Scanning Tunneling Microscopy

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This paper begins with a brief introduction the development of scanning tunneling microscopy (STM); in the second part, we will present some basic theory about STM, we will pay more attention on the theory for tunneling between the surfaces of the sample with the model probe tip. Next, we introduce the STM facility, include different modes of operation and other influence factors. In addition, some application of STM to nanofabrication and Nanocharacterization are reviewed. Finally, conclusion and outlook are made towards the future research on STM.

Keywords: STM, Tunnel current, Nanofabrication

I.   Introduction

The 1986 years Nobel prize is a warded to Gerd Binnig and Heinrich Rohrer for their design of the scanning tunneling microscope [1]. The invention of STM help scientist better understand the surface structure which means this technical solved the fundamental problem in surface physics. From 1986 until now, research go on improve this advance technical and apply this method into industry innovations of novel nanometer-scale product. Numerous advantages and versatility of STM make itself become a powerful tool [3]. STM with tunneling spectroscopy can be used to perform atomically resolved spectroscopy imaging functions such as energy-resolved local density of states (LDOS) mapping, spin-polarized tunneling imaging, molecular vibrational spectroscopy by inelastic tunneling, and tunneling-induced photon emission mapping. Further more, as a nanofabrication tool, STM also be used in atom manipulation, local deposition by the decomposition of organometallic gases. Moreover, STM can be adapted to various environments such as air, ultrahigh vacuum (UHV), controlled atmospheres and liquid [11]. In the following context, we will introduce both basic theory of STM and application of STM in nano-device industry.

II.   Theory of STM

Tunneling current

From the figure 1(a,b,c), we will show some basic idea of tunnel [2]. In the figure 1(a), we can show the scheme of tunneling into vacuum, the electron in a valence band are move in the Coulomb potential well of a atom core plus other valence electrons, the wave function of the electron is extend into the vacuum. In the vacuum, the wave function is decreasing exponentially, it tunnels into the vacuum. In real

materials, If two atoms come sufficiently close, just as shown in the figure 1(b), the wave function of the two atoms overlapped with each other, at this time, an electron can tunnel back and forth through the vacuum or potential barrier between them. In a metal, in the figure 1 (c), the potential barriers between the atoms in the interior are quenched, the electrons in the conduction band can move freely. as the same situation as a, at the surface, the potential rises on the vacuum side forming the tunnel barrier, only those electrons which their electronic states very near the Fermi level, can be excited and tunnel across the barrier. As figure 1 (c) shown, when the two metal surface are closed enough, because the different Fermi levels of those two metals which produced by the small bias V, an electron can tunnel to the surface atom of another metal close by. The electron in the left side of metal can tunneling to the right side. There are many factors determine this tunnel. First, tunneling require empty level for the tunnel electron, so the tunneling current is related with the density of available states in the sample; the current is also due to the bias voltage V, when V is positive, electron in tip tunnel into empty state in the sample surface, if V is negative, electron tunnel our of occupied states in the sample into the tip. The tunneling current is
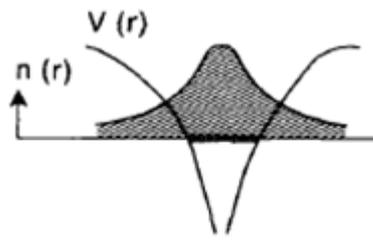
Figure 1(a). The wave function of a valence electron tunneling into vacuum

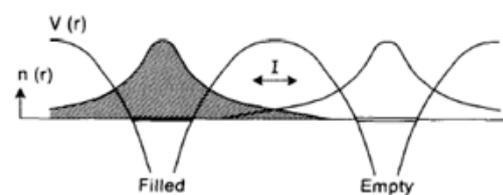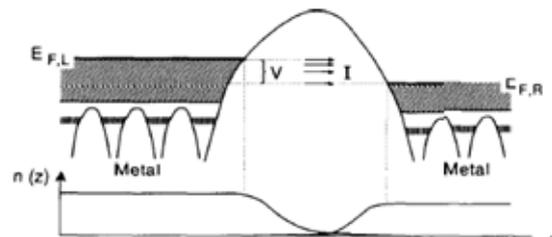Figure 1(b). Electron Tunneling through potential barrier between Atom to Atom

