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ADRIATICO RESEARCH CONFERENCE on

LASERS IN SURFACE SCIENCE

11–15 September 2000

Miramare – Trieste, Italy

Surface states at a graphite monolayer on Pt(111) studied by multi-photon photoelectron spectroscopy

Y. Matsumoto
the Graduate University for Advanced Studies
Kanagawa, Japan

Surface states at a graphite monolayer on Pt(111) studied by multi-photon photoelectron spectroscopy

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The Graduate University for Advanced Studies (Sokendai), Hayama

Adriatico Research Conference on

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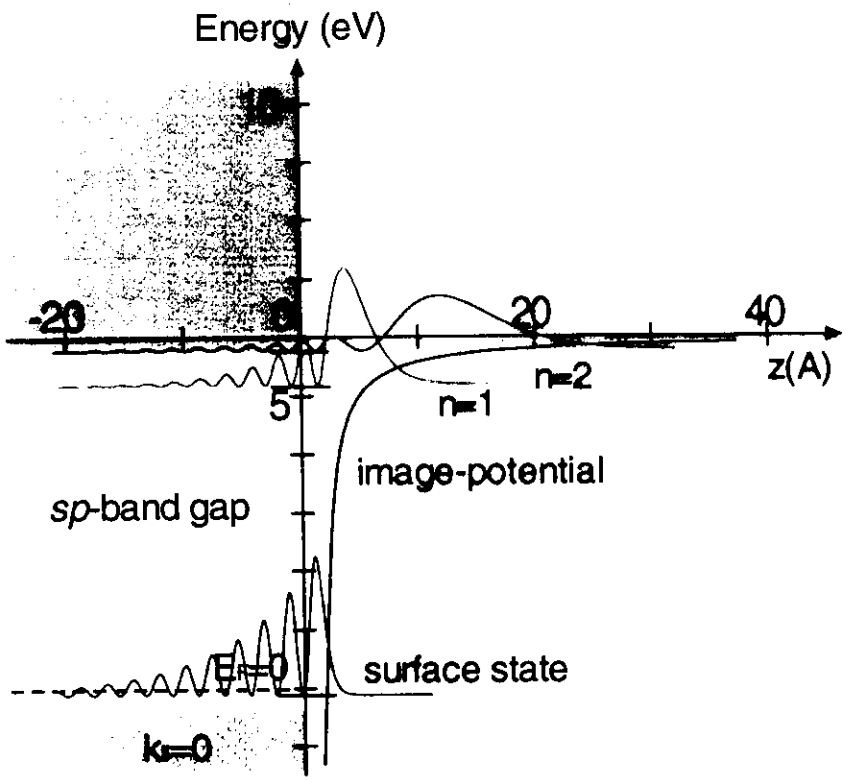
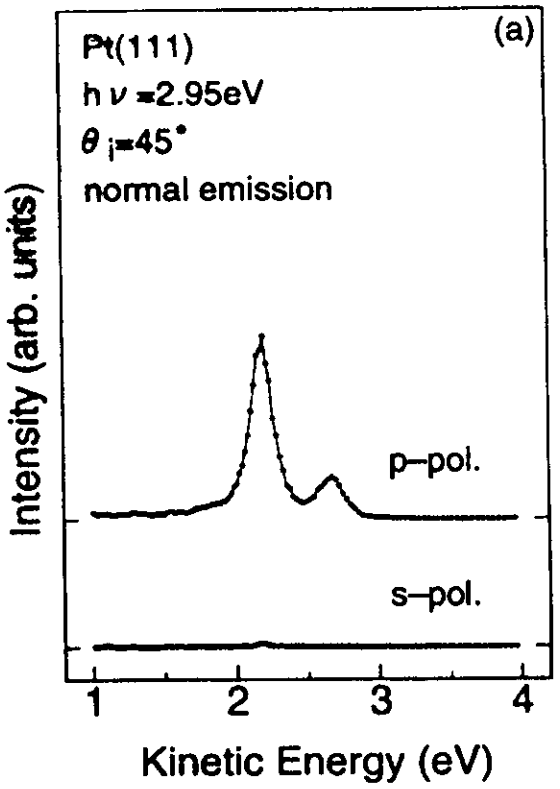
Surface States and Image Potential States at Pt(111)





