Modification of Fermi Velocity in Epitaxial Graphene

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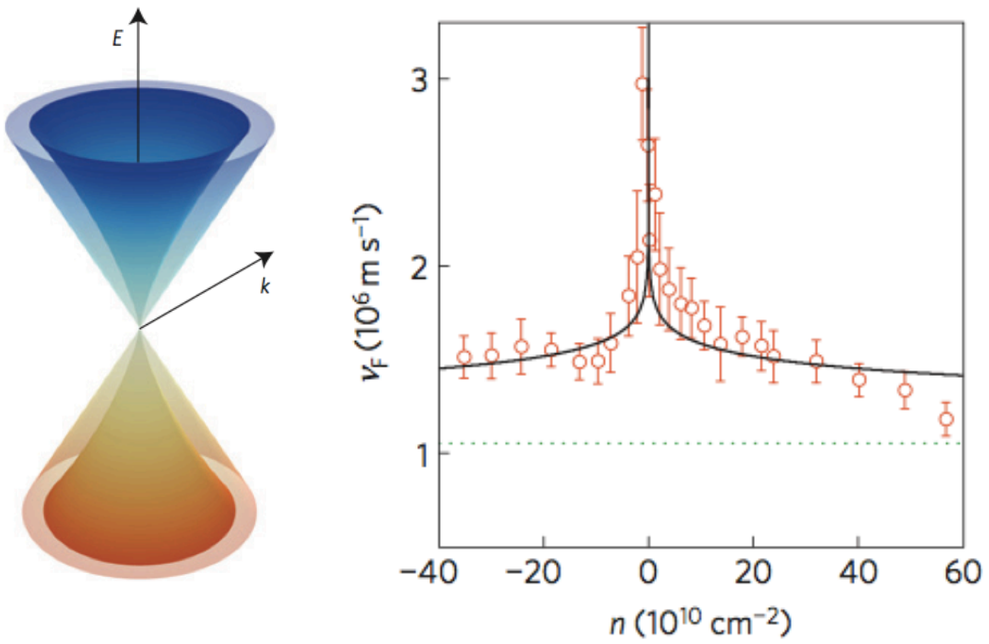
Fermi Velocity Modification in Graphene

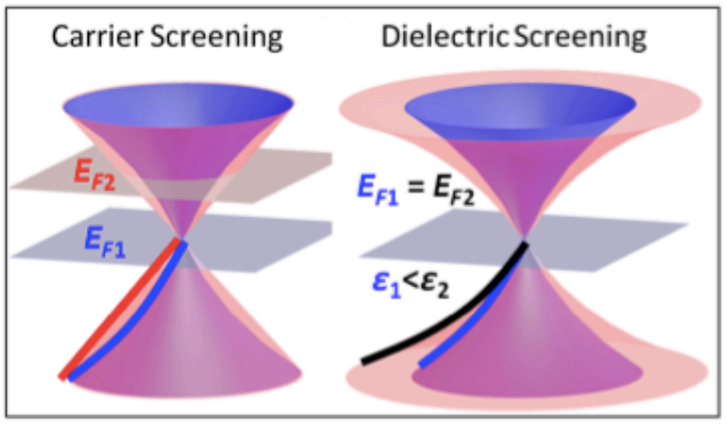
- Introduction of charges to a neutral graphene sheet (doping)
- screening of e-e interaction or long-range impurities (charges or impurities)

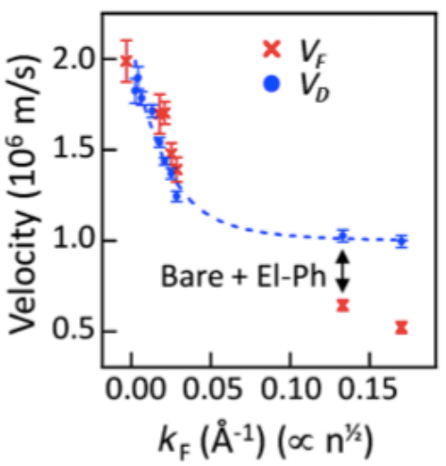


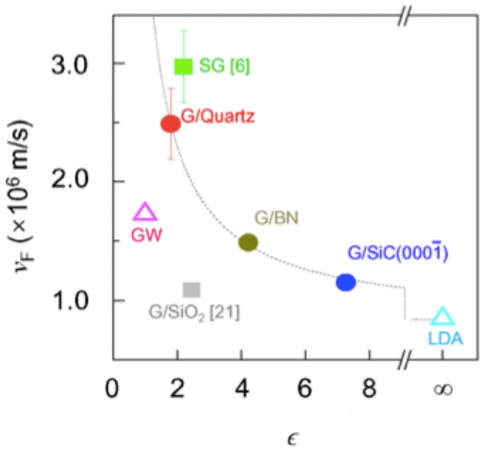
$$v_F(n) = v_F(n_0)\left[1 + \frac{\alpha}{8\varepsilon_G}\ln(n_0/n)\right]$$

- *e-e interaction considering*
- *Dirac cone reshaping*
- *e concentration tuning by gate*

Nature Physics **7**, 701 (2011)







- *carrier/dielectric screening effect*
- *Dirac cone reshaping*
- *few potassium deposition induced*

Phys. Rev. Lett. **110**, 146802 (2013)

Outline:

- Metal/Graphene Contact
  - *Work function difference: Surface charge transfer doping!*
- Metal deposition on Graphene
  - *No Work function difference: Ti and Graphene the work function is nearly the same!*
  - *Few Ti deposition on graphene (<3%)*
  - *Fermi velocity decrease: ARPES characterization*
- First-principle Calculation of Ti/Graphene system (Low concentration)
  - *Strong hybridization between Ti and C atoms*
  - *Modification of band dispersion*
- Take Home Messages

