silicon nitride tips were coated with 3-aminopropyltrimethoxysilane (APTMS) in order to improve the coating effectiveness of DNA. Micropipettes were also employed to deliver such molecules. A solution contained in a pipette was ejected by electrochemical current on a glass surface [106]. Likewise, cantilevered nanopipettes were employed to locally deliver proteins on surfaces [107]. The resolution of the micropipette-based technique is critically determined by the outer diameter of the tip as the solution tends to flood out of the aperture when brought into contact with surfaces – especially hydrophilic surfaces. The feature size is usually above $1 \,\mu m$ and the minimum feature size achieved so far is approximately 250 nm. To achieve this resolution, it is pivotal to fabricate tips with a small aperture. Unfortunately, reproducibility in micropipette or nanopipette fabrication is low; hence, micromachining techniques have attracted significant interest. For example, cantilevers were micromachined to mimic conventional pin-type microspotters. A buffer solution is transported via open microchannels to the gap between cantilever ends and deposited on a substrate by direct contact. Miniaturized gaps were produced by improved design to achieve patterned feature sizes as small as $2-3 \,\mu m$ [27]. However, it still remains a challenge to accomplish submicron patterning with such microspotters because the feature size is determined by the gap size, which is about 1 µm when conventional UV lithography is employed. The so-called NFP provides a much better resolution for the reasons elaborated in a previous section. Continuous molecular ink-feeding in closed microfluidic systems and high-resolution writing, as small as approximately 40 nm, were achieved with this technique [57]. Direct submicron pattering of DNA solutions, continuously supplied to the volcano tip rather than coated by dipping and *without* the need for APTMS priming, was also demonstrated. Capillary feeding was utilized to continuously supply ink to the tip from an on-chip reservoir. As presented in Fig. 23.25, the NFP device was used to pattern gold surfaces with alkanethiol-modified oligonucleotides. The patterned DNA spots were subsequently hybridized with complementary DNA functionalized Au nanoparticles (approximately 15 nm in diameter).

Patterning was performed with a commercial AFM (Thermomicroscopes CP), with one cantilever selected for deflection detection, while the other cantilevers passively made contact with the surface. The AFM was placed in an environmentally controlled glove box at a relative humidity of $70 \pm 5\%$ and room temperature.

The ink used was a solution of $6.60 \,\mu$ l phosphate buffered silane, $3.06 \,\mu$ l dimethylformamide and $0.34 \,\mu$ l water containing $0.3 \,M$ MgCl₂ and 10 mM hexanethiol-modified oligonucleotides. The solution was fed into the on-chip reservoir using a micropipette, but direct feeding via a capillary tube adapted to the chip is possible for large-scale applications. Immediately after the feeding, the chip was mounted into the AFM. Once the tip had been brought into contact with the gold surface, customized software was used to laterally move the tips. An array of dots was patterned with three different contact times of 2, 1 and 0.5 s, for each alternating row of the array. After the patterning, the surface was passivated by immersing the substrate in a 1 mM C6 hexanethiol solution of ethanol for 5 min. Subsequently, the substrate was rinsed with ethanol followed by distilled water, and then blown dry with nitrogen gas.



Fig. 23.25. DNA patterning by NFP

In order to examine the patterned DNA spots, complementary DNA functionalized Au nanoparticles (approximately 15 nm in diameter) were applied. A three-DNA-strand system was used, consisting of capture, target and probe strands [108, 109]. While the patterned DNA worked as a capture strand, target and probe strands were applied after the patterning and the C6 passivation. The Au nanoparticles had been functionalized with the probe strand and the target strand was used to link the capture and probe strands. The substrate with the patterned DNA array was immersed in a solution containing both linker and probe strands. After approximately 40 min of hybridization at 37 °C, the substrate was rinsed with ammonium acetate buffer to remove nonspecifically bound Au nanoparticles.

The hybridized spot array was imaged by dark-field optical microscopy and AFM topography (Fig. 23.26). In the dark-field optical micrograph shown in Fig. 23.26a, the assembled nanoparticles produced Rayleigh scattering. The larger dots in rows 1 and 4, produced by 2 s of contact time, are easily visible. Some of the smallest dots in rows 3 and 6, produced by 0.5 s of contact time, are less clear. The AFM topography was obtained in tapping mode, and the measured height was approximately 20 nm. All the dots are clearly defined except for a few missing dots.

The typical spot size routinely produced with this technique was about 200– 300 nm in diameter, depending on the contact time. The oblong shape of the spots is directly related to the tip shape and, eventually, to its mechanical deformation during the contact time as a result of the tip compliance within the volcano shell. The resolution achieved is much better than that obtained in previously reported cantilever-based tools. In contrast to micropipette-based devices, it has the advantage of scalability. With the simultaneous multi-ink patterning combined with the DNA patterning and scalability to a 2D array, the NFP has the potential of being the tool of choice to mass-produce microarrays of DNA and proteins. Since it does not need pretreatment of the tip prior to DNA patterning, it would require fewer preparatory steps and fewer opportunities for contamination or damage in the array of tips.



Fig. 23.26. Optical dark field image (*left*) and AFM topography (*right*) of the DNA dot array patterned by second-generation NFP. The contact times were 2, 1 and 0.5 s, respectively, for each alternating row of the array

23.2.5 Perspectives of NFP

The future of NFP will likely consist of the development of 2D arrays of probes capable of writing with several molecular species, with independent actuation, and eventual independent sensing. The developments are supported strongly on one hand by the need to increase writing speed and on the other by the capability to fabricate by standard micromachining processes probes of high complexity. Figure 23.27 illustrates a possible architecture for such a 2D NFP array.

When expanded to 2D arrays, the use of a scanning stage for the motion of the sample will be necessary because the z motion of the piezotubes in commercial AFMs is coupled with the x-y scanning and also because the mounting angle of a probe is usually not parallel to the scanning substrate (probes are mounted with tilt angle of approximately 15° to the substrate). X–Y scanning stages with feedback control, nanometer resolution and five degrees of freedom $(x, y, z, \theta_y, \theta_y)$ are commercially available [110]. Such stages can be used for the alignment and scanning of the 2D probe array. In order to align the substrate to the NFP array, avoiding independent sensing on each probe, three microfabricated deflection sensors placed on the periphery of the array can be used to control the plane of the NFP array. Since PZT is capable of both actuation and sensing, probes at three locations on the periphery of the array can be designed to work as sensors that could send feedback contact information to the corresponding stage actuators. Using feedback-control algorithms, the stage actuators can, in turn, adjust the substrate (stage) parallel to the array. With the distance between the array and stage maintained constant while scanning, the writing status of individual cantilevers can be turned on or off by applying an activation voltage to the independent PZT probe actuators. Ideally, each cantilever requires two electrical connections. When a 2D array becomes massively parallel for



Fig. 23.27. 2D array of NFP including multiple reservoirs and independent PZT actuation of cantilevers

higher throughput, the area needed for electrical connections and pads proportionally becomes massive. In order to reduce the complexity, pads can be shared row-by-row and column-by-column with use of an $N \times N$ multiplexed addressing schemes as in random access memories (RAM).

