

# Adsorption of Ammonia Molecules on Si(111)-7x7 Surface: an STM Observation

Rong-Li Lo (羅榮立)

Physics Department, NTHU

26, Dec. 2006

## **Outline:**

**(1) Introduction**

**(2) Experimental**

STM and Si(111)-7x7 surface

**(3) Review**

**(4) Results and Discussion**

**(5) Conclusion and future work**

# Introduction

Interfaces of silicon for thin film growth

$\text{Si}_3\text{N}_4$ : good thermal stability and dielectric property

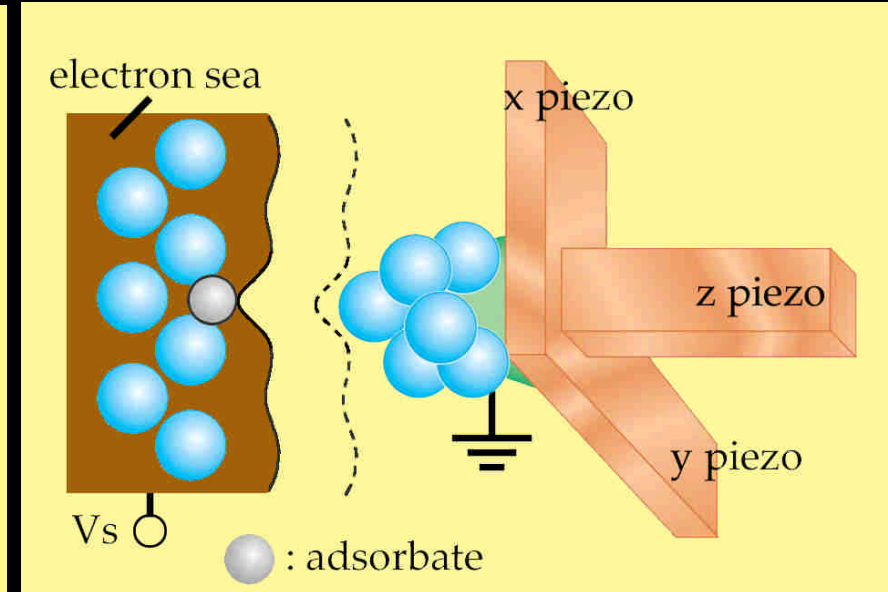
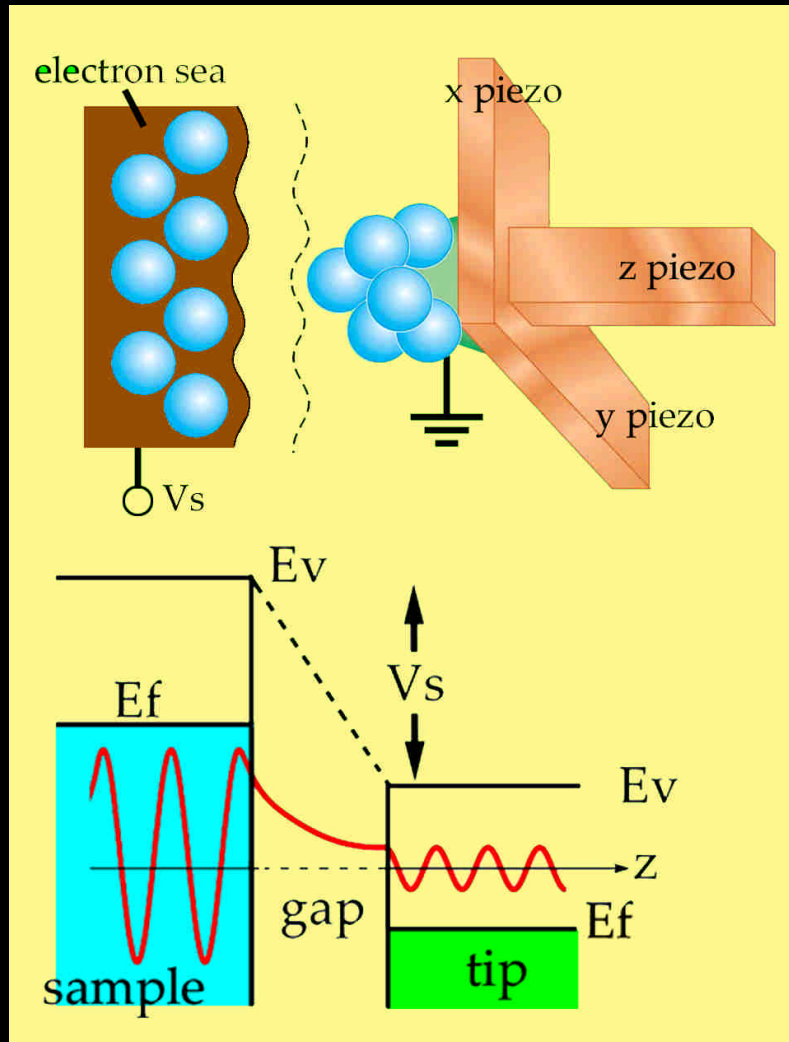
Epitaxial  $\text{Si}_3\text{N}_4$  thin films on Si(111):

lattice mismatch is  $\sim 1.1\%$  between  $\text{Si}_3\text{N}_4(0001)/\text{Si}(111)$

Thermal nitridation:

Expose Si wafers to  $\text{NH}_3$ ,  $\text{NO}$ ,  $\text{N}_2$ , N plasma, ...

