Buried SiO_x interfaces in CNT/Silicon heterojunctions unraveled by Angle-Resolved X-ray Photoelectron Spectroscopy

Gabriele Salvinelli

Doctorate School in Physics, Astrophysics and Applied Physics

Università degli Studi di Milano

Università Cattolica del Sacro Cuore (BS)

Monday, October 15, 2012

“Heterostructures, as I use the word here, may be defined as heterogeneous semiconductor structures built from two or more different semiconductors, in such a way that the transition region or interface between the different materials plays an essential role in any device action. Often, it may be said that *the interface is the device*”

Herbert Kroemer

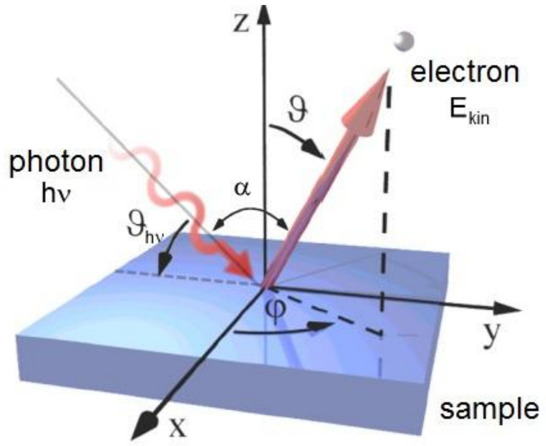
Nobel Lecture, December 8, 2000

Outlines

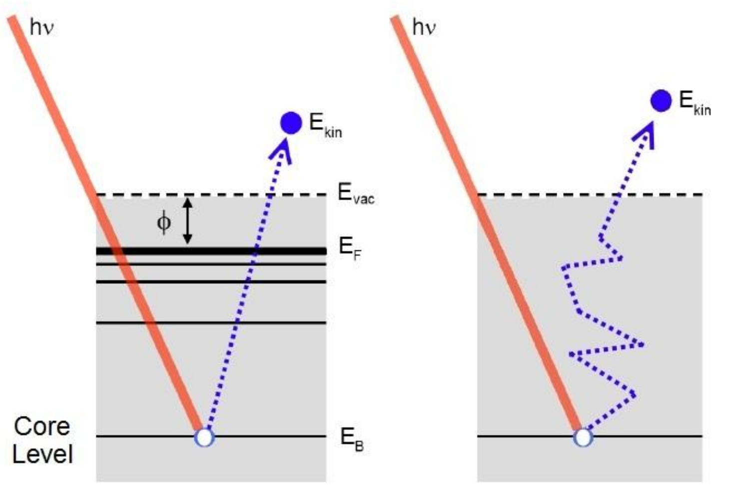
- **Experimental Techniques**
  - X-ray Photoelectron Spectroscopy (XPS)
  - Angle-Resolved X-ray Photoelectron Spectroscopy (AR-XPS)
- **A case study**
  - CNT/Silicon solar cells
  - Sample preparation
- **Experimental measurements**
  - The SiO_x – SiC issue and C 1s spectra
  - Si 2p fitting and ARXPS data
  - Global fitting and thickness evaluation
- **Future prospects**
  - ARXPS study on $LaAlO_3/SrTiO_3$ heterostructures