Doping Graphene with Metal Contacts

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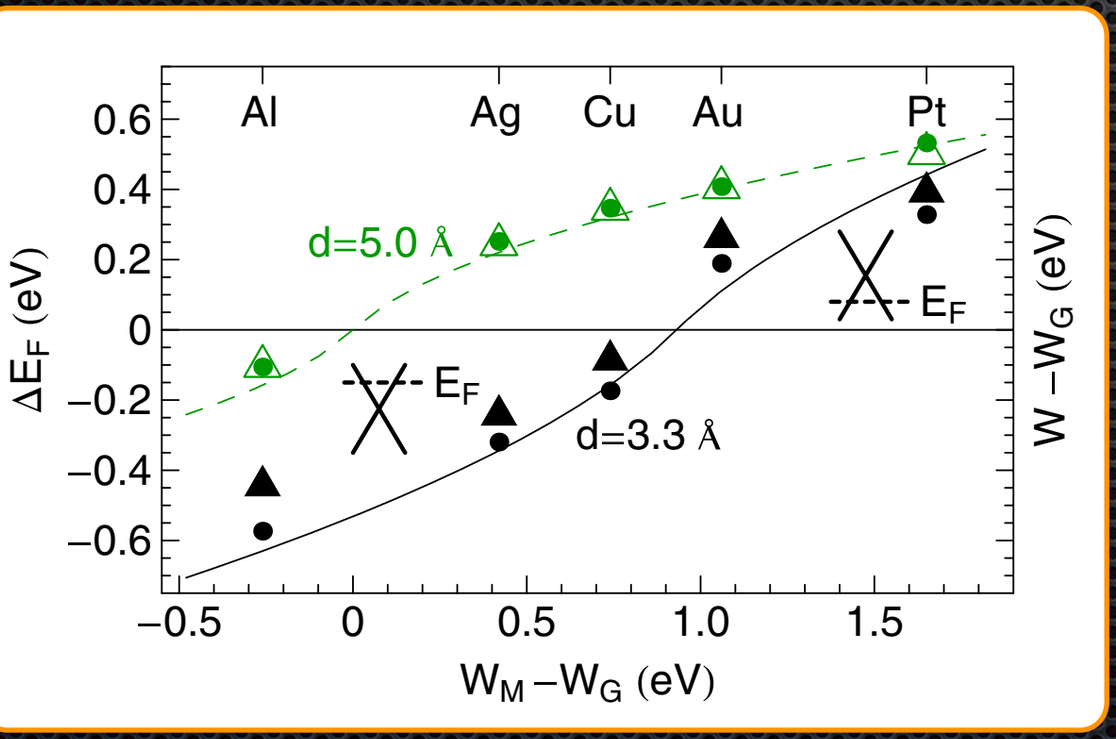
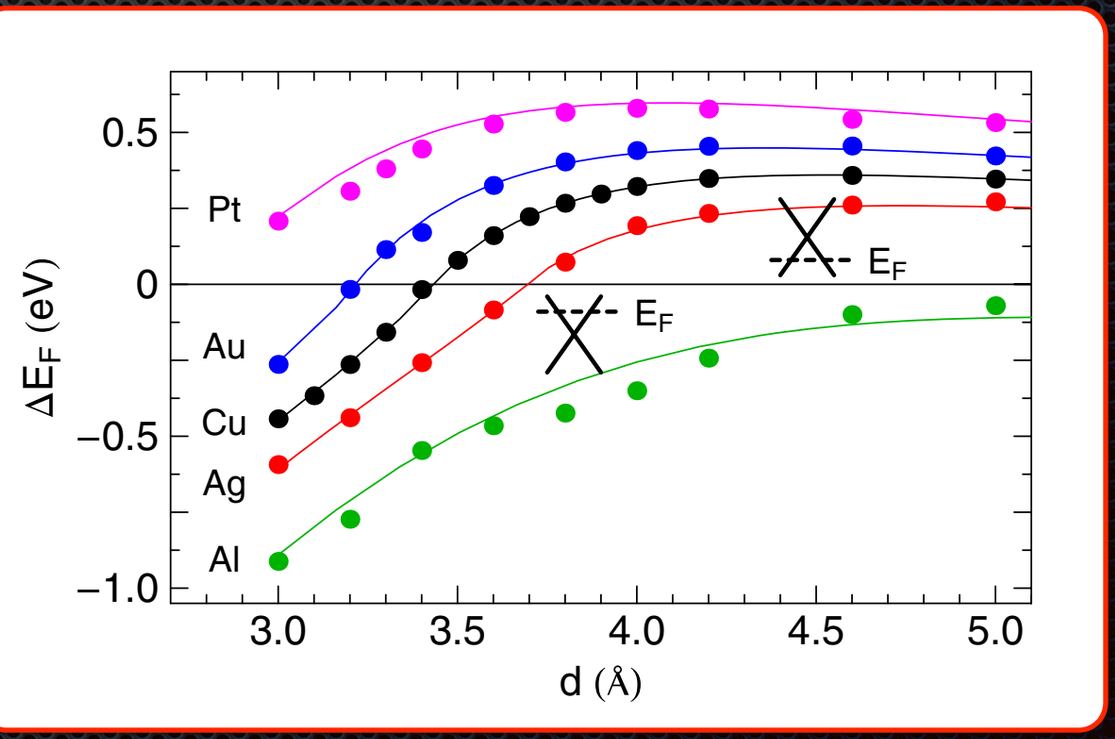
Making devices with graphene necessarily involves making contacts with metals. We use density functional theory to study how graphene is doped by adsorption on metal substrates and find that weak bonding on Al, Ag, Cu, Au, and Pt, while preserving its unique electronic structure, can still shift the Fermi level with respect to the conical point by ~0.5 eV. At equilibrium separations, the crossover from *p*-type to *n*-type doping occurs for a metal work function of ~5.4 eV, a value much larger than the graphene work function of 4.5 eV. The numerical results for the Fermi level shift in graphene are described very well by a simple analytical model which characterizes the metal solely in terms of its work function, greatly extending their applicability.



