Spectroscopy of electronic states of metals with a scanning tunneling microscope

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We have constructed a scanning tunneling microscope (STM) and have obtained current-voltage derivative spectra from metal surfaces. For Au(111) we have observed an electronic surface state 0.4 eV below the Fermi energy. This state has previously been observed with photoemission and oxide tunneling experiments. We have also observed strong peaks in spectra obtained from Pd(111) which we identify with surface states and effects derived from bulk energy bands. In the voltage range investigated here, tunneling takes place through the entire vacuum gap between the metallic tip of the microscope and the surface of the sample being examined. The STM spectroscopy results reported here are compared with previous experimental work and theory. These intrinsic surface states are the first which have been observed with the STM and demonstrate its unique applicability to the investigation of surface electronic structure.

Introduction

The power and potential of the scanning tunneling microscope (STM) have been demonstrated recently by Binnig and Rohrer and their colleagues [1, 2]. In the STM a metal tip is positioned a few angstroms away from a conducting surface and, with a voltage applied, the tunneling current passing through the gap is measured while scanning across the surface or sweeping the applied voltage. Feedback control of the piezoelectric positioner allows for excellent stability and resolution: less than 0.01 Å vertically and atomic distances in the surface plane. The STM has been used in the scanning mode to produce high-resolution topographic images of surfaces of semiconductors and metals and adsorbate-covered surfaces. Measurement of current versus voltage for nearly constant tip position allows for a spectroscopic mode of STM operation. Current-voltage measurements have been used to study electronic image states of the region between the tip and surface [3]. Most successful STM current-voltage measurements have been done with surfaces of single crystals prepared in high vacuum. This is in part due to the difficulty of obtaining stable STM operation free of excess noise in the presence of impurities and unstable surface layers and oxides.

We report here the results of measurements of current-voltage spectroscopy with an STM in which intrinsic surface electronic structure is observed. Our STM is operated in high vacuum and is sufficiently immune from vibrations and drift

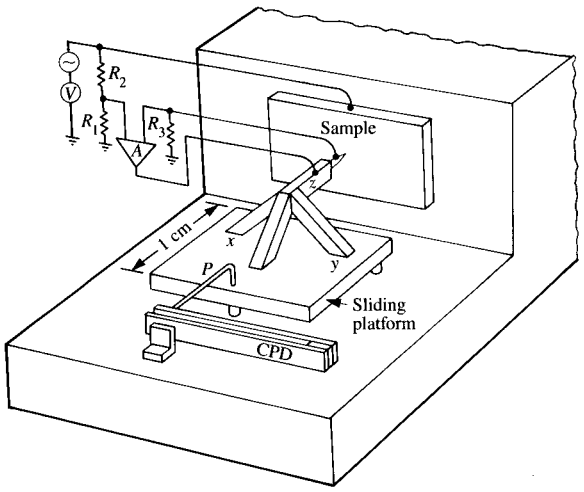

Figure 1

Sketch of the STM used in this study. The coarse positioner (CPD) is a wide-range piezoelectric actuator which can move the support table by means of the metal (gold wire) push rod (*P*). Micropositioning of the tip is accomplished with the three orthogonal *x*, *y*, and *z* piezoelectric elements. Also shown is a representation of the circuit which is used to obtain constant-resistance derivative spectra.

that current-voltage derivative spectra can be obtained at localized areas of single-crystal metal surfaces. For these measurements, the tunnel bias voltage is no more than a few volts. For this low bias, electrons tunnel directly through the vacuum space from one electrode to the other; i.e., the wave function in the gap region is a pure damped wave. This mode is clearly analogous to the classical tunneling experiments in which a metal-insulator-metal (MIM) thin-film structure is employed and tunneling takes place between the metals through the thin oxide insulator. With the STM, however, tunneling occurs through a thin vacuum gap. In contrast, STM spectroscopy experiments in which image states and other electronic reflection effects at surfaces are observed operate in the voltage range above about 5 eV [3]. For this large-voltage case, electrons tunnel through the barrier immediately in front of the emitting surface and can occupy real states in the gap between tip and metal surface.

For these experiments we chose the Au(111) surface, since this surface has been studied by a number of workers utilizing ultraviolet photoemission spectroscopy (UPS), inverse photoemission spectroscopy (IPS), and electron tunneling spectroscopy using the (MIM) structure. The bulk band structure of Au shows a forbidden gap in the (111) direction about 5 eV wide, extending from about 1.0 eV below the Fermi level to about 4 eV above the Fermi level [4]. Surface states have been reported within 1 eV of each band edge within the forbidden gap [5, 6]. These are of special interest because they have been observed in different experiments under conditions in which the Au surface has been exposed to air and other adsorbable atomic species [6]. The Au(111) single-crystal surface was studied by STM current-voltage spectroscopy methods, to be described below. A strong spectral peak was observed corresponding to a surface state at the Au(111) surface. The position of the observed peak agrees well with the energy values reported by other experiments. We also report results on Pd(111) in which new features attributable to surface states and bulk bands are seen. We believe that these results on Au and Pd surfaces are the first STM measurements of an intrinsic electronic state on single-crystal surfaces.