Figure 1(c). Electron tunneling in a metal

$$I \propto \sum_{v} \left| \Psi_v(\vec{r_0}) \right|^2 \delta(E_v - E_F) \Big|$$

Ψv is the state of the surface; Ev is the energy of state Ψv in the absence of tunneling. E_F is the Fermi energy [6]. From this equation, we can found that the right part of this equation is the surface local density of states (LDOS) at E_F , so the tunneling current is proportional to the surface LDOS. The microscope image represents a contour map of constant surface LDOS. When a electron transmission an barrier, the tunneling transitivity decreases exponentially with the distance of the barrier, in vacuum , when the distance of the barrier decreases 1Å ,the current increases by an order of magnitude, With one electrode shaped into a tip, the current flows practically only from the front atoms of the tip, in the best case from a specific orbital of the apex atom. This gives a tunnel-current filament width and thus a lateral resolution of atomic dimensions. The second tip shown is recessed by about two atoms and carries about a million times less current [4].

III.   Facility

A. Modes of operation

Basically, there are two kinds of modes for STM [5], one is called Constant current which is the one we discussed in the following part and another one is named constant height.

In the constant current mode, the tip is scanned across the surface at constant tunnel current, vertical tip position will be continuously changed to keep the tunnel current as a constant. Actually, in a homogeneous surface, constant current essentially means constant interval between sample surface and the tip. In this method, the function named height control mechanism will adjusting the tip move vertically up and down to keep the tunnel current to be constant through the feedback voltage. That means in this method, the tip topography the surface of the sample and gives a constant charge density surface image .The feedback voltage is a function of the height of the tip: Vz (Vx, Vy) $\propto$ Z(x,y).When the surface of the sample is smooth, there is another choice named Constant height mode. In this mode, people through change the current to make sure both the voltage and height are held as a constant , the image of this mode is made of current changes over the surface, which can be related to charge density[8].   The changing tunneling current as a function of surface charge density conveys the same information as obtained in constant current mode. I(Vx, Vy) $\propto \sqrt{\Psi}$*Z(x,y). This mode is much faster than the constant current mode. The only thing we should pay attention to is the surface should be smooth enough, or the scales of the ups and downs may even larger than the distance between the tip to the sample surface, at such situation, the tip may be destroyed by crashing with the sample.
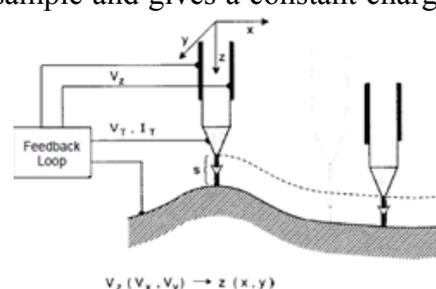

$V_z (V_x, V_y) \rightarrow z (x,y)$

Figure 2 (a). Constant current mode

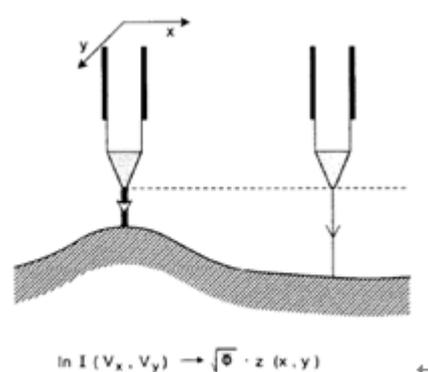$\ln I (V_x, V_y) \rightarrow \sqrt{\Phi} \cdot z (x,y)$

Figure 2 (b). Constant height mode

B. Instrument

To introduce the instrument, we use the constant tunnel current as a example, the sketch of this instrument is shown in figure3 [7], the three frictionless x-y-z piezodrive Px, Py, Pz, which is quite vibration sensitive, will control the movement of the tip.   Px, Py will scan the tip over the sample's surface, Pz will depend on the feedback voltage to determine the tip's vertical move to keep the constant tunnel current at constant tunnel voltage Vt. At the point B which is a contamination spot,

this lead the tip has a z direction displacement. As we mentioned before, a little change on the surface will lead a dramatic current change, commonly, the barrier height or we called work function Is nearly several electronvolts, when we change the tunnel barrier width with a single atomic step (2-5 Å), the tunnel current will change about three orders of magnitude. This is the basic principle for this instrument. Include, in the constant tunnel current modes, the surface topography has constant work function and constant gap width.
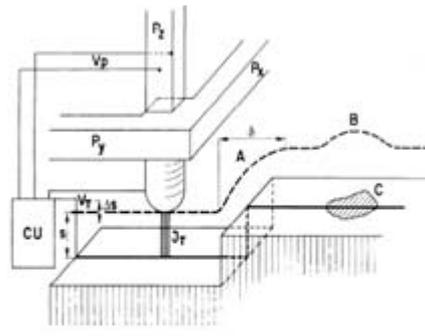
Figure 3. Principle of operation of the scanning tunneling microscope