Experimental Techniques

XPS

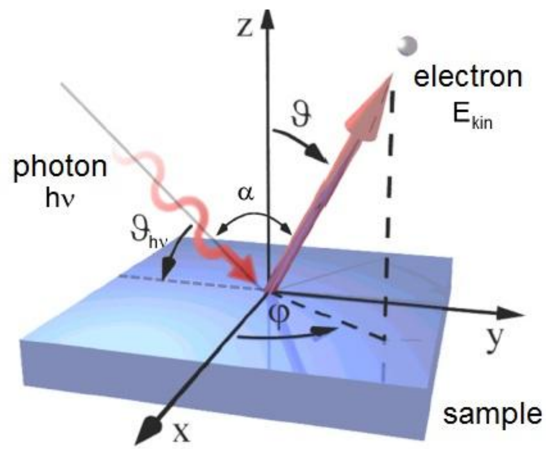


$$E_{kin} = h\nu - \phi - E_B \qquad (1)$$

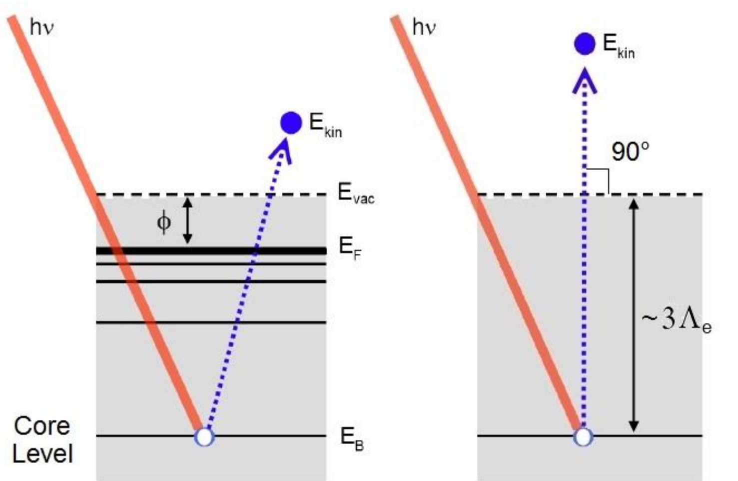


Experimental Techniques

XPS

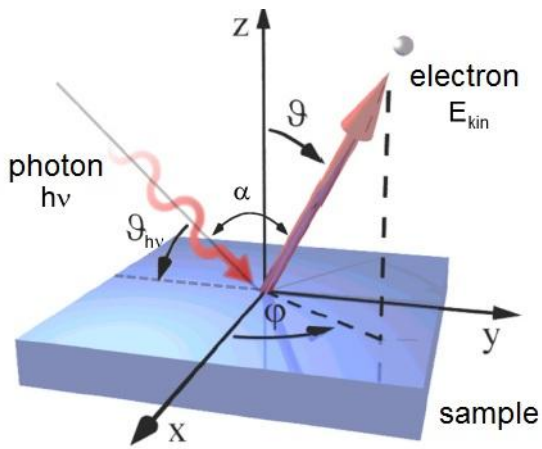


$$E_{kin} = h\nu - \phi - E_B \qquad (1)$$

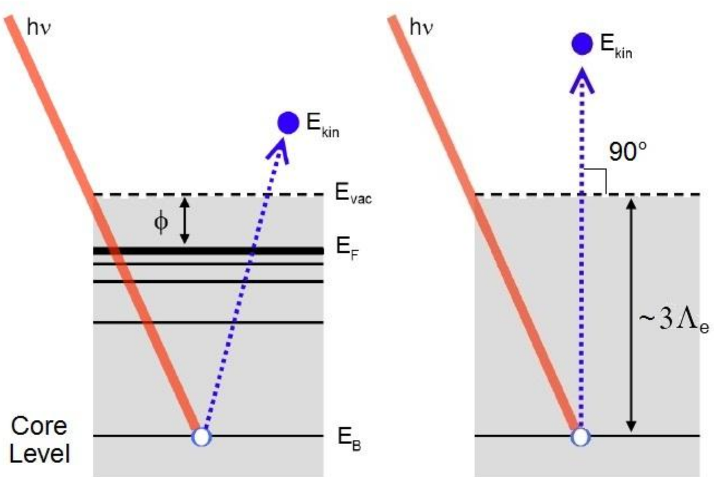


Experimental Techniques

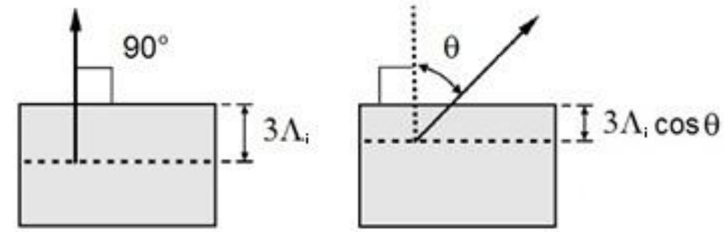
XPS



$$E_{kin} = h\nu - \phi - E_B \quad (1)$$

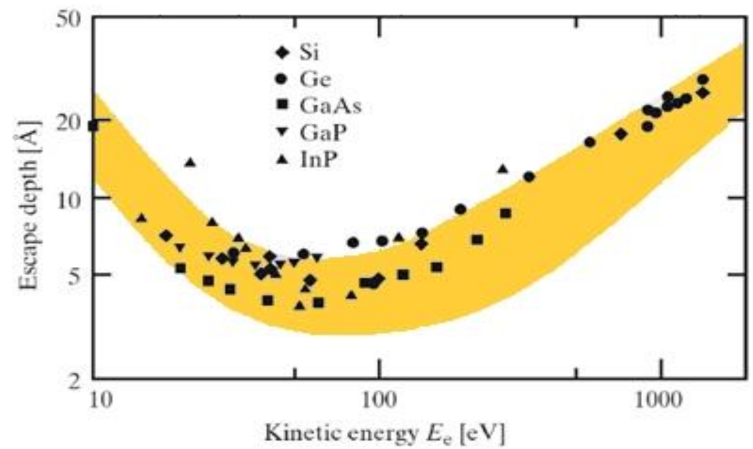


Angle-Resolved XPS



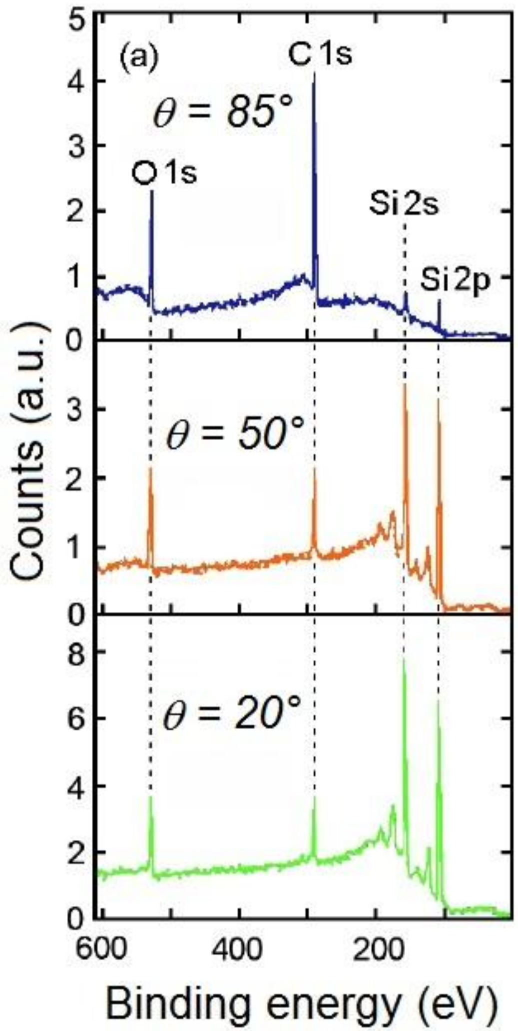
$$I(z) = I_0 exp\left(\frac{-z}{\Lambda_i cos\vartheta}\right) \quad (2)$$

$$\Lambda_i(\text{Å}) = \Lambda_i(E_{kin}, M, N_\nu, \rho) \quad (3)$$



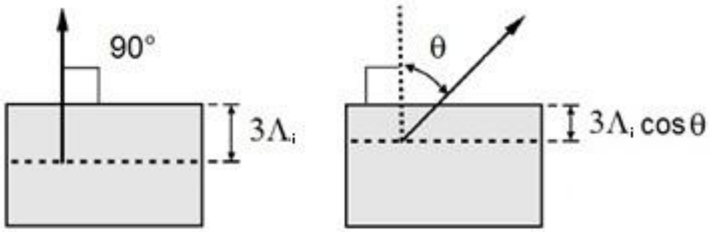
P.Y. Yu and M.Cardona: Fundamentals of Semiconductors, Springer (2005)

Experimental Techniques



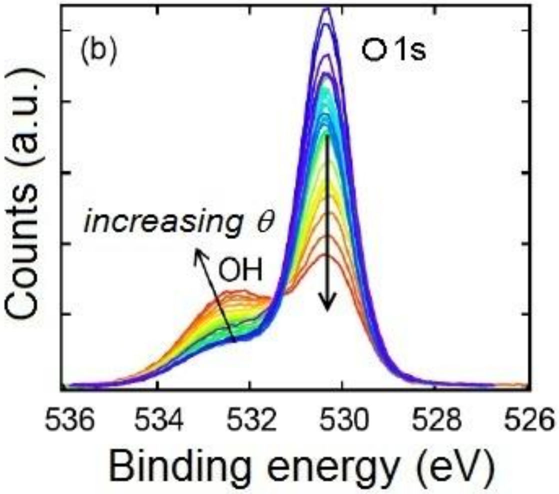
(a,b) S.A.Chambers et al., *Surface Science Reports* **65** (2010) 317

Angle-Resolved XPS

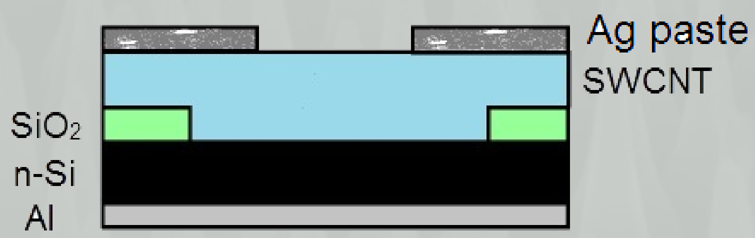


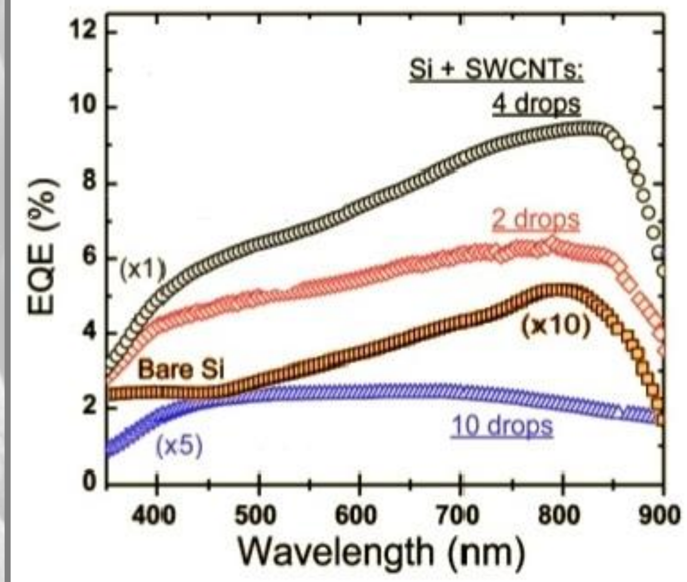
$$I(z) = I_0 exp\left(\frac{-z}{\Lambda_i cos\vartheta}\right) \quad (2)$$

$$\Lambda_i(\text{Å}) = \Lambda_i(E_{kin}, M, N_\nu, \rho) \quad (3)$$



A case study: CNT/Silicon solar cells





M. A. El Khakani et al., *Appl. Phys. Lett.* **95** (2009) 083114

CNT network role:

- Absorption of light
- Generation of photocurrent
- Transport of charges

Aims of research:

- Chemical analysis
- Study the relationship between the constituents
- Evaluation of a layer model

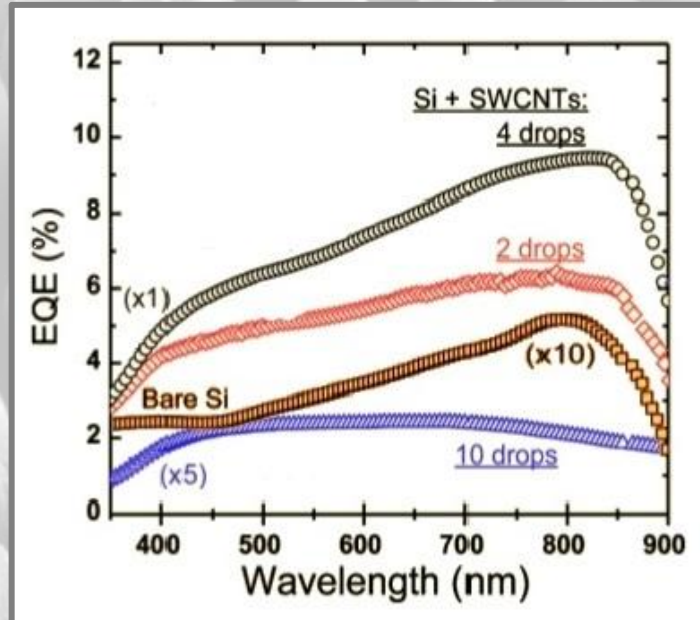
J. Wei et al., *Nano Lett.* **7** (2007) *2317*

Label	Type	Conductivity	Quantity of CNT	Series	Efficiency (η)
A	SWCNT	Metallic	1.5 ml	I	0.26 %
B	SWCNT	Semiconductor	2 ml	I	0.03 %
C	SWCNT	Semiconductor	---	II	2.72 %

F. De Crescenzi, Physics Department, University of Rome *Tor Vergata*

A case study: CNT/Silicon solar cells

n-Si [redacted]



M. A. El Khakani et al., *Appl. Phys. Lett.* **95** (2009) 083114

Aims of research:

- Chemical analysis
- Study the relationship between the constituents
- Evaluation of a layer model

CNT network role:

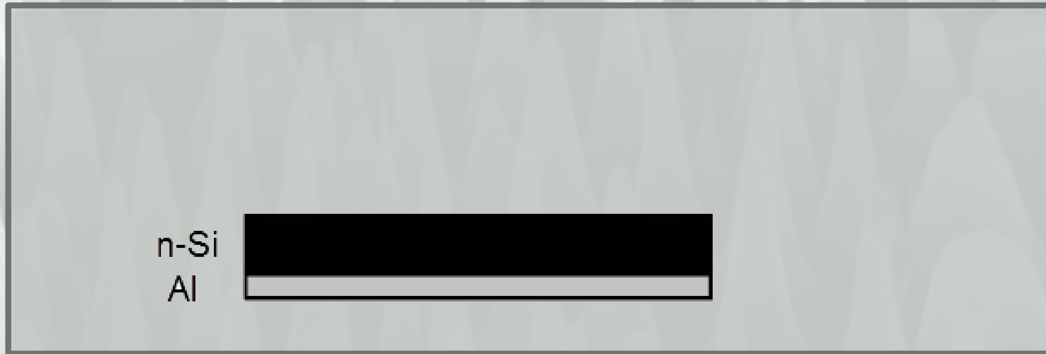
- ❑ Absorption of light
- ❑ Generation of photocurrent
- ❑ Transport of charges

