

Alternating current scanning tunneling spectroscopy of self-assembled monolayers on gold

S. J. Stranick and P. S. Weiss^{a)}

Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania 16802

A. N. Parikh

Department of Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania 16802

D. L. Allara

Department of Chemistry and Department of Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania 16802

(Received 4 February 1993; accepted 12 April 1993)

We demonstrate the spectroscopic capabilities of an ac scanning tunneling microscope. This ac scanning tunneling microscope has a bias voltage modulation frequency tunable over the range dc–20 GHz and is thus capable of recording images and local spectra of insulating as well as conducting substrates. In this article we detail the spectral sensitivity and the tip-sample separation dependence of the spectra recorded by simultaneously tuning the modulation and detection frequencies. Spectra of an evaporated gold film and of self-assembled monolayers of $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ and of $\text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_{15}\text{SH}$ on gold are presented.

I. INTRODUCTION

In conventional scanning tunneling microscopy^{1,2} a dc bias voltage is applied to a metal tip that is brought within a few atomic diameters of the surface of a conducting or semiconducting sample to give a tunneling current that depends strongly on the separation of tip and sample. The current is used for feedback control of the tip-sample separation as images of the surfaces are recorded. For an insulating sample, a dc tunneling current cannot be conducted through the sample. Kochanski showed that by using a high frequency ac bias voltage, the nonlinearity of the scanning tunneling microscope (STM) junction allows the third harmonic of the modulation frequency ($3f_0$) to be used for feedback control of the tip-sample separation in what he called an alternating current scanning tunneling microscopy (ACSTM).³ This allowed imaging of insulating films with a lateral resolution of ca. 1 nm. In Kochanski's design and in subsequent experiments by others, the ACSTM junction was placed in a microwave cavity resonant at the detection frequency ($3f_0$).³⁻⁵ This limited operation to an extremely narrow frequency range. Michel *et al.* placed an ACSTM in a tunable resonant cavity, but since the tuning required mechanical adjustment, spectra could not be obtained in this configuration.⁵ We have recently obtained atomic resolution images on graphite, and resolution comparable to Kochanski's on a number of metal, semiconductor, and insulator surfaces.^{6,7} Since we employ sensitive microwave network and spectrum analyzers for detection and low-loss transmission lines, we can work over a broad frequency range—dc to 20 GHz—without the need for a resonant cavity.^{6,7} As illustrated below, this allows us to record local microwave frequency ac tunneling spectra on insulators and other materials.^{6,7} A major impact of this mode of scanning probe microscopy is

expected to be in the evolution of a method to distinguish chemical features at a surface with molecular resolution. Since any given molecular group is likely to exhibit a unique dielectric response over a broad bandwidth, a potential signature is available to carry out such chemical imaging. With this in mind we have prepared surfaces covered with molecules with chosen chemical groups by taking advantage of the technique of self-assembly to produce air-stable monolayers. In particular, in this article we present results for self-assembled monolayers of $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ and of $\text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_{15}\text{SH}$ on Au{111}. These are a pair of molecules of very similar size and intermolecular interactions which in self-assembled monolayers have very similar surface presentation of terminal methyl groups. These alkane thiols have identical alkyl chain lengths; the only difference is the substitution of the terminal methyl group for a methyl ester group. We show that unique spectra (microwave amplitude versus frequency) are observed for these films.

II. EXPERIMENT

The experiments reported here we conducted in air using two different STM designs. One is based upon a modified louse,⁷ while the other is a Besocke beetle-style STM.⁸ In both microscopes, the sample connection is made on the same side of the tunnel junction as the ACSTM tip, and the sample approaches the ACSTM tip. The modulation/detection frequency is tuned so as to determine the optimum frequencies for imaging and to record spectra of the sample at the position of the ACSTM junction. All the spectra reported here were recorded at room temperature in air. The microwave frequency source is a Hewlett-Packard 83620C with a 1 Hz bandwidth.⁹ The signal at the modulation frequency is recorded with a Hewlett-Packard 8510C network analyzer.⁹ The signals at the modulation or other frequencies such as the harmonics of the modulation

^{a)} Author to whom correspondence should be addressed.