C. Tip materials influence

There are lots of factors may influence the image of the STM, now, we introduce a theory of STM imaging mechanism in terms of actual electronic states on real tip. If we pay some attention to those researches about STM, we may found that the commonly used tip materials are W, Pt and Ir [8], all of those materials are d-band metals. Take tungsten tips as an example, we know that, at the Fermi level, 85% of its density of states come from d states. Just as the some reference shown, the W atoms on the tungsten tip surface will have a thinner electron density surrounded [9], the reason for this phenomenon is because the tip atoms has experience a reduced force, this force is come from the electron wind. In such situation, the w atom at the top of the tip will show a positive charge, the electrical field will attract the W atoms move to the apex of the tip, as a result, we can get very sharp tip with one atom at its apex, this structure will gives a rise to the metallic d tip state. The early STM research think that the tip materials have no relationship with the STM resolution, however, during further research, we can see that the STM resolution is dependent on the tip materials which require localized metallic Pz or dz [10] tip stats. From that research, we can draw a conclusion that only d-bond metals and semiconductors which can form Pz like metallic dangling bonds can be used as tip materials. All in all, the localized surface states of the tip especially the chemical identity of the apex atom will help people better understand the STM imaging mechanism.

IV. Application

Just as mentioned before, because the advance characteristics and lots of advantages of the scanning tunneling microscope (STM), STM become a powerful tool to investigate surfaces of conductive materials since it's invented. Recently, through the trend of miniaturization both in magnetic and electronics devices, such as high-density information storage, high-resolution lithography, and production of nanoscale integrated chemical systems and electronic devices. So, now, the development of advanced fabrication and characterization technologies and science

for the nanofunctional materials is become the most important problem in this research area. As we know, the size of the advance micro devices is shrinking into the nanometer scale, continuing miniaturization of electronic and mechanical devices has led in recent years to an interest in the generation of nanometer-sized structures on surfaces. To achieve this goal, we need to find an effective and efficient way to resolve the bottleneck of nanotechnology. In this advance research area, the invention of scanning probe techniques, particularly scanning tunneling microscopy (STM), has made it possible to modify surfaces at the nanometer scale and to manipulate even single atoms with the STM tip. STM nanofabrication technique has potential applications to various technologies. For example, from the effect of single-electron tunneling, a nanometer-scale SET transistor is become an important candidate technology for high-speed, low-power large-scale integrated circuits [11], which with tens of thousands of transistors per chip. As figure 4 show, technical for the fabricating nanometer scale part such as nanowires and nanodots on semiconductor substrate it become the key point for the nanometerdevices.
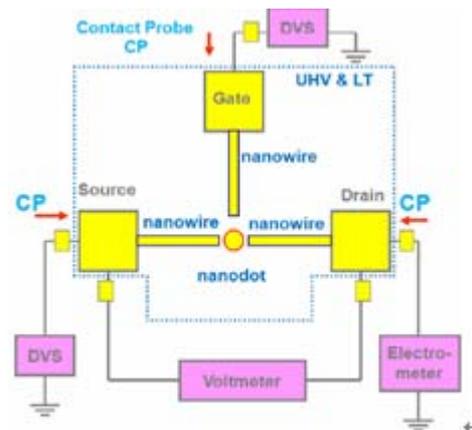