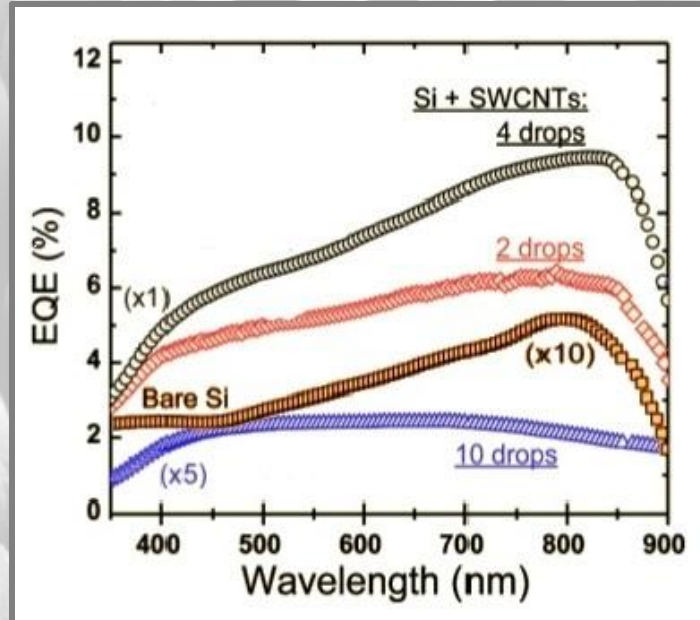
J. Wei et al., *Nano Lett.* **7** (2007) *2317*

Label	Type	Conductivity	Quantity of CNT	Series	Efficiency (η)
A	SWCNT	Metallic	1.5 ml	I	0.26 %
B	SWCNT	Semiconductor	2 ml	I	0.03 %
C	SWCNT	Semiconductor	---	II	2.72 %

F. De Crescenzi, Physics Department, University of Rome *Tor Vergata*

A case study: CNT/Silicon solar cells





M. A. El Khakani et al., *Appl. Phys. Lett.* **95** (2009) 083114

CNT network role:

- ❑ Absorption of light
- ❑ Generation of photocurrent
- ❑ Transport of charges

Aims of research:

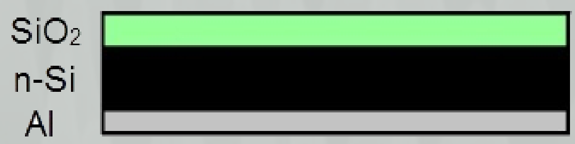
- Chemical analysis
- Study the relationship between the constituents
- Evaluation of a layer model

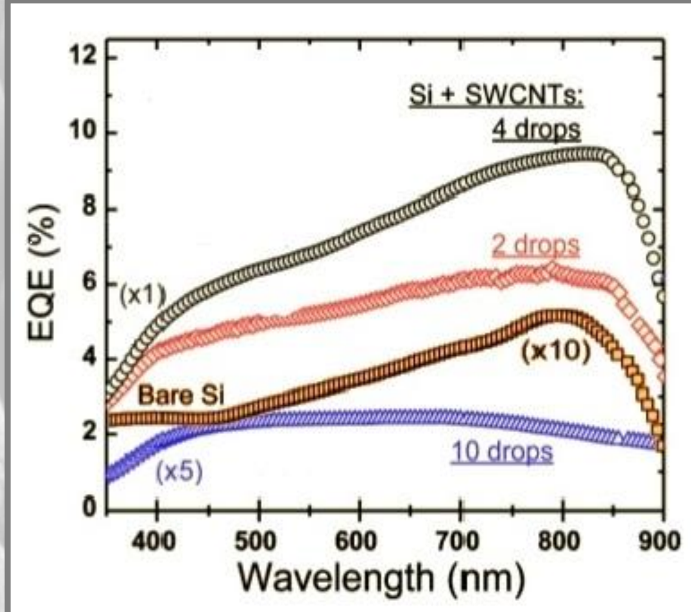
J. Wei et al., *Nano Lett.* **7** (2007) *2317*

Label	Type	Conductivity	Quantity of CNT	Series	Efficiency (η)
A	SWCNT	Metallic	1.5 ml	I	0.26 %
B	SWCNT	Semiconductor	2 ml	I	0.03 %
C	SWCNT	Semiconductor	---	II	2.72 %

F. De Crescenzi, Physics Department, University of Rome *Tor Vergata*

A case study: CNT/Silicon solar cells





M. A. El Khakani et al., *Appl. Phys. Lett.* **95** (2009) 083114

CNT network role:

- Absorption of light
- Generation of photocurrent
- Transport of charges

Aims of research:

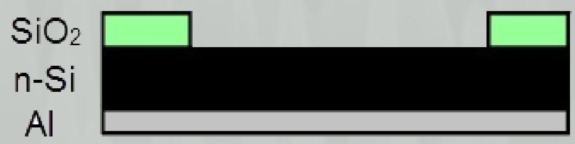
- Chemical analysis
- Study the relationship between the constituents
- Evaluation of a layer model

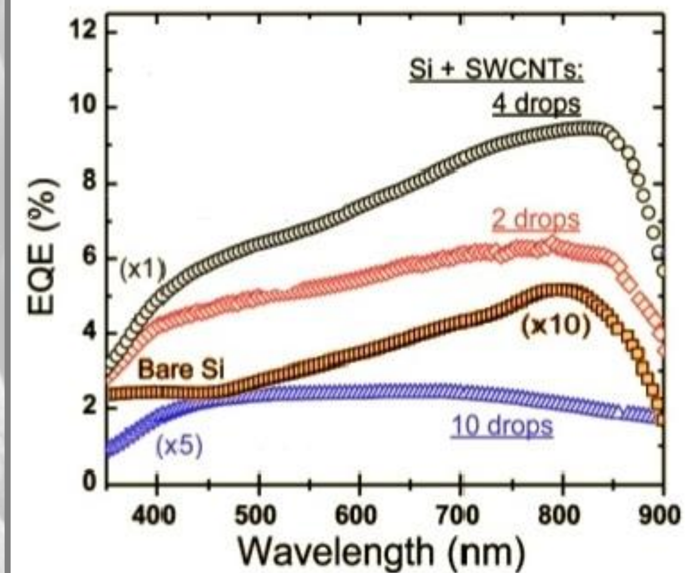
J. Wei et al., *Nano Lett.* **7** (2007) *2317*

Label	Type	Conductivity	Quantity of CNT	Series	Efficiency (η)
A	SWCNT	Metallic	1.5 ml	I	0.26 %
B	SWCNT	Semiconductor	2 ml	I	0.03 %
C	SWCNT	Semiconductor	---	II	2.72 %

F. De Crescenzi, Physics Department, University of Rome *Tor Vergata*

A case study: CNT/Silicon solar cells





M. A. El Khakani et al., *Appl. Phys. Lett.* **95** (2009) 083114

CNT network role:

- ❑ Absorption of light
- ❑ Generation of photocurrent
- ❑ Transport of charges

Aims of research:

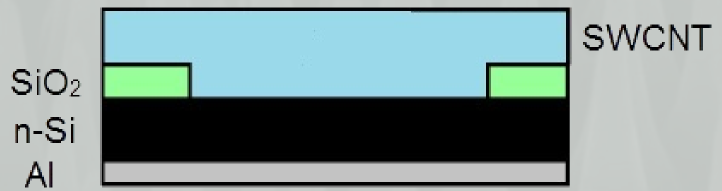
- Chemical analysis
- Study the relationship between the constituents
- Evaluation of a layer model

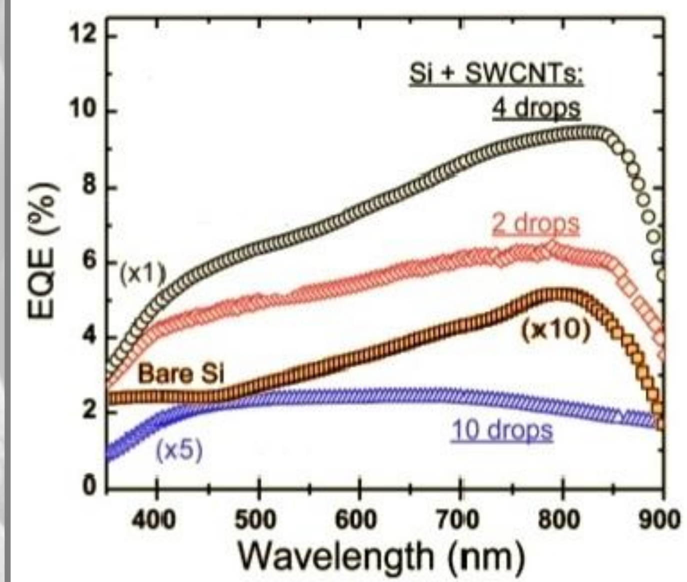
J. Wei et al., *Nano Lett.* **7** (2007) *2317*

Label	Type	Conductivity	Quantity of CNT	Series	Efficiency (η)
A	SWCNT	Metallic	1.5 ml	I	0.26 %
B	SWCNT	Semiconductor	2 ml	I	0.03 %
C	SWCNT	Semiconductor	---	II	2.72 %

F. De Crescenzi, Physics Department, University of Rome *Tor Vergata*

A case study: CNT/Silicon solar cells





M. A. El Khakani et al., *Appl. Phys. Lett.* **95** (2009) 083114

CNT network role:

- ❑ Absorption of light
- ❑ Generation of photocurrent
- ❑ Transport of charges

Aims of research:

