Gold monolayer islands on a polar AlN(0001) surface

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TNT 2017 Trends in NanoTechnology

TNT2017 Dresden Germany

June 05-09, 2017

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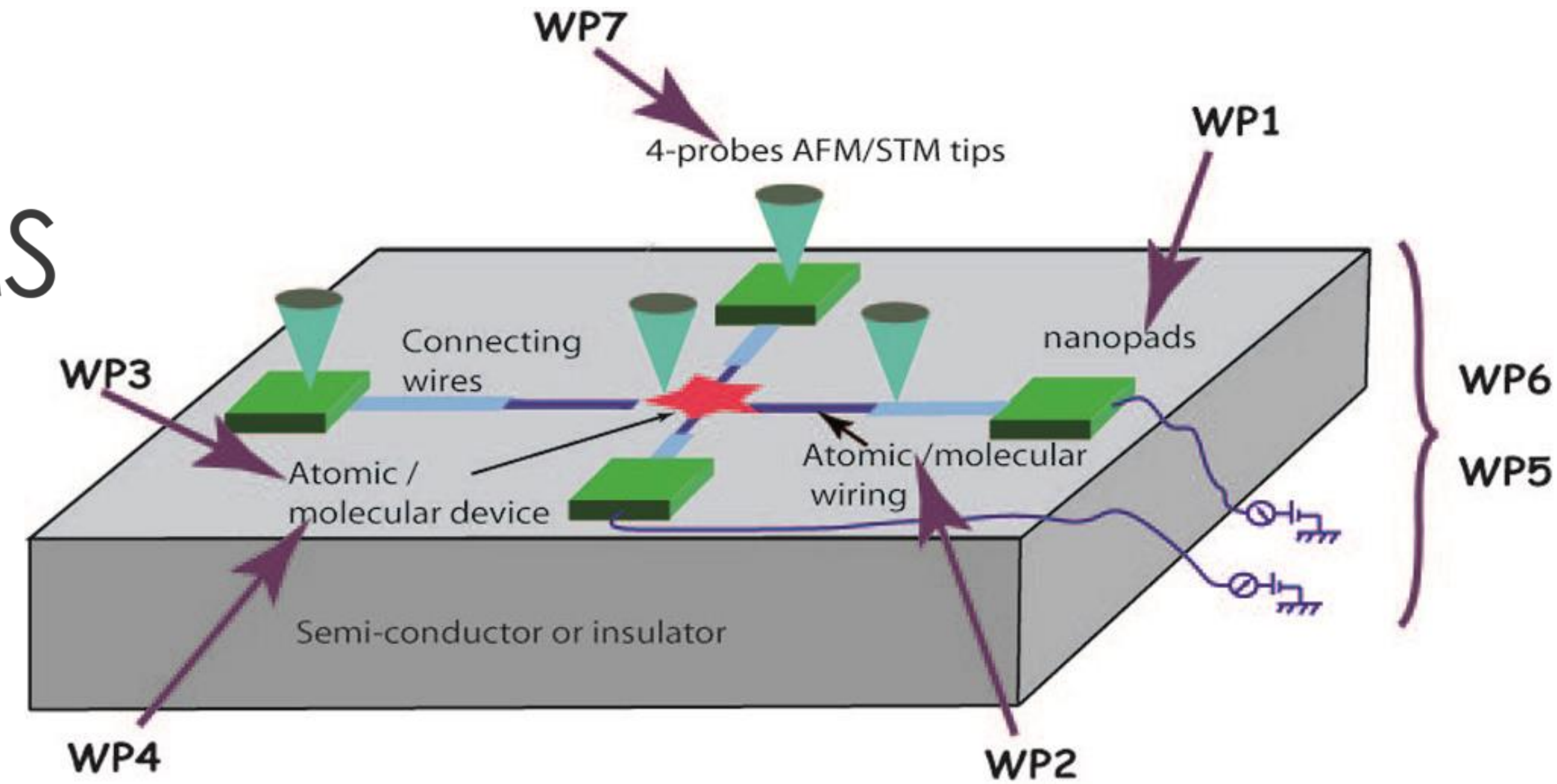
Goal: metallic nano-islands on an insulator molecular electronics applications



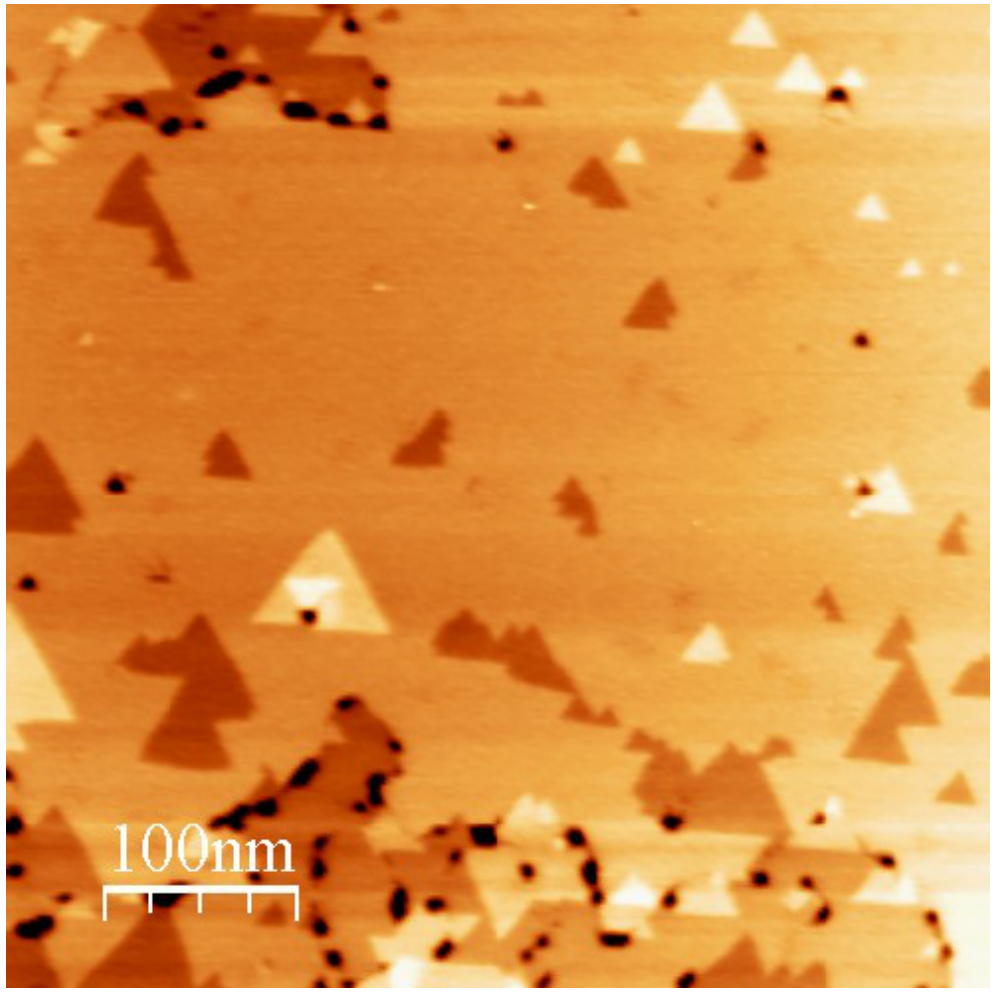
- Acting as electron reservoirs
- Relatively flat (one monolayer height ideally)
- Local-probe based methods: observation / manipulation
- Keep intact the electronic properties of a molecule
- Atomic control of the surface

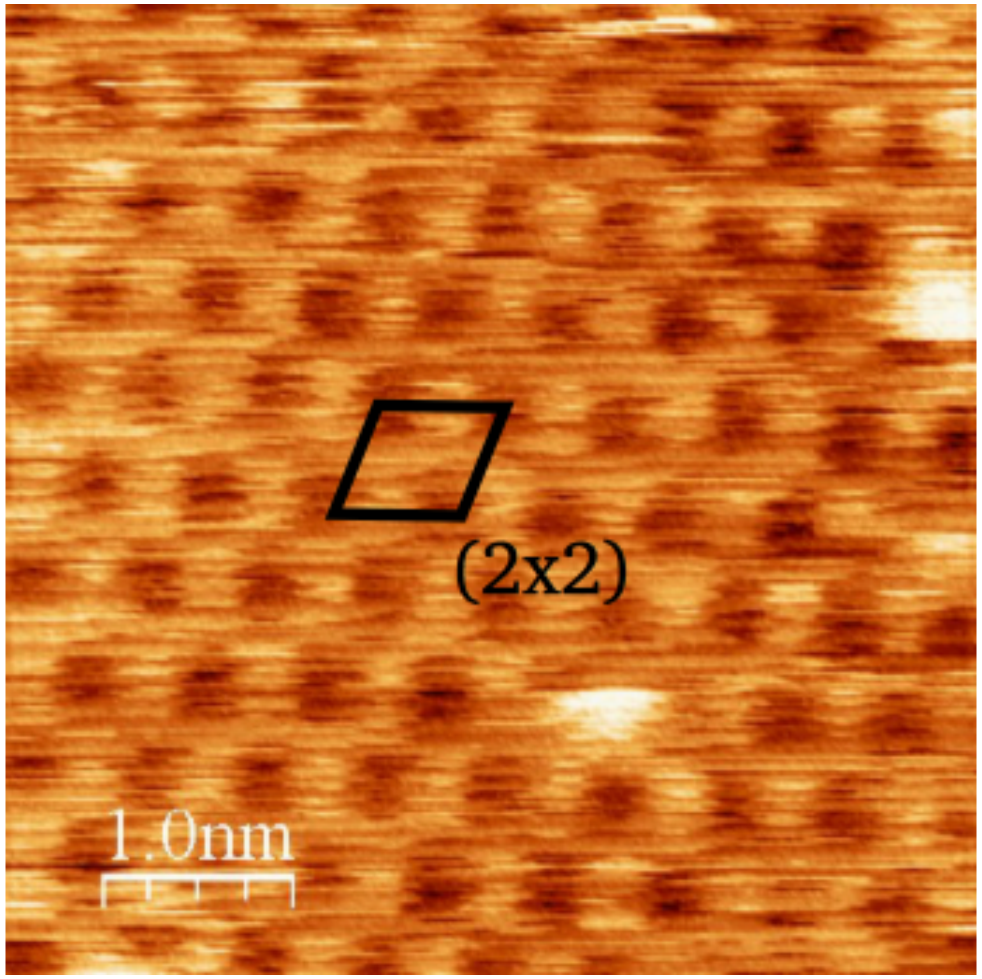
Aluminium nitride

III-V semiconductor with Eg = 6.2 eV

MBE growth (NH_3) ~100 nm 2H-AlN on a 4H-SiC substrate @ 990 °C

nc-AFM images @ RT





a = 6.22 Å

Aluminium nitride

Polar materials

Alternation of
positively and negatively charged planes

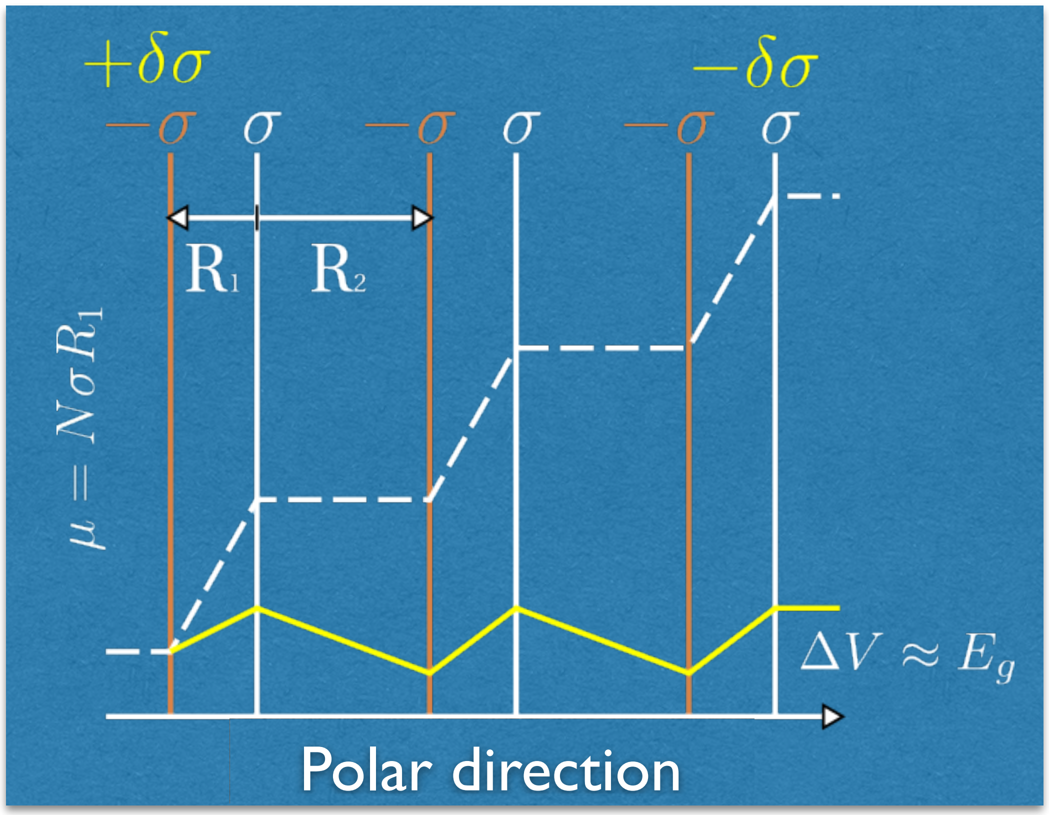
electrostatic divergence

Compensation

Aluminium nitride

Polar materials and electrostatic divergence, compensation

First order compensation:
lateral charge transfer



Thermodynamic limit

$$\delta\sigma_\infty = \frac{\sigma R_1}{R_1 + R_2}$$

J. Goniakowski *et al.*, Rep. Prog. Phys. **71**, 016501 (2008)
C. Noguera, J. Phys.: Condens. Matter **12** (2000) R367–R410

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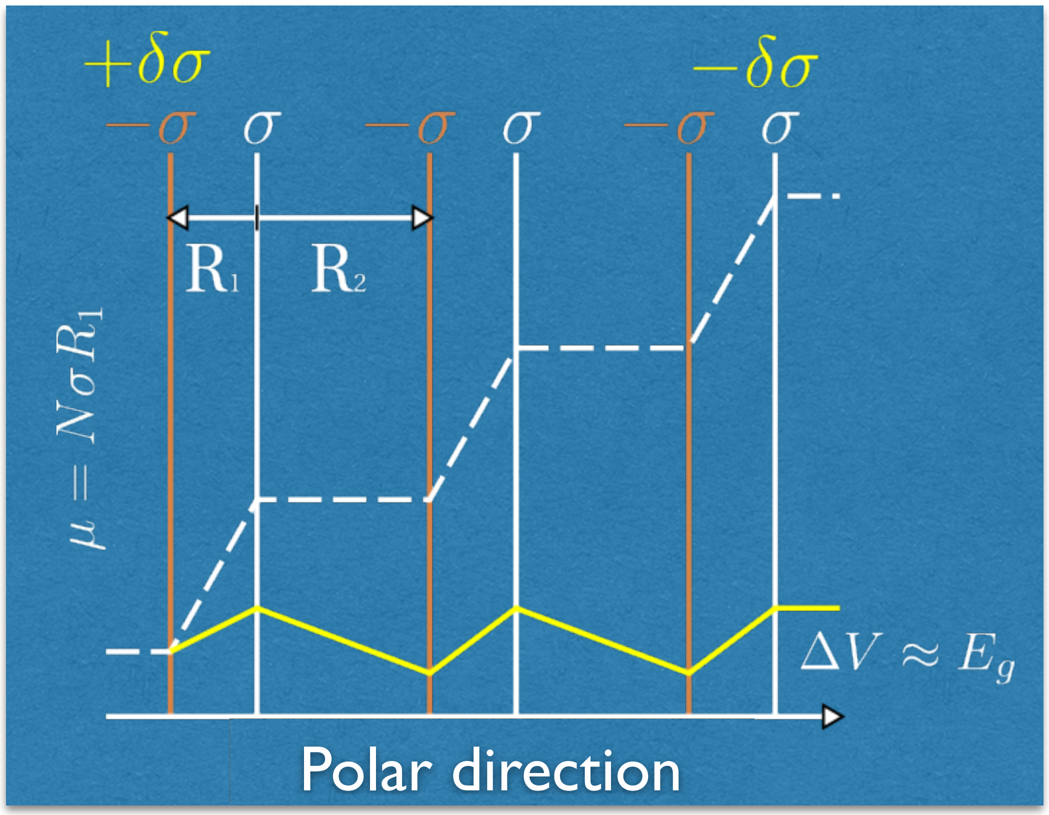
Aluminium nitride

