Near field emission scanning tunneling microscopy

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(Received 13 June 1994; accepted for publication 30 September 1994)

The close proximity between probe and sample in a scanning tunneling microscope interface may produce unwanted modifications of the interface. This is particularly severe when working with soft materials, as molecular films or biomolecules. Here, we propose the operation of the scanning tunneling microscope in the near field emission regime as an effective method to overcome those problems. A theoretical description of the probe–sample interface in the near field emission regime predicts subatomic resolution in the direction normal to the surface and lateral resolution of 3 nm for tip–sample separations of 3–5 nm. Furthermore, atomic resolution is demonstrated by imaging steps of carbon atoms. © *1994 American Institute of Physics.*

In the last decade the scanning tunneling microscope (STM) has emerged as the most versatile tool for studying at atomic and nanometer scales metallic and semiconducting surfaces.[1,2] The application of STM is, however, restricted to conducting or doped semiconductor surfaces. The atomic force microscope (AFM) was developed as a technique to study insulating as well as conducting materials.[1] Atomic resolution is obtained when the probe is in mechanical contact with the sample. The close proximity of probe and sample in STM and AFM may produce unwanted alterations of the sample. Indeed, the driving force behind some AFM works has been to minimize the interaction force between probe and sample.[3–5] To overcome some of the limitations associated to contact or near contact, the STM can be operated in the near field emission regime where probe–sample separations are of few nanometers. This also extends the application of the STM to study biomolecules. Some recent experiments show that the STM can image biomolecules[6,7] and manipulate them at nanometer scale[7] by using relatively high voltages and very low currents.

Attempts of using the field emitted current from a tip as a parameter for generating images were done by Young.[8] However, the field emission of electrons from a sharp tip is not exempt from drawbacks. The high energy of the electrons impinging the sample could modify it. In addition, the emission is very sensitive to the environment. For instance, adsorbates that may appear on the tip would produce instabilities in the emission characteristics. This is due to the changes produced in the work function and in the field very close to the adsorbate. However, the changes in the field decay very fast with the distance from the adsorbate.[9,10] They have a negligible effect on the field at the sample surface. The instabilities could be avoided if the polarity is reversed. Our goal is to show that the emission of electrons from the sample can effectively lead to a new STM mode for imaging surfaces. This is in contrast with field emission microscopy, where electrons are always emitted from sharp tips.[10]

Three regimes can be defined in the current (I) versus voltage (V) curves in a metal–insulator–metal junction. Tunneling when the applied voltage is lower than the work function; the intermediate region $\phi_e \leqslant eV \leqslant \phi_e + E_F$, it will be called near field emission regime hereafter and the standard field emission or Fowler–Nordheim regime for higher voltages.

Here, we describe the general features of the STM operated in the near field emission regime. Atomic resolution is predicted in the direction normal to the surface and verified experimentally by imaging monoatomic steps on graphite. Lateral resolution is in the nanometer range. It depends on the tip–probe distance and tip's radius.

Field emission from metallic tips is generally described by the Fowler–Nordheim theory.[10] This approach gives an approximate description of the I versus V characteristics of the emission. The emission area is usually treated as a constant fitting parameter. However, recent calculations show that the emission area depends on the applied voltage.[11]

To include the three-dimensional geometry of the interface we choose a prolate spheroidal coordinate reference system.[12] In this system, surfaces of constant η represent equipotential surfaces and lines of constant ξ and φ represent electric field lines. The tip and sample surfaces are an hyperboloid $\eta=\eta_0$ and a flat surface $\eta=0$, respectively. The radius of curvature of the tip apex R and the tip–sample distance S determine the choice of η_0, $\eta_0=[S/(S+R)]^{1/2}$. In the case of negative sample bias, the potential energy of an electron between two surfaces is

$$U(\eta)=\phi_s-[e|V|+(\phi_s-\phi_t)]\frac{\log[(1+\eta)/(1-\eta)]}{\log[(1+\eta_0)/(1-\eta_0)]}+U_{\rm im}, \quad (1)$$

where $U_{\rm im}$ is the image potential[13] and ϕ_s and ϕ_t are sample and tip work functions, respectively. To calculate the current we use the following semiclassical approach. The current density J at each point of the emitter surface (η_e,ξ,φ) is obtained from a planar model,[14]

$$J\approx 6.2\times 10^{-6}\Delta S^{-2}\{\phi\ \exp(-10.25\Delta S\phi^{1/2})-(\phi+e|V|)\times\exp[-10.25\Delta S(\phi+e|V|)^{1/2}]\}. \quad (2)$$