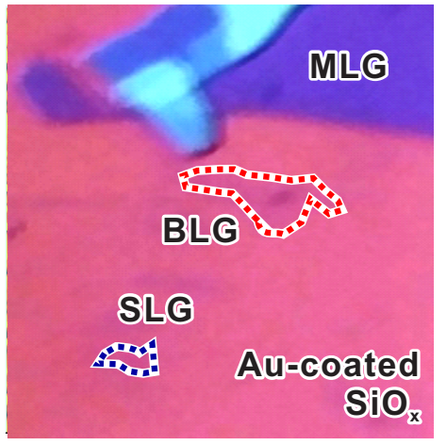
Fermi level shifts ΔE_F as a function of the graphene-metal work function difference

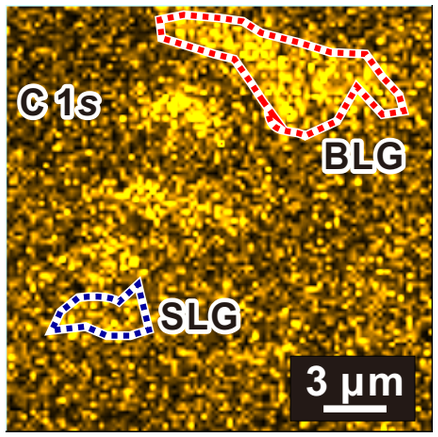


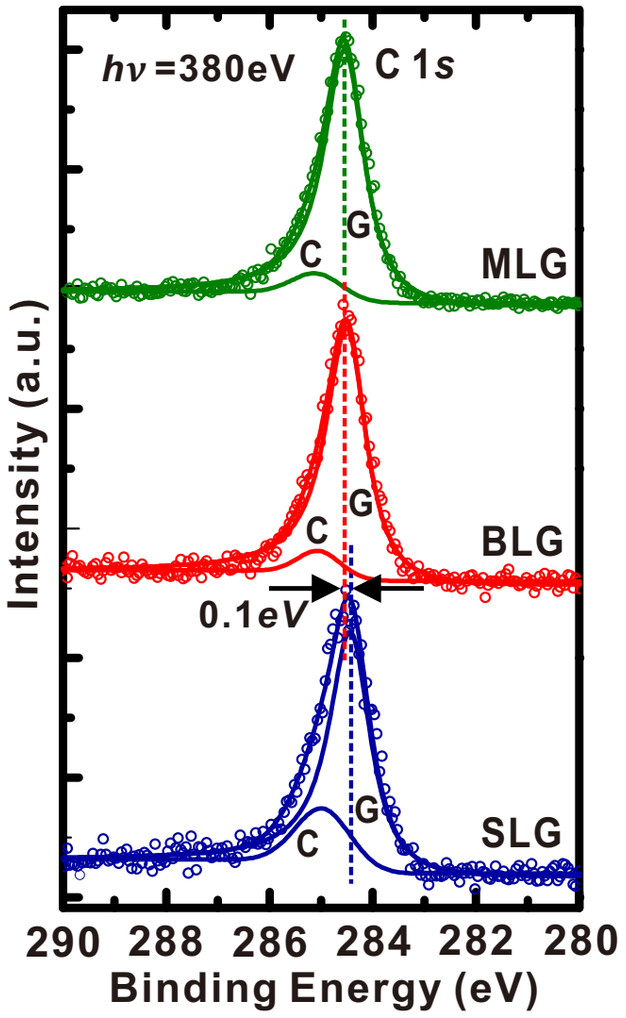
Fermi level shifts ΔE_F as a function of the graphene-metal surface distance

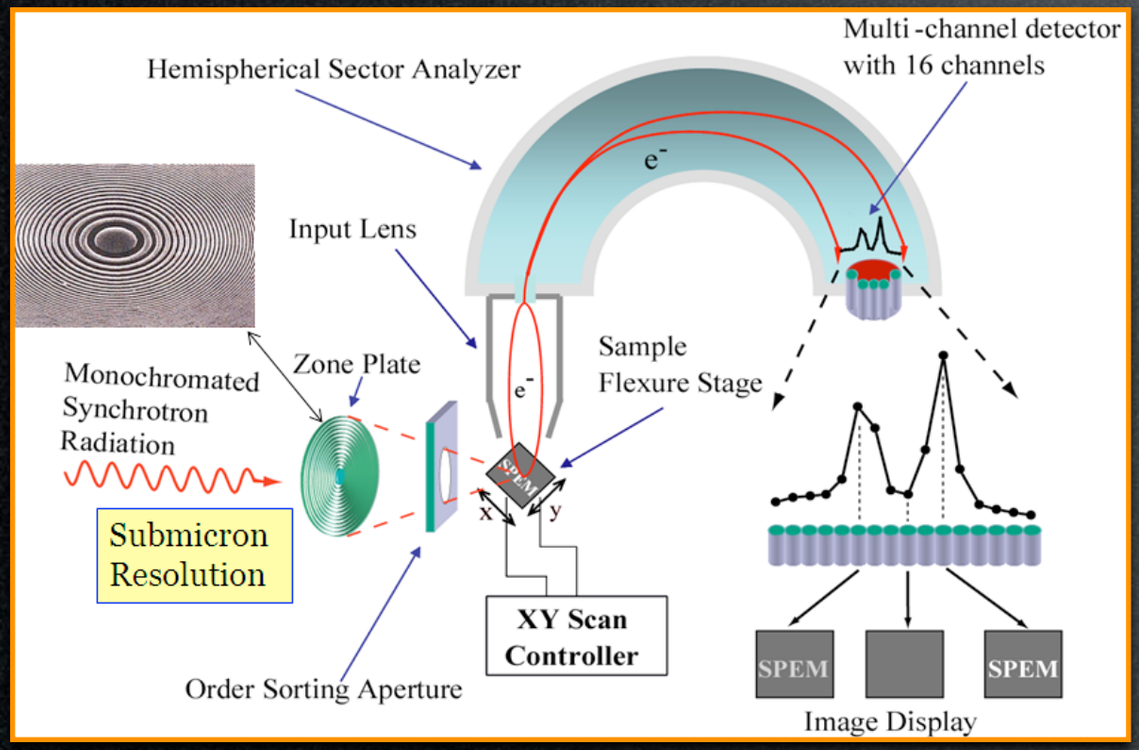
Photoelectron Spectroscopic Characterization of Graphene/Metal Contact

- Scanning Photoelectron Microscopy/Spectroscopy (SPEM/S) Measurement









SPEM Image

C 1s chemical mapping

- graphene area identification

- good agreement with OM image

μ-PES Characterization

C 1s PES spectra

- asymmetric line shape

- SLG component (G) at 284.4 eV with low α factor (~0.8)

