Chemical imaging of insulators by STM

Department of Physics, University of Wisconsin Madison, 1150 University Avenue, Madison, Wisconsin 53706-1390
(Received 1 December 1998)

Nanostructures of CaF$_2$ and CaF$_1$ on Si(111) are used to demonstrate a chemical imaging method for insulators. Chemical sensitivity is achieved in scanning tunneling microscopy via a sharp drop of the tunneling current for bias voltages below the conduction-band minimum. This imaging method has a spatial resolution of better than 1 nm and distinguishes different oxidation states. A resonance is found in $(dI/dV)/(dV/dI)$ at the conduction-band minimum that enables an accurate determination of its position. We observe enhancements by up to a factor of 5 and absolute values in the range of 20–50, compared to 1 for an Ohmic metal. A minimal model is given, explaining the resonance in terms of tunneling across a thin insulator film. These methods should be generally applicable for determining local Schottky barriers and band offsets in nanostructures and for chemically selective imaging of insulators and wide-gap semiconductors. [S0163-1829(99)07215-X]

I. CHEMICAL IMAGING IN SCANNING TUNNELING MICROSCOPY (STM)

Chemical imaging has been a long-standing goal in high-resolution microscopy. The finer the resolution becomes, the more difficult it is to obtain chemical information. Approaching the atomic resolution limit, there are only a few atoms within the resolution volume that can be sampled. In transmission electron microscopy, the energy loss spectrum has become a tool for identifying different chemical species. In STM such a general method has not been found yet, although a variety of effects can lead to chemical contrast in specific cases. For metals, two techniques have been employed utilizing the work function as identifier. One is based on resonant tunneling into image states, the other on a measurement of the tunneling barrier. On semiconductor surfaces, specific broken bond orbitals are distinguishable in the gap but their identity needs to be analyzed in detail before a chemical assignment can be made. Differences in the electron/hole confinement can provide contrast in cross-sectional STM. A general method that works for insulators has been lacking so far. It is desirable to have a complete set of tools identifying all classes of materials, particularly in the rapidly growing field of self-assembled nanostructures. In future nanodevices, insulators will necessarily play a crucial role in electrically separating wires or dots. In addition, the band structure of semiconductors and insulators is modified by atomic-scale effects including the electron/hole confinement that can provide contrast in cross-sectional STM. A method that works for insulators has been lacking so far. It is desirable to have a complete set of tools identifying all classes of materials, particularly in the rapidly growing field of self-assembled nanostructures. In future nanodevices, insulators will necessarily play a crucial role in electrically separating wires or dots. In addition, the band structure of semiconductors and insulators is modified by atomic-scale effects including the electron/hole confinement.

We have achieved chemical selectivity between different insulators and even different oxidation states of the same element. Essentially, we take advantage of a large jump in the conductivity at the CBM of insulators. The chemical identifier is the energy of the CBM relative to the Fermi level $E_F$. It represents the analog to the work function that has been used to identify metals. We are able to discriminate between Si, CaF$_2$, and CaF$_1$ in nanowire and island structures grown epitaxially on stepped Si(111). Height differences between terraces and across individual terraces are eliminated. The local conduction-band minima are determined with a spatial resolution of 1 nm making the spectroscopic sampling of individual nanostructures a reality.

II. CaF$_2$/Si(111) SYSTEM

CaF$_2$ on Si(111) has been selected as a prototype of a well-defined, epitaxial insulator structure. Previous work has established two types of atomically sharp interfaces, one F terminated, the other Ca terminated. The F-terminated interface contains a full F-Ca-F triple layer that is characteristic of the CaF$_2$(111) structure. The F-layer adjacent to Si desorbs at ~700 °C and a Si-Ca-F interface is formed, where the second valence of Ca is taken up by the broken surface bond of Si(111). This CaF$_1$ layer has an optical band gap of only 2.4 eV, as opposed to the 12-eV gap of CaF$_2$. When going from a flat Si(111) surface to a nanostructured topography at vicinal Si(111) surfaces, complex growth modes start to appear, such as islands attached to step edges, bunched steps, stripes, and double-layer structures. Determining the local chemistry in this case requires an analysis tool that operates on the nanometer scale and ignores these topographical variations.

