Surface Spectroscopy Utilizing Field Electron Emission from Thermal-field Treated Tips in STM

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We have demonstrated the potentials of a field emission scanning tunneling microscope (FE-STM), in which the STM tip can be operated as a stable field electron emission gun. The tips were treated by a thermal-field (T-F) method for remolding and cleaning. A well-controlled T-F treated tip can determine the electric field between tip and sample in the STM as a geometrical boundary condition. Using the treated tip the electron standing waves excited in a vacuum gap between tip and sample were analyzed, and the electric field near sample surfaces was evaluated by assuming a simple potential model. Furthermore, by irradiating sample surfaces with a high-energy electron beam emitted from the tip, we obtained electron energy loss spectra (EELS) and Auger electron spectra from semiconductors, HOPG and metals.

[ntroduction

: the last two decades the excellent imaging ›ability of scanning tunneling microscopy [M) has been successfully demonstrated h atomic resolution on sample surfaces [1], l its potential of atom manipulation as well . The spectroscopic methods using STM re been also developed, in which tunneling rent I [3,4] or differential conductance dV [5-7] is measured with changing bias .tage V at each pixel of an STM image. cently, vibrational spectroscopy with inetic tunneling in the STM has been also deoped to recognize molecular species on faces at low temperature [8]. Further›re, the combination with photon [9] and ctron [10-13] spectroscopies for surface ılysis has attracted much interest, in which STM tip is used as an electron source.

In spite of their excellent features, their ›lications using surface analytical methods nbined with STM have not seemed to exıd widely, because of rather poor repro:ibility of the electronic states at a prepared apex. In these spectroscopic proximity›be methods, the spectroscopic images are rays composed of the spatial convolution electronic states between a tip and a sam:. Thus, in order to improve their avail.lity, it is required to control the atomic nposition at the tip as well as the atomic ucture to regulate the tip electronic states.

One possible technique to fabricate such a well-controlled tip is the so-called thermal-field (T-F) treatment for a W tip [14,15]. It has been used in the preparation of electron sources in transmission electron microscope (TEM), scanning electron microscope (SEM), field emission microscope (FEM), field ion microscope (FIM), scanning Auger electron microscope (SAM) and so on. The W tip is heated while a high voltage is applied to the tip; contaminants on the tip are thermal-field desorbed while the tip being sharpened for a [111]-oriented W tip, owing to the surface tension of each facet and the inhomogeneous electric field over the tip end. We before reported the improvement of reproducibility of scanning tunneling spectroscopy (STS) with the treated tip [14]. We named the instrument, in which the STM tip can be operated as a stable field electron emission gun, field emission STM (FE-STM). In this report we describe the tip preparation for stable field emission in the FE-STM and its application for surface electron spectroscopy.

2. Tip preparation for FE-STM

Homemade STMs operated in a base pressure of $2x10^{-11}$ Torr were used in this study. A schematic diagram of the instrument is given in Fig. 1; the combined instrument consists of an STM head with three-dimensional mechanical stages driven by piezo inertia motion, an electron energy analyzer (Omicron, CSA300, a cylindrical sector analyzer with an

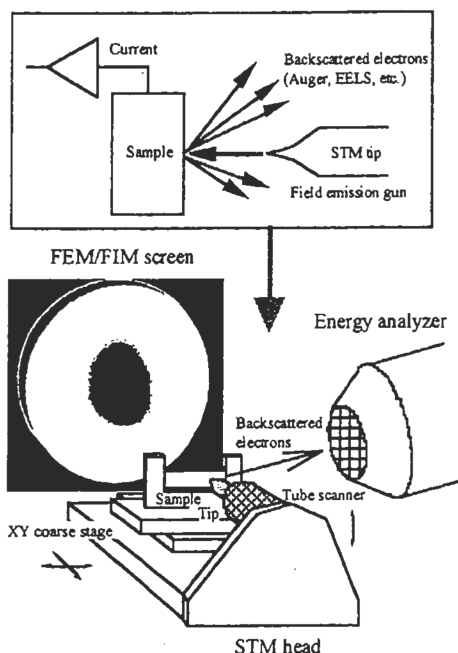


Figure 1 Schematic diagram of a combined instrument with a field emission STM, an electron energy analyzer and a phosphor screen for FEM, FIM and TFD imaging. The tip can be heated in the STM.

