Tunneling spectroscopy applied to PbS (001) surfaces: Fresh surfaces, oxidation, and sorption of aqueous Au

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ABSTRACT

Electron tunneling spectroscopy (ETS) makes possible the study of electronic structures of conductive mineral surfaces and can be applied under ambient or in-situ conditions rather than in a vacuum. We use ETS to study fresh, oxidized, and aqueous-Au-treated PbS (001) surfaces in order to demonstrate the strengths and limitations of the technique in the context of a geochemical application. Experimental tunneling spectra are in qualitative agreement with tunneling theory. Spectra for Au, fresh PbS, and oxidized PbS are different (primarily because of work function differences) and can be used to distinguish between, for example, Au and PbS when they are present on one surface. ETS is thus useful as a compositional probe with high spatial resolution. Spectra for fresh PbS show a small peak at about +250 mV that corresponds to conduction band states with mixed Pb and S character. Both the ETS spectra and STM images suggest that these states are lost upon oxidation. Au precipitated on PbS from aqueous AuCl₄⁻ solutions as isolated islands looks identical to metallic Au in ETS.

INTRODUCTION

For natural Earth surface systems, it may be argued that virtually all chemical processes are modulated or controlled by reactions involving mineral surfaces (Stumm, 1992). Understanding mechanisms of mineral surface reactions depends on a knowledge of surface electronic structures because, fundamentally, interactions between a solid surface and gases, H₂O, or aqueous solutes are interactions between the electronic structures of the adsorbates and of the surface.

Surface electronic structure is commonly studied by photoelectron spectroscopy (PES). X-ray PES (XPS) is often used to study surface compositions (e.g., surface leaching during dissolution) using relative intensities of core-level photoelectron peaks (e.g., Berner and Holdren, 1979; Hellmann et al., 1990). XPS peaks may also have structure that can be related to specific surface species (e.g., Stipp and Hochella, 1991). UV-PES (UPS) is used to examine valence-band electronic structures related to bonding. The valence band is also accessible to electron tunneling spectroscopy (ETS). Some forms of ETS have been in use for several decades, but the technique described here is based on scanning tunneling microscopy (STM), which, along with scanning force microscopy (SFM), is being used in geosciences primarily for imaging of microtopography and surface atomic and molecular structure. Here, we apply ETS to PbS (galena) surfaces and to changes in surface electronic structure associated with oxidation and sorption of aqueous Au. This system was chosen because it is an experimentally convenient analogue for natural systems for Au scavenging and concentration.

PREVIOUS WORK

ETS has been used in many vacuum-based studies of metal and semiconductor surfaces; Stroscio et al. (1986), Feenstra et al. (1987a, 1987b), and Avouris (1990) provided good examples. For minerals, Gilbert and Kennedy (1989) studied tunneling hysteresis on Fe₂O₃ and TiO₂ surfaces using ambient ETS, and Sakamaki et al. (1990) applied ambient ETS to TiO₂ to study surface density of states (DOS). Fan and Bard (1991) studied pyrite (100) surface DOS; their results are in agreement with those of Eggleston and Hochella (1992) based on UPS and STM. Eggleston and Hochella (1991) used ETS to distinguish between Au and PbS on PbS (100) surfaces that had been exposed to aqueous gold chloride; this paper presents the basis of, and an expansion upon, these earlier results.

THEORY

Electron tunneling theory, as applied to STM and ETS, is well summarized in Stroscio et al. (1986), Feenstra et al. (1987a), Avouris (1990), and references therein. For a tip-surface tunneling junction, the tunneling current ($I_t$)
can be written

$$I_t = \int_{E_{F_0}}^{E_{F_1} + eV_0} \rho_s(E, r) \rho_r(-E - eV_0, r) \exp[-s\sqrt{(2m/h^2)(\Phi - eV_0/2)}] \, dE$$

where $V_0$ is the bias voltage across the junction, $E_F$ is the Fermi level, $\rho_s$ and $\rho_r$ are sample and tip density of (electron) states (DOS) functions at the location of the tip $r$ and energy $E = eV_0$, $\Phi$ is the barrier height [$\Phi = (\phi_s + \phi_r)/2$, where $\phi_r$ and $\phi_s$ are the work functions of tip and sample, respectively], $m$ is the electron rest mass, $\hbar$ is Planck’s constant divided by $2\pi$, and $s$ is the tip-sample separation distance. The exponential term expresses the conductance of the junction.