The calcium fluoride samples in this study comprise the Ca-terminated interface as well as the F-terminated interface. The first type of the interface was obtained on a Si(111) surface miscut by 1.1° towards the [1 1 2] azimuth, with 1.5 triple layers of CaF$_2$ deposited at 610 °C and postannealed at 830 °C for 1 min and at 700 °C for 4 min. The sample with the F-terminated interface was grown on a Si(111) surface miscut by 1.3° towards the opposite azimuth, i.e., [1 1 2], with 1 of a triple layer of CaF$_2$ deposited at 650 °C.

III. CHEMICAL IMAGING BY SPECTROSCOPIC STM

Before getting into the details of chemically selective tunneling, it is useful to recall how tunneling into insulators becomes possible. As shown previously, electrons are able to tunnel from the tip into the conduction-band minimum of an insulator when applying a sufficiently large, posi-
tive sample bias (Fig. 1, left). Electrons injected into the conduction-band pass through the insulator and prevent it from charging, as long as the film is thinner than the mean free path at the CBM (typically in the 10-nm range). In the specific cases considered here, the CBM lies about 3–5 eV above \( E_F \) for CaF\(_2\) and 1.4–1.8 eV above \( E_F \) for CaF\(_1\).\(^{21}\) In CaF\(_2\), a stable tunneling current is obtained at a sample bias voltage of \( \approx 4 \) V (typically 0.3–1.0 nA). Attempts to stabilize the tunneling current at a bias voltage below the CBM causes the tip to approach the underlying Si and to pick up insulating CaF\(_2\) debris. The voltage drop across the CaF\(_2\) layer is drawn differently for the two cases in Fig. 1. It is small when tunneling above the conduction-band minimum (Fig. 1, left), where CaF\(_2\) is conducting. For tunneling into the gap (Fig. 1, right), we are almost in the electrostatic limit. Part of the applied voltage drops in the insulator. It is determined by the electric field of the tip, reduced by the dielectric constant \( \epsilon = 7 \) of CaF\(_2\).

For chemical imaging the feedback loop is turned off and current-voltage curves are acquired at each image point. Figure 2 shows such \( I(V) \) data, averaged over atomically-flat areas 3 × 3 nm\(^2\) in size. Typically, \( I(V) \) curves are taken at 400 image points in order to check for spatial homogeneity. In addition, the tip height is varied by changing the sample bias (different types of lines in Fig. 2). For each spectrum, the tip is stabilized near its highest voltage point, thereby avoiding overflow and underflow of the current. An approxi-
mate density of states can be derived\(^{22–24}\) by calculating the \( (dI/dV) / (dI/V) \) data points. The conduction-band edges correspond to onsets in the \( (dI/dV) / (dI/V) \) curves that become well-defined peaks in the normalized spectra. The onset behavior is reminiscent of data from semiconductors,\(^{6,7,24}\) the peaks have not been observed be-
fore. This feature will be discussed in more detail in Sec. IV.

\[ \text{FIG. 1. Schematic of chemically-selective tunneling into insula-
 tor films, using CaF}_2\) on Si(111) as an example: left, stabilizing the tip at a sample bias that allows tunneling of electrons from the tip into the CBM of the insulator; right, acquiring a current image at a bias where electrons from the tip enter the gap of the insulator. The insulator appears dark.\]

\[ \text{FIG. 2. Tunneling spectra of CaF}_2\) /Si(111) and CaF\(_1\)/CaF\(_2\)/Si(111). Two sharp onsets in the \( (dI/dV) / (dI/V) \) spectra char-
acterize the respective conduction-band minima and provide chemi-

