ナノ構造形成・新機能発現における電子論ダイナミクス

(

RSDFT Si

CONQUEST

OpenMX

FEMTECK   (

Car-ParrinelloMD

David Bowler (U College London) *CONQUEST*
Mauro Boero (U Strasbourg) *CPMD*

手法の開発とその応用

◆

➢

◆ LDA/GGA

➢

→ GGA+HFA　　　　　　　　　　　　　DMatrixFT

→

◆ 　　　　　　　10nm　　　10　　　　　　　DFT

➢

→ RSDFT, CONQUEST, OpenMX, FEMTECK

→

◆

➢

→ RS-CPMD, MetaDynamics

Why Alignment?

(TI)　　Jack Kilby　Novel prize in 2000

Selective Alignment of CNT on Al$_2$O$_3$ Substrate

*If carbon nanotubes (CNT) are used in next-generation technology, they should be aligned and integrated on some substrate.*

On Al$_2$O$_3$ surface,

SWCNT aligned along [-1101] on R plane (1-102) & [1-100] on A-plane (11-20) Selectively

Ago et al., CPL (2005)

Berber & Oshiyama: PRL 96, 105505 (2006)
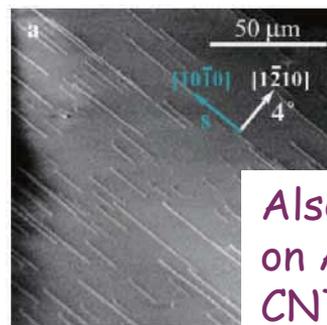
Also some particular facets on Al$_2$O$_3$ are used to align CNTs   Ismach et al., JACS (2005)

Chirality Selectivity
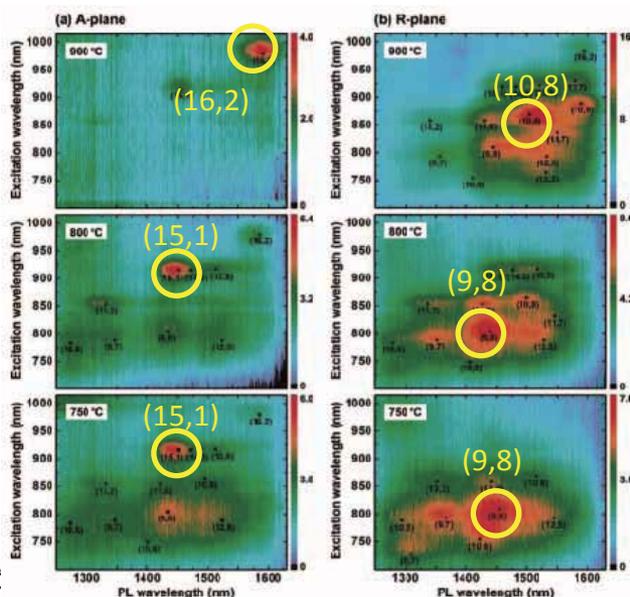
Issues:
- ✓ What is the reason of the selective alignment?
- ✓ Weak van der Waals OR some Covalency? Actually some debate based on nothing

In collaboration with Sukmin Jeong, 2011

Sapphire Al_2O_3, Complex Enough in Atomic Scale

[0001]
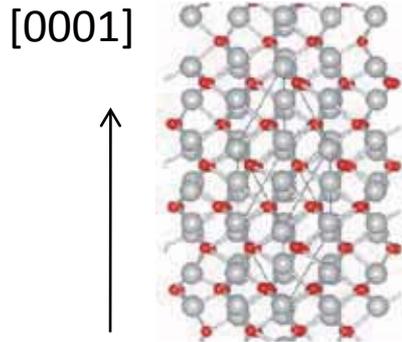
Al: gray
Oxygen: red
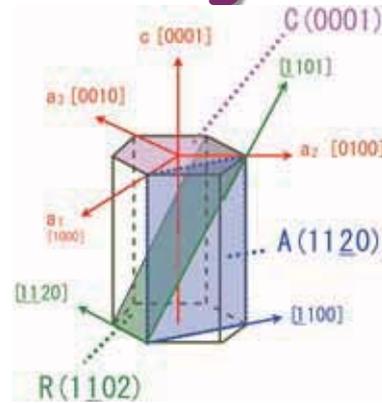
Structural Optimization and Energetics of Each Plane