Polar materials and electrostatic divergence, compensation

First order compensation: lateral charge transfer



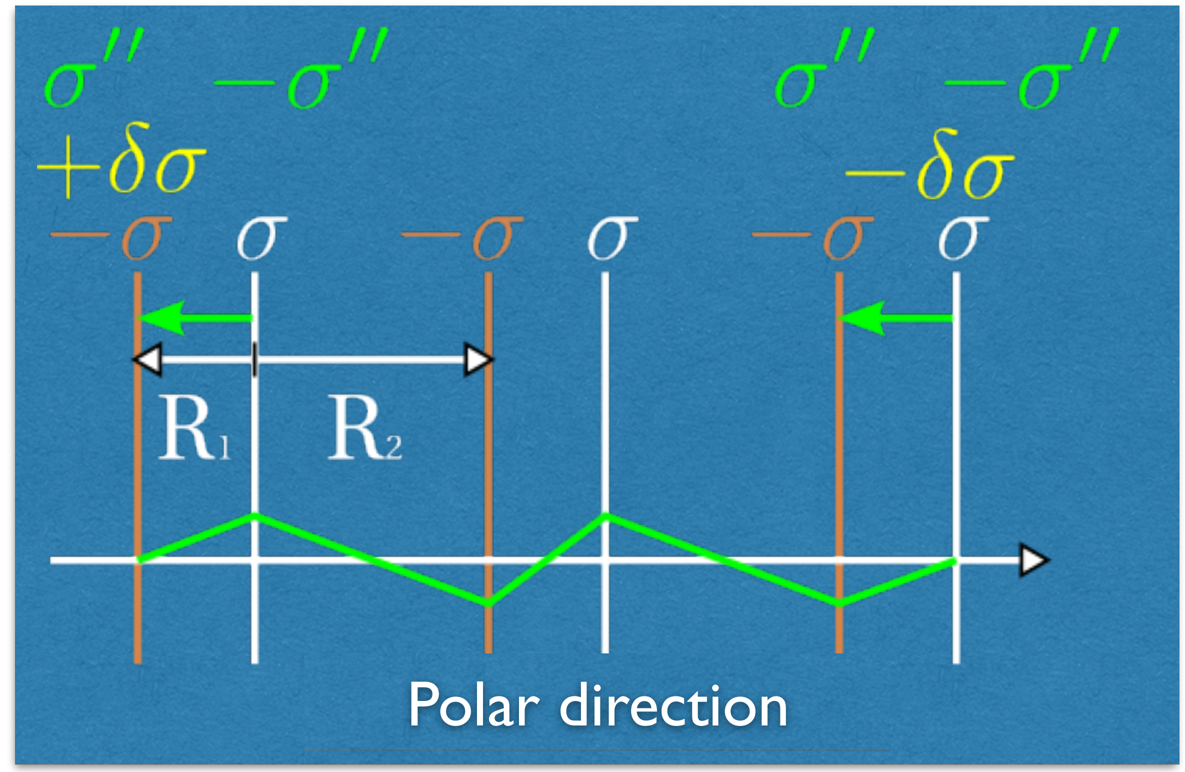
Thermodynamic limit

$$\delta\sigma_\infty = \frac{\sigma R_1}{R_1 + R_2}$$

Wurtzite AlN

$$\delta\sigma = \frac{\sigma}{4}$$

Second order compensation: Relaxation: surface dipoles



$$\sigma'' = \sigma \frac{R_1}{2(R_1 + R_2)}$$

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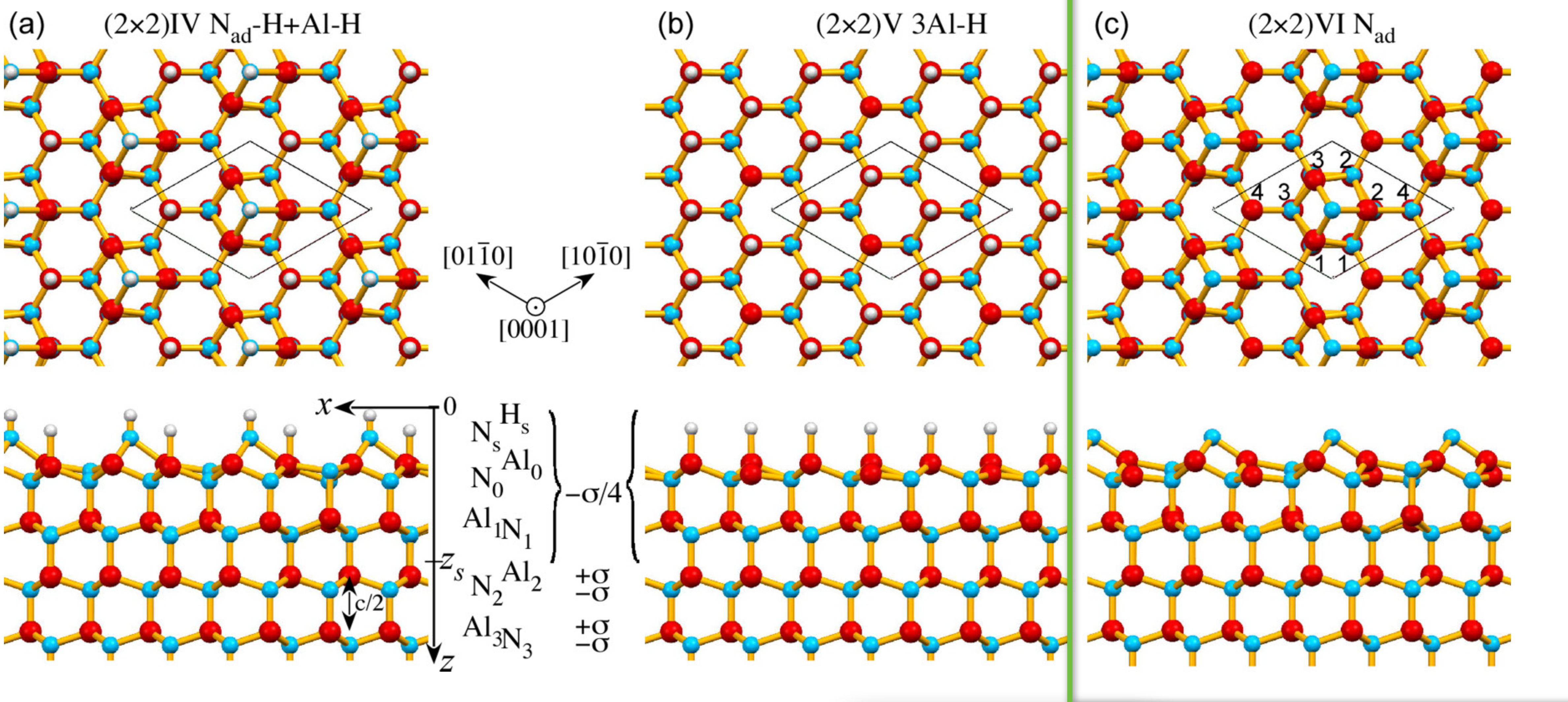
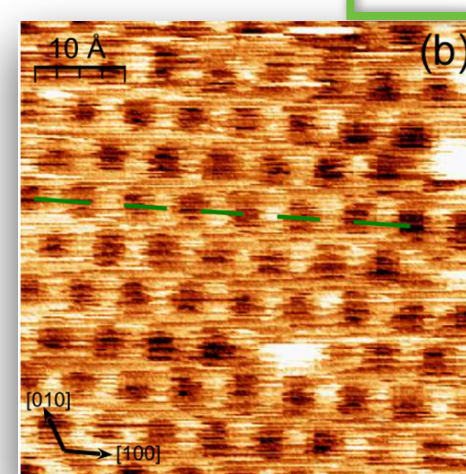
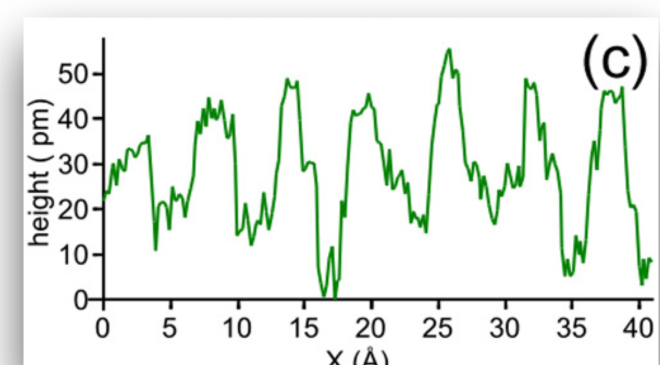
Aluminium nitride







F. Chaumeton *et al.* Phys. Rev. B **94**, 165305 (2016)

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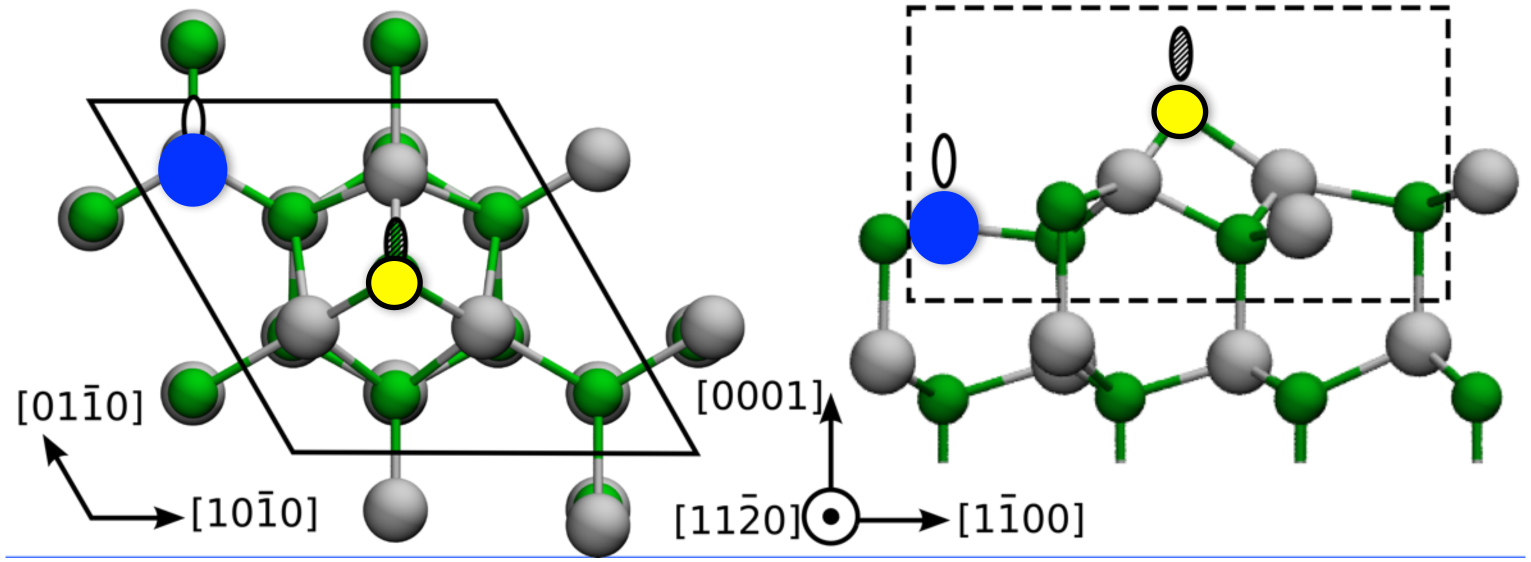
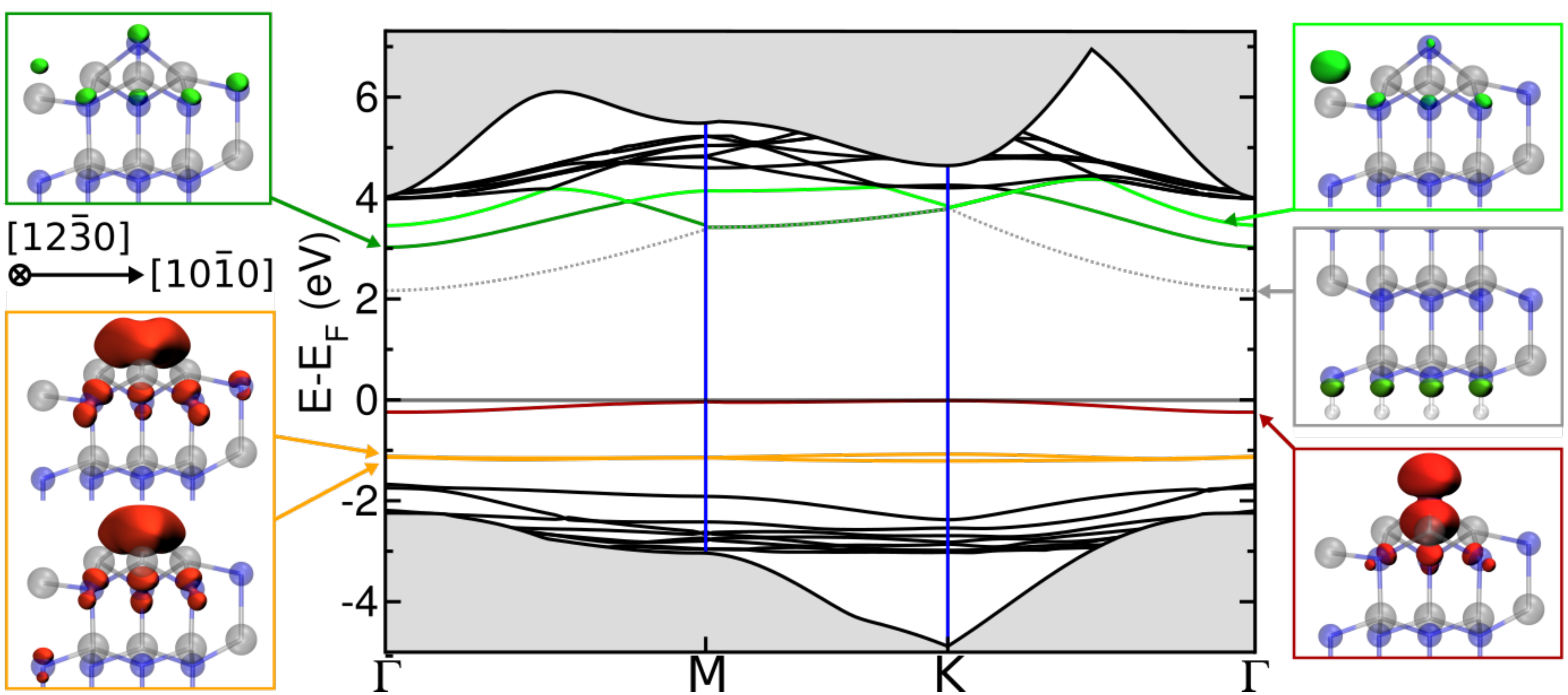
(2×2)-N_{ad} reconstruction

DFT
PBE
HSE06



- Al sp^3
- Al sp^2
- N bulk
- N_{ad}

Donor sites: N^{2-}
Acceptor sites: Al *sp*2



Surface states in the gap

- flat bands (N p_z)
- disperve bands (Al *sp*2)
- two bands

(σ bonds, N p_x and N p_y)

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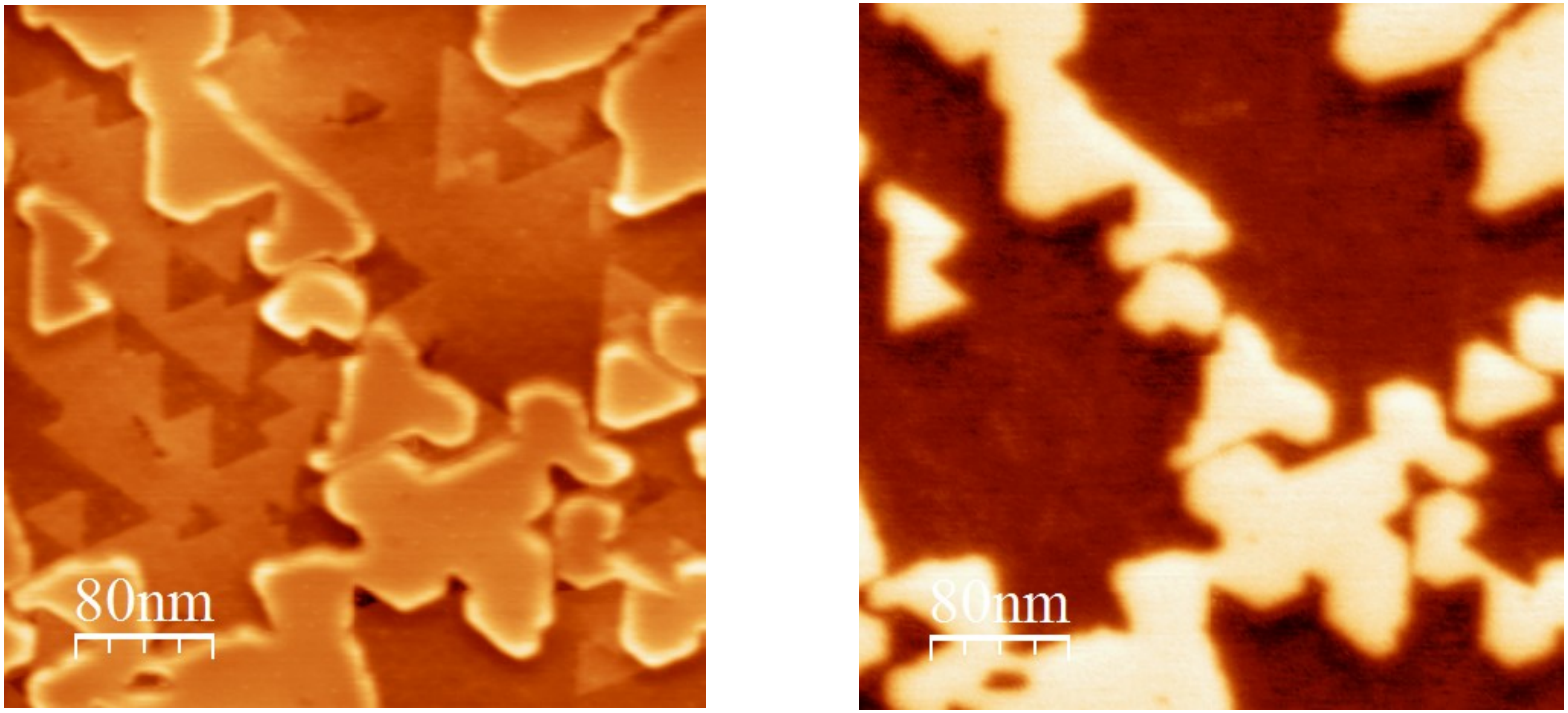
Aluminium nitride with gold



What is the atomic structure of the gold islands?

What is the stabilization mechanism of gold on this insulating substrate?

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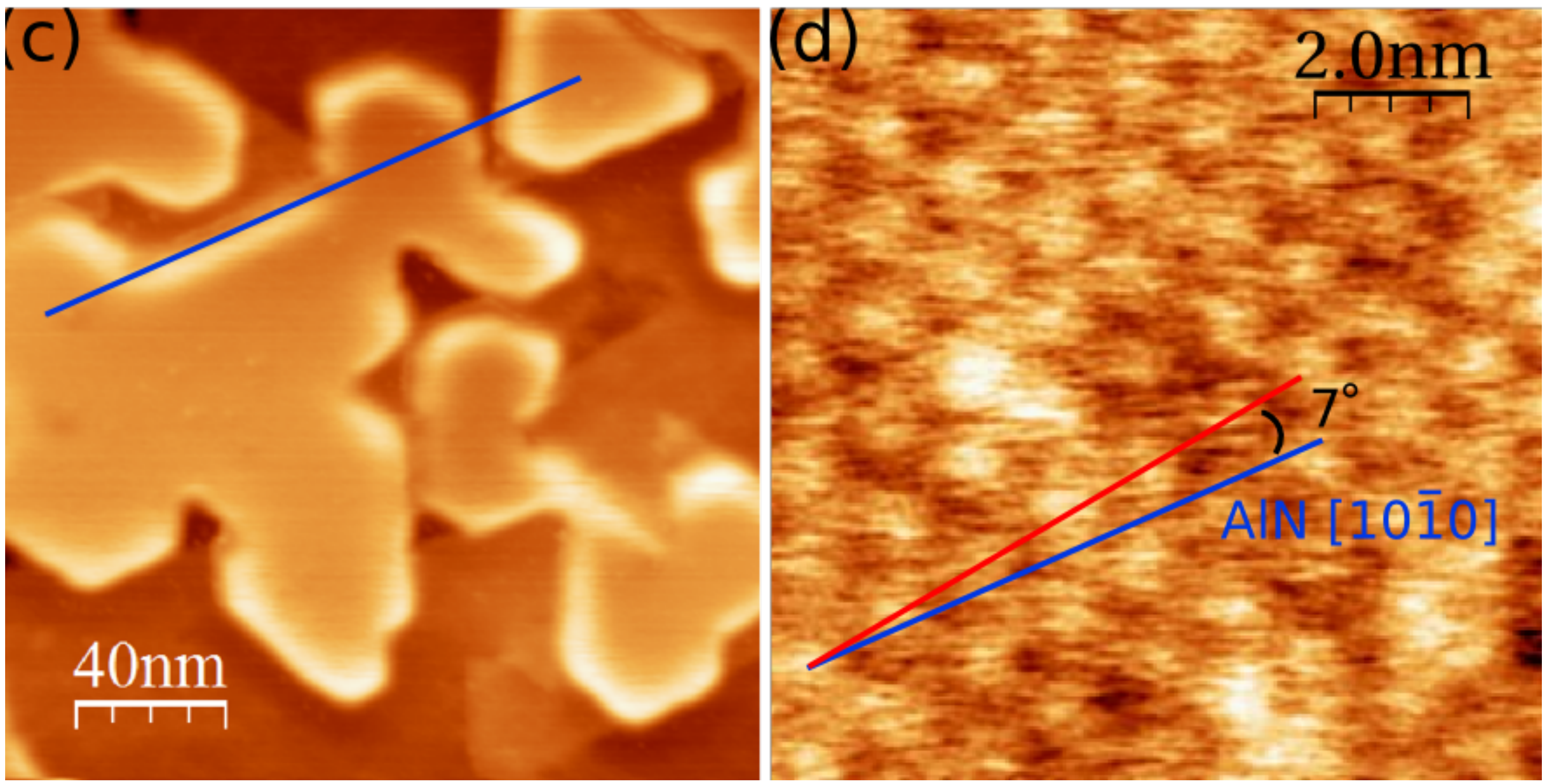
Aluminium nitride with gold

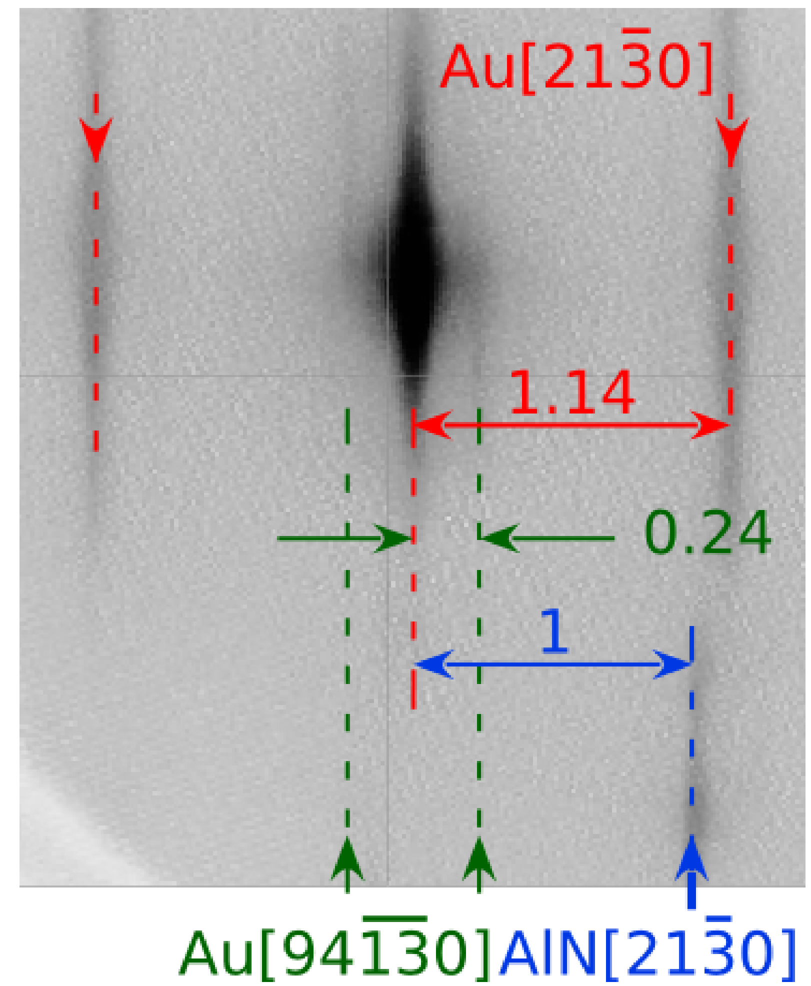
Au 2D monoatomic high islands on AlN(0001)

the experimental structure at **RT**



NC-AFM at RT: observation of an hexagonal pattern with A=2.6 ±0.1 nm and angle close to 7°

