Thermovoltage across a vacuum barrier investigated by scanning tunneling microscopy: Imaging of standing electron waves

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The thermovoltage of a vacuum barrier has been studied by heating the tip of a scanning tunneling microscope. It is extremely sensitive to minor variations of the electronic structure of the sample. As an example an electronic surface state on Cu(111) has been investigated. The reflection at step edges and other defects leads to an interference pattern modulating the thermovoltage by up to 2 μV/K. The findings are well described by a numerical calculation which confirms that the latter differs from a map of the electronic density of states.

Thermovoltages result from transport phenomena if an electric conductor is submitted to a temperature gradient. A special case arises if the conductor is formed by a vacuum barrier which allows electronic tunneling. The thermovoltage is given by the bias which is needed to balance forward and backward tunneling. Therefore a measurement of this quantity represents a critical test for the theoretical description of the tunneling process and the involved electronic states. Since tunneling occurs from occupied to unoccupied states only electrons in the small range of about $+/-$ 2 kT around the Fermi level may contribute in the absence of any external bias. In consequence the thermovoltage depends crucially on the density of states of both electrodes in the vicinity of the Fermi level.

Williams and Wickramasinghe[1] performed an experiment at ambient conditions analyzing the thermovoltage of a scanning tunneling microscope (STM). They found a lateral variation on MoS_2 between the Mo and S atoms.

We present an investigation of the thermovoltage across a vacuum barrier. Our measurements show that this quantity is extremely susceptible to minor variations of the electronic structure of both electrodes. This sensitivity, combined with extreme lateral resolution which can be obtained by using a STM, will make a promising tool in surface science.

For metallic sample surfaces and tunneling tips the observed thermovoltage, i.e., the thermovoltage per temperature difference, is about one order of magnitude larger than the values for metallic bulk.[2] In addition it is negative even for Au, Ag, and Cu samples with positive bulk values for the thermopower. Its absolute value depends on several parameters, e.g., the crystallographic orientation of the surface.

A particularly interesting example to analyze how the thermovoltage depends on the electronic system is found for the (111) surfaces of noble metals. They are known to support electronic surface states representing an almost free two-dimensional electron gas which is reflected at monoatomic steps and other defects.[3] By tunneling spectroscopy performed at low temperature, Crommie, Lutz, and Eigler[4] succeeded in imaging the electronic density of these waves on Cu(111) for different types of confinement. Hasegawa and Avouris[5] showed for Au(111) and Ag(111) that even at room temperature standing waves of the surface states can be observed; however, the coherence length is reduced due to the thermal energy spread.

Our experiments show that standing electron waves of surface states, e.g., on Cu(111), lead to a modulation of the thermovoltage observed in STM. Moreover the thermovoltage does not yield the same information as tunneling spectroscopy; it is related in a more subtle way to the electronic density of states of the tip and sample. A careful analysis of the data yields k as well as dE/dk of the surface state at E_F.

Experiments have been performed by a STM operated in ultrahigh vacuum. A temperature difference between tip and sample of about 10 K has been achieved by heating the shaft of the tip by laser irradiation of about 50 mW (568 nm).[6] Stable steady-state conditions with little thermal drift have been achieved by a constant laser output and a sufficient time for the system to equilibrate (several hours). The way the experiment is conducted excludes heating of the sample. The coupling across the vacuum barrier by radiation and by the tunneling electrons can be completely neglected in comparison to the thermal conductance of tip and sample.[7]

To measure the thermovoltage the STM has been operated in a potentiometry mode relying on the thermal noise of the vacuum barrier.[8] The square of the spectral density of the latter is proportional to the conductance of the tunneling gap, hence it shows the same exponential distance dependence on the gap width as the tunneling current in normal STM operation. However, it is independent of the bias voltage and does not disappear at 0 V. This permits us to use a second feedback loop to adjust the external bias such that the net current vanishes. The technique yields a typical resolution of about 3 μV. Without heating, the observed potential is constant within a few μV. To verify the experimental results which are presented, the direction and speed of the scan have been varied.

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Cu(111) has been prepared by evaporating 200 nm of Cu onto a mica substrate heated to 550 K. The sample is transferred in vacuum to the STM. The tunneling tips have been electrochemically etched from a tungsten wire. They have been cleaned *in situ* by field emission and covered with copper by a controlled touch with the copper surface shortly before the measurement.