STM current-voltage spectroscopy measurements

The STM (shown in **Figure 1**) used in these measurements is similar to that developed by Binnig et al. [1, 2]. The sample under study is rigidly mounted to a vibration-isolated platform. A dual spring and a magnetic eddy-current damper comprise the vibration isolation. A three-axis piezoelectric manipulator supports the tunneling tip. However, this STM differs from that of Binnig et al. in that a wide-range (1-mm travel) piezoelectric bimorph actuator, rather than a piezoelectric "louse" drive, is used for coarse positioning of the high-precision tip-manipulator. Motion of the bimorph element is transmitted to the tip-manipulator itself by a gold wire push rod about one cm in length. A feedback control system, shown schematically in Figure 1, controls the tunneling voltage V_T and the tunneling current I_T so that the ratio $R_T = V_T/I_T$ remains fixed. The tip-manipulator drive voltage, set by the feedback circuit, is a measure of tip displacement. The STM is compact in order to ensure that mechanical resonance frequencies are large and to minimize thermal expansion or drift. The noise in the tip displacement due to vibration is typically 0.1 Å peak to peak. The measured drift in position over the sample surface (due to thermal expansion and other effects) is less than 0.01 Å/s for the measurements reported here. Our experiments have been performed at room temperature because the structure of interest is sufficiently strong and broad in energy that cryogenic temperatures are not required.

In classical planar MIM tunneling, electronic states of a metal electrode may be seen in the derivative current-voltage characteristic of the tunneling junction [5]. This occurs because the current is determined by the availability of electronic states within the metallic electrodes, specifically bulk states such as energy bands, quantum size effects [7], and surface states whose wave functions are confined mainly to the immediate surface of the metal. Analogous dependence of the derivative current-voltage characteristic on surface electronic structure is expected for the STM geometry.

For low voltages, the approximate behavior of the tunneling current I_T related to the tunneling voltage V_T and

the tip-to-sample separation s is given by

$$I_T \propto V_T \exp(-as\sqrt{\phi}),$$

where ϕ in eV is the average work function of the two surfaces and $a = 1.025$ Å^{-1} (eV)$^{-1/2}$ [1, 2]. This expression is useful for understanding the behavior of the tunneling current at low voltages. At higher voltage, however, the current depends nonlinearly on voltage. Further, electronic structure effects and inelastic processes may introduce rich structure into the current-voltage characteristic. However, the simple behavior described by the above expression is useful for understanding the experimental approach. Spectroscopy with the STM is complicated by the need for feedback control of tunneling current or voltage simultaneously with measurement of the current-voltage characteristic. Further, it is necessary for simplicity of spectrum interpretation that the current-voltage derivative be measured at nearly constant s. The constant-resistance feedback circuit shown in Figure 1 was used to perform this task. The derivative of the tunneling current of the STM with respect to tunneling voltage, defined as the conductance G, was measured by adding a small high-frequency modulation to the tunneling voltage and monitoring the current modulation at that frequency by a lock-in detector [5]. The modulation frequency was chosen to be well above the bandwidth of the feedback control system to ensure that variations in s were decoupled from the modulation-induced variations in V_T. The ratio R_T was compared to a reference resistance in the bridge control circuit. As V_T was swept through the spectral range, I_T was varied to hold R_T constant. We note that the current-voltage characteristic at constant s is nearly linear for the values of I_T, V_T, and s employed here. The constant-resistance method therefore introduces negligible distortion in tunneling spectra because the variation of s with V_T is slight. If use is made of the constant-tunneling-current method, R_T varies with voltage, and distortion of the spectral features can occur. The polarity of the tunneling voltage was selected for occupied ($V_T < 0$) or unoccupied ($V_T > 0$) states. The energy scale, relative to the Fermi energy of the metal sample, was read in eV directly from the V_T axis.

The tunneling tips which were used were prepared by simple mechanical machining methods [1, 2]. The spectra discussed here were obtained with W tips. However, both Au and W tips were found to give similar spectra. The tip was advanced to within close proximity of the surface without actually touching it to avoid the exchange of tip and sample material. Tunneling current was in the range of 1 to 10 nA for the measurements reported here, resulting in nominal R_T values of 100 megohms. All measurements were made at room temperature.