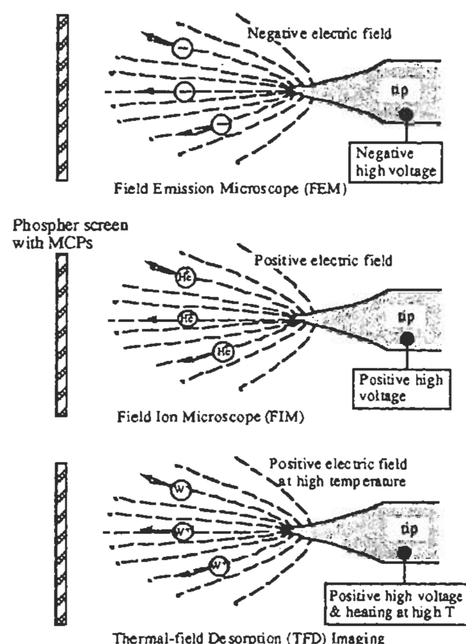


Figure 2 Schematics of field projection methods for tip evaluation and preparation.

entrance lens) and a phosphor screen with chevron-type micro-channel plates for FEM, FIM and thermal field desorption (TFD) imaging behind a sample in the STM. The emission patterns from the tip are projected on the screen through a hole of a sample holder at which the tip is aimed. The tip in the STM head can be biased up to a high voltage of 10 kV while being heated at 1500°C; we heat the tip by passing an AC current through a W loop, onto which the tip is spot-welded, and apply a high voltage through a high-voltage isolation transformer. The W tips electrochemically etched were treated by the T-F method in UHV to sharpen or remold them with cleanliness. Fig. 2 shows the projection imaging methods for tip evaluation. Fig. 3 shows their images observed on the way and at final stage [16]. The [111]-oriented W tip has a threefold symmetry around the [111] axis, which was surrounded by three expanding {112} facets, resulting in a corner at the tip apex. The images show a threefold symmetry with ridgelines formed by two adjacent {112} facets. At the final stage, since the apex of a (111) facet has a low work function, we obtain one bright spot from the apex in the FEM image. The spread of the beam energy and angle is 0.2-0.3 eV and within about 5°, respectively. The apex emitting the electron beam is the most protruding area to the sample. This indicates that the area irradiated with the electron beam on the sample surface corresponds to the area scanned with the tip in the STM imaging mode. On the other hand, for a [011]-oriented W tip, which is made from a polycrystalline W wire, a dark area expands at the tip end in the FEM image after the T-F treatment. The [011]-oriented tip has a clean flatten facet of (011) plane with a high work function at its end.

3. Electron spectroscopies with FE-STM

When the voltage to the STM tip exceeds the work function of a sample, the electrons that tunnel through the potential barrier around the tip have positive kinetic energy in the vacuum gap between the tip and the sample. Subsequently they are incident on the sample surface with a kinetic energy. In this field emission regime, electron scattering experiments can be performed in an STM setup. Here we show two examples with FE-STM. One for the tip bias voltage up to about minus ten eV resulting in electron standing waves in the vacuum gap, and the other up to minus a few keV enough to make Auger electrons and others emitted out of the sample surface.