figure 4. Nanometer scale SET transistor

A.   Z-piezo voltage pulse

As shown in figure 5, it is a STM image of a nanodot formed on a Si(111) surface after applying a single z-pulse. The main techniques for this nanodevices is try to fabricate metallic nanostructures on clean substrate. Now, let us show an example to explain this process. The material of the tip is made by tungsten wire with thin silver film deposited on it. At the beginning, we will apply a z-piezo voltage pulse on the tip. The duration time of this voltage pulse is 10sm. The reason why we need to apply a voltage pulse is because the adatoms on a surface will always migrate toward the center of the field which at that point, the field is highest. As shown in the figure 6 (a), in the absence of the voltage pulse, surface potential is periodic and the surface diffusion is in random direction. When we apply a voltage pulse, at the position which near the tip, the polarization energy is larger, this lead to the surface potential is inclined toward
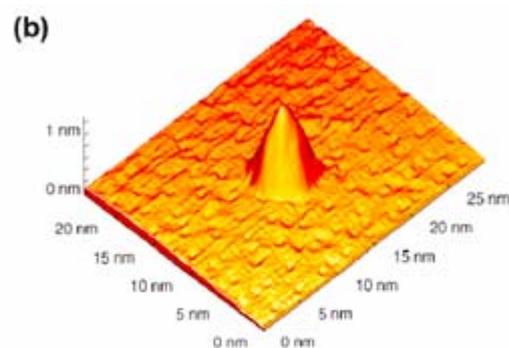

Figure 5. STM image of a nanodot formed on a Si(111) surface after applying a single z-pulse. the nanodot with 6nm in diameter and 0.9nm in height

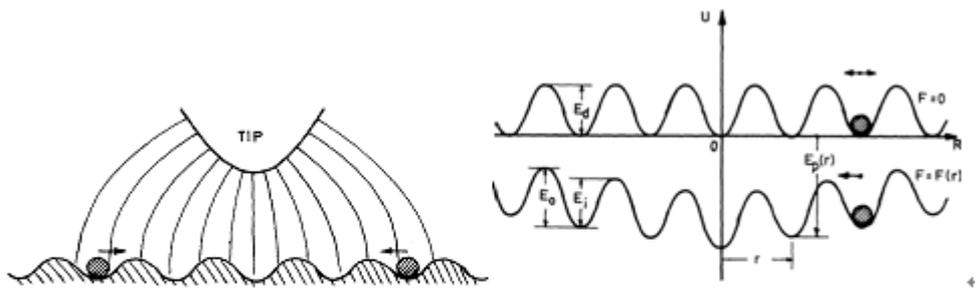the center. The atoms will be migrated toward the center, figure 6 (b) [15].

Figure 6 (a,b). Diagrams explaining why absorbed atoms
will migrate toward the tip by appliying voltage pulses to
the tip or to the sample

The whole process is shown in the figure, During the whole process, we use the constant current mode. At the beginning, the tip is stay at a certain height, the gap distance between the tip and the surface of Si(111) is approximately 0.5 nm, this gap distance is changed with different materials and different tunneling conditions. Then, we applied an externally generated voltage pulse directly to the z-piezo, which leads to a corresponding movement of the STM tip in the z direction. When this additional external voltage pulse is applied on the z-piezo, both tip height and the tunnel current will show simultaneous responses. Just as shown in figure 7. In the first millisecond of the pulse (figure 8), the tunnel current show a sudden and dramatic increase, showing that the STM tip approached the surface due to this additional voltage pulse on the z-piezo [14]. Through the tip is approaches to the surface, the gap distance will be shorter, when the gap distance is nearly to a typical bond length or approaches the atomic distance, the atoms on the apex of the tip will transferred to the sample surface and formed a nanodot on the sample surface. After 3ms, the feedback circuit will return a signal and causes the tip to retract in order that the tunneling current regains its predetermined value. All this process seems very simple, however, the principle of how the atoms on the tip can be migrated from the tip to the surface is complex. There are two ways can explain this transfer, one is called Field evaporation model, the other is caused by the spontaneous point contact.
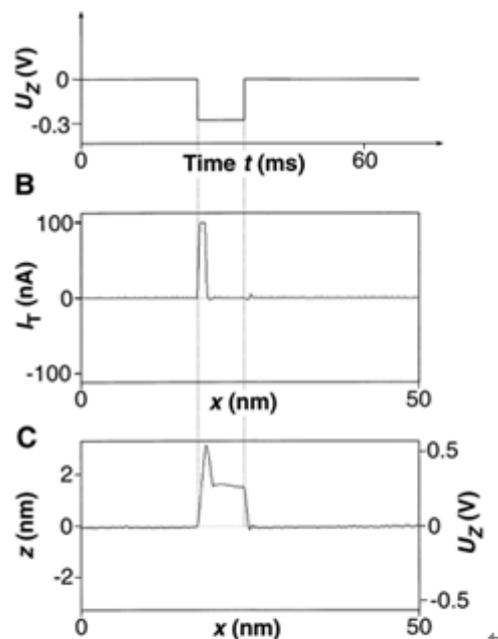