For future development of PZT actuated probes, special attention will be needed to minimize the hysteretic effects in the piezoelectric materials. The deflections presented in Fig. 23.20c were obtained for a monotonic increase in the applied voltage starting from a given material history. With further application of square waves, slightly different deflections were measured. This problem can be alleviated by optimizing the deposition of the piezoelectric material such that hysteresis is minimized. Fatigue and exhaustion of the piezoelectric response can also limit the function and life time of independently actuated probes. This and many other challenges remained to be addressed in the design of systems for massively parallel patterning of a variety of molecular species. One of them, tip wear, is addressed in the following section.

23.3 Ultrananocrystalline-Diamond Probes

Wear resistance and long functional life time become paramount when designing complex 1D and 2D arrays of AFM probes, especially for contact mode techniques such as DPN and NFP. Clearly the cost of fabricating such probes is high because of the number of processing steps. Hence, materials exhibiting low wear should be employed to maximize the life of the array and as a result produce more cost-effective probes. Wear resistance can be defined in terms of scanning distance and wear rate (i.e., amount of material removed per unit mechanical work). The materials in contact, the force applied on the probe, the environmental parameters (temperature, humidity, gas composition in the AFM chamber, contamination species) and the ink types are all important parameters controlling the wear rate. Even though the theory of friction in AFM applications has gained some attention, leading to interesting concepts such as wear or friction-free mechanical motion or nanoscale lubrication, systematic experimental measurements have not yet been reported.

Engineering new materials and developing simple fabrication processes is one way of addressing this problem. Both aspects will be discussed here. We also focus on probes which may be attractive for integrating new functions, such as independent sensing and actuation, arraying, multiple probing techniques, microfluidics and/or scanning probe machining. The life time of probes is typically shortened by mechanical failure in operation and handling, pickup of material and particles from the samples, and wear. While the former can be enhanced by more careful procedures, the latter is especially important in contact mode techniques, such as contact mode AFM imaging [111], scanning spreading resistance microscopy [112], atomic scale potentiometry [113], scanning thermal microscopy [114] and lithography [71, 115], for example, DPN and fountain-pen nanolithography [46, 57, 68, 69, 71]. To reduce probe wear, hard materials are typically employed, among which diamond is the obvious material of choice. Furthermore, diamond possesses surface and bulk properties that are ideal for probes: very low chemical reactivity, a low work function

when the surface is chemically conditioned, no oxide layer formation, tunable electrical conductibility by doping, and thermal conductivity ranging from relatively low (approximately 10 W/Km) for ultrananocrystalline diamond (UNCD) to extremely high (approximately 2000 W/Km) for single-crystal diamond [116].

In previous work, several species of diamond films have been employed in probe fabrication by different groups [117–122], differing mainly in the degree of crystallinity of the diamond. Initial attempts at producing conductive diamond probes for scanning tunneling microscopy involved boron-implanted macroscopic diamond crystals, which were machined by polishing and were mechanically assembled into AFM cantilevers [117]. Later attempts used boron-doped epitaxial CVD layers grown on natural diamond [120]. These approaches showed the feasibility of employing conductive diamond in probe manufacturing, but are obviously not well suited for integration. Microcrystalline diamond (MCD) or nanocrystalline diamond (NCD) films [121] have superior mechanical characteristics (wear, hardness) with respect to amorphous or diamond-like carbon (DLC) materials [122], but have higher surface roughness than the latter. DLC films are smoother and easier to integrate in more complex fabrication schemes but cannot be made highly conductive. Because of this, micromachining techniques based on molding methods [118, 119, 123] were developed to minimize the major problem of crystalline diamond films, i.e., their surface roughness when used as coatings. An alternative to molding is to use thin conformal films to cover probes made of other materials. The latter technique has the disadvantage of increasing the initial tip radius of the probes (10-20 nm) by the thickness of the diamond film (typically 70-100 nm to achieve full coverage of the substrate); thus, resulting in much lower tip sharpness. Typical commercial diamond-coated tips have radii in the 100-200-nm range. In particular cases, nanoroughness features can improve the radius of the contact area, but the general shape and aspect ratio of the probes is compromised. Molding of crystalline diamond works reasonably well, but leaves the growing surface of the diamond very rough, improper to continue the integration with other, later-deposited layers and further processes.

UNCD films [124], with grain sizes in the 2–5-nm range, retain most of the surface and bulk properties of crystalline diamond as well as the smoothness of the substrate [125, 126]. The material is deposited by microwave PECVD (MPCVD) from an Ar–CH₄ (99%:1%) gas mixture. Table 23.1 shows some of the remarkable properties of UNCD, compared with other forms of diamond. The term UNCD is used to distinguish this material from MCD [121], NCD [127] and DLC [122]. Owing to the small size of the UNCD grains, the ratio of grain boundary atoms (which consist of a mixture of sp^2 , sp^3 and other forms of carbon bonding) to bulk atoms (sp^3) is high, leading to interesting material properties, like a predictable fracture strength equal to or higher than that of single-crystal diamond and the ability to incorporate nitrogen into the grain boundaries, which gives rise to greatly increased (up to 250/ Ω cm) room-temperature n-type conductivities. A comparison between these species of diamond is given in Table 23.2.

The remarkable hardness of UNCD makes it the material of choice for contact mode nanoprobe tips. Erdemir et al. [127] measured wear rates on MCD films using a pin (SiC)-on-disc tribometer measurement technique. They found that MCD films exhibit wear rates from 0.48×10^{-6} to 55.0×10^{-6} mm³/N m. By contrast, UNCD

	Microcrystalline	Nanocrystalline	Ultranano-	Diamond-like carbon	
	diamond	diamond	crystalline diamond	ta-C	ta-H:C
Growth species	CH3* (H°)	CH3* (H°)	C ₂	С	С
Crystallinity	Columnar	Mixed diamond and non-diamond	Equiaxed diamond	Mixed diamond and amorphous	Amorphous
Grain size	$\sim 0.5-10\mu m$	50-100 nm	2-5 nm	Variable	_
Surface roughness	400 nm-1 μm	50-100 nm	20-40 nm	5–100 nm	1-30 nm
Electronic bonding character	sp ³	Up to 50% <i>sp</i> ² (secondary phase)	$2-5\% sp^2$ (grain boundary)	Up to 80% <i>sp</i> ³	Up to $\sim 40\% \ sp^3$
Hydrogen content (%)	< 1	< 1	< 1	< 1	15-60

Table 23.2. Characteristics of different diamond film species

films exhibit a wear rate as low as $0.018 \times 10^{-6} \text{ mm}^3/\text{Nm}$. It was also found that the as-grown UNCD films have friction coefficients roughly 2 orders of magnitude lower than those of MCD films of comparable thickness. The wear rate of a SiC pin rubbed against an UNCD film was found to be approximately 4000 times lower than that of a SiC pin rubbed against an as-deposited MCD film.

