Mechanism and development of dip-pen nanolithography (DPN)

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Abstract: Dip-pen nanolithography is a new scanning probe lithography (SPL) technique based on atomic force microscopy (AFM), and now has made a great progress. The process of dip-pen lithography involves the adsorption of ink molecules on AFM tip, the formation of water meniscus, the transport of ink molecules, and diffusion of ink molecules on the substrate. More factors such as temperature, humidity, tip, scanning speed and so on will influence the process of dip-pen lithography. The paper analyzes in detail the mechanism of this technique, introduces synthetically the latest development, including electrochemical DPN, more-mode DPN, multiple DPN, multi-probe array DPN and so on. Finally, the paper describes the characteristics and the application of DPN.
Key words: dip-pen; nanolithography; atomic force microscopy; nanofabrication

1 Introduction

Scanning probe lithography (SPL) technique that uses scanning probe microscope as the tool of nano-fabrication recently has made great progress with the requirements of micro-/nano-devices, high-density information storage, nanobiology, nanoelectronics, etc. This technique has broad application prospect, and now there are so many scanning probe lithography methods like mechanical nanolithography, AFM anodic oxidation, auto relocation, electrochemical lithography and so on[1-3]. As one of these methods, dip-pen nanolithograph (DPN) has attracted the scientists' increasing attention since invented by Chad A Mirkin in 1999. *SCIENCE* has reported it for several times. According to the latest researches, the paper summarizes the mechanism and advance of this technique.

2 Mechanism of DPN

Chad A Mirkin et al found AFM tip could directly lithograph nanostructure in the air when they studied on the influence of water molecules to the resolution of AFM in 1999. They found, water meniscus could be formed with the effect of the capillary force between the tip and sample surface adsorbing the water molecules in the air. The water meniscus transports the material molecules adsorbing on the tip to the substrate, thus the steady surface nanostructure could be obtained on the substrate by chemisorptions. Because this process is similar to writing with a pen dipped in the ink, it's named as dip-pen nanolithograph (DPN). Fig. 1 is the schematic diagram of dip-pen nanolithograph[4].

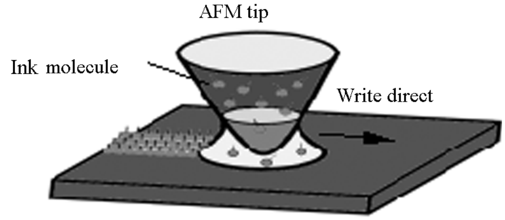

Fig. 1 Sketch map of DPN

The whole process of dip-pen lithography involves four phases: the adsorption of ink molecules on AFM tip, the formation of water meniscus, the transport of ink molecules, and the diffusion of ink molecules on the substrate. More factors such as temperature, humidity, tip, scanning speed and so on would influence the process of dip-pen lithography. Below, the concrete analysis of mechanism of this technique on various factors in different phases is carried out.

2.1 Adsorption of "ink" molecules

The adsorption force between the tip and "ink" molecules is the prerequisite of lithography. The adsorption depends on the property of the tips and "ink" molecules. Considering the influence of its property, the surface of the tip should be treated before adsorbing "ink" molecules to lithograph. In order to distribute the "ink" molecules evenly on the tip, the molecules can be resolved in the solution with suitable concentration, then be bleached and dried. Vaporization is an

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another way, which refers to place the tip and "ink" molecules into a sealed container, boil the "ink" molecules to make it vaporize, so the tip can fully adsorb the vaporized "ink" molecules, finally cool them to a room temperature[5]. However, this method only applies to the "ink" molecules with low melting point. The experiment indicates that the "ink" molecules can be distributed evenly on AFM tip via both methods.