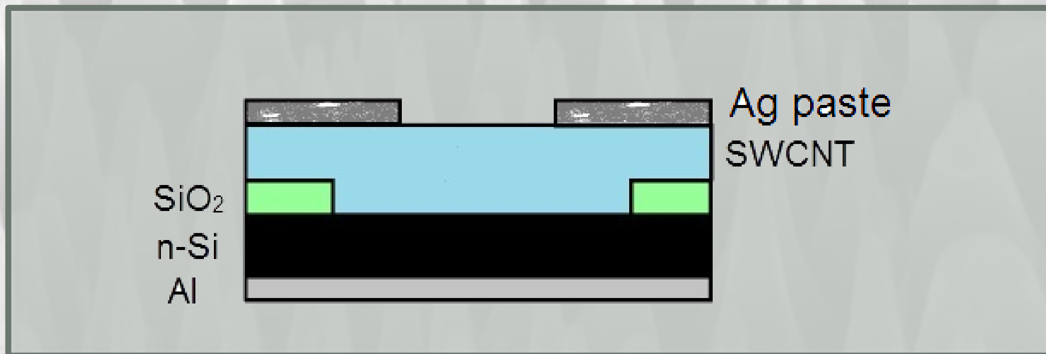
- Chemical analysis
- Study the relationship between the constituents
- Evaluation of a layer model

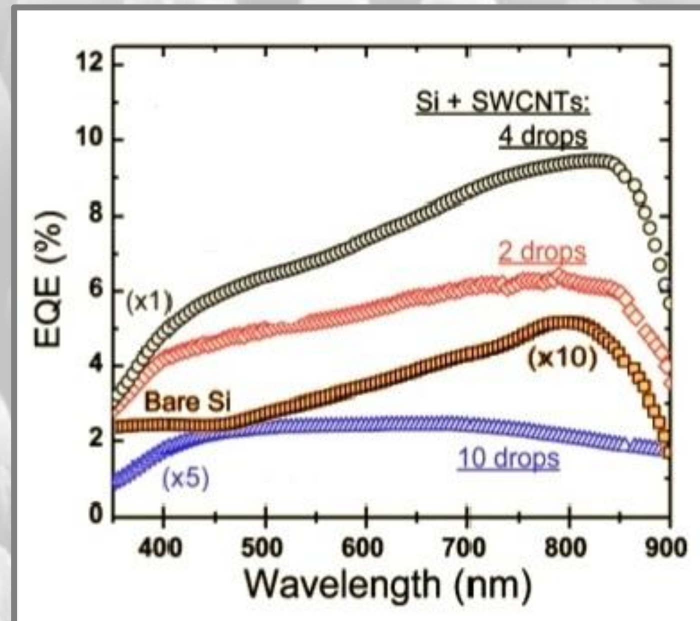
J. Wei et al., *Nano Lett.* **7** (2007) *2317*

Label	Type	Conductivity	Quantity of CNT	Series	Efficiency (η)
A	SWCNT	Metallic	1.5 ml	I	0.26 %
B	SWCNT	Semiconductor	2 ml	I	0.03 %
C	SWCNT	Semiconductor	---	II	2.72 %

F. De Crescenzi, Physics Department, University of Rome *Tor Vergata*

A case study: CNT/Silicon solar cells





M. A. El Khakani et al., *Appl. Phys. Lett.* **95** (2009) 083114

CNT network role:

- Absorption of light
- Generation of photocurrent
- Transport of charges

Aims of research:

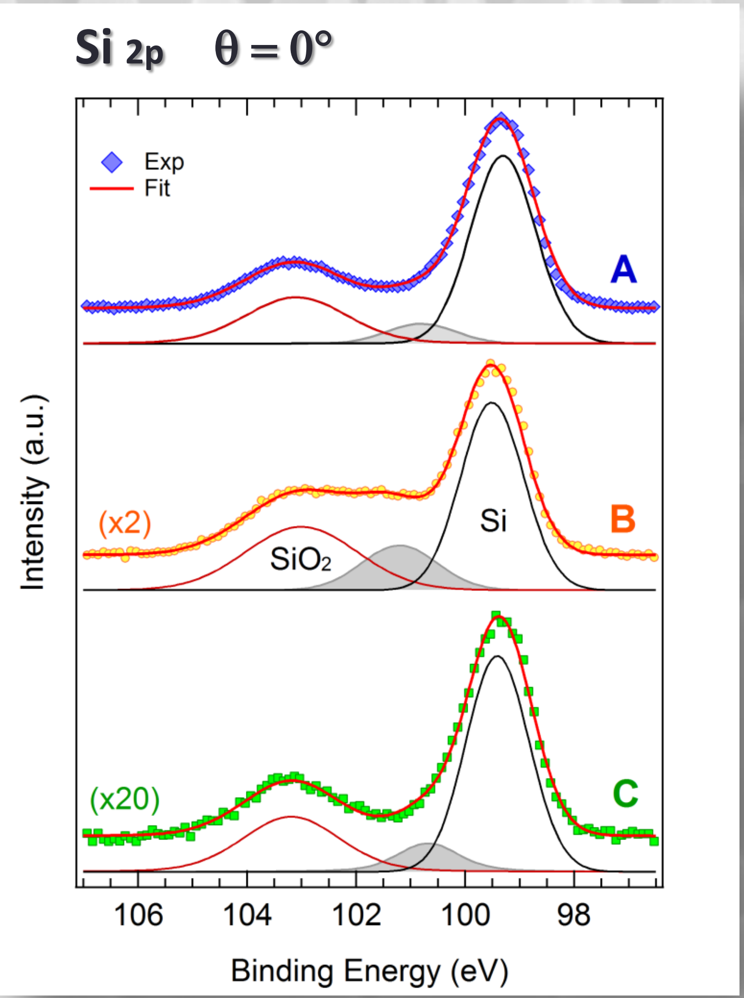
- Chemical analysis
- Study the relationship between the constituents
- Evaluation of a layer model

J. Wei et al., *Nano Lett.* **7** (2007) *2317*

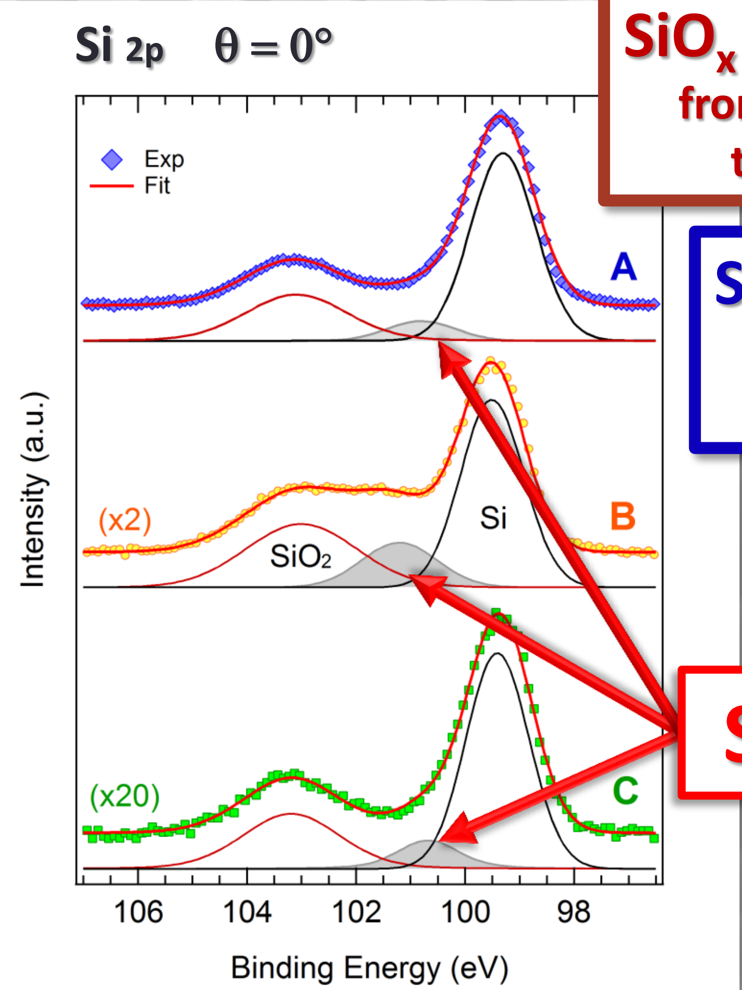
Label	Type	Conductivity	Quantity of CNT	Series	Efficiency (η)
A	SWCNT	Metallic	1.5 ml	I	0.26 %
B	SWCNT	Semiconductor	2 ml	I	0.03 %
C	SWCNT	Semiconductor	---	II	2.72 %

F. De Crescenzi, Physics Department, University of Rome *Tor Vergata*

Experimental results: XPS and AR-XPS



Experimental results: XPS and AR-XPS



SiO_x :
from 100.4 eV [1]
to 103.2 eV [1]

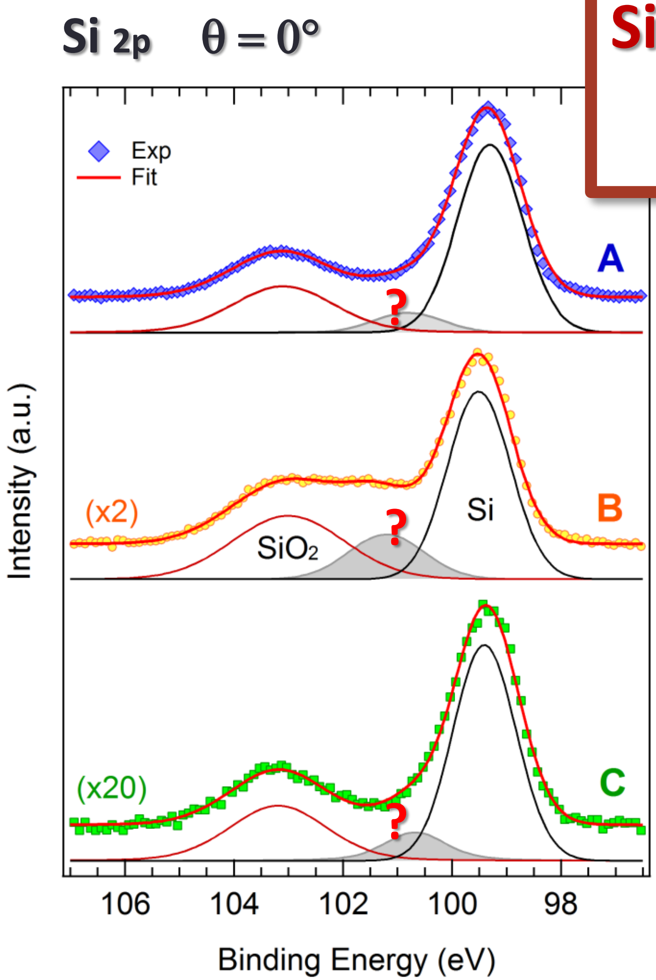
SiC :
from 99.85 eV [2]
to 100.8 eV [3]

?

