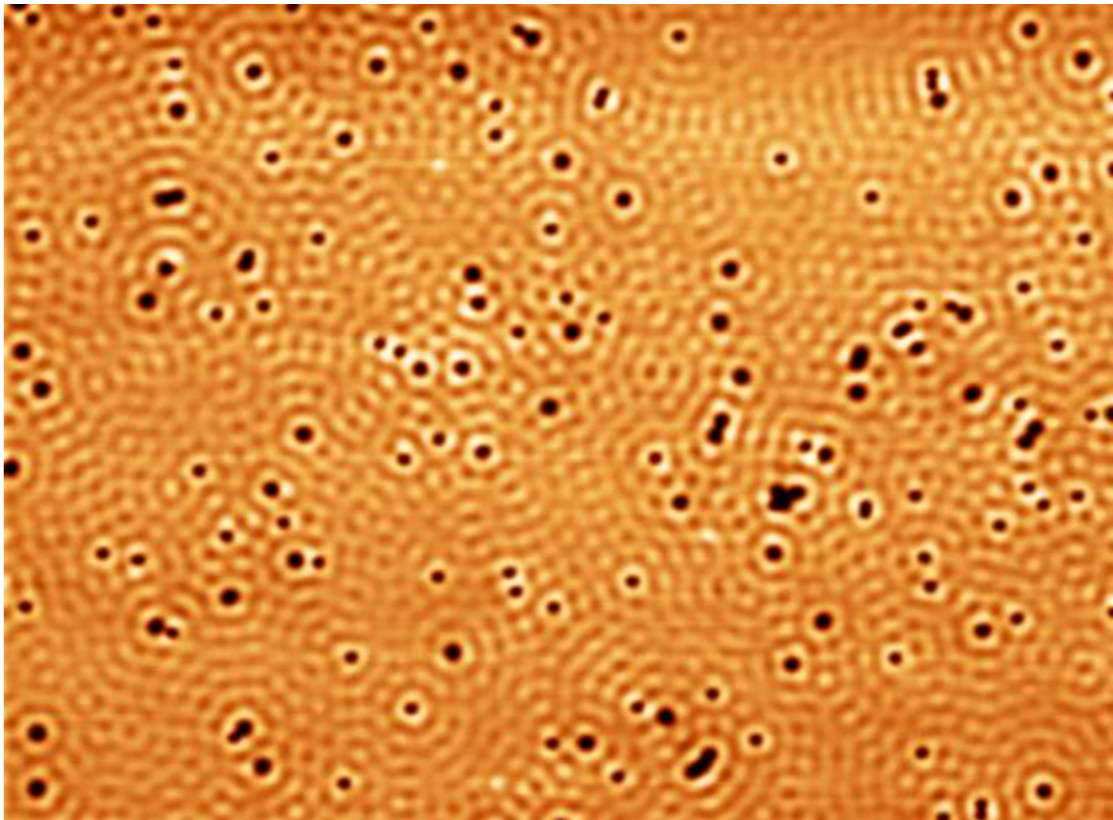


## Measurement of the surface state dispersion by low-temperature scanning tunneling microscopy (STM)

Liwei Jing ([liweijing@aalto.fi](mailto:liweijing@aalto.fi))

Viliam Vano ([viliam.vano@aalto.fi](mailto:viliam.vano@aalto.fi))

Peter Liljeroth ([peter.liljeroth@aalto.fi](mailto:peter.liljeroth@aalto.fi))



## 1 Introduction

This assignment introduces low-temperature scanning tunneling microscopy (STM) and spectroscopy (STS) that are able to provide structural and electrical information of surfaces with atomic spatial resolution. Since its conception in the early 1980s [1], there have been few techniques in the physical sciences that have had as large a conceptual impact as STM. Shortly after its development, the impact of STM was in providing atomically resolved images of well-defined surfaces, such as single crystals of semiconductors and metals. However, the past decade has seen an enormous increase of STM studies focusing specifically on the properties of single molecules and nanostructures [2,3]. The strength of STM lies in the combination of high-resolution imaging (STM) and spatially resolved electrical spectroscopy (STS), which is capable of providing the local density of states (LDOS) with atomic spatial resolution.

These techniques will be illustrated by imaging Cu(111) surface and measuring the dispersion of the two-dimensional free electron gas (surface state) present on the surface. This can be achieved by measuring the oscillations in the local density of states arising from the scattering of the surface state off surface impurities.