2.2 Formation of water meniscus

As the transmission channel of the "ink" molecules from tip to substrate, water meniscus is crucial in the whole dip-pen nanolithograph. The formation of water meniscus depends on the relative humidity of the air and the relative distance between the tip and the substrate. According to the mode proposed by Brunauer, Emmett, Telle, et al, the adsorption of vapor on the surface of the substrate is a dynamic process with multi-layers adsorption and desorption. The thickness of water film adsorbed is related to the relative humidity of the air. According to the experiment performed by Thomes, the quantity of water molecules adsorbed by the solid surface is approximately in direct proportion to the relative humidity of the air. Humidity is the necessary condition to the formation of water meniscus. Though the tip and the surface of the substrate adsorb enough water molecules, the water meniscus also can't be formed if the distance between the tip and the substrate exceeds a certain value, that is, there's a critical distance H_c. Many factors influence H_c such as humidity, temperature, tip's hydrophilicity and geometric shape. The improvement of the tip's hydrophilicity can increase H_c. Comparatively, geometric shape of the tip and temperature has less influence on H_c. Therefore the humidity is the most important factor to H_c. The relationship between the humidity and H_c is similar to a quadratic function[6]. Capillary force is the impetus of the water meniscus. As it involves nanometer scale, the Kelvin formula that usually analyses the capillary phenomena is inadaptable[7]. Using Monte Carlo simulation, Joonkyung Jang studied on the formation of the water meniscus when the hydrophobic tip's humidity was 30 %. The result revealed the capillary force was related to the relative distance between the tip and the substrate, and the smallest capillary force existed when the relative distance between the tip and the substrate was two lattices[8].

The width of water meniscus is affected by humidity, temperature, tip's hydrophilicity and geometric shape. It is one of the most important influences to the linewidth of the fabrication. Based on the researches, the width of water meniscus is in direct proportion to the humidity but in inverse proportion to the relative distance between the tip and the substrate as well as the temperature; the tip with finer cone will obtain smaller width of the water meniscus; and a tip with good hydrophilicity has a great influence to the water meniscus as it decides the quantity of the water molecules adsorbed, with the tip's infiltrating reducing, the width of water meniscus is decreasing[6]. In addition, the width of water meniscus is related to the roughness of the substrate's surface. The rougher the surface is, the wider the water meniscus will be[9]. Fig. 2 shows the factors such as humidity, the relative distance between the tip and the substrate, the tip's infiltrating, geometric shape, temperature and the surface roughness that influence to the formation and width of the water meniscus.

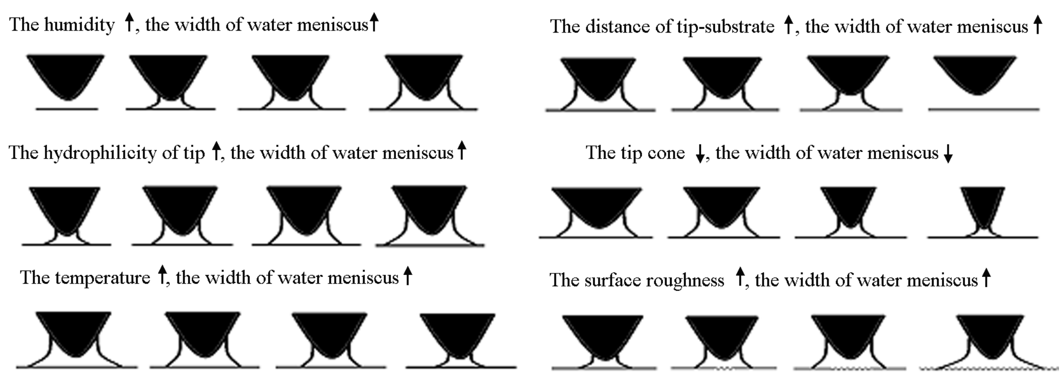

Fig. 2 Sketch map of water meniscus that formed and influenced by conditions

2.3 Transportation of "ink" molecules in the water meniscus

There are many action modes between the "ink" molecules adsorbed on the tip and the water meniscus. The water-soluble "ink" molecules dissolve in the water meniscus, which transports these "ink" molecules to the substrate. Through the chemical reaction with the surface of the substrate, the "ink" molecules can be deposited on the substrate. The concentration gradient in the solution is the impetus of transportation, which is related to the quantity of the "ink" molecules, the volume of the water meniscus and the deposition speed of the "ink" molecules on the substrate. The deposition speed depends on the intermiscibility of the "ink" molecules and the substrate.

Lloyd Whitman et al found the deposition speed of the hydrocarbon "ink" molecules which couldn't solve in water wasn't related to the humidity. This also revealed there might be other transportation mechanism besides the concentration gradient[10].

