分光分析による表面物理化学

近藤剛弘

筑波大学 数理物質系 物質工学域

筑波大学 数理物質融合科学センター (CiRfSE)
物質変換材料部門

共同研究者

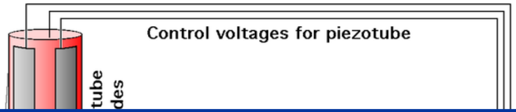
筑波大学：中村潤児教授、Guo研究員
中村近藤研究室のメンバーと卒業生
岡田晋教授

Web掲載用のため
イントロダクションのスライドを
一部割愛いたします

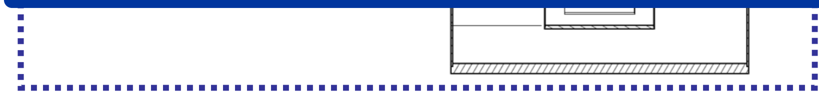
極低温走査トンネル顕微鏡

Scanning tunneling microscope (STM)

Low temperature STM

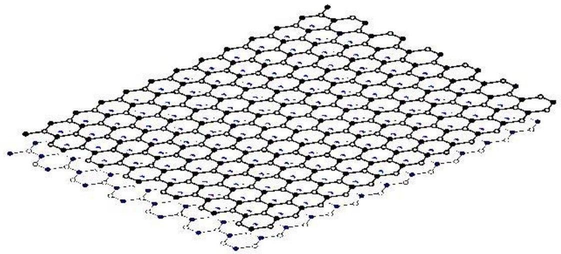


**STM･STS計測では
固体表面の物理化学的な知見
特に物性や化学反応過程などを
原子分解能での顕微鏡観察と
局所分光計測で
明らかにすることが可能**

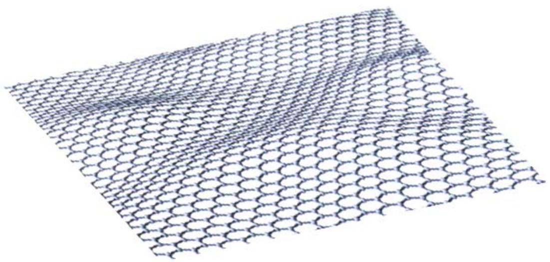


Background and motivation

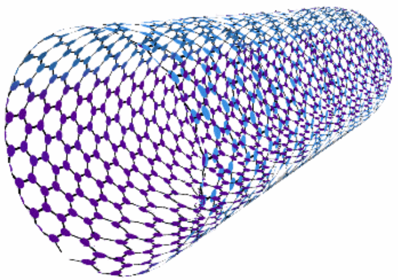
Graphitic material



Graphite (3D)



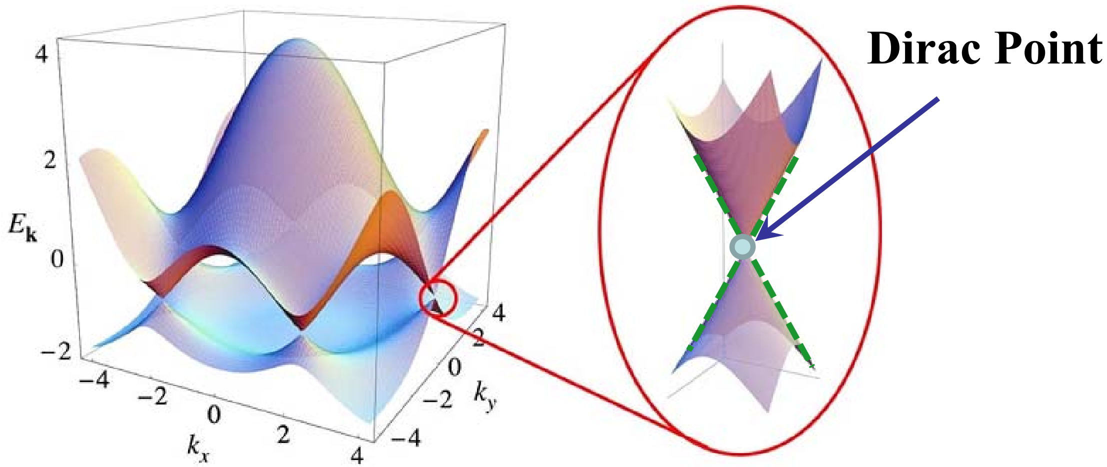
Graphene (2D)



Carbon nanotube (1D)

Graphene shows specific physical and chemical properties among the graphitic materials due to its unique electronic structure

Zero-gap semiconductor

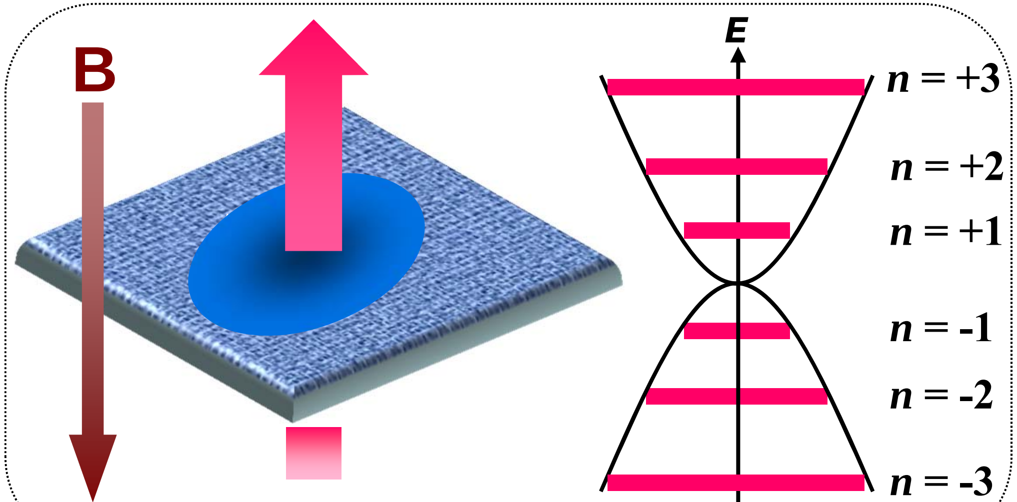


Massless Dirac fermions

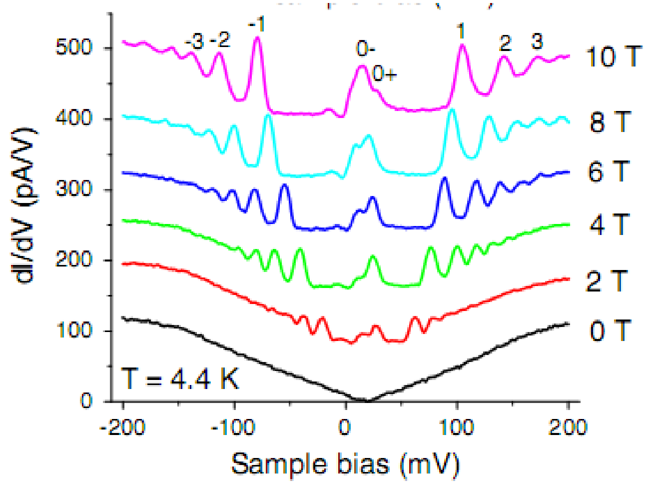
Graphene band structure

Graphene shows specific Landau levels under magnetic fields

Landau levels in 2D electron gas



Schematic image of Landau level



STS of Graphene on graphite under magnetic field

La

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Room-Temperature Quantum Hall Effect in Graphene

Science AAAS

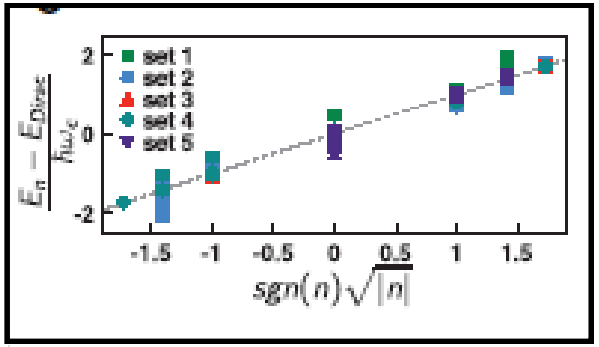
K. S. Novoselov,[1] Z. Jiang,[2,3] Y. Zhang,[2] S. V. Morozov,[1] H. L. Stormer,[2] U. Zeitler,[4] J. C. Maan,[4] G. S. Boebinger,[3] P. Kim,[2*] A. K. Geim[1*]