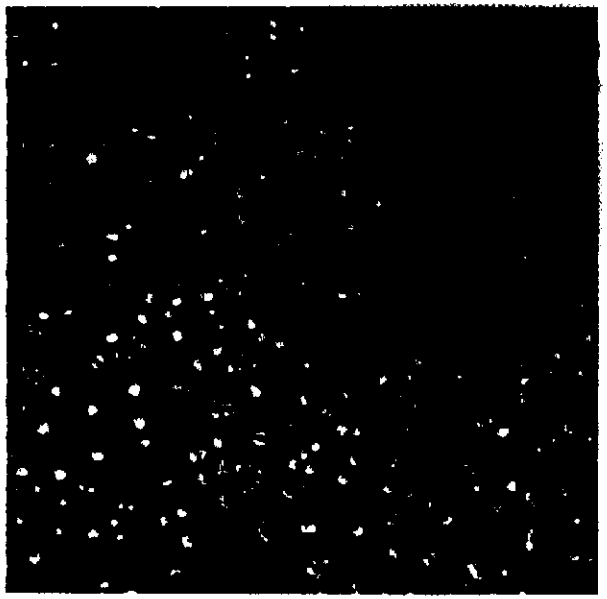
3PPE from clean Pt(111)

I.Kinoshita, et al., *Chem. Phys. Lett.*, **229**, 445 (1996).

Graphene on Pt(111)

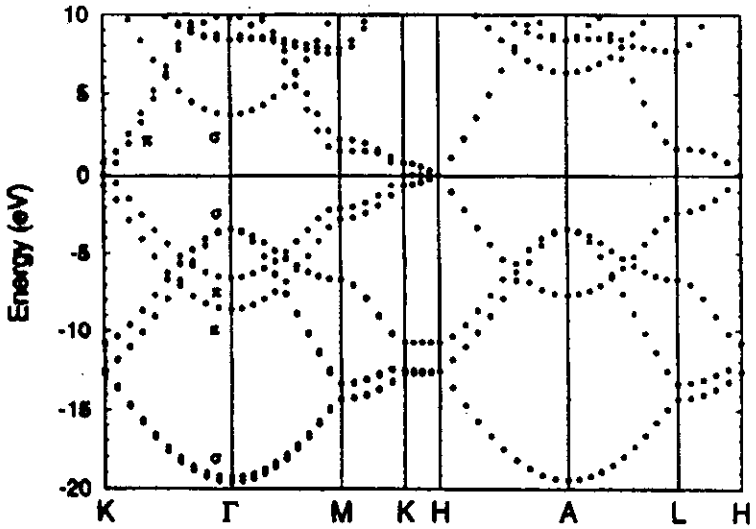
How are surface states on clean Pt(111) affected by a graphite monolayer?
Cf. Xe, heptane/Ag(111) etc.

Island of graphene on Pt(111)



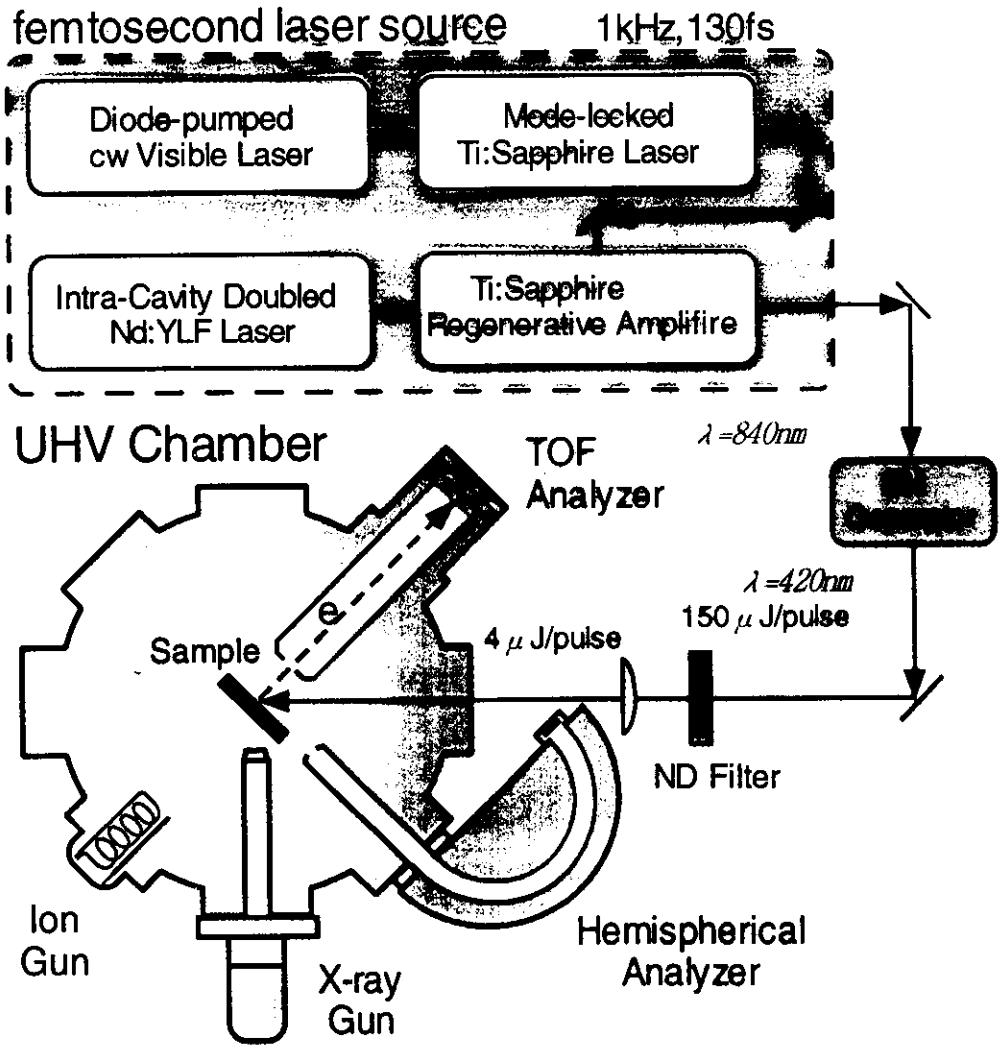
STM image (1000 Å × 1000 Å)
T.A.Land et al. Surf. Sci. 264 (1992) 261