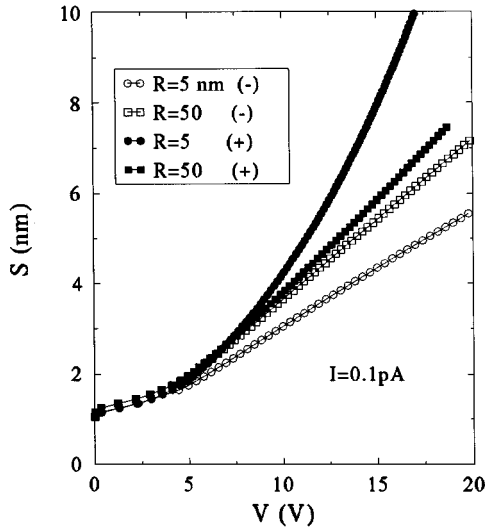

FIG. 1. Tip–sample distance vs applied voltage curves (I=constant). In the field emission regime the current is controlled by the electrical field at the emitter surface. Consequently, the current increases with decreasing tip's radius if emission is from the tip (positive bias). The opposite happens when the polarity is reversed. I=0.1 pA, $\phi_s=\phi_t$=4.7 eV.

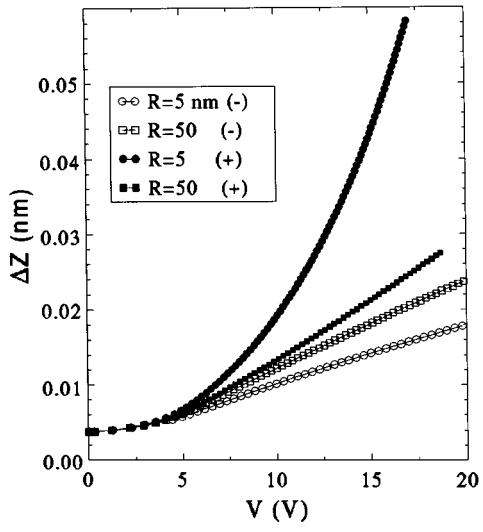

FIG. 2. Vertical resolution as a function of the applied voltage and tip radius. The resolution is calculated assuming that variations in the current of 10^{-2} pA can be detected. I=0.1 pA.

The effective barrier ϕ associated to each emitting point is averaged along its corresponding field line,

$$\phi(\xi)=\frac{1}{\Delta S}\int_{\eta_1}^{\eta_2} U(\eta)\sqrt{\frac{\xi^2-\eta^2}{1-\eta^2}}\,\frac{S}{\eta_0}\,d\eta \tag{3}$$

and the barrier width is

$$\Delta S=\frac{S}{\eta_0}\int_{\eta_1}^{\eta_2}\sqrt{\frac{\xi^2-\eta^2}{1-\eta^2}}\,d\eta, \tag{4}$$

where η_1 and η_2 are the curvilinear coordinates that define the tunneling region. Energies are in eV, distances in nm, and J in A/nm^2. The total intensity is obtained after integration of J over the emitter surface $\eta=\eta_e$ ($\eta_e=0$ for negative polarity and $\eta_e=\eta_0$ otherwise),

$$I=2\pi(S/\eta_0)^2\sqrt{1-\eta_e^2}\int_1^{\infty} J(\xi)\sqrt{\xi^2-\eta_e^2}\,d\xi. \tag{5}$$

The dependence of the distance with the applied voltage for several tip's radius is presented in Fig. 1. In near field emission, the results are almost independent on the polarity as long as the potential drops linearly in the gap region. This is the case for relatively blunt tips ($R\approx$50 nm). For ultrasharp tips, if electrons are emitted from the tip S increases exponentially with the applied voltage (I=constant). The relationship is approximately linear for negative polarities.

The vertical resolution is given by $\Delta Z\approx\Delta I/(dI/dS)$, where ΔI is the minimum detectable change in the current. In Fig. 2 we have plotted ΔZ versus the voltage for a constant current of 0.1 pA and ΔI=0.01 pA. Subatomic resolution is obtained for a wide range of voltages (from 5 to 20 V). This is true even for tip–sample distances of 10 nm. In the tunneling regime, atomic resolution is obtained due to overlapping of tip and sample electronic orbitals. In near field emission vertical resolution comes from the dependence of the current with the field and the sensitivity of the latter to small changes in S.