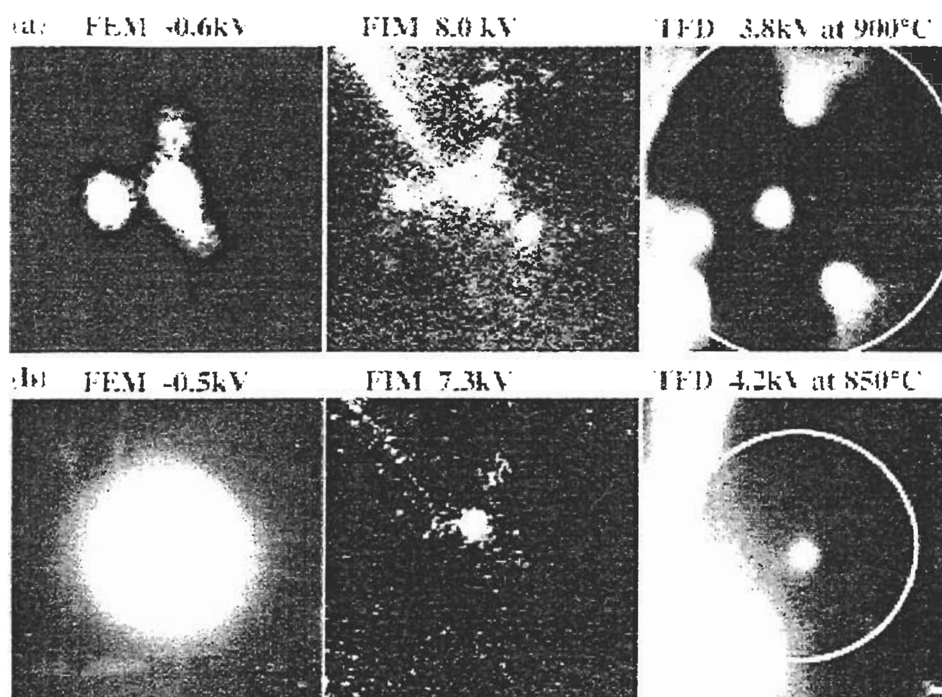


Figure 3 Images of projection methods for a [111]-oriented W tip treated by the T-F method, (a) on the way and (b) at the final stage, respectively. In the FEM image of (b), the applied voltage was increased much to confirm the spherical symmetry, leading to a large bright spot. The bright areas outside circles in TFD images are discharge from other parts than the tip. TFD makes clean the tip including its shank, while its apex being sharpened.

3.1 *Electron standing waves in a vacuum gap*

For a tip biased at a negative voltage of from a work function of sample to about 10 V and brought close to the sample, the phase coherence of field-emitted electrons causes a series of peaks in a differential conductance (dI/dV) versus the bias voltage (V) curve [5-7]. The voltage of the first peak corresponds almost to the work function. The incident electrons field-emitted from the tip are partially reflected at the sample surface with an abrupt potential change, and the reflected electrons are reflected again at the tunneling barrier partially. Consequently, by repeating the reflection, the electron standing waves (ESW) are generated in the vacuum gap under specified biased boundary conditions involving the tunneling barrier and a potential near the sample.

In this differential conductance measurement, the tunneling current is kept constant to avoid the damage of the tip and the sample surface from tip burst due to rapid current increase, causing tip retraction as the bias voltage is increased for dI/dV-V measurements. Under the condition of a constant field emission current, the electric field over the tip is required to be constant independently of the voltage. Thus, adjusting the separation between tip and sample with an STM feedback circuit regulates the potential barrier close to the tip, depending on the tip geometry. If the tip has the same geometry, the change in ESW excitation among various samples can be attributed to the change in the confinement potential near the samples.

We prepared the tips having almost the same structure by the T-F treatment. Recently we found that the electric field near the sample surface can be evaluated from the energy intervals of a series of peaks in a dI/dV-V curve according to the Airy function, because, roughly speaking, the ESW states are confined in a triangle potential near the sample surface [17,18]. The eigenstates confined in a potential near the sample surface are pictured in a Muffin tin potential with an abrupt change at the surface, which shifts the phase of propagating electron wave, leading to the reflection. Here we approximate it to be a simple triangle potential biased at the voltage. For the evaluation of electron confinement in