2.4 Diffusion of the "ink" molecules on the substrate

The diffusion of the "ink" molecules on the substrates is another great influence to the linewidth of the fabrication, which involves the diffusion coefficient, scanning speed (staying time) and deposition speed. The diffusion coefficient is related to the properties of "ink" molecules and the substrate's material besides the roughness of the substrate's surface. It decreases as the roughness increases. Joonkyung Jang's research also revealed the different diffusion coefficients in multimolecular layer and monomolecular layer[11].

The staying time is an important factor which is much related to the radius of the fabricated dot structure when the tip and the substrate are relatively static. The researches of Mirkin, et al. indicated the square of the dot structure's radius is in direct proportion to the staying time[12,13].

E Antoncik assumes AFM tip can provide enough "ink" molecules when the tip stays on the substrate. The centre is the diffusion source, whose radius is r_0. The initial density is c_0, which is an unknown constant.

According to the diffusion formula:

$$\frac{\partial c}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(rD\frac{\partial c}{\partial r}\right) \qquad (1)$$

The density flow (F) in the diffusion is supposed to be:

$$F = -2\pi D c_0 / \text{In}\left(\frac{R}{r_0}\right) \qquad (2)$$

D is the diffusion coefficient. R is the diffusion radius. From

$$F\mathrm{d}t = c_m 2\pi R \mathrm{d}R \qquad (3)$$

It can be deduced:

$$t = \frac{c_m}{2Dc_0}\left\{R^2\left[\text{In}(R/r_0) - \frac{1}{2}\right] + \frac{r_0^2}{2}\right\} \qquad (4)$$

c_m is the density of monomolecular layer[14].

Considering the influence of multimolecular layer diffusion, Joonkyung Jang proposed the radius of the point structure was more related to the number of deposited molecules than deposition speed in the fabrication.

The relationship between the staying time and the number of deposited molecules are as follows:

$$t = n\pi\rho R^2 \qquad (5)$$

(When the diffusion speed is slow).

$$t = R^2 / \left[4D\ln\left(\frac{n}{4D\pi\rho}\right)\right] \qquad (6)$$

(When the diffusion speed is fast).

ρ is the density of molecular layer. D is the diffusion coefficient.

The movement of AFM tip on the substrate is more complicated. The linewidth of the fabrication is related to the scanning speed. According to the theory of diffusion mode, Schwartz P. V. deduced the relationship between the scanning speed of the probe and the linewidth of the nanostructure as follows:

$$w \approx G/(2vl_0) \qquad (7)$$

(When the scanning speed is fast).

$$w \approx (D/v)^{\frac{1}{2}} \qquad (8)$$

(When the scanning speed is slow).

G is a constant. l_0 is the distance between the top of the tip and the surface of the substrate. w is the linewidth. v is the scanning speed[15].

The experiment of Jason Haaheim et al also indicated that the linewidth decreased with the increase of the scanning speed at the same diffusion speed. The linewidth is inversely proportional to the scanning speed[9].

Unlike the dot structure, the linewidth is much related to the deposition speed of the "ink" molecules. Small linewidth can be got both from a fast scanning speed and a slow deposition speed as well as a slow scanning speed and a fast deposition speed. However, it's impossible to get the linewidth when both scanning speed and deposition speed are fast.

Joonkyung Jang, et al. used the random walk simulation to acquire the 3D relationship among the linewidth, the scanning speed and the deposition speed[18]. In real fabrication, if the water meniscus isn't fully formed for the too fast scanning speed, the dot structure will have fracture. The force of the tip would take some of the deposited "ink" molecules in scanning, which makes a ridge on the top of the line. The regularization of the pattern is related to the roughness of the substrate's surface, considering the influence of the diffusion.

3 Development of DPN

Considering the application prospects of DPN in many fields such as functional nano-devices, micro-miniaturize sensors, high-density information storage, biochip, genetic engineering and cell detection, scientists do a lot of researches for its further development while studying its mechanism. With the great progress made in DPN, the accuracy at present can reach 15 nm in the linewidth and 5 nm in the resolution. Various "ink" molecules including organic molecules, peptides molecules, DNA molecules, virus, protein molecules, polymer, inorganic nano-particles and sol particle can be transported to the substrates which can be made of different material such as metal, semi-conductor, insulator and bimolecular. Many new technologies have developed such as electrochemical DPN, various AFM fabrication modes of DPN, combined fabrication of multi-"ink" molecules and concurrent fabrication of the multi-probe array.