Next we report the fabrication of UNCD probes for AFM, integrating tips and cantilevers made entirely of this material, both in nonconducting (undoped) and in conducting (nitrogen-doped) states. The probes were characterized by electron microscopy and resonance measurements, and their performances were tested in imaging, DPN writing and conductive modes. Wear tests were also conducted to demonstrate the superior behavior of the microfabricated UNCD tips compared with that of commercial silicon nitride tips.

23.3.1 Chip Design

Two types of cantilevers with different designs were fabricated. One featured a highstiffness triangular cantilever and the other a low-stiffness arrow-shaped cantilever. The length of both cantilevers was 170 μ m, while the width of the arrow-shaped cantilever was 12 μ m and the width of the arms of the triangular cantilevers was 18.8 μ m. The thickness of the diamond (UNCD) was between 0.8 and 1.4 μ m, depending on batch and wafer-level deposition nonuniformities. The arrow-shaped cantilever was chosen instead of a simple rectangular cantilever to increase the reflective area of the probe near the tip while keeping the stiffness at a minimum. The chip body was of rectangular shape with dimensions 1.6 mm × 3.6 mm. Four cantilevers of the same type were placed on each chip, one pair spaced 300 μ m and the other pair spaced 600 μ m on opposite sides of the chips. This design follows roughly the geometry employed in commercial tips (Veeco, Ultralever). A view of the two types of cantilevers is seen in Fig. 23.28a and b, while a zoom-in of the tip apex is shown in Fig. 23.28c.



Fig. 23.28. SEM pictures of the two types of ultrananocrystalline diamond (UNCD) cantilevers with tips: (**a**) arrow-shaped cantilever, (**b**) triangular cantilever; (**c**) detail of a tip, with the *inset* showing the apex and a 30-nm-radius circle for reference. The 2–5-nm-scale grain size makes us believe that ultimately the tip vertex is much sharper

23.3.2 Molding and Other Fabrication Techniques

Molding is well known as a fabrication method for ultrasharp tips of a large variety of materials [128, 129], including diamond [130], for which tip radii of 30 nm have been reported [131]. However, the reports on diamond molding did not include oxidation sharpening as an option for increased sharpness of the probes. Tip radii were limited by the geometrical precision of the pyramidal pit etched into silicon, and by the diamond deposition and seeding parameters. The ultimate shape of such a pyramidal pit in Si(100) is given by many factors, including the accuracy of alignment with respect to the crystallographic orientation, and the lithographic performances in providing optimum geometries for windows in the masking layer used for pyramidal etching. A slight increase in the window size in one direction may result in formation of a line-edge probe rather than a point-tip probe. Since the alignment, lithography and etching processes are never perfect on the nanometer scale, one expects lineedge probes to be always obtained, depending on how much magnification is used in observing the tip end. In the approach presented, besides a sufficiently rigorous lithography ($\pm 0.1 \,\mu$ m) and care in alignment (better than $\pm 1^{\circ}$ for both flat-to-crystal and mask-to-flat alignment), an oxidation sharpening step was added (Fig. 23.29). This step, besides the additional sharpening due to constraints in the oxide growth in pyramidal pits [128], performed well in leading to single-point tip geometries.

The molding method has the general inconvenience that the tip is fabricated facing towards the substrate; thus some microfabrication effort is required to reverse the probe cantilevers with respect to the handling chip body. Several methods were reported for reversing the diamond tips: (1) building chip bodies by micromachining on separate silicon or glass wafers and gluing them onto the tip-fabrication wafer [123]; (2) fabricating tips and portions of the cantilevers on one wafer and gluing them onto cantilevers fabricated on other wafers (eventually, made of other materials), followed by releasing [132]. All these methods require aligned bonding procedures and a good resistance of the glue joint during the chip release and



Fig. 23.29. Molding of UNCD by (**a**) forming a pyramidal pit in Si(100) by orientation-dependent etching, (**b**) oxidation sharpening, (**c**) deposition of UNCD and (**d**) removal of the Si and SiO₂ mold by chemical etching

operation processes. In order to simplify this sequence, we investigated the use of metal electroforming to build a chip body within an SU-8 photoresist mold, followed by release through dissolution of the silicon substrate. Although bonding of a complementary wafer for the chip body has the advantage of offering a medium to develop electronic circuitry without interfering much with the tip fabrication, it is an unnecessary effort in the case of simple conductive probes. In our approach, simple sensors/actuators in film form, such as piezoactuators or piezoresistors, can be still integrated on top of the diamond by proceeding from the mold-side silicon wafer. Additional precautions in protecting them during the silicon mold removal may be required. Less harsh methods to remove the silicon substrate can be also considered, such as XeF_2 etch or sequential combinations of partial etch with KOH solution and finalizing with XeF_2 .

The processing steps employed in fabricating molded UNCD probes are summarized in Fig. 23.30. The fabrication starts by forming an oxide mask (thermal oxidation, 500 nm), which was patterned lithographically by mask M1 with square openings $(12 \,\mu\text{m} \times 12 \,\mu\text{m})$, followed by KOH (30%, 80 °C) etching of pyramidal pits in the Si(100) wafer. Several groups of different sized squares and rectangles were fabricated simultaneously with mask M1, corresponding to different alignment marks, such that a large variety of tip geometries could be obtained. A thermal oxidation sharpening process at 900 °C followed, which resulted in a SiO₂ layer greater than 1 μ m in thickness on the {100} surface of the Si wafer. Figure 23.31a shows one sharpened pyramidal mold, exhibiting a central black area corresponding to the recessed (sharpened) zone. An ultrasonic seeding procedure was applied with a 4–6-nm grain diamond powder suspended in methanol (5 mg/l), to which the wafers were exposed for 30 min and rinsed with 2-propanol, then ultrasonically cleaned in methanol for 5 min and dried. Growth of an UNCD layer (0.5-1-µm thick) was achieved by MPCVD in a methane-argon gas mixture, containing also nitrogen in the case of the n-doped films [124]. Next, an Al mask (80 nm) was deposited by electron beam evaporation and patterned with mask M2, defining the cantilevers. The pattern was transferred into the UNCD by RIE, using oxygen