In situ RHEED after gold deposition in the MBE



Reconstructed RHEED pattern obtained by summation from 6 to 11° after AlN[21-30]

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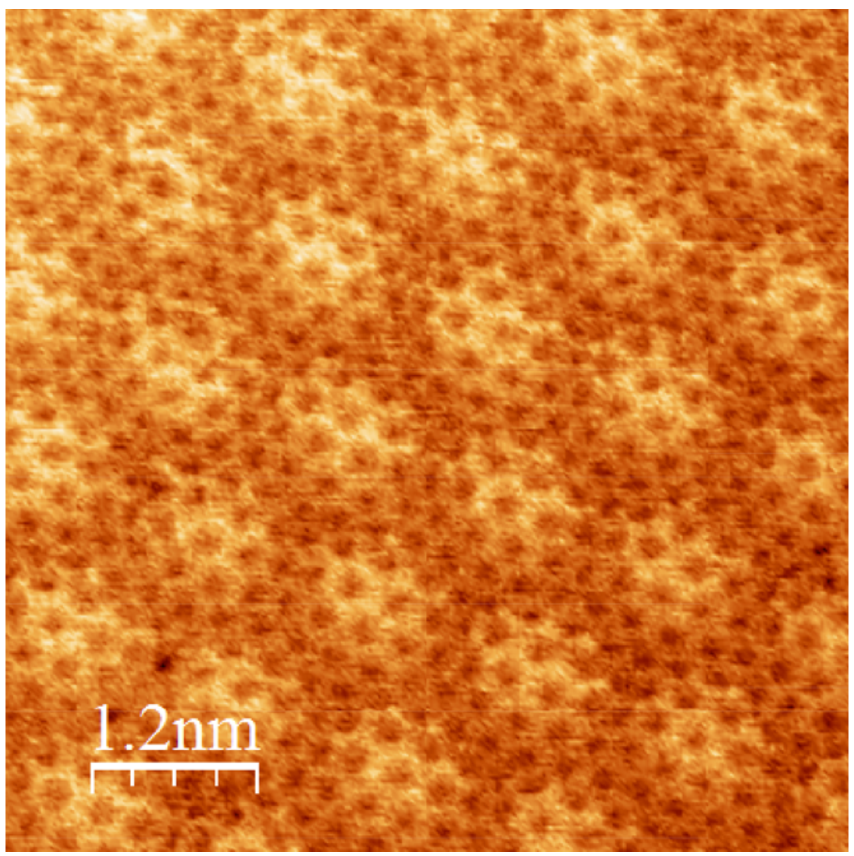
Aluminium nitride with gold

Au 2D monoatomic high islands on AlN(0001): atomically resolved structure at **4K**

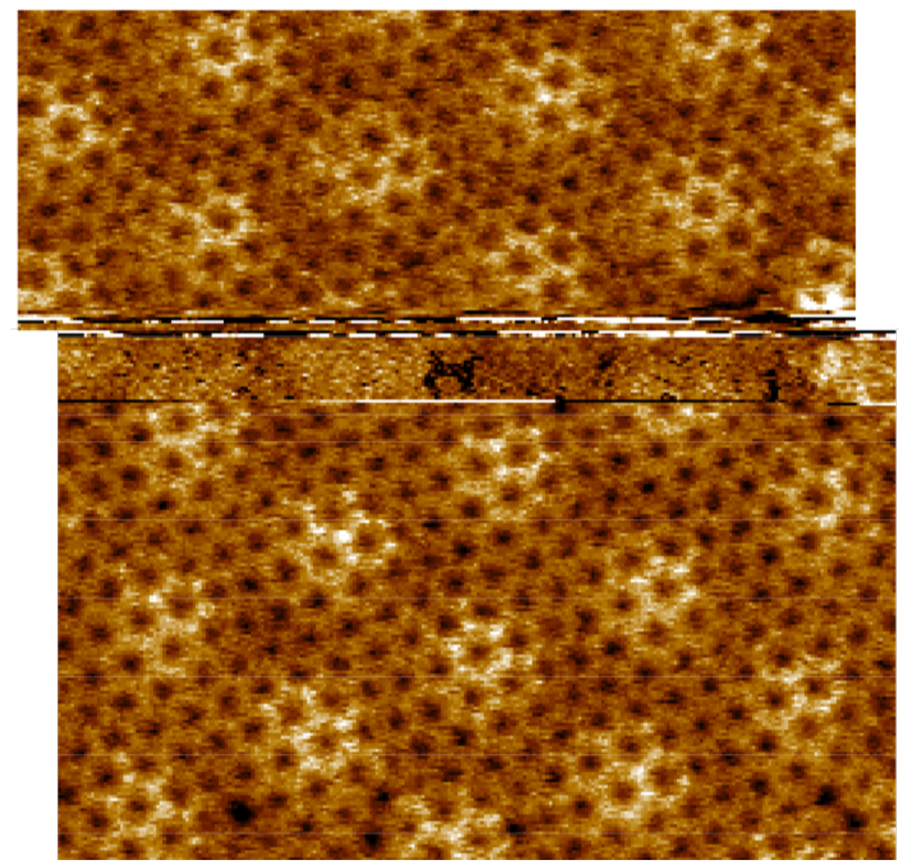
⇒ Sample was transferred under UHV for low temperature characterization with Qplus ncAFM

⇒ Observation of two moiré with atomic resolution

Moiré M1

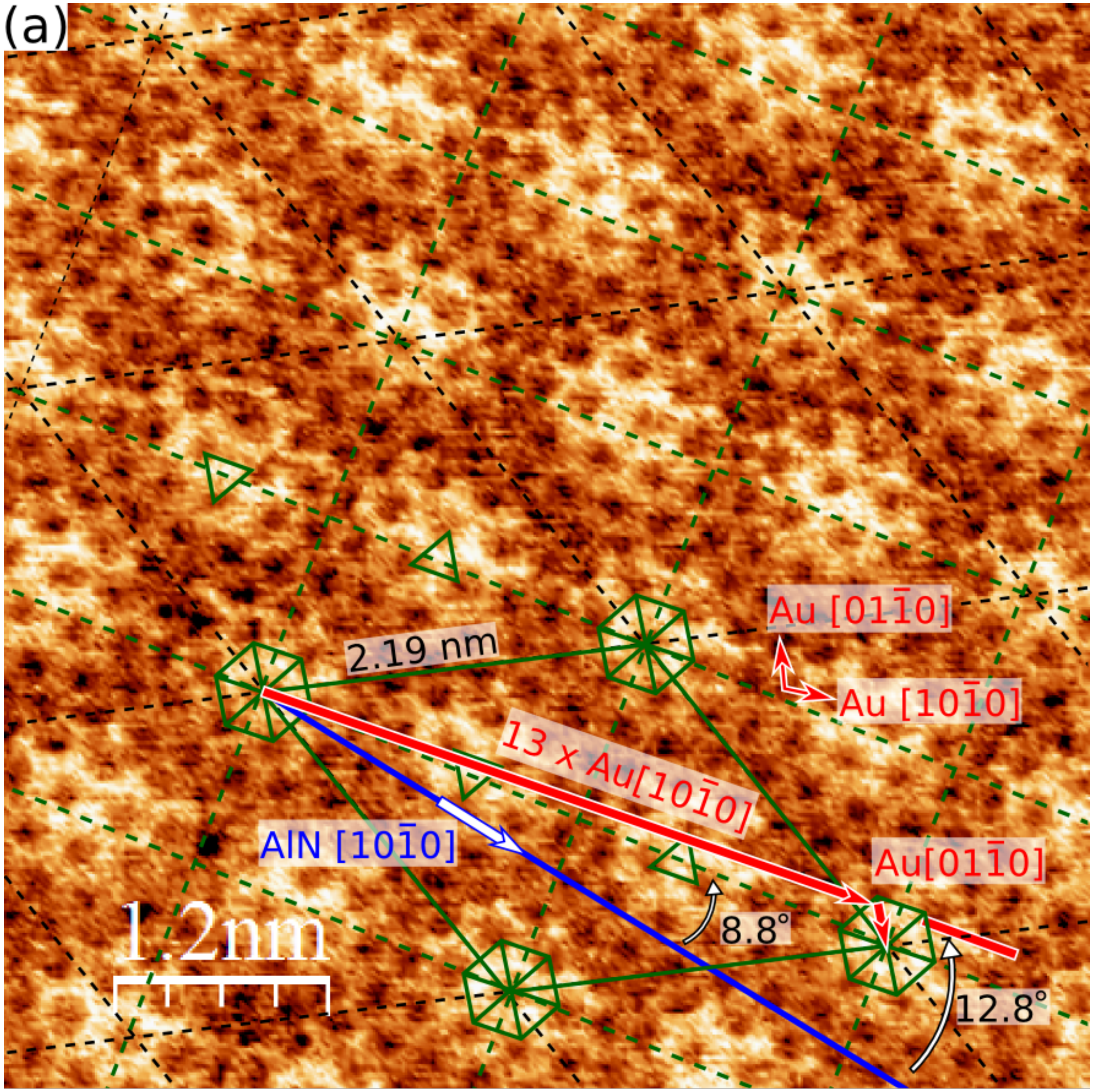


Moiré M2



The topography contrast is reversed which was already observed in Qplus with very small amplitude

Aluminium nitride with gold



EXPERIMENTAL RESULTS

1 - Distance between nearest neighbor :

$d_{Au\text{-}inplane}$ = 2.8 ± 0.1 Å

(gold bulk value : 2.88 Å)

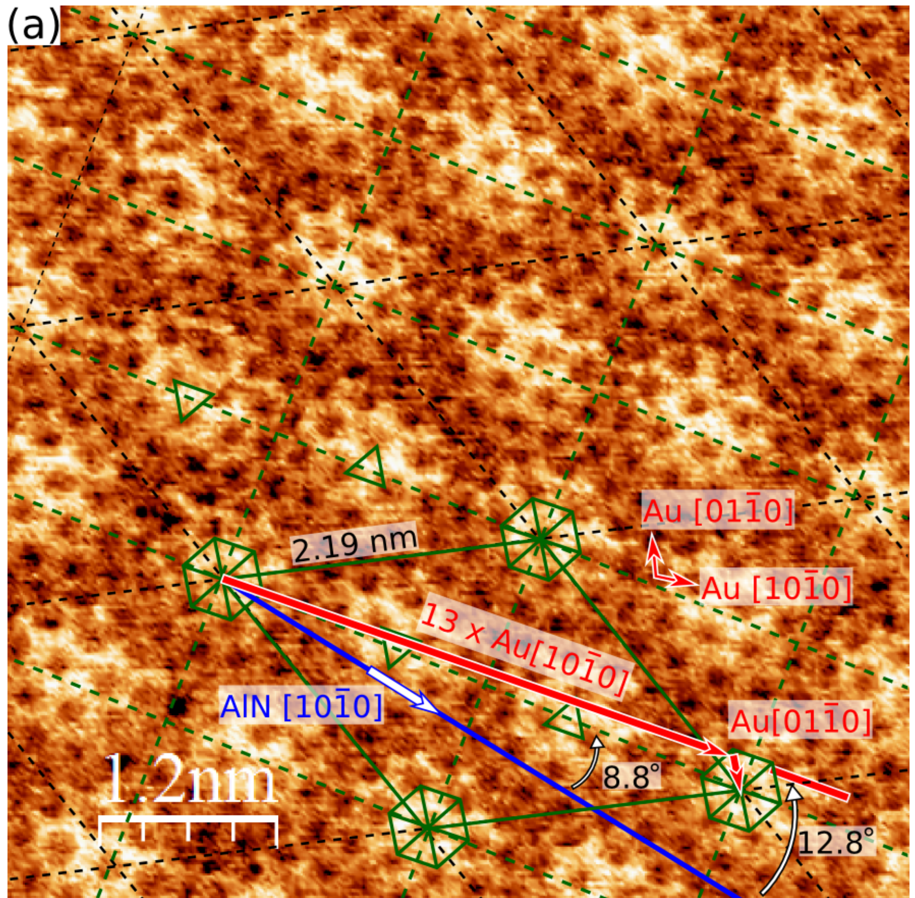
2 - Hexagonal modulation (moiré) :

12.6 ± 0.5 Å, angle 8.8 ± 1°

3 - Supercell parameters :

a = b = 21.9 ± 0.2 Å, alpha = 12.8 ± 1°

Aluminium nitride with gold



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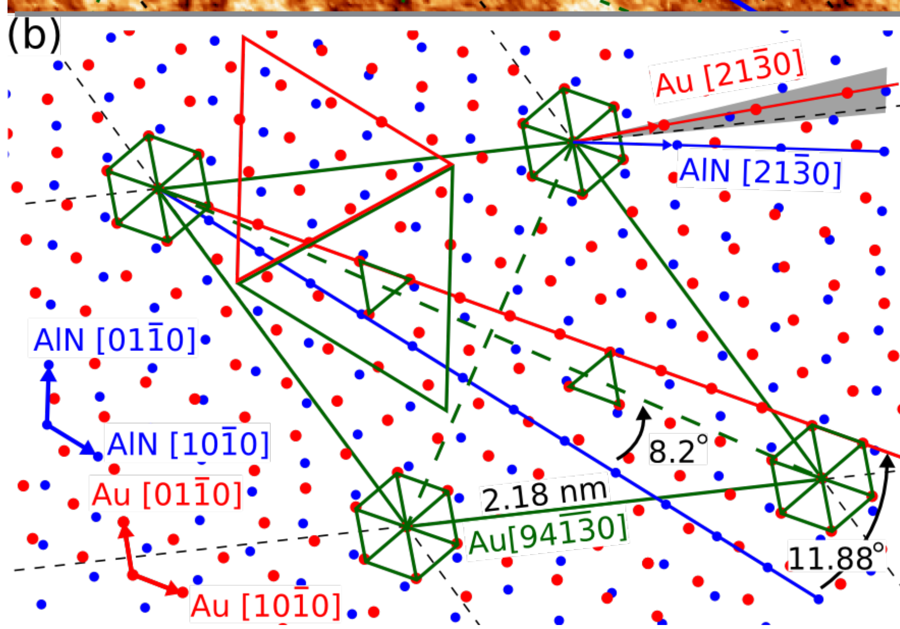
Model for the moiré M1



EPITAXY MODEL RESULTS

1 - $d_{Au\text{-}inplane}$ = 2.79 Å

2 - Hexagonal modulation (moiré) :

12.5 Å, angle 8.21°

3 - Supercell parameters :

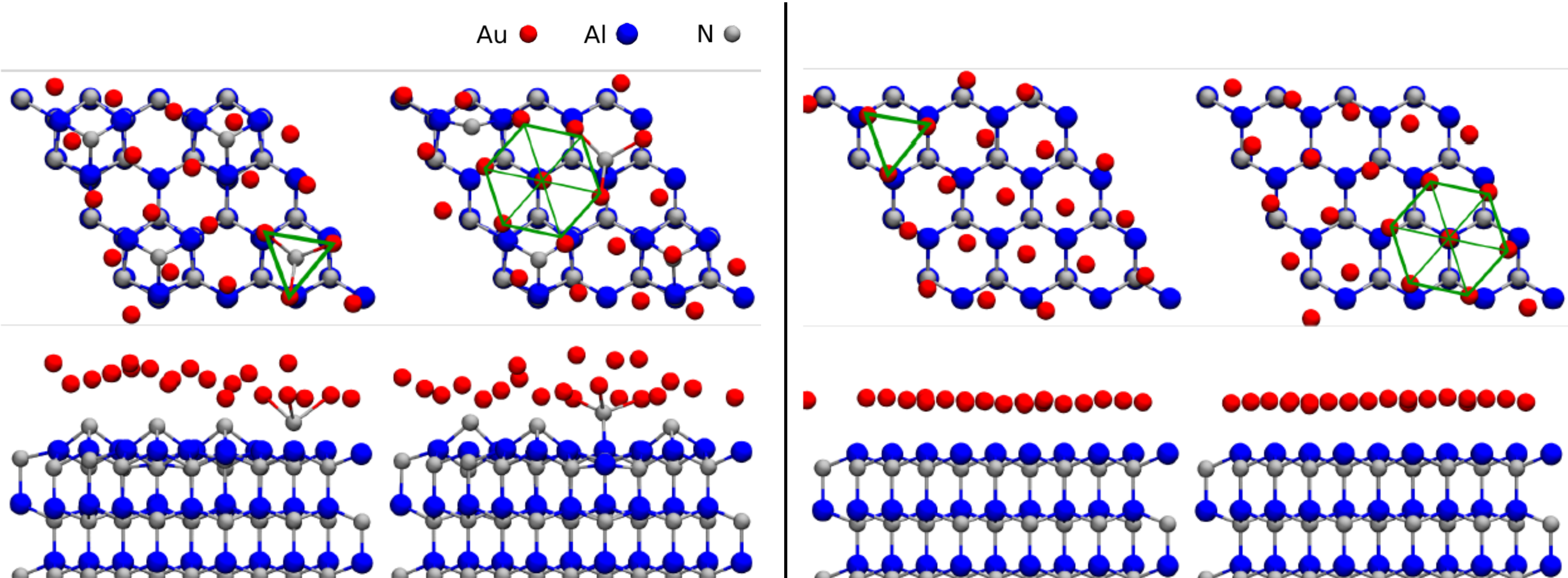
a = b = 21.8 Å, alpha = 11.88°

4 - Epitaxial relation :

Au[94$\bar{13}$0] // AlN[85$\bar{13}$0]

Aluminium nitride with gold

DFT calculations: model on (2x2)-N_{ad} and bare AlN(0001)



