SCANNING-TUNNELING-SPECTROSCOPY DETERMINATION OF BARRIER POTENTIALS IN AIR OR MODERATE VACUUM

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INTRODUCTION

A scanning tunneling microscope (STM) can be used to obtain images of surface topology with resolution approaching atomic dimensions. It can also be used to measure localized surface energy barriers. The combination of these two features results in scanning tunneling spectroscopy (STS), which can provide barrier-potential maps of solid surfaces. Computer-controlled nanometer probes in general and the STM/STS techniques in particular have important applications in quantitative nondestructive evaluation.

Electron tunneling between two conductors separated by an insulating barrier is characterized by an exponential dependence of the tunneling current (I) on the thickness (s) of the insulator [1]. A plot of log(I) versus s is a straight line the slope of which is related to the mean barrier potential (ϕ) characteristic of models of metal-insulator-metal (MIM) tunnel junctions. Thus, if I(s) is carefully measured over a range of several orders of magnitude, ϕ can be determined. It has been demonstrated that localized barrier potentials can be determined from measurements of tunneling current as a function of probe-tip displacement (u) using a scanning tunneling microscope in vacuum [2,3]; however, the value of ϕ so determined is often less than that calculated from MIM models. If the tip and sample surface are progressively cleaned in vacuum and ϕ remeasured, it has been found that its value increases, approaching the value calculated using photoelectric work functions [2,4].

The possibility of determining barrier potentials using an STM for various tip-sample combinations in moderate vacuum and in air or other gases at atmospheric pressure has been investigated [5]. Rapid scans of z-displacement

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transducer voltage (V_z) as a function of tunneling current for constant tip-sample voltage (V) were measured under computer control. Values of ϕ were determined from the slope of transducer-drift-corrected log(I) versus V_z curves and the transducer calibration, which relates u to V_z. Results of these experiments for a W tip and a Au sample at 10^{-4} torr and in N_2 at atmospheric pressure gave values of ϕ of the order of 0.1 eV [5]. Such diminished values of ϕ have been reported by others for samples in air or low vacuum [4,5,6].

We have discovered that measurements of V_z as a function of V for constant I reveal a characteristic voltage, V_c, which may be a measure of the transition from tunneling to field emission. A similar transition has been observed in measurements of dV_z/dV versus V using modulation spectroscopy. Comparison of the experimental results with Simmons's MIM model suggests that the characteristic voltage may be related to ϕ, at which value of V the transition from tunneling to field emission occurs. These results, the theoretical basis for the above interpretation, and other interpretations are discussed in this paper.

EXPERIMENT

The STM instrument utilized a segmented-tube transverse-**E**-length-expander transducer [7] rigidly mounted to the scanner base plate. A mechanical vertical positioner with submicrometer resolution was used for coarse approach of the sample to the tip. Because of the large dynamic range of the z displacement of the transducer-about 5 μm perpendicular to the sample surface-and efficient feedback electronics, tunneling current could be established without "crashing the tip". Calibration of V_z in terms of u was accomplished using an optical-beam-deflection technique [8].

Determination of ϕ from measurements of log(I) versus V_z was effected by operating the STM in constant-current mode. The current and corresponding transducer voltage were measured and displayed on the CRT monitor by rapidly stepping the current under computer control with 26 values of increasing I followed by 26 values of decreasing I over a range of about 3 orders of magnitude. Correction for drift during each scan pair and relation of u to V_z were accomplished as previously described [5,8].

Determination of the characteristic tip-sample voltage (V_c) was accomplished in two ways. The first was by measurements of V_z versus V at constant I by stepping V in constant-current mode with data recorded as above. In the tunneling regime, a gradual change in V_z as V is changed is observed as expected, corresponding to the feedback-controlled adjustment of the tip-sample spacing to maintain constant current. At some value of V, $V=V_c$, an abrupt change in the variation of V_z with V occurs.

The second method for determining V_c involves an abrupt change in dV_z/dV at $V=V_c$. This measurement was made by modulating V in constant-current mode and measuring the resulting change in V_z with a lockin amplifier.

The results discussed below were obtained for a variety of tip-sample combinations, different scanning transducers, and different preamplifiers (logarithmic and linear). Before the measurements, the tip was typically cleaned in vacuum by applying 9 VDC between tip and sample for 20-30 minutes. It should be emphasized that although the spectroscopic data were obtained without intentionally moving the probed position on the sample during the many scans, the tip position was subject to drift for several reasons and certainly varied on a microscopic scale. Furthermore, the tip may have been relatively large. Thus, the values of measured parameters are probably characteristic of a surface area more global than atomic in range.