Fig. 23.30. Fabrication of UNCD probes – processing sequence. (**a**) Oxide growth followed by lithography with mask M1, and then etching in KOH solution. (**b**) Oxidation sharpening. (**c**) UNCD and Al deposition. (**d**) Lithography (mask M2) followed by Al etching. (**e**) UNCD etching using RIE. (**f**) Al removal. (**g**) After lithography (mask M3), oxide etching on the backside. (**h**) Ti/Ni deposition followed by patterning (mask M4). Ti layer (not shown in the figure) used as an adhesion layer between UNCD and Ni. (**i**) SU-8 spin-coating and patterning (mask M5). (**j**) Ni electroforming. (**k**) Lapping/polishing. (**l**) SU-8 removal. (**m**) Etching in KOH solution. (**n**) Oxide etching



Fig. 23.31. (a) An anisotropically etched pyramidal hole, after sharpening by thermal oxidation. (b) Molded UNCD probe. (c) Zoom-in showing the probe apex with approximately 30 nm radius. A more exact calculation of the radius is presented in Sect. 4.3.1

plasma (30 mTorr, 50 standard cm³/min, 200 W), according to a process described in [133], after which the Al mask was removed by wet chemical etching. The backside oxide was patterned with mask M3, for subsequent release of the structures. A top metal was then deposited by electron beam evaporation and patterned on the front side, forming a plating base for the subsequent electroforming of the chip body.

The plating base metal must suit the electroforming metal, for example, Ni 150-nm plating base in the case of Ni electroforming, or Ti 10 nm/Au 200 nm for electroforming of gold. The choice of the electroforming metal is based on compatibility with the release procedure. Patterning of the plating base layer (mask M4) is required for avoiding the presence of the metal in the area adjacent to the cantilevers, where it may result in metal debris hanging around the cantilevers after their release. At the same time, the plating base pattern has to be continuous, for providing electrical contact to all the areas that need to be plated. Optionally, the plating base can be left on the cantilevers, to act as a reflective coating, provided no electroplating will be performed there.

In our process, a negative-tone SU-8 photoresist (MicroChem, 330-µm thickness) layer was deposited and patterned with mask M5, to form a mold for the metal handling chip body. For the chip discussed here, we used gold electroforming, but other metals may be considered for cost reduction (Ni, Cr) or for special applications including piezoactuators where Pt would be the metal of choice to subsequently grow a piezoelectric layer on top. The electroforming of the gold layer was performed in two steps: it started with the deposition of 3 µm of gold with a neutral pH Techni-gold 25E (Technic) sulfamate solution [134], to provide a good adhesion, and continued with the deposition of the thick chip body from a mildly acid pH Neutronex 309 (Enthone-OMI) bath. Both processes were performed at 40 °C, with a current density of 1 mA/cm^2 . The metal thickness ranged between 250 and $300\,\mu\text{m}$. The gold roughness and incidental side wall overplating were removed by mechanical polishing. The SU-8 resist mold was then removed in a piranha solution. The removal of the Si substrate was performed by KOH etching (30%, 80 °C), and the remaining oxide was removed by a buffered HF solution. After the removal of the sacrificial silicon mold, the chips remained suspended on a Si and gold frame, each supported by two bridges from where they could be easily clipped off using tweezers.

23.3.3

Performance Assessment and Wear Tests

The tips were characterized and sorted using field-emission SEM. The high conformity of the UNCD deposition enabled a good coverage of the pyramidal pits used as molds, resulting in tips with a nanometer-scale apex. In most cases very sharp tips were achieved from protruding features (Fig. 23.31). Owing to the nanograin size (2-5 nm) of the material, the ultimate tip radius could be in the 2–5-nm range.

Examination of the UNCD surface morphology revealed that film growth is achieved from seeding nanoparticles, which leads to clustering. As discussed in the context of UNCD strength [135,136] a large number of grains is present in each clus-

ter and imperfections between clusters were observed in the form of voids [135,136]. In the pit area, larger voids are clearly visible between grain clusters (Figs. 23.28c inset, 23.33). Growth of UNCD on ultrasonically seeded SiO₂ is more challenging than growth on Si; hence, cluster and void sizes generally tend to increase. Similar structures, but made of crystalline grains, have been observed in MCD films grown on side walls of pyramidal pits in Si [131]. The nucleation of MCD grains and intergrain gap formation on tilted surfaces were linked by Scholtz et al. [131] to the size of the diamond particles used in the ultrasonic seeding process. In their experiments, ultrasonic abrasion with 4- μ m-diameter diamond particles produced minimal intergrain gaps on flat surfaces, while for pyramidal holes, the optimum diamond particle size for uniform coverage was found to be 1 μ m. In the case of UNCD, the initiation of the film growth is done mostly by the nanometer-size diamond nanoparticles used in the seeding step, but the nucleation and growth obeys similar rules. The inset of Fig. 23.28c is a zoom-in view of one of the top clusters. A coral-like surface morphology is observed.

The surface roughness of UNCD films can be minimized to values in the 4–7-nm root-mean-square range by depositing a very thin (5–10-nm thick) metallic layer, for example, W, Mo or other carbide-forming materials, as a nucleation promoter. We have found that SiO_2 is a more difficult nucleation medium than Si, resulting in poor UNCD film adhesion, especially in the case of doped UNCD. Nonetheless, it is indispensable for maximum sharpening. In a variant of the processing sequence, we used an additional lithography step to selectively remove the oxide prior to the UNCD deposition from all areas, except the pyramidal pits. For this purpose, mask M1 was realigned, but using a reversible (negative) photoresist (Shipley AZ5214E), through which the oxide was removed in BOE.

A vibration test on the arrow-shaped UNCD cantilevers was performed using a Polytec vibrometer in differential interferometric mode (the reference beam on the chip body and the measuring beam on the cantilever). The first three resonant frequencies were measured at 32.2, 52.31 and 53.94 kHz, respectively (movies are provided as supporting materials [137]). The first and the last vibration frequencies correspond to vibration modes in which the pyramid axis oscillates with rotation around the perpendicular to the chip surface. The intermediate frequency corresponds to a motion in which the pyramid axis oscillates without rotation, i.e., it remains perpendicular to the chip surface during the whole motion. This vibration mode is well suited for AFM techniques involving cantilever oscillations perpendicular to the surface being scanned (tapping mode) [4]. Note that the high stiffness achievable with UNCD cantilevers makes it possible to increase the working frequencies, with obvious benefits in sensitivity and resolution.