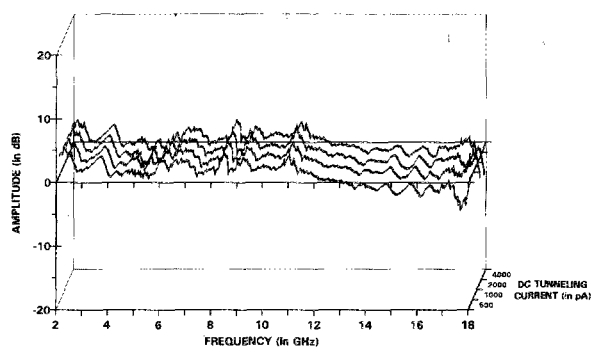


FIG. 1. Amplitude detected at the modulation frequency with the ACSTM probing an evaporated gold film, recorded as described in the text. Spectra are shown for tip-sample separations which with a dc bias voltage of -10 mV give dc tunneling currents of: 500 pA, 1 nA, 2 nA, and 4 nA, as indicated. Note that the detected amplitudes are plotted logarithmically.

frequency are recorded using a Hewlett-Packard 71210C spectrum analyzer.⁹ The narrow bandwidth used allows us to reduce the effect of broadband noise.

The gold films were prepared by evaporating gold onto hot mica (temperature = 340°C , pressure = $(1-6 \times 10^{-7})$ Torr). The self-assembled monolayers of $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ and of $\text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_{15}\text{SH}$ were prepared by soaking the substrate in a solution of the desired thiol in ethanol ($1 \times 10^{-3}\text{M}$) for four days. Companion samples were characterized by infrared spectroscopy, liquid drop contact angle, and ellipsometry to verify the quality of the assembled films.¹⁰ All the samples studied here were sufficiently conductive that we were able to use a simultaneous dc tunneling current to control the tip-sample separation while recording spectra. In the data shown, we reference the tip-sample separation by indicating the dc bias and tunneling current.

III. RESULTS AND DISCUSSION

In Fig. 1, we show microwave frequency ac tunneling spectra recorded with the tip within tunneling range of an evaporated gold film (in air) as the modulation and detection frequency are simultaneously tuned. The tip height was held constant during each measurement by leaving the feedback loop locked onto a preset dc tunneling current present due to dc bias voltage of -10 mV applied to the ACSTM tip. Note that the logarithm of the measured amplitude is plotted.

In Fig. 2 we show spectra recorded with the tip within tunneling range of a self-assembled monolayer of $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ on an evaporated gold film (in air). Once again spectra are shown for various tip-sample separations as measured and controlled by a dc tunneling current for a dc bias voltage of -10 mV applied to the ACSTM tip. The spectra are nearly identical for different dc tunneling currents, but are substantially different than the spectra of bare gold shown in Fig. 1. In Fig. 3, we show spectra recorded on a self-assembled monolayer of $\text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_{15}\text{SH}$ on an evaporated gold film (in air) as for Fig. 2. For this molecule the methyl termination is

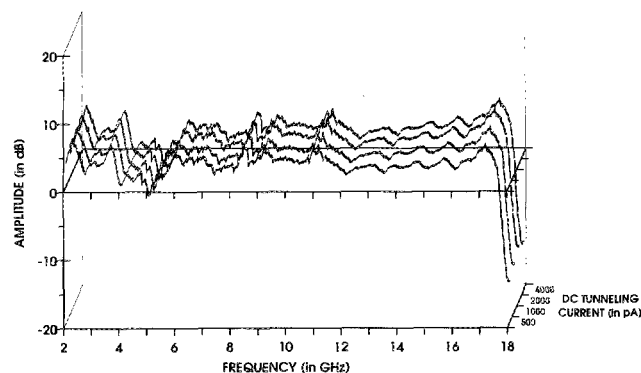


FIG. 2. Amplitude detected at the modulation frequency with the ACSTM probing a self-assembled monolayer of $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ on an evaporated gold film, recorded as described in the text. Spectra are shown for tip-sample separations which with a dc bias voltage of -10 mV give dc tunneling currents of 500 pA, 1 nA, 2 nA, and 4 nA, as indicated. Note that the detected amplitudes are plotted logarithmically.

replaced with a methyl ester termination. Once again, the spectra shown for the film are nearly identical. There is substantial similarity with the spectra of the closely related methyl-terminated thiol shown in Fig. 2, but differences in the 2–4 GHz and other regions.