Differentiation of Equation 1 and normalization to Ohm's Law conductance ($I/V$) gives a function $(dI/dV)/(I/V)$ proportional to the convolved DOS of the tip and sample (Stroscio et al., 1986) in the limit of low $V_0$. A plot of $(dI_t/dV)/(dI_t/dV_0)$ vs. $V_0$ should give peaks at energies corresponding to high DOS. However, because the conductance of the tunnel junction does not follow Ohm's Law but is a function of $V_0$, DOS information is superimposed on a smoothly varying background whose characteristics depend on $\Phi$ and $s$.

To show the dependence of the background on $\Phi$ and $s$, we calculated $I_t$ vs. $V_0$ and $(d \ln I_t)/(d \ln V_0)$ vs. $V_0$ curves for various $s$ and $\Phi$ values using the equation $I_t = AV_0 \exp(-sB\sqrt{\Phi - eV_0/2})$, a simplified version of Equation 1 used by Binnig et al. (1982) and Binnig and Rohrer (1986) in describing their original STM and ETS work. The constant $A$ ($A = 10^{-15}$/Ohm in our case) was chosen to give realistic currents for a given $V_0$, and $B = (2m/h^2)^{1/4} = 1.025 \, eV^{-1/4}/\AA$.

Figure 1 shows calculated $I_t$ vs. $V_0$ curves, and Figure 2 shows the corresponding $(d \ln I_t)/(d \ln V_0)$ vs. $V_0$ curves. Figure 1A shows $I_t$ vs. $V_0$ for different tip-sample separations, $s$; $I_t$ is very sensitive to $s$, as expected from theory. The corresponding $(d \ln I_t)/(d \ln V_0)$ curves (Figure 2A) are not very sensitive to $s$, however, unless $s$ varies by $\pm 2 \, \AA$. Figure 1B shows $I_t$ vs. $V_0$ for different barrier heights; Figure 2B shows that the slope of $(d \ln I_t)/(d \ln V_0)$ vs. $V_0$ is very sensitive to factor of two changes in $\Phi$.

Figures 1 and 2 thus show the form of the smoothly varying background in the absence of varying DOS structure. For samples exhibiting DOS structure, peaks in $(d \ln I_t)/(d \ln V_0)$ or $(dI_t/dV_0)/(I_t/V_0)$ spectra are found to correspond to bands of high DOS; excellent examples of this for UHV conditions may be found in Stroscio et al. (1986) and Avouris (1990).
Because our STM and ETS were performed in ambient conditions, we must consider differences between ambient and vacuum tunneling. First, under ambient conditions, the tip-sample gap contains positive charge (the intervening atomic nuclei) that may alter the shape and height of the tunneling barrier \( \Phi \) (Simmons, 1963). Generally, \( \Phi \) is lower under ambient conditions that in UHV. Second, chemisorbates alter the surface electronic structure.

These problems present serious complications for ambient ETS, but do not preclude its usefulness in well-defined applications. In practice, only resonant processes (those whose frequency or time scale is similar to that of data measurement) are likely to hamper data collection seriously. For example, if the tip is slightly oxidized, the tip-sample gap contains an oxide layer, but the dielectric properties of the oxide may be treated as constant unless the oxide layer grows during use of the tip. A more serious problem is that adsorbates diffuse and may exchange onto and off of surface sites at high frequency. A variety of sorbate-induced electronic structures may occur and recur locally; peaks from particular structures are likely to be averaged out, leaving only a featureless background. However, if a particular structure dominates the time average and the tip is also temporally stable, specific peaks may be observed. The fact that STM imaging is possible under ambient conditions supports this conclusion; when imaging is successful, we are probing states that should also be spectroscopically observable.