The stiffness of the UNCD cantilevers was measured by the cantilever deflection method, using an AFM probe after calibration with a reference cantilever of known stiffness. We measured a stiffness value of 3.6 N/m for a 1.2-µm-thick triangular cantilever, and a stiffness of 0.94 N/m for a 0.9-µm-thick arrow-shaped cantilever. Knowing the geometry of the cantilever, we could deduce a value of $923 \pm 50 \text{ GPa}$ for Young's modulus of UNCD, which correlates well with the value of $960 \pm 60 \text{ GPa}$ measured by membrane deflection experiments [125, 126]. The stiffness of the arrow-shaped cantilever is close to the stiffness of one of the triangular nitride cantilevers of a commercial nitride probe (tip A of Veeco Si₃N₄ contact

mode probes, 0.58 N/m). This information was used to perform a comparative test on wear resistance of the tips. For this purpose, a Digital Instruments 3100 AFM was used for repeated scanning in contact mode. Imaging of an UNCD surface, $10 \,\mu\text{m} \times 10 \,\mu\text{m}$ in area, was performed with a constant force of 30 nN. The scanning of the UNCD tip was performed on the surface of an UNCD film deposited on Si for the purpose of accelerating the wear tests. The tests were run for UNCD and Si₃N₄ tips. The tips were imaged before and after the test using a field-emission SEM (LEO Gemini 1525). After 1 h of scanning, the nitride tips showed visible wear, while the UNCD tips showed no appreciable change (Fig. 23.32). The degrading of the silicon nitride tip could be detected also in the quality of topographic AFM images, while the images recorded with the UNCD tip showed no appreciable change.

In an attempt to look for the dominant wear mechanisms in UNCD, we looked for changes in the diamond tip after long scans performed for 3 h with an increased constant force of 50 nN using the triangular-shaped UNCD cantilever. Figure 23.33 presents a view of the tip apex before and after the wear experiment. One can notice the absence of a relatively large portion of the tip apex and debris gathered on the side walls of the pyramid. The geometry of the worn tip suggests that the observed wear is due to the dislodgment of a cluster of UNCD grains as a result of intercluster cracking, rather than a gradual atom-by-atom removal. This finding shows that when increasing the wear resistance of UNCD probes, one has to optimize the intercluster strength or eliminate the formation of clusters. The role of seeding in UNCD surface morphology and strength is discussed in [125, 126, 136]. Elimination of clustering



Fig. 23.32. Si_3N_4 tip before (a) and after (b) the wear test, showing damage. UNCD tip before (c) and after (d) the same test, showing no visually detectable damage



Fig. 23.33. High-resolution SEM image of an UNCD tip before (**a**) and after (**b**) a prolonged wear test. The absence of portions of the material roughly following the *intercluster contour line* suggests failure happens mainly by detaching of clusters, rather than a continuous smooth wear

would also have a positive impact in obtaining smoother, high-conformity filling of the mold template with diamond, resulting in sharper tips with controlled geometry at the nanoscale. Research on the optimization of seeding and deposition parameters was performed. In order to decrease the agglomeration of the powder in the solution, a couple of droplets of surfactant (sodium dodecyl sulfate, Fluka) were also added using a regular glass pipette.

23.3.4 Applications

Besides wear resistance, the performance of the UNCD AFM probes resides in their low work function, low chemical reactivity and high conductivity when doped. These features enable advanced conductive AFM techniques such as AFM potentiometry and nanoelectrochemistry. Molecular writing and lateral force imaging with UNCD probes were also demonstrated. Hence, combinations of conductive and writing techniques such as electrochemical DPN [46] or EPN [67] are possible. These applications are discussed next.

23.3.4.1 AFM Potentiometry

UNCD can be doped with nitrogen to enhance its electrical conductivity [138]. Since a very high concentration of dopant results in the weakening of bond strength at the grain boundaries, there is a trade-off between mechanical strength and electrical conductance of the material. We have found that a good balance between strength and conductivity can be achieved when UNCD is grown from gas mixtures containing 10% nitrogen, which leads to a material with a conductivity of $30/\Omega cm$ [139]. This material was used to prepare AFM cantilevers for various applications, following the fabrication method presented in the previous section.

To theoretically evaluate the contact resistance of a doped UNCD probe with a highly conductive substrate (such as a gold substrate), we began by computing the electrical resistivity of the probe on the basis of the geometry described in Figs. 23.34

Fig. 23.34. Probe in contact with a gold substrate and equivalent electrical circuit



and 23.35. The electrical scheme of the total resistance of the probe can be viewed as composed of the resistance of the approximate pyramidal body of the probe, the resistance of the tip end (approximately a hemisphere of radius r_0) and the resistance of the gold substrate. The resistance of the probe cantilever was neglected, being approximately 4 Ω , owing to a gold coating of approximately 50 nm, on the backside of the cantilever, deposited to improve the reflectivity. This layer is present also in the inner side of the pyramid body, as schematically depicted in Fig. 23.34.

For the calculation of the resistance of the pyramid body, an exact shape of the body must be considered, since the main contribution to the resistance comes from the vortex of the probe, where an important geometrical change is induced by the oxidation sharpening. The exact shape of the probe can be determined from a digitized SEM frontal image of the probe, taking into account the tilts. The tilt calibration can be avoided by knowing the angle of the probe pyramid from the



Fig. 23.35. (a) Geometry of the tip defined by digitizing an SEM image of the probe shown in Fig. 23.31b; the drawing is not at scale. (b) Same procedure applied at a smaller scale for the tip end radius, based on the image shown in Fig. 23.31c

crystallographic orientation of its facets [(111) planes]. Figure 23.35 shows the digitized shape corresponding to a transversal section through the probe, derived from an SEM image similar to that in Fig. 23.31b.

Figure 23.35 shows the profile resulting from a digitized SEM image after tilt compensation. The data points were fit by the least-squares method using the function

$$y(x) = y_0 - |x| \tan \alpha + \frac{a}{|x|^{\mu}}$$
 (23.1)

The values identified for y_0 , *a* and μ are those listed in Table 23.2. The origin of the *x*-axis was considered at the tip point. The radius r_0 of the tip was calculated in a similar way from a high-magnification SEM image (Fig. 23.35b). Alternatively, it can be obtained by deconvolving scans of spherical beads of known diameter [139]. The tip radius was used to calculate the contact area, which in turn was employed in computing the contact resistance.

In the following, the pyramidal part of the probe will be considered to fit the hemisphere of radius r_0 forming the tip, although is it evident that one has a square cross section, while the other has a circular base. Better approximations can be eventually adopted, but more important errors are supposed to come from the value of the resistivity and other geometrical imperfections.

For an estimation of the pyramid body resistance, note that the material under the horizontal line in Fig. 23.35a (in contact with the gold layer) has a small contribution to the total resistance. This will become more evident in the following developments. Thus, a good approximation of the contact resistance can be obtained by calculating the resistance of the pyramid trunk extending from point $y(r_0)$ to $y(x_1)$ in the vertical direction, where the origin of the axes was chosen at the apex of the gold layer, and x_1 is the coordinate at level y = 0.