After reading these instructions and before starting the actual measurements you should be able to answer the following questions:

1. Explain the working principle of STM.
2. How can the local density of states be measured with STM?
3. What is a surface state and what is its electronic structure?
4. How can dispersion be measured with STM?

### 2.1 Scanning tunneling microscopy

An STM works on the principle of quantum mechanical tunneling of electrons between an atomically sharp probe ("tip") and a conductive surface through a thin (typically ~1 nm) vacuum barrier. The STM setup is shown in Figure 1a. Here, the tip raster scans the sample surface while recording the tunnel current at a chosen bias voltage  $V_b$ . This voltage refers to the potential of the sample with respect to the tip. The tip is attached to a scanner with piezoelectric elements that can be used to control the x-, y-, and z-position with picometer accuracy. Scanning is typically carried out in the constant-current mode, where the tip height is controlled by a feedback loop such that the tunnel current between tip and substrate is maintained constant. The obtained image contains z-position of the tip in the xy-plane and the image is referred as topograph. A typical STM image of a (111)-terminated copper surface is shown in Figure 2a. The black depressions are carbon monoxide (CO) and oxygen impurities. It is important to realize that the resulting 'apparent height' of the surface features contains information on both the electronic and topographic properties ('true height') of the sample. This can be easily understood. On the one hand, the tunneling matrix element between the STM tip and the surface depends exponentially

on their separation  $d$  (see Figure 1b):  $T \propto \exp(-2\kappa d)$ , where  $\kappa$  is the decay constant. For a vacuum barrier, the tunnel current decreases by roughly one order of magnitude per one Ångström change in  $d$ . This would relate to the “true height” of the features (such as surface steps) on the surface. On the other hand, the tunnel current depends on the local density of states (LDOS) of the sample  $\rho_s$  and the tip density of states (DOS)  $\rho_t$ :

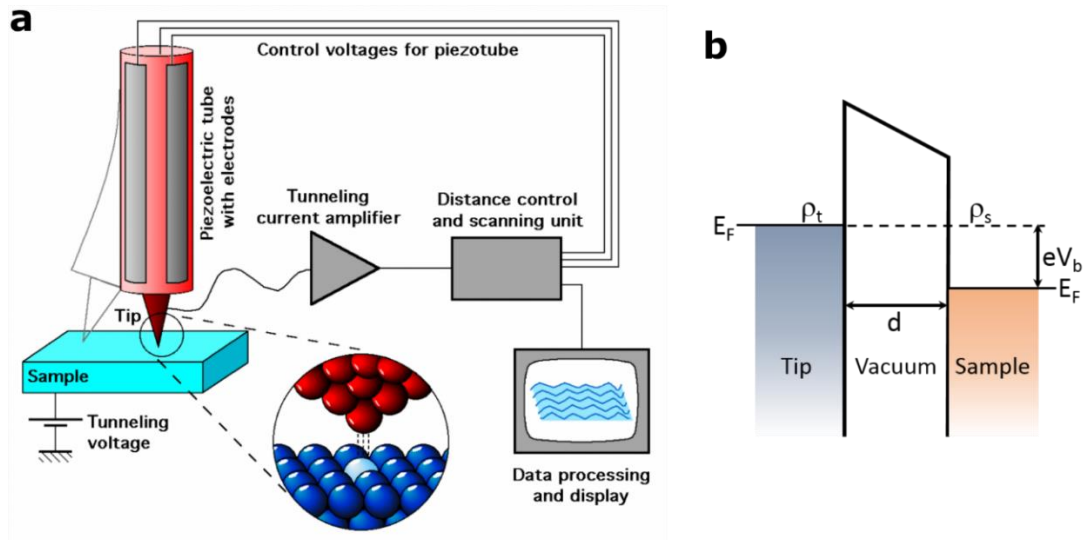
$$I(V_b) \propto \int_0^{V_b} \rho_t(E - eV) \rho_s(E) T(E, V, d) dV \quad (1)$$

Going back to Figure 2a, it is now clear that the impurities reduce the local density of states and hence, the tip has to approach the surface in order to maintain a constant tunneling current even though the impurity itself topographically protrudes from the surface.

