Nanostructured formation of crystalline SiC obtained by acetylene interaction with silicon (111) and (100) surfaces

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Introduction

Silicon carbide is one of the most interesting material for many electronic, optoelectronic and thermophotovoltaic applications.

The thermal, mechanical and chemical stability makes 3c-SiC a promising wide gap semiconductor for electronic working at high temperature and in corrosive atmosphere.

However great efforts should be devoted to produce high quality silicon carbide samples without carbon segregation or microvoids formation.

The adsorption of acetylene on silicon surfaces received great attention as a promising carbon source for epitaxial growth of 3c-SiC, because the processing temperatures can be reduced below 1000 ^{o}C.

-The main obstacle to the realization of this program with carbon (Diamond Eg=5.5 eV) is the extreme low solubility of C in silicon (only few percent %) induced by the large lattice mismatch (52%).

-The goal is to fabricate thin pseudomorphic $Si_{(1-x)}C_{(x)}$ on Silicon with enhanced carbon concentration without formation of SiC precipitates.

-To describe how hydrocarbon molecules (acetylene, C_2H_2) chemisorb on Si, dissociate and penetrate into subsurface substitutional sites.

- UHV Techniques: Auger, EELS, XPS, UPS, XPD, LEED, KED
ex-situ: SEM, IR Luminescence

Experimental

- Samples prepared in a UHV system : $p=2x10^{-10}$ Torr
- Si substrate reconstruction obtained by resistive heating
- C2H2 pressure during growth $p=1\text{-}2 \times 10^{-5}$ Torr
- Time of exposure 30 minutes
- Exposure performed for different substrate temperature

LEED patterns:

- To check the quality of silicon substrate reconstruction
- To study the morphology an structural change after C2H2 exposure

Auger spectra:

- To check the atomic purity of substrates and grown layers
- To follow the evolution of the electronic properties around the carbon atoms

Auger Carbon CVV lineshape studies
Electron Eergy Loss Spectroscopy (EELS)
Electron Energy Loss Fine Structure (EELFS)

- **to monitor the local structure**

Luminescence spectra :

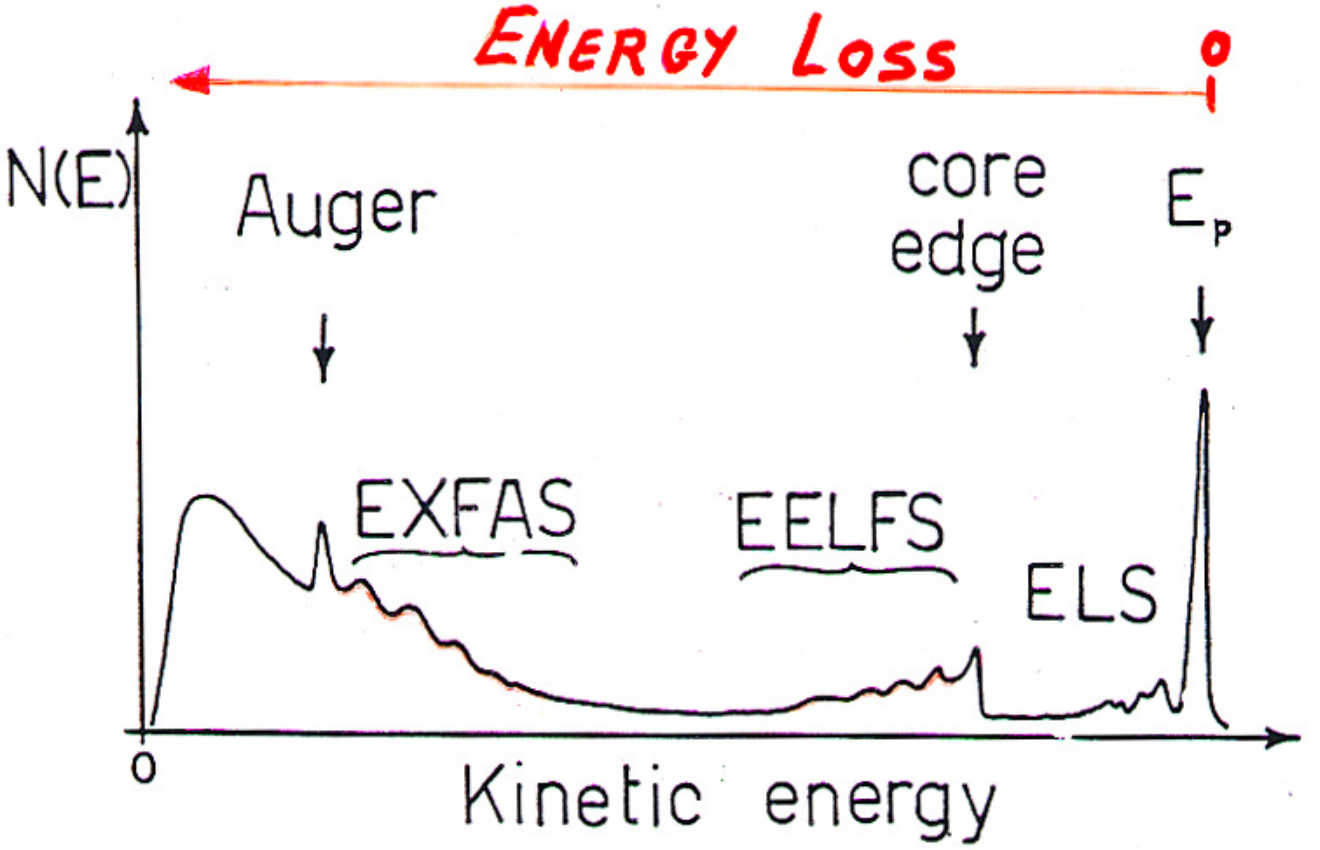
- **To assess any change in the electronic properties of the semiconductor system because the technique is sensitive to the formation of new radiative channels**

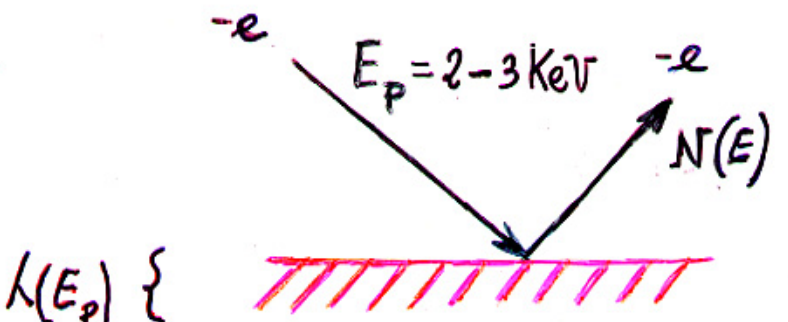
Scanning Tunneling Microscopy (STM)

- **To investigate the morphology, down to nanometric scale, of the formed thin silicon carbide layer**
- **local density of states around E_F through the I-V spectra**