Unoccupied states of graphene?



J.C.Bottger, Phys. Rev. B55 (1997) 11202

Experimental



Sample preparation

[Graphite/Pt(111)]

1. Pt(111) cleaning
   - Ar^+ ion sputtering
   - Annealing
   - O_2 treatment
2. C_2H_4 dose @110K
3. Annealing to 900K or 1100K

The processes of 2 and 3 are repeated to obtain high coverage.

Image potential states

Binding energies of the image states :

$$E_e - h\nu = \Phi - E_b(n)$$
$$= \Phi - \frac{0.85\text{eV}}{(n+a)^2}$$

$E_e = 6.93\text{eV}\ (n=1)$ ··· B

$E_e = 7.55\text{eV}\ (n=2)$ ··· C

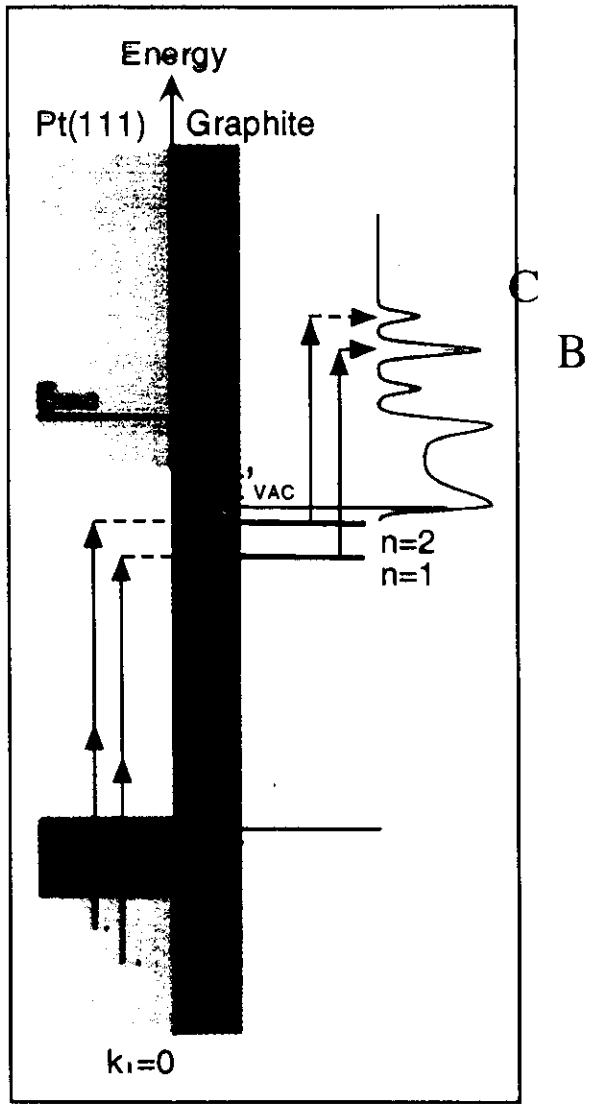
$E_b(n=1) = 0.83\text{eV}$

$E_b(n=2) = 0.21\text{eV}$

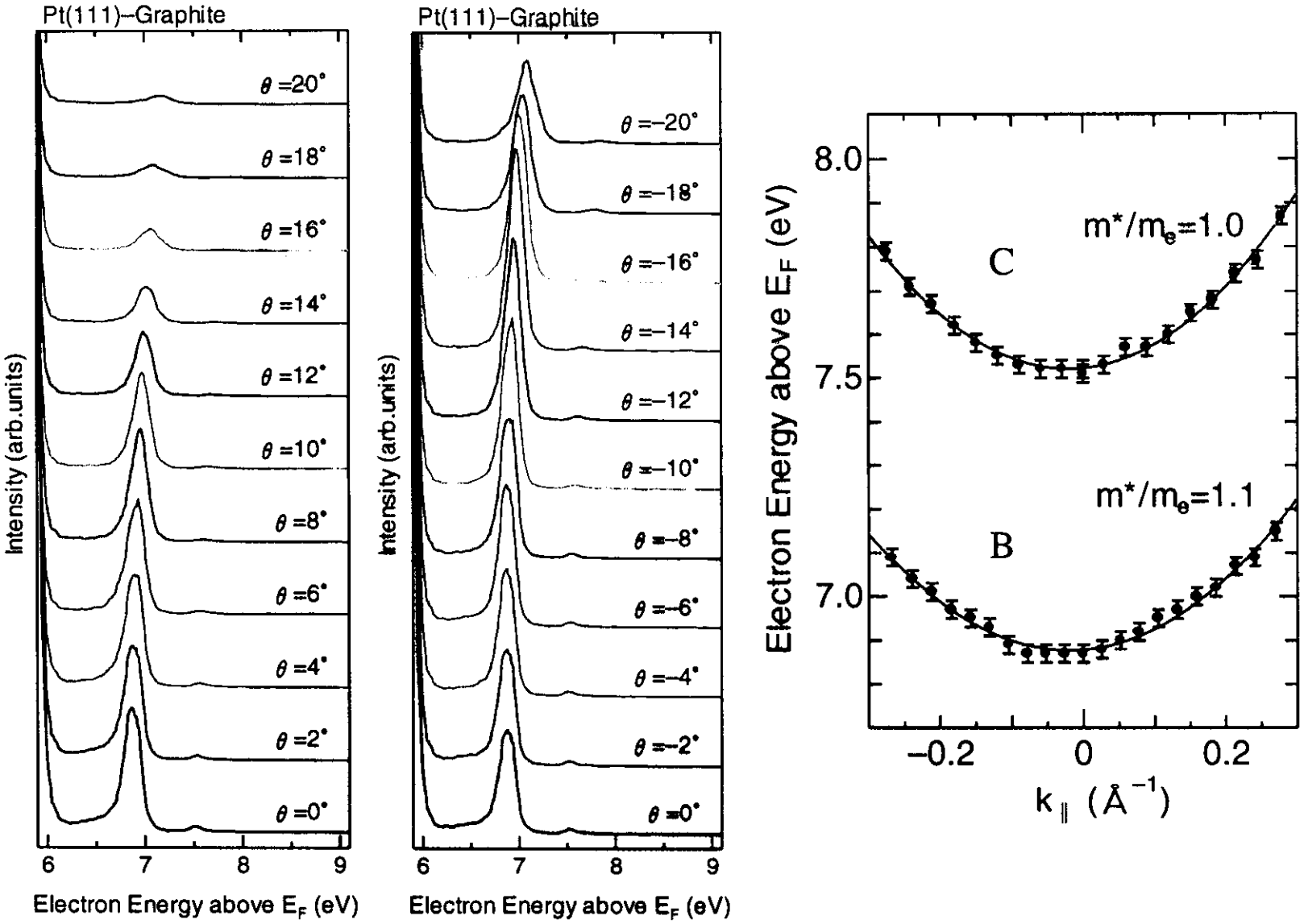
$\Phi_{\text{grp}} = 4.81\text{eV}$ cf. 4.7eV for Bulk graphite