Differentiating Eq. (1) w.r.t. to the bias voltage and assuming that the transmission and tip DOS are constant, one gets

$$dI/dV_b \propto \rho_s(eV_b) \quad (2)$$

at the position of the STM tip. This very important result forms the basis for all scanning tunnelling spectroscopy (STS) experiments, in which the  $dI/dV_b$  signal is interpreted as being proportional to the LDOS of the sample at the position of the tip. While the procedure for rigorously recovering LDOS from the measured  $dI/dV_b$  spectra has been discussed at length in the literature [4-6], the interpretation that  $dI/dV_b(V_b, x, y) \propto \text{LDOS}(eV_b, x, y)$  is usually sufficiently accurate.

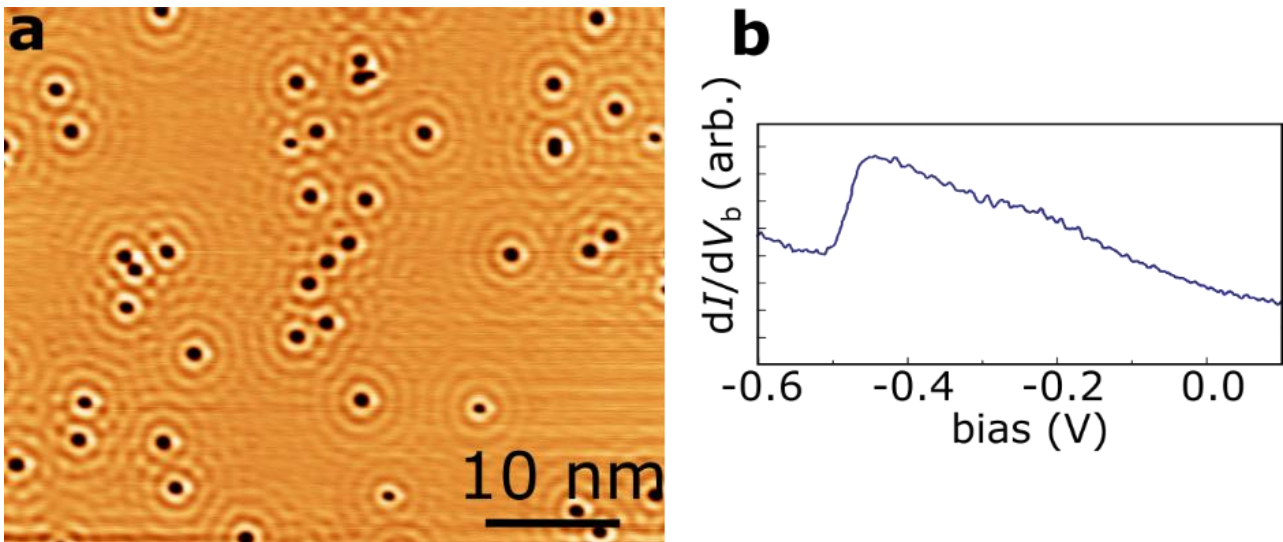


**Figure 1.** (a) Schematic of the STM set-up: bias voltage is applied to the sample and the current between the tip and the sample is measured. The tip position is controlled by piezoelectric elements. Figure credit: Michael Schmid, TU Wien. (b) Schematic energy diagram as a positive bias voltage is applied to the sample. In this case, the current is the result of electrons tunneling from the tip to empty states of the sample over the energy window set by the bias voltage (0 to  $eV_b$ ). This corresponds to measuring empty states of the sample.

The simplest way to obtain the  $dI/dV_b$  spectrum is to obtain an  $I(V_b)$  curve and subsequently differentiate it with respect to  $V_b$ . Numerical differentiation would amplify any noise present in the data. This in turn leads to a masking of the spectral features. This can be avoided using a lock-in amplifier to obtain  $dI/dV_b$ , which helps to improve significantly the signal-to-noise ratio. The lock-in uses a periodic signal  $V = V_m \sin(\omega t)$  (sinusoidal voltage modulation with amplitude  $V_m$  and frequency  $\omega$ ) added to sample bias  $V_b$ . The sample bias now reads  $V = V_b + V_m \sin(\omega t)$ . By applying a Taylor series expansion at  $V = V_b$ , tunneling current  $I$  can be rewritten as:

$$I(V_b + V_m \sin(\omega t)) \sim I(V_b) + \left. \frac{dI(V)}{dV} \right|_{V=V_b} \cdot V_m \sin(\omega t) + \left. \frac{dI(V)^2}{dV^2} \right|_{V=V_b} \cdot V_m^2 \sin^2(\omega t) + \dots \quad (3)$$

By means of a lock-in amplifier we can extract the first harmonic signal, which is proportional to the differential conductance signal  $dI/dV_b$ .