- CMA
- LEED
- HA

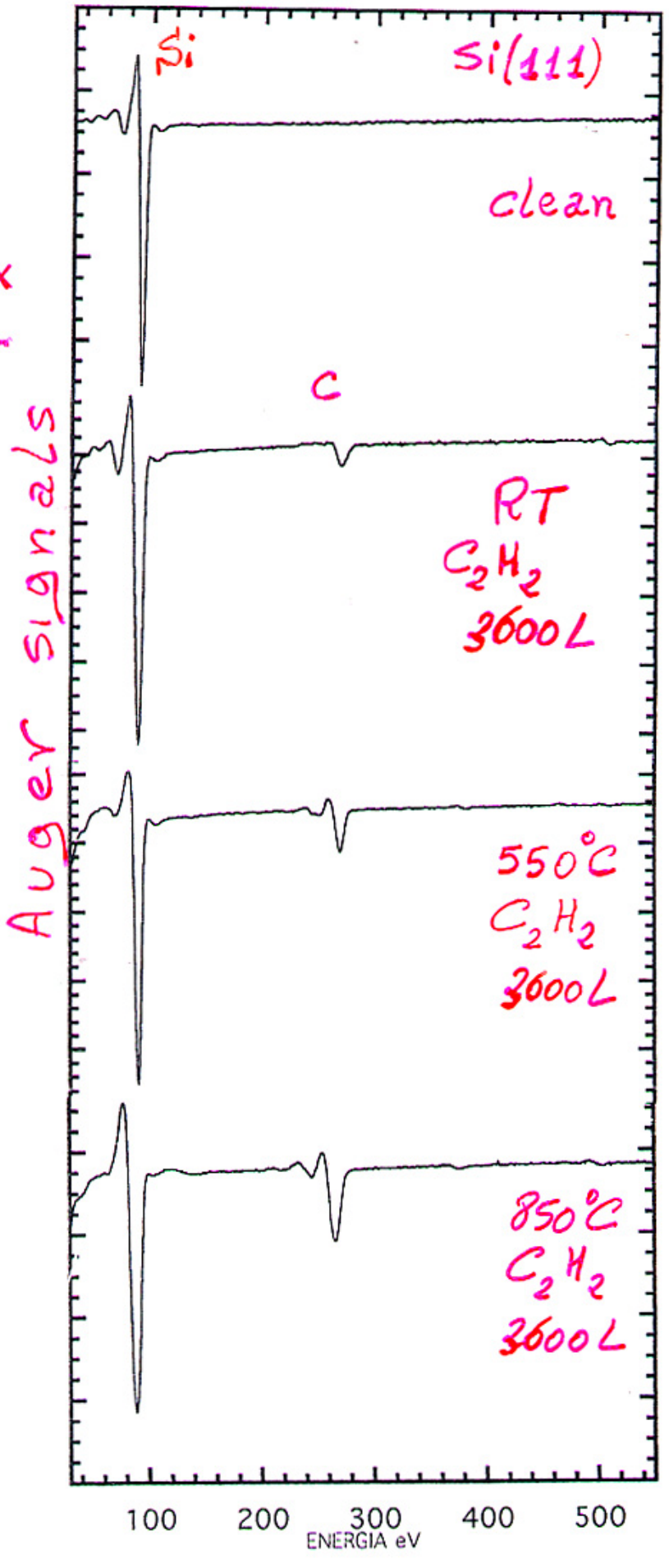
} -e spectrometers



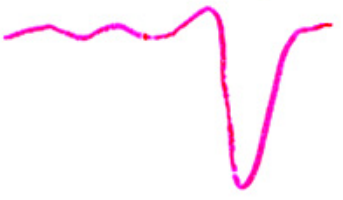


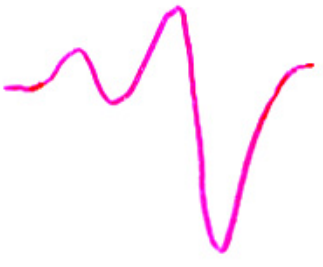
$\lambda(E_p)$ { $\lambda(\text{Å}) \sim 5-10$ Å