$(\Phi_{\text{Pt(111)}} = 5.98\text{eV})$

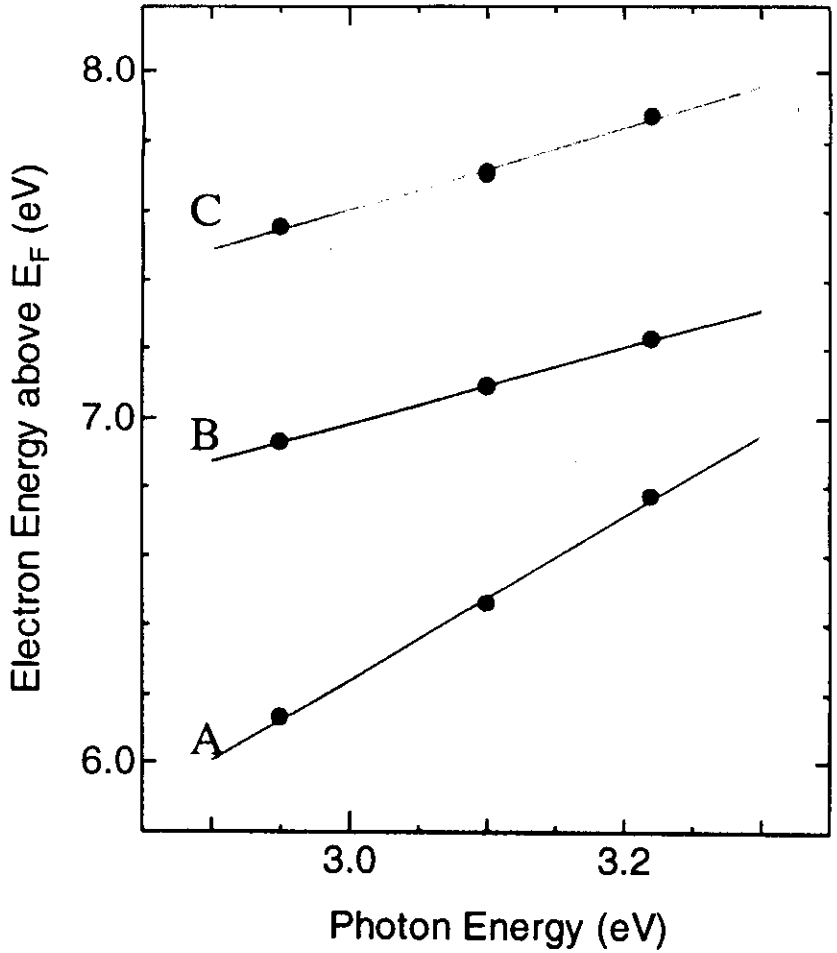
$a = 0.012$

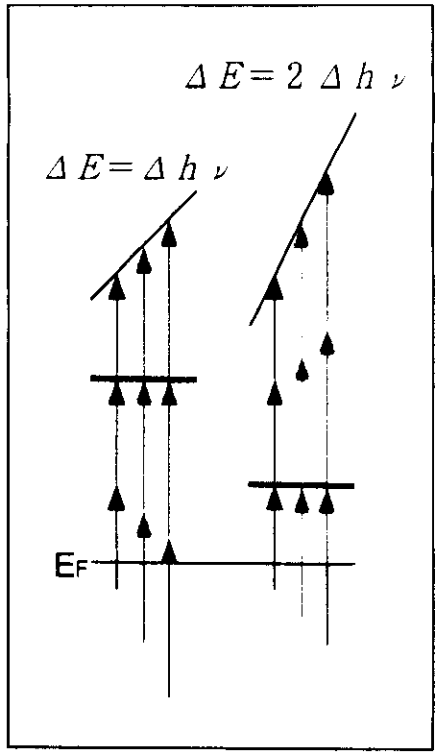


Angle-Resolved 3PPE & Dispersion



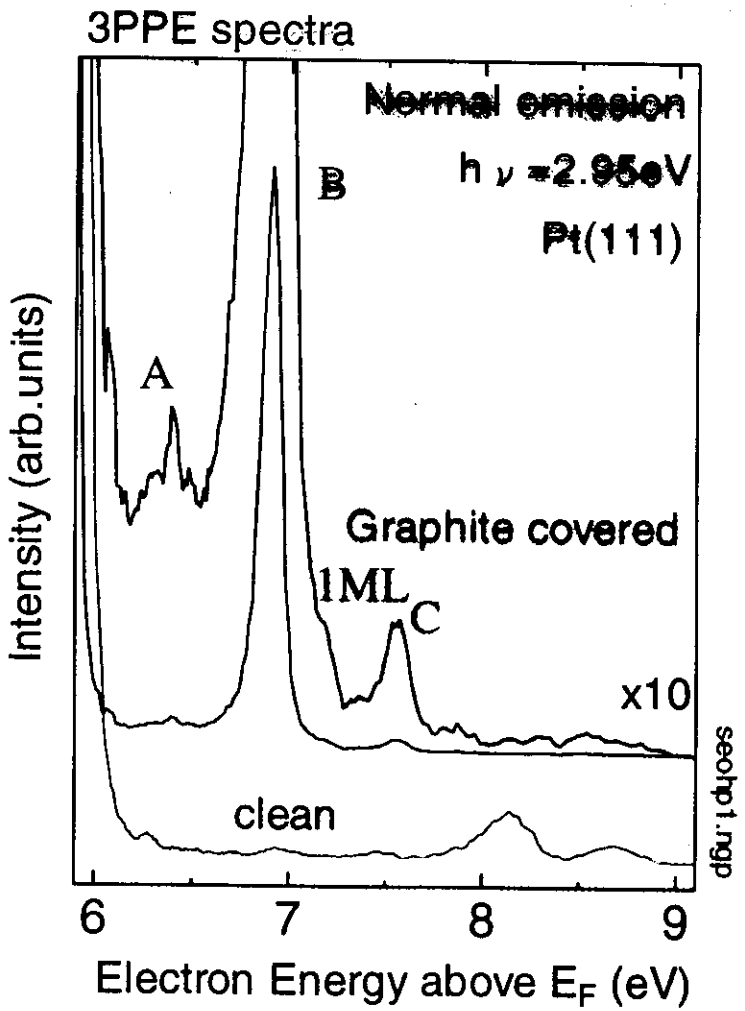
Peak Energy vs. Photon Energy

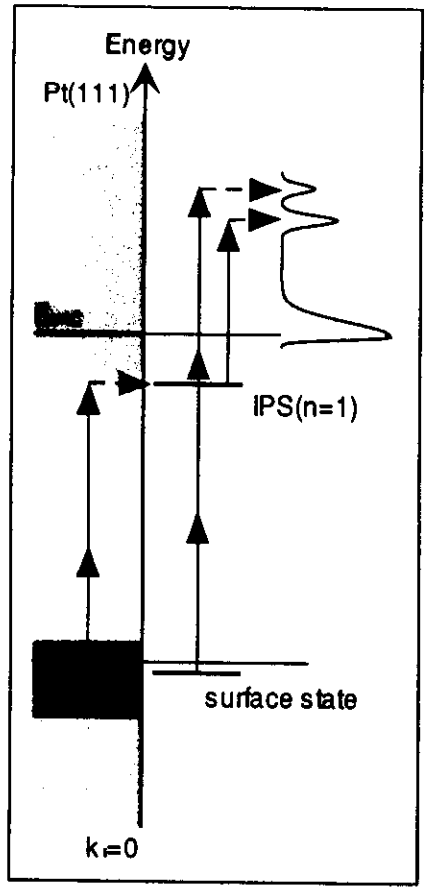




E_A= 0.29 eV, E_B= ~~6.93~~ 3.98 eV, E_C= ~~7.66~~ 4.60 eV above E_F

3PPE from clean & Graphite covered Pt(111) surfaces





Calculations: Crystal-induced surface state