Novoselov et al., Science, 315 (2007) 1379

Large energy difference of graphene Landau levels is known to lead to Quantum Hall effects at room temperature

Graphene Landau level appeared at *B* = 0 T

Nano-bubble of graphene on Pt(111)

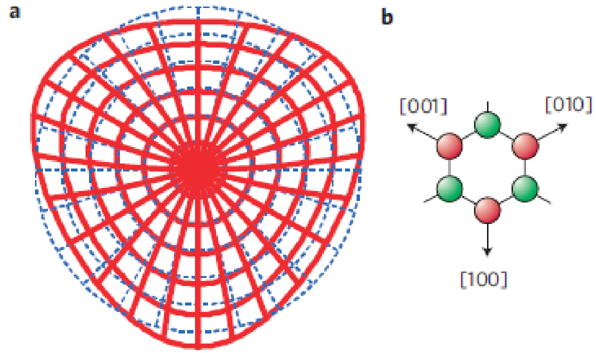


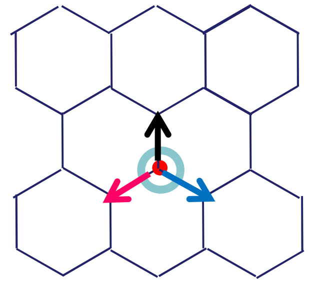
$$E \propto \sqrt{n}$$

N. Levy et al.,
Science, **329** (2010) 544.

Strain

Inequivalent hopping





Non-uniform shear strain

Inequivalent hopping

$$u_{xx} = \frac{\partial u_x}{\partial x}, \quad u_{yy} = \frac{\partial u_y}{\partial y}, \quad 2u_{xy} = \frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x}$$

Ando, et al., Phys. Rev. B **65** (2002) 235412.
Neto et al., Rev. Mod. Phys. **81** (2009) 109.

Gauge field

$$\mathbf{A} = \frac{\beta}{a}\begin{pmatrix} u_{xx} - u_{yy} \\ -2u_{xy} \end{pmatrix} \qquad B_S = \frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y}$$

Geim, et al.,Nature Phys.**6** (2010) 30

Pseudo-magnetic field

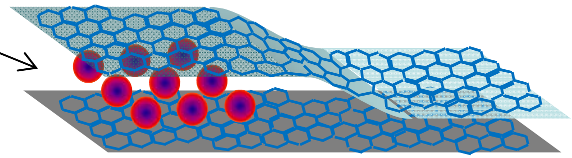
$$\vec{B}s = \vec{\nabla} \times \vec{A}$$

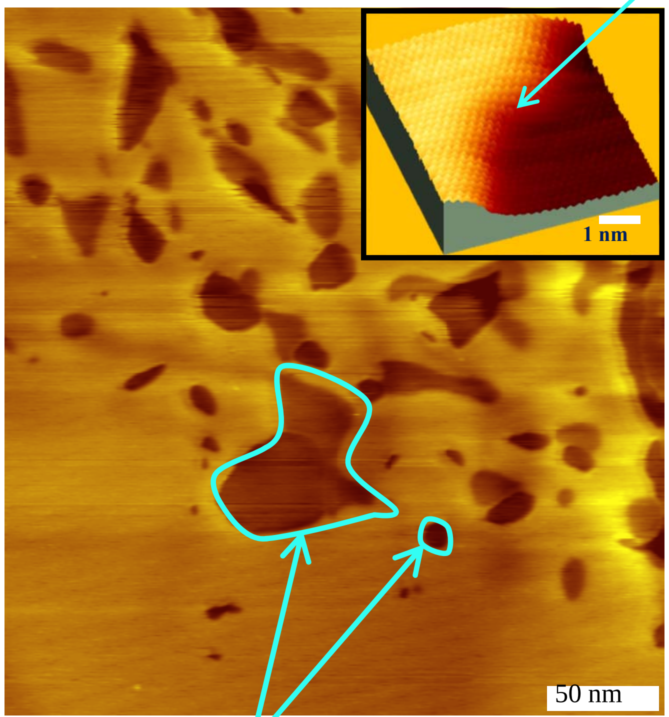
Landau levels appearance are ascribed to the strain-induced pseudo-magnetic fields

We have also observed Landau levels at B = 0T

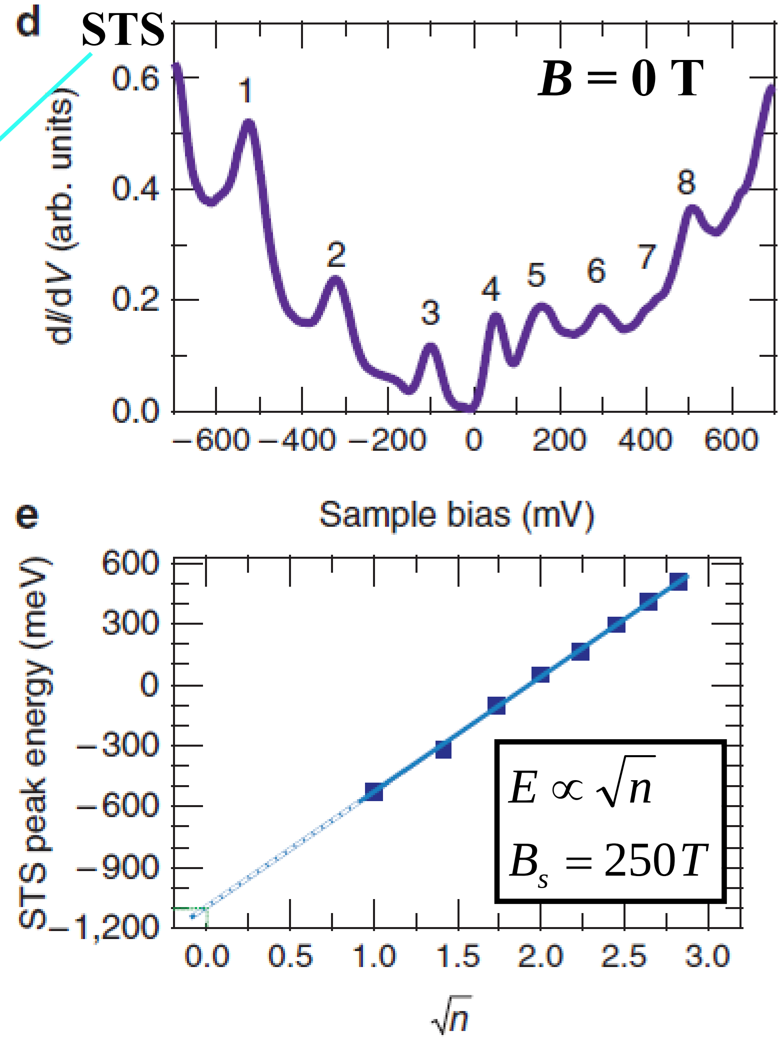
Potassium (K) partially intercalated graphite

K





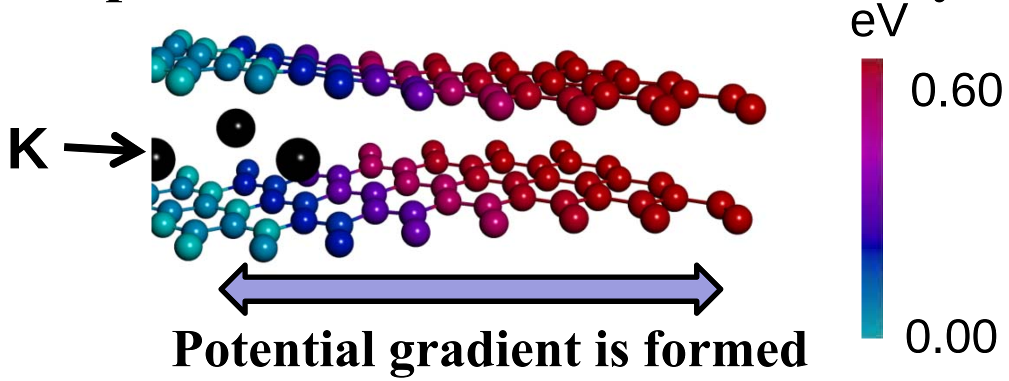
K-free domains (Nanovalleys)