RESULTS

A very substantial amount of experimentation to determine ϕ from log(I) versus V_z was done with a W tip and a Au film deposited on a glass substrate. These measurements were made at 10^{-4} torr with V as a parameter for values from -0.1 to -2.0 V (Positive V indicates that the tip is positive with respect to the sample.). For $0.1 < |V| < 1.5$ V, the scans were well behaved and the values of ϕ determined from these scans were consistently about 0.09 eV. It may be that the cause of the diminished values of ϕ is contamination-mediated deformation of the sample surface where the relative displacement of tip and sample is less than the transducer displacement [4]. In any case, such low values are common as obtained from the slope of log(I) versus V_z curves. For $1.5 < |V| < 2.0$ V, the scans were not well behaved, it was difficult to infer ϕ from the scans, and values of ϕ were significantly less than those inferred for $|V| < 1.5$ V.

Results of measurements of V_z as a function of V for constant I are exemplified by Fig. 1. For these data, I=2.7 nA, the tip is W, the sample is Pt, and the sample chamber contained N_2 at atmospheric pressure. The value of the characteristic voltage is seen to be about 2.1 V. Similar results were obtained for tip/sample combinations: W/Au and Pt/Au. The value of V_c for each of the tip/sample combinations was observed to depend on the polarity of V, but to be independent of I. The many-scan-average values of V_c ranged from 2.2 to 2.5 V for the above tip/sample combinations.

An example of the modulation-spectroscopy data is shown in Fig. 2 for a W tip and Au sample in N_2 at atmospheric pressure, I=10.7 nA, modulation voltage=V_m=1.2 mVRMS, and a modulation frequency of 50.1 Hz. It can be seen that a transition in dV_z/dV occurs at about V=2.2 V.

It is interesting to compare the data shown in Figs. 1 and 2 with Simmons's one-dimensional model of a symmetrical MIM junction. Theoretical expressions for current density, J, in terms of s and V are developed for a rectangular barrier with the effects of image forces included. Equations are presented for the tunneling regime, $V < \phi_o$, and the field-emission regime, $V > \phi_o$ [1]. These equations

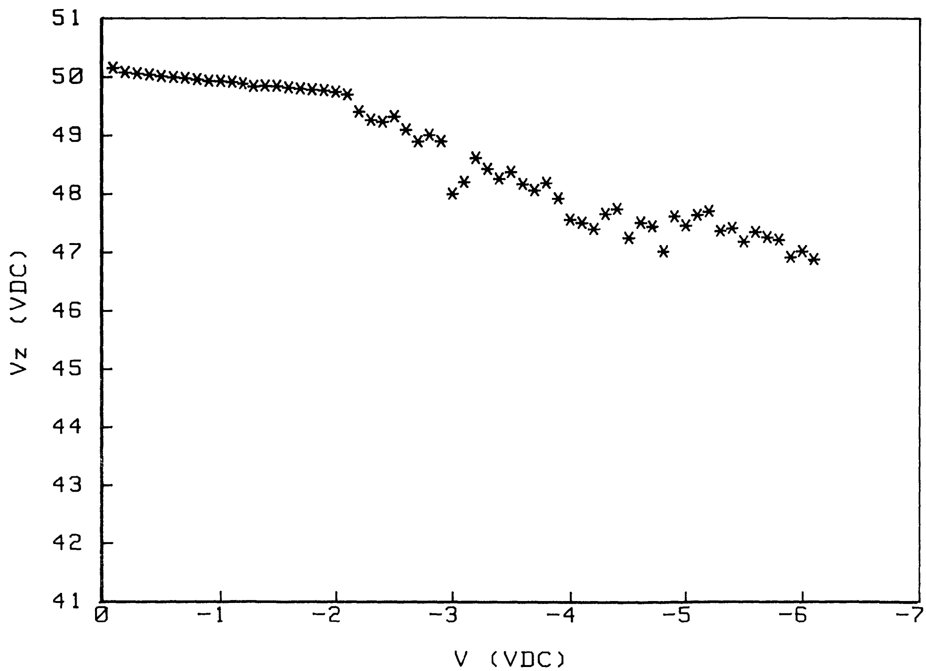

Fig. 1. Transducer voltage (V_z) versus tip-sample voltage (V) for a constant current (I) of 2.7 nA: W tip, Pt sample.