Numerical integration of the Schrödinger equation

The wave function in the sp-band gap :

$$\psi = e^{qz}\cos(\frac{G_0}{2}z + \delta)$$

The wave function outside the crystal is numerically integrated.

Potential energy:

$z_1 < z$: image potential

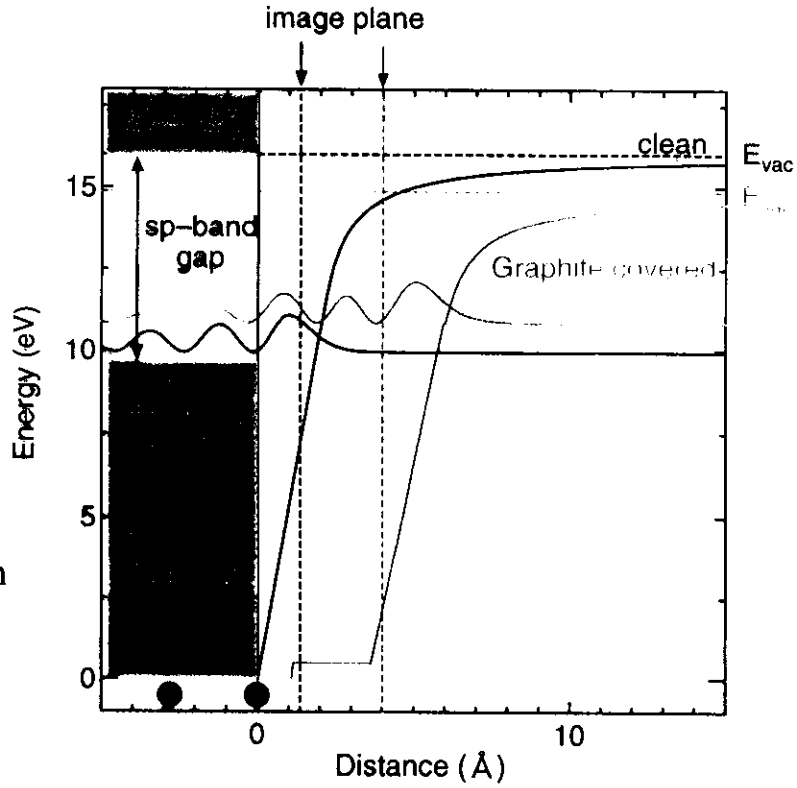
$0 < z < z_1$: liner form connected with the image potential at $z = z_1$

Both wave functions are matched smoothly at the half an interplaner distance from the surface.