$1L = 1\,sec \times 10^{-6}\,Torr$

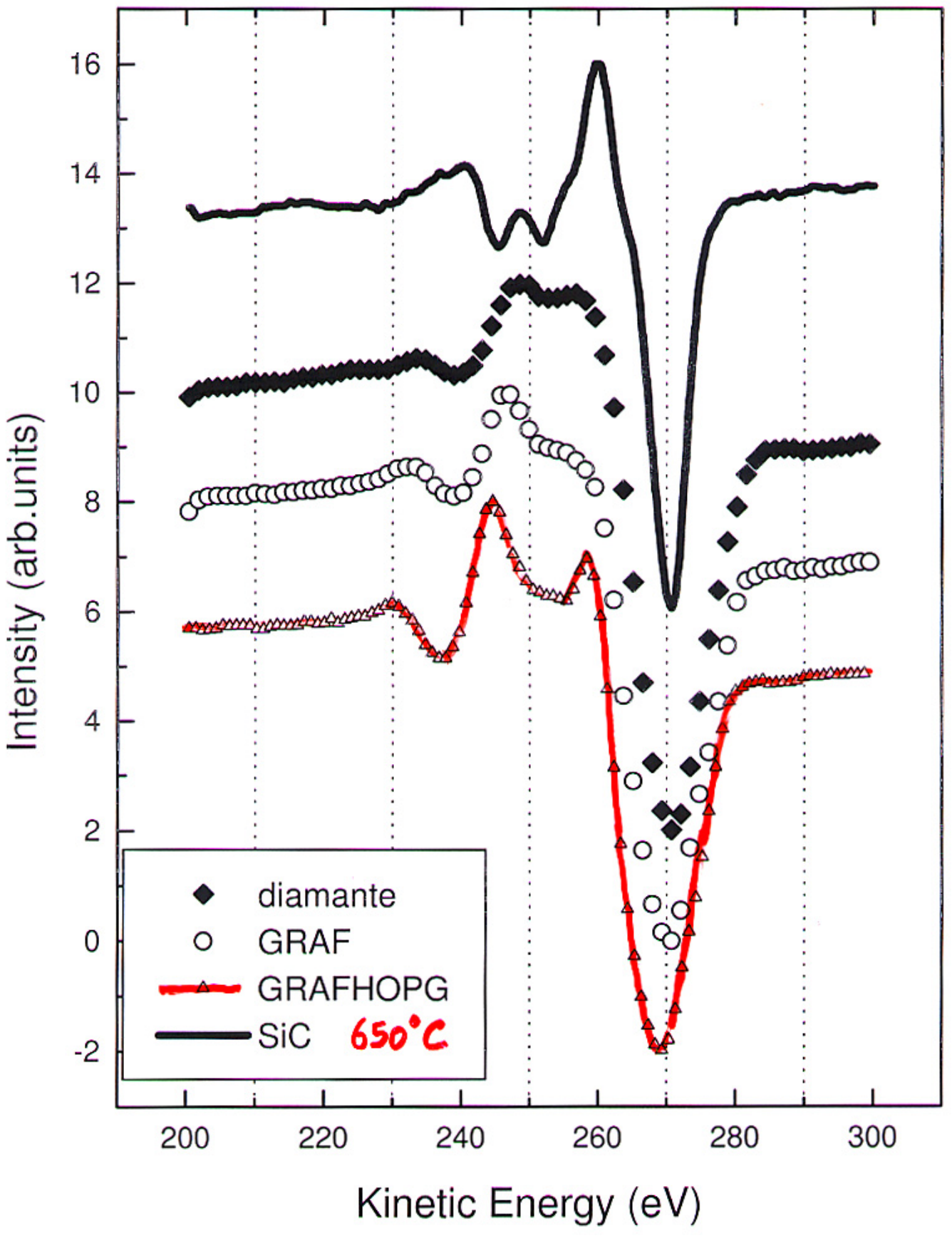


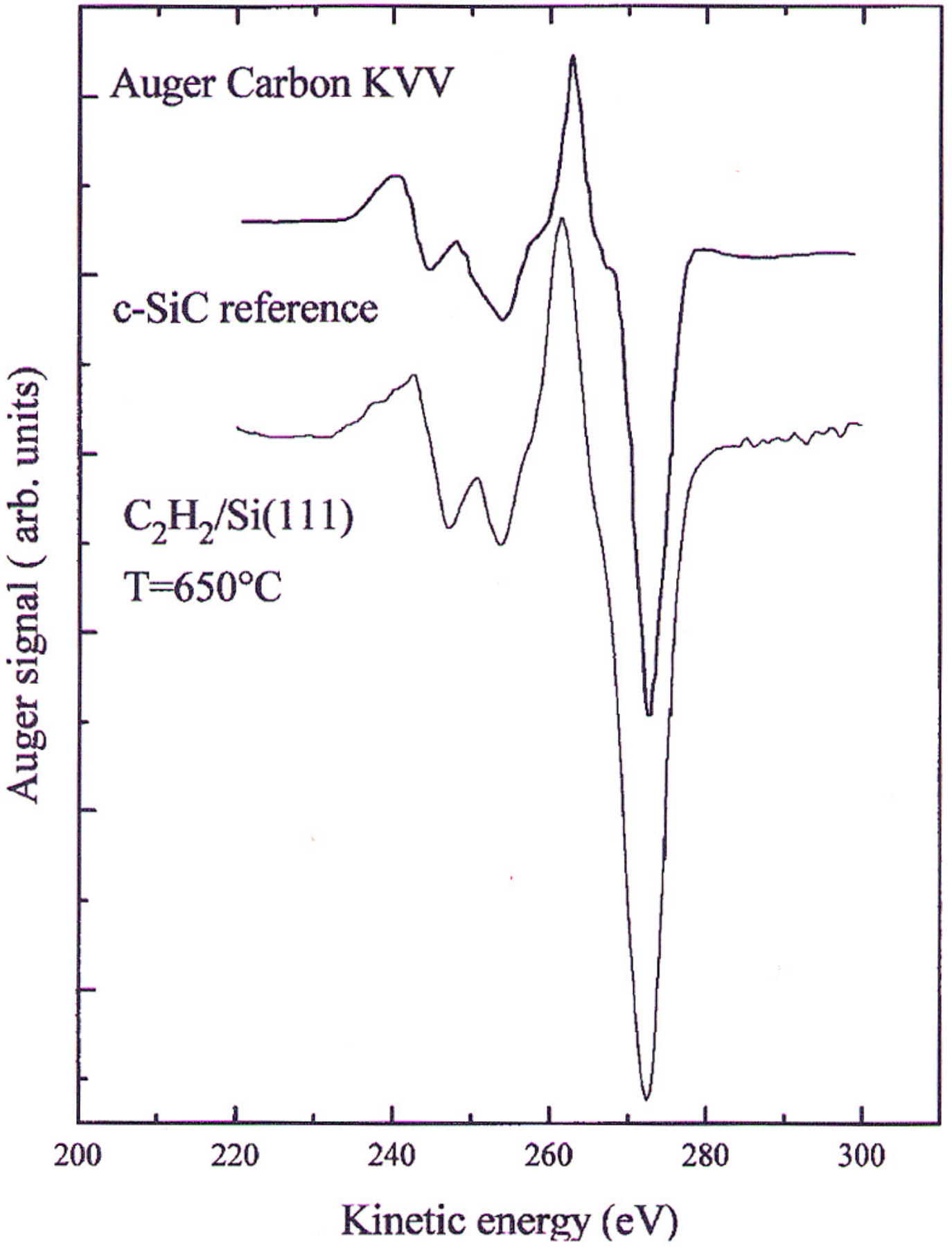
carbon Lineshape



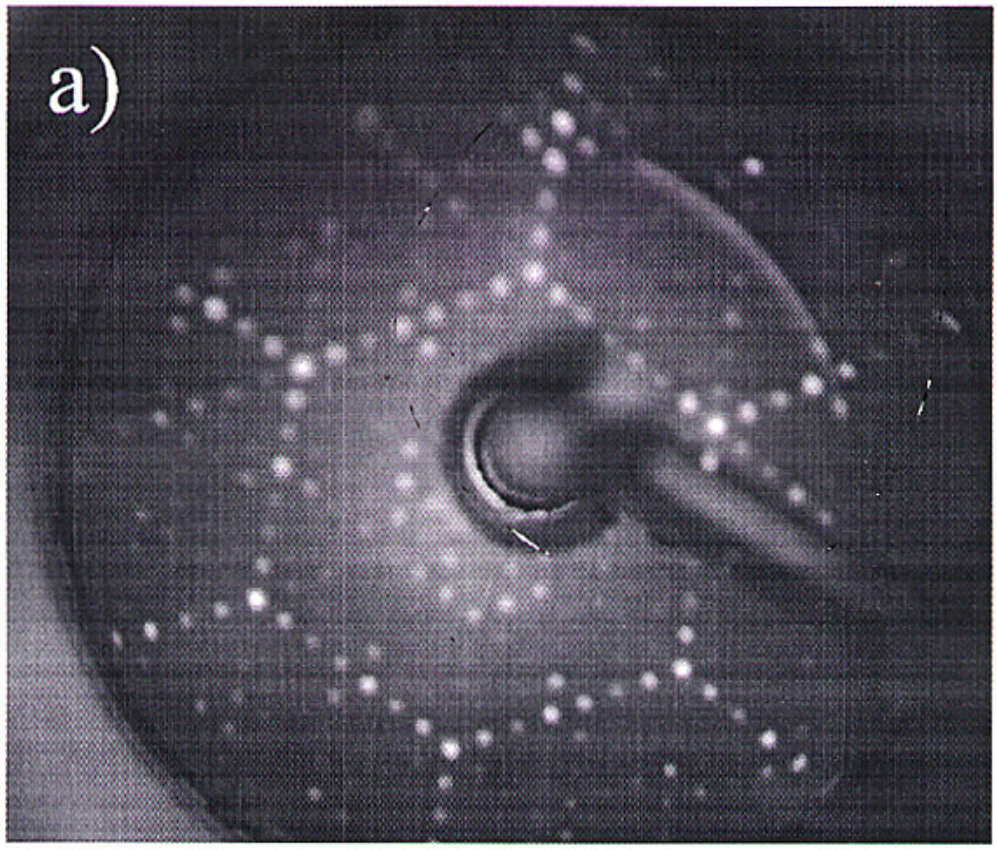


carbidic carbon


16
14
12
10
8
6
4
2
0
-2
Intensity (arb.units)
200
220
240
260
280
300
Kinetic Energy (eV)
diamante
GRAF
GRAFHOPG
SiC
650°C


Auger Carbon KVV
c-SiC reference
C_2H_2/Si(111)
T=650°C
Auger signal (arb. units)
200
220
240
260
280
300
Kinetic energy (eV)

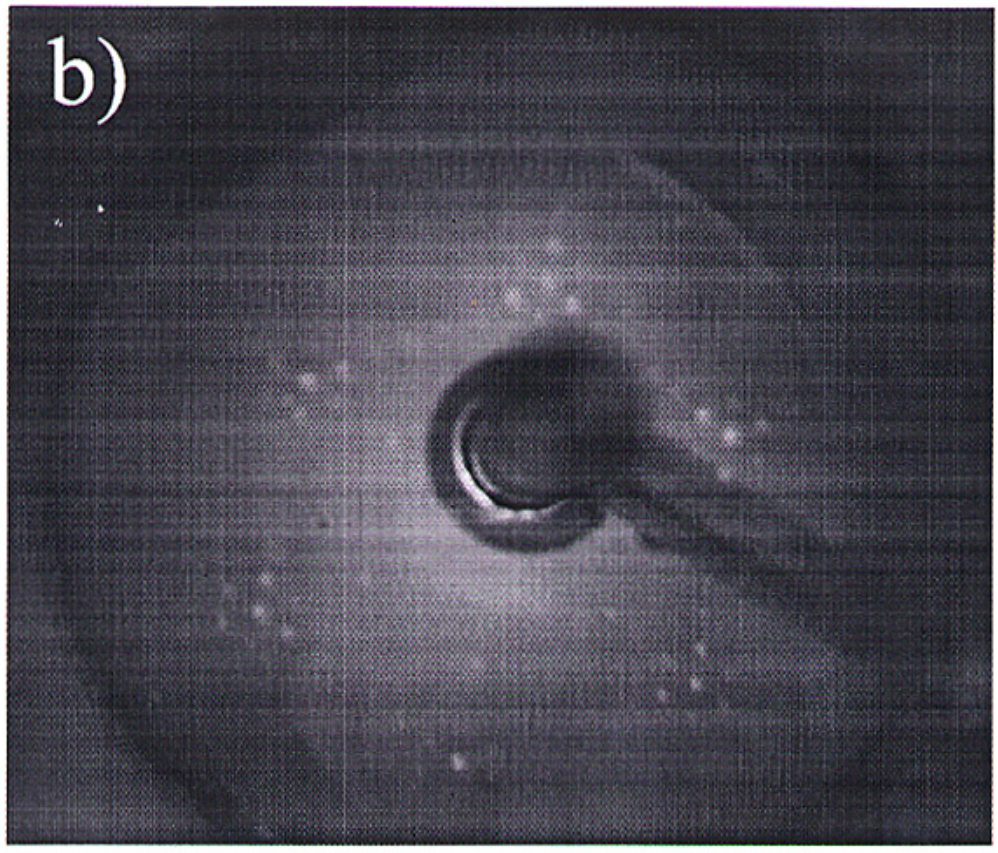
LEED



Si(111)