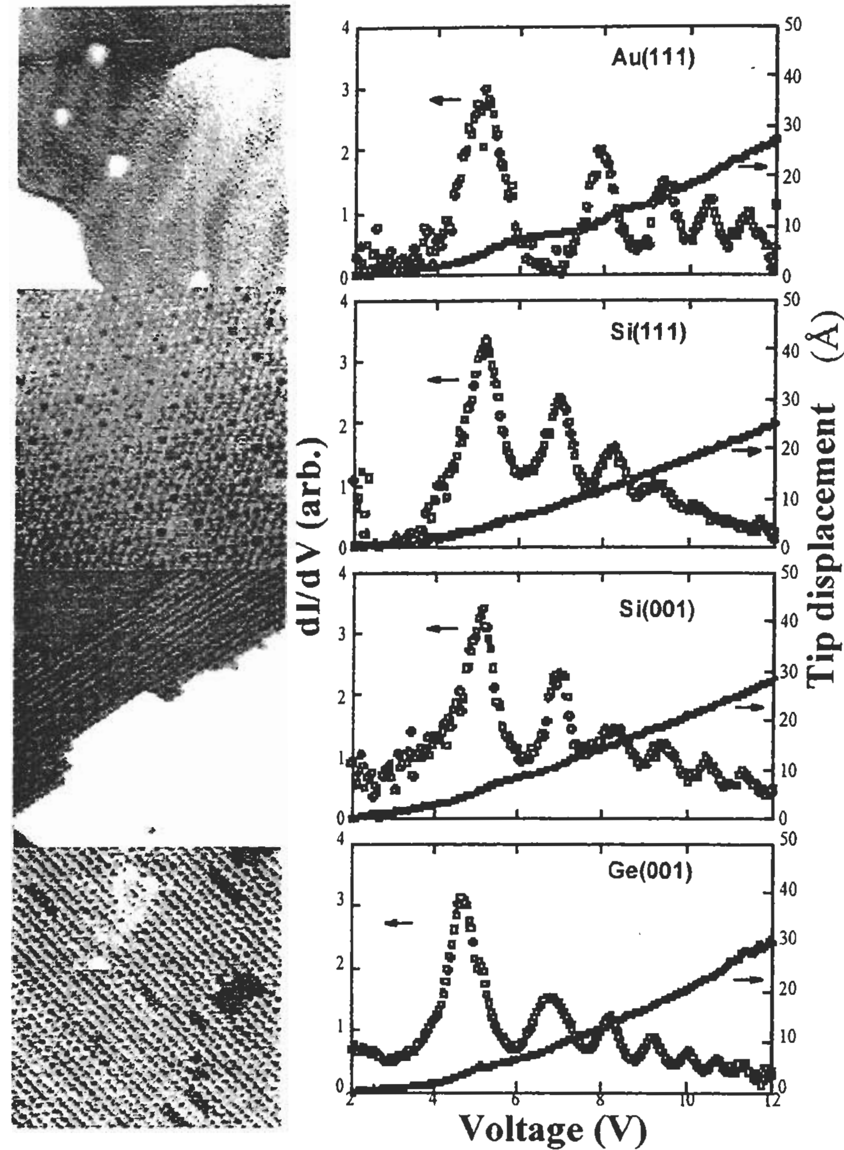


Figure 4 STM images and differential conductance spectra for Au(111), Si(111), (001) and Ge(001): STM images were obtained at Vsample = -0.25 V, It = 1 nA and the scanning area of about 40x40 nm^2 for Au(111), 1.5V, 0.1 nA and 20x20 nm^2 for Si(111), -1.3V, 0.1 nA and 20x20 nm^2 for Si(001), and -2 V, 1 nA and 20x20 nm^2 for Ge(001), respectively. The similar retraction in the conductance curves roughly indicates that the tips have the same radius for each measurement. The current was kept constant at 1 nA for the dI/dV measurement.

a triangle potential near the sample surface, we used a T-F treated tip of [011]-oriented W tip with a clean flatten facet of (011) plane, to regulate the electric field near the tip. Moreover, the flattened facet is expected to enhance the electron interference as the Fabry-Pérot type interferometer does. Fig. 4 shows the dI/dV-V curves with ESW peaks for several samples; Au(111), Si(111)7x7, Si(001)2x1 and Ge(001)2x1. Fig. 5 summarizes the electric field near the sample surface estimated from the first and the second peak with low eigen-energies, which are found at sample voltages of about 5 to 8 V in Fig. 4. The electric field corresponds to that at about 0-2 Å close to the sample surface under a tri-