**Figure 2.** (a) Zoomed-in STM topographic image of a Cu(111) surface. The surface state is scattered of surface impurities (typically carbon monoxide). (b)  $dI/dV_b$  spectrum measured on a Cu(111) surface showing the onset of the surface state at a bias of ca. -0.5V.

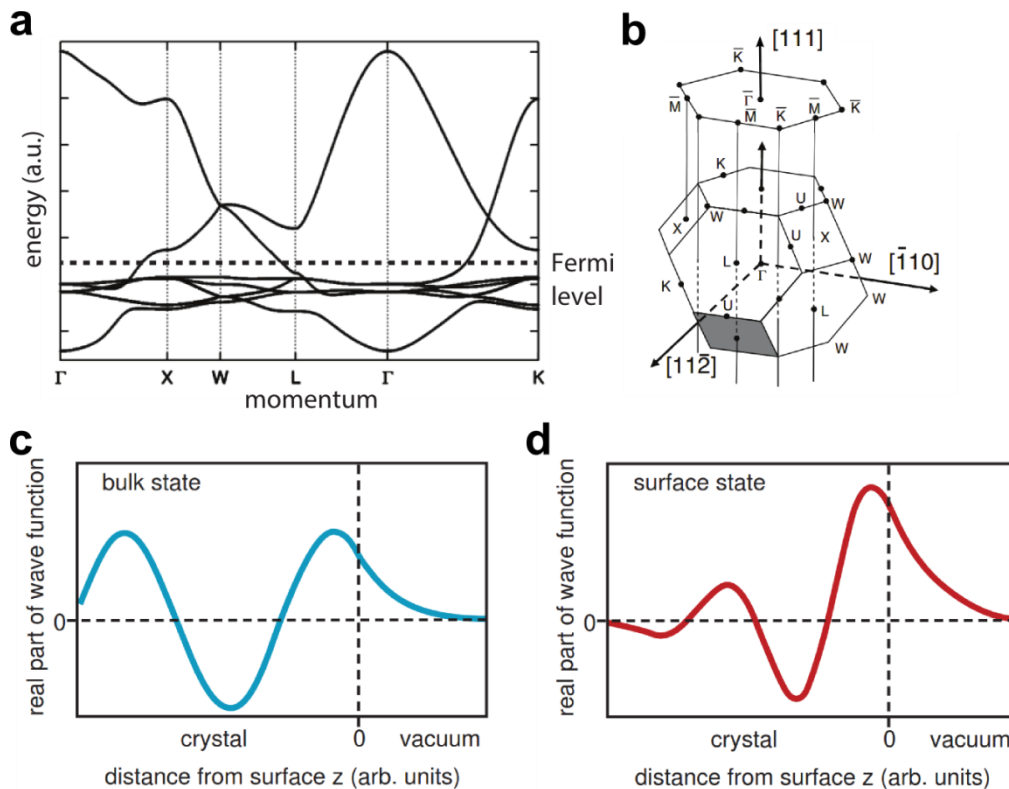
An example of such a spectroscopic STM measurement can be found in Figure 2b, which shows the measured  $dI/dV_b$  signal as a function of the bias voltage on a Cu(111) surface. The onset of the surface state can be seen as a step in the  $dI/dV_b$  signal at a bias of around -0.5V. From the definition of the bias (sample w.r.t. to the tip), we can infer that at negative bias, we are probing occupied states in the sample, and at positive bias, the unoccupied part of the DOS (see Figure 1b). This means that the Cu(111) surface state onset is located ca. 0.5 eV below the copper Fermi level.