# Experimental : STM



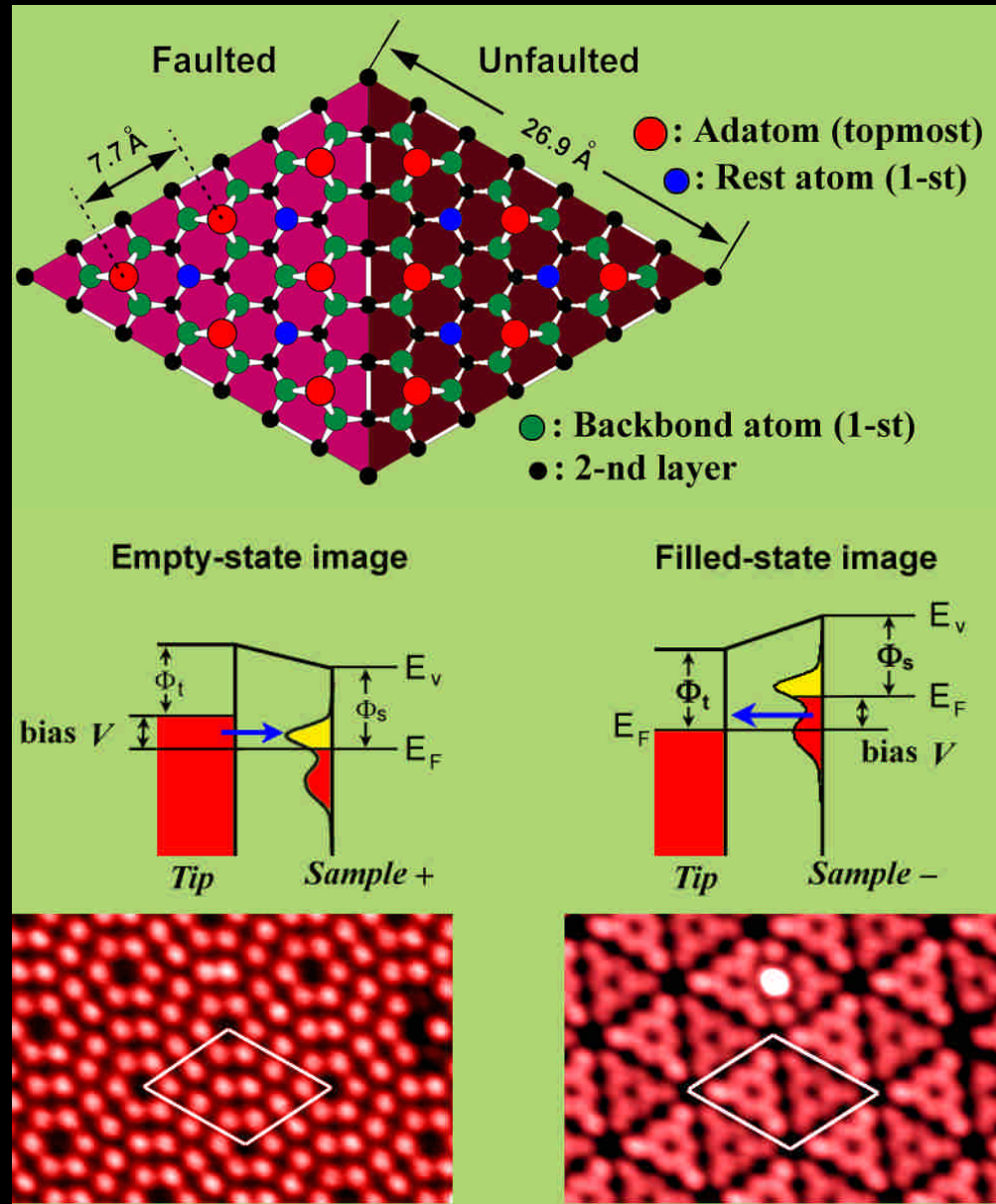
Tunneling current  
 $I \propto F(V_s) e^{-kz}$

# Experimental

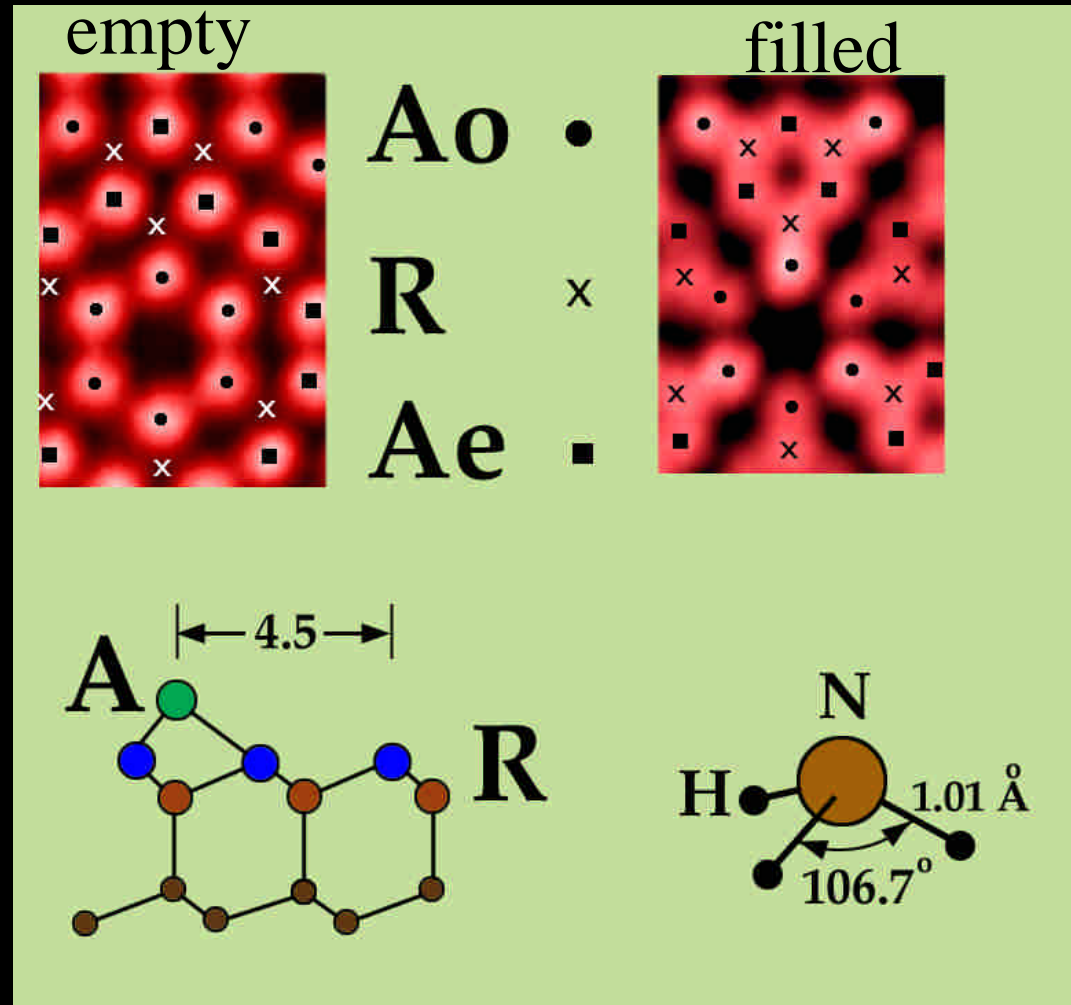
Si(111)-7x7 surface:  
DAS model

STM image:

empty state (left)  
and filled (right) state  
images

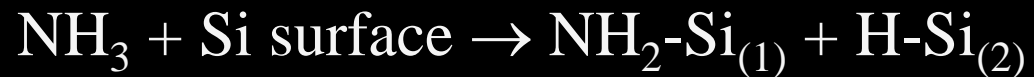


# Adsorbed sites on 7x7 surface

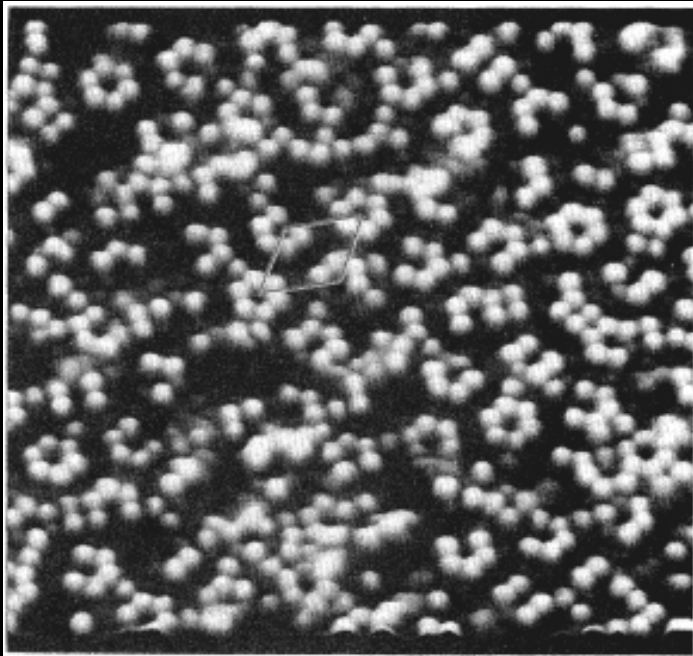


# Review

Dissociative adsorption:



$\text{Si}_{(1)}$  and  $\text{Si}_{(2)}$  are a pair of adjacent A-R dangling bond.



- (i) R is more reactive than A.
- (ii) Reacted ratio:  $A_e/A_o > 4$ , originating from electronic structure.

STM results  
[PR B 39(89)5091]

## Question remained:

### The $x$ of $\text{NH}_x$ ( $x = 0 \sim 2$ ) and $\text{NH}_x$ adsorption sites

Theoretical:

- (i) No site selectivity
- (ii)  $\text{NH}_x$  prefers on A site

Experimental:

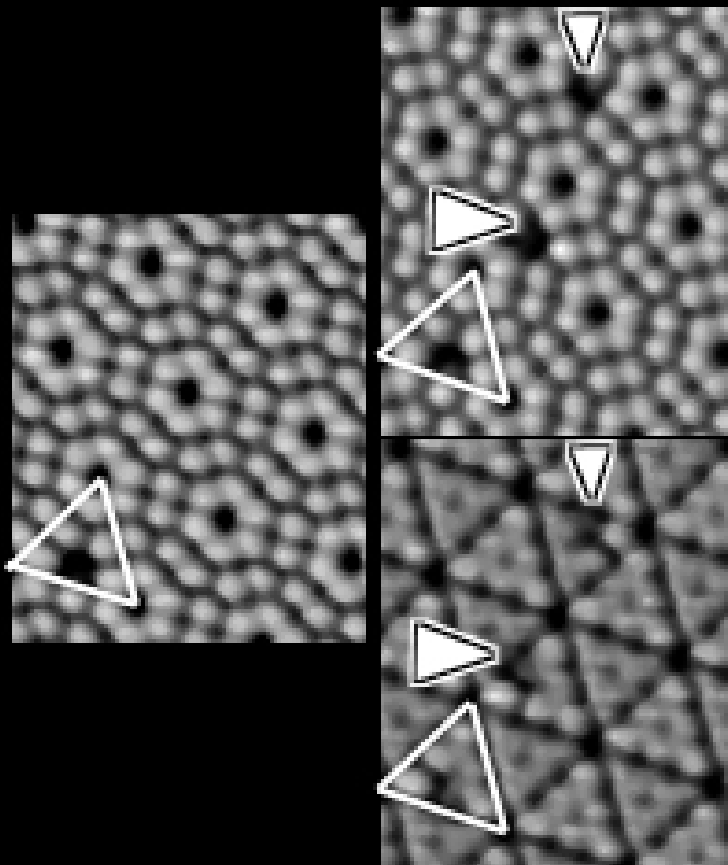
- (i)  $\text{NH}_2$  is adsorbed at R site,  
 $8 \pm 7\%$  of the  $\text{NH}_x$  is adsorbed at A site
- (ii)  $\text{NH}_x$  is adsorbed at A site



## Results and Discussion

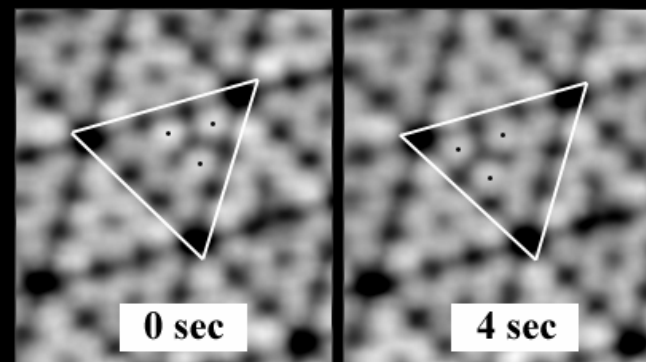
An  $\text{NH}_3$  is dissociated and adsorbed on an A-R pair.