The spectra shown are typical of those recorded over different areas of each surface away from surface defects. Our main point here is that the structure shown in the spectra are reproducible. The structures in the spectra are not critically dependent on the changes in the impedance matching at the bias supply cable and tunneling current transmission line terminations formed by the tunnel junction. Rather, the spectral structure is determined by the identity of the molecule(s) in the tunnel junction.

Among all these spectra the one region where there are some differences for various tunneling impedances for a single film is for 16–18 GHz over the bare gold film shown in Fig. 1. It is known that Au atoms move rapidly on this surface in air, and that in addition there is a contamination

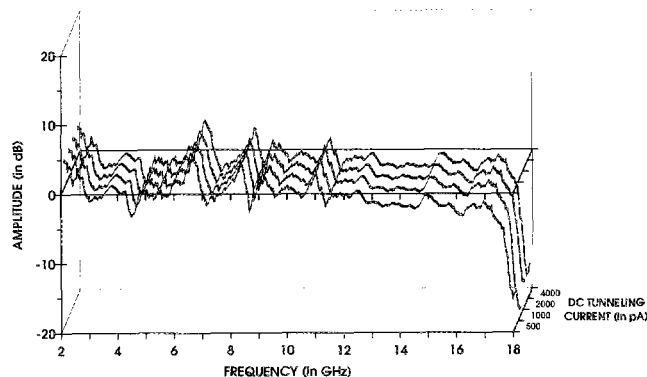


FIG. 3. Amplitude detected at the modulation frequency with the ACSTM probing a self-assembled monolayer of $\text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_{15}\text{SH}$ on an evaporated gold film, recorded as described in the text. Spectra are shown for tip-sample separations which with a dc bias voltage of -10 mV give dc tunneling currents of 500 pA, 1 nA, 2 nA, and 4 nA, as indicated. Note that the detected amplitudes are plotted logarithmically.

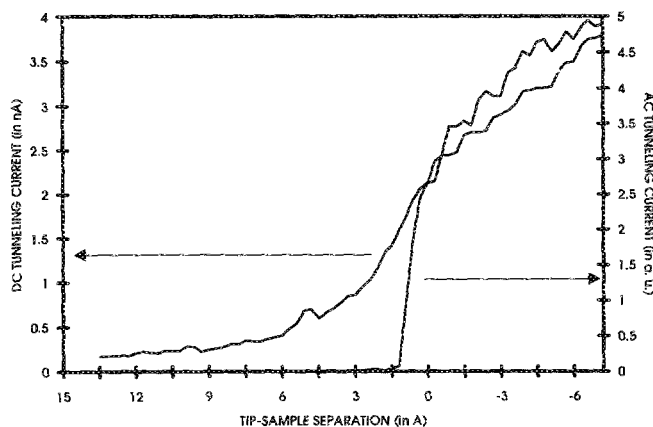


FIG. 4. Microwave frequency amplitude detected at the modulation frequency of 2 GHz and dc tunneling current with the ACSTM probing a single crystal Au{111} surface in air, as the tip-sample separation (z) is varied. The zero of tip-sample separation is assigned to point contact between tip and sample.

layer that presumably also moves.¹¹ We tentatively assign the spectral variations observed in this case to motion of the gold and/or this adsorbed layer.