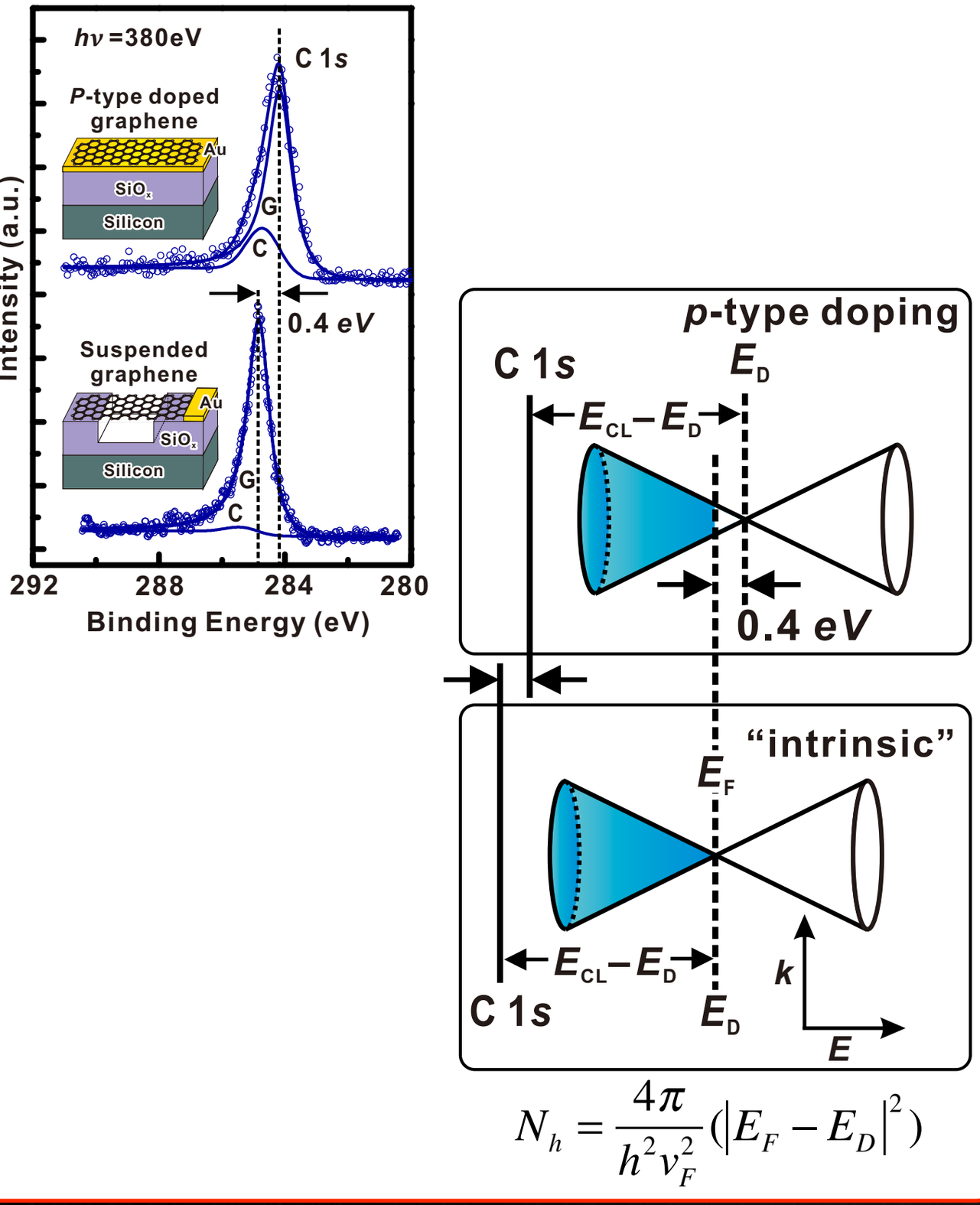
- Doniach-Sunjic function

- carbon contamination (C)

Chung-Lin Wu* *et al*, "Graphene on Au-coated SiO_x substrate: Its core-level photoelectron micro-spectroscopy study" *Appl. Phys. Express* **5**, 085101 (2012)

Charge Transfer between Graphene and Metal

- C 1s Core-level Characterization



$$N_h = \frac{4\pi}{h^2 v_F^2}(|E_F - E_D|^2)$$

Doping Level Examination

C 1s core-level shift

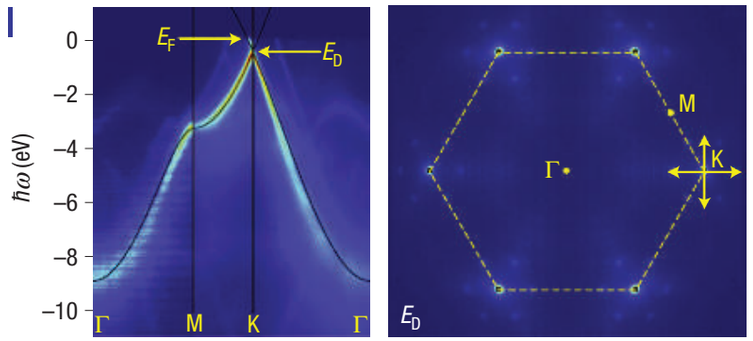
- material constant (E_{CL}-E_D)
- directly related to E_D shift
- SLG having lower work funtion (4.6 eV) than Au (5.54 eV)
- *p*-type doping (1.1×10^{13} cm^{-2})
- larger work function of BLG (4.7 eV)
- less *p*-type doping of BLG

How about if the metal has the same work function with graphene?