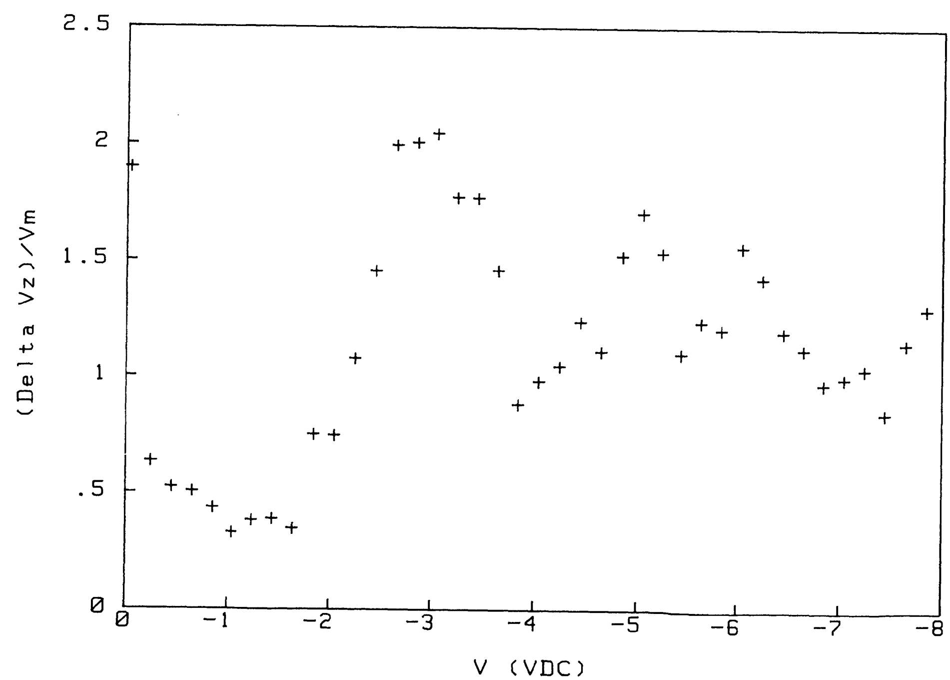

Fig. 2. Change in transducer voltage (Delta V_z) divided by tip-sample modulation voltage (V_m) versus V for a constant current (I) of 10.7 nA, f=50.1 Hz, V_m=1.2 mVRMS: W tip, Au sample.

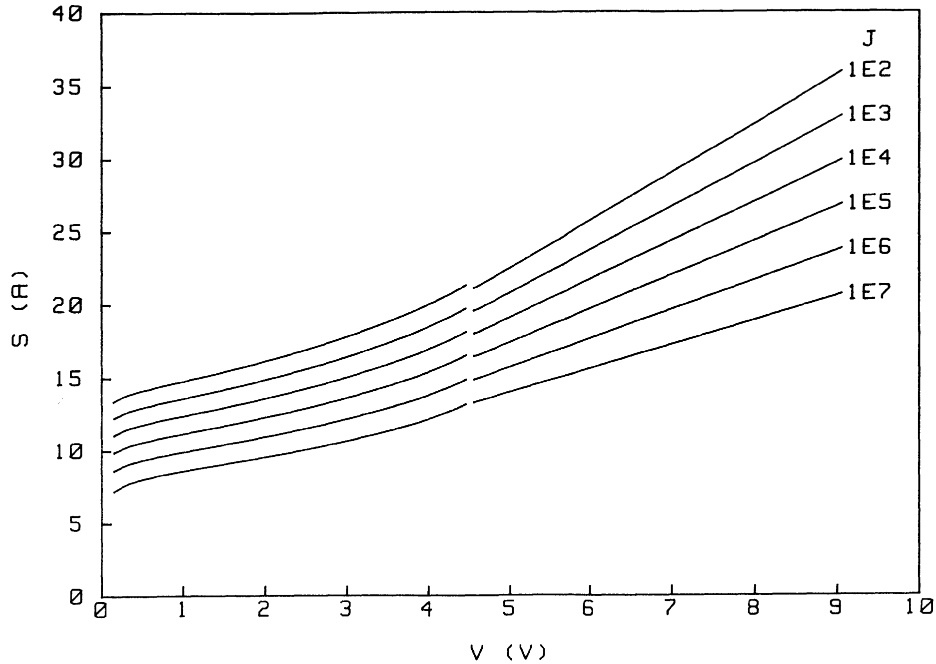

Fig. 3. Theoretical insulator thickness (s) versus potential difference (V) between metals for constant current density (J) in A/cm^2 from one-dimensional model of MIM junction, ϕ_0=4.5 eV.