The thickness of the UNCD layer was measured as $d = 0.9 \,\mu\text{m}$ and the thickness of the gold film (for increase of reflectivity) as 50 nm. From the geometry of the silicon v-grove, tan $\alpha = \sqrt{2}$ and the half-width of the probe at the point of the gold layer can be calculated as

$$x_1 = \frac{d}{\sin \alpha} = d\sqrt{\frac{3}{2}} . \tag{23.2}$$

For an elementary segment of thickness dy and cross section $(2x)^2$ in the probe body region, the resistance is given by $dR_{pr} = \rho \frac{dy}{(2x)^2}$, where ρ is the resistivity of UNCD. For the total resistance, we have to integrate over x from x_1 to r_0 :

$$R_{\rm pr} = \int_{x_1}^{r_0} \rho \frac{\mathrm{d}y}{(2x)^2} = \frac{\rho}{4} \int_{x_1}^{r_0} \left(\sqrt{2} + \frac{a}{x^{\mu+1}}\right) \frac{\mathrm{d}x}{x^2}$$
$$= \frac{\rho}{4} \left[\sqrt{2} \left(\frac{1}{r_0} - \frac{1}{x_1}\right) + \frac{a\mu}{(\mu+2)} \left(\frac{1}{r_0^{\mu+2}} - \frac{1}{x_1^{\mu+2}}\right) \right], \qquad (23.3)$$

where (23.1) for the function y(x) was taken into consideration and the absolute value was omitted since the calculation is performed in the positive half plane. This

expression shows that, since $r_0 \ll x_1$, $(r_0 \sim 25.7 \text{ nm}, x_1 \sim 1200 \text{ nm})$ the terms in x_1 accounting for the larger side of the pyramid trunk considered are not significant. This supports the fact that the approximations done on that side of the object are of minor significance. For the values being considered (Table 23.3) the resistance of the probe body as function of the tip radius r_0 is given in Fig. 23.36.

From this graph, the resistance of the pyramidal part for the case being considered, $r_0 = 25.7 \pm 1.5$ nm, is $R_{\rm pr} = 560 \pm 51 \,\Omega$, where the error in $R_{\rm pr}$ stems mainly from the accuracy of the resistivity (5% error) and the error in the tip radius calculation (Fig. 23.35b).

The resistance of the hemispherical tip can be calculated in a similar way, i.e., by considering the elementary resistance dR_{tip} of a layer of circular cross section and infinitesimal thickness dx (Fig. 23.34). Integrating over the domain x = 0 to $r_0 - \varepsilon$, where ε is the indentation depth, we obtain

$$dR_{\rm tip} = \frac{\rho \, \mathrm{d}x}{\pi y^2} \tag{23.4}$$

and

$$R_{\rm tip} = \int_{0}^{r_{\rm o}-\varepsilon} \frac{\rho \, \mathrm{d}x}{\pi y^2} = \frac{\rho}{\pi} \int_{0}^{r_{\rm o}-\varepsilon} \frac{\mathrm{d}x}{r_{\rm o}^2 - x^2} = \frac{\rho}{2\pi r_{\rm o}} \int_{0}^{r_{\rm o}-\varepsilon} \left(\frac{1}{r_{\rm o}-x} + \frac{1}{r_{\rm o}+x}\right) \, \mathrm{d}x$$
$$= \frac{\rho}{2\pi r_{\rm o}} \left[\ln(r_{\rm o}+x) - \ln(r_{\rm o}-x)\right]|_{0}^{r_{\rm o}-\varepsilon} = \frac{\rho}{2\pi r_{\rm o}} \ln\left(\frac{2r_{\rm o}-\varepsilon}{\varepsilon}\right) \,. \tag{23.5}$$

The contribution to the total resistance from the gold side can be evaluated from the formula of a circular contact of radius r_c on a semi-infinite conductor of resistivity ρ_{Au} , for our case [140]:

$$R_{\rm Au} = \frac{\rho_{\rm Au}}{4r_{\rm c}} = \frac{\rho_{\rm Au}}{4\sqrt{\varepsilon(2r_{\rm o} - \varepsilon)}} \,. \tag{23.6}$$



Fig. 23.36. Resistance of the probe body as a function of the tip radius, calculated from the *fitted curve* representing the shape of the tip, with the parameters given in Table 23.3. The *thickness of the line* corresponds to the error domain

d	$1000\pm100~\rm{nm}$
x_1	$1225\pm125~\mathrm{nm}$
ρ	$3.85 \times 10^{-5} \ \Omega m$
μ	0.588 ± 0.08
a	$80 \pm 20 \text{ nm}^{\mu+1}$
yo	$3840 \pm 25 \text{ nm}$

Table 23.3. Values of the parameters used to obtain the plot shown in Fig. 23.36

Combining (23.3), (23.5) and (23.6), we can write

$$R_{\text{tot}} = \frac{\rho}{4} \left[\sqrt{2} \left(\frac{1}{r_{\text{o}}} - \frac{1}{x_{1}} \right) + \frac{a\mu}{(\mu+2)} \left(\frac{1}{r_{\text{o}}^{\mu+2}} - \frac{1}{x_{1}^{\mu+2}} \right) \right] + \frac{\rho}{2\pi r_{\text{o}}} \ln \left(\frac{2r_{\text{o}} - \varepsilon}{\varepsilon} \right) + \frac{\rho_{\text{Au}}}{4\sqrt{\varepsilon(2r_{\text{o}} - \varepsilon)}} .$$
(23.7)

Neither the tip resistance nor the gold substrate resistance can be evaluated without knowing the indentation depth ε . To gain insight into the working of the tip-to-substrate contact for the case of UNCD probes in contact with highly conductive metal substrates, we will estimate the indentation depth from a mechanical calculation based on the applied force and the constitutive behaviors of the materials.

For low contact forces, the radius of the contact spot is a function of the applied force. The substrate material in this experiment was chosen to be gold such that plastic indentations would develop at relatively low contact forces. The force applied to the tip in the experiments was evaluated to be $0.20 \pm 0.08 \,\mu$ N. The evaluation was based on the deflection sensitivity of the piezotube (75 nm/V) and a prescribed displacement equivalent to 3 V. The stiffness of the cantilever was computed to be $0.88 \pm 0.32 \,\text{N/m}$. This cantilever stiffness was determined from its geometry and confirmed by load-deflection measurements performed with an X-ray photoelectron spectroscopy nanoindenter.