7×7

$E_p = 56\ eV$



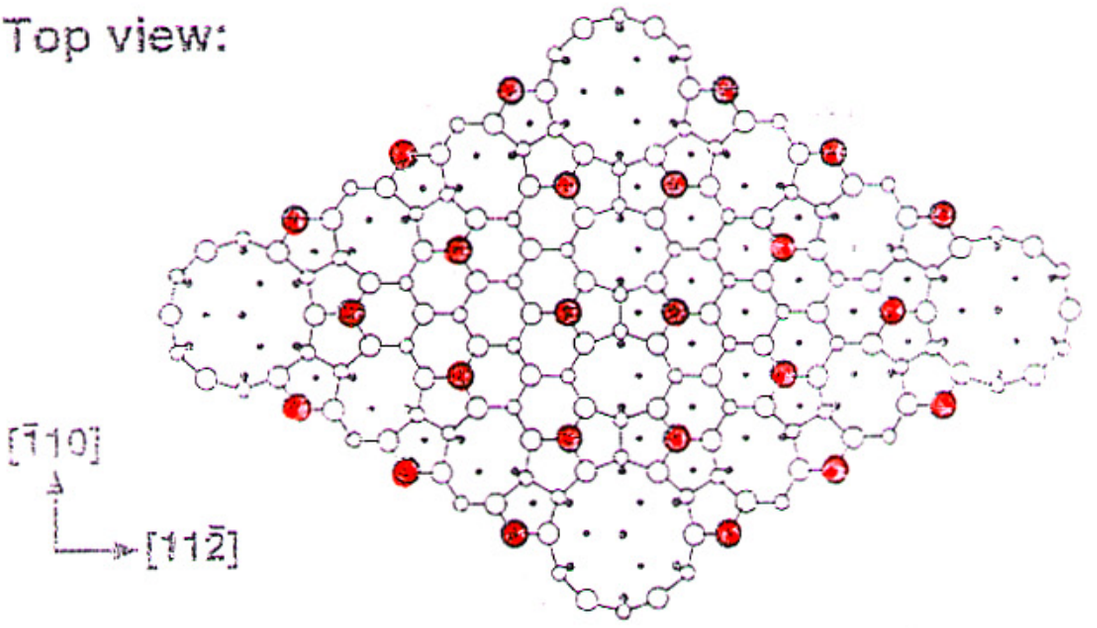
C_2H_2 /

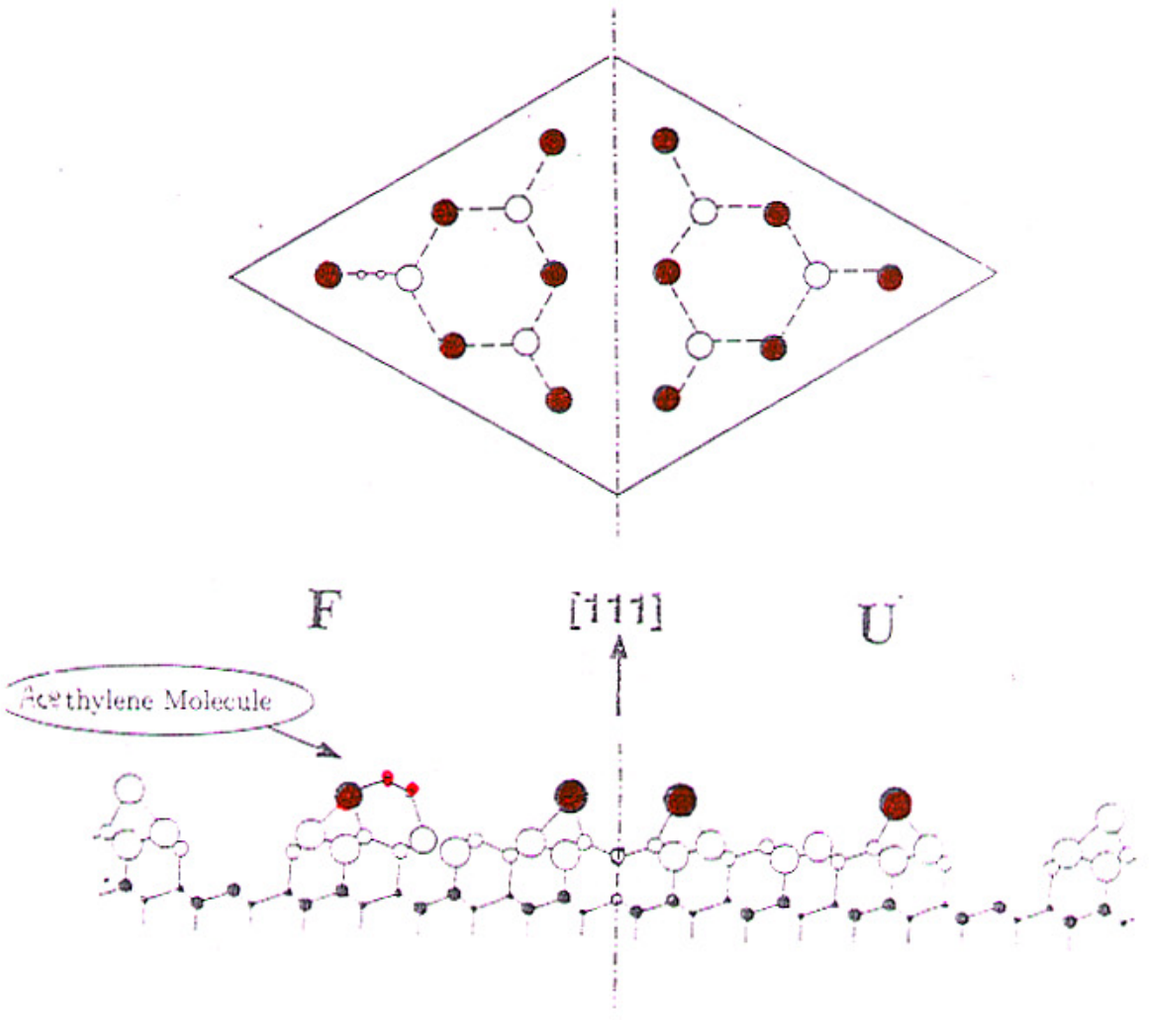
Si(111)

RT

2000 L

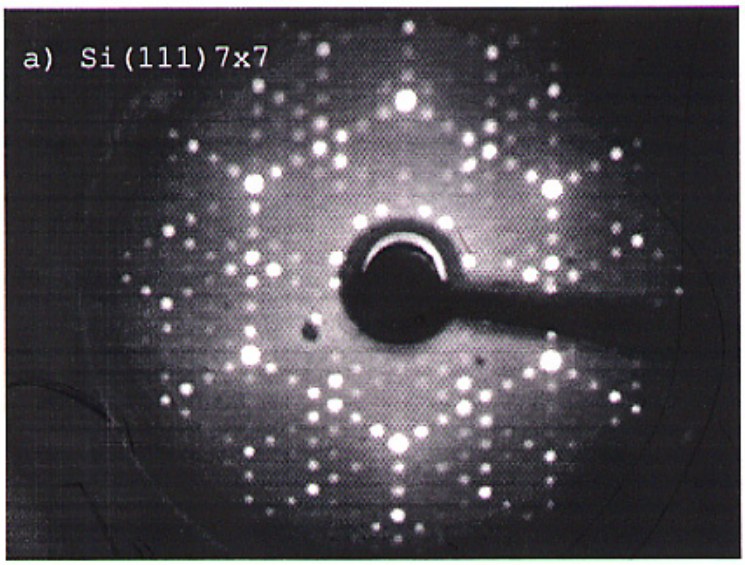
Si(111) 7×7 reconstruction

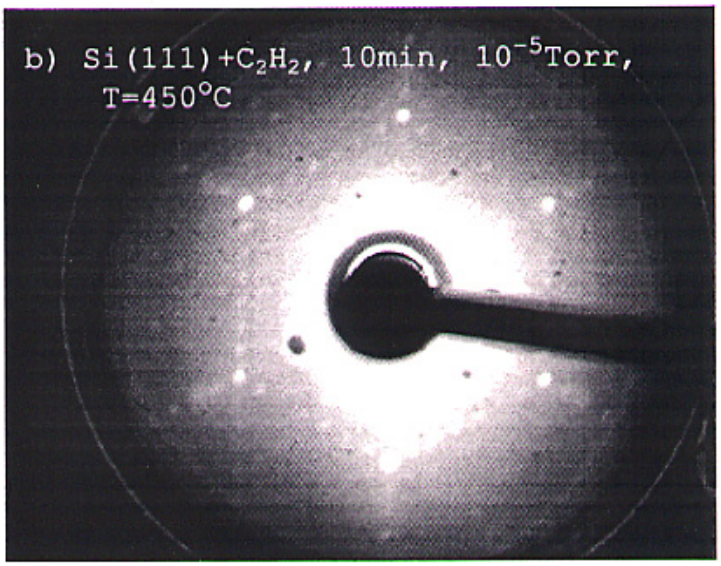


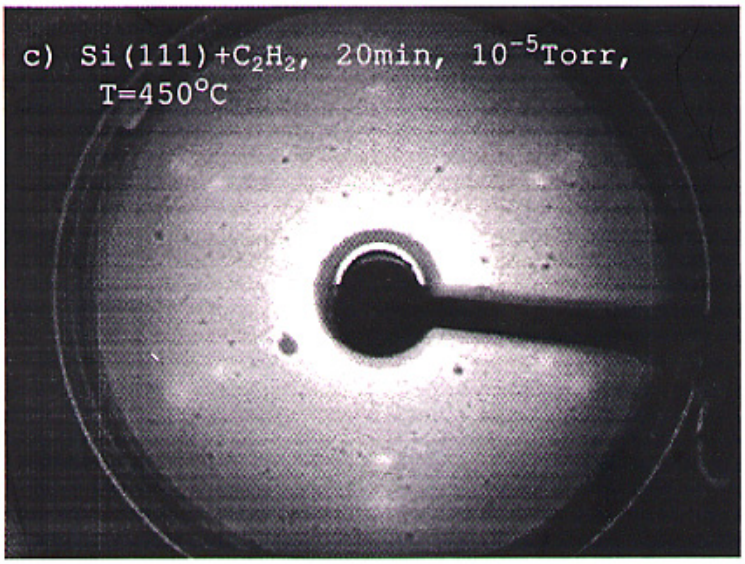


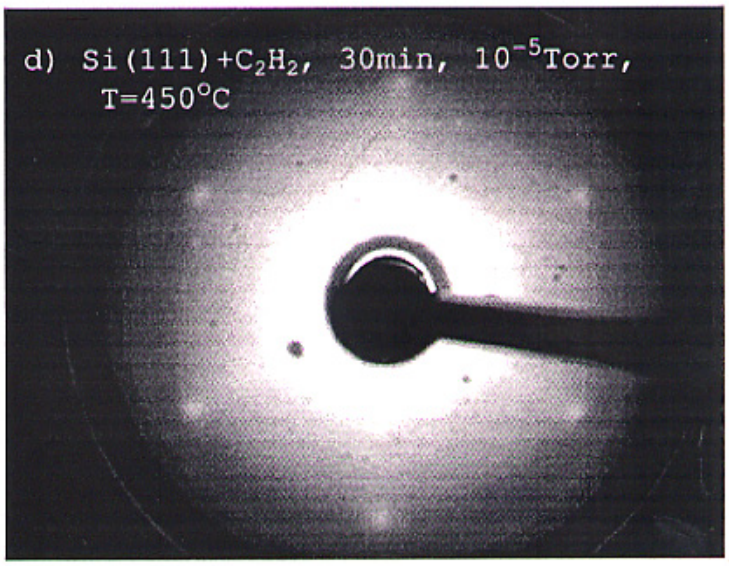
Schematic drawing of the proposed adsorption site.