cal selectivity. The normalized \( (dI/dV) / (dI/V) \) spectra exhibit reso-
nances at the CBM. Different line types represent different tip

\[ \text{expected CBM of 1.4–1.8 eV for a CaF}_1\) layer but consistent with the CBM of the underlying Si along the [111] tunneling direction.\]

\[ \text{For a chemical image it is not necessary to acquire a complete I(V) curve at each pixel. A single voltage point per chemi-

cal species is enough, as demonstrated in Figs. 3 and 4. In Fig. 4, CaF}_2\) is distinguished from Si, in Fig. 3 from CaF\(_1\). In both cases, the tip is stabilized at a bias corresponding to the CBM of CaF\(_2\). The chemical image is acquired at a 0.5–2 eV lower bias. A larger bias reduction provides better chemical contrast at the expense of a lower absolute current.}\]

\[ \text{In such chemical images the height difference between Si steps is eliminated. In fact, the chemical contrast is opposite to the topographic contrast in Fig. 3: CaF}_2\) stripes appear bright in the topographic image (top) but dark in the chemi-
cal images (bottom). The chemical composition of the sur-

\[ \text{face determines the contrast exclusively, with CaF}_2\) being dar-
est, Si brightest, and CaF\(_1\) in between.}\]

\[ \text{The spatial resolution better than 1 nm, as demonstrated in Fig. 5 by a line scan across a chemical image of a small CaF}_2\) island on Si(111). It was grown at 550 °C, where the diffusion length is only a few nm. Taking the sharpness of the edges as criterion we find a spatial resolution of better than 1 nm. That makes it possible to determine the CBM of individual nanoclusters and other quantum structures. The energy shifts expected from confining electrons to nanometer-size objects are expected to be in the 0.1–1 eV range. For example, the difference between the lowest two states in a linear quantum well of length \( l \) and infinite depth is \( (E_2 - E_1) = \frac{3\hbar^2}{8ml^2} \), which amounts to 1 eV for \( l = 1 \) nm. That should be easily resolvable with our technique.}\]
thanks to the sharp resonances observed in Fig. 2.

IV. RESONANCE AT THE CONDUCTION-BAND MINIMUM

The \((dI/dV)/(I/V)\) tunneling spectra in Fig. 2 exhibit a surprising resonance at the conduction-band minimum (CBM). The peak is three times as high as the continuum above it for CaF₂ and five times as high for CuF₂. In search of an explanation for this phenomenon we consider several options.

a. Divergence of \((dI/dV)/(I/V)\) at the band edge. It has been pointed out that normalized scanning tunneling spectra of bulk semiconductors diverge at the conduction-band minimum. The current \(I\) approaches zero faster than the differential conductance \((dI/dV)\) when approaching the conduction-band edge from above. Inside the gap, \((dI/dV)/(I/V)\) is undetermined because \(I=0\). We utilize thin films, where the tunneling current \(I\) remains finite inside the band gap. The states of the silicon substrate decay exponentially through the CaF₂ film, leaving a finite density of states at the CaF₂ surface available for tunneling. The normalization problems encountered with bulk semiconductors are averted. We will develop a model for tunneling through a thin-film insulator film below that is based on established approaches for planar tunneling.

b. Tip-surface interaction. Tip-induced modifications of

FIG. 3. Discrimination of CaF₁ from CaF₂ by chemically selective tunneling. Stripes of CaF₂ reside on top of a monolayer of CaF₁ that completely coats a stepped Si(111). Top: Topography obtained at a sample bias of +4.3 V with a tunneling current of 0.4 nA. Bottom: Chemical image, obtained from the tunneling current distribution at a sample bias of +3.8 V while stabilizing the tip height at +4.3 V. The patches with the higher band gap (CaF₂) appear dark, leading to an inversion of the topographic contrast. 100×100 nm².

