

Spring 2008 MSAE E4990y  
Introduction to STM and AFM

Lecture 3  
STM in Catalysis Research  
January 30, 2008

Outline

- The Tersoff-Hamann model of STM
- The concept of local density of states
- Atomic-scale imaging by STM
- Catalysis research with STM  
Ni-Au catalyst for steam reforming  
MoS2 catalyst for hydrodesulphurization
- Outlook

The Tersoff-Hamann model of STM  
-- tip considered as a geometrical point --

- In principle, the STM image is determined by a convolution of tip wavefunctions and the sample wavefunctions.
- However, the tip wavefunction is difficult to determine, and the combined problem is pretty complicated.
- A particular model is proposed to take out the tip problem.
- The tip is modeled as a structureless geometrical point, and the STM image is related to a property of the sample alone.
- A detailed mathematical analysis showed that a STM image is a contour of equal local density of states at the Fermi level.
- The model works very well as long as the bias voltage is low and the features to be observed are much greater than 0.3 nm.

Local density of states (LDOS)

Definition: density of electron states per unit volume per unit energy at position  $\mathbf{r}$  and energy level  $E$ .

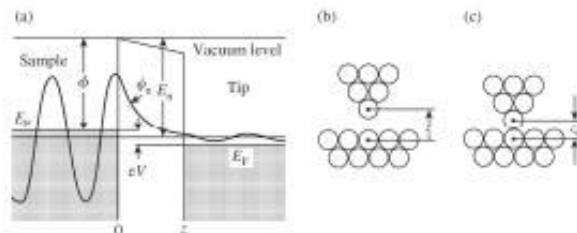
For a series of wavefunctions  $\psi_\mu(\mathbf{r})$  with energy value  $E_\mu$ ,

$$\rho(\mathbf{r}, E) = \lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon} \sum_{E_\mu = E}^{E+\epsilon} |\psi_\mu(\mathbf{r})|^2 = \sum_{\mu} |\psi_\mu(\mathbf{r})|^2 \delta(E - E_\mu)$$

The quantity can be calculated using first-principle numerical methods. The Tersoff-Hamann model concludes that at low bias, an STM image is a contour of the Fermi-level local density of states.

Here we make an elementary explanation of its meaning, and a heuristic derivation of the Tersoff-Hamann model.

An explanation of the Tersoff-Hamann model (1)



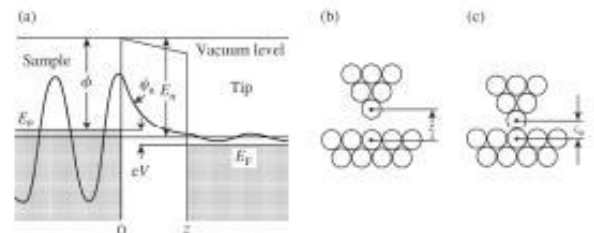
For uniform free-electron metals,

$$I = VG_0 e^{-2\kappa(z-z_0)}$$

The electron state density near the Fermi level also follows the exponential law,

$$\rho(z, E_F) = \rho(0, E_F) e^{-2\kappa z},$$

An explanation of the Tersoff-Hamann model (2)



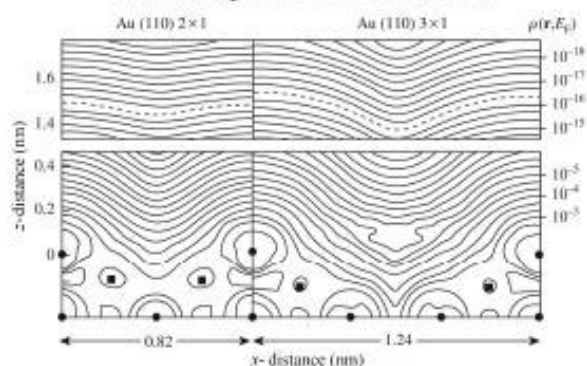
Combining these two equations, in a one-dimensional case,

$$I(z) \propto V \rho(z, E_F).$$

The relation is, heuristically, valid for all surfaces at any distance,

$$I(\mathbf{r}) \propto V \rho(\mathbf{r}, E_F).$$

### An Example of LDOS contours



Calculated LDOS contours of Au(110) surface. Two types of reconstruction are shown. The dotted curves show theoretical predictions of STM images.

### Criterion of validity of the Tersoff-Hamann model

The Tersoff-Hamann model is valid when the characteristic length of the features of interest is much greater than the atomic diameter:

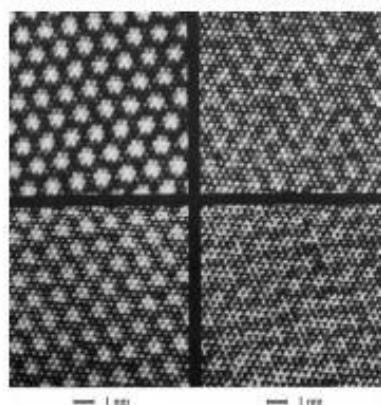
$$a \gg \frac{\pi}{\kappa},$$

$$\kappa \cong 10 \text{ nm}^{-1},$$

$$a \gg 0.3 \text{ nm}.$$

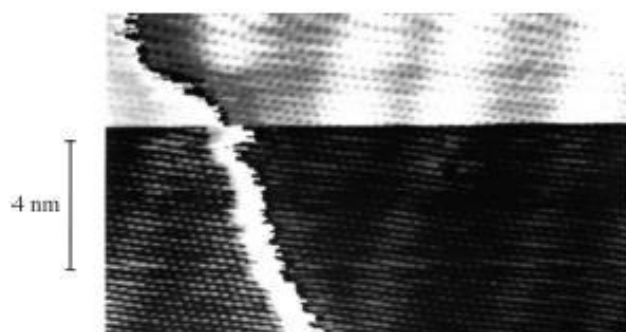
For atomic-scale features, the tip electronic states play a critical role.