SiO_x or SiC

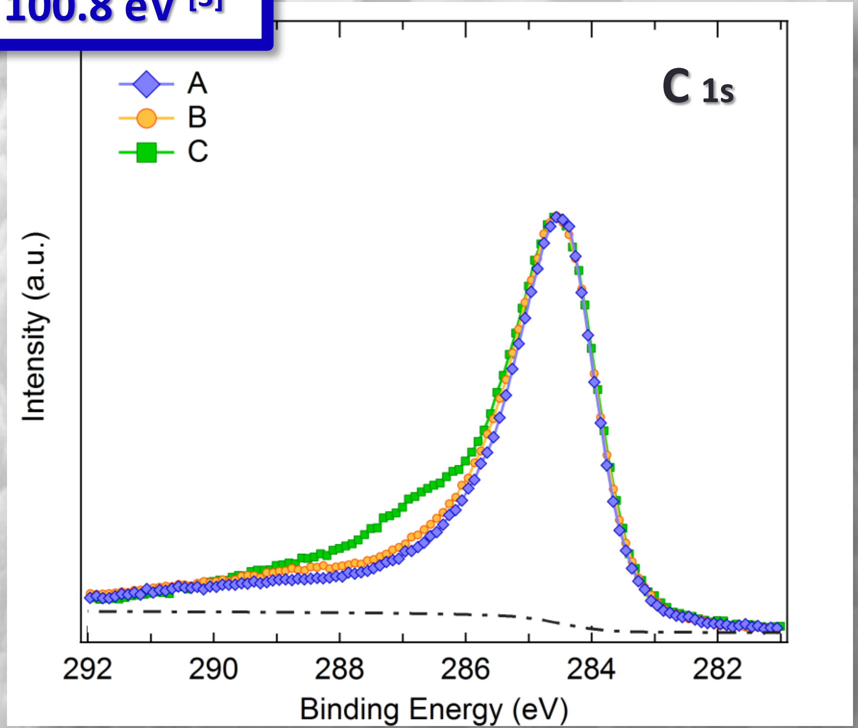
[1] W.A.M. Aarnik et al., *Appl. Surf. Sci.* **45** (1990) 37
[2] T. Aoyama et al., *Appl. Surf. Sci.* **41** (1989) 584
[3] A.A. Galuska et al., *J. Vac. Sci. Technol. A* **6** (1988) 110

Experimental results: XPS and AR-XPS



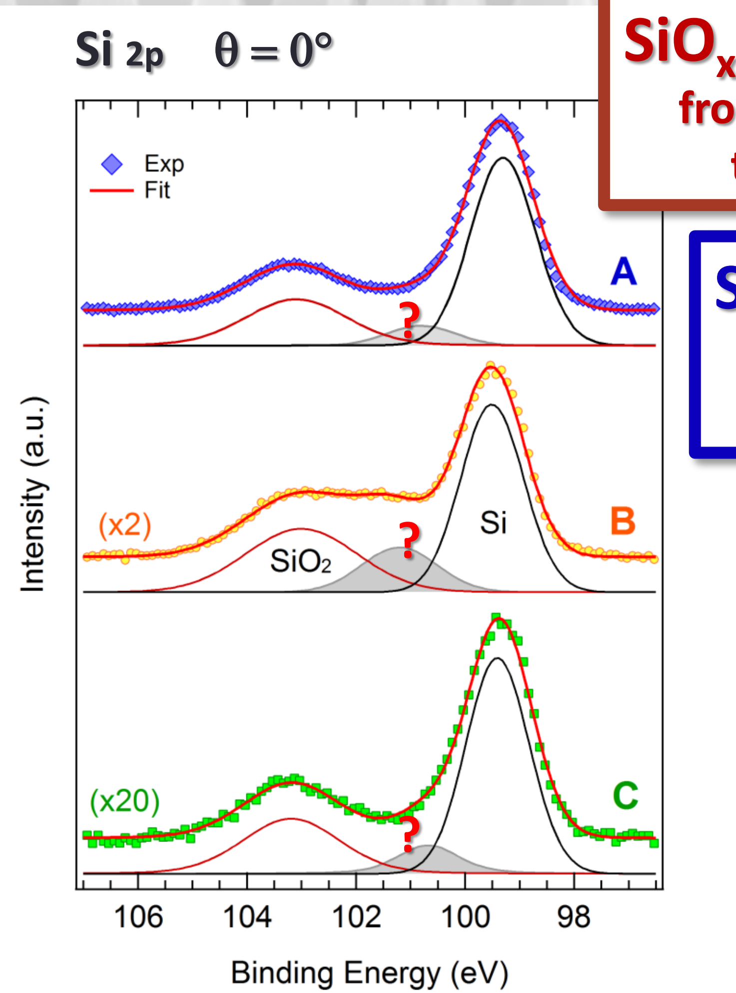
SiO_x :
from 100.4 eV [1]
to 103.2 eV [1]

SiC :
from 99.85 eV [2]
to 100.8 eV [3]



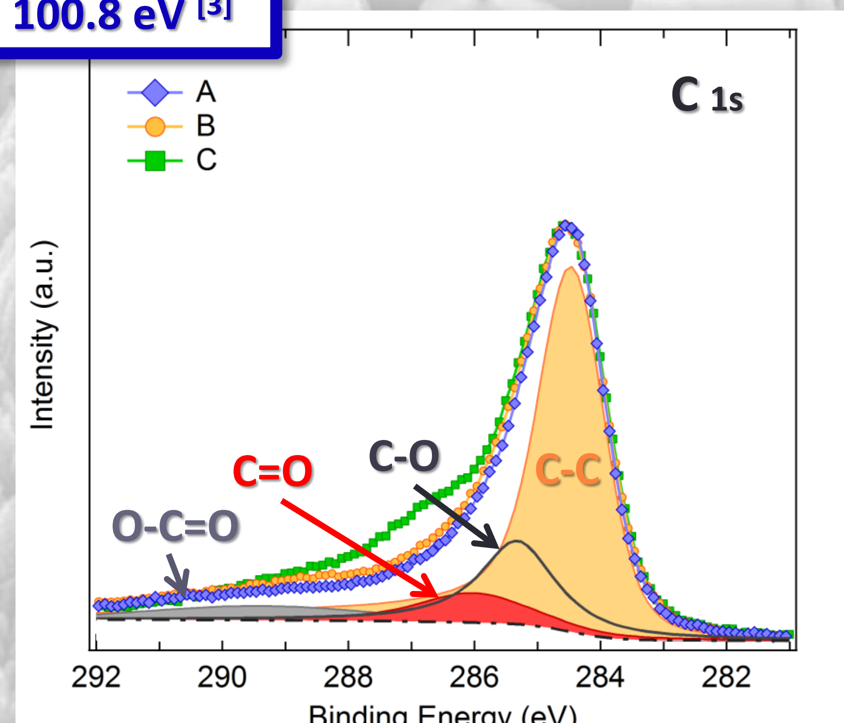
[1] W.A.M. Aarnik et al., *Appl. Surf. Sci.* **45** (1990) 37
[2] T. Aoyama et al., *Appl. Surf. Sci.* **41** (1989) 584
[3] A.A. Galuska et al., *J. Vac. Sci. Technol. A* **6** (1988) 110

Experimental results: XPS and AR-XPS



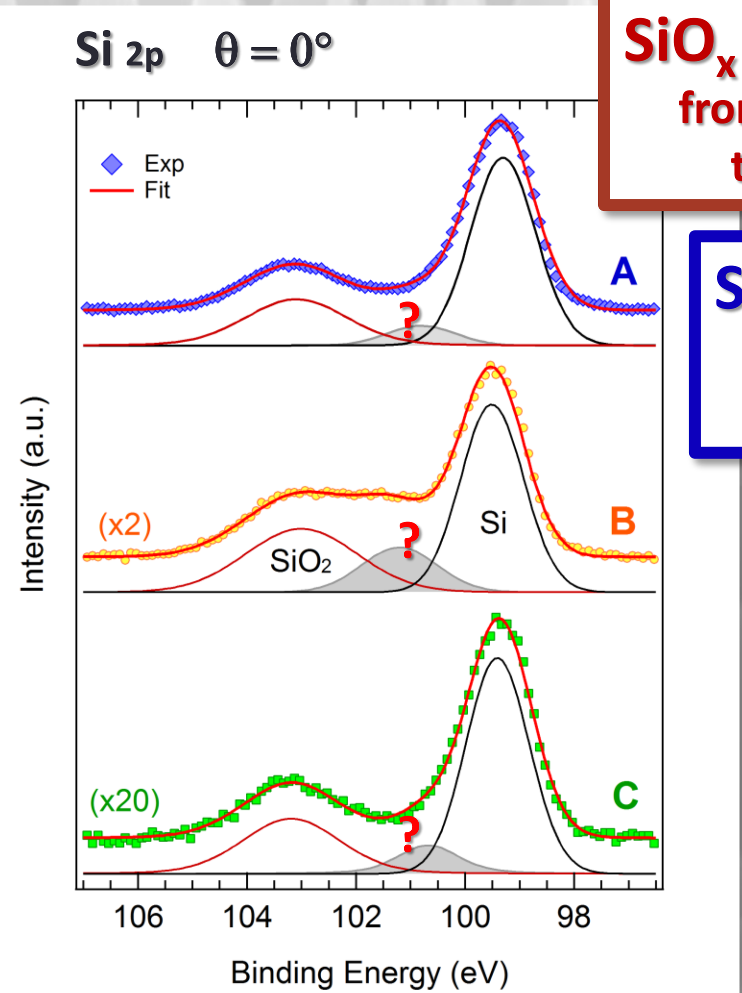
SiO_x :
from 100.4 eV [1]
to 103.2 eV [1]