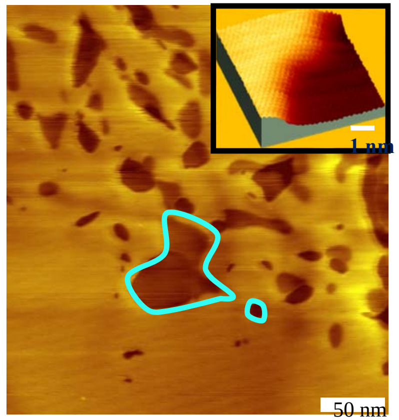


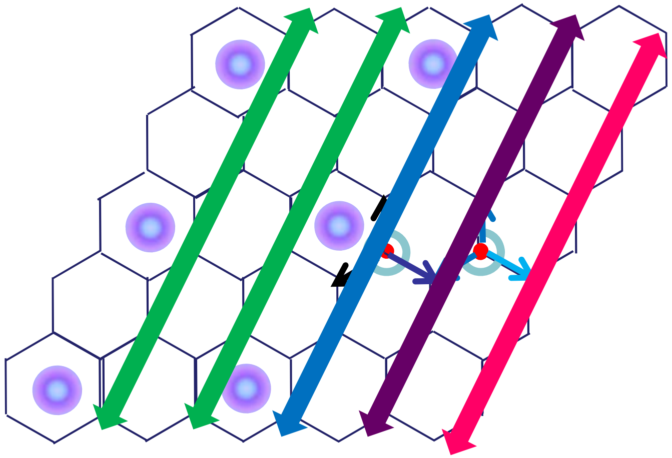
D. Guo, T. Kondo, J. Nakamura, et al., Nature Communications **3** (2012) 1068

Our proposed “domain model” for pseudo magnetic fields

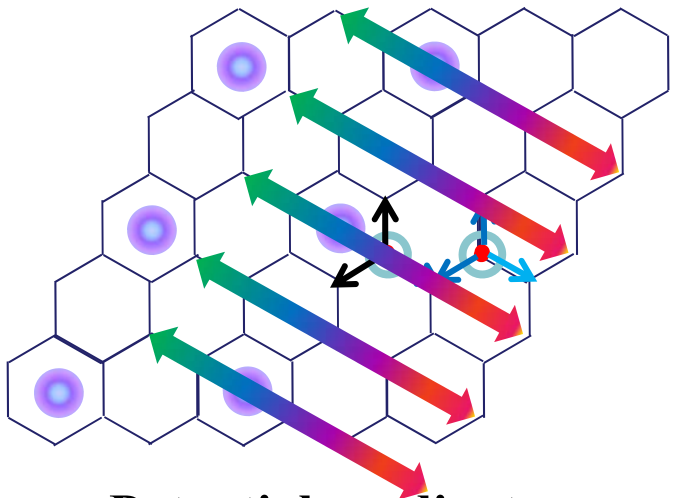
On-site potential of carbon calculated by DFT







Equipotential contour



Potential gradient

Equivalent hopping in the contour direction

Inequivalent hopping along the gradient direction

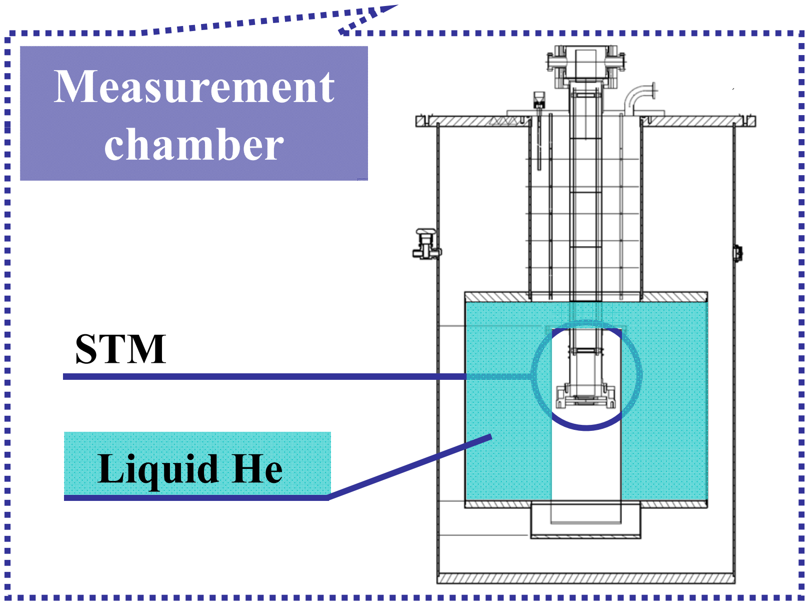
Gradient of on-site potentials results in inequivalent hopping

Recent progress

To prove the domain-model as another origin for the pseudo-magnetic field

We have observed Landau levels of bilayer graphene at the atomically flat area of nitrogen-doped graphite at $B = 0$ T