Figure 7. The imposition of an external voltage
pulse Uz on the z-piezo (A) causes a change in
the tunnel current IT (B) and a tip movement in
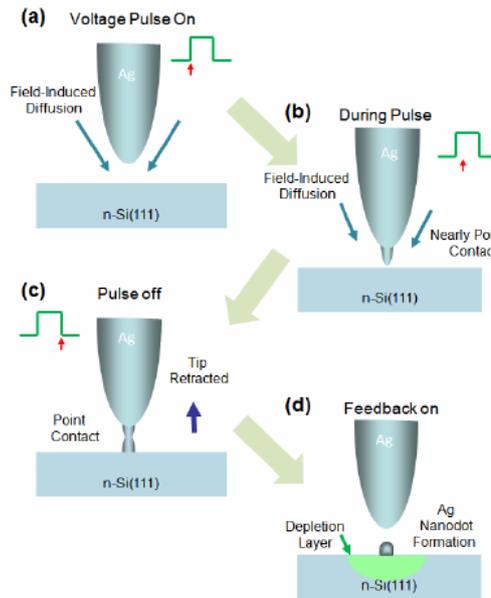the z direction (C). Pulse duration was $\Delta t = 10$ ms.

Figure 8. Schematic model of tip-material
transfer mechanism by applying voltage pulse

C. Field evaporation model

We can get the general idea of this model from the figure 9(a,b) [15] and figure 10(a,b,c). When the distance between the tip and sample surface are closed enough, a potential barrier will formed, the atoms can transfer between them. When we apply a field between them, the energy barrier will be lower. In a metal-vacuum-metal model, the height of the barrier will be decreased a lot when apply a field. In the process of

deposition, we apply a z direction voltage pulse on the tip and sample surface, when the tip and the surface are closed enough, the barrier which the atoms will be tunneled is very low. So the atoms can easier transfer from the tip to the sample surface [16]. This is the reason why atoms can be deposited on the surface.
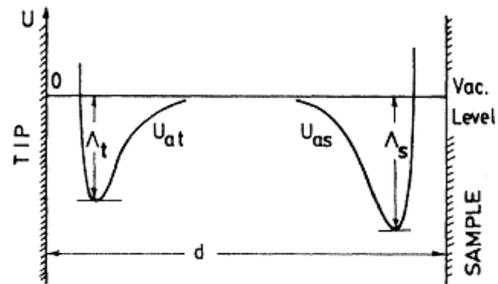

Figure 9 (a). When the distance between tip and sample is large, the atom-tip and atom-sample interaction U_{at} and U_{as} don't overlap
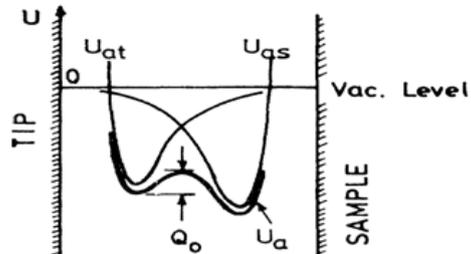

Figure 9 (a). When distance is small, the two start to overlap, there will form a small activation barrier. Atom can transfer between the tip and sample
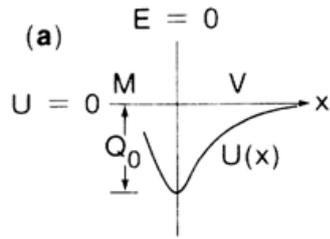
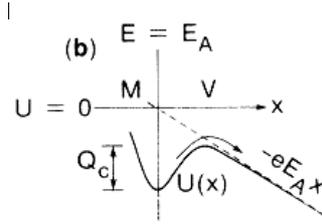Figure 10 (a). Single metal vacuum interface with no applied field

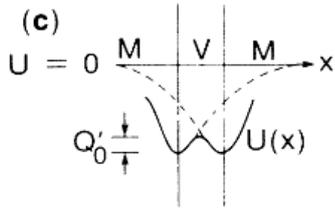Figure 10 (b). Interface with applied field, the ion can lower its energy by leaving the metal