Before



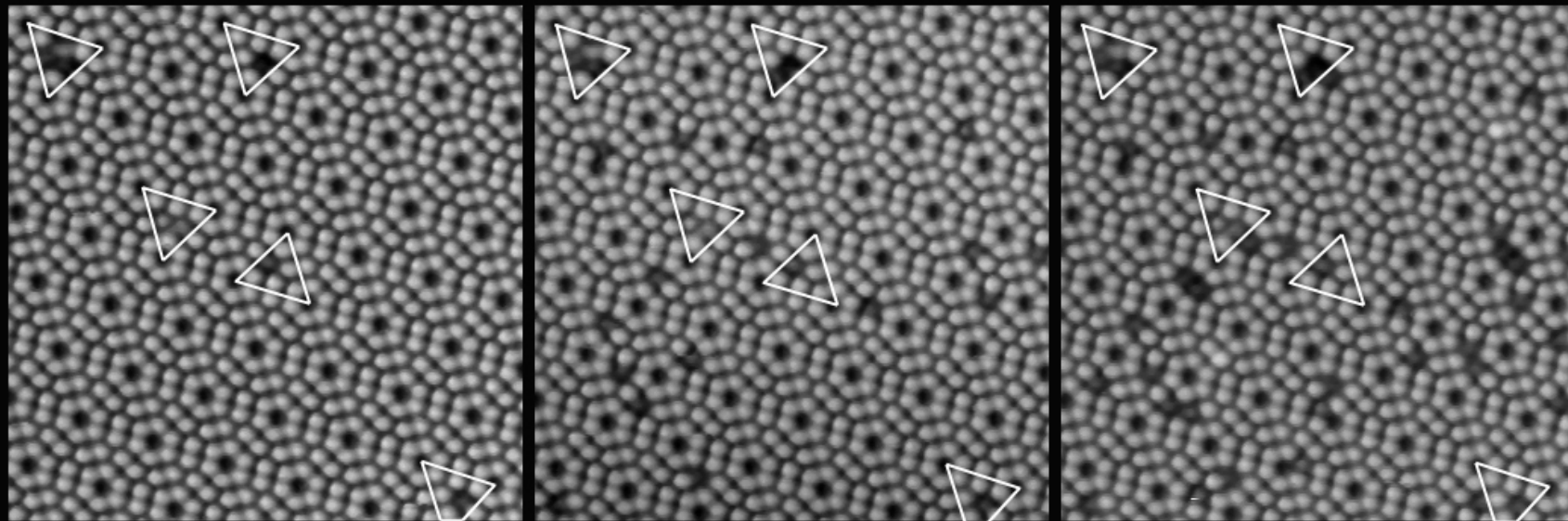
**A reacted R site:**

H-adsorbed R site  
at 340° C



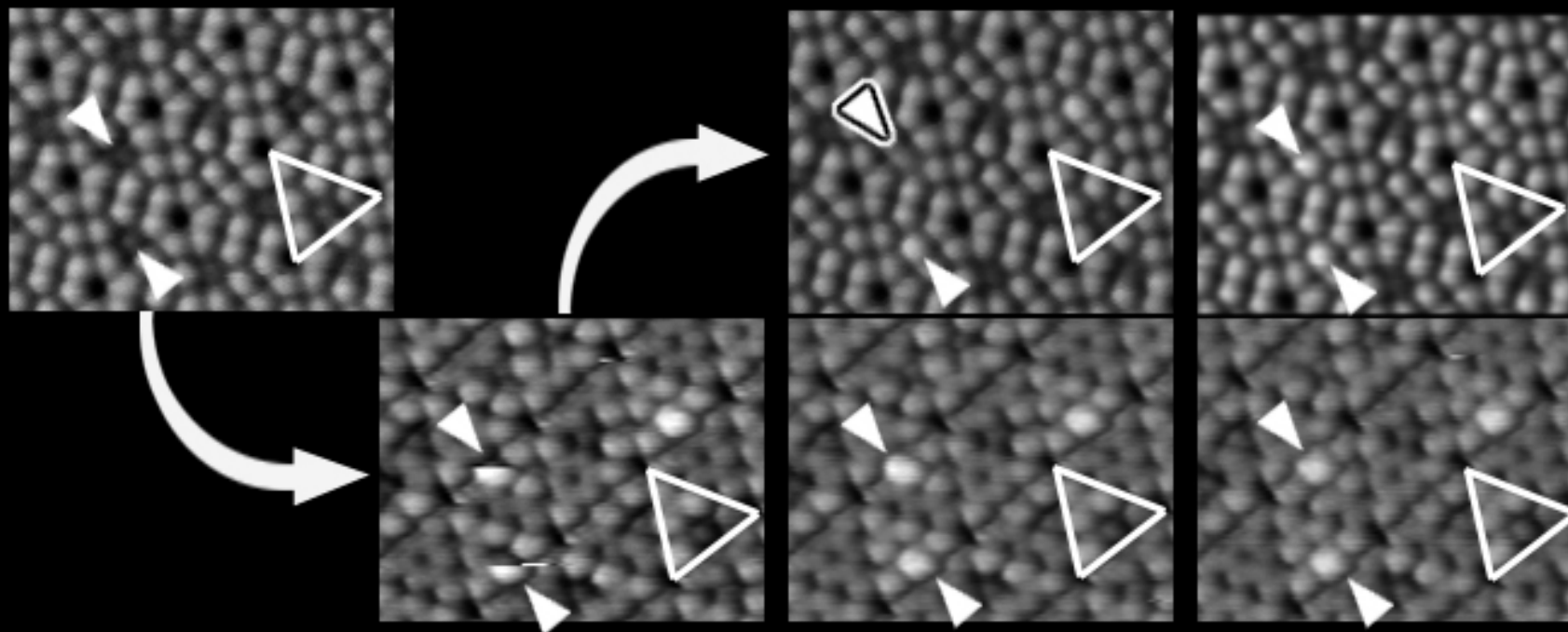
# Distribution of reacted adatom sites

**in-situ** cumulative exposure



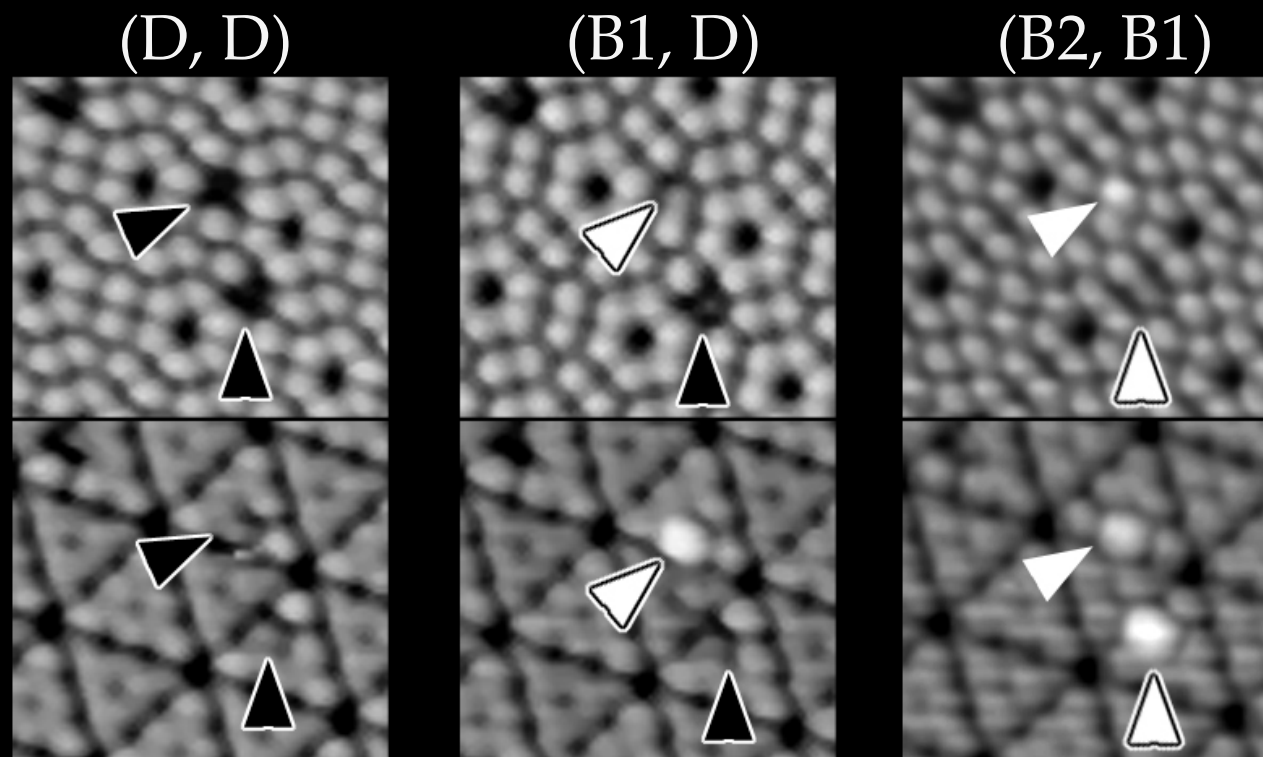
In-situ + (empty and filled state images) exclude defect sites.