M1 — E=-1797.59 eV

M1-h — E=-1797.63 eV

U1 — E=-1772,86 eV

U1-h — E=-1772,86 eV

< 25 eV

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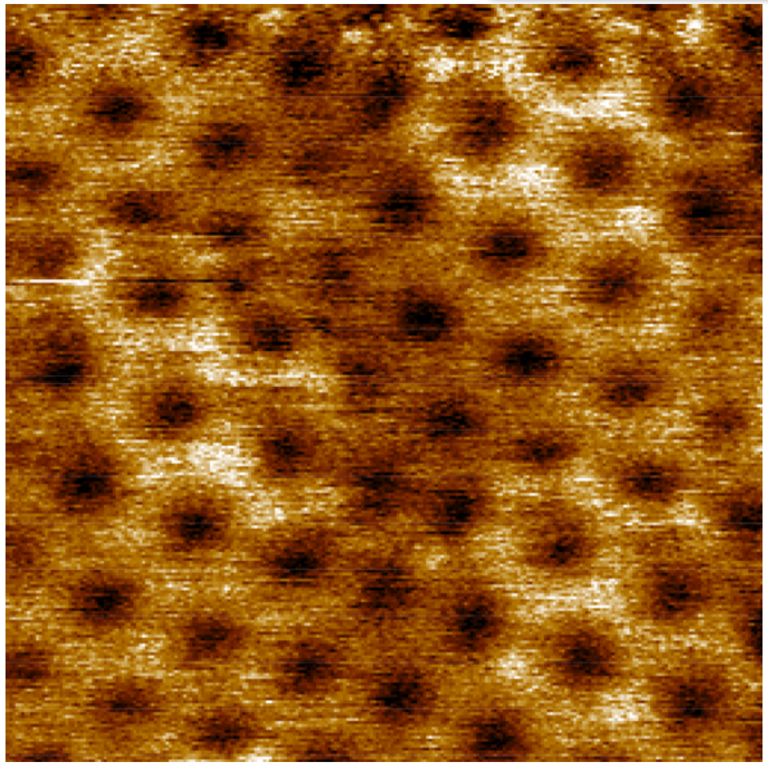
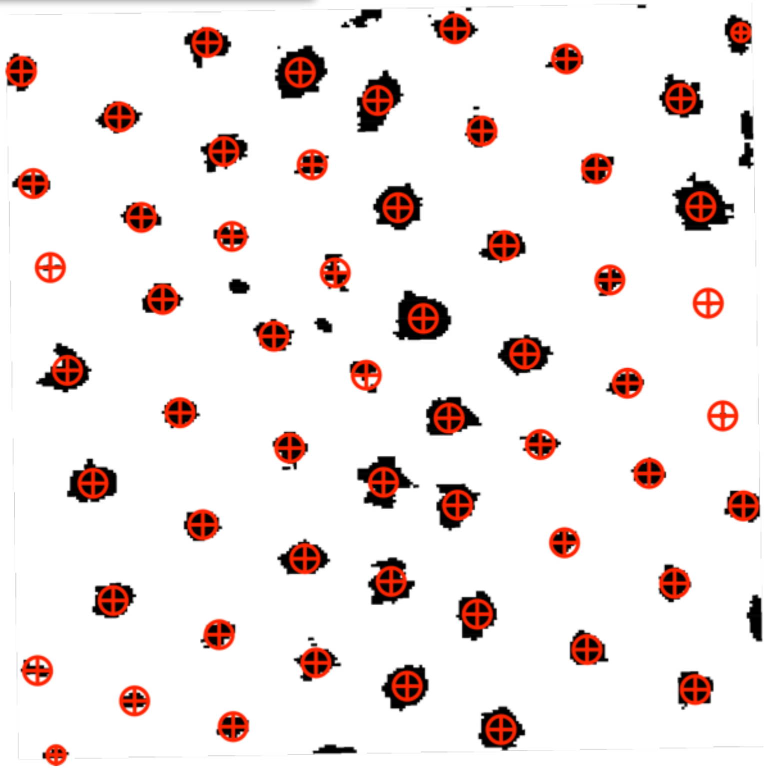
Aluminium nitride with gold



extracting position →

Calculate $d_{Au\text{-}inplane}$ values



Experiment and DFT comparison for $d_{Au\text{-}inplane}$

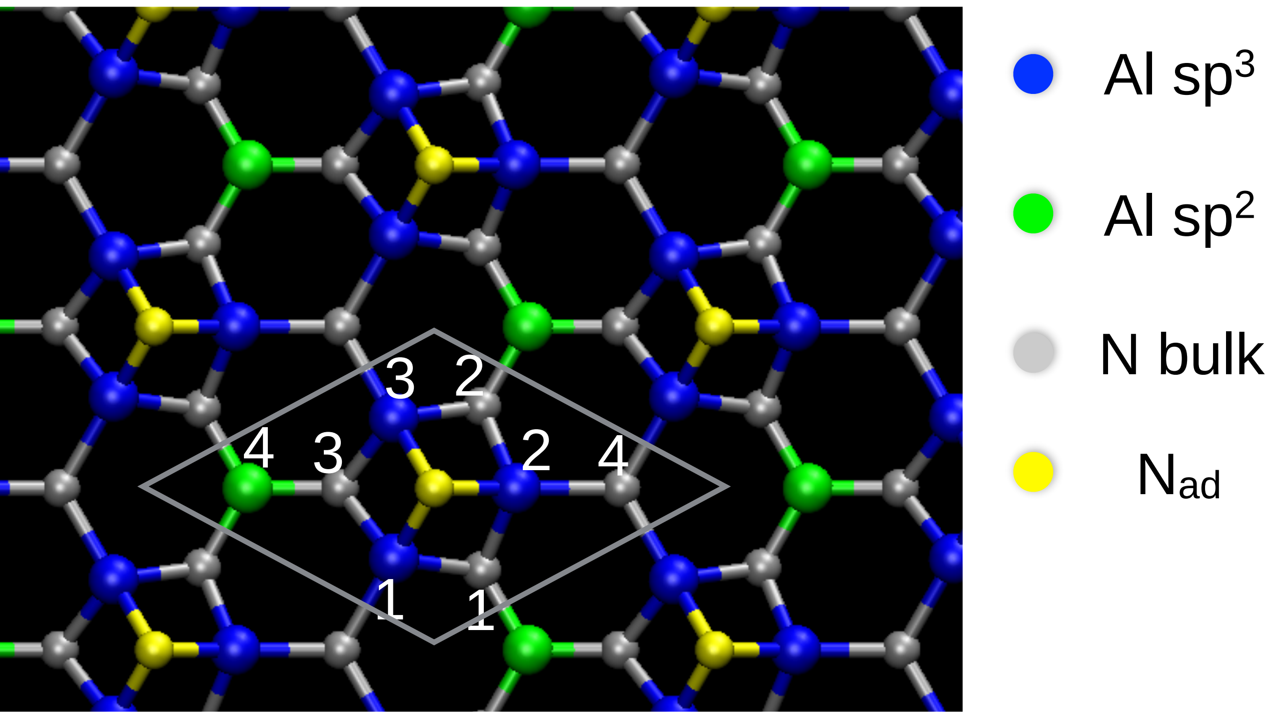
$d_{Au\text{-}inplane}$	Experiment	DFT-Au-U1t	DFT-Au-M1t
Minimum (Å)	2.01	2.70	2.44
Maximum (Å)	3.16	2.77	3.15
Mean (Å)	2.74	2.73	2.74
RMS	2.76	2.73	2.75
Std Deviation (Å)	0.255	0.0166	0.153

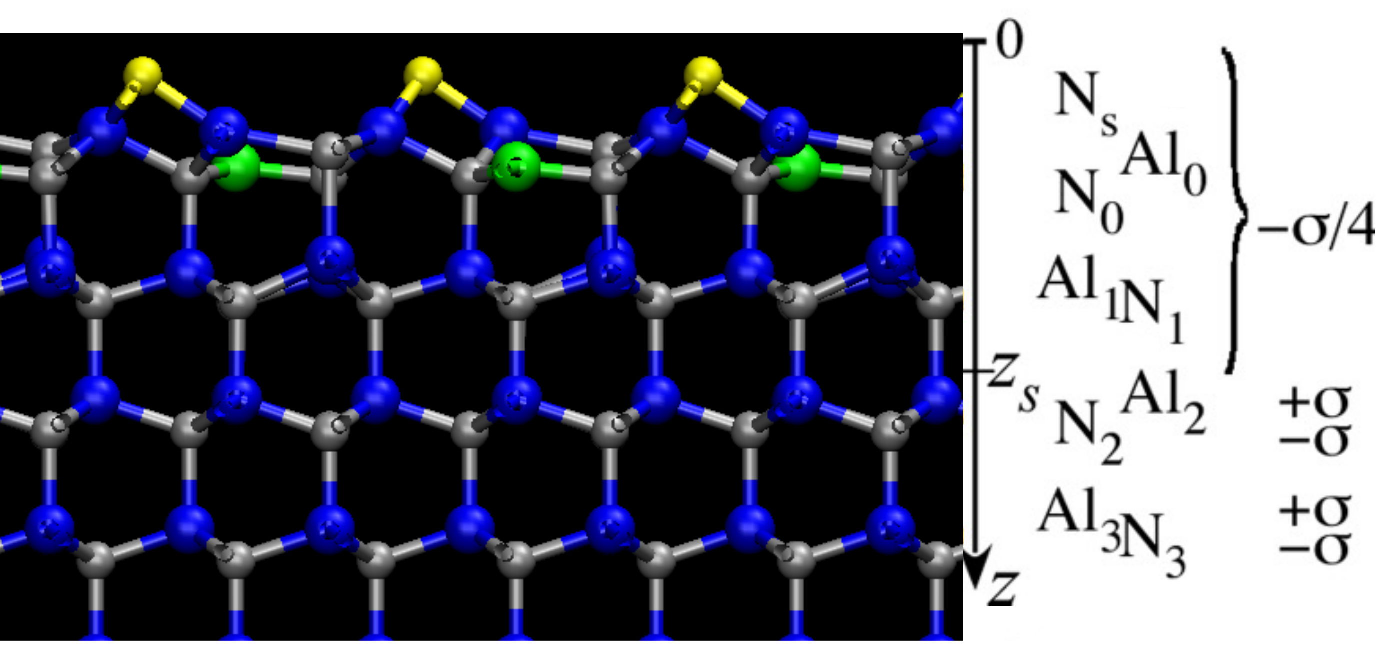
Dispersion matching GOOD

CONCLUSION: the N atoms of the (2x2)-N_{ad} stay below the Au layer

Stabilization mechanism of the Au on AlN(2x2)-N_{ad}

1 - the surface charge on the 2H-AlN(0001) (2x2)-N_{ad} surface





For 2H AlN(0001) polar direction :

$$\sigma_S = -\sigma/4$$

Bader charge analysis

(in |e| and |e| per (1x1) unit surface for σ_S)

Atom	1	2	3	4	σ_S
N_s	−2.201				−0.550
Al_0	2.322	2.322	2.322	2.348	
N_0	−2.386	−2.385	−2.385	−2.305	−0.587
Al_1	2.388	2.388	2.388	2.354	
N_1	−2.381	−2.381	−2.381	−2.405	−0.595
Al_2	2.387	2.387	2.387	2.386	
N_2	−2.387	−2.387	−2.387	−2.388	−0.595

$$\sigma = 2.387 \Rightarrow \sigma_S = -\sigma/4 = -0.597$$

The additional N atom is responsable of 90 % of the surface charge.

F. Chaumeton et al., PHYSICAL REVIEW B **94**, 165305 (2016)

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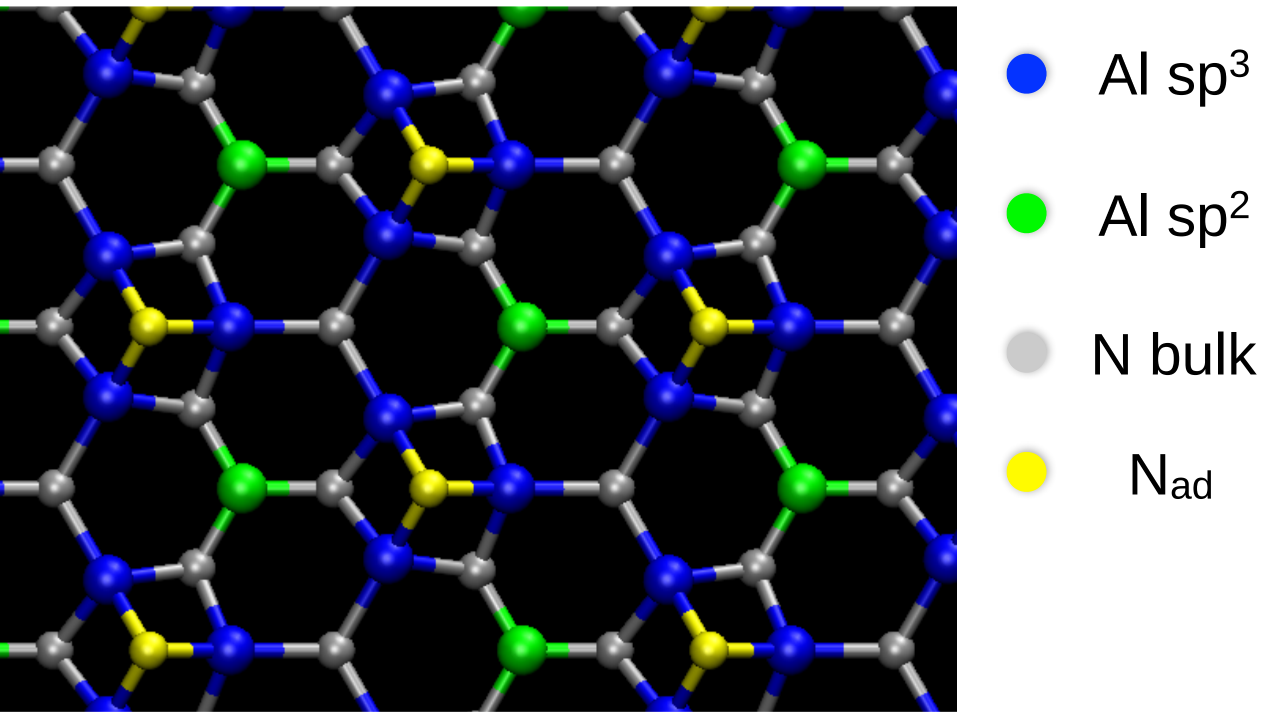

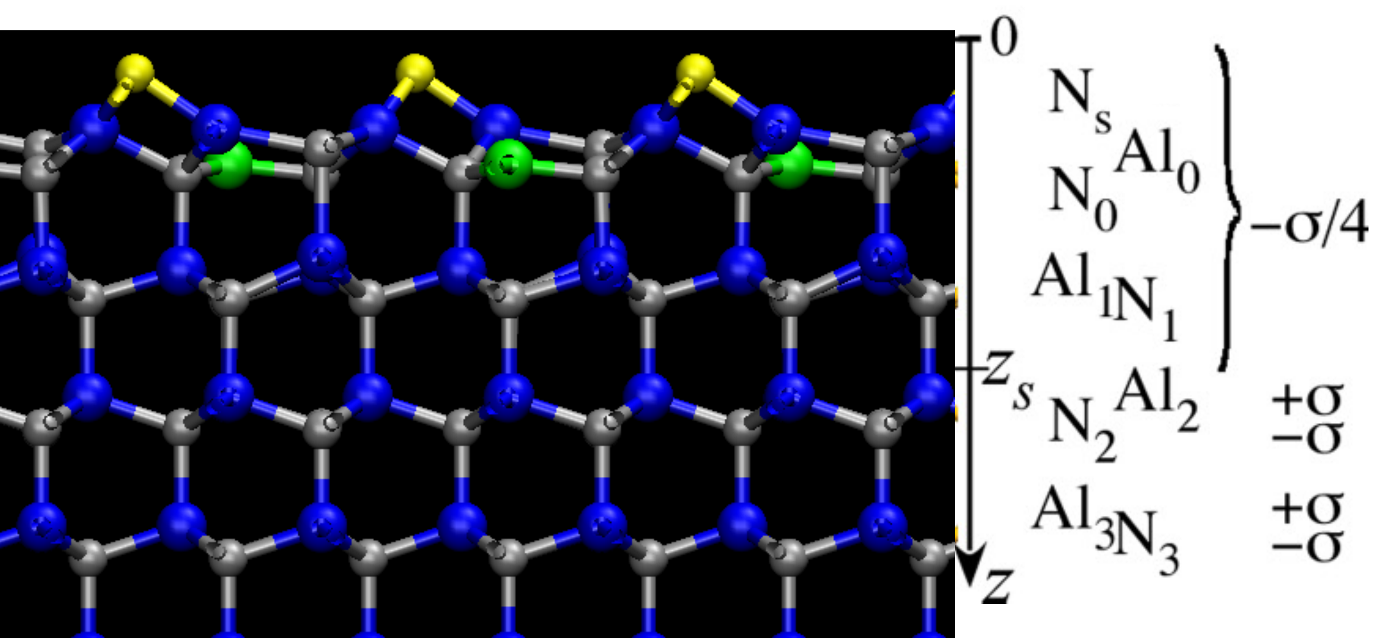

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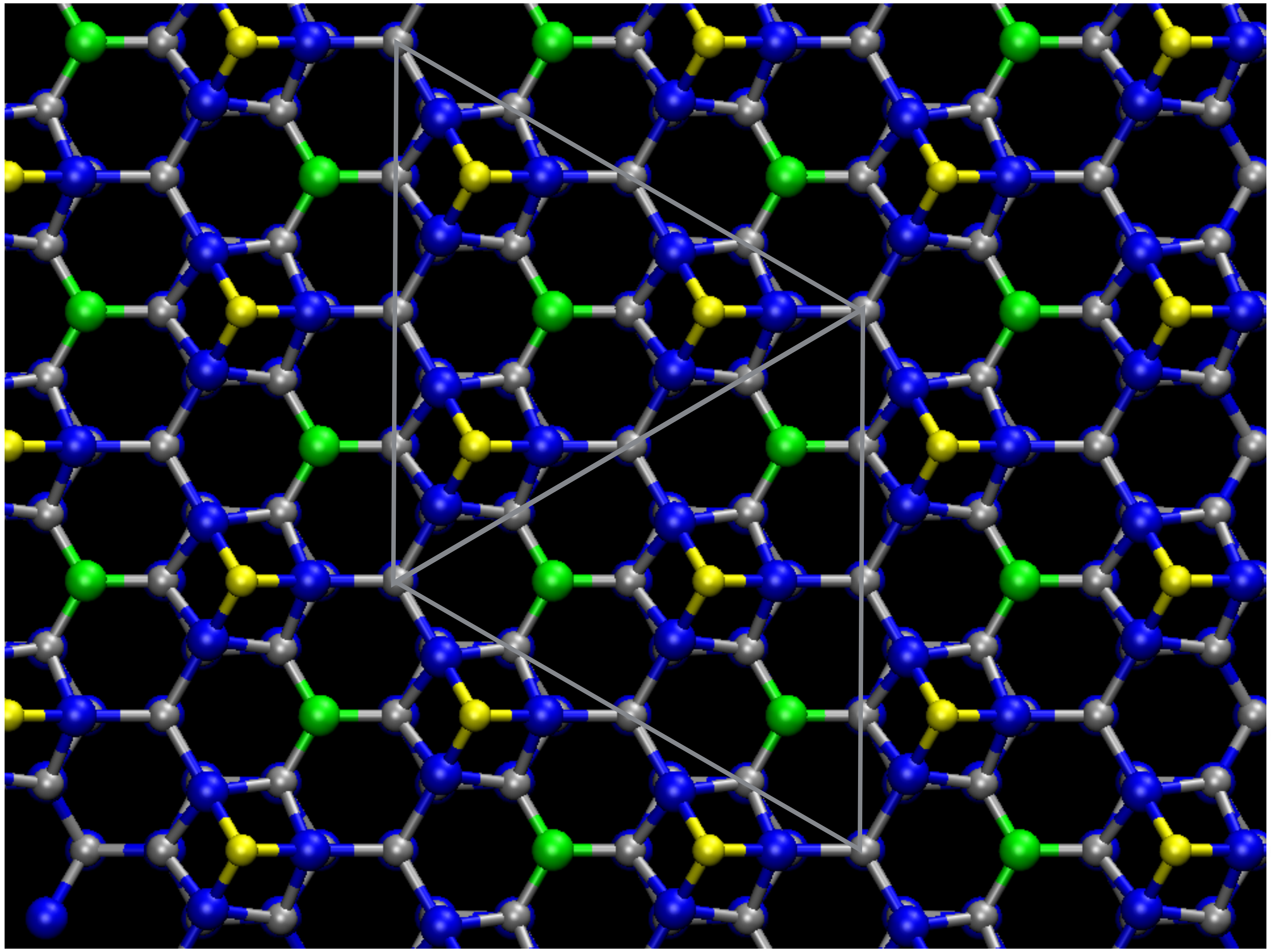
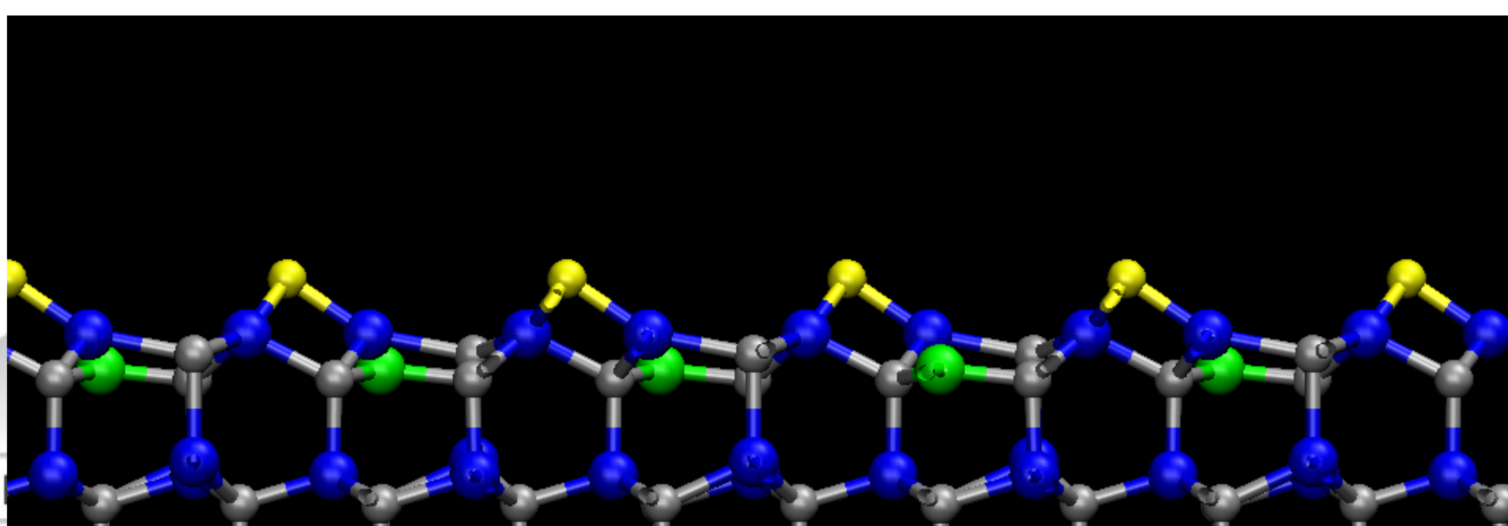
$$\sigma = 2.387 \Rightarrow \sigma_S = -\sigma/4 = -0.597$$

The additional N atom is responsable of 90 % of the surface charge.