Experiment



1. Cleaning of HOPG surface

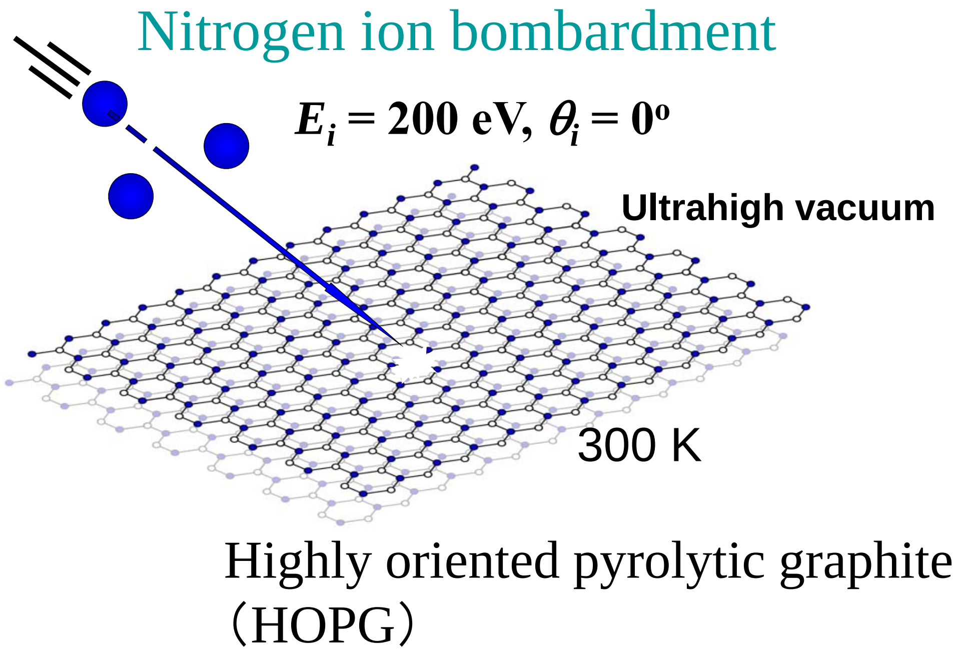
(1) Cleaving HOPG at atmosphere

(2) 940K annealing (30 min.) in UHV

2. Nitrogen doping

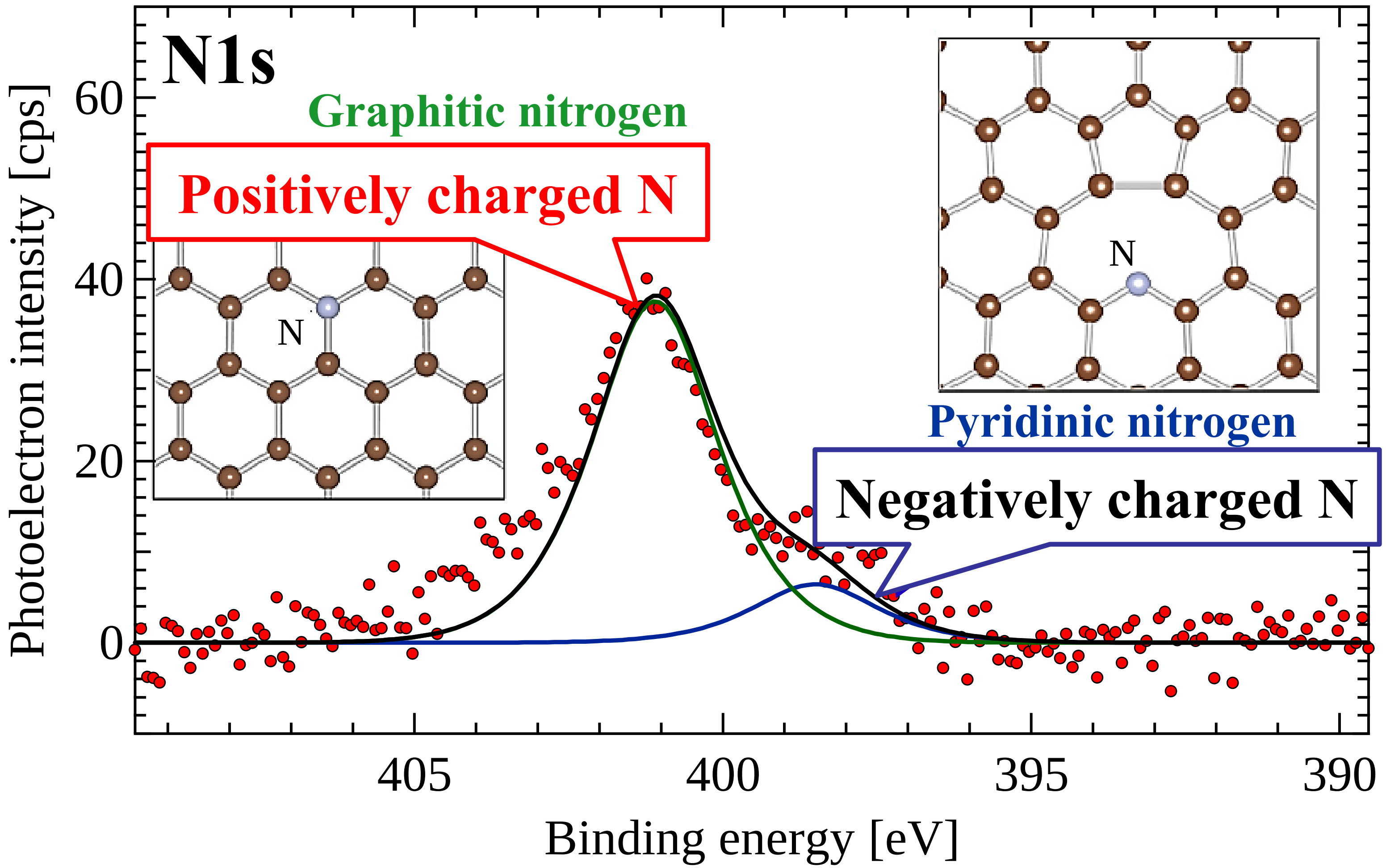
(1) Nitrogen ion bombardment
(N/C : <0.04, 0.04, 1.9 at %)

(2) 940 K annealing (30 min.)



N1s XPS spectrum of nitrogen doped graphite

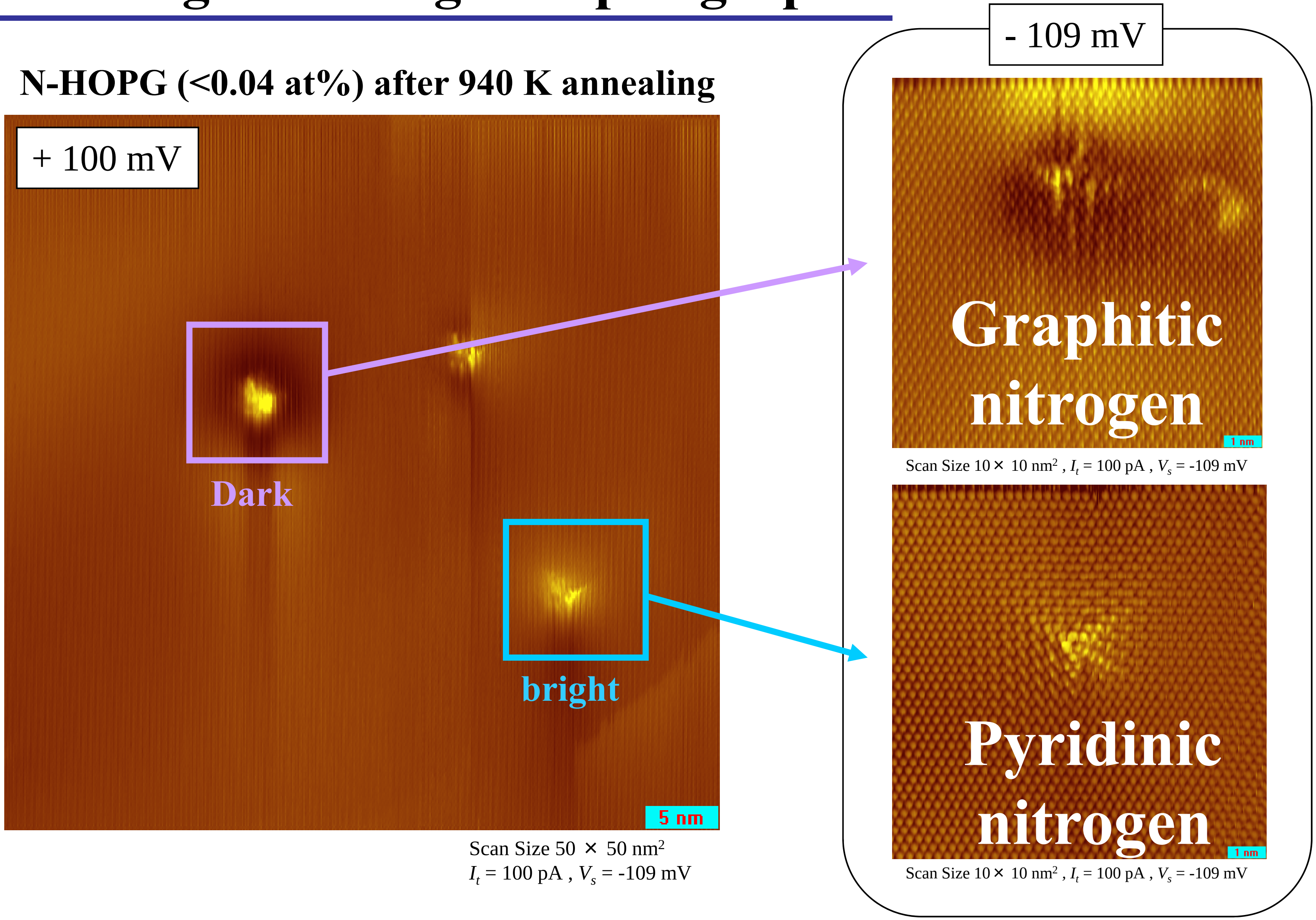
N-HOPG (1.9 at%) after 940 K annealing



Graphitic nitrogen (positively charged N) is dominant

STM image of nitrogen doped graphite

N-HOPG (<0.04 at%) after 940 K annealing

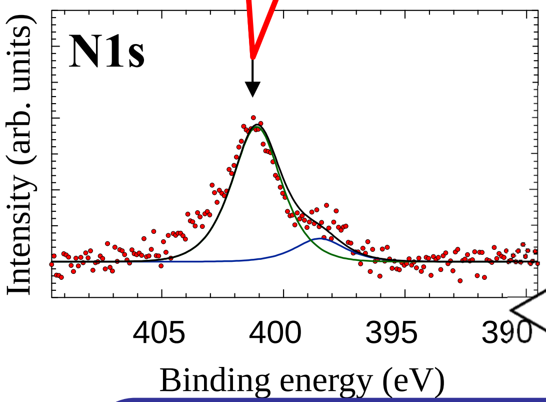


Two types of defect are observed !