FIG. 4. Chemical distinction between CaF₂ and Si, using islands and stripes of CaF₂ on a Si(111) surface with bunched steps. Top: Topography obtained at a sample bias of +4 V with a tunneling current of 1 nA. The \(x\) derivative of the tip height is given, simulating side illumination from the left. Bottom: Chemical image, given by the tunneling current distribution at a sample bias of +2 V while stabilizing the tip height at a sample bias of +4 V. Electrons from the tip cannot enter the gap of CaF₂, resulting in a low current for CaF₂ patches (dark areas). 200×200 nm².
the band structure, such as tip-induced band bending, have been discussed in the context of semiconductors.\textsuperscript{23} With ionic insulators, one might expect the electric field of the tip to influence the ions. In order to test for such effects, the spectra in Fig. 2 have been taken for different tip spacing by changing the sample bias at which the tip is stabilized. The edge enhancement is larger in the curves taken for a lower sample bias range, which corresponds to the tip being closer to the surface.

\textit{c. Resonant tunneling via image states.} At metal surfaces, resonant tunneling into image states just below the vacuum level has been observed.\textsuperscript{3} Such states are possible in insulators, too, except that their binding energy is reduced for a finite dielectric constant $\varepsilon$. Although tunneling into a bound image state is conceivable for the resonance in CaF\textsubscript{2}, it cannot explain the resonance in CaF\textsubscript{1}. That lies too far below the vacuum level.\textsuperscript{9}

\textit{d. Enhancement of the density of states near the CBM.} An interesting metal-semiconductor interaction has been predicted\textsuperscript{26} that enhances the density of states near the band edges. Metal and insulator states form bonding-antibonding pairs that repel each other. Metal states near the bottom of the insulator band are pushed down and accumulate just below the band edge. In our case, such an enhancement of states might take place in the tip or at the underlying silicon.

In the following, we focus on option $a$ and provide the simplest possible model for it. The agreement with the data is rather suggestive (compare Figs. 2 and 6), although it will be difficult to rule out the other options without getting into detailed calculations. The key idea is tunneling across two barriers in series, first across the vacuum gap and then through the insulator film. The standard theory of planar

\begin{equation}
I(V) \approx \int D_{\text{Sample}}(E + eV)T(E, V)D_{\text{Tip}}(E)dE.
\end{equation}

Here, the energy $E$ is referenced to the Fermi level of the tip. We take the Si substrate as sample and the combination of the CaF\textsubscript{2} film and the vacuum gap as barrier. The simplest approximation for $D_{\text{Sample}}$ and $D_{\text{Tip}}$ is a constant,\textsuperscript{27} multiplied by the Fermi function $f(E)$:

\begin{equation}
D_{\text{Sample}}(E) \approx 1 - f(E),
\end{equation}

\begin{equation}
D_{\text{Tip}}(E) \approx f(E),
\end{equation}

\begin{equation}
f(E) = \frac{1}{1 + \exp(E/kT)},
\end{equation}

$kT = 0.026$ eV at room temperature. That reduces the problem to a calculation of transmission probability $T(E, V)$, which is decomposed into the component $T_{\text{Vac}}(E, V)$ for the vacuum barrier and $T_{\text{Ins}}(E, V)$ for the insulator film:

\begin{equation}
T(E, V) = T_{\text{Vac}}(E, V)T_{\text{Ins}}(E, V),
\end{equation}

\begin{equation}
T_{\text{Vac}}(E, V) = \exp[-2\sqrt{2m/\hbar}(\Phi - 1/2eV_S - E)^{1/2}d_{\text{Vac}}],
\end{equation}