Determination of adsorption sites of H and NH<sub>2</sub>  
⇒ **activation of tunneling electrons**



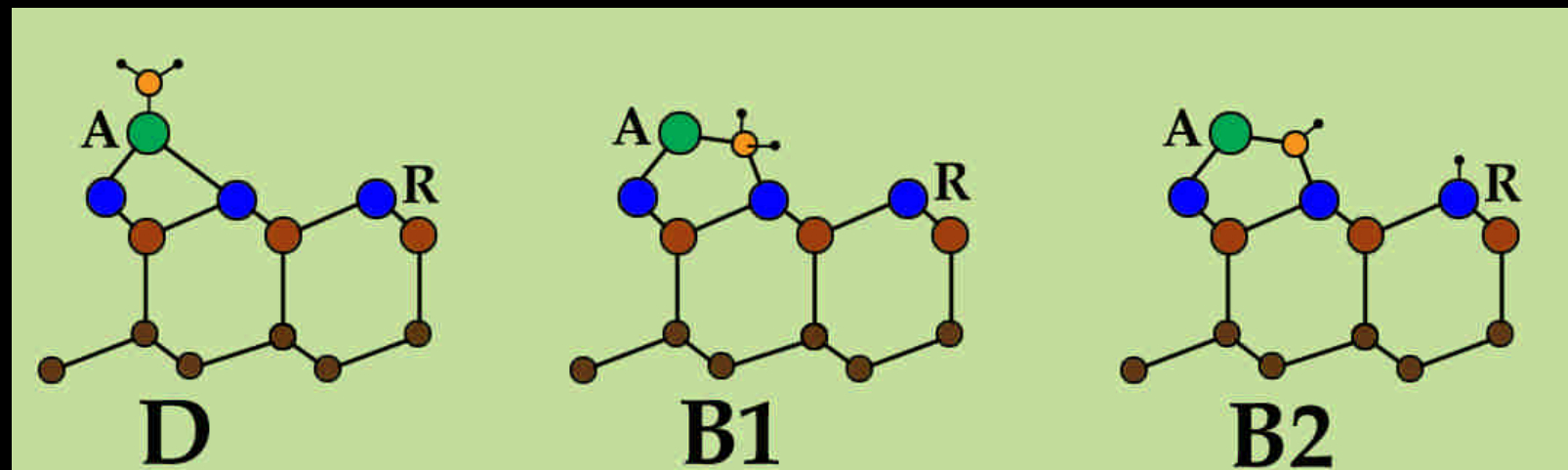
Scanning direction: up to down and left to right.

## Adsorption states of NH<sub>2</sub> on A site



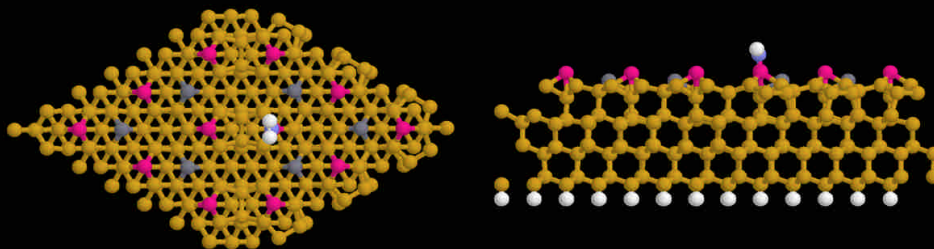
Transformation by tunneling electrons: D → B1 → B2