SiC :
from 99.85 eV [2]
to 100.8 eV [3]



[1] W.A.M. Aarnik et al., *Appl. Surf. Sci.* **45** (1990) 37
[2] T. Aoyama et al., *Appl. Surf. Sci.* **41** (1989) 584
[3] A.A. Galuska et al., *J. Vac. Sci. Technol. A* **6** (1988) 110

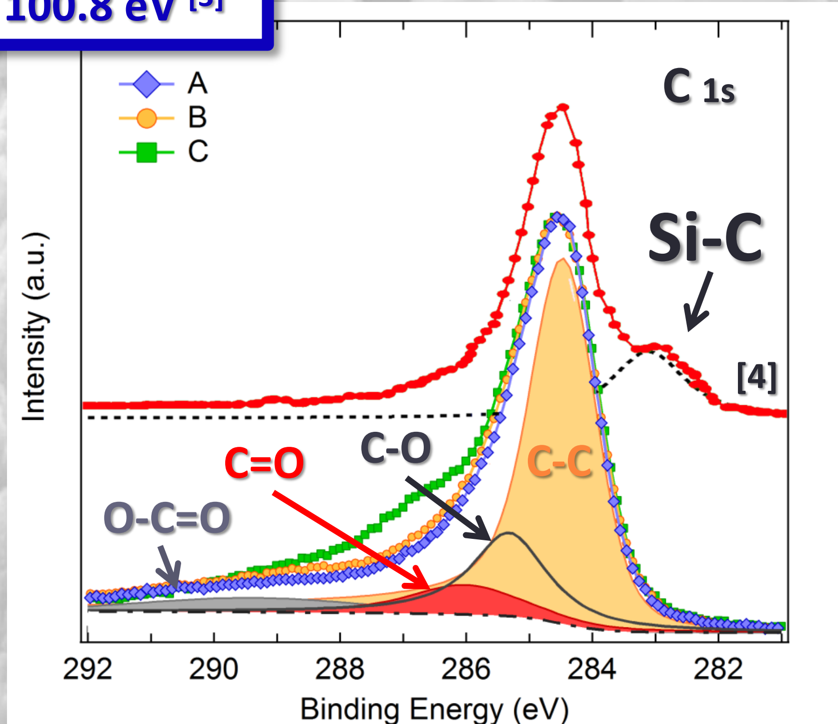
Experimental results: XPS and AR-XPS



SiO$_x$:
from 100.4 eV [1]
to 103.2 eV [1]

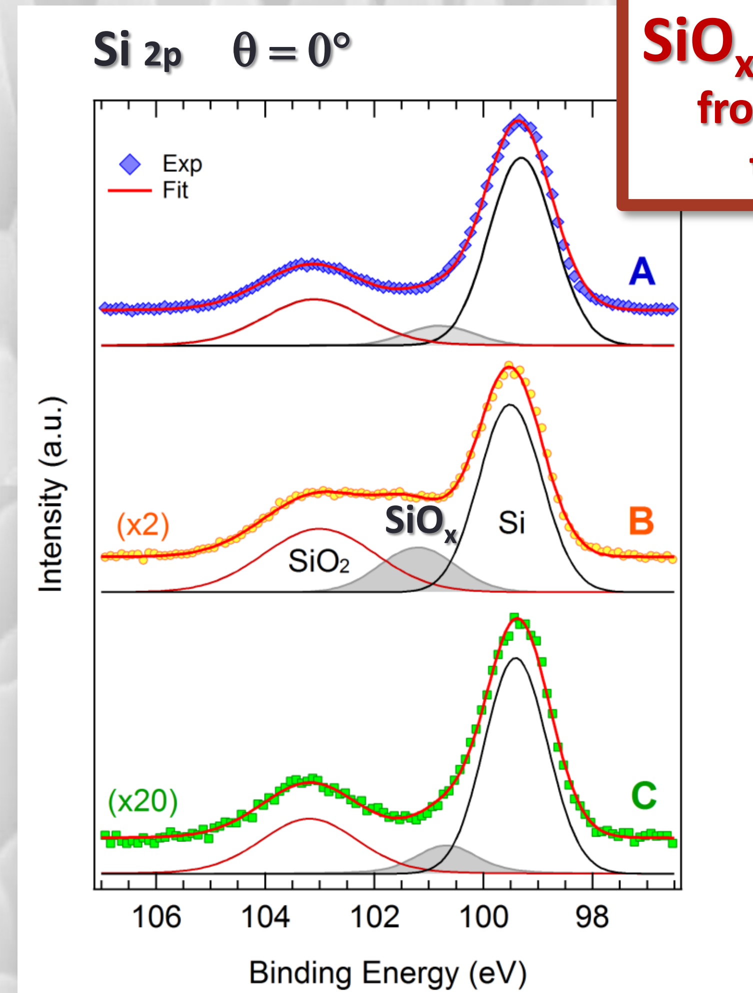
SiC :
from 99.85 eV [2]
to 100.8 eV [3]

[4] **T. Maruyama et al. : *Diamond & Related Materials* 16 (2007) 1078**

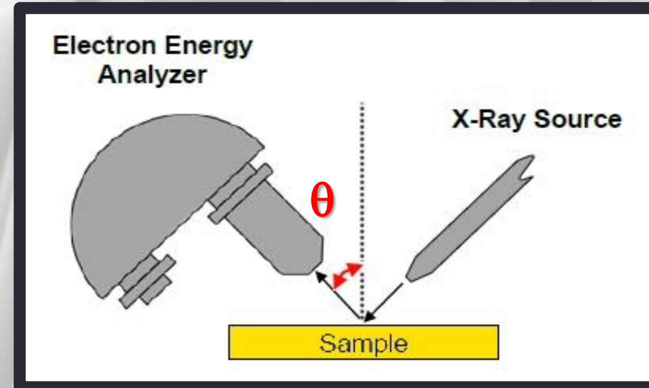


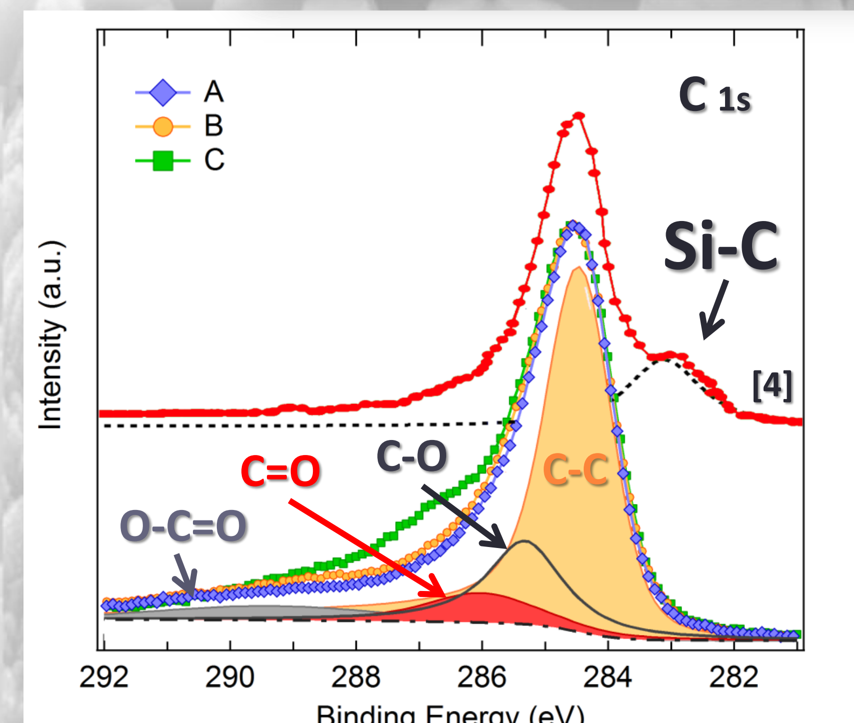
[1] W.A.M. Aarnik et al., *Appl. Surf. Sci.* **45** (1990) 37
[2] T. Aoyama et al., *Appl. Surf. Sci.* **41** (1989) 584
[3] A.A. Galuska et al., *J. Vac. Sci. Technol. A* **6** (1988) 110

Experimental results: XPS and AR-XPS



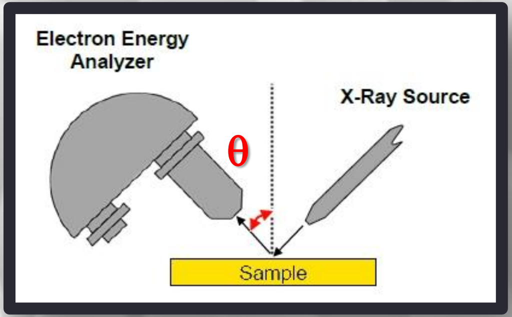
SiO_x :
from 100.4 eV [1]
to 103.2 eV [1]