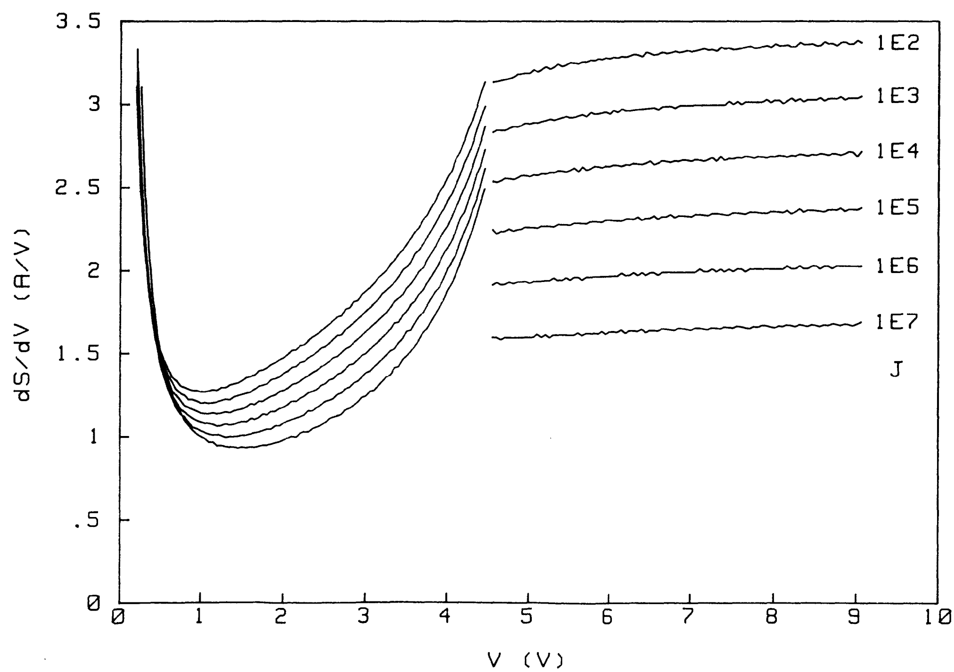

Fig. 4. Theoretical ds/dV versus V for constant J in A/cm^2 from one-dimensional model of MIM junction, ϕ_0=4.5 eV.

have been numerically inverted to obtain s(V,J) for comparison with the data of Fig. 1. For ϕ_o=4.5 eV and the insulator dielectric constant equal to unity, s is shown as a function of V for several values of J in Fig. 3. It should be noticed that (allowing for the lack of continuity resulting from the use of different equations for each regime) the slope varies for $V < \phi_o$ and is constant for $V > \phi_o$. This effect is more dramatically shown in Fig. 4, which results from the numerical differentiation of Fig. 3. Since $s=s_o + \beta V_z$, where β represents the transducer calibration factor, dV_z/dV should have the same shape as ds/dV. The similarity of the shape of dV_z/dV shown in Fig. 2 to ds/dV shown in Fig. 4 for $V < V_c$ is remarkable.

DISCUSSION

Graphs of measurements of V_z vs V for constant I show a change in slope at $V=V_c$, where $V_c \approx 2$ VDC for tip/sample combinations: W/Pt, and Pt/Au. The characteristic voltage, V_c, is polarity dependent and current independent. Similar results have been obtained from dV_z/dV vs V measurements. Comparison of these results with a one-dimensional model of an MIM junction indicates that this transition may be associated with the transition from tunneling to field emission. If this is the case, then the characteristic voltage (V_c) can be associated with the barrier height (ϕ_o). The importance of this interpretation of V_c is that the method we have developed would make possible the determination of barrier potentials in circumstances where measurements of log(I) versus s fail.

Another possible interpretation of the transition is the onset of a surface reaction and material transfer. We have some indications from STM images of the same area, before and after V is increased above V_c, that the surface is modified. Furthermore, Li, et al. [9] have reported that electroetching of Au using an STM becomes improbable for V less than about 2.7 V. It may be that the transition from tunneling to field emission and surface modification are essentially coincident.

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