## Model of D, B1, and B2 adsorption states

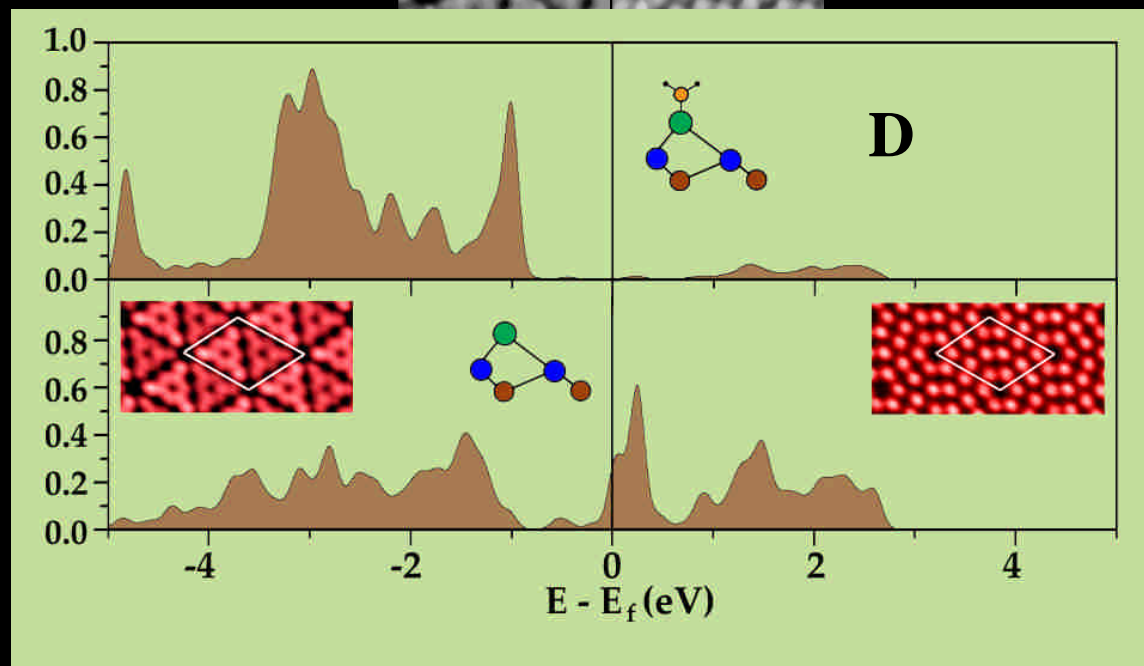
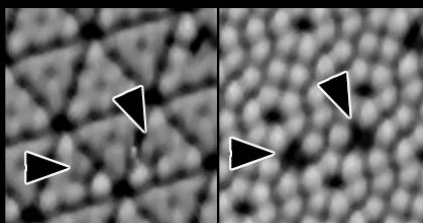


Probability of  $\text{NH}_2$  on A =  $X$  %; on R =  $(1 - X)$ %.

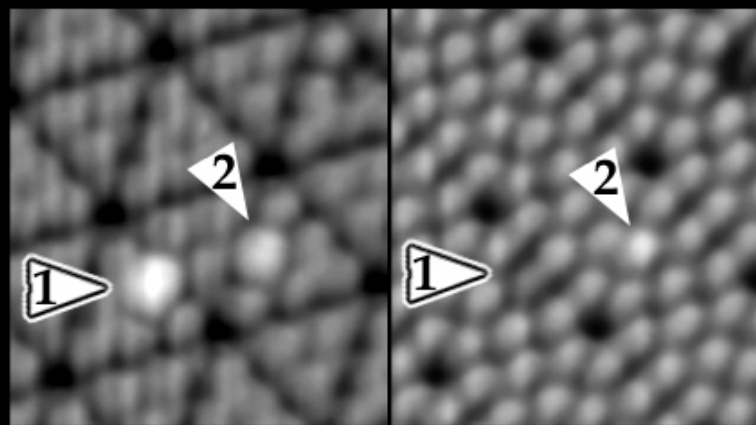
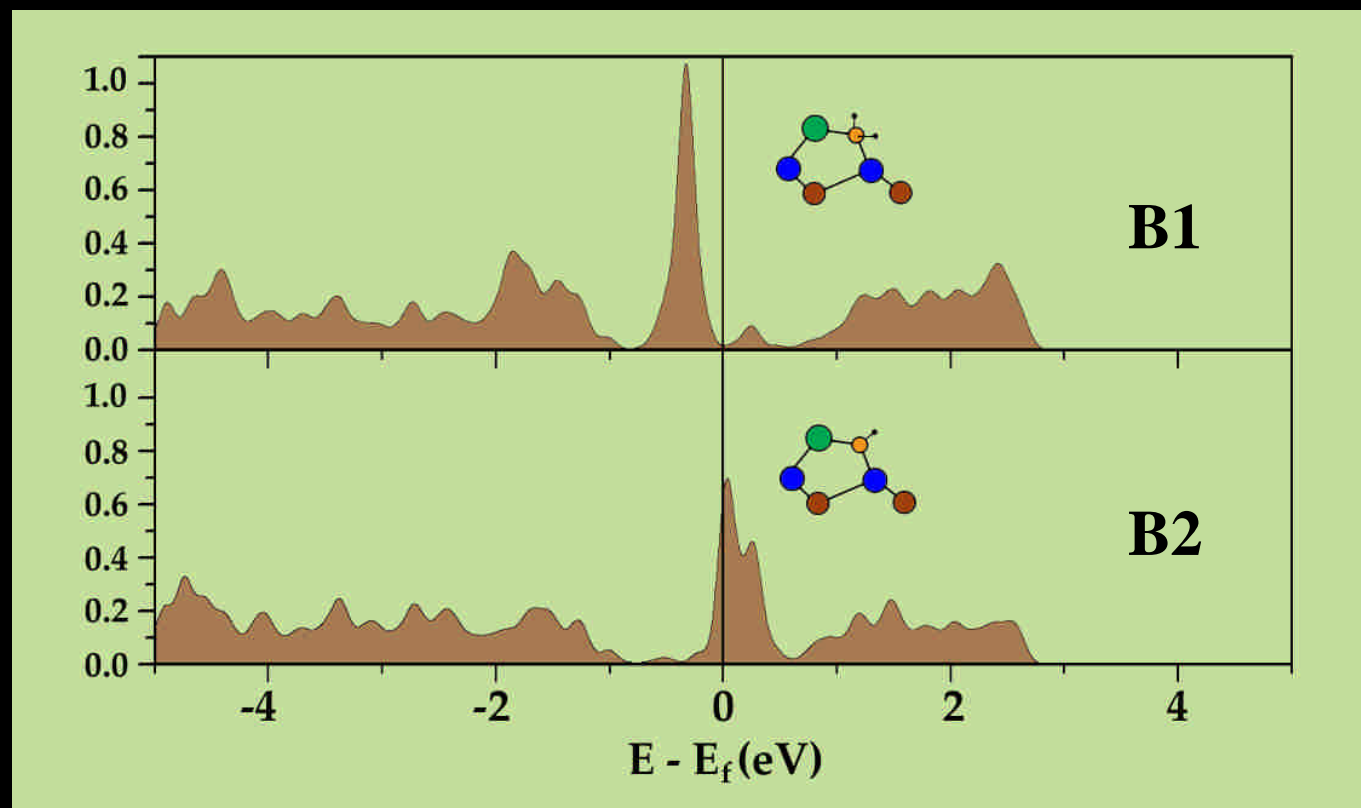
# Theoretical support (東華大學 張俊明)