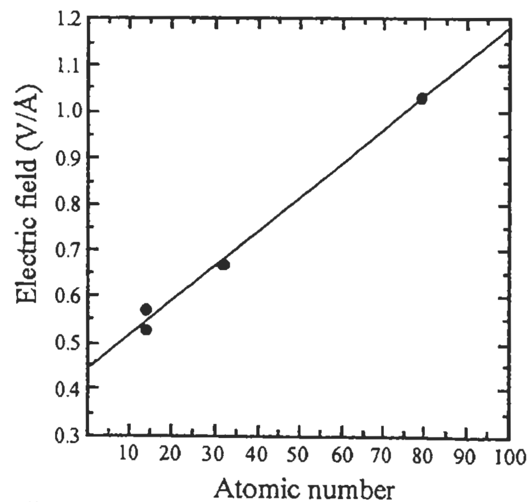
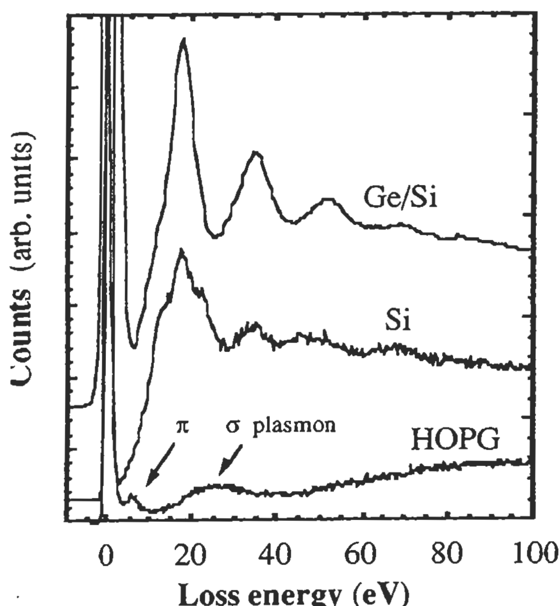


Figure 5 Evaluated electric field intensity near the sample surface versus atomic number.

igle potential approximation at a bias voltge. The field increases with the atomic imber of the surface element, although we ive only a small number of measurements. iis implies that the method has a potential recognizing surface elemental species.

2 *Auger electron and energy loss spectra*

y raising the applied voltage to several kV, e can obtain field-emitted electrons having iergy enough to make Auger electrons nitted out of sample surfaces. For this ectroscopy, we used a [111]-oriented W tip well as for STM imaging. The tip was T-treated and evaluated by FEM before the periments. The sample was electrically ounded. The emission current was about 1



igure 6 Electron energy loss spectra for Ge deosited Si(111), Si(111)7x7 and HOPG obtained ith the instrument combined with an FE-STM. he primary electron energies were 1.2, 1.2 and .79 keV, respectively.

μA, and the separation between tip and sample was changed from 3 mm to less than 0.1mm.

We have obtained the energy spectra of electrons backscattered from Si(111), Ge deposited Si(111), HOPG (highly oriented pyrolytic graphite), and polycrystalline metals of Mo and Ag, and so on. The elastic scattering peak with satellite peaks on the lower energy side due to plasmon (bulk and surface) energy losses, Auger electron peaks strongly depending on the elements and true secondary electrons were detected. The spectra around the elastic peak with plasmon loss peaks for Si(111), Ge deposited Si(111) and HOPG are obtained with a resolution less than a few eV, in Fig. 6. The Ge coverage was about 0.04 bilayer grown at 400 °C. A series of satellite peaks corresponds to multiple losses due to bulk plasmon excitation, and a shoulder around 10 eV to surface plasmon for Si(111) and Ge deposited Si(111): the plasmon loss peaks appeared at almost the same energies. The plasmon loss peaks of HOPG were clearly detected at around 7 eV and 25 eV, which are attributed to plasmons of π and δ band, respectively [13]. These spectra imply that the electron energy loss spectra (EELS) are quite useful for surface spectroscopy combined with the FE-STM.