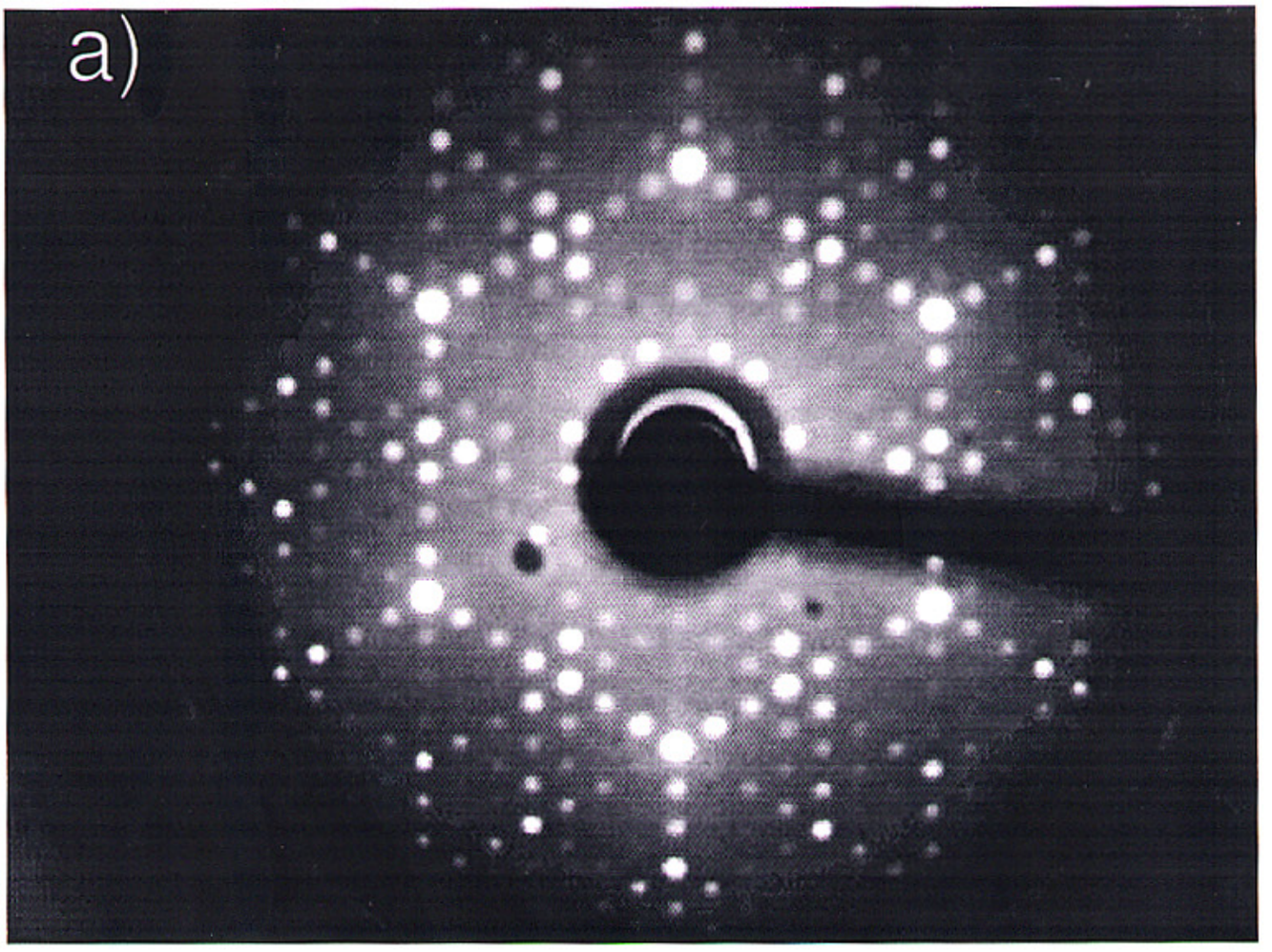
LEED $E_p = 62eV$


a) Si(111)7x7

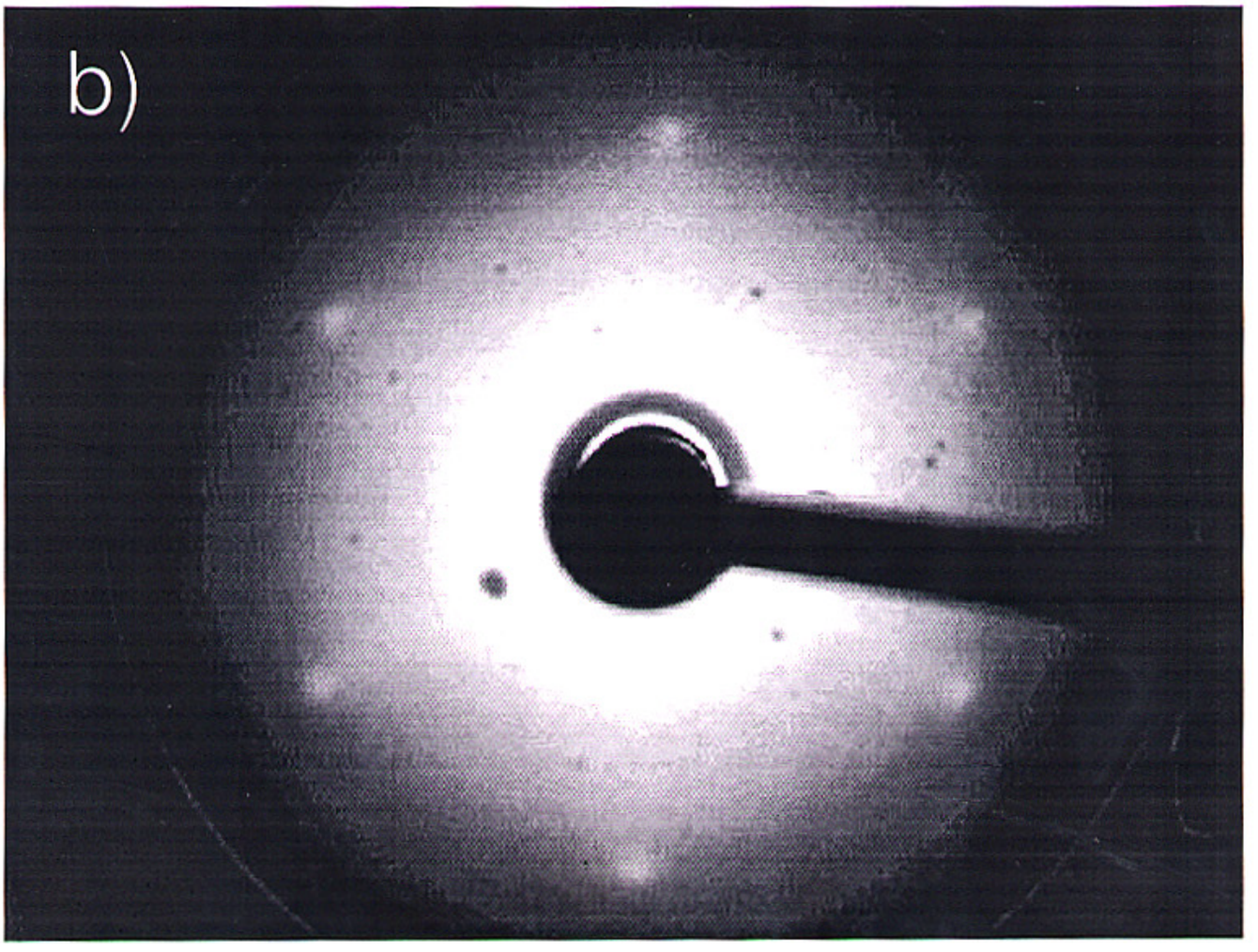

b) Si(111)+C_2H_2, 10min, 10^{-5}Torr,
T=450°C

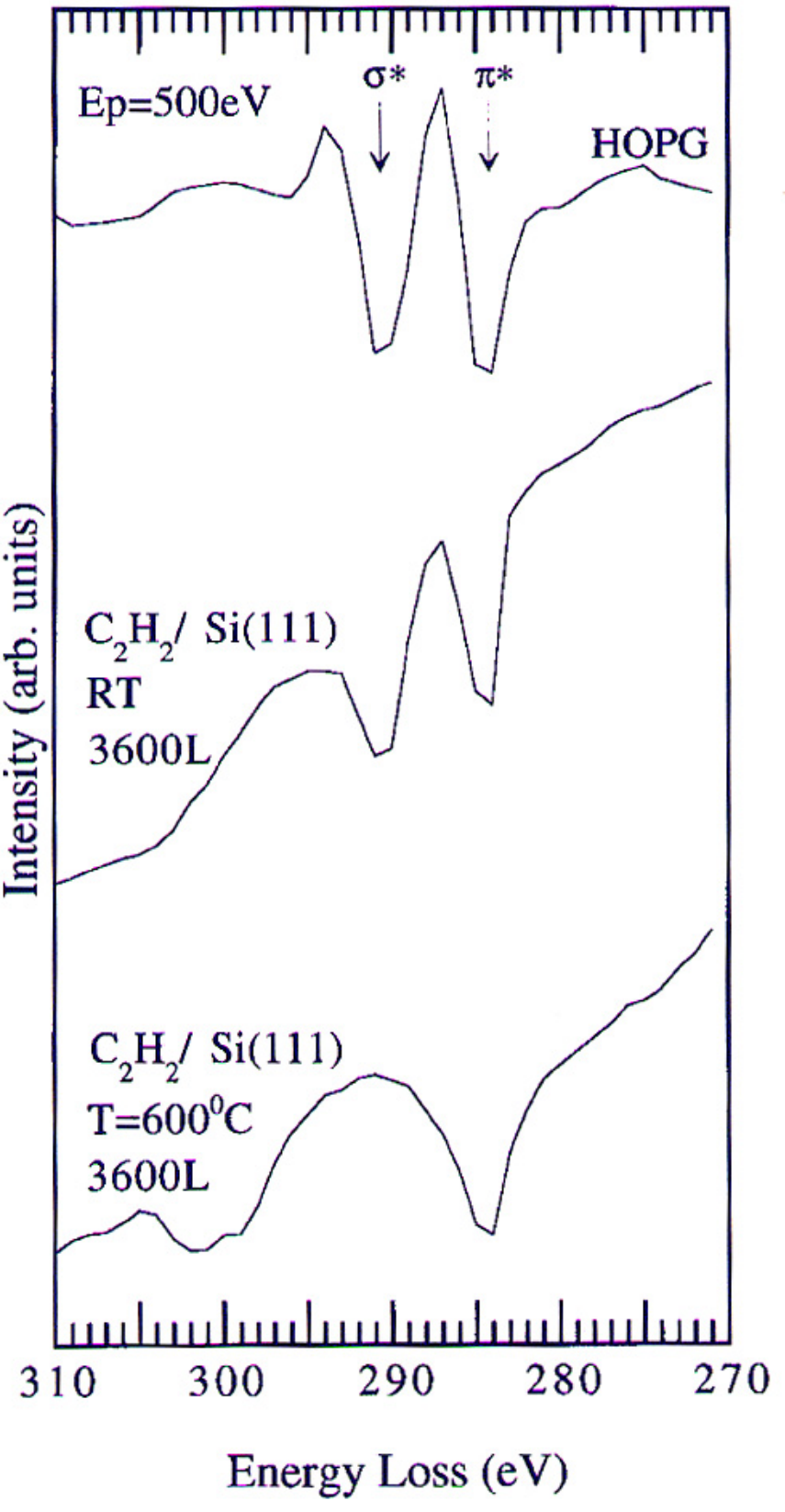

c) Si(111)+C_2H_2, 20min, 10^{-5}Torr,
T=450°C

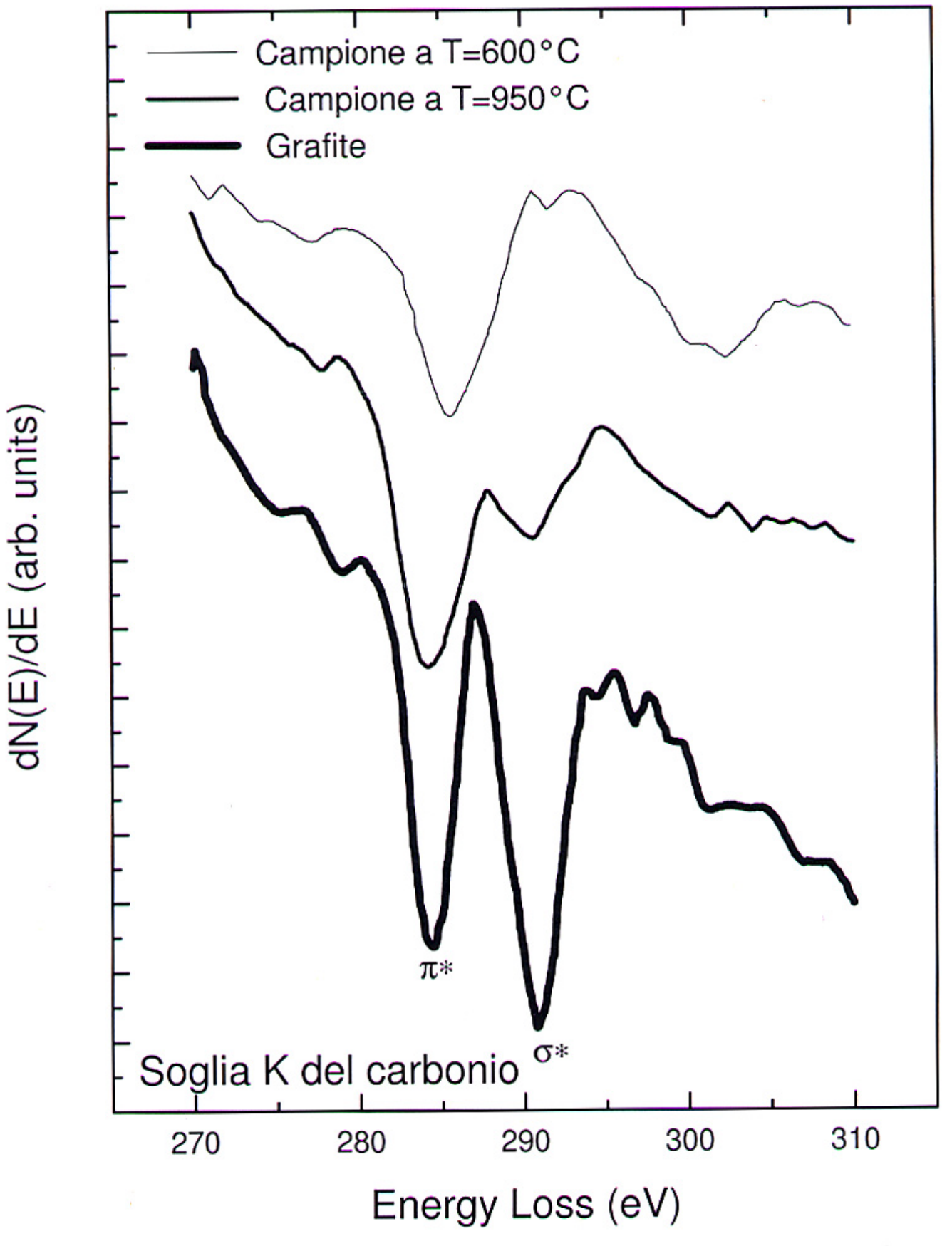

d) Si(111)+C_2H_2, 30min, 10^{-5}Torr,
T=450°C