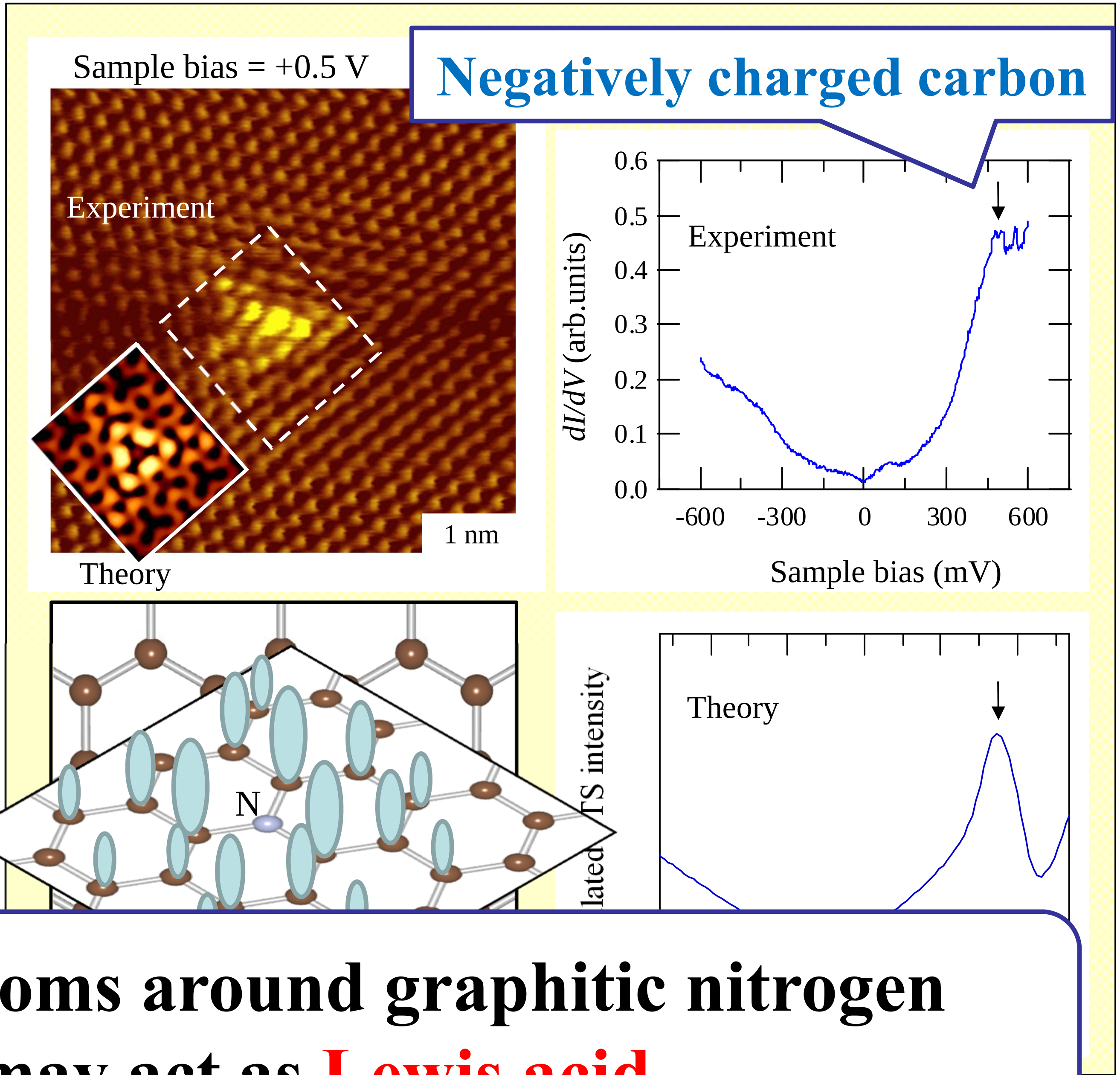
T. Kondo J. Nakamura et al., Phys. Rev. B **86** (2012) 035436

Graphitic nitrogen

Positively charged nitrogen



Negatively charged carbon



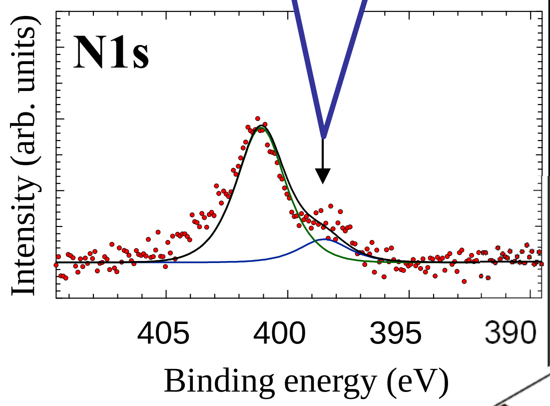
Carbon atoms around graphitic nitrogen may act as Lewis acid

Ca … s
at occupied region !

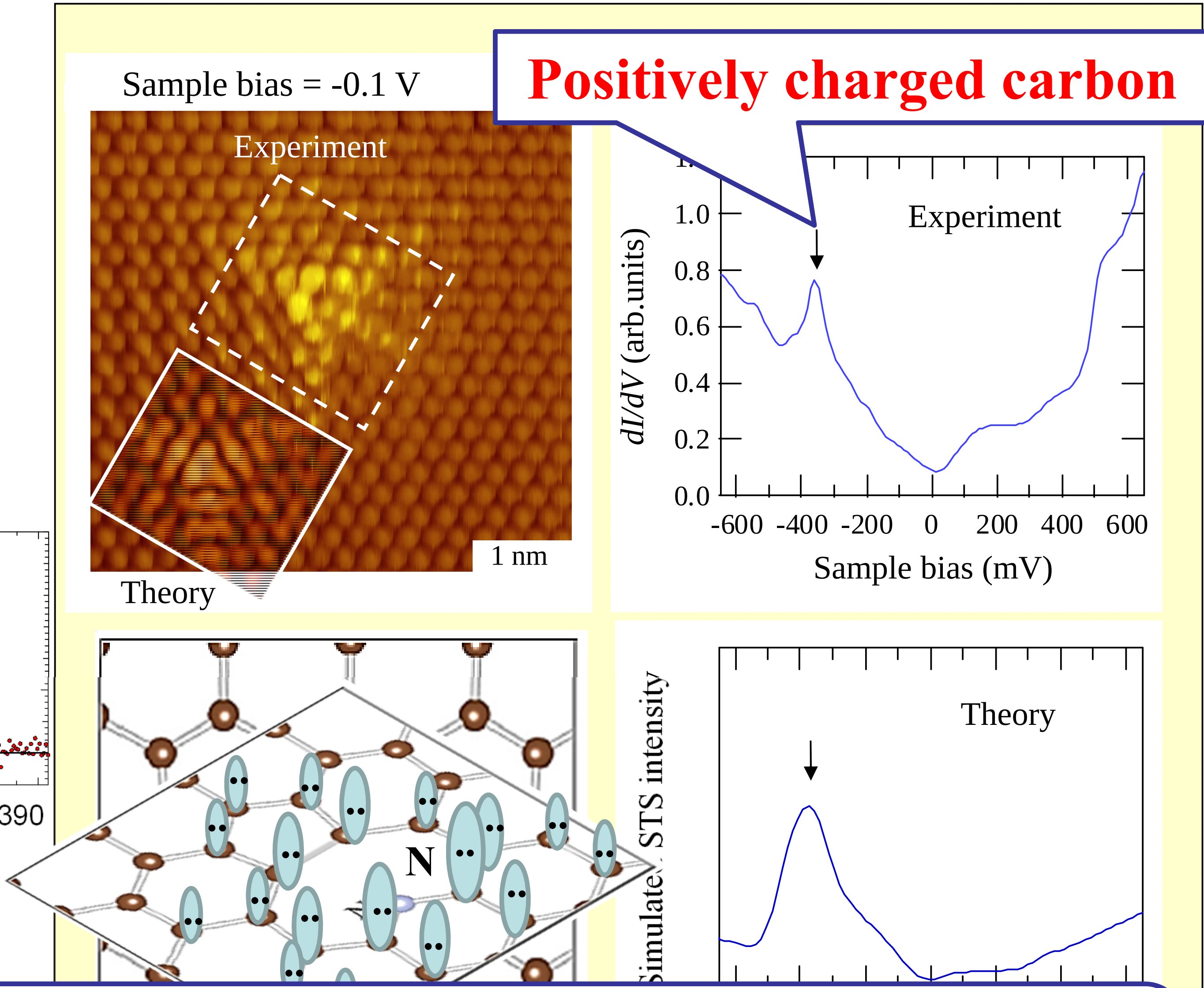
T. Kondo J. Nakamura et al., Phys. Rev. B **86** (2012) 035436