Figure 1 shows the topography of a small area of a Cu(111) surface and the thermovoltage which has been measured simultaneously. To enhance the visualization of the thermal signal, Fig. 1(c) shows a shaded representation of the data. The area is characterized by a strip of a single additional layer of copper with a width of 10 nm. Approximately in the center of the area is a small defect which can hardly be recognized in the topography. Its nature cannot be deduced from our data; however, it strongly influences the thermovoltage. The latter shows a wavy signal which looks like an interference pattern caused by the monoatomic steps and the defect near the center. Beside the structure parallel to the steps, additional features in a perpendicular direction can be observed in the vicinity of the defect.

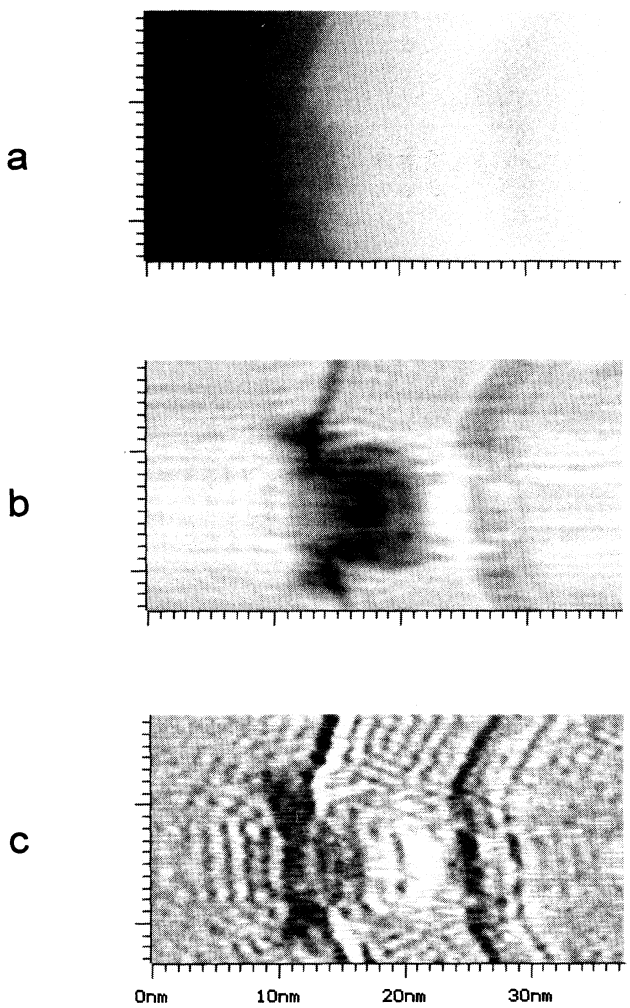

FIG. 1. Topography and thermovoltage for a Cu(111) surface. (a) Gray scale representation of the topography obtained at an average current noise of 5 pA. (b) Gray scale representation of the thermovoltage at the sample for a temperature difference of about 10 K. The thermovoltage is about $-50\ \mu$V on the flat part, and decreases by about 50 μV at a step. (c) Shaded representation of the thermovoltage.

Figure 2, curves *a* and *b*, shows cross sections taken to the left of the first step in the upper part of Fig. 1. The position has been chosen because no other defects are close by. The topography is represented by *a*; the monoatomic step can be well recognized. The measured thermovoltage is given by *b*. The periodicity of the signal is approximately 15 Å; about 4–5 oscillations can be resolved. At the step itself an additional contribution to $V_{\rm th}$ of about $-60\ \mu$V appears which is probably due to the modification of the projected bulk states in the vicinity of the step.[2]

To explain thermoelectric effects observed in STM, the tunneling current caused by the difference of the Fermi distributions of both electrodes has to be analyzed. This current will charge the electrodes till the tunneling current caused by the resulting bias voltage equals the first one. As outlined by Støvneng and Lipavský[9] the thermovoltage $V_{\rm th}$ at the electrode with the higher temperature is given by the ratio of the thermal-induced tunneling current to the conductance of the tunneling barrier:

$$V_{\rm th}=-\frac{I_{\rm th}}{\sigma}\ .$$

The thermally generated tunneling current at zero bias is

$$I_{\rm th}=a\int\rho_T\rho_S\left[f\left[\frac{E}{kT_T}\right]-f\left[\frac{E}{kT_S}\right]\right]dE\ ,$$

where a is a constant; ρ_T is the electronic density of states of the tip at its surface; and ρ_S is the density of states of the sample taken at the tip surface, and thus contains the decay of the wave functions into the vacuum, and hence