\begin{equation}
T_{\text{Ins}}(E, V) = \begin{cases} 
\exp[-2\sqrt{2m/\hbar}(E_{\text{CBM}} - eV_S - E)^{1/2}d_{\text{Ins}}], & \text{for } eV_S + E < E_{\text{CBM}}, \\
1, & \text{for } eV_S + E > E_{\text{CBM}}.
\end{cases}
\end{equation}
$E$ is the energy of a tunneling electron relative to the Fermi level of the tip, ranging from a few $kT$ positive to $-eV_S$. $V_S$ is the sample voltage, which is positive for tunneling into the conduction band. $\Phi$ represents the average work function between tip and insulator. For $T_{\text{Vac}}$ we use the average barrier$^3$ $(\Phi - eV_S)$ across the vacuum gap. $E_{\text{CBM}}$ is the energy of the conduction-band minimum of the insulator relative to its Fermi level. Any voltage drop across the insulator is neglected. $d_{\text{Trp}}$ is the distance of the tunneling tip from the insulator surface, and $d_{\text{Ins}}$ the thickness of the insulator film. Most of these parameters can be estimated from independent measurements$^{28}$ Only the position of the conduction band minimum $E_{\text{CBM}}$ is adjusted to match the observed peak position in the $(dI/dV)/(I/V)$ spectra, which gives $E_{\text{CBM}} - E_F = 2.3$ eV for CaF$_2$ and in $E_{\text{CBM}} - E_F = 3.7$ eV for CaF$_2$.

Figure 6 shows the results of the model applied to our experimental conditions. It is to be compared with the data in Fig. 2. The general peak shape, and even the absolute peak height in the $(dI/dV)/(I/V)$ spectra is reproduced surprisingly well, given the simplicity of the model and the lack of adjustable parameters (apart from $E_{\text{CBM}}$). That suggests that we have captured the salient features of the resonance effect. Since the density of states is assumed to be constant, the resonance must be due to the change in the transmission near the conduction-band minimum. The model also provides predictions. For example, the height of the resonance scales with $E_{\text{CBM}}$ and $d_{\text{Ins}}$ approximately like

$$(dI/dV)/(I/V)_{\text{max}} \approx 2.4 \text{ (eV Å)$}^{-1}d_{\text{Ins}}E_{\text{CBM}}.$$ (4)

The resonance becomes stronger for larger $E_{\text{CBM}}$, making the technique particularly useful for insulators and wide-gap semiconductors. The calculated spectra are insensitive to the tip distance $d_{\text{Trp}}$, but they depend on the film thickness $d_{\text{Ins}}$. As the film becomes thicker, $(dI/dV)/(I/V)$ keeps increasing for energies inside the gap and diverges in the limit of an infinitely thick film. That is exactly the divergence problem that has plagued the interpretation of $(dI/dV)/(I/V)$ spectra from bulk semiconductors and has led to various schemes for artificially removing the divergence, such as adding a small constant to $(I/V)$ or applying some amount of broadening to the $(I/V)$ values.\textsuperscript{24} The use of thin films in our work turns this difficulty around and converts it into an accurate tool for determining conduction-band minima and Schottky barriers in nanostructures. The value of $E_{\text{CBM}} - E_F$, which corresponds to the n-type Schottky barrier, corresponds directly to the peak position in the $(dI/dV)/(I/V)$ spectrum.

Currently we are exploring refinements\textsuperscript{39} of the minimal model given in Eqs. (1)–(3). They include a more realistic distribution of the voltage drop across insulator and vacuum. The two limiting cases are depicted in Fig. 4. The CaF$_2$ layer is conducting above the CBM, and the voltage drops completely across the vacuum gap (left). Tunneling deep inside the gap one approaches the electrostatic limit (right). In this case there is a significant voltage drop across the CaF$_2$ film, which is analogous to the tip-induced band bending discussed for semiconductors.\textsuperscript{30,31} Another refinement is an explicit integration of the one-dimensional Schrödinger equation across the combined barrier, which yields more accurate transmission coefficients. That allows the inclusion of the image potential and the effects discussed in option $b$. The increasing influence of the image potential qualitatively explains why the peaks in the tunneling spectra slightly shift towards lower voltages when the tip approaches the surface. Further possible refinements are an effective mass for the conduction band of CaF$_2$ and the inclusion of three-dimensional effects, such as a finite escape cone.\textsuperscript{22–24}

V. SUMMARY AND OUTLOOK

In summary, we have developed a chemical imaging method for insulators that has sub-nanometer resolution. Terraced height differences are eliminated completely from the chemical image. Different oxidation states can be distinguished (CaF$_2$ versus CaF$_3$). The method is based on a steep drop of the conductivity inside the gap, together with a newly found resonance in $(dI/dV)/(I/V)$ at the conduction-band minimum. A minimal model is given, which explains the resonance as an effect of tunneling across two barriers, the vacuum gap and the insulator film.