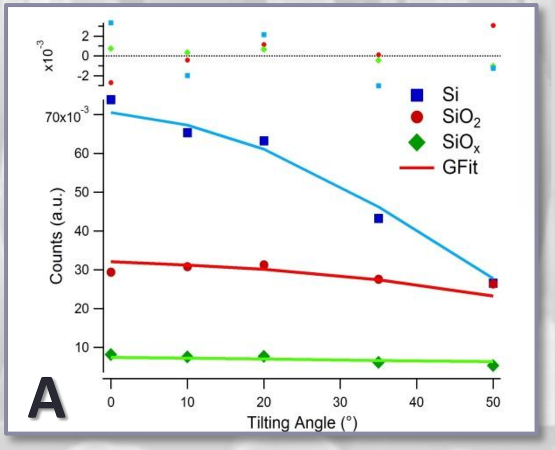


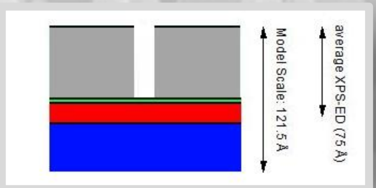


[1] W.A.M. Aarnik et al., *Appl. Surf. Sci.* **45** (1990) 37
[4] **T. Maruyama et al. : *Diamond & Related Materials* 16 (2007) 1078**

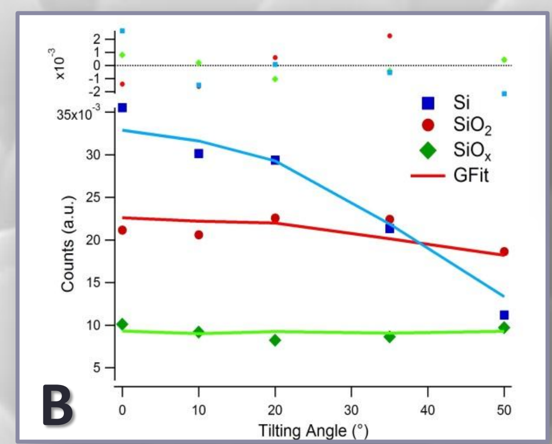
AR-XPS Depth Profile Model

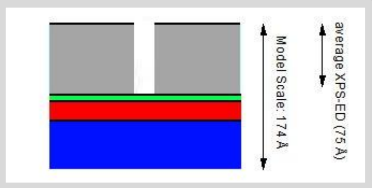




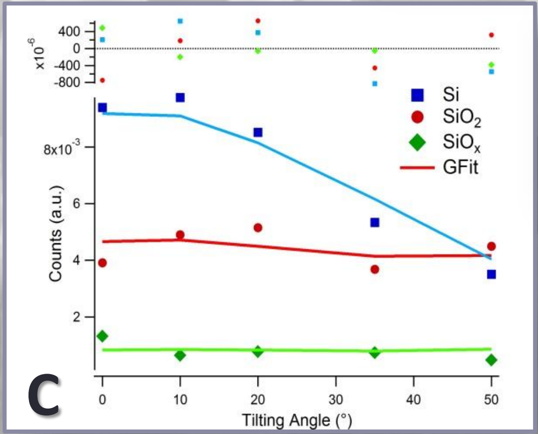


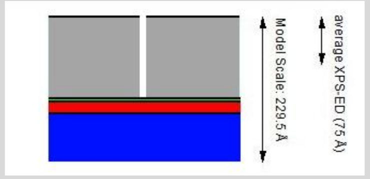
CNT = 60.4 Å
SiO_x = 1.7 Å
SiO_2 = 17.1 Å
isl.% = 0.91





CNT = 84.9 Å
SiO_x = 3.5 Å
SiO_2 = 23.2 Å
isl.% = 0.91

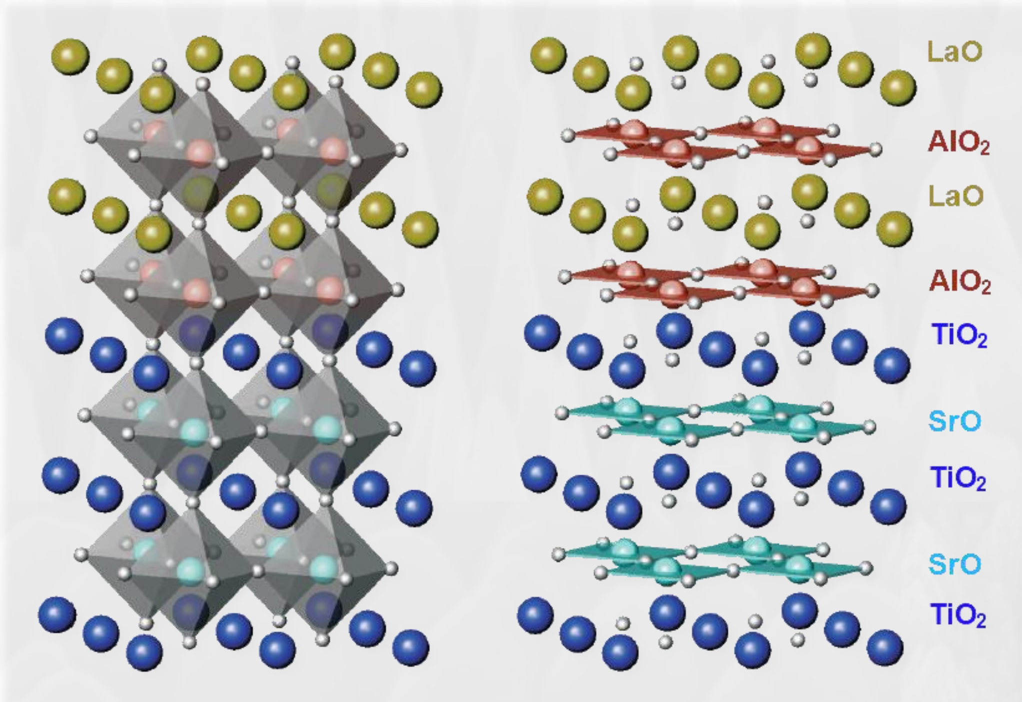


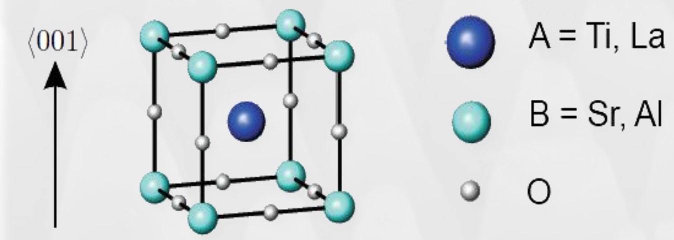


CNT = 130.4 Å
SiO_x = 1.4 Å
SiO_2 = 18.5 Å
isl.% = 0.98

Label	Series	CNT (Å)	Si-O (Å)	Efficiency (η)
A	I	60.4	18.8	0.26 %
B	I	84.9	26.7	0.03 %
C	II	130.4	19.9	2.72 %

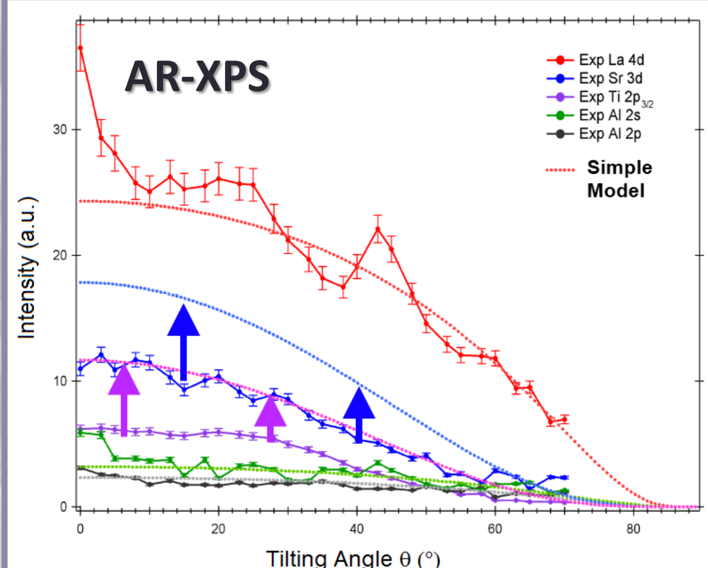
Future prospects : $LaAlO_3$ / $SrTiO_3$





$$I(z) = I_0 exp\left(\frac{-z}{\Lambda_e cos\vartheta}\right) \qquad (1)$$

$$\Lambda_e(\text{Å}) = \Lambda_e(E_{kin}, M, N_\nu, \rho) \qquad (2)$$



Surface Science and Spectroscopy Lab

Members:

- Prof. Luigi Sangaletti
- Giovanni Drera - Post-doc
- Chiara Pintossi - PhD student
- Federica Rigoni - PhD student
- Davide Visentin - graduate student
- Giorgio Lanti - graduate student
- Matteo Bovo - undergraduate student

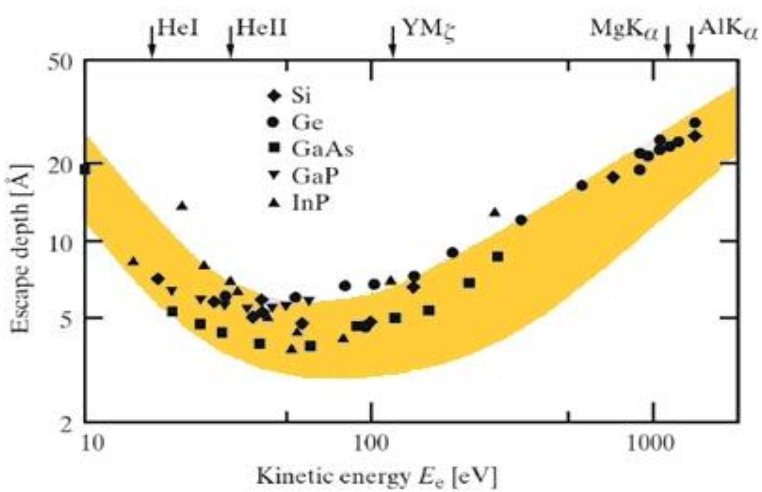
Thank you for the attention

Appendix A : TPP-IMFP

$$\Lambda_e(\text{Å}) = \frac{E_{kin}(eV)}{\left\{E_p^2\left[\beta\ln(\gamma E_{kin}) - \left(\frac{C}{E_{kin}}\right) + \left(\frac{D}{E_{kin}^2}\right)\right]\right\}}$$