## 2.2 Physics of surface states

The bulk electronic properties of crystalline solids can be described by their band structure, i.e. the dependence of the electron energy on its momentum. An example of a calculated band structure can be found in Figure 3a. The letters on the x-axis refer to different symmetry points in the 1<sup>st</sup> Brillouin zone shown in Figure 3b. In the bulk, the wavefunctions are given by the three-dimensional Bloch waves

$$\psi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}) u_{\mathbf{k}}(\mathbf{r}) \quad (4)$$

where  $u_{\mathbf{k}}(\mathbf{r})$  is a function that has the same periodicity as the lattice. The presence of a surface results in a behaviour similar to what happens at the edge of a particle in a box problem (with finite barrier height). Considering only the situation perpendicular to the surface, the Bloch wave function and its derivative have to be matched continuously to an exponentially decaying wavefunction in the vacuum. This is shown in Figure 3c.



**Figure 3.** (a) Calculated band structure of copper. (b) 1<sup>st</sup> Brillouin zone of an fcc crystal, with the projection onto the (111) surface. (c) Schematic wavefunction of a bulk Bloch state at the surface. (d) Schematic wavefunction of a surface state.

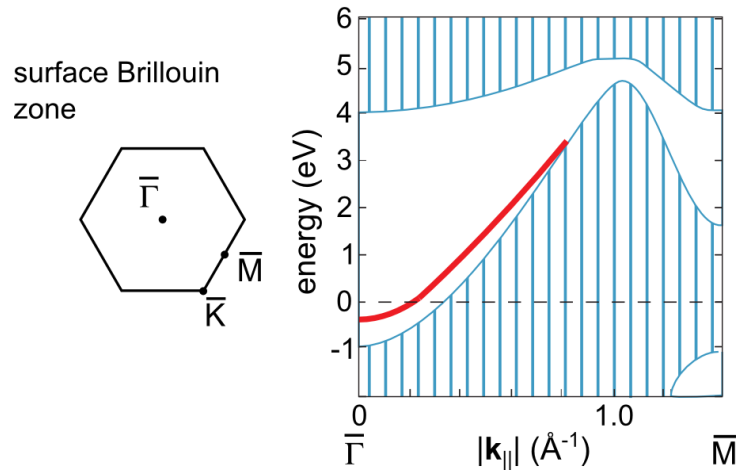
The presence of the surface destroys the translational periodicity perpendicular to the surface but the periodicity parallel to the surface is maintained. Therefore, parallel to the surface, the electronic states are still two-dimensional Bloch waves. The wave vector  $\mathbf{k}$  of a bulk Bloch wave is purely real but this is not a restriction stemming from the Schrödinger equation. In the case of a particle in a box, the wave vector outside the box is purely imaginary, which results in an exponential decay of the wavefunction. In a similar manner, we can see what would happen if the wave vector was complex inside the solid. If we

assume that the perpendicular component of  $\mathbf{k}$  is complex, the Bloch states can be expressed as

$$\psi_{\mathbf{k}_{\parallel}}(\mathbf{r}) = \exp(i\mathbf{k}_{\parallel} \cdot \mathbf{r}_{\parallel}) u_{\mathbf{k}}(\mathbf{r}) \exp(i\kappa z) \quad (5)$$

where  $\mathbf{k}_{\parallel} = (k_x, k_y)$  and  $\mathbf{r}_{\parallel} = (r_x, r_y)$ . This type of a wavefunction is not physically meaningful in a bulk solid as it is exponentially increasing in the  $+z$ -direction. The existence of the surface makes such solutions with a complex wave vector possible and an example is given in Figure 3d. The solution has a complex wave vector in the  $z$ -direction, which means that it is exponentially increasing in that direction. However, as the crystal is terminated by the surface, it has to be matched to an exponentially decreasing wave function outside the surface and it can still be normalised. This solution is a surface-localised electronic state. Note that the wave number  $\kappa$  in the  $z$ -direction is complex, not just imaginary. Therefore, the wave function in the  $z$ -direction is not just exponentially decaying but still has an oscillating Bloch character.

These states are characterised by the quantum number  $\mathbf{k}_{\parallel}$  and an energy  $E(\mathbf{k}_{\parallel})$ . Momentum parallel to the plane  $\mathbf{k}_{\perp}$  is not a good quantum number because the periodicity is broken in the direction perpendicular to the surface. A true surface state cannot be degenerate with any bulk state. This means that for a surface state with  $\mathbf{k}_{\parallel}$  and  $E(\mathbf{k}_{\parallel})$ , there cannot be any bulk states with the same energy and  $\mathbf{k}_{\parallel}$  for any value of  $\mathbf{k}_{\perp}$  i.e. along the entire  $\mathbf{k}_{\perp}$ -rod that is passing through the  $\mathbf{k}_{\parallel}$  of the surface state. If there was such a state, the surface state could couple to it and penetrate infinitely into the bulk and not be a surface state any more. This requirement gives a necessary condition for the existence of a surface state: The surface state must lie in a projected band gap of the bulk electronic structure. The projected band structure for a specific  $\mathbf{k}_{\parallel}$  is defined as all the energies for which bulk states exist that have the same  $\mathbf{k}_{\parallel}$  and an arbitrary value of  $\mathbf{k}_{\perp}$ .