The STM and its vibration isolation system were enclosed in an ion-pumped vacuum chamber having a 10^{-7} Pa base pressure. Sample surfaces were prepared in a separate UHV (2×10^{-8} Pa base pressure) chamber by repeated cycles of argon ion bombardment and annealing. The single-crystal samples were characterized by LEED and Auger analysis and were initially free from contamination. Samples were exposed to air in the brief transfer between the UHV chamber and the STM chamber. Subsequent mild cleaning of the sample surfaces in the STM system was performed by operation of an argon glow discharge at 3 to 4 Pa near the negatively biased sample surface. Local area cleaning was also investigated; at high voltage (10 to 30 V), field emission current was passed between sample and tip in the presence of argon at about 5×10^{-3} Pa [8].

The constant-resistance conductance spectra were obtained by sweeping the voltage between tip and sample while recording the dc output of the lock-in detector operating at the modulation frequency. Modulation voltage amplitude was in the range of 100 to 400 mV at a frequency of 8 kHz. A complete spectrum consisted of the average of about 10 to 30 sweeps collected over a period of about 100 seconds. Individual sweeps showed the main details of the averaged spectrum. Further, averaged spectra recorded at a single location on the sample surface were completely reproducible.

The spectral measurements reported here applied to a small area of the sample surface defined by the resolution of the STM (the tip was not scanned over the surface during the spectroscopic measurements). The STM was used in the imaging mode to study the surface topography in the region which was examined by constant-resistance spectroscopy. The spectra discussed here were collected from surface regions which were flat and featureless to within a few Å over areas of about 50 Å by 50 Å surrounding the point being probed. Surface electronic structure is expected to depend sensitively on the local surface conditions. Some regions of the sample were apparently contaminated and showed excessive noise and featureless conductance spectra.

Figure 2(a) shows a typical constant-resistance STM conductance versus voltage spectrum (normalized to conductance at zero voltage) for Au(111) in the range from −1.0 to 1.0 V. Also shown **[Figure 2(b)]** is a sketch of an experimentally determined portion of the Au band structure, obtained by means of MIM tunneling measurements [5]. A prominent conductance peak is seen at −0.4 V in Figure 2(a), indicating structure below the Fermi energy. For positive V_T the conductance shows only a weak increase corresponding to the wide gap of forbidden states. The Au(111) surface possesses interesting structure, including the wide gap of forbidden states as well as a surface state near the bottom of the gap. This state has been studied by MIM tunneling [5] and by UPS [9]. MIM tunneling locates the state at −0.7 eV [5] and UPS at −0.4 to −0.5 eV, both with a full width at half maximum about 0.5 eV. The difference in energy values for these may be accounted for by the MIM experimental configuration in which the oxide layer is in

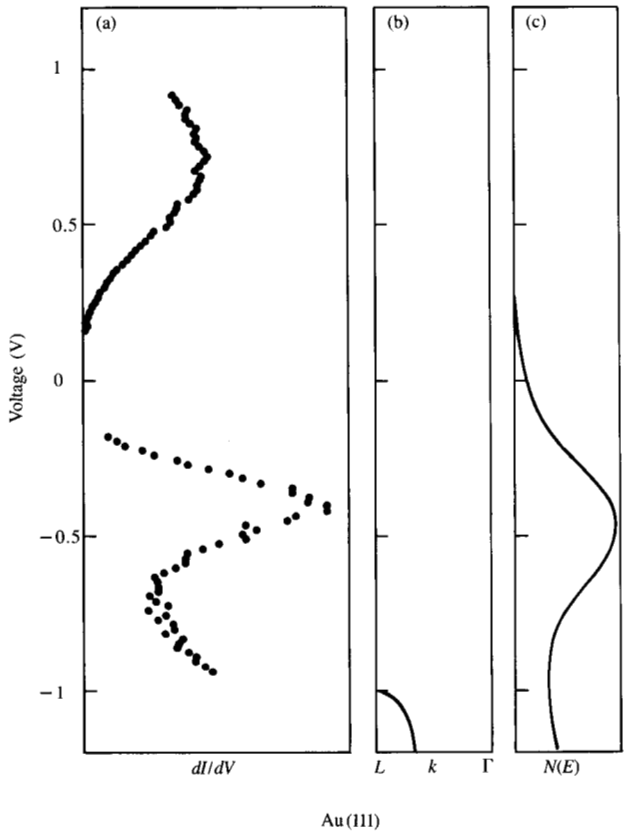

Figure 2

(a) Typical constant-resistance conductance versus voltage spectrum for Au(111) obtained at room temperature with 180-mV p-p modulation. (b) Experimentally determined portion of the Au(111) band structure; there is a wide forbidden gap extending upward from the saddle point at L at -0.9 V. The UPS results for the surface state are shown in (c). (From [9], reproduced with permission.)