The small difference in the amplitude for the various tip heights we believe to be due to rectification of the ac bias of 0 dBm (224 mV rms into 50 Ω) dominating the dc current measurement under the conditions used. We typically find a stronger distance dependence for the ac amplitude than Figs. 1–3 would indicate. This is shown in Fig. 4 for the ac amplitude at 2 GHz and the dc tunneling current versus ACSTM tip-sample separation over a bare Au{111} surface in air. Simultaneous tip bias voltages of -10 mV dc and 0 dBm at 2 GHz were applied, and both the ac and dc currents were measured. The tip-sample separation was decreased from being out of tunneling range into point contact, and then the ACSTM tip was pressed into the sample. Each measurement was done at a fresh position on the surface and the data shown in Fig. 4 are typical of a single scan. We assign the zero of tip-sample separation as point contact between tip and sample.^{12,13} When the tip is pushed beyond point contact, stepwise increases in both ac and dc current are found as has been observed in previous measurements.^{12,14} Note that in tunneling range where images and spectra are recorded, the ac tunneling current varies more rapidly with tip-sample separation than does the dc tunneling current.

By removing the large capacitive term in "linear impedance" we are able to use the amplitude at the modulation frequency for feedback for obtaining images and for re-

ording spectra as shown above. By linear impedance we mean loss at the modulation frequency (f_0) as opposed to amplitude detected at harmonics of this frequency (nf_0). We note that for bare Au in air the amplitude at $2f_0$ is 92 dB down from the amplitude at the fundamental, and the amplitude at $3f_0$ is 118 dB down from the fundamental. For insulating substrates, we have observed the amplitude of the harmonics to be within 18 dB of the fundamental due to the highly nonlinear tunnel junction formed in that case.⁶

IV. CONCLUSIONS AND FUTURE PROSPECTS

We have shown that spectral features in microwave frequency ac tunneling spectra remain substantially constant with tip-sample separation. We have shown that adlayers on surfaces determine the measured spectral features, and that we are sensitive to the chemical identity of the molecule in the ACSTM tunnel junction. The goal of our research is molecular scale chemical imaging. Experiments are in progress toward this end utilizing a series of mixed composition self-assembled monolayers.

ACKNOWLEDGMENTS

The support of the Biotechnology Research and Development Corporation, Hewlett-Packard, the Office of Naval Research, and the National Science Foundation Chemistry Division, Presidential Young Investigator Program (the above for S.J.S. and P.S.W.), and Materials Research Division (Grant No. DMR-9001270 for A.N.P. and D.L.A.) are gratefully acknowledged.

¹G. Binnig and H. Rohrer, *Helv. Phys. Acta* **55**, 726 (1982).

²R. Wiesendanger and H.-J. Güntherodt, in *Scanning Tunneling Microscopy I*, edited by H.-J. Güntherodt and R. Wiesendanger (Springer, New York, 1992), p. 1.

³G. P. Kochanski, *Phys. Rev. Lett.* **62**, 2285 (1989).

⁴W. Siefert, E. Gerner, M. Stachel, and K. Dransfeld, *Ultramicroscopy* **42-44**, 379 (1992).

⁵B. Michel, W. Mizutani, R. Schierle, S. Jarosch, W. Knop, H. Benedickter, W. Bächtold, and H. Rohrer, *Rev. Sci. Instrum.* **63**, 4080 (1992).

⁶S. J. Stranick and P. S. Weiss (unpublished).

⁷S. J. Stranick and P. S. Weiss, *Rev. Sci. Instrum.* **64**, 1232 (1993).

⁸K. Besocke, *Surf. Sci.* **181**, 145 (1987); J. Frohm, J. F. Wolf, K. Besocke, and M. Teske, *Rev. Sci. Instrum.* **60**, 1200 (1989).

⁹Hewlett-Packard Corporation, Palo Alto, CA.

¹⁰P. E. Laibinis, G. M. Whitesides, D. L. Allara, Y. T. Tao, A. N. Parikh, and R. G. Nuzzo, *J. Am. Chem. Soc.* **113**, 7152 (1991).

¹¹D. R. Peale and B. H. Cooper, *J. Vac. Sci. Technol. A* **10**, 2210 (1992); H. J. Mamin, H. Birk, and D. Rugar (unpublished).

¹²J. K. Gimzewski and R. Möller, *Phys. Rev. B* **36**, 1284 (1987).

¹³N. D. Lang, *Phys. Rev. B* **36**, 8173 (1987).

¹⁴D. M. Eigler, P. S. Weiss, E. K. Schweizer, and N. D. Lang, *Phys. Rev. Lett.* **66**, 1189 (1991).