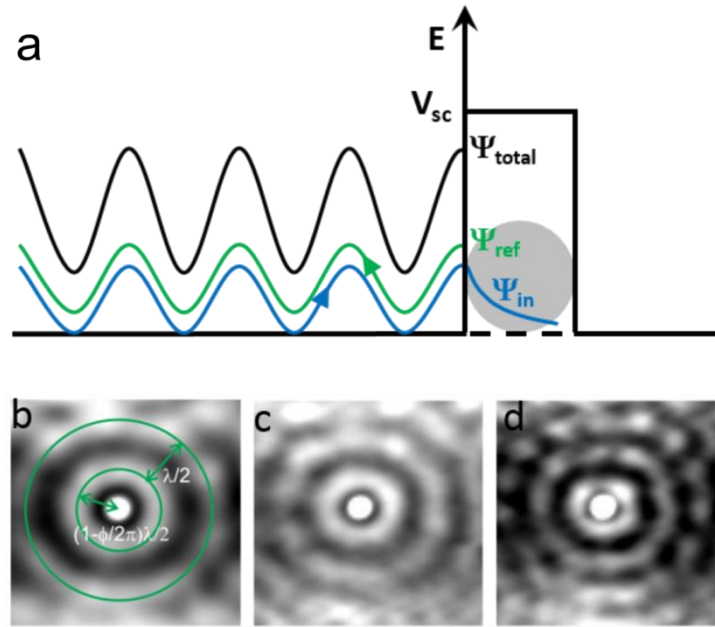


**Figure 4.** The surface Brillouin zone of Cu(111) and the projected bulk band structure (shaded in blue). The sp-derived surface state (red line) exists inside the projected gap of bulk band structure.

This is illustrated for the case of Cu(111) surface in Figure 4, which shows the surface Brillouin zone (left) and the projected band structure along the  $\bar{\Gamma} - \bar{M}$  axis. The bulk bands cover the energies and momenta indicated with blue shading. There is a gap around the Fermi energy at the  $\bar{\Gamma}$ -point. The surface state living inside this gap is indicated with the red line and it shows free-electron like dispersion

$$E = \frac{\hbar^2}{2m_{\text{eff}}} |\mathbf{k}_{\parallel}|^2 \quad (6)$$

with an effective mass of ca.  $m_{\text{eff}} = 0.4$ .



**Figure 5.** (a) One-dimensional schematic of scattering of an electron wavefunction due to a scatterer shown by a grey circle representing potential barrier of height  $V_{sc}$ . The wavefunctions have been shifted vertically up for clarity. (b-d)  $dI/dV_b$  maps recorded in the vicinity of a Cu adatom on Cu(111) surface at (b) -300 mV, (c) -200 mV, and (d) -100 mV. Antinodes of the standing waves are shown by green circles in (b).

### 2.3 Scattering of surface electrons

The surface state electrons scatter from surface impurities (e.g. CO and oxygen on Cu(111)) and step-edges present on the surface. The scattering of the surface states refers to what happens to a travelling electron wavefunction when it encounters a scatterer on the surface. We can understand this from a one-dimensional schematic shown in Figure 5a where the scatterer (shown in grey circle) constitutes a rectangular potential barrier of height  $V_{sc}$ . The actual potential shape and size of a real scatterer can be different from this. As the incident electron wavefunction ( $\Psi_{in}$  with energy  $E_b$ ) impinges the barrier from the left side a part of it gets reflected back ( $\Psi_{ref}$  with energy  $E_b$ ). When the phase of the reflected wave matches constructively to the incident wave, a standing wave ( $\Psi_{total}$ ) forms due to the interference. The resulting standing wave pattern can be probed by STM