3.1 Electrochemical DPN (E-DPN)

Electrochemical DPN was invented by Li Yan of Duck University. Fig. 3 is the schematic diagram of electrochemical DPN. The experiment was done with the 40 % humidity and the Nasnocope Ⅲa AFM, NSCS15 probe. It was fabricated while there was 4 V DC voltage between the tip adsorbing H_2PtCl_6 and the Si(100) substrate. The substrate connected the cathode and the tip's scanning speed on the substrate was 5 nm/s. The electrochemical reaction in the cathode was: $PtCl_6^{2-} + 4e \rightarrow Pt + 6Cl^-$. Pt nanostructure with a 50 nm-wide and 0.5 nm-high line was gained[16,17].

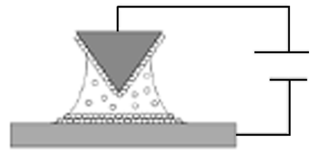

Fig. 3 Sketch map of electrochemical DPN

The principle of DPN is using the water layer between the tip and the substrate as an electrolysis pool, reducing the metal salt to the metal through electrochemical reaction and depositing the metal to the substrate. Such nanostructure of metal and semi-conductor can be gained as Au, Ge, Ag, Cu, and GaN[18]. The linewidth is related to the humidity, scanning speed and voltage. The voltage should be kept below 10 V; otherwise the substrate would have oxidation reaction. Directly using the water meniscus as a reactor, Mirkin et al developed E-DPN thereafter. The molecules on the tip depositing on the substrate form the nanostructure after they had chemical reaction with the water[19]. Fig. 4 is the dot structure and nanopattern of the MHA molecules depositing on the gold substrates, which is fabricated by Zhang Yi, Chad A Mirkin using E-DPN[20].

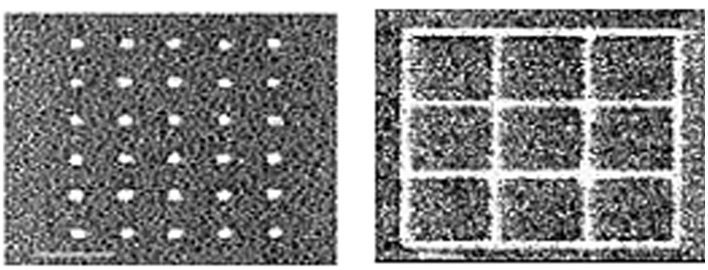

Fig. 4 Nanodot and nano-pattern lithographed by E-DPN

With the use of E-DPN, the sorts of "ink" molecules are extended; the thermal stabilities of the structures are improved; the structures are diversed; the fabrication of metal and semi-conductor can be controlled from higher place; as well as the functional nanodevices are made more efficiently. In addition, E-DPN can decorate the nanostructure. Because of the high speed of the inorganic reaction, how to control the reaction speed of "ink" molecules in water meniscus is the key to apply E-DPN to making nanostructure and nanodevices.

3.2 Various AFM fabrication modes of DPN

AFM fabricates in many ways. The researchers have developed DPN fabrication technique combined different fabrication ways of AFM, based on the different substrate materials and "ink" molecules.

Contact mode: the fabrications and images are both made by contact mode. It is fit for nanolithograph on the surfaces of hard substrates such as metal, semi-conductor and insulator. Tapping mode: the fabrications and images are both made by tapping mode. It can make home position image for biomacromolecules.

The limitation is that it is hard to make nanostructure for the tip which vibrates frequently. Contact and tipping mode: it makes good use of the advantages of above two modes, using contact mode to make its nanostructure and tipping mode to make its image. The patterns of the biomacromolecules can be made. The limitation is the tips should be changed while fabricating. CDDPN: it makes nanostructure and image at the same place without changing the tip through shifting the working condition of AFM and transferring the contact mode and the tipping mode promptly. The advantage is that it simplifies the fabrication as well as solves the problem of difficult nanolithography on the soft substrates. Using CDDPN, Li Bin, et al. successfully made nanostructure through putting AFM tip with protein solution on DNA molecules[21,22]. The DNA enzyme on AFM tip decomposed DNA, which made biochemical reaction of monomolecules under the control of nanoscale[23].