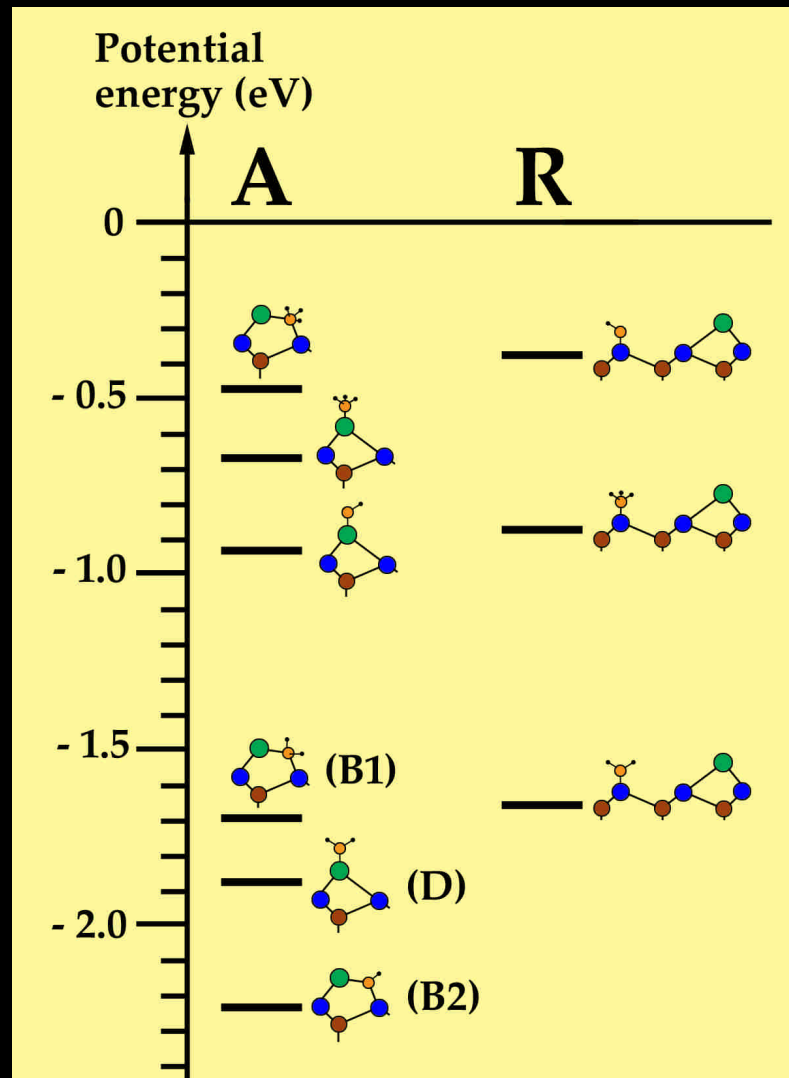
Full 7x7 DAS model





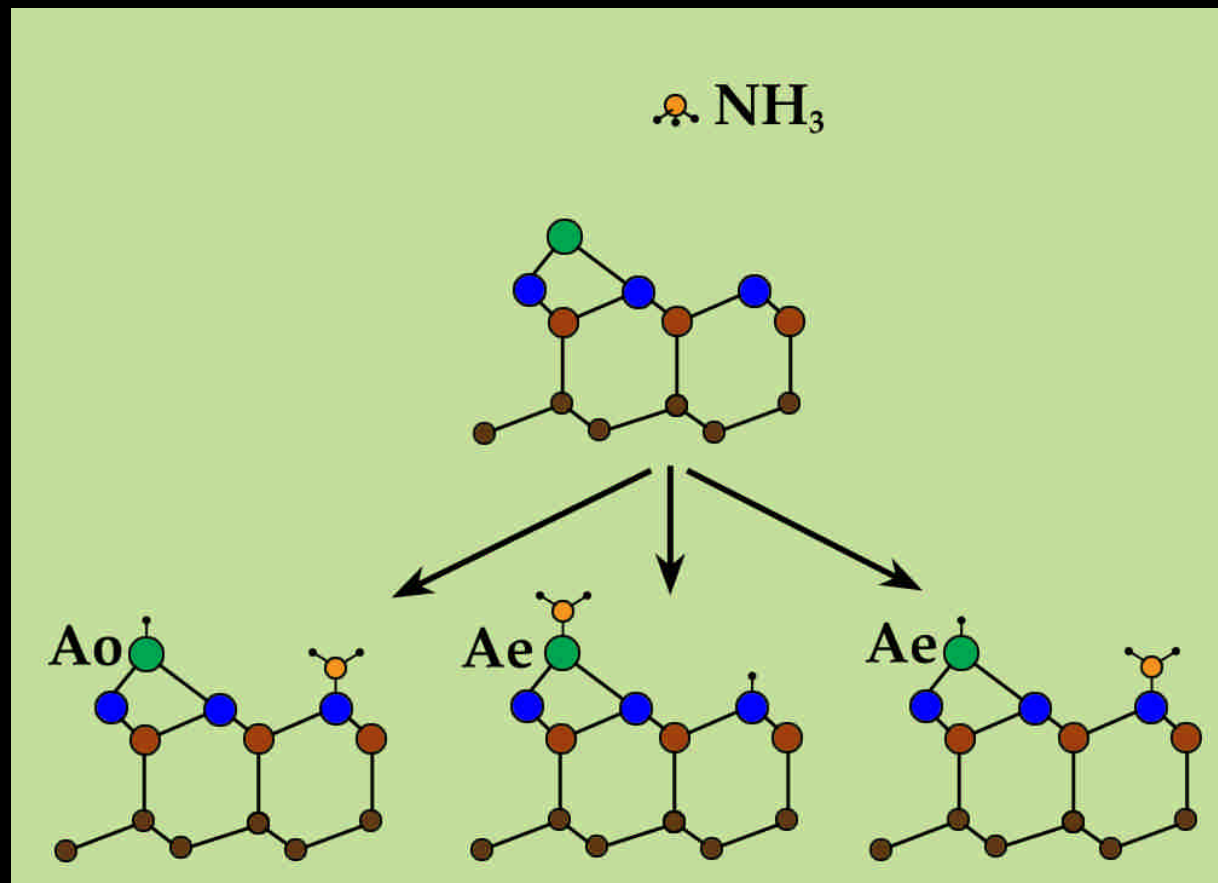


# Potential energy levels of $\text{NH}_x$ on A and R

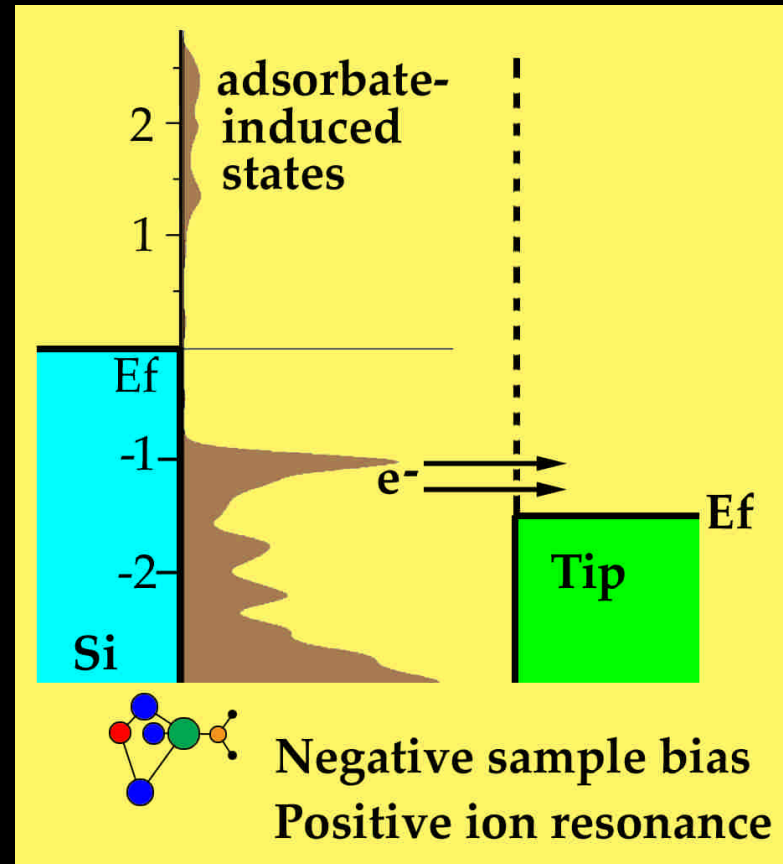




# Distribution of adsorbed fragments



# Mechanism behind the transformation ⇒ Adsorbate-induced state resonance



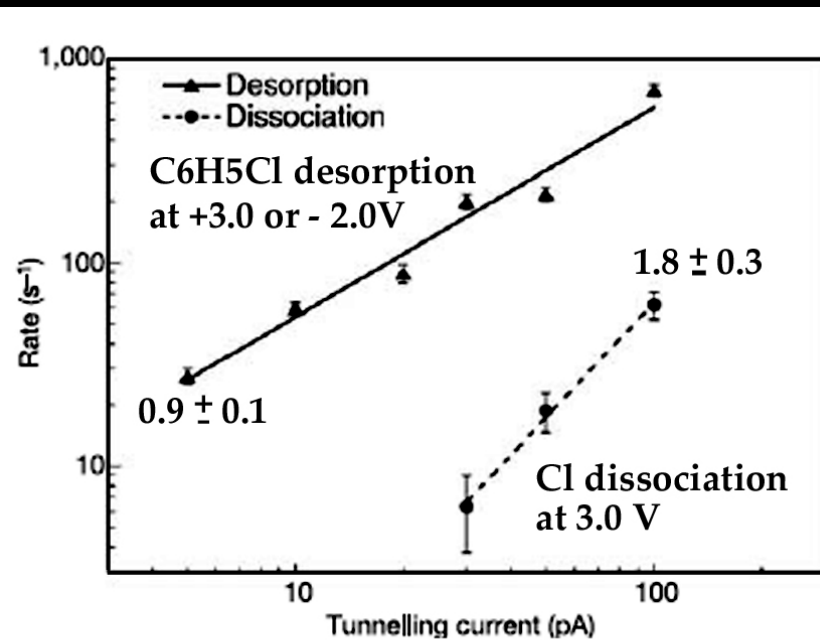
Tunneling electron's energy → vibrational energy of  $\text{NH}_2\text{-ad}$   
→ conversion to  $\text{NH}_2\text{-ins}$

## Conclusion:

- (a)  $\text{NH}_3$  is dissociatively adsorbed at a pair of A-R dangling bonds.
- (b)  $\text{NH}_2$  is adsorbed at rest atom (R) with probability  $(1 - X)$  %, while  $X$  % at center adatom site (Ae).
- (c)  $\text{NH}_2\text{-ad-Ae}$  is stimulated to transform into  $\text{NH}_2\text{-ins-Ae}$  which is a metastable state of  $\text{NH-in-Ae}$ .
- (d) The STM-induced transformation is fulfilled by a positive ion resonance

# Work in the future

## Determination of n-electron process



Chlorobenzene on Si(111)-7x7 at RT

Desorption: one-electron process

Dissociation of Cl: two-electron process

From *Nature* 434 (2005) 367

## Acknowledgement:

東華大學 物理系 張俊明 教授

中興大學 物理系 何孟書 教授