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 remodeling 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.

Introduction

The last two decades the excellent imaging ability of scanning tunneling microscopy (STM) has been successfully demonstrated at atomic resolution on sample surfaces [1, 2]. Its potential of atom manipulation as well. The spectroscopic methods using STM have also been developed, in which tunneling current $I$ [3, 4] or differential conductance $dV/dI$ [5-7] is measured with changing bias voltage $V$ at each pixel of an STM image. Centrally, vibrational spectroscopy with inelastic tunneling in the STM has been also developed to recognize molecular species on faces at low temperature [8]. Furthermore, the combination with photon [9] and electron [10-13] spectroscopies for surface analysis has attracted much interest, in which STM tip is used as an electron source. In spite of their excellent features, their applications using surface analytical methods obtained with STM have not seemed to expand widely, because of rather poor reproducibility of the electronic states at a prepared apex. In these spectroscopic proximity methods, the spectroscopic images are rays composed of the spatial convolution electronic states between a tip and a sample. Thus, in order to improve their availability, it is required to control the atomic composition at the tip as well as the atomic structure 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 [16]. 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^-10 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 actuation, an electron energy analyzer (Omicron, C3A300), a cylindrical sector analyser with an
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.
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 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
a triangle potential near the sample surface, we used a T-P 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-
ngle potential approximation at a bias voltage. The field increases with the atomic number of the surface element, although we have only a small number of measurements. This implies that the method has a potential for recognizing surface elemental species.

2 Auger electron and energy loss spectra raise the applied voltage to several kV, and can obtain field-emitted electrons having enough energy to make Auger electrons sputtered out of sample surfaces. For this spectroscopy, we used a [111]-oriented W tip well as for STM imaging. The tip was T-treated and evaluated by FEM before the experiment. The sample was electrically grounded. The emission current was about 1 µA, and the separation between tip and sample was changed from 3 mm to less than 0.1 mm.

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 bands, 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 electric 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 6](image)

**Loss energy (eV)**

Figure 6. Electron energy loss spectra for Ge deposited Si(111), Si[110]x7 and HOPG obtained with the instrument combined with an FE-STM. The primary electron energies were 1.2, 1.2 and 2.79 keV, respectively.

![Figure 7](image)

**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.
An 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.

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References

4. Summary
We presented the tip preparation method for a field emission STM for electron spectroscop- ies. 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 df/dV-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.