To estimate the lateral resolution we calculate the effective width of a monoatomic step at constant current for different radii (Fig. 3). For a given tip position over the sample, the current density is calculated over both terraces neglecting the effects of the step edge. This approximation does not include contributions due to the field enhancement near the

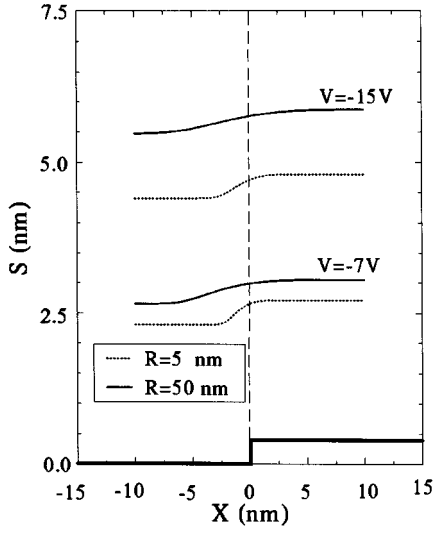

FIG. 3. Simulated images of a monoatomic step as a function of the applied voltage and tip radius. Electrons are emitted from the sample (negative bias). I=0.1 pA.

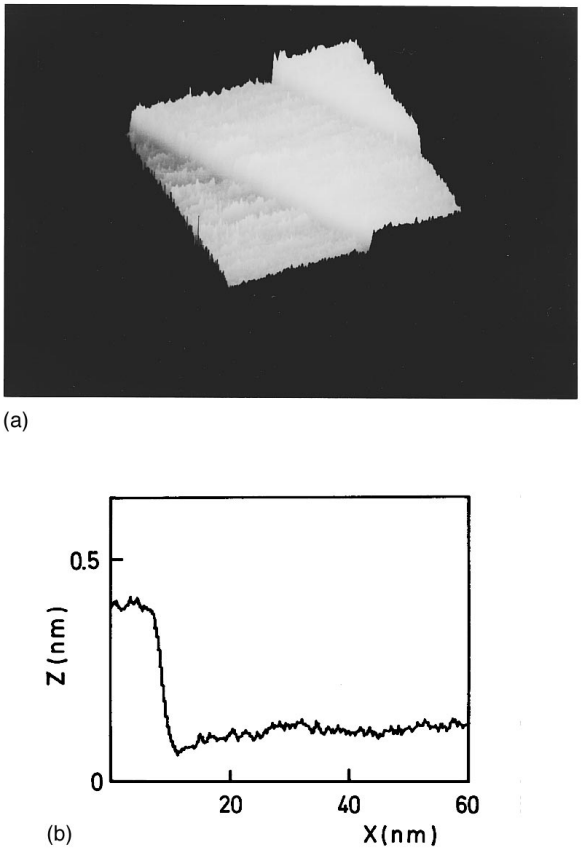

FIG. 4. Near field emission image of a graphite surface (HOPG). (a) It shows several terraces separated by monoatomic steps of carbon atoms (0.33 nm). It also illustrates the asymmetry between lateral and vertical resolution in near field emission. (b) A scanline across a monoatomic step. Its apparent width is 5.5 nm. The images are raw data; $I=0.2$ pA and $V=-8$ V.

step. At constant current, those contributions would appear as small bumps parallel to the step lines. However, those effects have not been observed in STM images or in the present experimental results (Fig. 4).

The lateral resolution Δx depends on tip's radius and tip–sample separation. We found that Δx is proportional to the¬ scale¬ factor¬ S/η_0 in¬ the¬ region¬ of¬ interest $\{\Delta x \approx 0.7*[(R+S)*S]^{1/2}\}$. For tips with $R\sim 5$ nm, effective widths as small as 3.5 nm are obtained.

As a test of the above properties we have performed preliminary experiments in air with a low current STM, operated in near field emission ($I=0.2$ pA and $V=-8$ V).[15] According to Fig. 1, the above parameters imply $S\sim 2.5$–3 nm. We have imaged monoatomic steps of carbon atoms (Fig. 4). The step (0.33 nm height) is clearly imaged above the background noise. For an apparent width of the step of 5.5 nm and $S\approx 3$ nm, the above expression gives a tip radius of about 20 nm.

The development of the STM has fostered a new breed of techniques, globally called scanning probe microscopies for studying surfaces at nanometer and atomic-scale resolution.[16] Here, we have described a mode of operation of the STM that combines the scanning and feedback characteristics of the STM with the emission of electrons governed by an electrical field. A compromise between vertical and lateral resolution and minimum contact forces defines the optimum working conditions. We have shown that in the near field emission regime there is atomic vertical resolution for tip–sample separations of 3–5 nm. The lateral resolution is of few nanometers. Emission from the sample increases stability and minimizes electron induced damage.

We think that one of the main applications of this STM mode is the imaging and controlled modification of molecular films and thin oxide layers. Furthermore, near field emission provides a direct, noninvasive approach for investigating at nanometer scale and low energies electron transport processes in molecular films and biomolecules.

The authors acknowledge stimulating discussions with F. Briones, C. Bustamante, J. Méndez, and J. M. Soler. J. J. S. acknowledges financial support from DGICYT under Contract No. PB92-0081.

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