R-plane

Kurita, Uchida & Oshiyama, PRB 82, 155319 (2010)
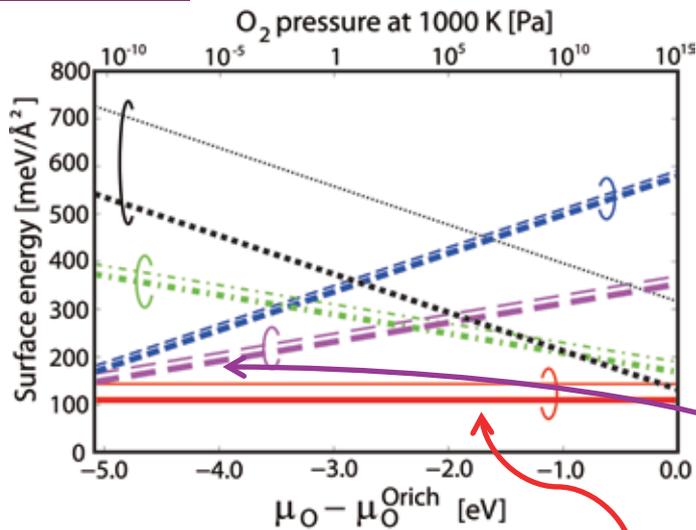
A-plane
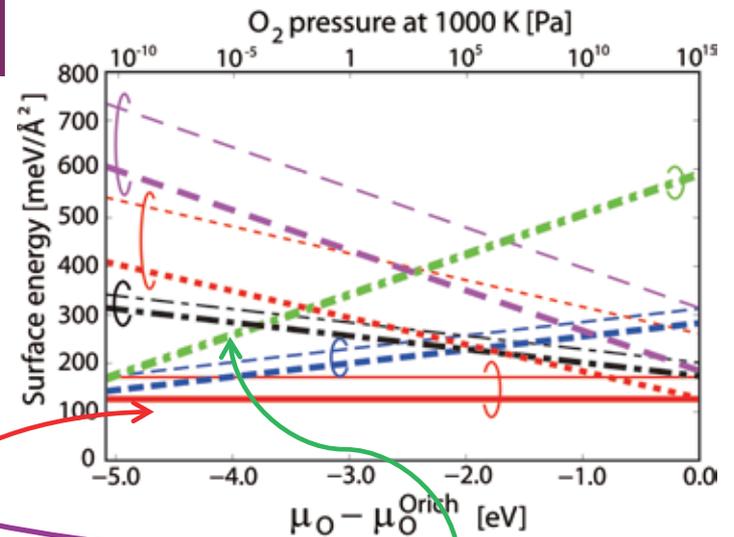
Stable Surfaces: stoichiometric surfaces and then Al-rich surfaces

On the Stoichiometric Surfaces

Along the <u>observed</u> direction,

(9,9)
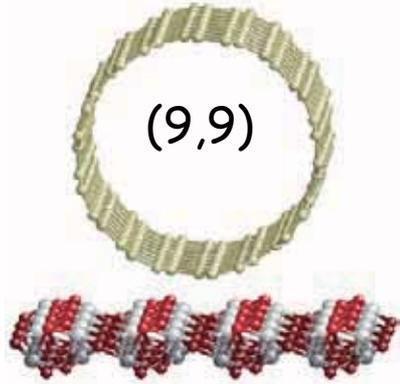
$d_{C-Al} > 3.20$
$d_{C-O} > 3.11$
cf. $d_{Al-C} = 1.90 - 2.21$
 in Al-carbides
No chemical bonds
$E_{ad} = 0.73$ eV/nm

Along the <u>different</u> (perpendicular) direction,

(9,9)
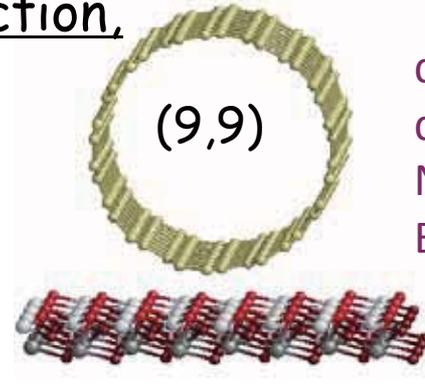
$d_{C-Al} > 3.02$
$d_{C-O} > 2.91$
No chemical bonds
$E_{ad} = 0.81$ eV/nm

Electron Localization Function

(a)
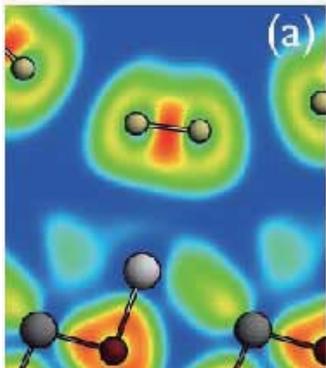
Weak (van der Waals) Interaction

Adsorption Energies (eV / nm)

Substrate orientation	CNT direction	LDA	GGA	VdW	GGA+ VdW
R-plane	[-1101]	0.73	-0.29	2.15	1.87
R-plane	[-1-120]	0.81	-0.30	2.41	2.11
A-plane	[1-100]	0.58	-0.59	1.95	1.36
A-plane	[0001]	0.47	-0.43	1.62	1.19