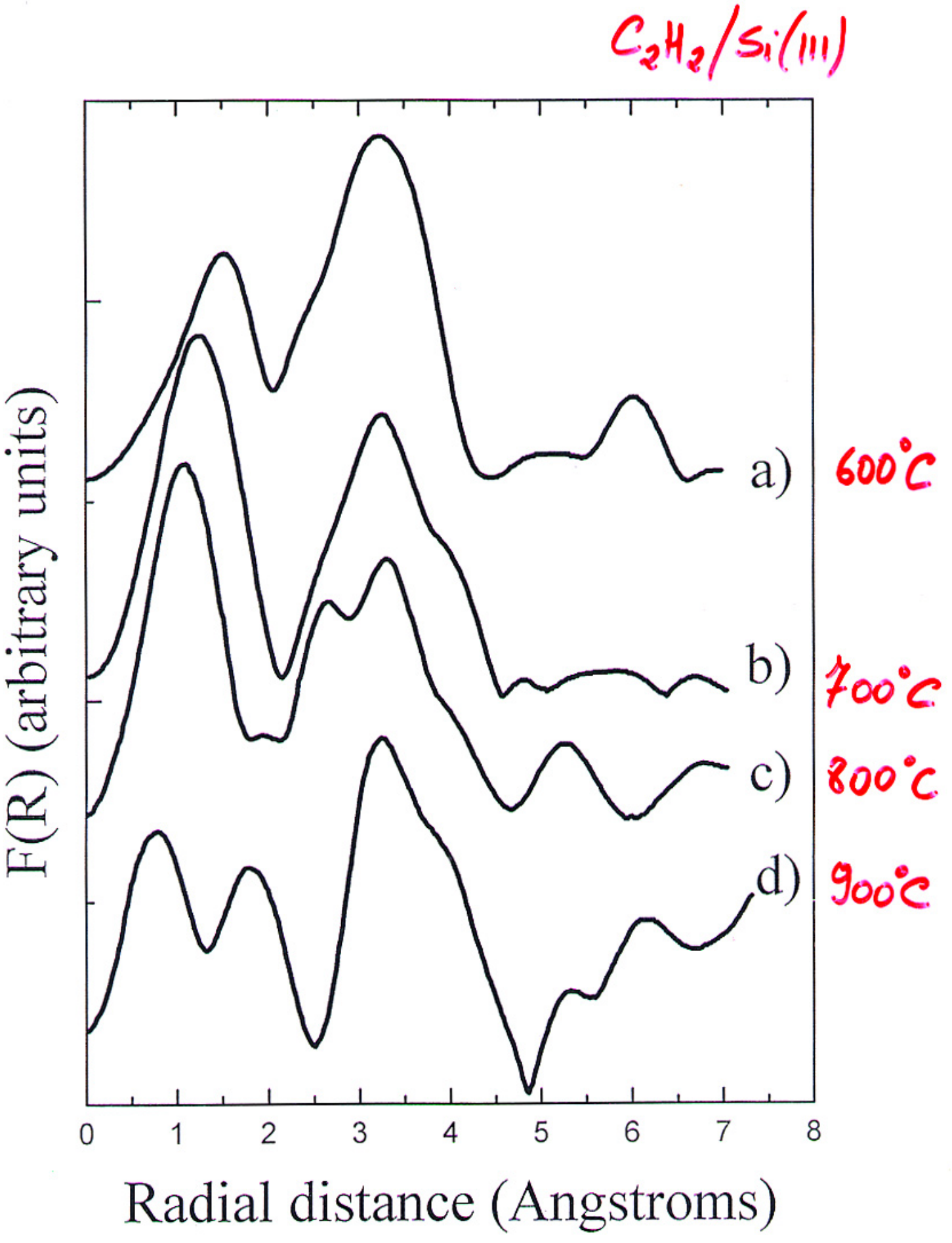


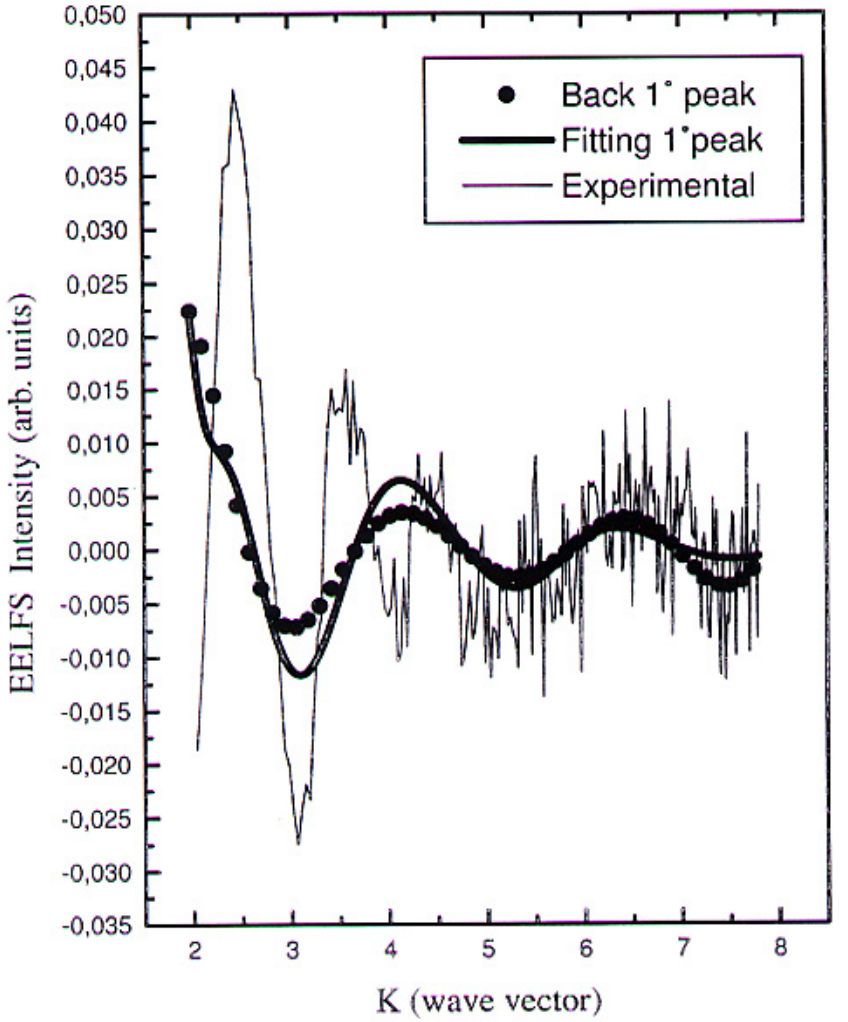
LEED $E_p = 62\ eV$

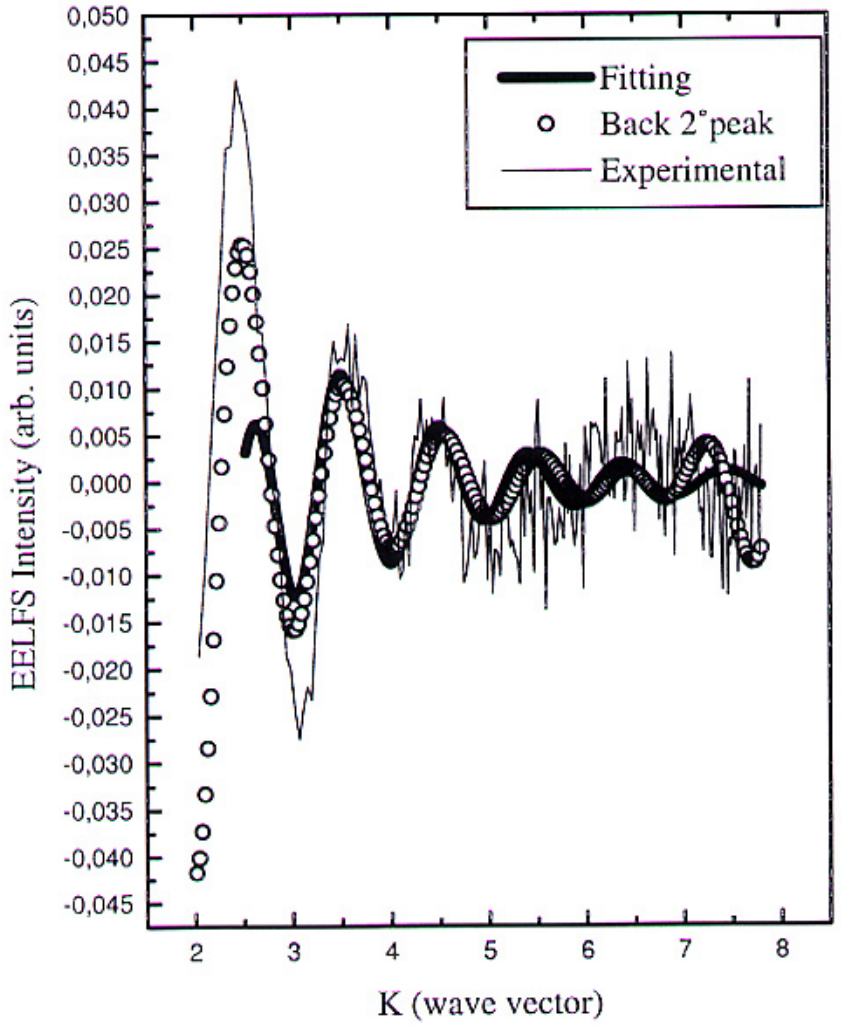


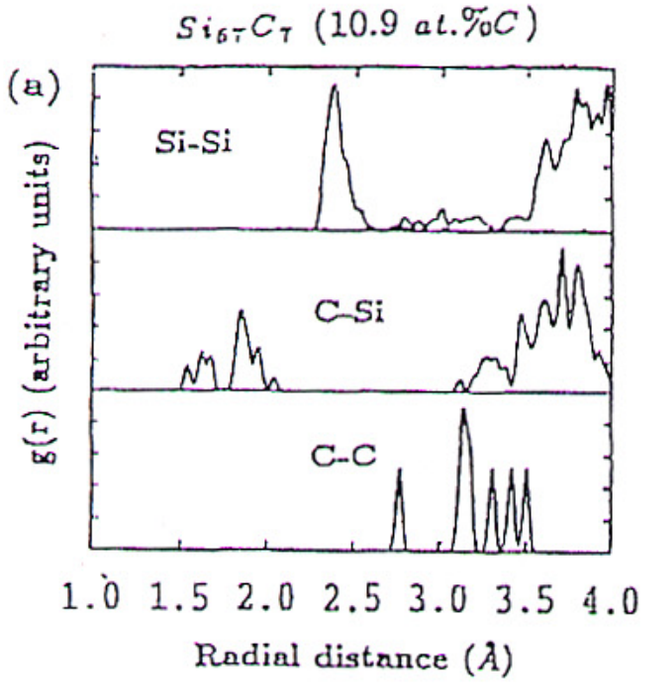

Ep=500eV
σ*
π*
HOPG
C2H2/ Si(111)
RT
3600L
C2H2/ Si(111)
T=600°C
3600L
Intensity (arb. units)
310
300
290
280
270
Energy Loss (eV)


Campione a T=600°C
Campione a T=950°C
Grafite
π*
σ*
Soglia K del carbonio
dN(E)/dE (arb. units)
270
280
290
300
310
Energy Loss (eV)


C2H2/Si(111)
F(R) (arbitrary units)
a)
600°C
b)
700°C
c)
800°C
d)
900°C
0
1
2
3
4
5
6
7
8
Radial distance (Angstroms)


Back 1° peak
Fitting 1°peak
Experimental
EELFS Intensity (arb. units)
K (wave vector)


Fitting
Back 2°peak
Experimental
EELFS Intensity (arb. units)
K (wave vector)