DPN can nanolithograph on different "ink" molecules and substrate materials using different AFM fabrication modes. More attention has been paid to the treatment of the AFM tips' surface, for the sake of efficiency. Most of the AFM tips used in DPN are Si_3N_4 business probes. In order to combine the biomacromolecules and the tip efficiently, the Si_3N_4 business probes can be coated with silane and mercaptan to make the molecules more attractive when such molecules as DNA and protein molecules are fabricated. Wang Xuefeng, et al. successfully made OTD nanopattern with AFM probes made of dimethylsiloxane[24]. This method makes a good combination of DPN and nano-indentation. But the linewidth of the pattern is about 330 nm. The accuracy can still be improved. As AFM probes are completely made of polymer, if it's lack of the reflector at the back of the cantilever, AFM feedback control will be limited. Based on these, Zhang Hua et al made Si_3N_4 probe covered with PDMS known as DPN indentation probe. This high-accuracy, low-cost probe can adsorb plenty of "ink" molecules as well as make hollow nanostructures. Moreover, it makes the AFM have a good feedback control. Fig. 5 is the fabrication of the indented tip[25].

3.3 Combined fabrication of DPN

DPN can not only fabricate the self-assembled monolayer, but also implement combined fabrication. Owing to the specific location of AFM, DPN also can use the same "ink" molecules to "write" on the fabricated pattern for many times. What's more, DPN can use different "ink" molecules to "write" on the same substrate. Fig. 6 shows the combined pattern including three kinds of materials. First, the tip with MHA molecules lithographes triangle, square and pentagon on Au (111) fabricated substrate. Second, the tip with ODT molecules lithographes a 3 μm × 3 μm square pattern. Finally, extending its scanning scale, the tip without any molecules gets a 4.3 μm × 4.3 μm combined pattern[5]. Prior to other lithographies, DPN has several features: the fabrication is accurate and simple without masks, extends the usable materials, can produce steady patterns with pure chemicals and has little destruction to the patterns.

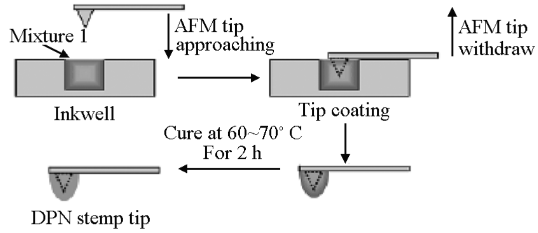

Fig. 5 Process for fabricating a DPN stamp tip

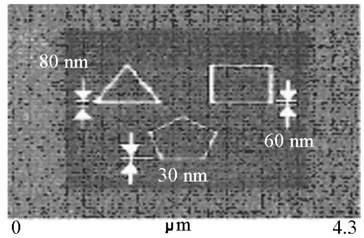

Fig. 6 Multiple nano-pattern lithographed by DPN

DPN can also combine other ways in making combined pattern and structure. Amro et al invented nanopen reader and writer (NPRW) which combine nanografting and DPN. This method uses the tip to adsorb the substitute molecules beforehand. The substitute molecules will fill the bare area of the substrate where the SAMs are moved away by the tip which is given a certain force. DPRW can construct different patterns and multi-layer combined patterns. It can also efficiently protect the patterns from diffusing and abrasing.

Usually, it takes several steps to make combined patterns. As mentioned, DPN indentation probe can make hollow nanostructures and the linewidth is influenced by writing speed. If the hollow nanostructures are filled with other materials by using DPN or other ways, combined nanopatterns or duple molecules structure can also be gained. It's relatively simple. As MHDA and ODT having different hydrophilicities, Jennifer R. Hampton, et al. studied the mechanism through using one AFM probe to transport MHDA and ODT to the substrate in order to make a combined nanopattern[26]. Lloyd Whitman and Paul Sheehan in US Navy laboratory Nano-surface-science and Sensor Centre acquire the 3 D combined structure through selectively growing a 6 nm-high disulfide crystal on the surface lithographed by DPN[10].