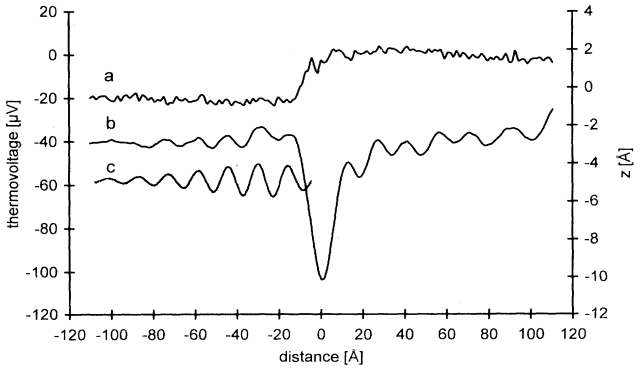

FIG. 2. Cross section through the interference pattern normal to a step edge. (Curve *a*) topography of a section of a single line of Fig. 1. (Curve *b*) measured thermovoltage. (Curve *c*) calculated thermovoltage. (Curve *d*) calculated tunneling conductance.

the tunneling probability. f is the Fermi distribution, E is the energy, k is Boltzmann's constant, and T_T and T_S are the temperature of the tip and sample, respectively. The conductance is given by

$$\sigma = -\tfrac{1}{2} ea \int \rho_T \rho_S \frac{\partial}{\partial E} \left[f\left[\frac{E}{kT_T}\right] + f\left[\frac{E}{kT_S}\right] \right] dE \ ,$$

where e is the elementary charge.

To solve the above integrals in an analytical form, Støvneng and Lipavský used several approximations, which unfortunately cannot be applied to our problem. To provide a more quantitative understanding of our results we have numerically evaluated the thermovoltage assuming that ρ_S, the total density of states for the sample, is given by the sum of the projected bulk states and the surface state. The density of the latter can be described by a Bessel function[4]

$$\rho_{SS} = g[1 - J_0(2k_{\parallel} x)] e^{-2\alpha z} \ ,$$

with the k vector parallel to the surface $k_{\parallel} = (1/\hbar)\sqrt{2m^*(E - E_S)}$ and the decay length of the electronic wave function into the vacuum $\alpha = (1/\hbar)\sqrt{2m(\phi - E) + \hbar^2 k_{\parallel}^2}$, using m^* the effective electron mass E_S the energy at the band edge for the surface state. z is the coordinate normal to the surface, and x is parallel to the surface and perpendicular to the step. Details of the calculation will be published elsewhere.[10]

The calculation yields a large thermovoltage $V_{\rm th} = -I_{\rm th}/\sigma$ with a small modulation due to the surface state. $V_{\rm th}$ is negative since $I_{\rm th}$ and σ are positive. It is only slightly influenced by the choice of parameters for states of the tip, the projected bulk states, or the relative weight of the surface state. Only the offset and the overall amplitude of the oscillation are affected. However, the relative amplitude of the maxima and minima depends strongly on dE/dk, the slope of the dispersion relation of the surface state. Trace c in Fig. 2 shows the result of the calculation. For comparison with the experiment the data have been scaled in the vertical direction by an arbitrary factor. Within the experimental errors the periodicity as well as the envelope of the oscillations is well described. The best agreement with the experimental data is found for the surface state using the parameters $m^* = 0.46$ m and $E_S = -0.39$ eV given by Kevan and Gaylord.[11] To compare with data obtained by tunneling spectroscopy, the calculated conductance which corresponds to dI/dV is plotted in curve d. While the periodicity is the same the envelope strongly differs, i.e., it decreases monotonically. In addition there is a phase shift relative to the thermovoltage which approaches $\pi/2$ with increasing distance from the step.