### Experimental observation of tip-dependence of STM images (1)



Four images of 4Hb-TaS<sub>2</sub> taken under identical conditions within 2 hours.

### Experimental observation of tip-dependence of STM images (2)



Corrugation reversal observed during a scan of an STM image on Au(111) surface, show the effect of spontaneous tip restructuring.

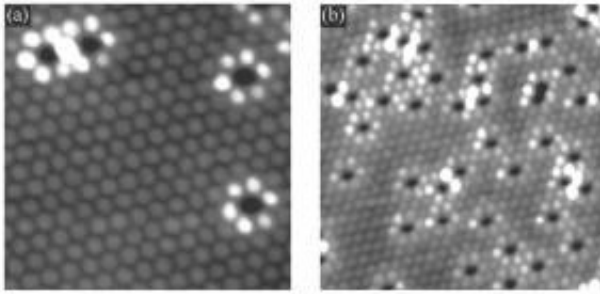
### Catalysis Research Using STM (1)

- **catalysis** is the acceleration of a chemical reaction by means of a substance called a **catalyst**, which is itself not consumed by the overall reaction.
- A catalyst provides an alternative route to products, the catalytic route being subject to lower activation energy than in the uncatalyzed reaction. A lowered activation energy increases the reaction rate. Catalysts generally change in the course of a reaction but are regenerated.

### Catalysis Research Using STM (2)

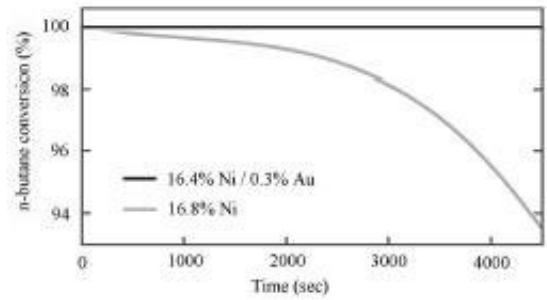
- Backbone of synthetic chemistry
- Important to environment protection
- To date, the catalysis process has been developed almost entirely through costly trial-and-error experimentation.
- The nature of catalysis is the single-molecule reactions at the atomic sites on the surface of catalyst.
- STM can provide information on atomic sites on the surface.
- STM can visualize the interaction of reactant molecules with those atomic sites.
- STM can also visualize the process at an atomic scale.

### The Steam Reforming Process (1)

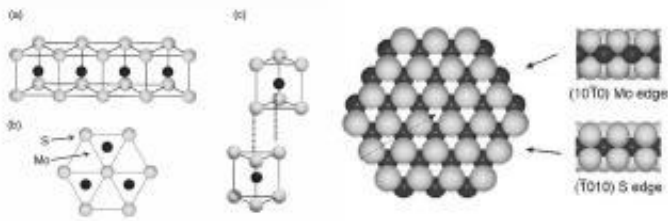


Two STM images of Ni(111) surface with 2% (left) and 7% of Au. The Au atoms appear as depressions, that is, low LDOS; while the adjacent Ni atoms appear as protrusions, that is, high LDOS and high reactivity.

### The Steam Reforming Process (2)



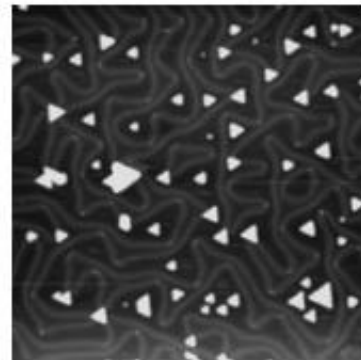
### The Hydrodesulphurization Process (1)



The atomic structure of a sheet of MoS<sub>2</sub>      The structure of a nanocrystal of MoS<sub>2</sub>

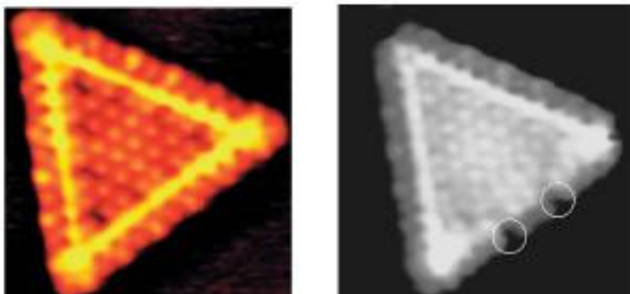
The theoretical structures of the catalyst: MoS<sub>2</sub>.

### The Hydrodesulphurization Process (2)



The STM image of MoS<sub>2</sub> nanocrystals are almost all triangular.

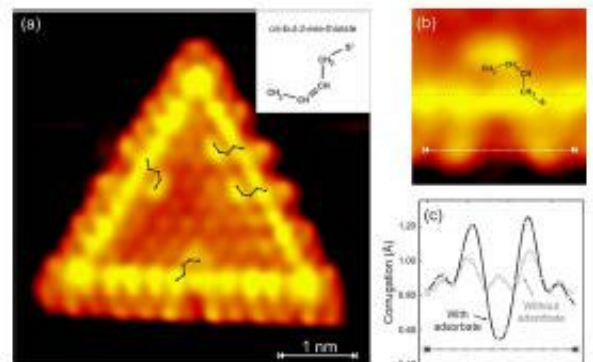
### The Hydrodesulphurization Process (3)



The fresh MoS<sub>2</sub> nanocrystal.  
No catalytic activity.

After reacting with hydrogen.  
Good catalytic activity.

### The Hydrodesulphurization Process (4)



A more complicated case.