close proximity to the Au surface. The Au(111) surface state appears as a strong and narrow peak in the STM constant-resistance spectrum. In the STM experiments, as the tip is scanned over the surface, there is a slight variation in position and intensity of the peak. During scanning over a contaminated area, the peak disappears completely. The broad maximum at positive voltage seen in the constant-resistance spectrum for Au(111) is at present unidentified. The measured changes in peak energy and intensity over the surface may be the basis for obtaining scanning-mode surface topograms based on the surface state. The data rate does not allow this for the present system.

The Au(100) surface was also studied by constant-resistance spectroscopy. In contrast to Au(111), the spectra for Au(100) show only smoothly varying behavior. In particular, there is no structure in the Au(100) spectrum in the voltage range where the surface state is detected at the Au(111) surface. Also, the lower edge of the bulk energy gap in the [100] direction is located about 1 eV above the Fermi level [4]. The lack of spectral structure over a wide voltage range is consistent with the presence of the wide conduction band below the energy gap. These observations also indicate that the measured spectra display features derived from the electronic structure of the sample surface and not from the tip.

Figure 3(a) shows a typical constant-resistance conductance versus voltage spectrum for Pd(111), where conductance (normalized to the conductance at zero voltage) is plotted over the range from -2.5 to 2.5 V. Also shown **[Figure 3(b)]** is a sketch of an experimentally determined portion [10] of the Pd band structure [11]. We observe structure for both positive and negative V_T. The large conductance peak at -1.4 V in Figure 3(a) occurs at the position of the d-band edge. Another prominent conductance peak at 1.0 V corresponds to the location of the saddle point at L in the band structure. These features do

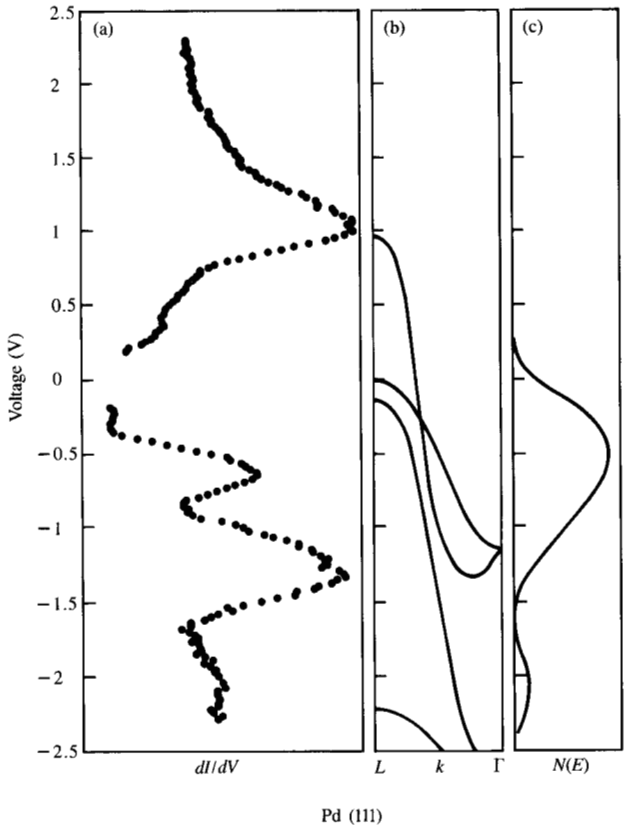

Figure 3

(a) Typical constant-resistance conductance versus voltage spectrum for Pd(111) obtained at room temperature with 200-mV p-p modulation. (b) Experimentally determined portion of the Pd(111) band structure (from [10], reproduced with permission). The s-d bands are prominent in this energy range, and there is a forbidden gap extending above the saddle point above 0.94 V. Surface-state peaks derived from UPS measurements are shown in (c) (from [12], reproduced with permission).

not vary considerably in intensity with the position of the tip over the surface. However, those near −0.6 V and near −2.1 V appear with variable intensity. Surface states have been identified on Pd(111) by UPS methods [12] and also have been studied theoretically [13]. **Figure 3(c)** shows the UPS results; good agreement is indicated between the position of the peaks and our data. The peak at 1.0 V in Figure 3(a) is accompanied by a second peak, or shoulder, at about 0.4 V. This feature also shows variable intensity with tip position; further study would be needed to identify this as a surface state.