To estimate the indentation depth ε , using contact mechanics solutions, we can begin by using the Hertzian elastic solution:

$$a = \left(\frac{3Pr_{\rm o}}{4E^*}\right)^{1/3} \,, \tag{23.8}$$

$$\varepsilon = r_{\rm o} - \sqrt{r_{\rm o}^2 - a^2} , \qquad (23.9)$$

where *P* is the applied force, E^* is the reduced modulus of the UNCD–gold interface and *a* is the contact radius. For a contact force of 0.20 µN and tip radius of 25.7 nm, we compute a penetration depth of 0.256 nm and a contact stress of 7.3 GPa, which is much higher than the yield stress of gold. Therefore, an elastoplastic solution needs to be considered to estimate the actual penetration depth. A model proposed by Zheng and Cuitino [141] corresponding to the contact of two spheres pushing against each other was used. One sphere of radius r_0 is considered for the UNCD tip, while the other, of radius $r \to \infty$ is considered for a flat gold surface. The penetration depth can then be calculated from the following expression [141]:

$$\frac{P}{\pi r_{o}^{2} \Gamma} = B(m) \left[2c^{2}(m) \right]^{1 + \frac{1}{2m}} k(m) \left(\frac{\varepsilon}{r_{o}} \right)^{1 + \frac{1}{2m}} , \qquad (23.10)$$

where *m* is the hardening exponent defining the plastic regime of gold, which is modeled to follow a power law. $B = 0.74 + 0.26^{1/m}$ (m < 3), $c^2 = 1.5 - (1/m)^{0.5}$ and $k = 3.07 \times 0.16^{1/m}$ are constants depending on the value of *m*. Γ is the equivalent reference stress calculated on the basis of the yield stress values for gold and UNCD, i.e., $(1/\Gamma)^m = (1/\sigma_{Au})^m + (1/\sigma_{UNCD})^m$; with $\sigma_i = \sigma_y^{1-1/m} E_i^{1/m}$. The value of *m* and the yield stress of gold were obtained from the tensile testing of gold thin films reported by Espinosa and Prorok [142]. A yield stress of 165 MPa and a hardening exponent m = 1.664 were identified from the reported stress–strain curves. For a contact force of $0.20 \pm 0.08 \,\mu$ N, the penetration depth was then calculated to be $\varepsilon = 0.7 \pm 0.21$ nm, which corresponds to a contact radius $a = 6.0 \pm 0.8$ nm.

Substituting this value for the penetration depth, along with the other parameters listed in Table 23.3, into (23.7), we obtain an estimated value for the total resistance of approximately 1.04 k Ω . It is interesting to consider the various contributions to the total resistance $R_{\text{tot}} = 2.1 \text{ k}\Omega$ as predicted from this calculation. The pyramidal resistance is $R_{\text{pr}} = 0.56 \text{ k}\Omega$, the tip resistance is $R_{\text{tip}} = 1.04 \text{ k}\Omega$ and the gold substrate resistance is only $R_{\text{Au}} = 0.5 \Omega$. This shows that the small volume at the tip apex, with its possible deviations from the considered geometrical model, is responsible for most of the probe resistance.

If a simpler model consisting of a contact region with radius *a* and a half space is used for the contact resistance, the formula for the contact resistance is $R_c = \rho/4a$, with ρ being the average resistivity. Using the values of ρ for UNCD and gold, and *a* from the mechanical analysis, we obtain $R_c = 2.09 \text{ k}\Omega$.

For an experimental evaluation of the total contact resistance R_{tot} , the UNCD probe (previously characterized in terms of shape) was brought into contact with a gold thin film, deposited on a silicon substrate, by applying controlled forces. Figure 23.37a shows the electrical circuit used in the measurement. A sweep voltage varying between -50 and 50 mV was applied using a Keithley SCS instrument and the current flowing through the circuit was simultaneously measured. An I-V curve is plotted in Fig. 23.37b, from which the effective resistance of the circuit can be



Fig. 23.37. (a) The electrical circuit used for getting the contact resistance. The substrate shown is a gold surface. (b) I-V curves obtained showing ohmic behavior of the contact

calculated. The same experiment was repeated several times to ensure the consistency of the measurements. A total resistance of $R_{\text{tot}} = 6.25 \pm 0.05 \text{ k}\Omega$ was obtained, which is larger than the value calculated theoretically. This shows that the tip-to-substrate contact contains a resistance (approximately $4 k\Omega$) that can be attributed neither to the probe nor to the gold substrate or electrodes; thus, it must be a material of high resistivity entrapped between the probe and the gold. This can be a thin oxide layer, a contamination layer, an alteration of the diamond tip owing to nanoscale discharges and heat generated during the conductive measurements or, more likely, a combination of these features. It is worth mentioning that the values enabling the comparison stem from measurements under a relatively high contact force. At lower contact forces, the electrical contact area is not formed simply by the geometrical indentation footprint, but involves contamination layers (oxides, adsorption layers) and roughness features of the two surfaces in contact. These features change both the electrical and the mechanical models. It may involve tunneling or dielectric breakdown and the mechanical response is more size-dependent. From a practical viewpoint, at low contact forces, the contact I-V characteristics of the type shown in Fig. 23.37b are history-dependent and become unreliable owing to noise and deviations from the ohmic behavior.

To evaluate the UNCD probe capabilities for AFM conductivity measurements, a thin film of gold deposited on a silicon substrate was scanned using the conductive



Fig. 23.38. (a) Electrical scheme used for getting a conduction map of the sample shown (b) A CCD image of the scanned region. The *bright portion* is gold film deposited on Si substrate (*dark region*). (c) Topography of the scanned region. (d) Conduction map, showing spikes of voltages in the conductive region

UNCD probe. A small anodic voltage V (of the order of millivolts) was applied to the gold surface with the UNCD probe grounded. The current in the circuit was amplified using a preamplifier, the output of which was inputted to the AFM Nanoscope III controller. Figure 23.38a shows the schematic of the electrical setup used during scanning and Fig. 23.38b shows the scanned region. When the tip comes in contact with the conductive substrate, a current is established in the circuit. This current is amplified by the preamplifier, and converted into a voltage signal with a known I-V sensitivity. The voltage plots were recorded simultaneously with the topographic and lateral force images using the AFM Nanoscope software. Figure 23.38c and d shows the topography and the conduction map of the scanned region.

The direct measurement of current and voltage through the conductive probe has the limitation that the probe continuously perturbs the voltage distribution on the sample. If this is to be avoided, the AFM probe can also be used in a potentiometric scheme (Fig. 23.39a). If the current through the probe I_p is kept sufficiently low, the overall voltage distribution on the sample is not affected by the measurement, provided the current through the main sample circuit is much higher ($I_s \gg I_p$). The example shown in Fig. 23.39 used a thin Cr film resistor of resistivity 0.635 Ω/cm and a total resistance of 100 k Ω with an applied voltage of 10 V. A resistor, $R_p \gg R$,



Fig. 23.39. (a) Electric circuit used for AFM potentiometry. (b) CCD image of the scanned region, where the *bright lines* are the metal traces and the *dark lines* are the spaces. (c) Conduction map of the two fins shown. (d) Cross-sectional profile along the line shown

was connected in series with the tip to limit the probing current. A CCD image of the scanned region is shown in Fig. 23.39b. Two fins of the resistor are scanned and a potential difference between the voltages at the two fins is observed. Figure 23.39c shows the corresponding conduction map and Fig. 23.39d shows a cross section of the voltage profile along the line shown (in red). For the plots shown, an amplification factor of 10⁶ is used and $R_p = 1 M\Omega$. These values correspond to a voltage difference of approximately 0.6 V between the two fins. The voltage applied across the fins is 10 V and the total length of the resistor is around 40 cm, which means a voltage gradient of 25 V/m. Therefore, a voltage difference of 0.6 V means a difference of around 1.5 cm between the locations of the two fins. The distance between the centers of the two locations is measured to be around 1.35 cm, which matches well with the electrically calculated value.