3.4 Multi-probe array fabrication of DPN

For the slow speed of the mono-probe DPN, the key to develop DNA further is to make it low-cost and efficient. The fabrication of the multi-probe array is the main access to make the lithography mass production. There are two modes in the multi-probe array fabrication of DPN, that is, active mode and passive mode. Passive mode: many identical AFM probes adsorbed on the same clamping chip. All the probes draw the same figures when touching the substrate. The probe array can be made of such materials as silicium, silicium oxide and magnetic iron nickel alloy[27]. Fig. 7 is the nanopattern made by the 8-probe array[28]. Urbana-Champaign, et al have already invented the 1000-probe array which is anticipated to apply to the industry, not only in the research. Multi-probe array improves the fabrication; meanwhile, it makes combined patterns by dipping different "ink" molecules. But it is difficult to control the movement of the single probe because of sharing one clamping chip when using the passive mode.

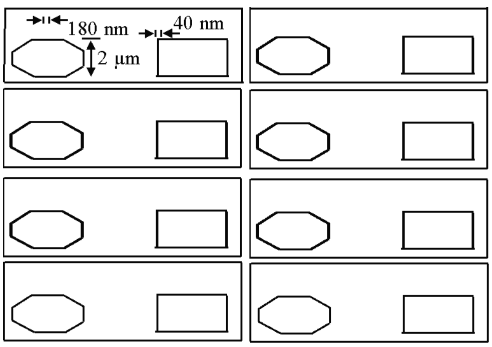

Fig. 7 Nano-pattern that lithographed by 8-tip

Prior to passive mode, active mode can solve this problem. Thermal bimetallic actuation DPN (TA-DPN) and electro statically actuated DPN (EA-DPN) are two kinds of active mode extensively studied. The cantilever adopted in TA-DPN consists of two kinds of material, which have different thermal conductivity coefficients such as Au-Si and Au-SiN_4. The gold surface of the cantilever's substrate is designed as a resistance heater. The heat produced by the resistance heater changes the probe's shape to control the probe. TA-DPN can control the single probe. But there are still two problems: while fabricating, the temperature is 10 ~40 ℃ higher than the air temperature, which destroys the properties of certain "ink" molecules such as protein. The heat conductivity and convection of air disturb the movement of adjacent tips, which makes it impossible to make smaller intervals between tips. Comparatively, EA-DPN is an ideal one. It consists of probes and a reversed electrode, showing in Fig. 8[29]. Putting the voltage between the tips and the reversed electrode produces static power to make the tips move. Though the tips of EA-DPN can also be disturbed by the adjacent tips, the disturbance is relatively small. So it can get smaller intervals between tips. Moreover, there's no heat in EA-DPN, so it can deposit the chemicals which are sensitive to the temperature.

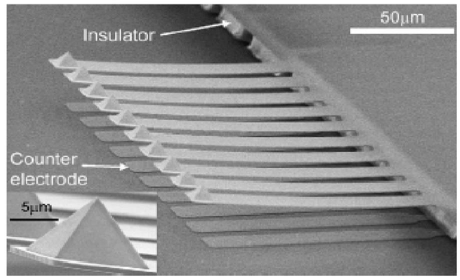

Fig. 8 DPN tip-array drove by static

4 Conclusions

Compared with other lithographies, DPN has characteristics following:

1) Higher accuracy of fabricated structures. The smallest unit of DPN fabricated structures can be nanometer. The linewidth can reach 15 nm and space resolution can be 5 nm in the experiments. The smallest linwith can even reach 1.9 nm in theory.

2) Fewer requirements to the environment. There are no special requirements as to extreme heat, vacuum and so on. It can also write without mask. So the fabrication is simple.

3) The diversity of patterns. Many kinds of "ink" molecules can be applied in DPN. The "ink" molecules which can be directly transported including organic molecules, polypeptide molecules, DNA molecules, protein molecules, polymer, inorganic nanoparticles, and sol particles and so on[30-34]. The surface of the substrates can be various: hard substrate including metals, semi-conductors, insulators and so on; soft substrates including biomacromolecules[35-37]. The fabrication can be repeated on the substrates. The patters can be either combined or redesigned[29].

DPN has been applied to many fields. Liu Jie of Duke University made many functional nanodevices and miniature sensors, as well as metal leads to connect carbon nanometer pipes. The researchers of Northwestern University used DPN technology to write the speech of on the Annual Meeting of Physics in 1960 in nanometer, which was given by the Nobel Prize winner Professor Feynman. Ki-Bum Lee et al used DPN in the cell detection[38]. Professor Brugger proposed to use nanoprobe to write through punching on the tips[10]. As the researches of DPN mechanism going on, more and more imaginative DPN methods come out. DPN will be applied to more fields.

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