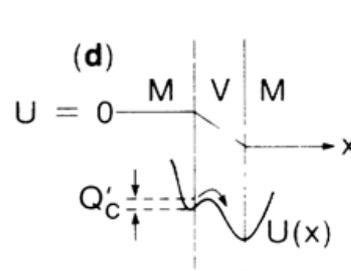Figure 10 (c). Metal-vacuum-matal structure with two like metals and no applied field

Figure 10 (d). With applied field, Qc reduced

D. Spontaneous point contact

Another way to explain the atom transfer is use mechanical point-contact model. In this model, tip-material transfer is caused by spontaneous formation of a point contact. This can be confirmed by an abrupt jump in current, as shown in the figure 12. We can prove this point contact from the I-z curve [13]. At the beginning, the tip is gradually moving to the surface when we apply a z-direction voltage, the current is exponentially increased through the tip close to the surface, the tip is in the tunneling regime during this process. When the distance between tip and surface is close to a typical bond length of -0.2nm, the current suddenly jumped to a very high value, this dramatically change of current suggests the formation of a mechanical point contact between the tip and Si(111) surface. The reason for this atomic-sized contact is various, it may be caused by field-induced diffusion (high electric field causes atoms at the tip Shank to diffuse to the apex by field-gradient-induced surface diffusion [15]) or by the formation of a chemical bond.
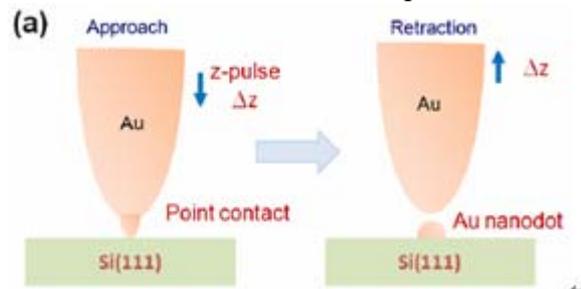

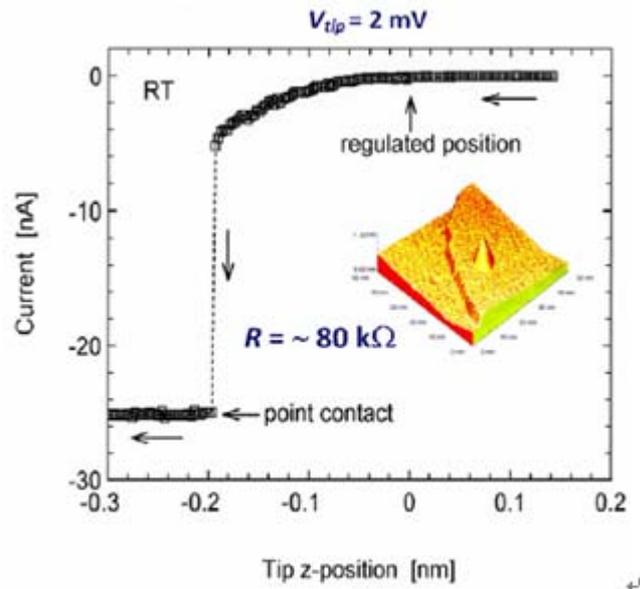Figure 11. Mechanical point-contact model

Figure 12. I-z curve obtained during the
deposited process at room temperature

Field-induced diffusion

The first model is called Field-induced diffusion. For this model, when we apply a z-piezo voltage pulse on the tip, the field electrons can be emitted either from the tip or the sample surface, this electron current will heat up or even melt the tip. For another way, because there exist a field gradient on the tip surface, so the atoms on the tip shank will flow to the tip apex either by a directional surface diffusion or by a hydrodynamic flow. Then, at the apex of the tip , a liquidlike-metal cone will form, the atoms on the apex of the tip are very easier to contact with the atoms on the sample surface. After 10 ms, the voltage pulse is over and the liquidlike-metal cone will cools down. The neck between the tip and the surface will be broken and a mount of atoms migrated from the tip to the sample surface[15]. Just as shown in the figure 13.
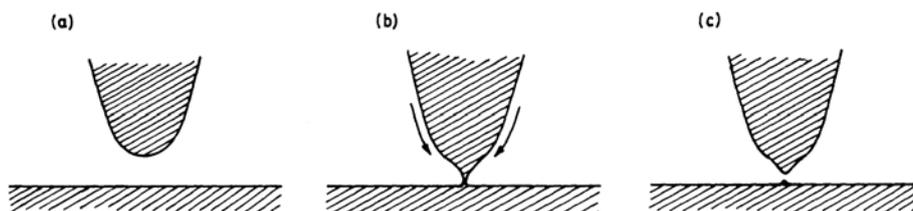