If the previous examples were obtained with relative large samples, the true advantage of AFM potentiometry is demonstrated by nanometer-scale measurements. Figure 23.40 shows an example of scanning with the potentiometric setup of a Pt



Fig. 23.40. Topographic image of a focused ion beam (FIB) deposited Pt nanowire (**a**), LFM image of the device (**b**) and AFM potentiometry map (**c**), showing that the voltage does not follow a uniform linear decrease along the nanowire resistor, owing to small shortcuts between the elements of the resistor, which occurred during the FIB deposition nanowire, deposited by a focused ion beam between two electrodes, through which a current $I = 33 \,\mu\text{A}$ was established by applying a voltage of 50 mV. Figure 23.40a is a topographic image of the Pt nanowire, while Fig. 23.40b is a lateral force image. The AFM potentiometric map is shown in Fig. 23.40c.

In the potentiometric map, it can be observed that the resistor is short-circuited at some places, a feature that is not evident in the topographical image. By contrast, the conduction map reveals that all the dark regions are electrically connected and are therefore at the same potential.

23.3.4.2 Molecular Writing

For DPN, the UNCD tip was dipped into a 10% MHA solution in acetonitrile, dried and mounted on the AFM head (Digital Instruments 3100). Writing was performed on the surface of a freshly deposited thin film of gold (100-nm Au electron-beam-evaporated onto a microscope glass slide). Writing of the letters U-N-C-D with the molecular ink was achieved with a line width of about 200 nm (Fig. 23.41).

The writing speed, which is controlled by the rate of molecular diffusion, was compared between the UNCD arrow-shaped and commercial nitride tips by performing static contact depositions of MHA dots on gold, with contact times of 5, 10 and 20 s. Both experiments were performed in similar conditions (contact force 50 nN, humidity $50 \pm 5\%$, temperature 23 °C). The results are shown in Figs. 23.42 and 23.43. The UNCD tips showed a slightly faster deposition rate, but within the limits of variability encountered among different nitride tips. This is consistent with the wetting properties of diamond, which is slightly more hydrophilic than silicon nitride. The smallest features that could be written with UNCD tips, using the DPN technique, were 80-nm-diameter dots (Fig. 23.42b).

The imaging of the DPN-deposited dots and letters was performed in all cases with the same tips used for deposition by running the instrument in frictional force mode. This also demonstrates that the UNCD probes developed produce high-quality frictional force AFM images.

Experiments also showed that the UNCD tips can be used to write by scratching the relatively soft gold surface. In this continuous writing mode, the tip is moved between a discrete number of points while keeping it in contact mode at relatively high contact force. The result of such a scratch test is shown in Fig. 23.44.

Fig. 23.41. "UNCD" written with MHA on a freshly deposited gold film, using a UNCD triangular-shaped probe. The line width is 200 nm. Imaging of the MHA pattern was performed with the same UNCD tip in lateral force mode





Fig. 23.42. (a) Three MHA dots on gold, obtained by contacting the surface with the arrow-shaped UNCD probe for 5, 10 and 20 s (from *top right* to *bottom left*, respectively). The image was recorded with the same probe in lateral force imaging mode. The diameters of the dots are 360, 540 and 710 nm, respectively. (b) Dots of 80-nm diameter are the best resolution features obtained so far



Fig. 23.44. AFM topography image of a scratch on a gold surface obtained by translating an UNCD tip in contact mode between two specified points



23.3.5 Perspectives for Diamond Probes

Diamond is expected to play an important role in future implementations of complex scanning probe systems owing to its excellent wear resistance, biocompatibility and

the potential to make it conductive by doping. Complete diamond probes or probes with diamond forming only the probe tips are envisioned. For such applications, the use of diamond becomes a matter of integration, i.e., microfabrication processes and materials compatibility. Diamond in its various forms is still difficult to integrate. Problems related to adhesion, particulate and impurities contamination, film uniformity, reproducibility and selectivity in dry etching relative to some of the standard MEMS/nanoelectromechanical systems (NEMS) materials, for example, Si, SiO₂ and Si₃N₄, need to be addressed.

A class of applications for which diamond will be extremely useful is AFM-based microelectrochemistry or nanoelectrochemistry. In such cases, a critical aspect of the experimental measurement is the choice of material for the conducting AFM tip. In air, highly doped Si tips suffer from the growth of a native oxide layer that quickly deteriorates the tip conductivity. Metal-coated tips also fail to provide a continually low contact resistance as the metal wears from the tip apex during scanning [143, 144]. One approach to minimize metal wear is to operate the AFM predominantly in tapping mode to minimize lateral forces on the tip. An alternative solution is the use of diamond-coated Si tips [145], or the much sharper molded diamond tips presented before.

Although doped diamond can serve as an electrode for electrochemistry and conductive scanning probe techniques, including eventually EPN, it is likely that its superior wear-resistance properties will not last under all possible environmental and electrical conditions employed in probing or writing. Recent conductive scanning probe microscope studies performed with metal probes on various diamond surfaces have shown that diamond can be etched [146], oxidized [147] or its surface modified [147, 148], thus providing a good substrate for AFM lithography and the formation of surface nanoelectronic circuits [148]. Oxidation of conductive diamond happens especially at anodic biases of a few volts (4-10 V) in air, which supplies the oxygen for the reaction. Oxidation occurs, likely with an initial swelling of the diamond surface [146], and then a surface recess is formed in a few minutes. However, swelling was observed even while performing the experiments in a vacuum, and persisted as long as the vacuum was maintained. Thus, the swelling may be a form of local carbon atom disorder, different from diamond, with high oxygen reactivity, or the accumulation of water molecules on oxidized carbon sites, desorbed later and leaving behind patterns of oxidized or etched diamond [147]. The low wear rate of diamond species is related also to the low friction coefficient, owing to the presence of hydrogen-terminated surface bonds. Local removal of hydrogen atoms during conductive techniques may thus increase the friction coefficient and wear. To gain insight into these mechanisms, to define the range of optimal material applications and to develop new diamond probes, extensive research is needed. Clearly, like any material, diamond is the right choice only for applications that exploit its superior properties. Among them, certainly are the probes of various future scanning probe microscopes, nanolithography, molecular pulling and data storage techniques.

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