The method developed here should be useful for chemical imaging of insulators and wide-gap semiconductors. The conduction band edge of an individual nanostructure can be determined accurately from the resonance in the normalized conductance. Consequently, the local tunneling barrier and the band offset can be measured, which represent key parameters of potential devices, such as quantum dots using Coulomb blockade and single electron tunneling.

ACKNOWLEDGMENT

This work was supported by NSF under Grant Nos. DMR-9624753 and DMR-9632527.

---

\textsuperscript{1}Permanent address: Institut für Festkörperphysik, Universität Hannover, D-30167 Hannover, Germany.
\textsuperscript{2}Permanent address: Department of Physics, National Chung Cheng University, Taiwan, R.O.C.
\textsuperscript{7}R. J. Hamers, STEM on Semiconductors, Springer Series in Surface
The scanning tunneling spectrum in this work exhibits an onset at 1 V and a small peak at 2.2 V. The latter agrees with our CaF\textsubscript{1} values of CBM at \(\Gamma\) of 1.8 and 1.4 eV above \(E_F\) have been given in Refs. 11 and 12, respectively.

The energy of the peak in the \((dI/dV)/(I/V)\) spectrum of CaF\textsubscript{1} would be consistent with the CBM of Si in the [111] direction, which corresponds to the \(L_1\) point at 2.4 eV [see F. J. Himpsel, Surf. Sci. Rep. 12, 1 (1990)]. Possibly, the \(L_1\) state of Si hybridizes with the Ca 4s state.

The assumption of a constant tip density of states is often made, lacking detailed knowledge of the tip states. The Si density of states has little structure at the energies under consideration, i.e., about 4 eV above the valence-band maximum.

The parameters used in the calculation are estimated from independent measurements: For the work functions \(\Phi\) of the tip and of CaF\textsubscript{2}, we take 4 eV (compare Refs. 5 and 9). As tip distances we use typical values (Refs. 5 and 24) at the respective tip stabilization voltages, i.e., \(d_{\text{tip}}=11\) Å at 4.3 V for CaF\textsubscript{2} and \(d_{\text{tip}}=10\) Å at 3.5 V for CaF\textsubscript{1}. The \((dI/dV)/(I/V)\) spectra are insensitive to variations in tip distance and work function, the \((dI/dV)\) spectra change by a scaling factor. As sample thickness we use \(d_{\text{ins}}=3.93\) Å for CaF\textsubscript{2} and \(d_{\text{ins}}=2.7\) Å for CaF\textsubscript{1}. The CaF\textsubscript{2} thickness is composed of 3.15 Å for the CaF\textsubscript{2} triple layer plus 0.78 Å for the \(F^–\) layer of the underlying CaF\textsubscript{1}. The \(F^–\) is likely to exhibit the full CaF\textsubscript{2} gap because of its closed shell character. Using \(d_{\text{ins}}=3.15\) Å instead for CaF\textsubscript{2} gives a resonance curve of similar shape but with the peak height reduced from 34 to 28. For the CaF\textsubscript{1} thickness we add half of the Si-Ca distance (Ref. 13) of 2.25 Å plus half of the CaF\textsubscript{2} thickness of 3.15 Å. These estimates are based on interfaces located halfway between lattice planes.

The scanning tunneling microscopy of Pt/CaF\textsubscript{2}/Si(111) at 4.5 V is assigned to the density of states of the CaF\textsubscript{2} intralayer, which is consistent with our finding.