Peak intensities are found to be sufficient to obtain good spectra within a few minutes, and reproducibility is not a problem when the STM is sufficiently free from drift. For example, the Au(111) surface-state peak appears as a 20% conductance change with about a 0.25-V linewidth. The electrical noise level is about two orders of magnitude larger than is to be expected for the intrinsic shot noise limit. We speculate that some of the excess noise is due to electrical instabilities in the high-field and high-current tunneling region, possibly due to impurities and oxides. The noise contribution due to vibration of the STM system must also be considered.

The Au(111) surface state in particular was expected to be observable under the conditions of our experiment, since Au is a relatively inert metal and past experience has shown that the surface state survives exposure to air and other external influences [5, 6]. Observation of the Au(111) surface with LEED immediately after initial cleaning and then again after a few minutes' exposure to air showed only a slight deterioration in the diffraction pattern. Spectra for the Pd(111) surface show several peaks clearly correlated with d-bands, the L saddle point, and surface-state features as measured by UPS. Partial cleaning by exposure to the mild gas discharge is an important aid in obtaining these results for the Pd(111) surface, but more experiments are necessary to reach full understanding of the detailed influence of surface conditions on the measured spectra.

Discussion

A number of comparisons may be made between the use of STM spectroscopy and other methods for measuring surface electronic structure. The STM can yield information for both filled and unfilled states above and below the Fermi energy. Those states are favored which have appreciable amplitude close to the surface, i.e., within a few Å of the surface. Tunneling electrons must be able to couple to the states of interest immediately outside the surface by the overlap of the wave functions of the electrons' states in the two electrodes. This is in contrast to studies carried out using UPS and IPS, where the mean free path for the electrons can be 50 Å or more. In addition, the need for a light source and monochromator is avoided when the STM is used. Compared to the MIM oxide-tunneling method of studying electronic states, the STM method is not limited by the need to produce high-quality oriented thin films of the metal to be studied. Also, perturbation of the surface states from the presence of an oxide tunneling layer is absent from the STM method. Thus, it should be possible to use the STM for study of the electronic levels of a large variety of metals. While the STM can be used to detect only electronic states with appreciable amplitude at the surface, this does not rule out bulk band observations, because electron reflection experiments have shown that bulk levels can be observed by surface-sensitive techniques [14]. Also, the STM method is not affected by electrical breakdown problems which restrict oxide tunneling experiments to lower voltage ranges and are coincidentally a source of noise and background problems. Because of the small area of the surface region probed by the STM and the ability of the STM "junction" to withstand higher current densities than MIM junctions, operation is possible at an electrode separation approximately one half of the oxide thickness used in the MIM method. Both theory and experiment [15] show that the background conductance variation over several volts is much less for this thickness range, a considerable practical advantage.

The resolution of the STM, as operated in the spectroscopic mode, involves several factors. First, there will be a thermal limit determined by the width of the edge of the Fermi distribution of the electrons in metal electrodes. This amounts to approximately 2 kT, about 50 meV at room temperature, and is small enough to allow resolution of most features of interest on metals. For an inelastic process the limit should be 5.4 kT [16], or about 150 meV at room temperature, which should be adequate for many electronic excitations. This resolution would not be sufficient, however, for other inelastic processes such as excitation of vibrational modes of adsorbed molecules which have a width of about 5 meV. However, the option of cooling the STM is available, although this is not routine at present. Second, modulation amplitude of sufficient size is required to observe a derivative spectrum, a consideration closely related to the time needed to acquire a reasonably noise-free spectrum. Typically, for the intensities and current levels currently employed, a modulation of at least 0.1 V is required to obtain a spectrum in a few minutes. Third, electronic states in metals are lifetime-broadened by an amount which is energy dependent but can be several tenths of an eV or more in width for energies of one eV and greater [17]. Finally, the narrow region of tunneling in the STM geometry will result in a broadening caused by "wavevector smearing" of these electronic states. No accurate model calculation of how much this will affect resolution is available at present. The results reported here indicate that there is reasonable agreement between available signal levels and the observed peak intensities.

These experiments demonstrate the usefulness of the STM in conjunction with first-derivative current-voltage

spectroscopy for studying the electronic states of a metal surface. They show that it is possible to obtain valuable information about surface and bulk electronic states, even for surfaces which may have a degree of contamination. Thus the STM can in some applications fill the role of conventional techniques and in others provide important complementary information. The fundamentally important questions concerning spatial variation of electronic structure over a surface may be addressed by use of STM spectroscopy in the surface-scanning mode, so that a particular feature such as a surface state can be mapped over an extended region.

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