Pyridinic nitrogen

Negatively charged nitrogen



Positively charged carbon



Carbon atoms around pyridinic nitrogen may act as Lewis base

electron lone pair

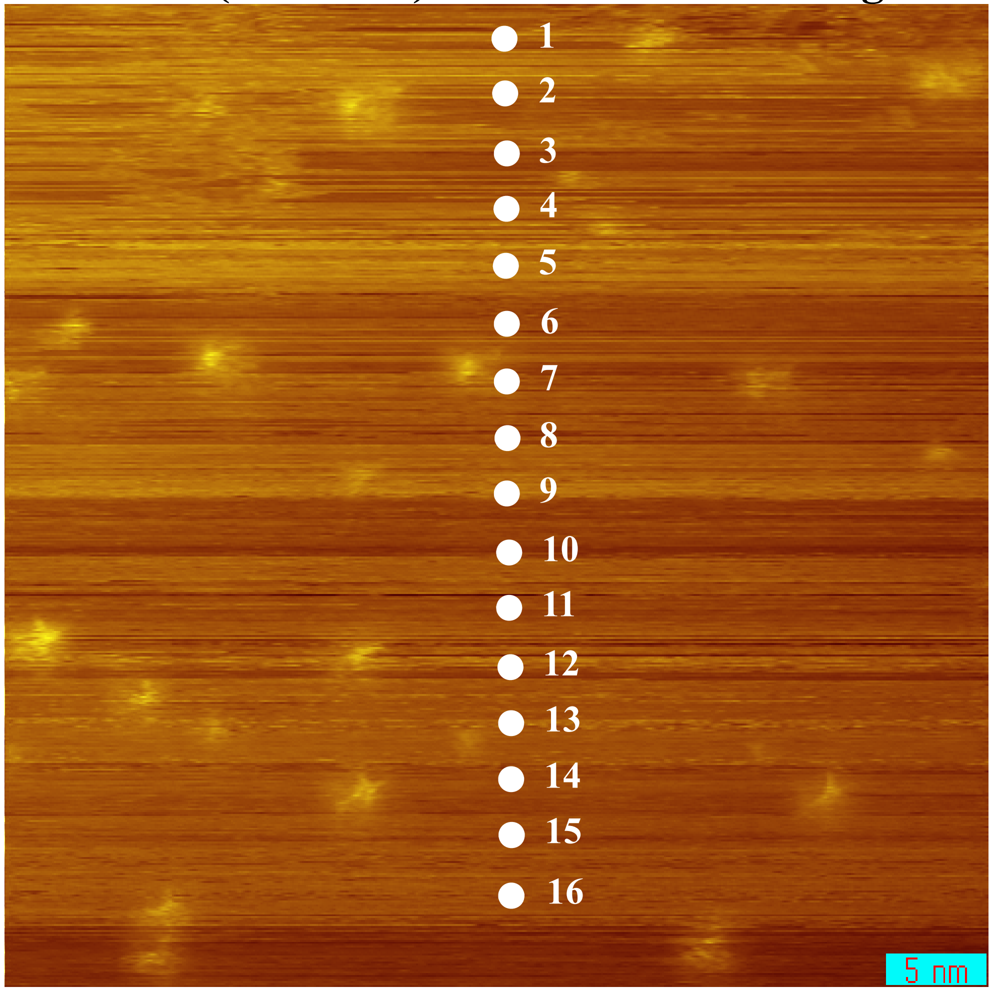
Car

at occupied region !