Crystal-induced surface state:

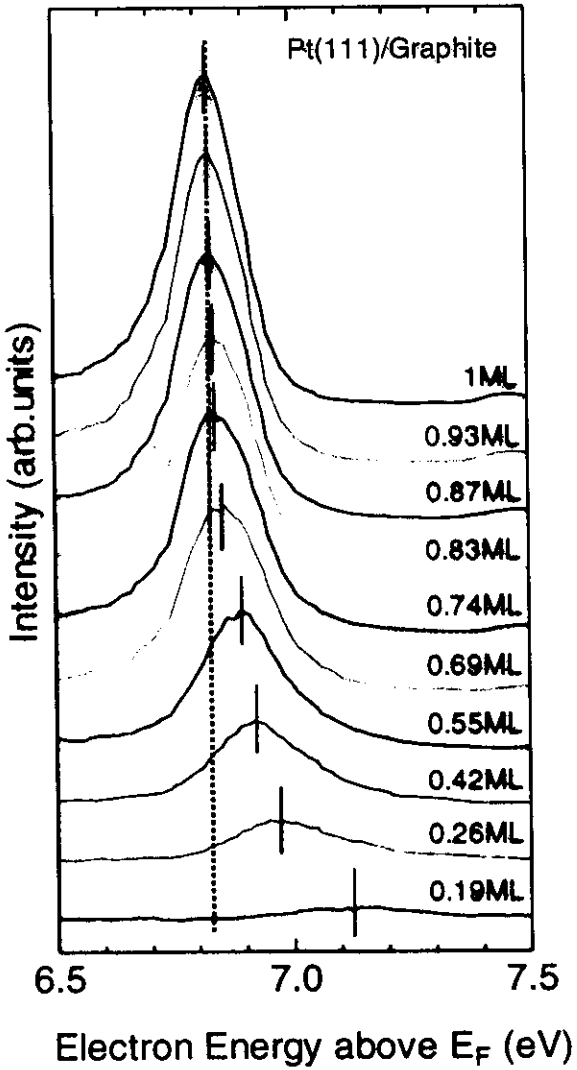
⇒ clean Pt(111) : -0.13 eV from E_F

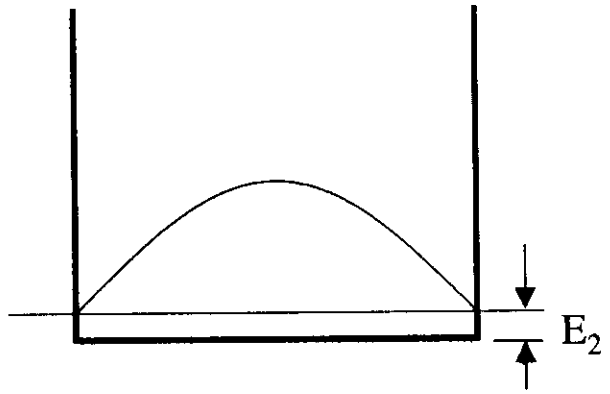
⇒Graphene / Pt(111) : +0.77 eV from E_F (graphene layer at 3.7 Å, inner potential 14.5 eV with respect to E_{vac}



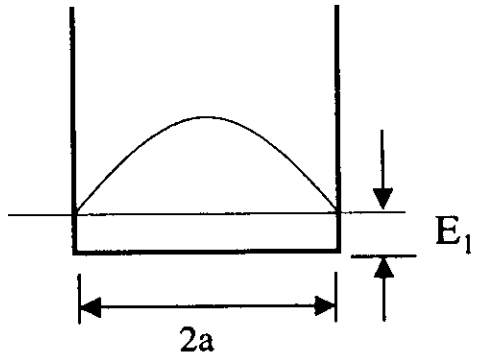
Coverage Dependence of 3PPE Spectra

Image-potential state (n=1)