Chung-Lin Wu* *et al*, "Graphene on Au-coated SiO_x substrate: Its core-level photoelectron micro-spectroscopy study" *Appl. Phys. Express* **5**, 085101 (2012)

Characterization of Fermi Velocity in Graphene

- quasi-free-standing graphene @ SiC



- *angle resolved photoemission spectroscopy (ARPES)*
- *Energy dispersion of Graphene*

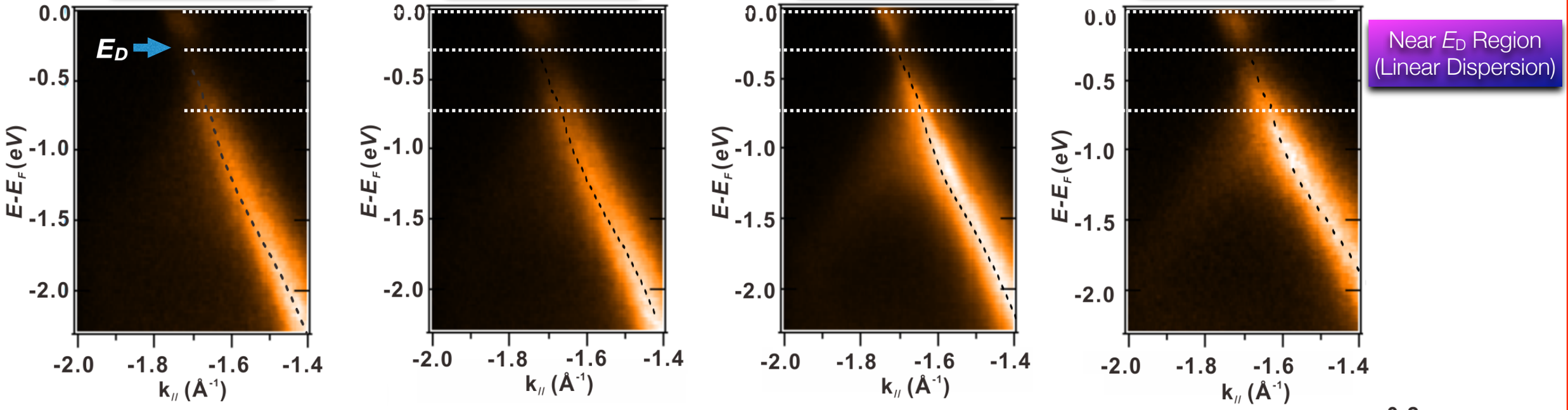
$E=hkV$; $V_F \propto \Delta E/\Delta k$

Nature Physics **3**, 36 (2007)