On the other hand, the Auger peaks were also detected for those samples, but shifted toward lower energies and reduced as the electric field between tip and sample was increased. The electron trajectories in the electric field were simulated to confirm the peak deterioration; the electrons with low energies are deflected strongly by the electric field. Thus an electric shield or an electron

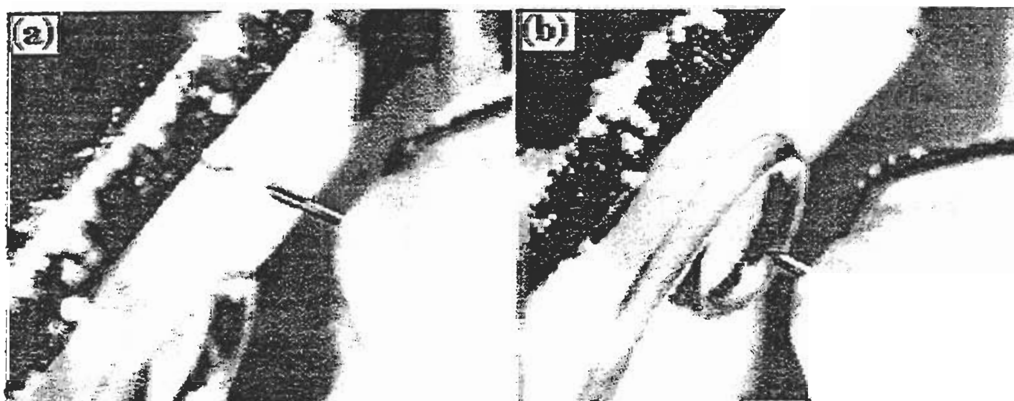


Figure 7 Photo of a simple electric shield of a Mo wire loop. In (a) a mirror image of a W tip is seen on a Si sample surface. On the right below, a tip holder of sapphire and a part of W loop for heating the tip.

extractor is required. One simple example of an extractor with a metal wire loop is shown in Fig. 7. In spite of its simplicity, the deflection was reduced. An Auger electron spectrum for HOPG using an extractor with a hole of about 1 mm in diameter between a tip and a sample is shown in Fig. 8, indicating less energy shift of the carbon KLL peak. A cylindrical shield around the tip is also promising for its compactness [19]. A metal plate with a small hole, the position of which can be controlled with a fine mechanical stage, should be inserted to optimize the electric field, which is under development.

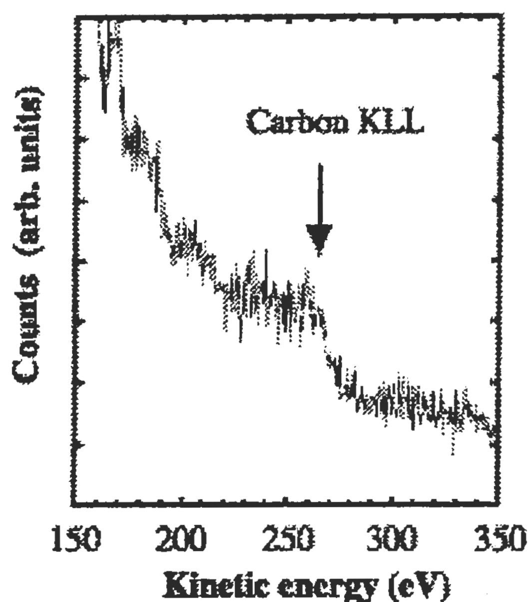


Figure 8 Auger electron spectrum for HOPG with an extractor between a tip and a sample. The primary electron energy was 1.7 keV.

4. Summary

We presented the tip preparation method for a field emission STM for electron spectroscopies. The T-F treated tip can be operated as a stable field emission gun and a geometrical boundary condition. A series of peaks appeared in dI/d*V*-*V* curves, which are attributed to the electron standing waves excited in a vacuum gap between the tip and the sample. From the peak interval we evaluated the electric field close to the sample surfaces. By raising the energy of field emission, EELS and Auger spectra were also obtained. By improving the electric shield between the tip and the sample the application of this combined instrument can be spread, which has great potential with a good spatial resolution.

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