CHARGE TRANSFER to the Au layer ?

Stabilization mechanism of the Au on AlN(2x2)-N_{ad}





2 - Bonds and charge transfer on the Au layer

DFT cell: AlN(0001) (4x4) with the reconstruction (2x2)N_{ad}
+
21 Au atoms

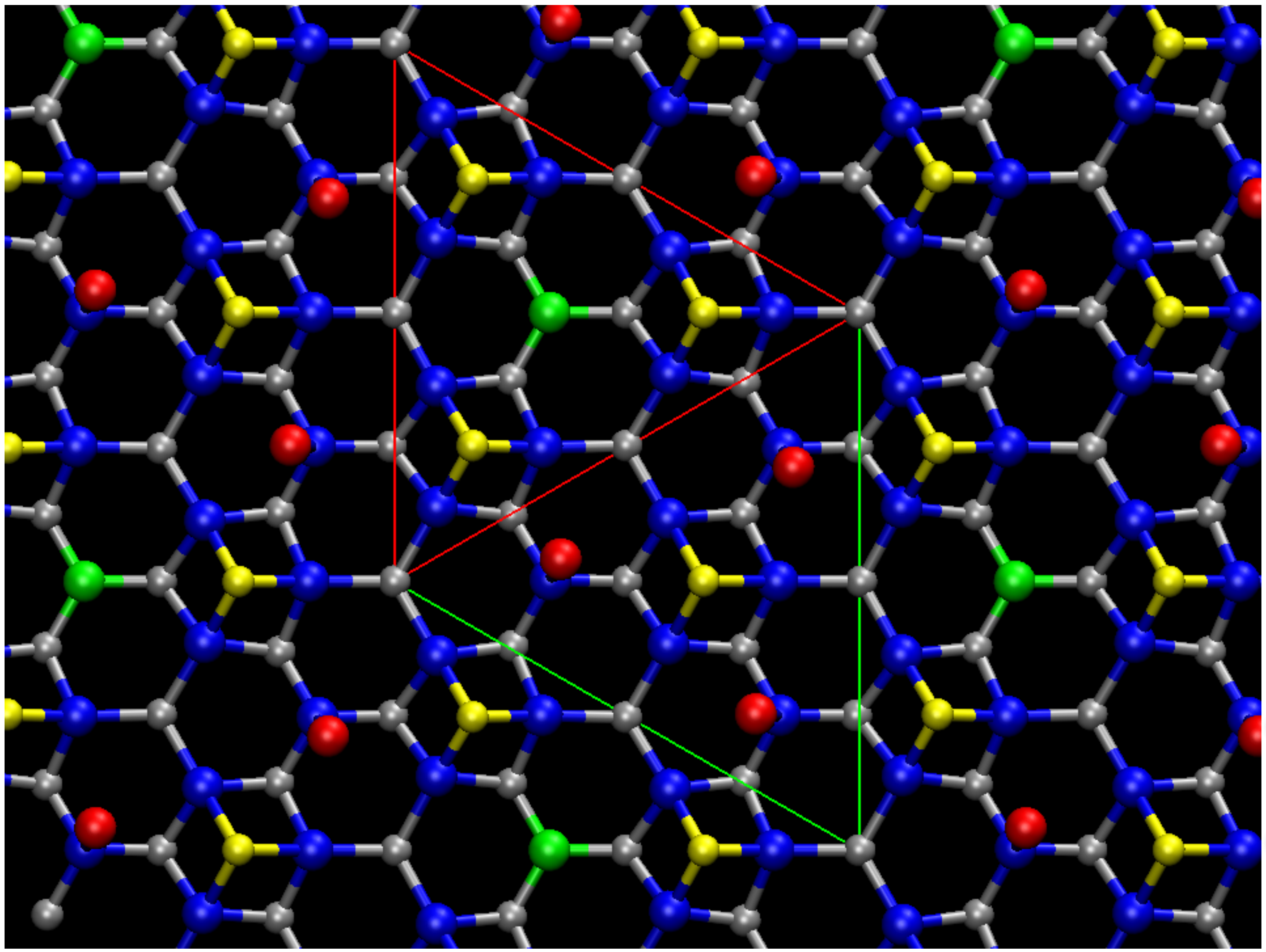
Due to the three-fold symmetry:
7 groups of
3 Au atoms

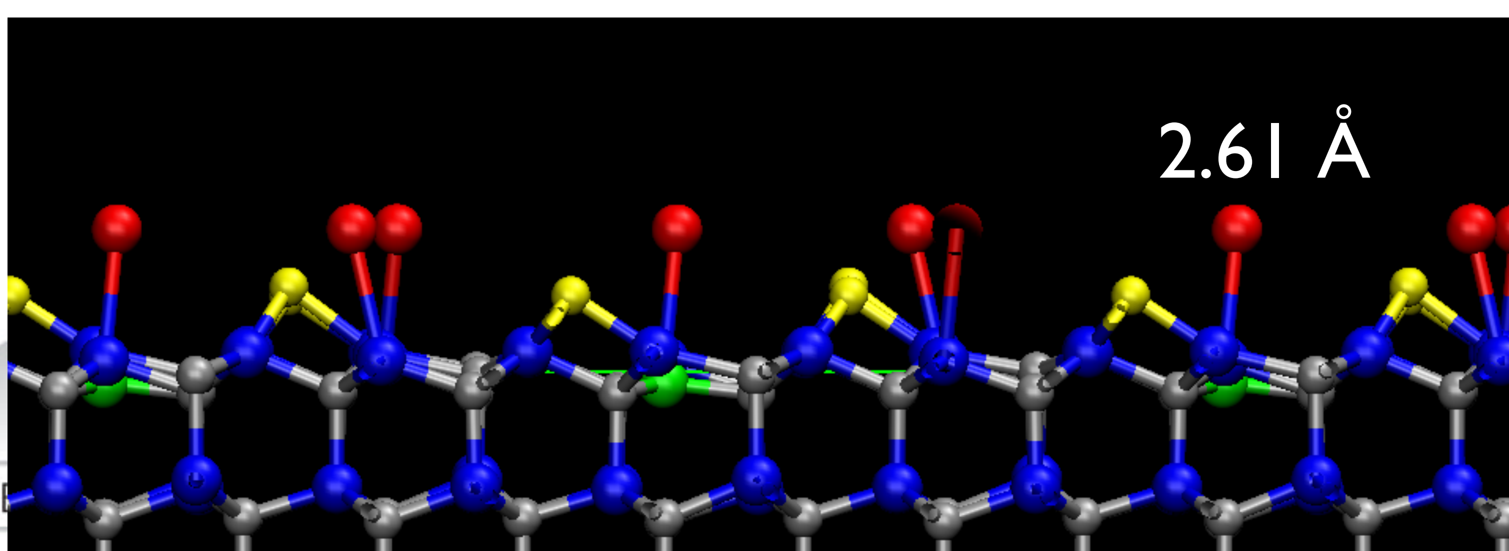
- Al sp^3
- Al sp^2 (acc)
- N bulk
- N_{ad} (don)

Stabilization mechanism of the Au on AlN(2x2)-N_{ad}

2 - Bonds and charge transfer on the Au layer

Due to the three-fold symmetry:
7 groups of 3 Au atoms

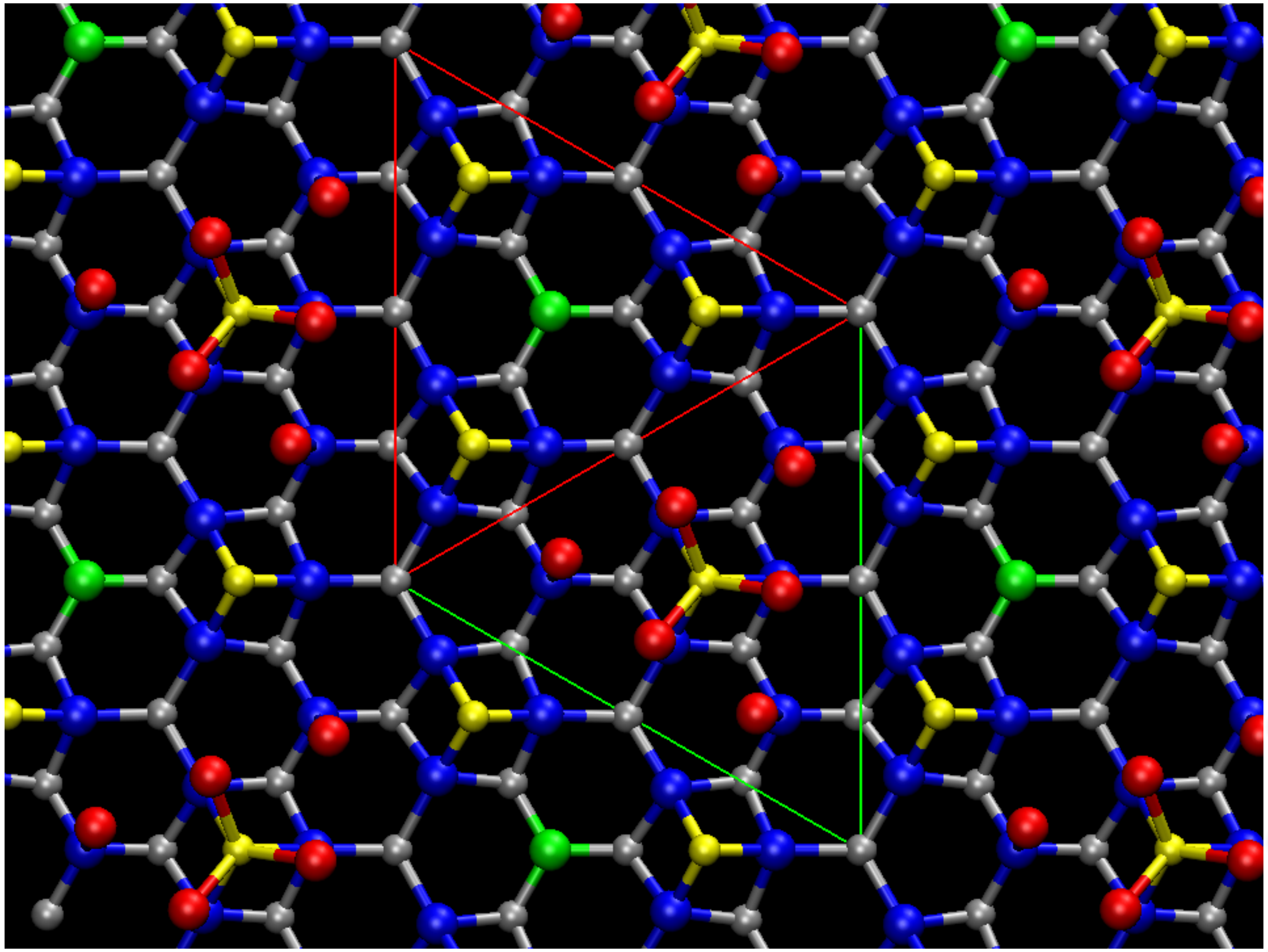


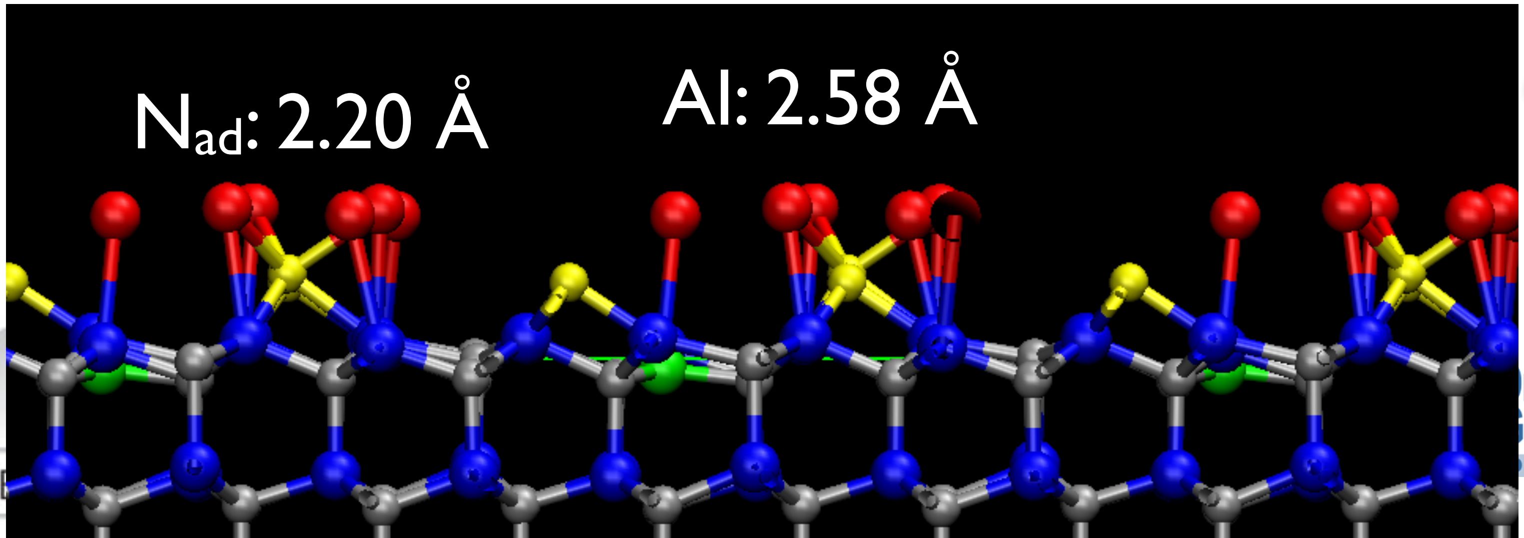


- Al sp^3
- Al sp^2
- N bulk
- N_{ad}

Group	Bonds with the AlN surface	Q_b |e|
1	Al sp^2	- 0.48
2		
3		
4		
5		
6		
7		

Stabilization mechanism of the Au on AlN(2x2)-N_{ad}





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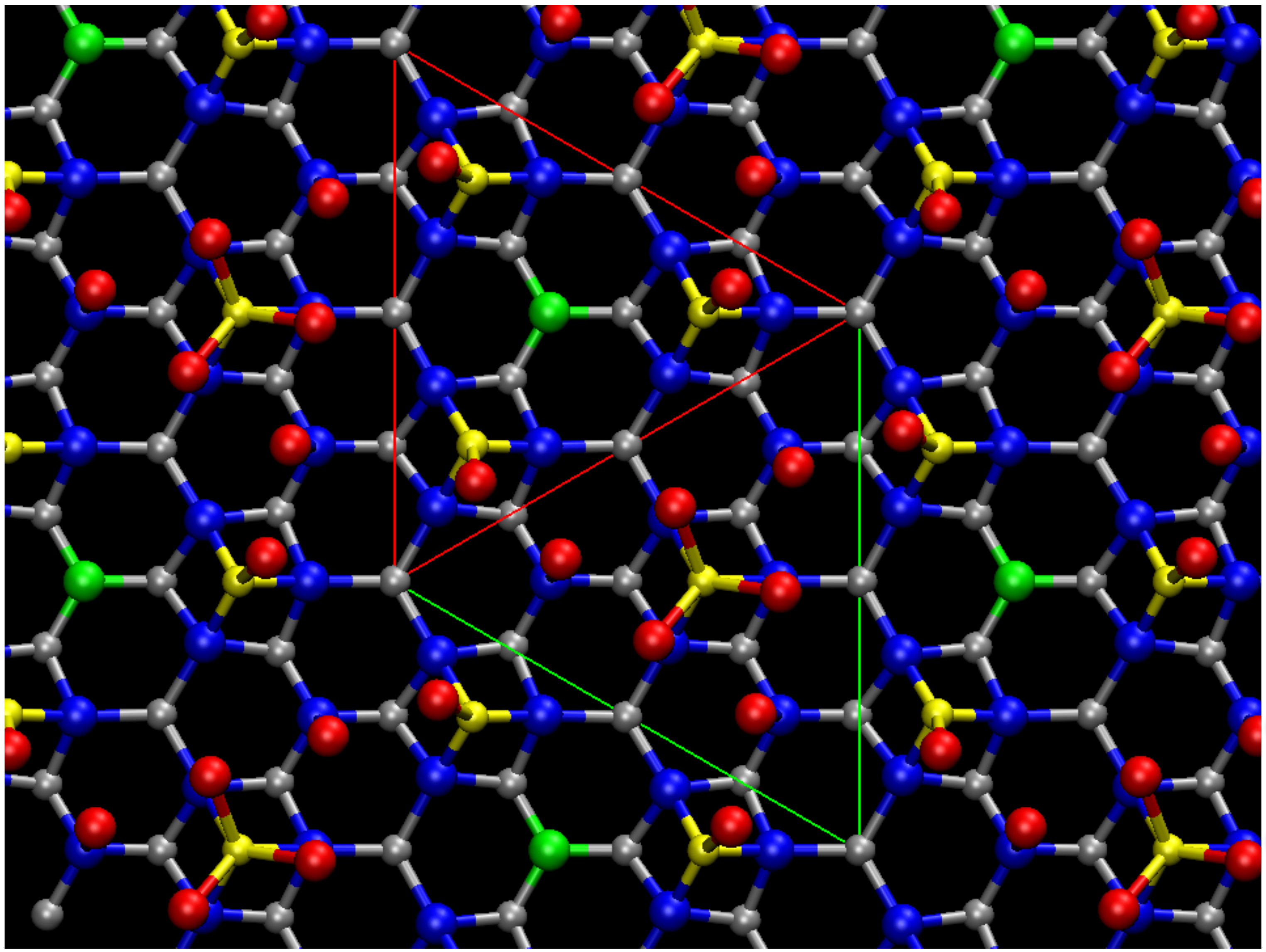
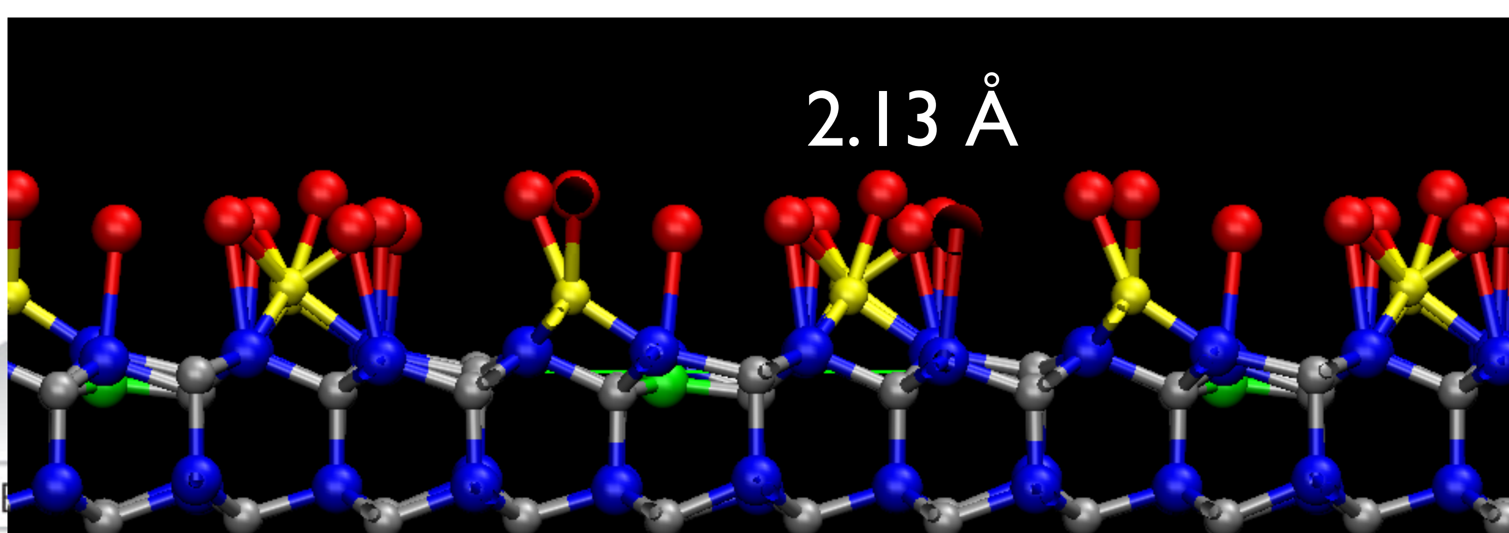
Due to the three-fold symmetry:
7 groups of 3 Au atoms