**EXPERIMENTAL**

STM and ETS were performed using a Digital Instruments NanoScope II. W tips were made by electrochemical etching in 1 M solution of KOH. Instrument conditions are reported in the figure captions. Tunneling spectra were obtained using a cycle in which the feedback loop ran for 300 \( \mu \text{s} \) at a given \( V_T \) and setpoint \( I_* \) (in units of nanoamps), which fixes \( s \); the higher \( d_{22} \), the lower \( s \). The data in Figures 3 and 4 suggest that ETS may be constrained systems. The reasons for the differences in estimation is less than the \( V_{s} \) desired by an amount that depends on \( I_* \) (an Ohmic effect of the \( I_* \) measurement system, approximately 1 mV/nA). The effects are sufficiently small so that no important consequences were observed.

STM images and ETS spectra were obtained for several materials, all at room temperature. Au films were grown on cleaved muscovite at \( 10^{-7} \) torr and 500 °C (see Lang et al., 1989). PbS crystals were cleaved under polyphenyl ether, a nonpolar oil (in order to exclude air; see Eggleston and Hochella, 1990 or 1991); these surfaces give relatively stable images and spectra. PbS surfaces that had been in \( \text{H}_2\text{O} \) for 1 min or in air for five months were also examined under oil in order to maintain comparability of the tunneling medium and to prevent further reaction with air. XPS studies of PbS oxidation (e.g., Buckley and Woods, 1984) show that after five months of air exposure PbS surfaces exhibit evidence of Pb-O bonding and sulfate-like species; we designate this surface “oxidized PbS.” Finally, fresh PbS surfaces were exposed to 1.3 ppm \( \text{KAuCl}_4 \), 1.1 M NaCl solution at pH = 3.2 (adjusted with HCl) at room temperature for periods from 1 min to 60 h.

**RESULTS AND DISCUSSION**

Figure 3 shows \( I_* \) vs. \( V_T \) spectra for (A) Au foil, (B) fresh PbS, and (C) oxidized PbS, at several tip-sample separations, \( s \), in each case; the exact value of \( s \) is unknown, but the \( s \) variation is probably <2 or 3 Å. The data in Figure 3 are labeled with the feedback \( I_* \) (in units of nanoamps), which fixes \( I_* \); the higher \( I_* \), the lower \( s \). The data are nonlinear with increasing \( V_T \), as expected for tunneling conduction (Fig. 1).

The spectra for different materials have different shapes; note, for example, the curves marked 1 nA in each case. The spectra for Au foil are easily distinguished from those for both fresh and oxidized PbS, and at least the 1-nA curves are distinct for fresh and oxidized PbS. Because the feedback loop ran at \( +200 \) mV and at the \( I_* \) marked on each curve, the data in Figure 3 should intersect these \( I_* \) values at \( +200 \) mV. That is not always the case, probably because of drift in \( s \) during data measurement. Figure 3C shows variability in \( I_* \) vs. \( V_T \) curves for a sequence of ten spectra (labeled 1 nA). Uncertainties were a small fraction of 1 nA at low \( V_T \) and ±8 nA at high \( V_T \).

The differences among the \( I_* \) vs. \( V_T \) spectra for the different materials were also apparent in the \( (\text{d} \ln I_*)/(\text{d} \ln V_T) \) spectrum in Figure 3 (i.e., the greater \( d_{22} \), the steeper the \( (\text{d} \ln I_*)/(\text{d} \ln V_T) \) function in Figure 4, as expected (e.g., see Figs. 1B and 2B). For example, \( d_{22} \) for the data for Au foil in Figure 3A is nearly constant, so \( d_{22} \) should also be nearly constant, as in Figure 4A. The data in Figures 3 and 4 suggest that ETS may be used as a high spatial-resolution compositional identification or differentiation tool, at least for compositionally constrained systems.
As discussed above, variation in the slope of \( \frac{d \ln I_t}{d \ln V_o} \) spectra may arise from (1) differences in tip-sample separation, \( s \), (2) different barrier heights, and (3) DOS variations. We collected spectra for Au and oxidized PbS for different tip-sample separations and found little dependence of the slope of the \( \frac{d \ln I_t}{d \ln V_o} \) curves on \( s \), in agreement with Figure 2A. The work function of Au metal \( (\phi_{Au}) \) is about 5.2 eV (Zangwill, 1988), and the work function of PbS \( (\phi_{PbS}) \) is about 3.7 eV (Evans and Raftery, 1982). The work function of oxidized PbS is not well defined but is almost certainly less than for fresh surfaces. According to the calculations (Fig. 2B), these differences should cause the slope of the \( \frac{d \ln I_t}{d \ln V_o} \) vs. \( V_o \) curves to be arranged in the order PbS\textsubscript{oxidized} > PbS\textsubscript{fresh} > Au, in agreement with observation (Fig. 4). Therefore, the different slopes are probably due at least partly, and perhaps mostly, to work function differences among the materials.