In summary the lateral variation of the thermal-induced voltage across a vacuum barrier has been investigated. It allows us to map details of the electronic structure of the surface. This was demonstrated for the example of interference structures of the two-dimensional (2D) electron gas of a surface state on the Cu(111) surface. The periodicity of the observed modulation agrees with the data of Crommie, Lutz, and Eigler,[4] who measured the tunneling conductance by dI/dV spectroscopy at low temperature. However, the envelope and the phase of the oscillations in the thermovoltage is completely different. The latter is given by the ratio between the thermally generated tunneling current and the tunneling conductance. Numerical calculations reveal that the amplitude of the oscillations depends crucially on dE/dk for the surface state at the Fermi energy. A good agreement with the experimental data is obtained by using parameters known from photoemission experiments.

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[1] C. C. Williams and H. K. Wickramasinghe, Nature **344**, 317 (1990).

[2] D. Hoffmann, A. Rettenberg, J. Y. Grand, K. Läuger, P. Leiderer, K. Dransfeld, and R. Möller, Thin Solid Films **264**, 223 (1995) (see also B. Koslowski, Dissertation, University of Constance, 1993).

[3] L. C. Davis, M. P. Everson, R. C. Jaklevic, and W. Shen, Phys. Rev. B **43**, 3821 (1991).

[4] M. F. Crommie, C. P. Lutz, and D. M. Eigler, Nature **524**, 363 (1993).

[5] Y. Hasegawa and Ph. Avouris, Phys. Rev. Lett. **71**, 1071 (1993).

[6] The temperature has been measured in a separate experiment by using a small thermocouple of negligible thermal conductance attached to the tunneling tip.

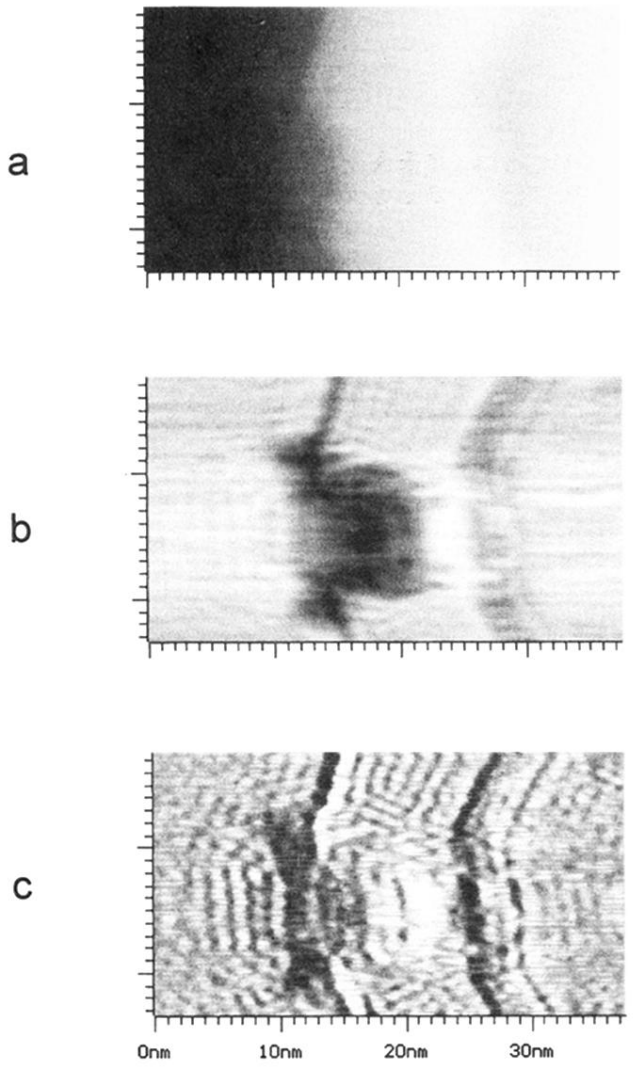
[7] J. B. Xu, K. Läuger, R. Möller, K. Dransfeld, and I. H. Wilson, J. Appl. Phys. **76**, 7209 (1994).

[8] R. Möller, C. Baur, A. Esslinger, U. Graf, and P. Kürz, J. Vac. Sci. Technol. B **9**, 609 (1991).

[9] J. A. Støvneng and P. Lipavský, Phys. Rev. B **42**, 9214 (1990).

[10] D. Hoffmann, A. Rettenberger, K. Läuger, J. Y. Grand, and R. Möller (unpublished).

[11] S. D. Kevan and R. H. Gaylord, Phys. Rev. B **36**, 5809 (1987).



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