T. Kondo J. Nakamura et al., Phys. Rev. B **86** (2012) 035436

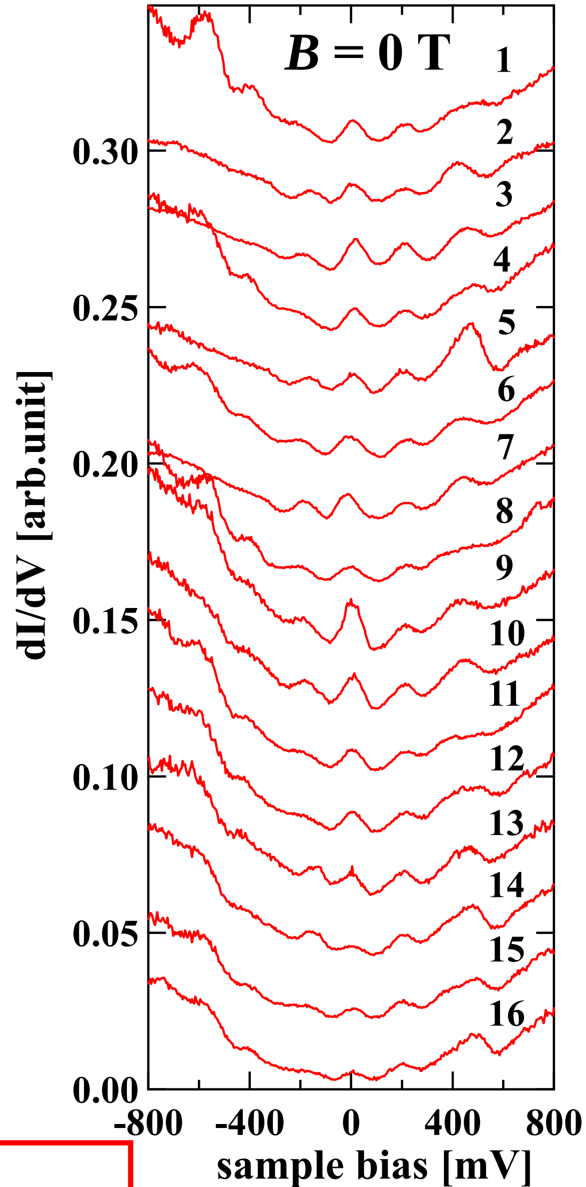
STS spectra on nitrogen doped graphite

N-HOPG (0.04 at%) after 940 K annealing



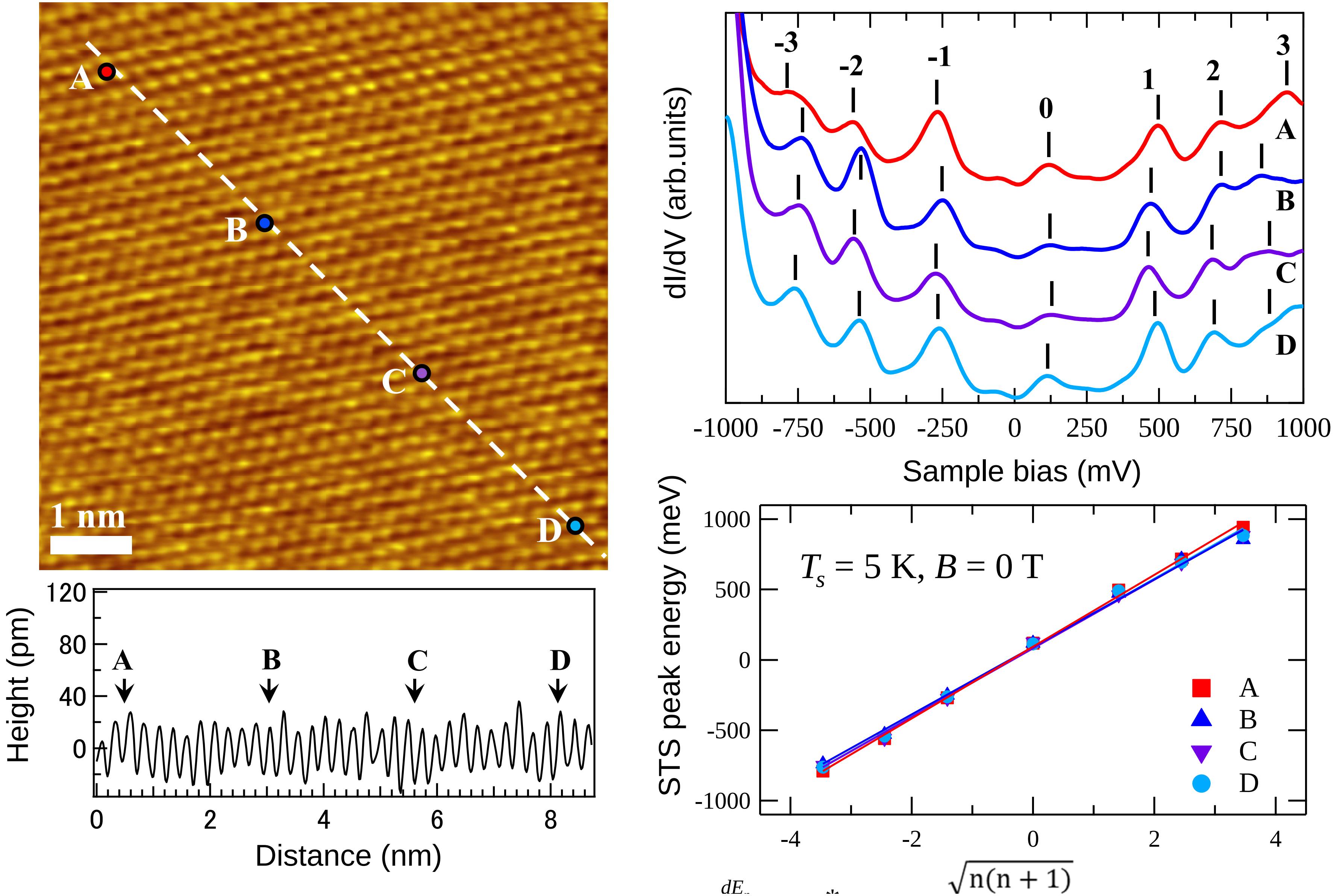
50×50 nm², 800 mV, 100 pA

T_s = 5 K, B = 0 T



Many peaks appear in STS spectrum

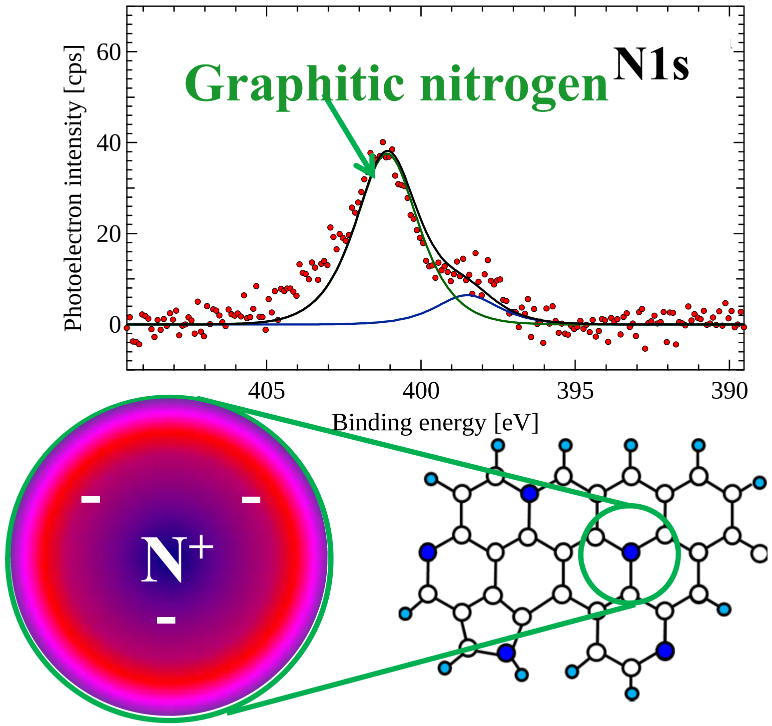
STM and STS on nitrogen doped graphite at $B = 0$T



Landau levels of bilayer graphene appear at FLAT area !

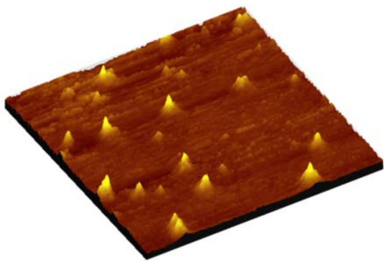
Why LL-like peaks appear in STS at $B = 0$ T