The data in Figure 4 seem consistent with the expectation for the DOS of a metal relative to a semiconductor; a metal should have a relatively even DOS across \( E_F \), whereas a semiconductor such as PbS, with a surface band gap of 0.1–0.4 eV, should show increasing DOS away from \( E_F \). However, if the DOS were the only contribution, the \( \frac{d \ln I_t}{d \ln V_o} \) function should have a more abrupt increase in slope as \( E_F \) exits the band gap and valence or conduction band states begin to contribute to the tunneling current. Figure 4, with the exception of Figure 4B, instead shows a steady increase in \( \frac{d \ln I_t}{d \ln V_o} \) with \( V_o \), a form more consistent with the form of curves in the absence of DOS structure (e.g., see Fig. 2). The exception, Figure 4B, is discussed below in regard to PbS oxidation.

**PbS oxidation**

Figure 4B shows a broad peak in the \( \frac{d \ln I_t}{d \ln V_o} \) function at about +250 mV. Although we did not expect DOS peaks to be observable in ambient (rather than vacuum) conditions, the reproducibility of this peak (in sev-
Fig. 5. STM image of a PbS surface taken after a 1-min exposure to deionized H₂O, at +200 mV and 1 nA in the constant height mode. Contrast is due to variation in \( I_r \). This image was taken only a few nanometers from the area imaged in Eggleston and Hochella (1991). According to the interpretation of Eggleston and Hochella (1990), the bright sites correspond to S and the less bright sites correspond to Pb. A unit cell with corners on S sites is marked. The measured edge length is 6 ± 0.2 Å, within error of the expected unit-cell edge length of 5.97 Å. The fresh galena surface structure is seen in most of the image (compare with Eggleston and Hochella, 1990); in addition, five apparent vacancies (probably oxidized sites) are evident. The image is low-pass filtered (cutoff: 0.4 Å) to remove high-frequency noise. Drift causes slight distortion of the nominally square unit cell.

General hundred successive spectra) suggests that it is real. Figure 5 is an STM image taken at similar \( V_s (+200 \text{ mV}) \). We interpret the peak in Figure 4B as the spectroscopic expression of the same band of states imaged in Figure 5 (excluding the apparent vacancies), i.e., a band of conduction-band states with mixed Pb and S character.

The DOS spectra for oxidized PbS do not show a discernible peak at +250 mV and were quite variable. Eggleston and Hochella (1991) showed that the apparent vacancies in images similar to Figure 5 probably correspond to oxidized S sites. These sites are probably not vacant but rather are sites of reduced \( I_r \) resulting from shifts in electronic structure related to oxidation. It seems reasonable to suggest that we do not observe the +250 mV DOS peaks in \( \frac{d \ln I_r}{d \ln V_o} \) spectra of oxidized PbS for the same reason that we see vacancies in the STM images of incipiently oxidized PbS surfaces; i.e., oxidation of surface S sites reduces the local DOS at this energy. It can be argued that we are observing, on the atomic scale, the beginnings of the process by which Pb-O and S-O bonding widens the band gap by removing state density near \( E_o \). However, it must be remembered that ETS spectra and STM images depend on stable tip configurations and other variables, and our inability to observe an ETS peak on oxidized surfaces may merely reflect unstable tips or the averaging out of peaks from a variety of individually short-lived structures. The important result is that the PbS conduction band states within 200–250 mV of \( E_o \) can be observed in both ETS and STM under ambient conditions, given stable tip, tunneling medium, and drift conditions.