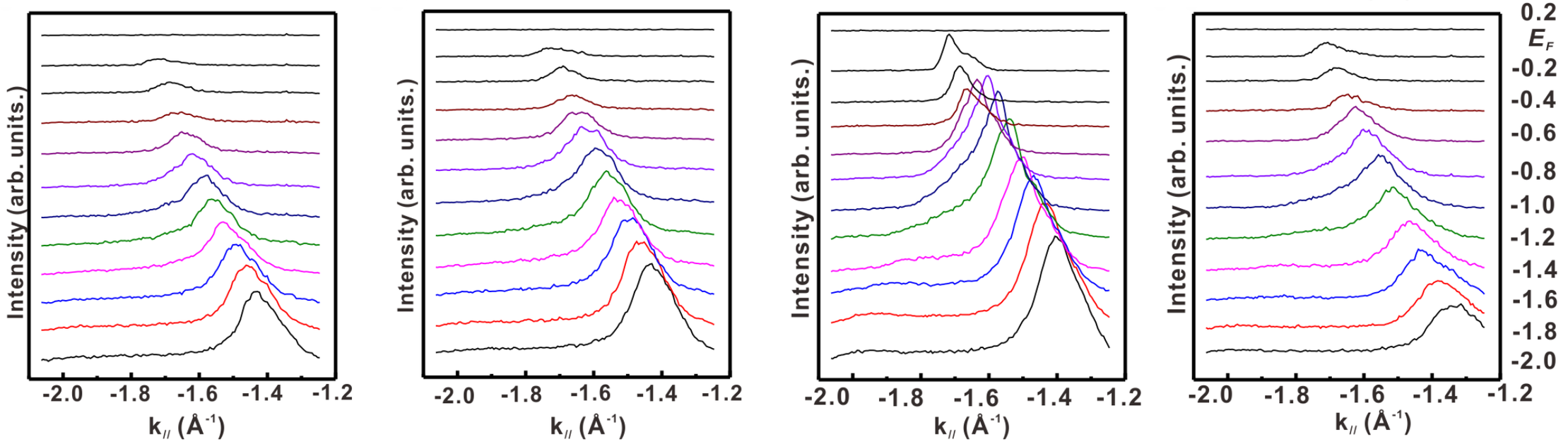
Increased Ti Coverage on SLG

As grown

SLG@SiC | 30s Ti@SLG | 60s Ti@SLG | 90s Ti@SLG

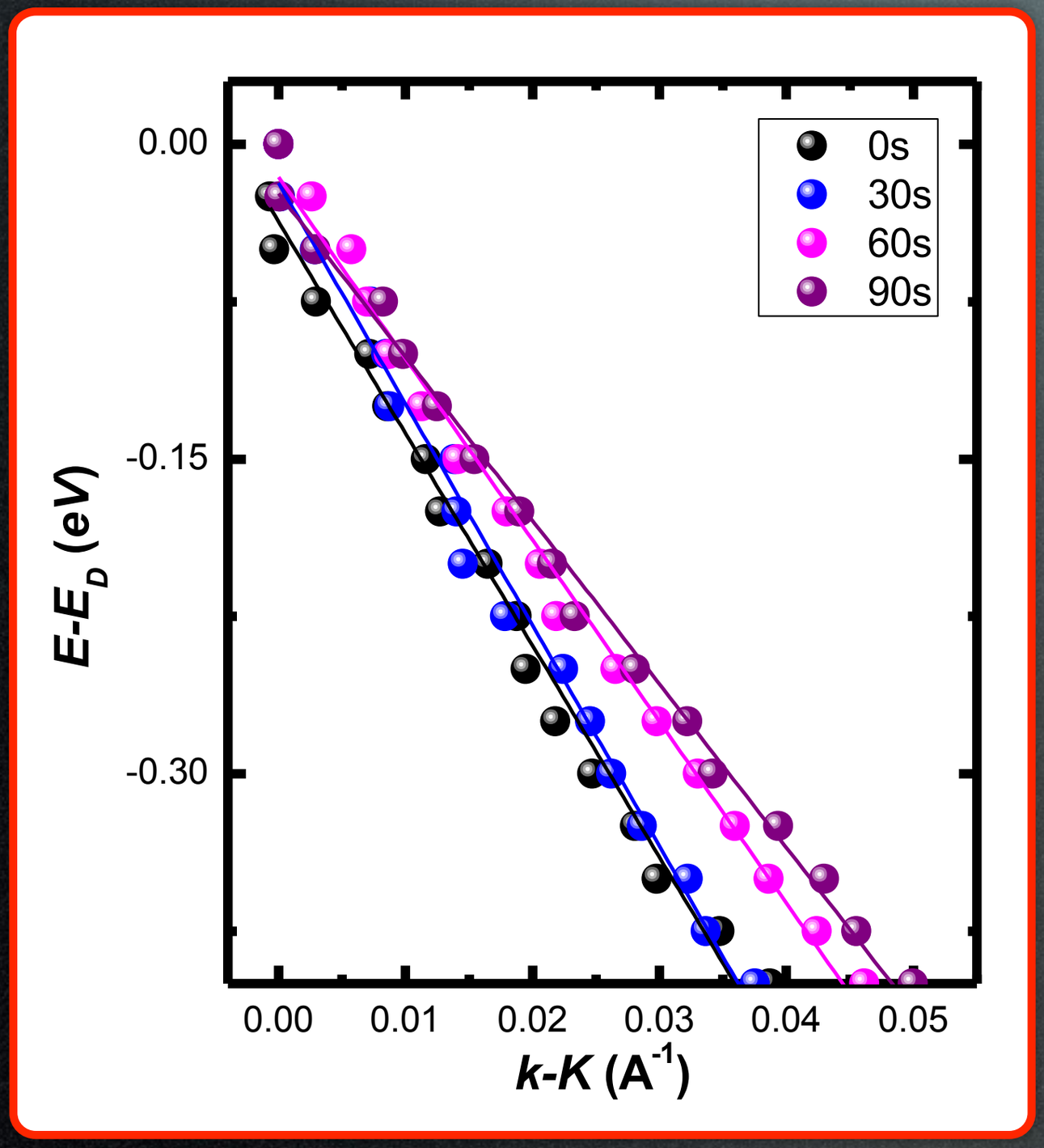


Near E_D Region (Linear Dispersion)



Characterization of Fermi Velocity in Graphene

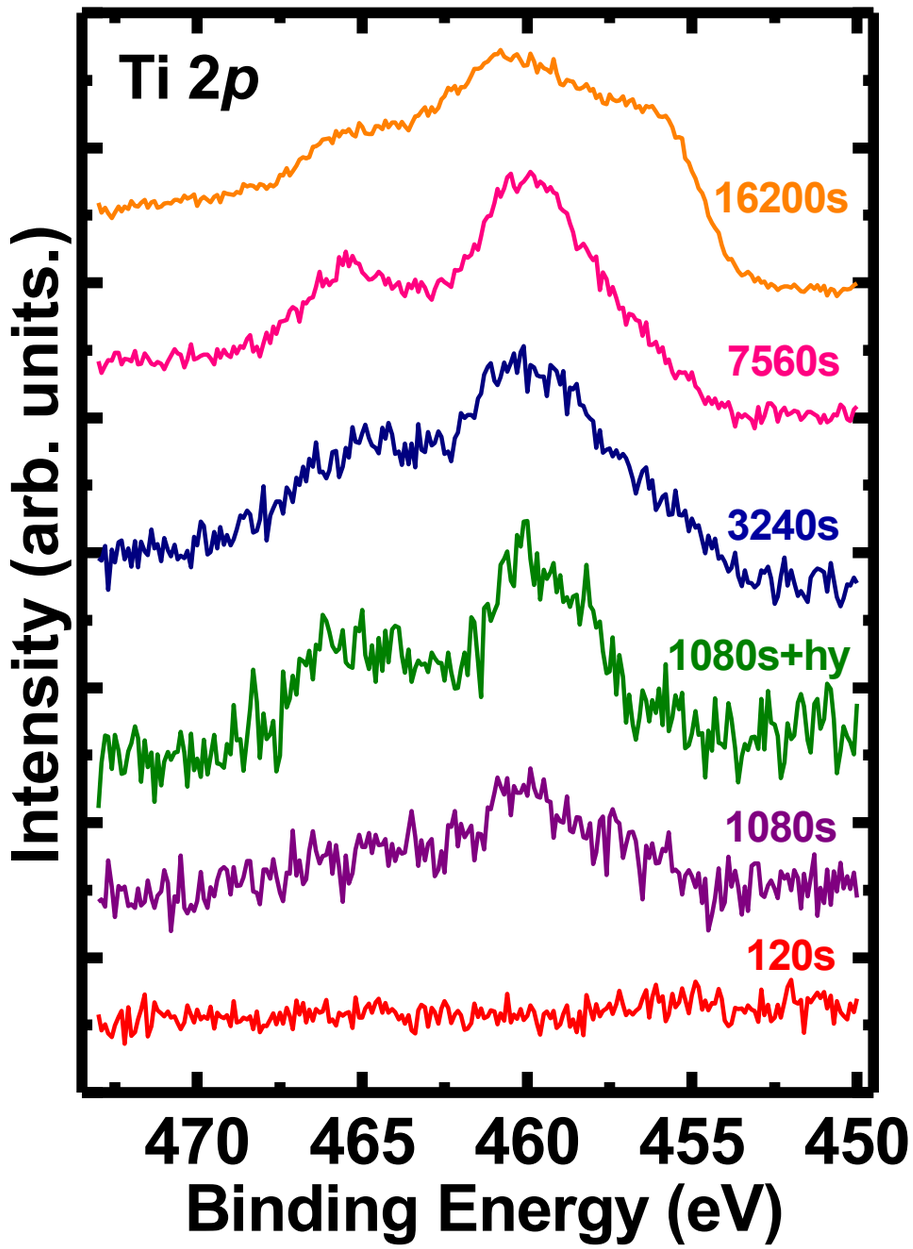
- Linear Dispersion near ED
-Dirac Cone Reshaped
- Determined by dE/dk (slope)
- Decreased with Ti coverage on SLG



Deposition Time	Slope (eV	Velocity (10
0 Sec (as grown)	10.10	1.53
30 Sec	10.53	1.60
60 Sec	8.65	1.31
90 Sec	7.794	1.18

Fermi velocity decrease about 25%!!