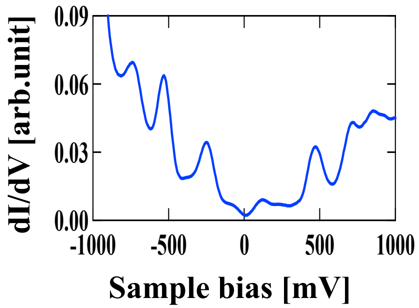
Nitrogen doped-graphite



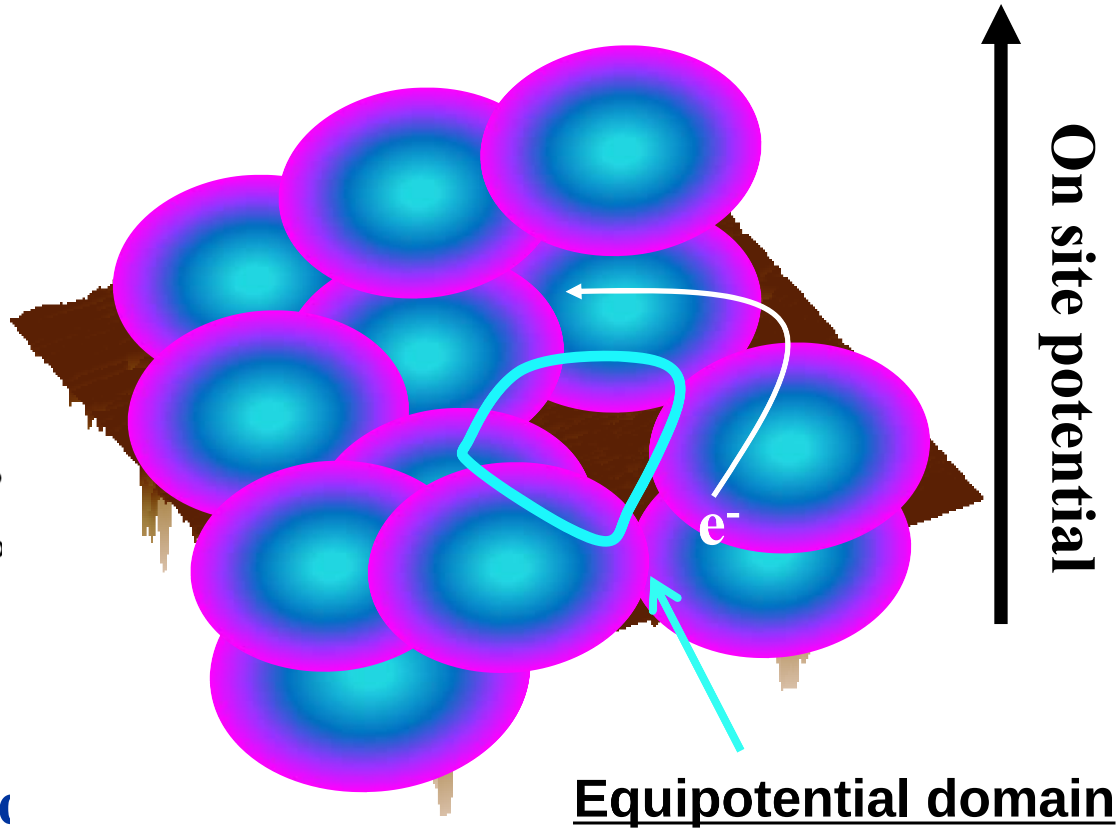
Graphitic nitrogen

Nitrogen is positively charged





Schematic image of potential

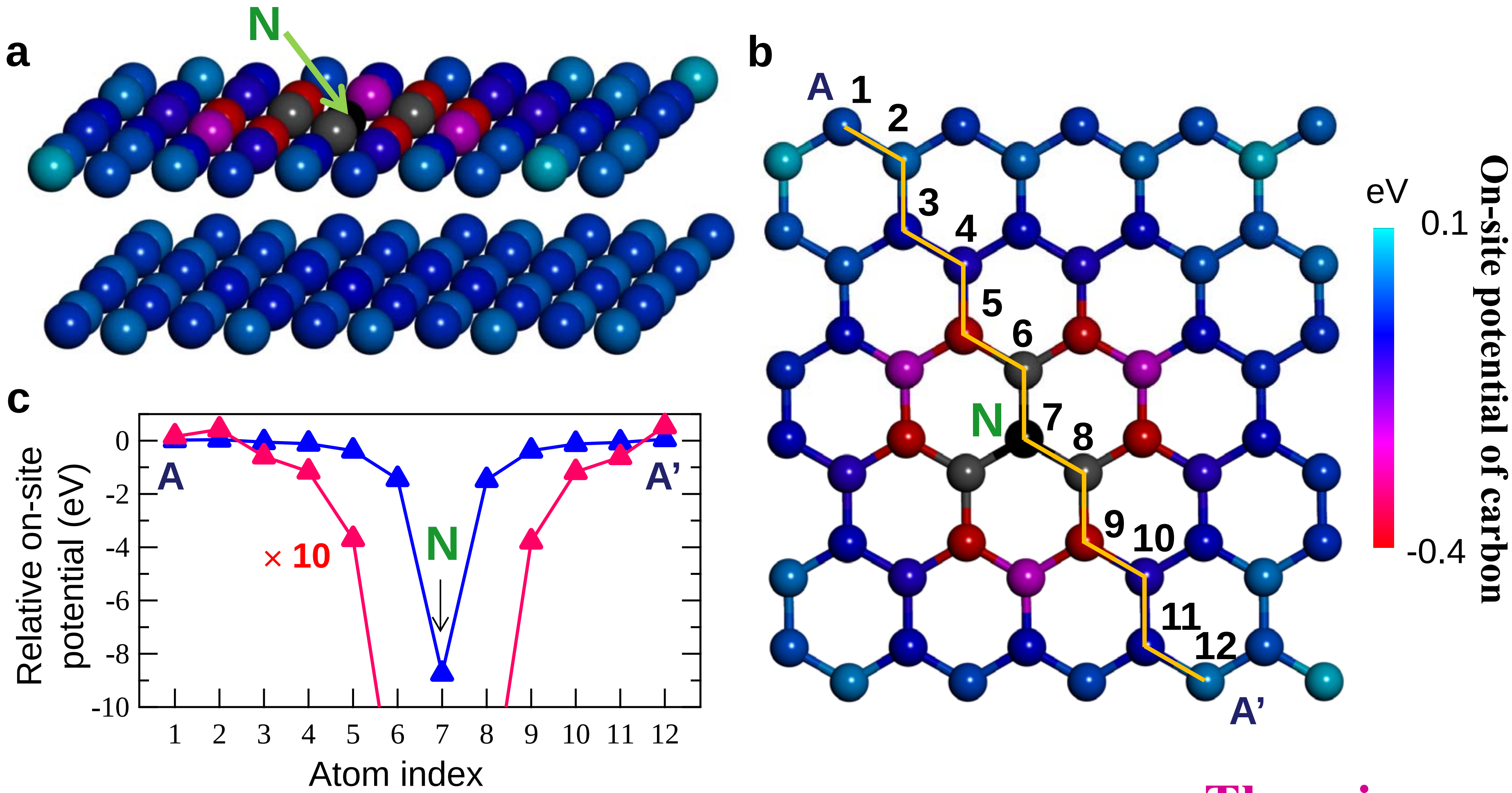


Inequivalent hopping along the potential gradient

LLs formation at $B = 0$ T

Gradient of on-site potentials around graphitic nitrogen

DFT calculation of nitrogen dope bilayer graphene



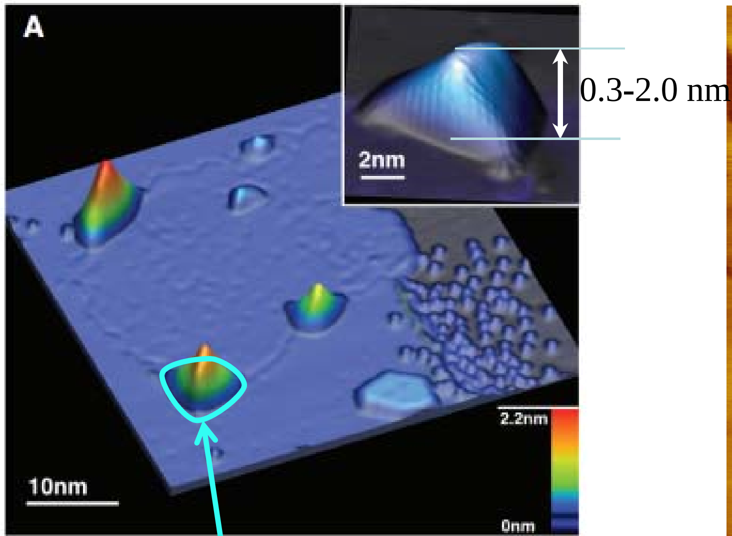
On-site potential of carbon next to nitrogen is 1.5 eV lower than carbon far from nitrogen!

There is a gradient of on-site potentials

Summary

- **Landau level peaks of bilayer graphene are observed in STS at the atomically flat area of nitrogen doped HOPG at $B = 0$ T.**
- **Domain model can explain the LL appearance.**
  (difference in the on-site potential)

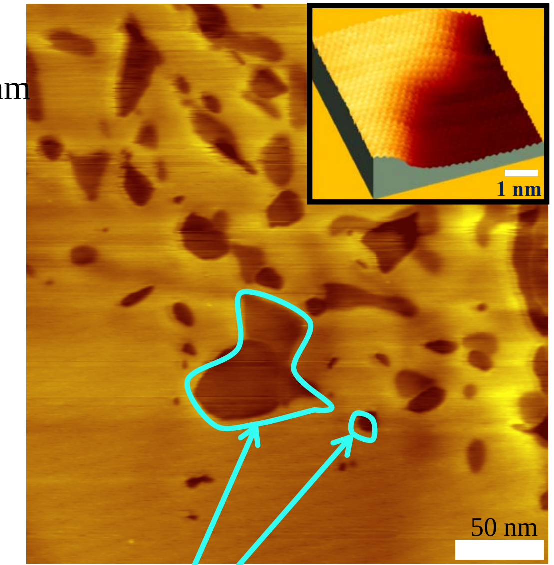
Strain



Science, 329, 544 (2010)

Nanobubble on Pt

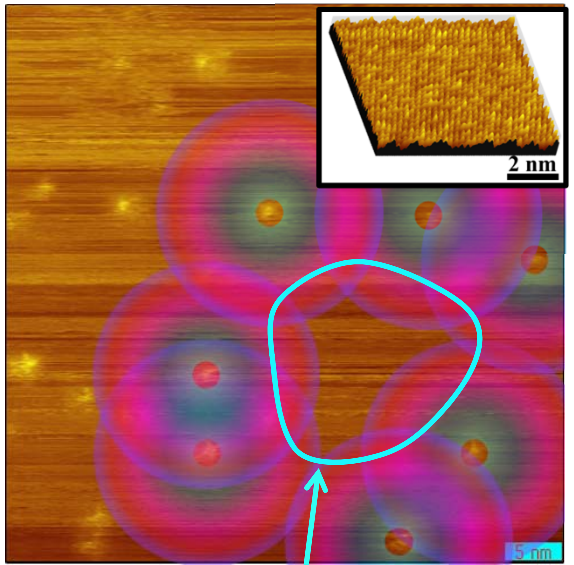
K-intercalated



Our work
Nature comm., 3, 1068 (2012)

K-free domains (Nanovalleys)

Nitrogen



Our work
Scientific Reports 5, 16412 (2015)

N doped-graphite