- Al sp^3
- Al sp^2
- N bulk
- N_{ad}

Group	Bonds with the AlN surface	Q_b lel
1	Al sp^2	- 0.48
2	Al + N_{ad}	- 0.13
3		
4		
5		
6		
7		

Stabilization mechanism of the Au on AlN(2x2)-N_{ad}





- Al sp^3
- Al sp^2
- N bulk
- N_{ad}

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Due to the three-fold symmetry:
7 groups of 3 Au atoms

Group	Bonds with the AlN surface	Q_b |e|
1	Al sp^2	- 0.48
2	Al + N_{ad}	- 0.13
3	N_{ad}	0.1
4		
5		
6		
7		

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2 - Bonds and charge transfer on the Au layer

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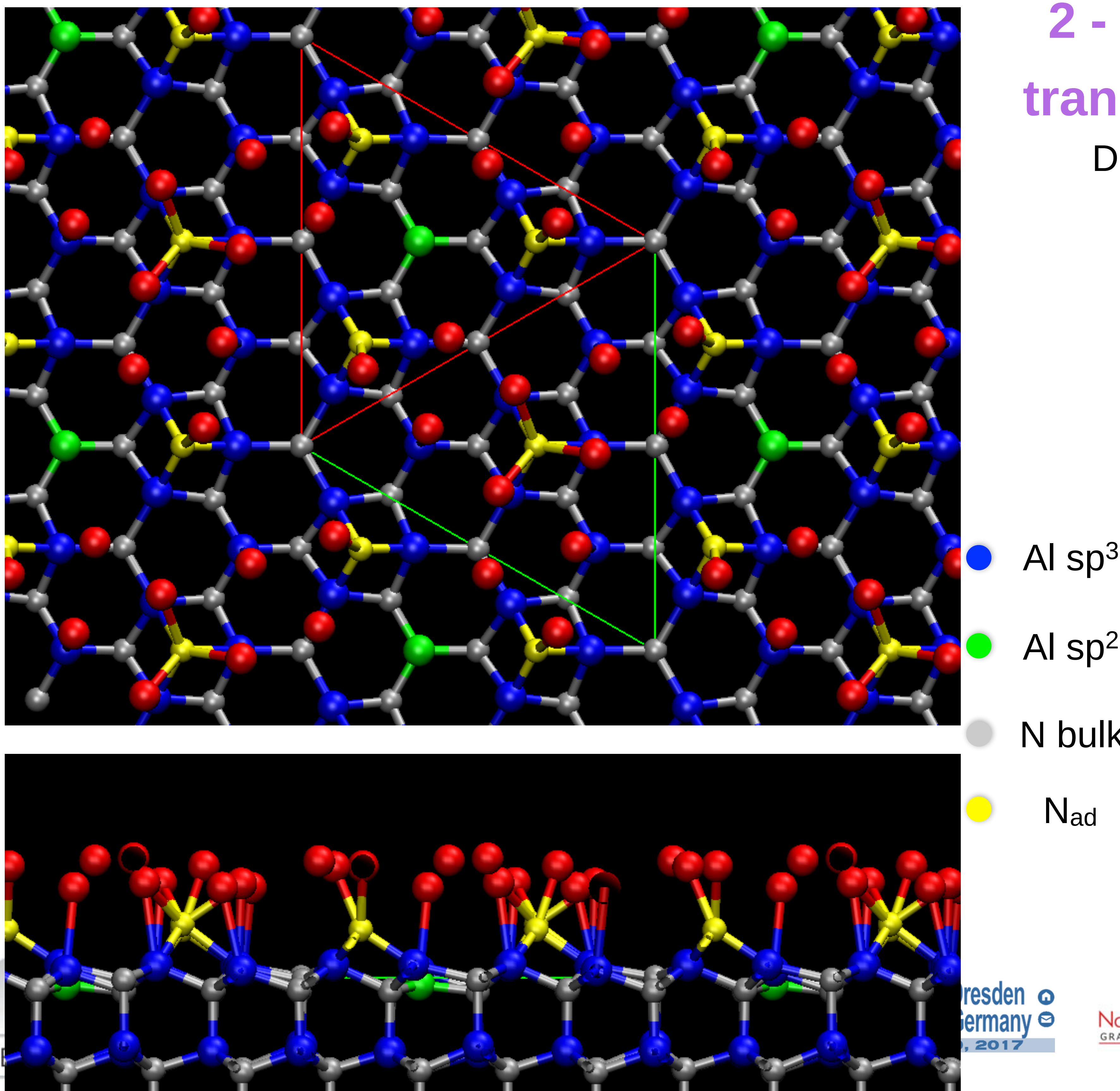
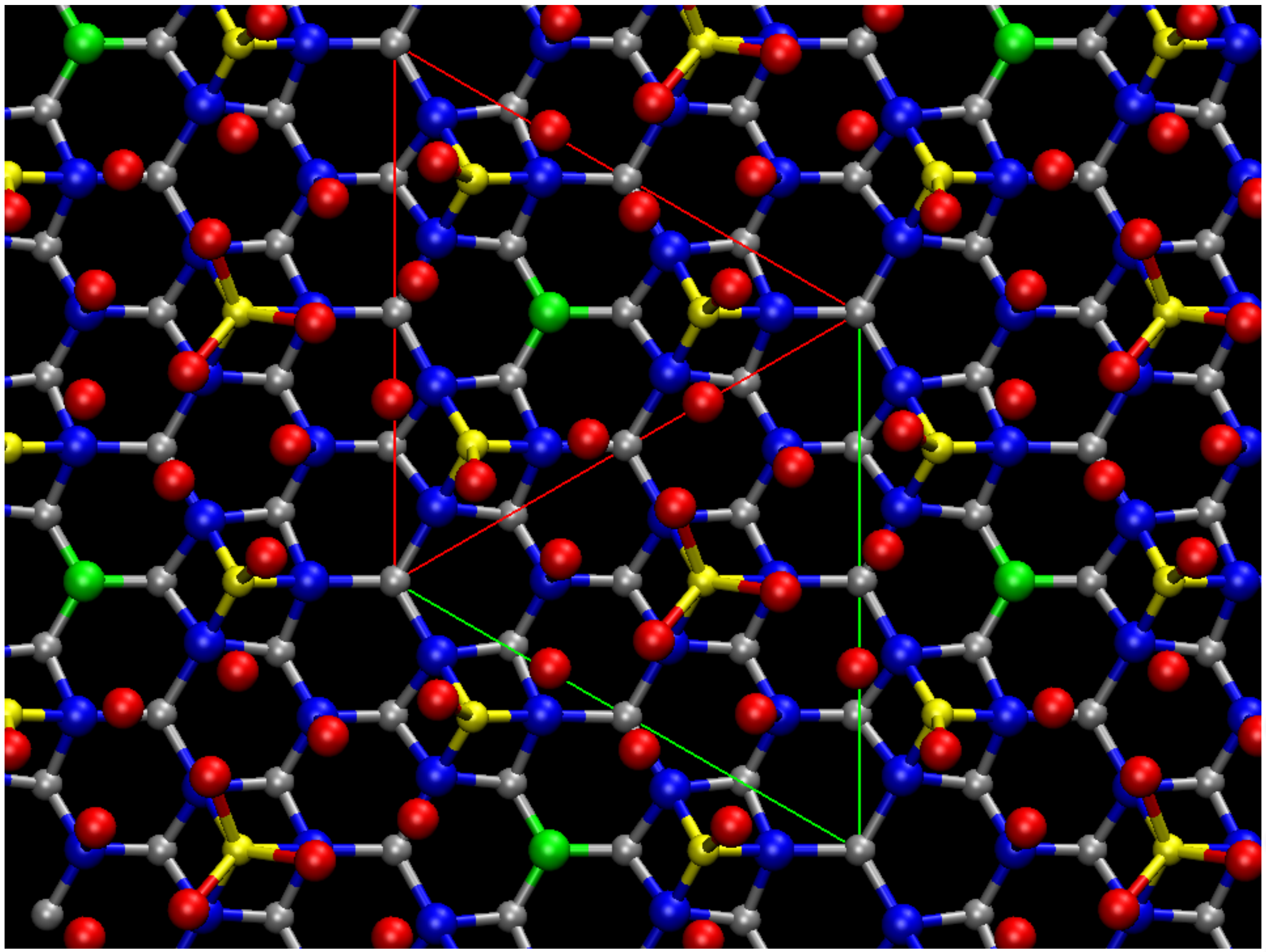
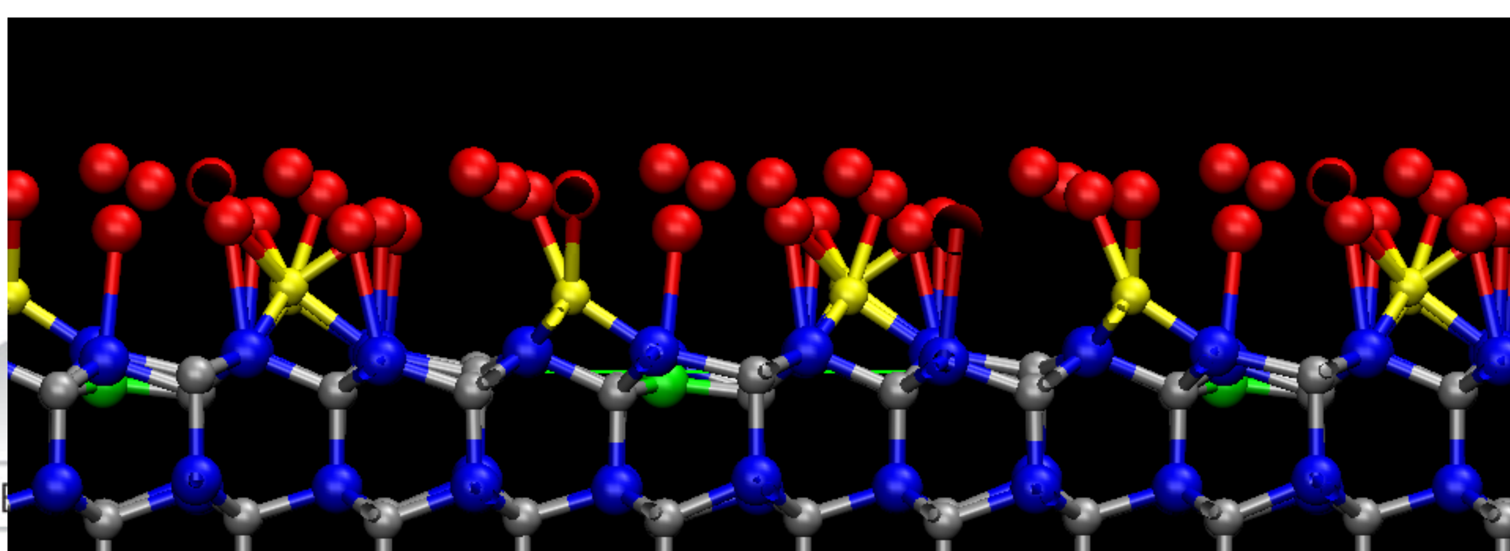


Group	Bonds with the AlN surface	Q_b lel
1	Al sp^2	- 0.48
2	Al + N_{ad}	- 0.13
3	N_{ad}	0.1
4	no	- 0.09
5		
6		
7		

Stabilization mechanism of the Au on AlN(2x2)-N_{ad}





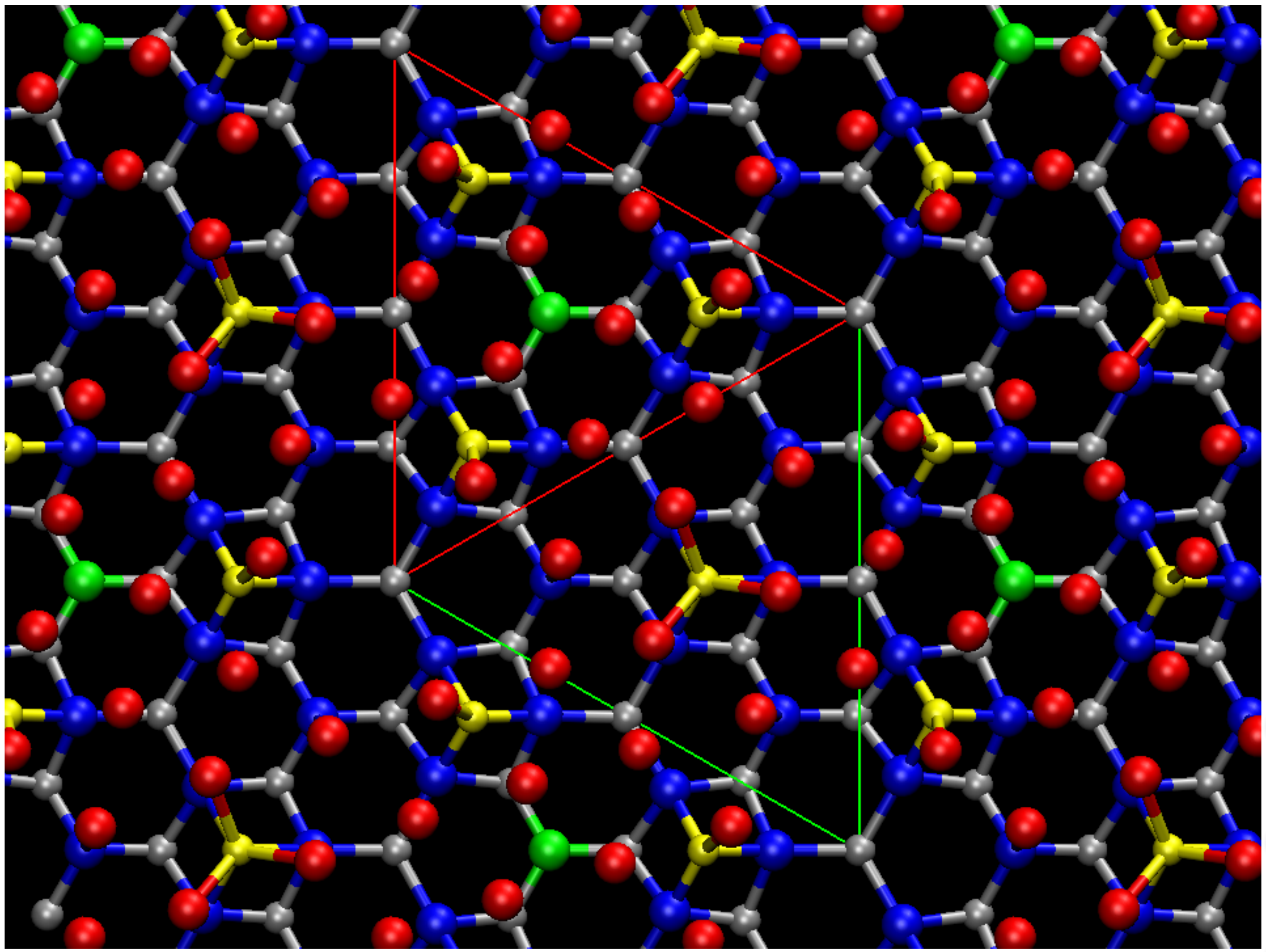
- Al sp^3
- Al sp^2
- N bulk
- N_{ad}

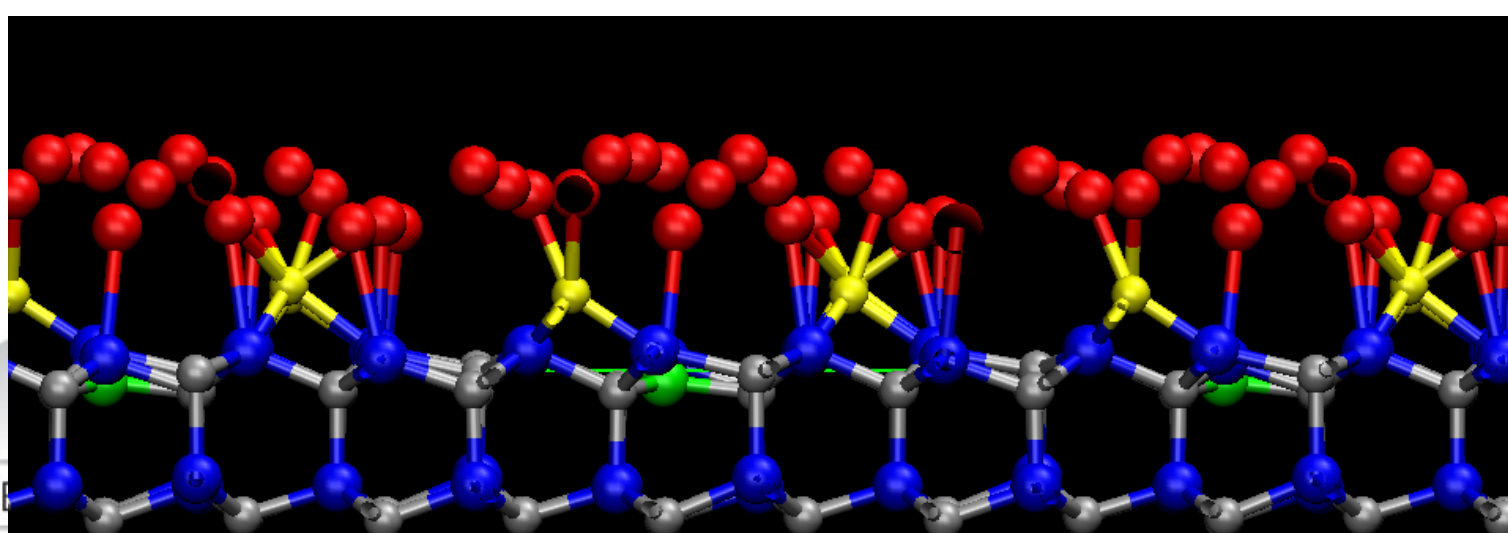
2 - Bonds and charge transfer on the Au layer

Due to the three-fold symmetry:
7 groups of 3 Au atoms

Group	Bonds with the AlN surface	Q_b |e|
1	Al sp^2	- 0.48
2	Al + N_{ad}	- 0.13
3	N_{ad}	0.1
4	no	- 0.09
5	no	- 0.05
6		
7		