Characterization of Ti Coverage on Graphene



- Ti 2p core-level (CL) spectra at different Ti coverage up to maximum deposition of 16200s
- Constant deposition flux
- Ti CL signal appearing until 1080s deposition - about 3% (XPS detection limit) Ti coverage under 1080s deposition

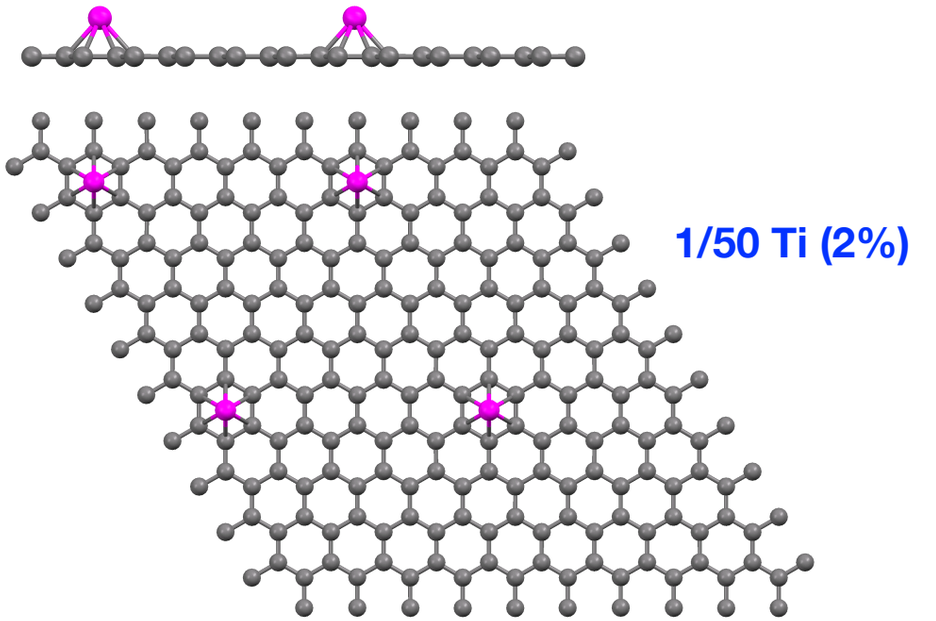
- 60 s → 0.16 %
- 90 s → 0.25 %

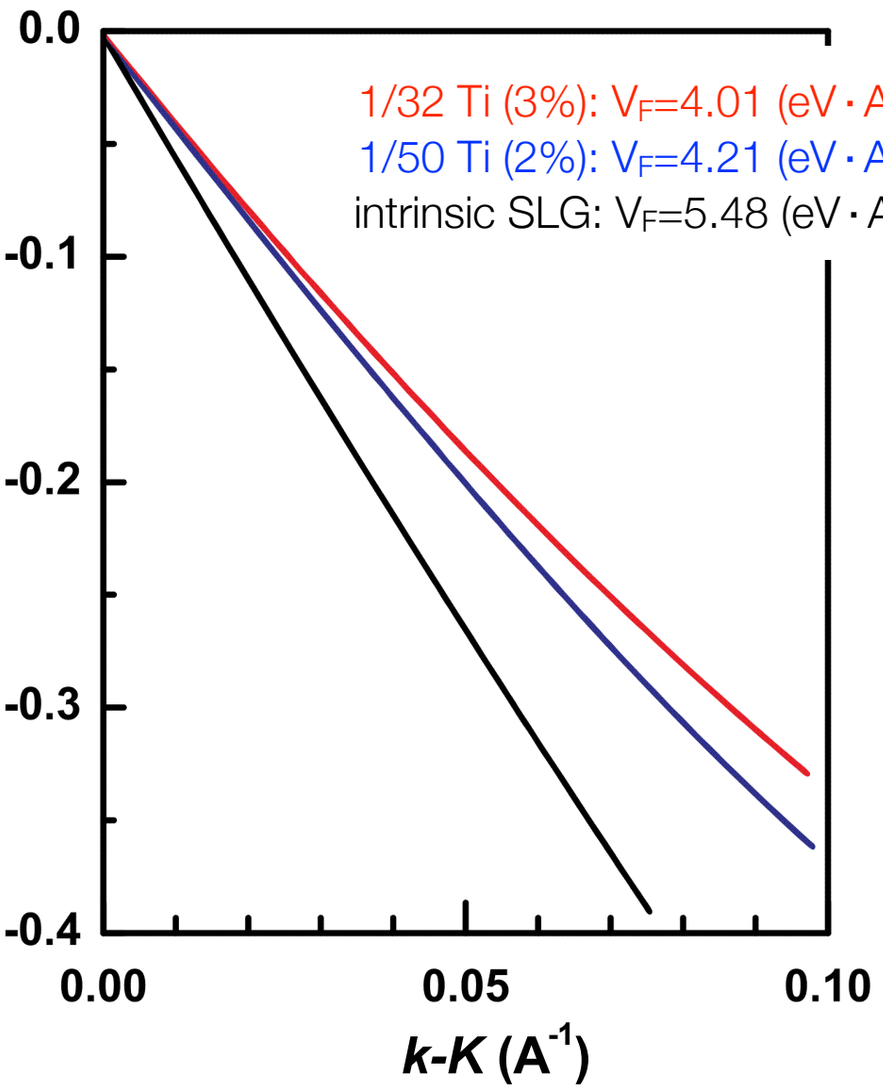
Few Ti make Fermi velocity decrease a lot!! ~ -25%

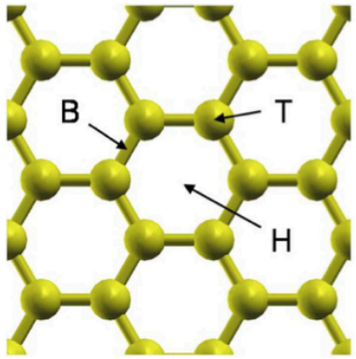
First-principle study of Ti adatom adsorption on graphene