On the Al-Rich Surfaces

Along the observed direction,

[-1101] direction
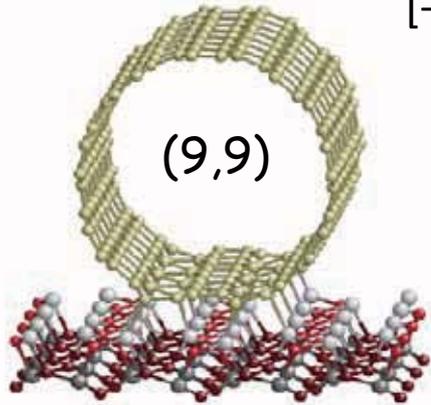
Flattening of CNT
CNT: sp2 → sp3
Four Al-C bonds
                    per unit
d_{Al-C} = 2.04 ~ 2.15
E_{ad} = 5.74 eV/nm

(9,9)

Along the different (perpendicular) direction,

Similar to
    [-1101] direction
But Three Al-C bonds
    per unit
d_{Al-C} = 2.05 ~ 2.20
E_{ad} = 2.99 eV/nm

(9,9)
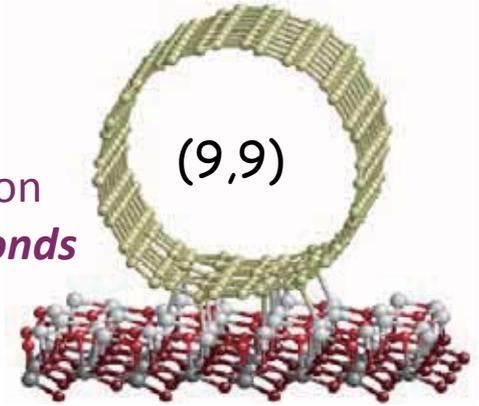
A-Plane

Along the observed direction,

[1-100] direction
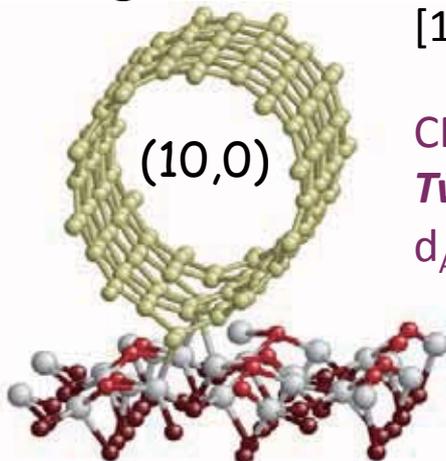
CNT: sp2 → sp3
Two Al-C bonds
d_{Al-C} = 2.06, 2.10
        E_{ad} = 1.62 eV/nm

(10,0)