Stabilization mechanism of the Au on AlN(2x2)-N_{ad}





Al sp^3

Al sp^2

N bulk

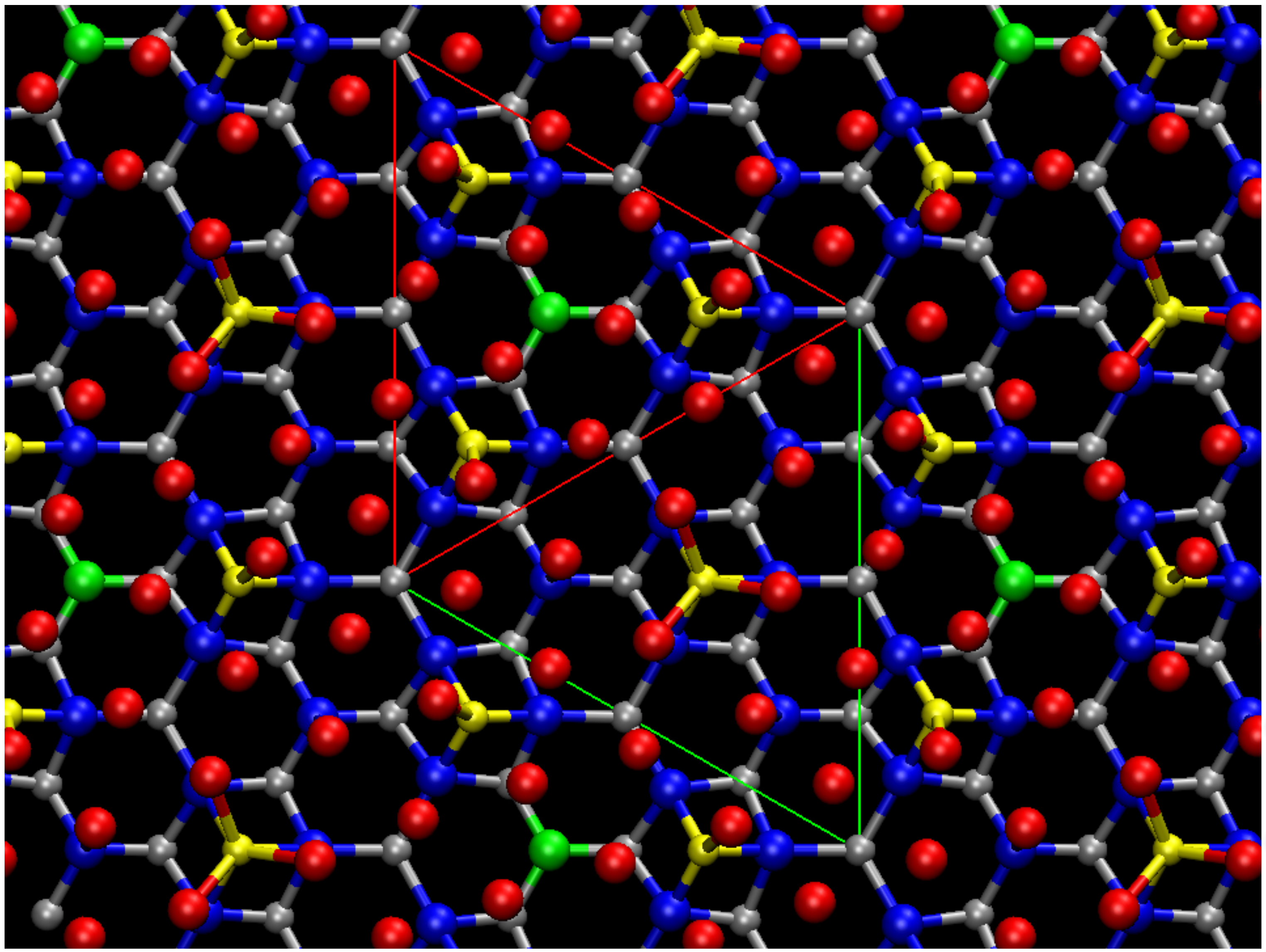
N_{ad}

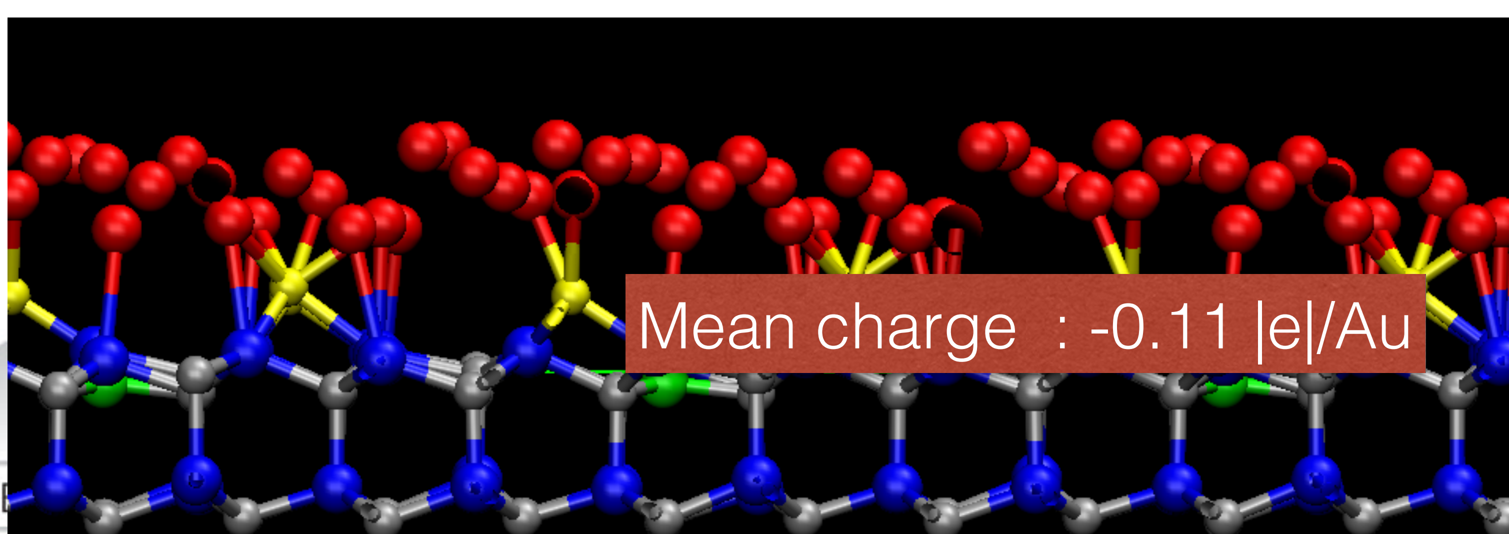
2 - Bonds and charge transfer on the Au layer

Due to the three-fold symmetry:
7 groups of 3 Au atoms

Group	Bonds with the AlN surface	Q_b |e|
1	Al sp^2	- 0.48
2	Al + N_{ad}	- 0.13
3	N_{ad}	0.1
4	no	- 0.09
5	no	- 0.05
6	no	- 0.03
7		

Stabilization mechanism of the Au on AlN(2x2)-N_{ad}





Al sp^3

Al sp^2

N bulk

N_{ad}

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Due to the three-fold symmetry:
7 groups of 3 Au atoms

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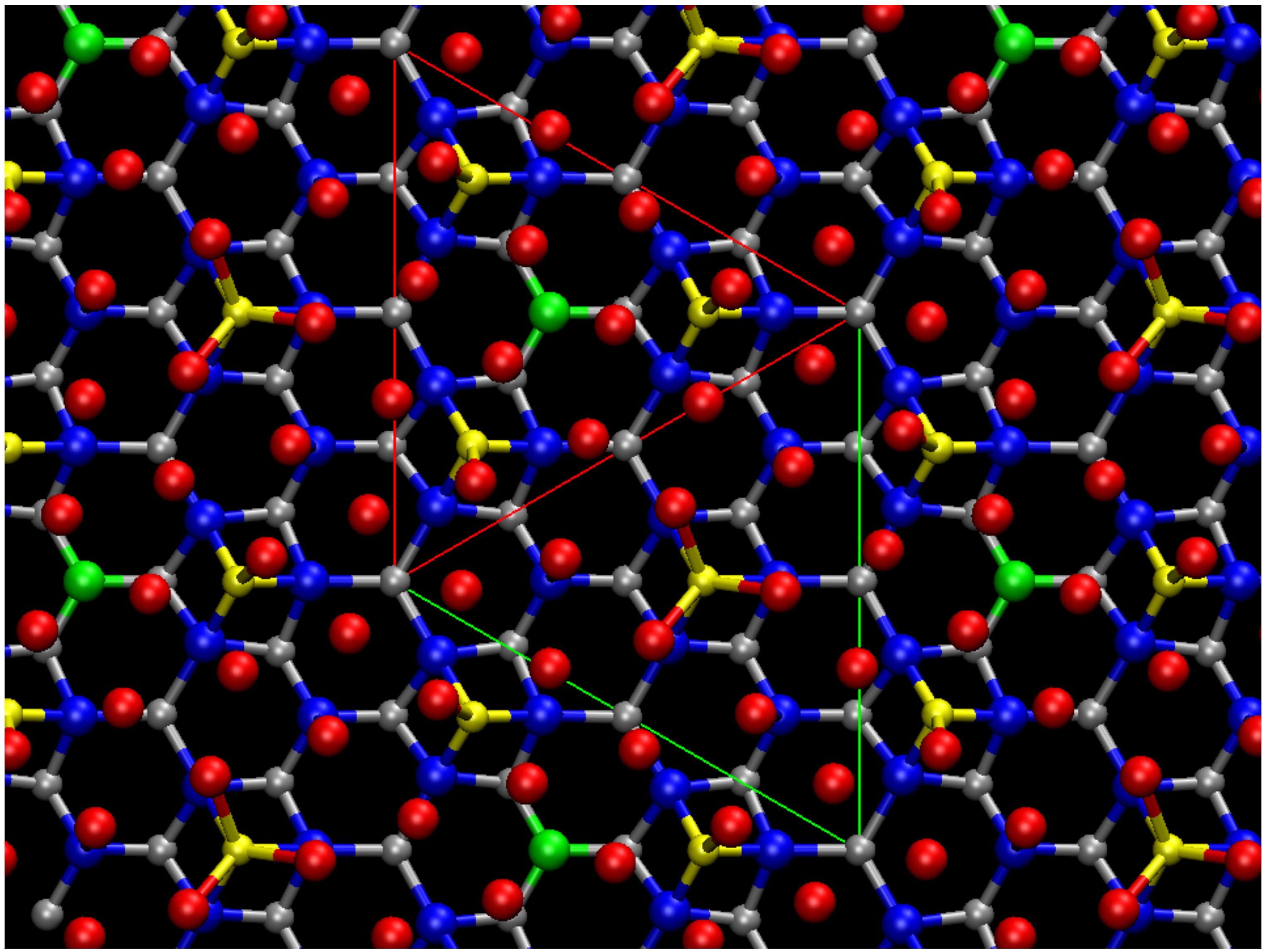
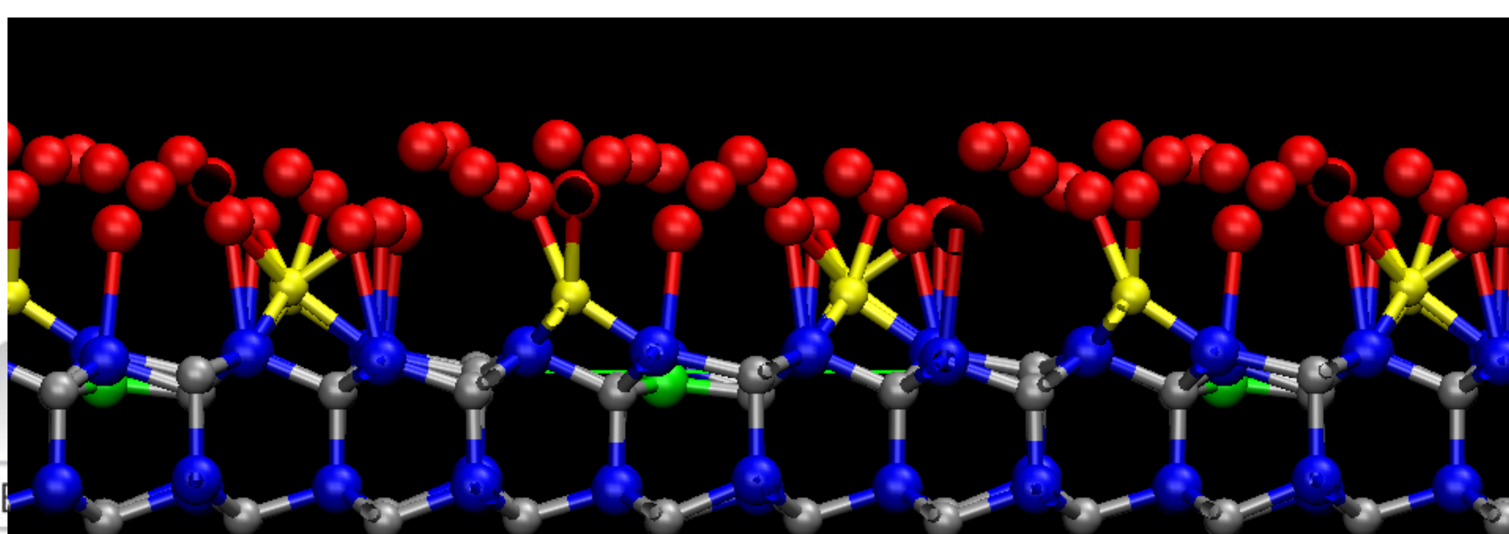
1	Al sp^2	- 0.48
2	Al + N_{ad}	- 0.13
3	N_{ad}	0.1
4	no	- 0.09
5	no	- 0.05
6	no	- 0.03
7	no	- 0.08

Stabilization mechanism of the Au on AlN(2x2)-N_{ad}



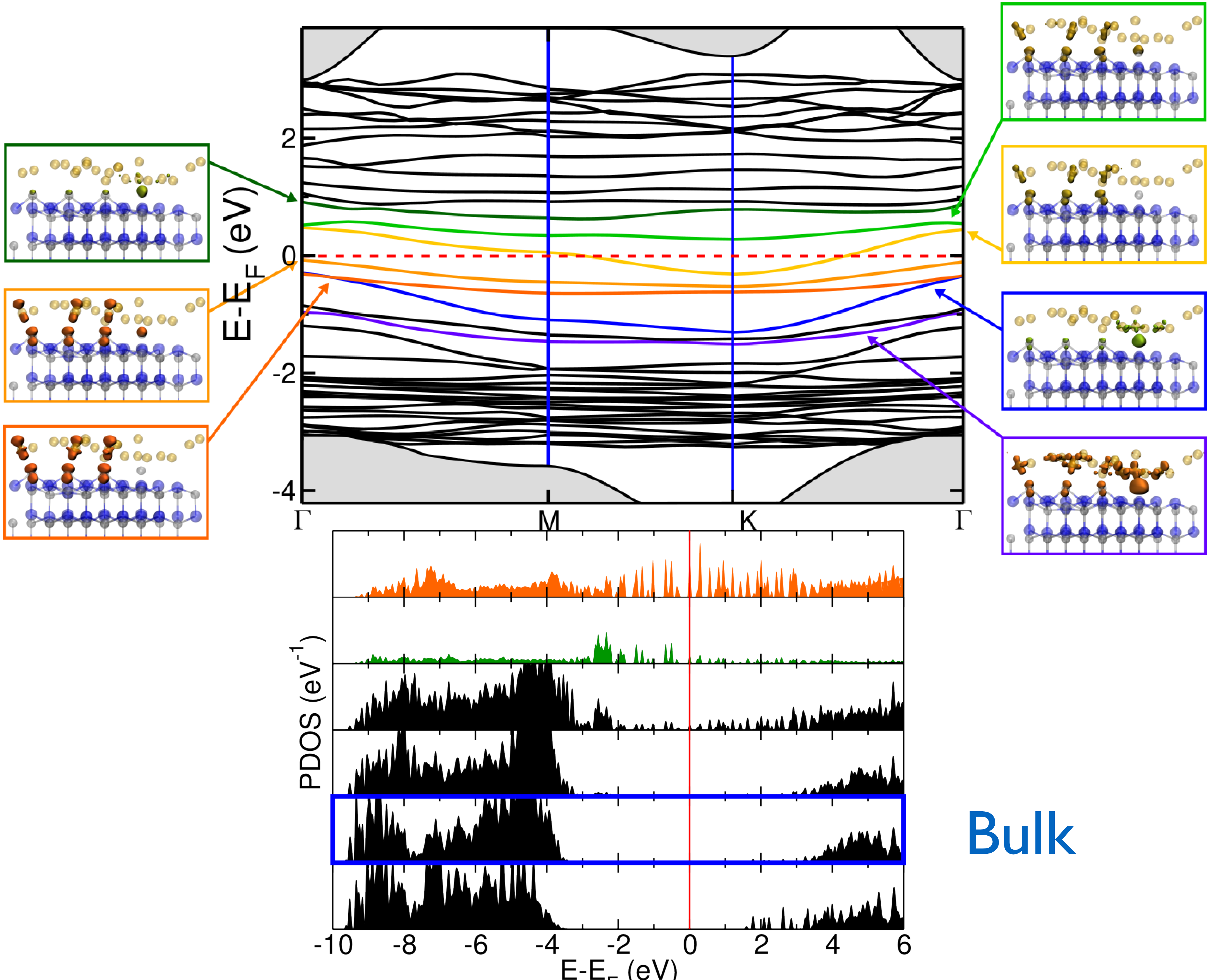


2 - Bonds and charge transfer on the Au layer

	AlN (2x2)Nad		21Au/AlN(4x4)	
	atom mean charge	(1x1) mean charge	atom mean charge	(1x1) mean charge
Au	—	—	-0.11	-0.144
N_{ad}	-2.18	-0.545	-1.73	-0.432
Al_1	2.31	0.577	2.33	0.578
N_1	-2.35	-0.587	-2.34	-0.585

25 % of charge transfer from the (2x2)N_{ad} to the Au layer

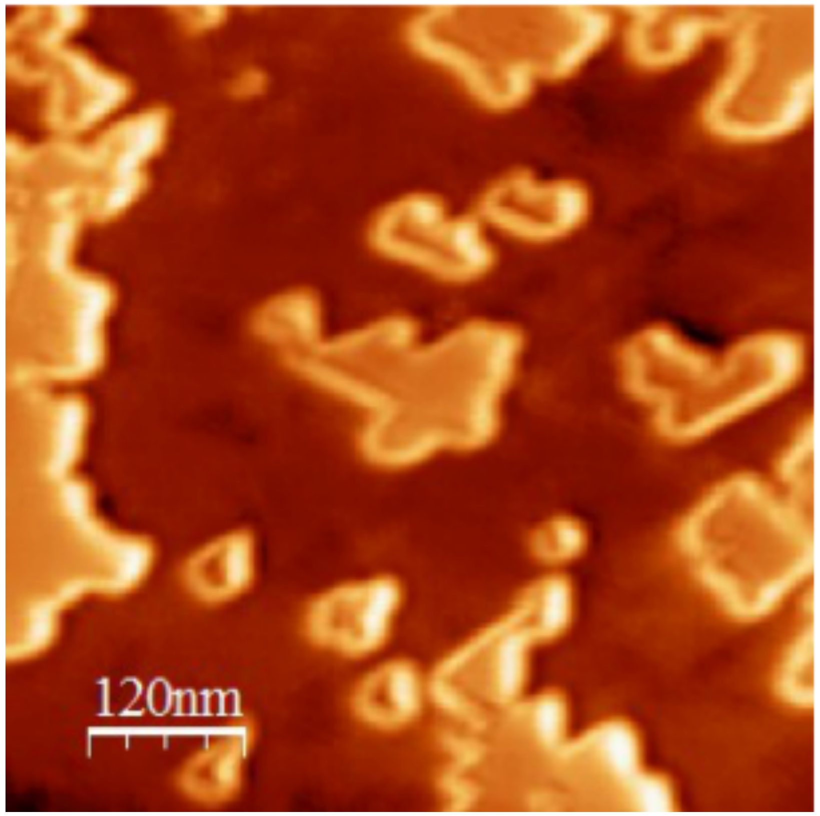
Stabilization mechanism of the Au on AlN(2x2)-N_{ad}