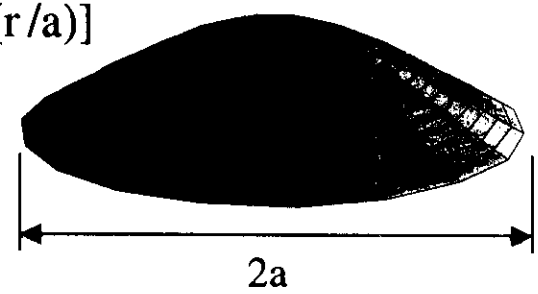


$E_1 > E_2$



The Particle-in-a-round-box model

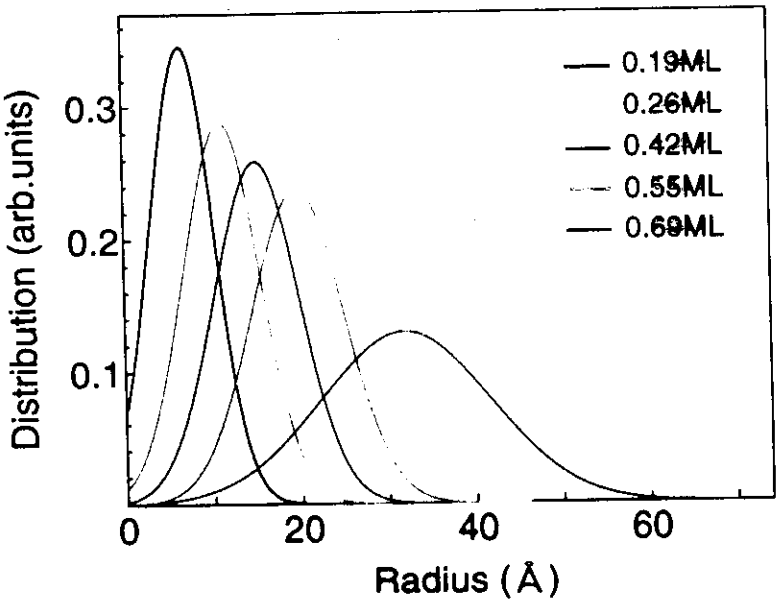
$\Psi(r) \propto J_0[z_{01}(r/a)]$

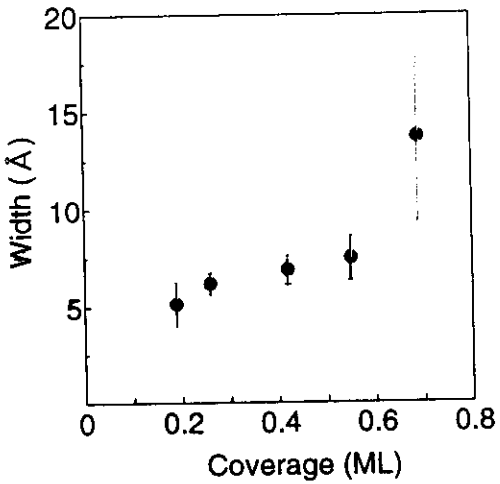


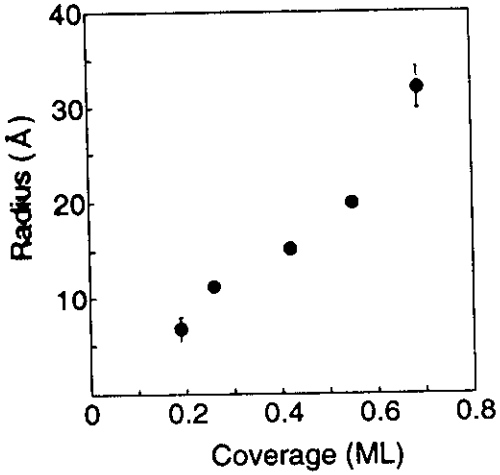
1. $E(a) = 22.03/a^2$ [eV],
   a : Radius of a graphene island[Å]
2. Take the lineshape at 1 ML as a reference.
   $\Rightarrow$ The peak energy and the width
3. Least-squares fitting of the spectral lines (< 1 ML) with

$$I(x) = \text{const} \int_{r1}^{\infty} \frac{1}{2\pi} \frac{\gamma}{(x - c/r^2) + (\gamma/2)^2} \frac{1}{\sqrt{\pi}\, w} \text{Exp}\left[-\frac{(r-a)^2}{w^2}\right] dr$$

Island size distributions of graphene







Annealing temperature: 900 K

Summary

1. Three peaks are observed by three-photon photoemission from the graphene/ Pt(111) surface.

- The higher two peaks: image-potential states for n=1,2
  $\Rightarrow$ Local work function = 4.81 eV.
- The lowest peak: an unoccupied *sp*-derived surface state of Pt(111) modified by graphene.

2. The binding energy of the image-potential state (n=1) at graphene/Pt(111) depends on the coverage of graphene.

- Using a particle-in-a-box model, the size distributions of graphene islands are estimated.

3. Photoemission from the σ^* state is missing. Why?