by measuring local density of states ( $\rho_s \propto |\Psi_{\text{total}}|^2$ ) at energy  $E_b$  ( $E_b = eV_b$ ) at each point of the standing wave. Alternatively, a two-dimensional  $dI/dV_b$  map can be recorded at bias  $V_b$  to map the standing wave pattern. The standing wave pattern will appear as oscillations in LDOS map [7]. Examples of such maps are shown in Figure 5b-d at energies -300 meV, -200 meV, and -100 meV. Wavelength (or wavevector  $k_{||}$  at energy  $eV_b$ ) of the standing wave can be extracted from a line profile of recorded  $dI/dV_b$  map. It is obvious that extracted wavelength will depend on the energy of the electron wavefunction. It is possible that in the presence of large density of scatterers, the resulting pattern will look very complex rather than circular. In that case, the wavevector of the standing wave can be extracted from the fast Fourier transform (FFT) the image. Plotting the energies as a function of the extracted  $k_{||}$  can then be used to reconstruct the dispersion curve of two-dimensional surface state.

### 3 The experiment

The assistant will help you setting up the measurement. The procedure is briefly outlined here.

#### 3.1 Sample preparation

(111)-terminated copper single crystal is cleaned by sputtering / annealing cycles in an ultra-high vacuum (UHV) environment. This cycle consists of Ne ion bombardment at 1 keV (pressure  $\sim 10^{-5}$  mbar) for 10 minutes followed by heating the crystal to 600°C. After three cycles, the sample is inserted into the low-temperature STM (UHV) and let it cool down to 5 K. All this will have already been carried out when you enter the laboratory. The assistant will give you an introduction to the STM machine and the control software. You will carry out imaging and spectroscopy measurements of the already cleaned and cold Cu(111) sample. Freely available software on internet such as WSxM 4.0 Beta 8.1 or Gwyddion can be used to process the data and extract useful information. FFT option is available in both the softwares.

#### 3.2 STM imaging and spectroscopy

Start the experiment by approaching the tip to the sample (using the control software). Take a couple of large and small scale STM images to make sure that the tip-sample tunnel junction is stable. Check the local density of states by recording  $dI/dV$  point spectra. The  $dI/dV$  spectra should have a step-like feature with an onset at around -0.5 V. If the tip is not stable, or the spectrum does not have the expected shape, follow the instructions from the assistant to gently modify the atomic structure of the tip apex by voltage pulses and controlled contacts with the sample. The  $dI/dV_b$  signal is measured using a lock-in amplifier by adding a small voltage modulation to the sample bias as described above.



### 3.3 Measurement of the surface state dispersion

Find a suitable terrace of the Cu(111) surface to measure the LDOS of the sample as a function of the bias voltage. The experiment involves measuring the  $dI/dV_b$  signal over an area containing some impurities (why?) in the constant-height mode (why?) at different bias voltages through the onset of the surface state band. The  $dI/dV_b$  maps contain information on the scattering of surface state electrons by the impurities. The wavelength of the standing waves can be extracted from the map for different bias voltages. The plot of bias voltage as a function of wave vector will give the dispersion of the surface states from where effective mass of electrons can be extracted.

### 5 Report

The report will consist of:

- (a) A large scale (typically 100 nm x 100 nm) and a small scale image (typically 10 nm x 10 nm) of Cu(111) image. Find the step height of the Cu(111) surface from the line profile. Comment on the features present on the image. Why can we not use topographic image to extract wavelength ( $k_{||}$ -vector) of the standing wave?
- (b)  $dI/dV_b$  point spectrum recorded on the surface to show the surface state onset. The range of  $V_b$  is typically -1 V to +1 V. Discuss the shape of the spectra.
- (c) Constant height LDOS maps at different bias values ( $V_b$ ) to cover the energy range tentatively. Using either the line profile or the fast fourier transform (FFT) to obtain the wavelength (or  $k_{||}$ -vector) of the surface standing waves. Extract the wavelength (or  $k_{||}$ -vector) from the raw data provided to you in a similar way.
- (d) Make the  $E$ - $k_{||}$  plot to generate the dispersion curve. Extract the electron effective mass by fitting with dispersion relation given in equation (6). Comment on the calculated effective mass.
- (e) Extract the surface state onset energy from the  $E$ - $k_{||}$  plot and compare it to value extracted from  $dI/dV_b$  point spectrum.

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