- Energetic and structural properties of different adsorption sites
- Band dispersion modification with changing Ti adsorption concentration

contributed by **Prof. M.-F. Lin, NCKU Phys**







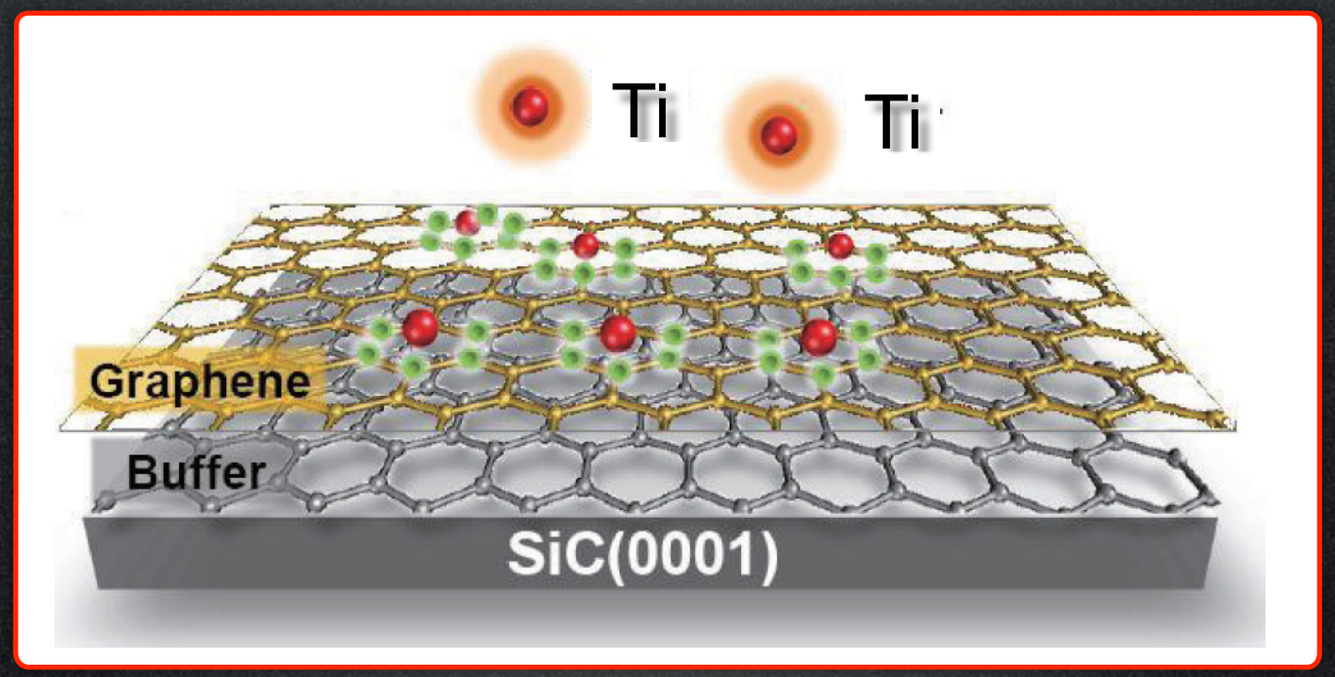
Phys. Rev. B **77**, 235430 (2008)

	Site	ΔE (eV)	E_c (eV)	$\Delta E/E_c$	$E_a^{max}-\Delta E$ (eV)	h (Å)	d_{AC} (Å)	d_{GC} (10^{-1} Å)
	H	1.096	1.630	0.672		1.71	2.23	0.0
	B	0.773			0.322	1.88	2.09	0.2
	T	0.754			0.342	1.89	2.02	0.3
	H	0.462	1.113	0.415		2.28	2.70	0.1
	B	0.393			0.069	2.44	2.59	0.1
	T	0.389			0.074	2.49	2.54	0.1
	H	0.802	0.934	0.859		2.60	2.99	0.1
K	*B*	0.739			0.063	2.67	2.85	0.3
	T	0.733			0.069	2.67	2.77	0.2
	H	0.632	1.840	0.343		2.29	2.72	0.1
Ca	*B*	0.484			0.148	2.33	2.53	0.2
	T	0.478			0.154	2.34	2.46	0.2
	H	1.042	3.390	0.307		2.13	2.56	0.1
Al	*B*	0.927			0.115	2.22	2.33	0.1
	T	0.911			0.131	2.22	2.24	0.2
	H	0.858	2.810	0.305		2.20	2.63	0.0
Ga	*B*	0.762			0.096	2.30	2.41	0.0
	T	0.749			0.109	2.31	2.33	0.1
	H	0.690	2.520	0.274		2.45	2.83	0.1
In	*B*	0.622			0.069	2.53	2.63	0.0
	T	0.614			0.077	2.55	2.56	0.1
	H	0.114			0.142	3.19	3.48	0.1
Sn	*B*	0.253			0.003	2.79	2.81	0.8
	T	0.256	3.140	0.082		2.82	2.75	0.7
	H	1.869	4.850	0.385		1.80	2.33	0.2
Ti	*B*	1.301			0.568	2.05	2.27	0.3
	T	1.301			0.568	2.00	2.18	0.3
	H	0.748	4.280	0.175		1.53	2.11	0.1
Fe	*B*	0.231			0.517	2.22	2.35	0.0
	T	0.149			0.599	2.18	2.13	0.5
	H	0.852			0.230	2.03	2.46	0.3
Pd	*B*	1.081	3.890	0.278		2.21	2.18	1.4
	T	1.044			0.038	2.21	2.10	1.1
	H	0.085			0.011	3.53	3.80	0.0
Au	*B*	0.089			0.007	3.06	3.11	0.4
	T	0.096	3.810	0.025		2.69	2.55	1.4

Ti has the largest binding energy (energetically favorite) at the H site, rather B and T sites!!

Take Home Messages:

- With the progressive deposition of small quantities of Ti, we observe an renormalization of the near-E_D valence band, a decrease in the Fermi velocity.
- These results might due to the strong bonding formation between Ti and C at the graphene hollow site.
- First-principle studies shows consistent results with ARPES measurements.



Thanks for Your Attention