Sorbed Au

Reductive sorption of aqueous Au complexes to sulfides is thought to be important in the formation of certain Au deposits (Seward, 1973; Hyland and Bancroft, 1989; Bakken et al., 1989). The Au-PbS system is ideal for the application of ETS and STM because both the substrate and adsorbate are conductive. Eggleston and Hochella (1991) used ETS to distinguish between Au and PbS on surfaces containing both materials; here, we give further examples of ETS application to the Au-PbS system and compare it with similar systems studied in UHV.

Figure 6A shows a \( \frac{d \ln I_r}{d \ln V_o} \) spectrum for a PbS surface that had been exposed to the Au (III) chloride solution (see experimental section) for 60 h. The surface was completely covered by Au after this treatment and appeared visibly gilded. The Au precipitated on the PbS surface is spectroscopically indistinguishable from the Au foil (see Fig. 4A). Figure 6B shows a \( \frac{d \ln I_r}{d \ln V_o} \) spectrum taken atop an island grown on a PbS surface after 1.5 h of exposure to the Au solution (STM images in Eggleston and Hochella, 1991, show that the Au exists on the surface as discrete islands up to 1000 Å in length). The spectrum appears identical to that of Au foil and of Au on PbS after longer exposure times. In contrast, Figure 6C shows a \( \frac{d \ln I_r}{d \ln V_o} \) spectrum taken on the same sample as in Figure 6B, but on an area between the
islands; in this case, the spectrum appears similar to those for oxidized galena (see Fig. 4C).

Another example is given in Figure 7. The tip was positioned over an Au island and a sequence of spectra collected. Although the spectra are quite noisy, the first two (Fig. 7A, 7B) are typical of Au. During several minutes the tip was allowed to drift, and when the tip had drifted entirely off of the Au island, oxidized PbS-type spectra were obtained (Fig. 7C, 7D).

Despite the difficulties of ambient ETS, our results are remarkably similar to those for comparable systems studied in UHV. The use of ETS to identify small Au islands on a semiconductor (Si) surface on the basis of work function differences was the first spectroscopic application of STM (Binnig et al., 1982; Binnig and Rohrer, 1987). Another comparable study is summarized in Figure 8, which shows spatially averaged ETS spectra for different coverages of Au on a GaAs(110) surface in UHV (Feenstra, 1989). Because Au forms clusters on the GaAs(110) surface, the data for what is ideally called one monolayer coverage (ML) consist of average spectra for both Au and GaAs (although the author suggests that this is not the case, his STM images show some GaAs between the Au clusters, and, given that what is imageable is also observable spectroscopically, the spectra should contain a contribution from GaAs). At higher coverages (e.g., 5 ML), the GaAs is completely covered by Au. Although Feenstra’s data cover a wider voltage range than ours, his spectra are very similar to ours for Au on PbS in the range sample in our study, -750 to +750 mV; the spectrum for Au is flat, whereas that for GaAs rises away from $E_F$.

This is a clear demonstration that differences between Au metal and a semiconductor, particularly work function differences (expressed in the tunneling barrier), are apparent in both UHV and ambient conditions.

**Concluding Remarks**

STM images of topographically complicated surfaces often contain little clue as to the compositional identity of features in the images. We have demonstrated that ETS can be used to identify such features in STM images, if the compositional possibilities are limited. The ETS differences among materials in this study are probably mostly due to work function differences. With stable tips,
we observed a DOS peak in ETS spectra taken in ambient
conditions of a fresh PbS surface; the peak corresponds
to PbS conduction band states. Spectra of Au precipitated
on PbS from aqueous Au(III) solutions confirm that the
Au is metallic. This has been demonstrated using XPS
(e.g., Hyland and Bancroft, 1989), but it shows that ETS
is applicable as an in-situ or ambient-conditions probe
with ultrahigh spatial resolution that can, in some cases,
be used instead of a UHV technique.

With the minimization of drift and maximization of
data collection speed, chemical characterization of con-
ducting or semiconducting mineral surfaces may also be
performed in situ and ultimately with near-atomic reso-
lation. ETS is thus a promising tool for the study of sur-
face electronic structure under ambient (rather than UHV)
conditions, with applications in mineralogical and geo-
chemical research.

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