Along the different (perpendicular) direction,

CNT: sp2 → sp3
One or Two Al-C bonds
d_{Al-C} = 2.04, 2.43
E_{ad} = 0.71 eV/nm

(10,0)
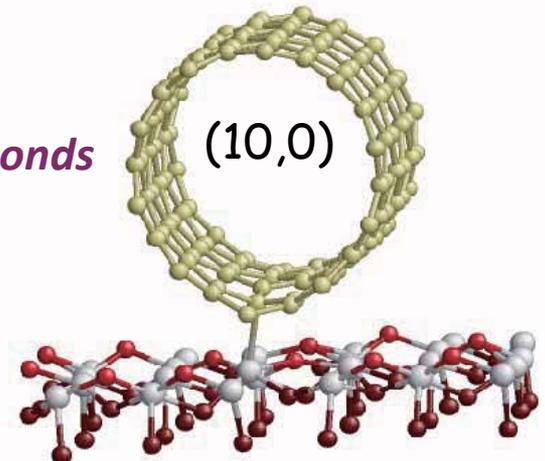
On the Al-Rich Surfaces

Covalent Bonding between substrate and CNT for Al-rich Surfaces

Stoichiometric   Al Rich
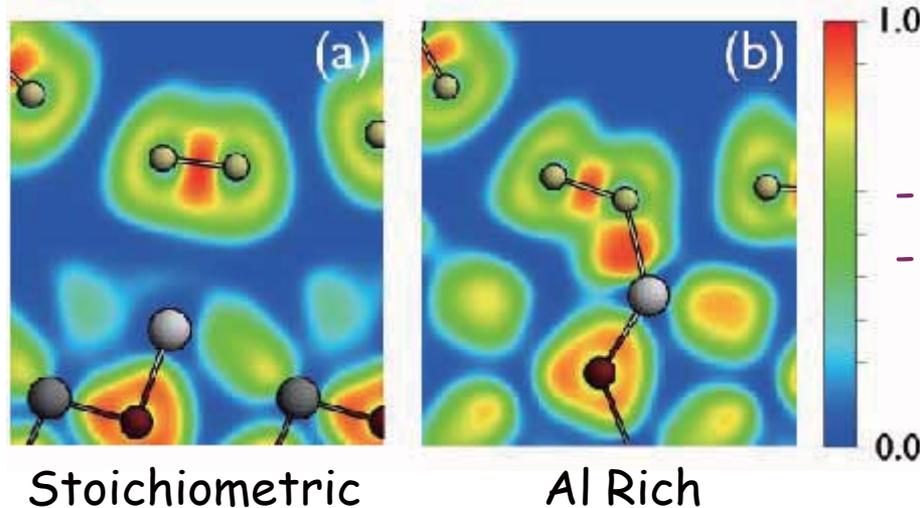
- Covalent bond between Al & C
- Partly ionic: $\Delta Q \approx 0.46e$ per bond (Bader charge)

Anisotropic Adsorption Energy (eV /nm) for Al-rich Surfaces

Substrate orientation	CNT direction	Stoichiometric	Al-Rich
R-plane	[-1101]	0.73	5.74	← Observed on R
R-plane	[-1-120]	0.81	2.99
A-plane	[1-100]	0.58	1.62	← Observed on A
A-plane	[0001]	0.47	0.71

*Surface anisotropy makes the difference in numbers of possible covalent bonds, then SELECTIVE ALIGNMENT*

Covalent Bonds Still Keep the Metal Metallic

Energy Bands and Orbitals for Adsorbed (9,9) CNT on R-Plane
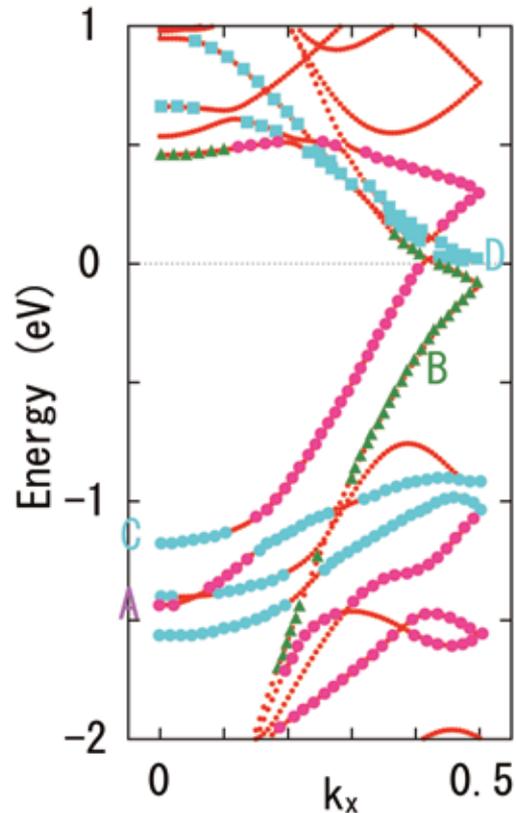
B: CNT State
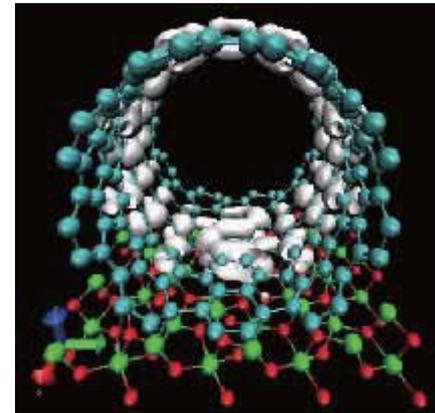
D: Substrate State
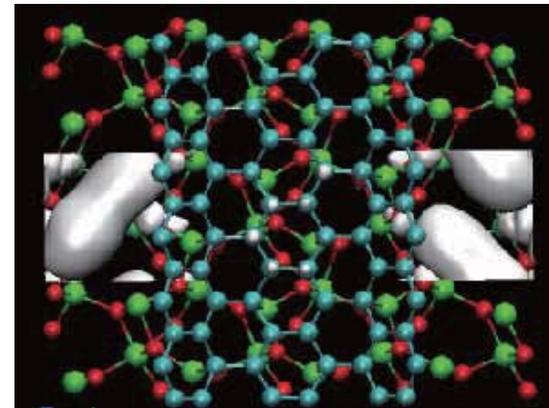
Let me finish,

confessing anti-computics fact:
Sukmin Jeong got these results by using
<u>V</u>ienna <u>A</u>b-initio <u>S</u>imulation <u>P</u>ackage

....

But I should add
he knows everything about our original
plane-wave code now known as TAPP,
PHASE?, STATE?,,,