Figure 13. Field-induced diffusion model of the atom contact

Chemical bond

Some other research shows that for some materials, we can use the chemical bond to explain the mechanism for nanodots deposited. Such as Silicon, on the Si(111) surface contains lots of adatoms, those adatoms have dangling bonds protruding into the vacuum, when the gap distance is become very small, the dangling bonds will

extracting the tip, a nanoscale silver dot will left on the surface of the silicon because the chemical bonding between the silver and silicon atoms [18]. After this, the feedback circuit causes the tip to retract in order that the tunneling current regains its predetermined value. This is the whole procedure for how tip-material transfer mechanism from an tip to n-Si(111) by applying a z-direction pulse.

With the method we shown, people now can generate patterns on even a larger scale. Figure 14 is a picture show an 20*20=400 single Cu clusters array which is fabricated on an area 245 nm by 275 nm , the time of this fabricate is less than 90 s [14]. The whole process for this is the same as we mentioned before. We were able to achieve this relatively fast patterning process by apply the additional voltage pulses on the z-piezo for the tip approach at the right moments, then the tip to approach the surface while it was scanning over the surface as in the usual imaging mode.
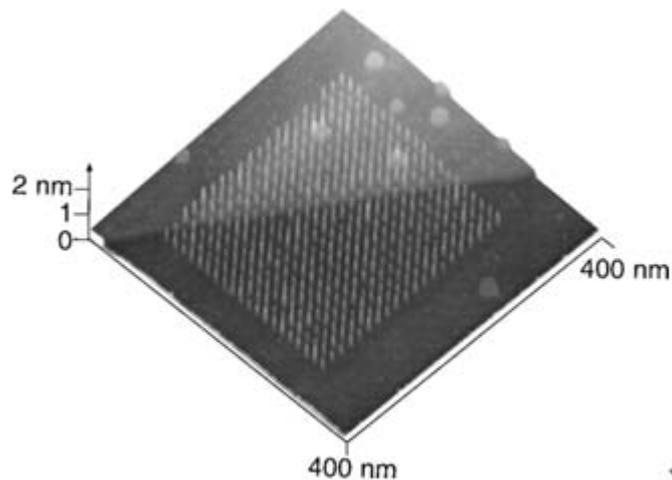

Figure 14. 20*20=400 single Cu clusters array

Figure 15 is a picture provided by IBM company which have positioned 48 iron atoms into a circular ring in order to "corral" some surface state electrons and force them into "quantum" states of the circular structure [19]. The ripples in the ring of atoms are the density distribution of a particular set of quantum states of the corral. We were able to achieve this relatively fast patterning process by allowing the tip to approach the surface while it was scanning over the surface as in the usual imaging mode. It was necessary to apply the additional voltage pulses on the z-piezo for the tip approach at the right moments.
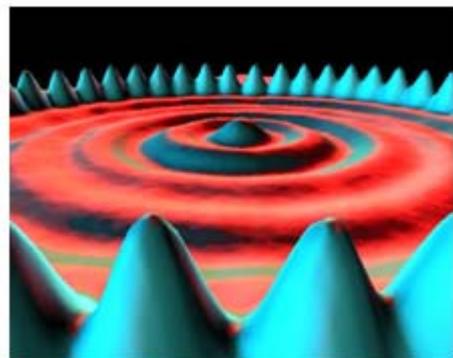

Figure 15. Quantum Corral (Iron on Copper (111))

V.   Conclusion

Basic theory and application of STM were reviewed. From the year 1986 Gerd Binnig and Heinrich Rohrer receive the Nobel prize, STM has experienced a very fast development during the past decades, nowadays, it already become the most

important method when research try to determine the surface structure. This method first time provides a possibility of direct, real-space determination of surface structure in three dimensions. Now，STM use its own advantages and combine its nanofabrication and nanocharacterization capabilities together，become the most powerful tool in the nanomaterial research field.

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