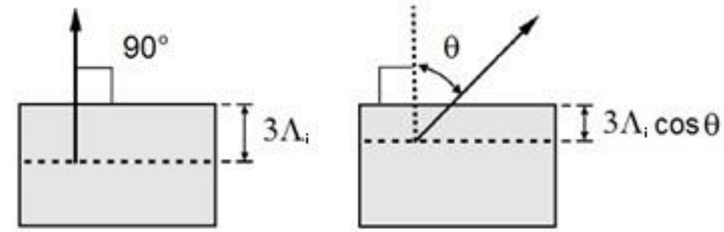
$$E_p = 28.8\left(\frac{N_v\rho}{M}\right)^{\frac{1}{2}} \qquad \beta = -0.10 + \frac{0.944}{(E_p^2 + E_g^2)^{\frac{1}{2}}} + 0.069\rho^{0.1}$$

$$\gamma = \frac{0.191}{\sqrt{\rho}} \qquad C = 1.97 - \frac{0.91 N_v\rho}{M} \qquad D = 53.4 - \frac{20.8 N_v\rho}{M}$$



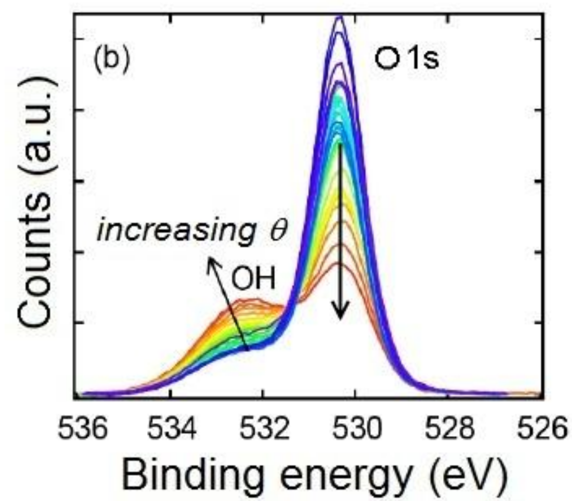
P.Y. Yu and M.Cardona: Fundamentals of Semiconductors, Springer (2005)

Angle-Resolved XPS

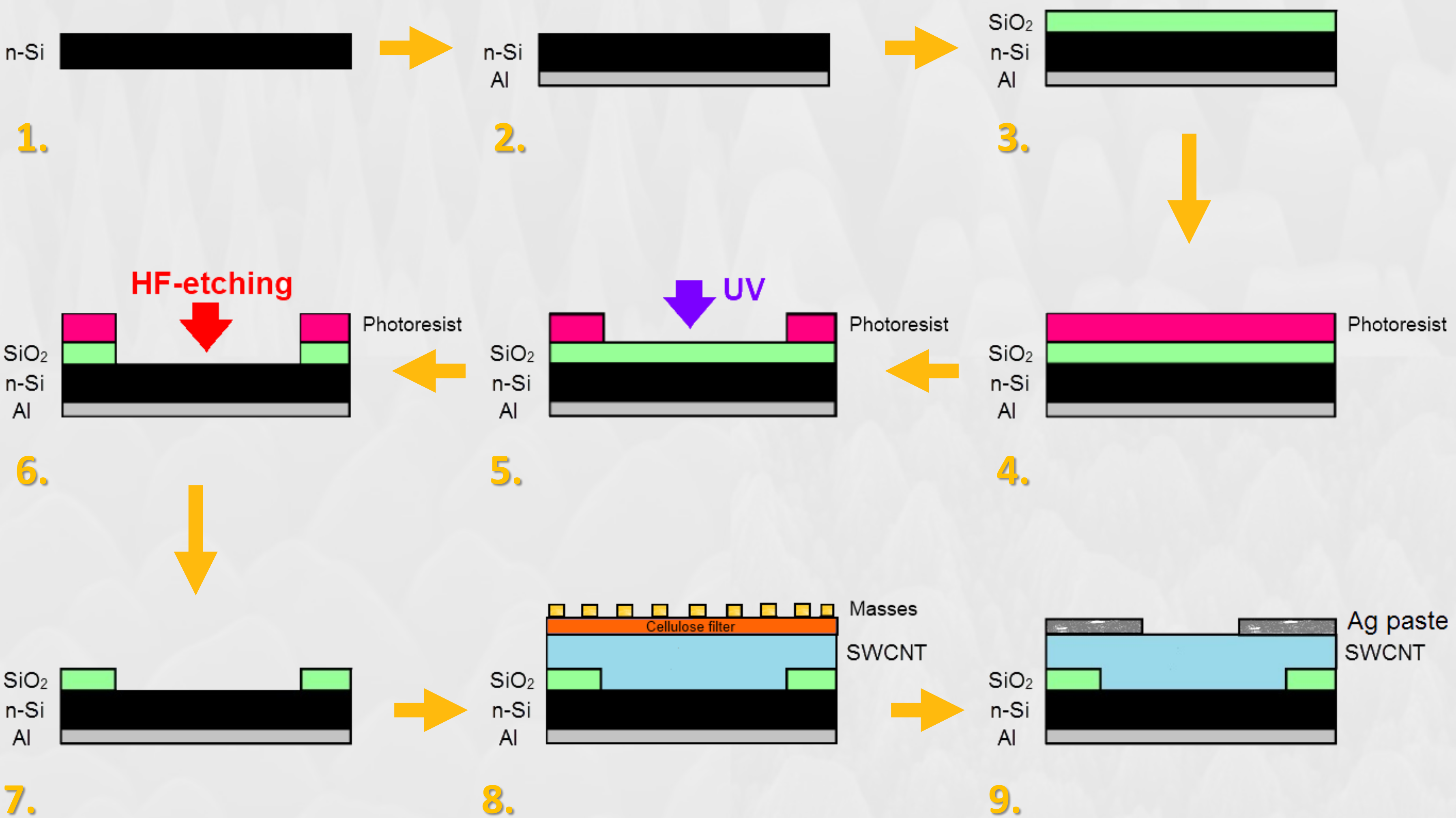


$$I(z) = I_0 exp\left(\frac{-z}{\Lambda_i cos\vartheta}\right) \qquad (2)$$

$$\Lambda_i(\text{Å}) = \Lambda_i(E_{kin}, M, N_v, \rho) \qquad (3)$$



Appendix B : Sample preparation



F. De Crescenzi, Physics Department, University of Rome *Tor Vergata*

Appendix C : Depth Profile Model

Depth Profile Model:

(1) $I(E_k,\theta) = N\, X_s \int_d^{d+t} \phi(E_k,\theta,z)dz$

(2) $X_s = \frac{\sigma_p h}{4\pi}\left[1-\frac{\beta}{4}(3\cos^2\varphi - 1)\right]$

(3) $\phi(E_k,\theta,z) \cong exp\left(\frac{-z}{\Lambda_i(E_k)\cos\theta}\right)$

(4) $\phi(E_k,\theta,z) \cong exp\left(\frac{-z}{\Lambda_{tot}\cos\theta}\right)$

(5) $\Lambda_{tot} = \frac{\Lambda_{tr}\Lambda_i}{\Lambda_{tr}+\Lambda_i}$

(6) $\Lambda_e(\mathring{A}) = \frac{E_{kin}(eV)}{\left\{E_p^2\left[\beta\ln(\gamma E_{kin}) - \left(\frac{C}{E_{kin}}\right) + \left(\frac{D}{E_{kin}^2}\right)\right]\right\}}$

$E_p = 28.8\left(\frac{N_v\rho}{M}\right)^{\frac{1}{2}}$ $\beta = -0.10 + \frac{0.944}{(E_p^2+E_g^2)^{\frac{1}{2}}} + 0.069\rho^{0.1}$

$\gamma = \frac{0.191}{\sqrt{\rho}}$ $C = 1.97 - \frac{0.91N_v\rho}{M}$ $D = 53.4 - \frac{20.8N_v\rho}{M}$

(7) $\Lambda_{tr} = \left(N\sum_{k=1}^{n} x_k\sigma_{tr,k}\right)^{-1}$

(8) $I(E_k,\theta) = N\, X_s \int_d^{d+t} exp\left(\frac{-z}{\Lambda_{tot}\cos\theta}\right)dz$

Simple Model:

(9) $I(z) = I_0 exp\left(\frac{-z}{\Lambda_e \cos\vartheta}\right)$

(10) $\Lambda_i(\text{Å}) = \Lambda_i(E_{kin}, M, N_v, \rho)$

(2) J. J. Yeh and I.Lindau, *Atomic Data and Nuclear Data Tables*, 32 (1985) 1-155
(5) W. S. M. Werner, *Surf. Interface Anal.* 31 (2001) 141–176
(6) S. Tanuma, C. J. Powell e D. R. Penn, *Surf. Interf. Anal.* 35 (2003) 268-275
(7) A. Jablonski, *Phys. Rev. B* 58 (1998) 24
[*] I. S. Tilinin et al., *J. Electr. Spec. Rel. Phen.* 97 (1997) 127