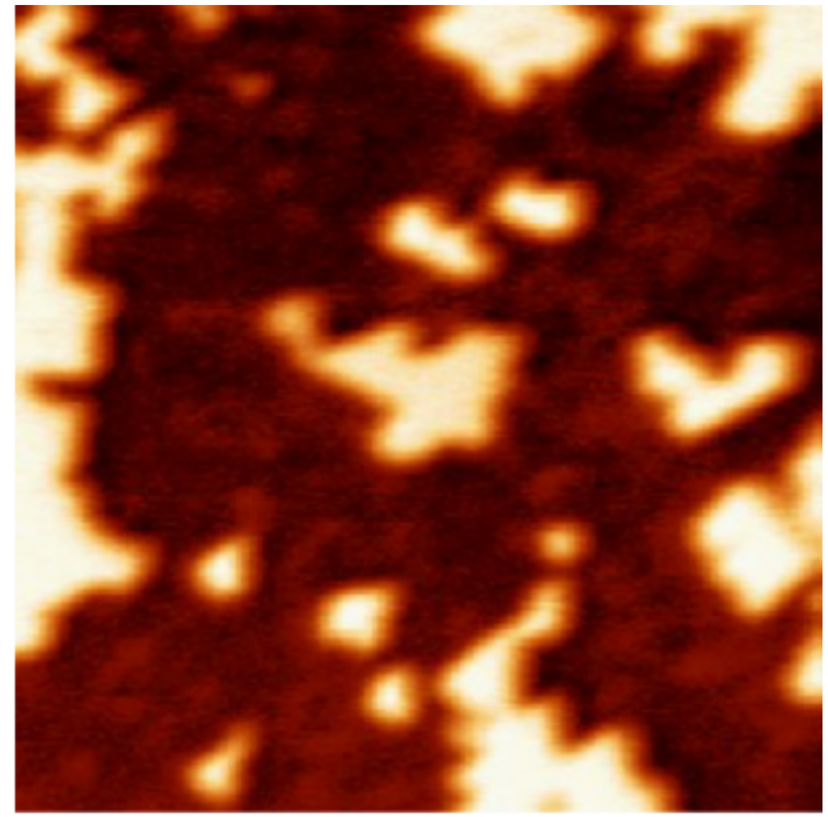
Bulk

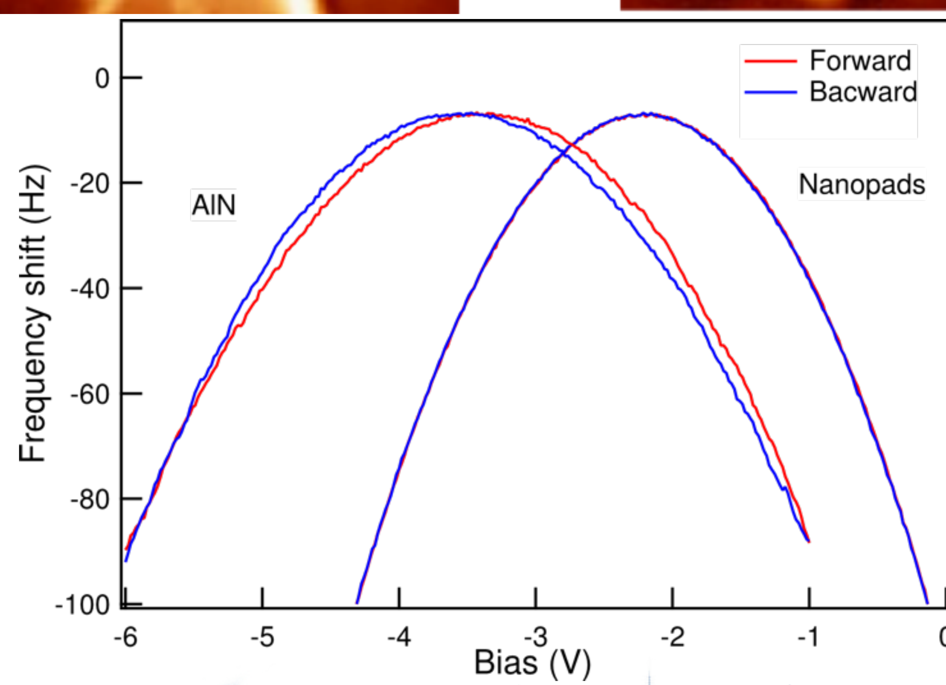
Au / AlN(0001)

nc-AFM Topo



KPFM





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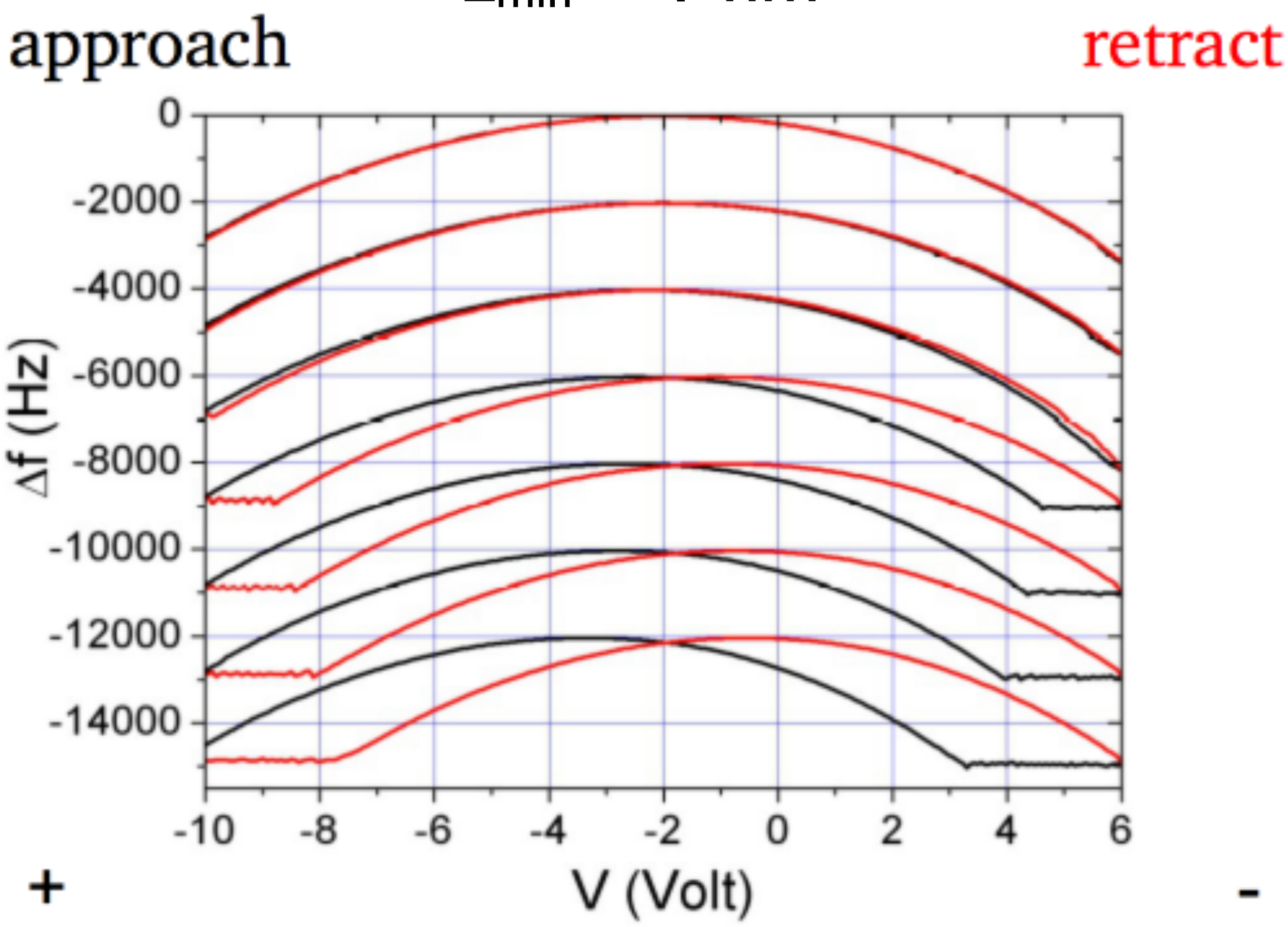
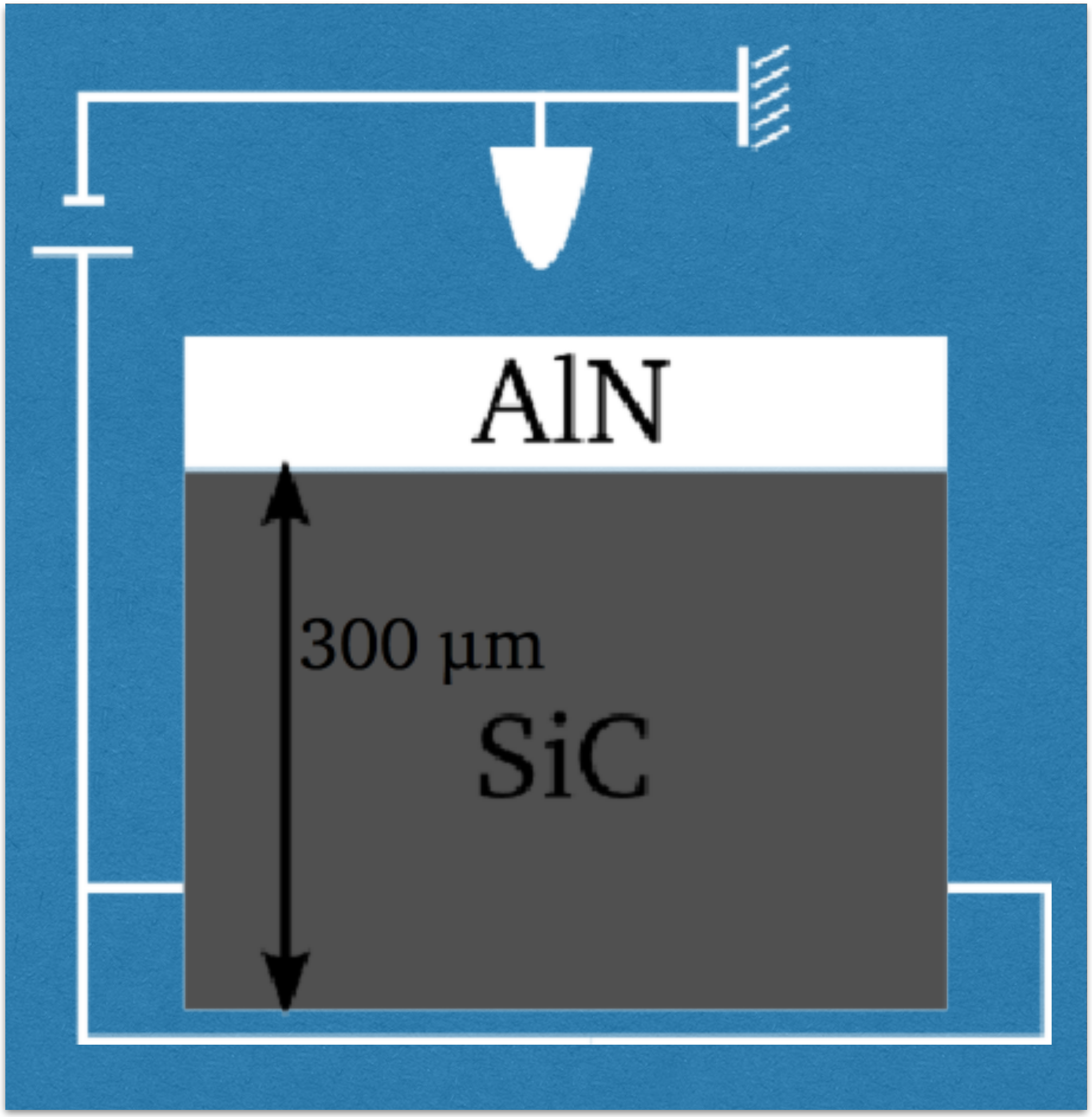
Au / AlN(0001)

Charging the islands

$\Delta z = 0.1$ nm
$z_{min} \sim 1$ nm





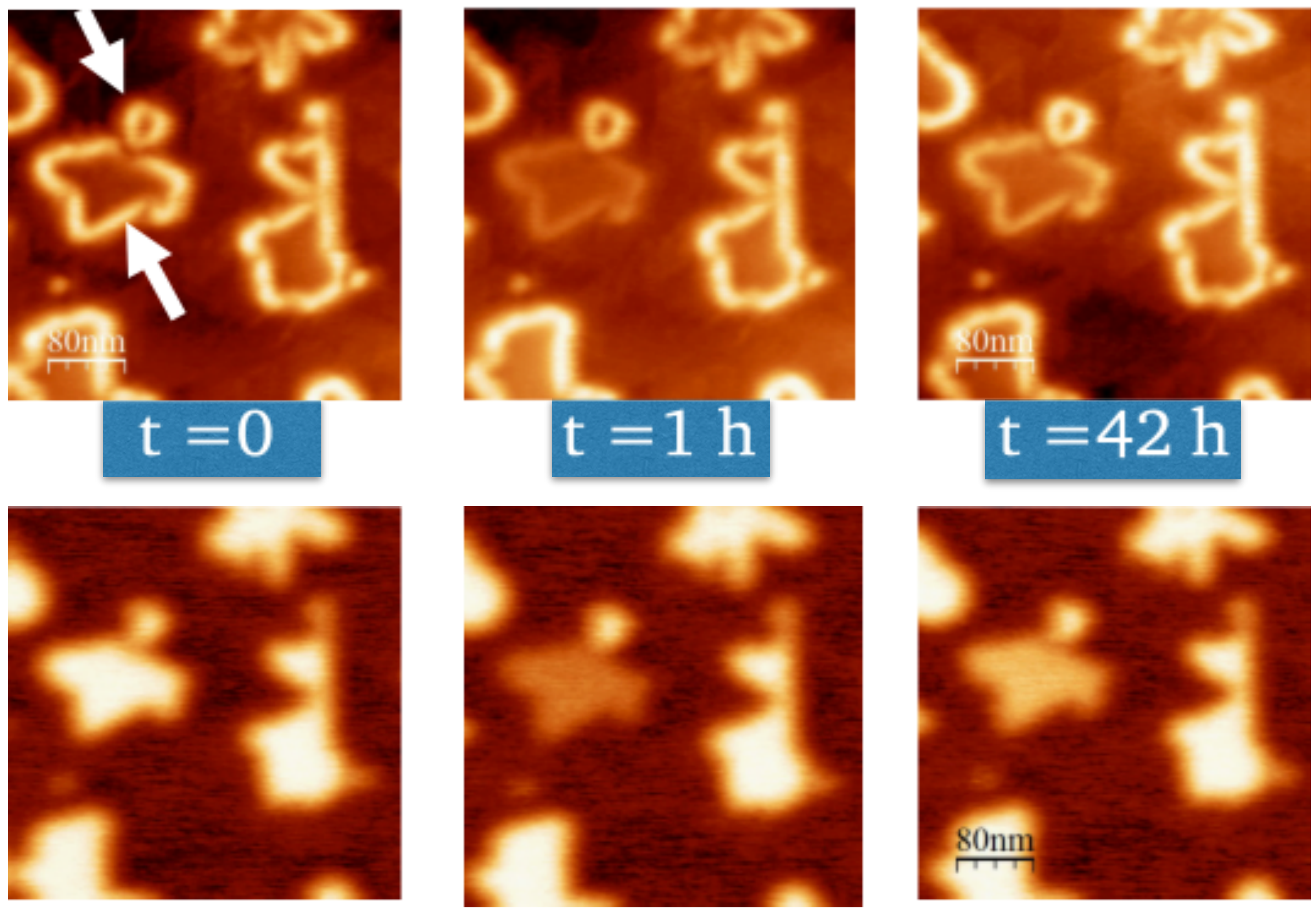
Charge transfer occurs

Au / AlN(0001)

Discharge?

Topo

KPFM



Charge is localized

No leakage to neighboring islands

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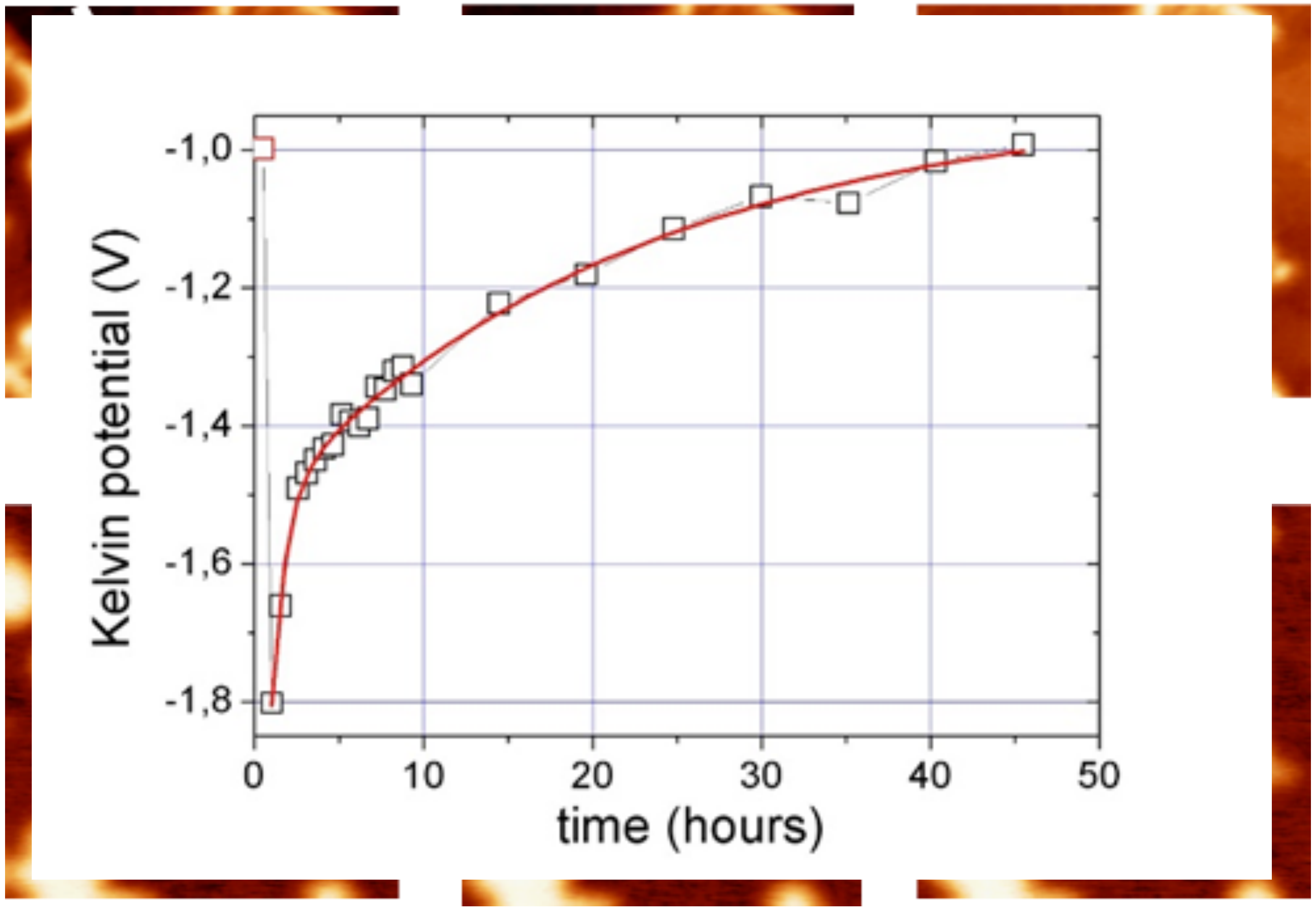
Au / AlN(0001)

Discharge?

Topo

KPFM

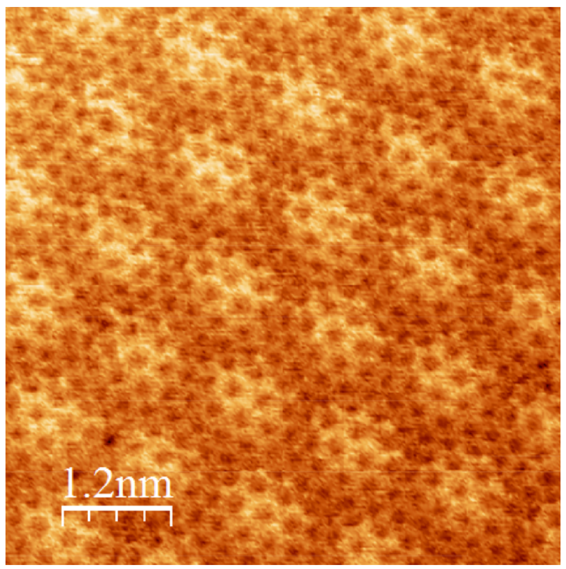


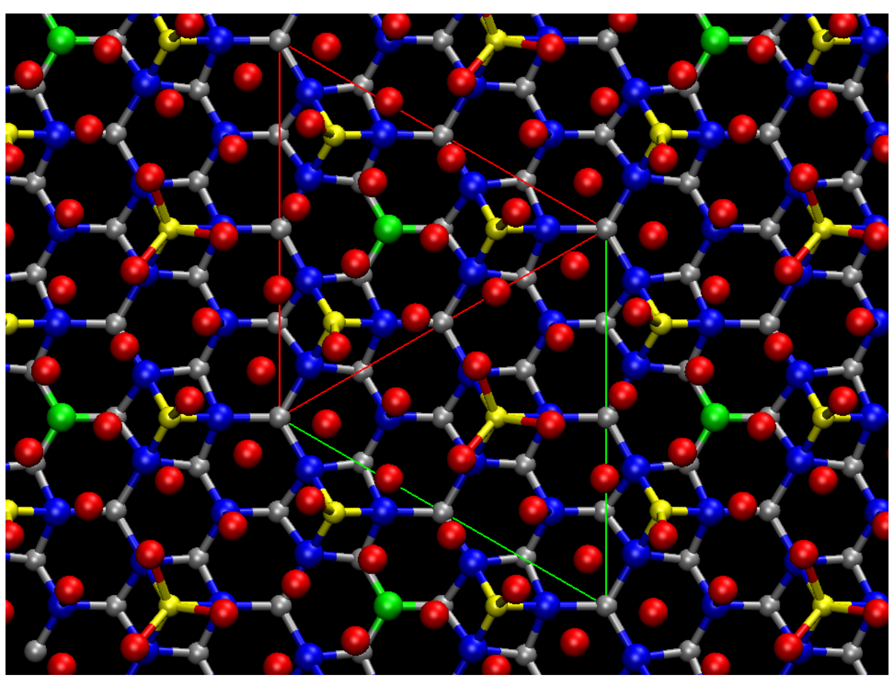
Charge is localized

No leakage to neighboring islands

Summary

Au 2D monoatomic high islands on AlN(0001)





Experiments:

- two moiré observed by NC-AFM with Qplus at 4K
- Two models with hexagonal pattern explained the observed moiré

DFT calculations :

- models on AlN(4x4) cells with 21 atoms allow to mimic the moiré
- DFT energies and $d_{Au\text{-}inplane}$ analysis confirm that the N_{ad} atoms are still present

Stabilization mechanisms :

- 9 of the 21 Au atoms create bonds with Al sp^2 and N_{ad}
- charge transfer of 25 % from the N_{ad} atoms to the Au layer
- AlN(0001) polar surface drives the stabilization of the Au layer

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Acknowledgments

Support

NanoSciences GRAND SUD - OUEST

Funding

SEVENTH FRAMEWORK PROGRAMME

PAMS

Calculations

Benoit Eydoux

Experiments

Bulent Baris
Hassan Khoussa
Olivier Guillermet
Sébastien Gauthier
David Martrou

CEMES