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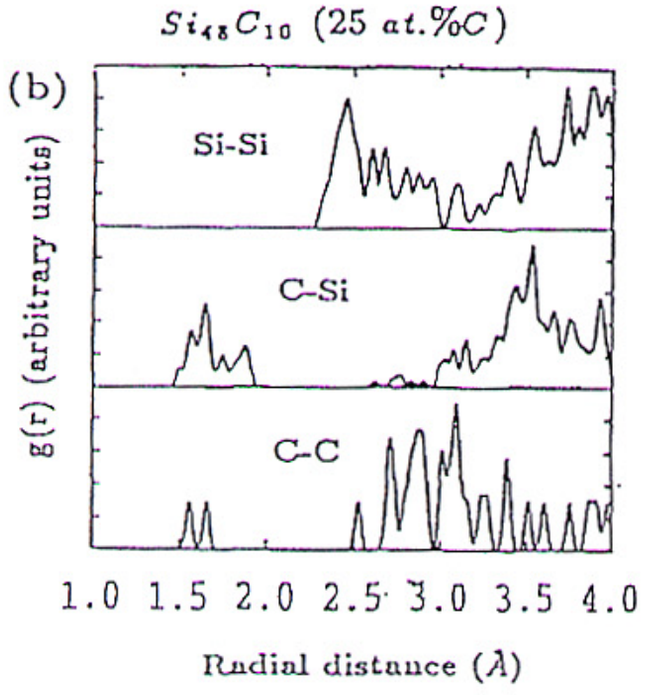
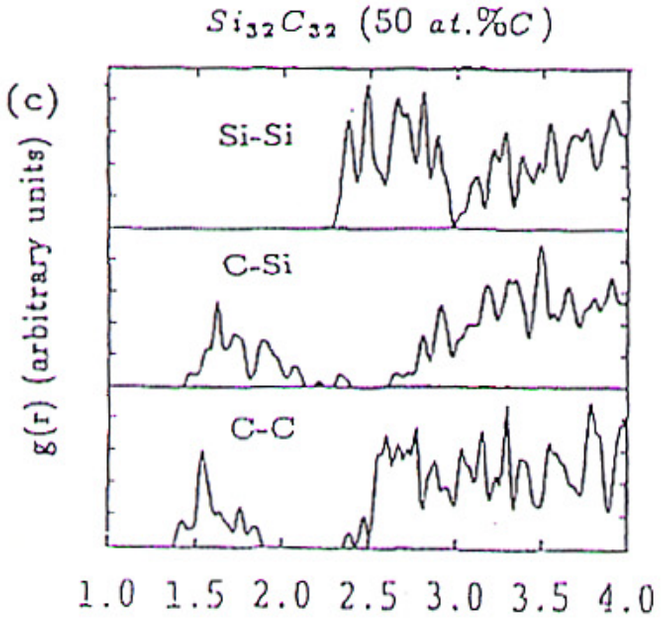
AND
OTTO F. SANKEY





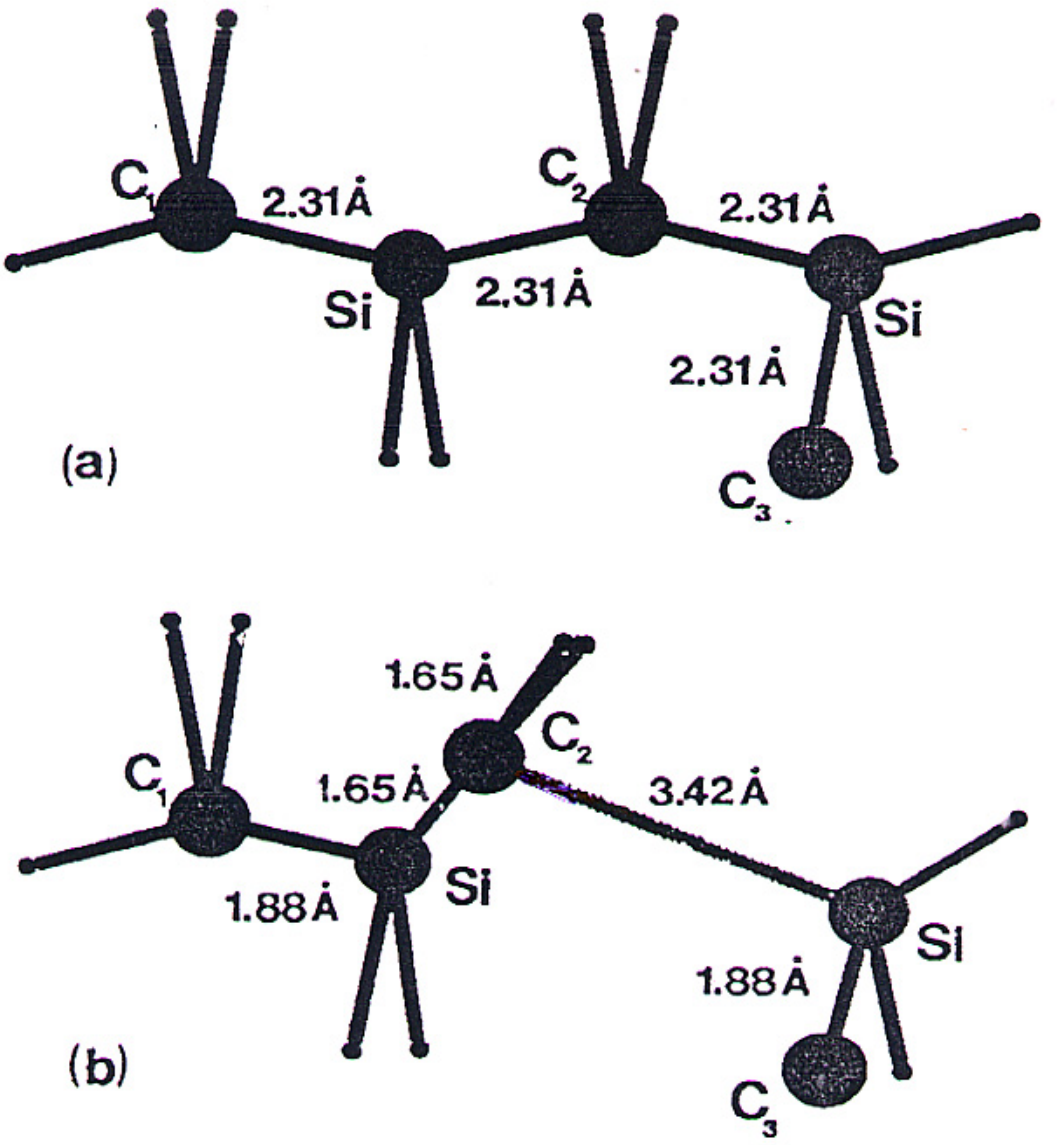
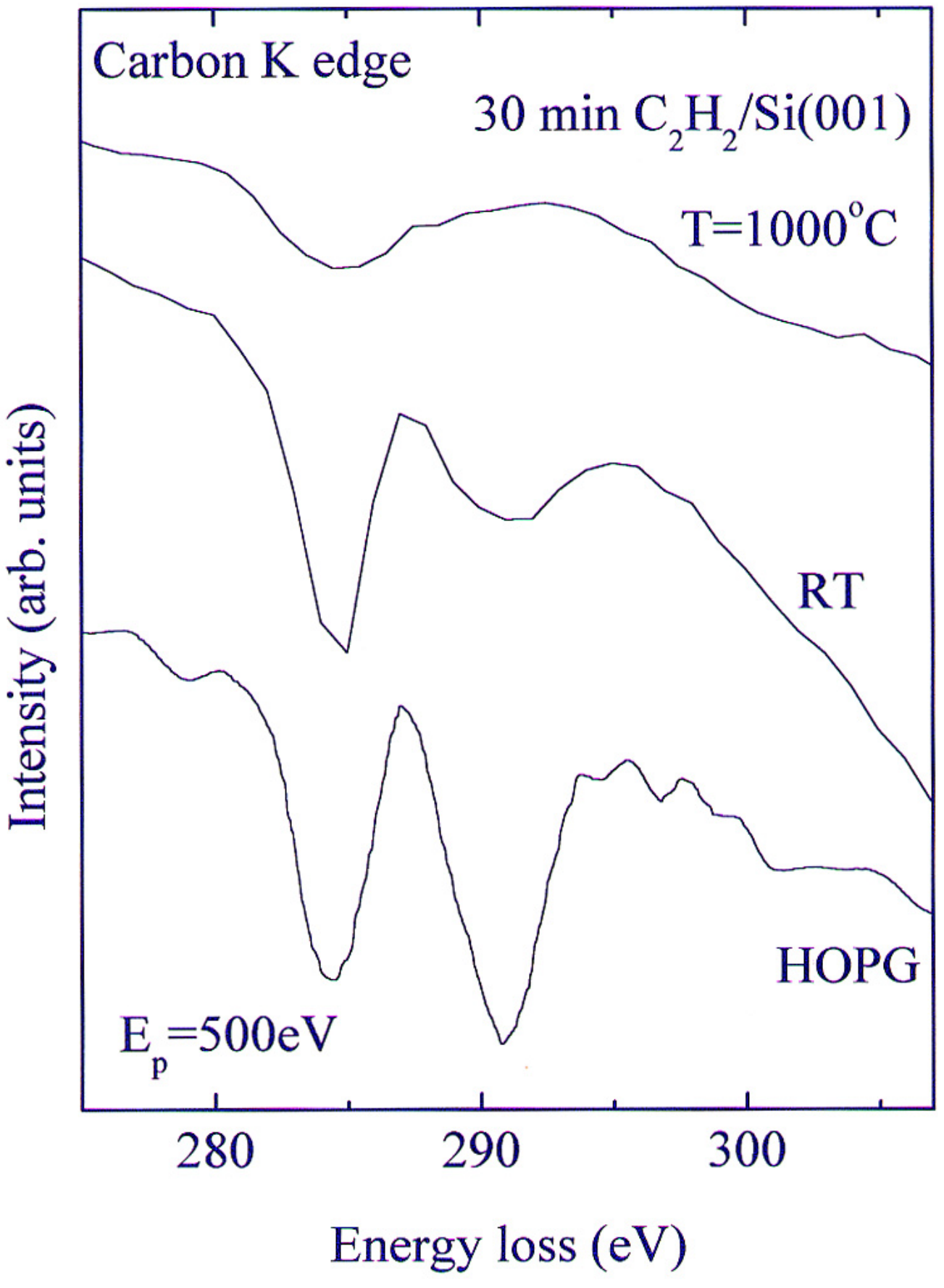
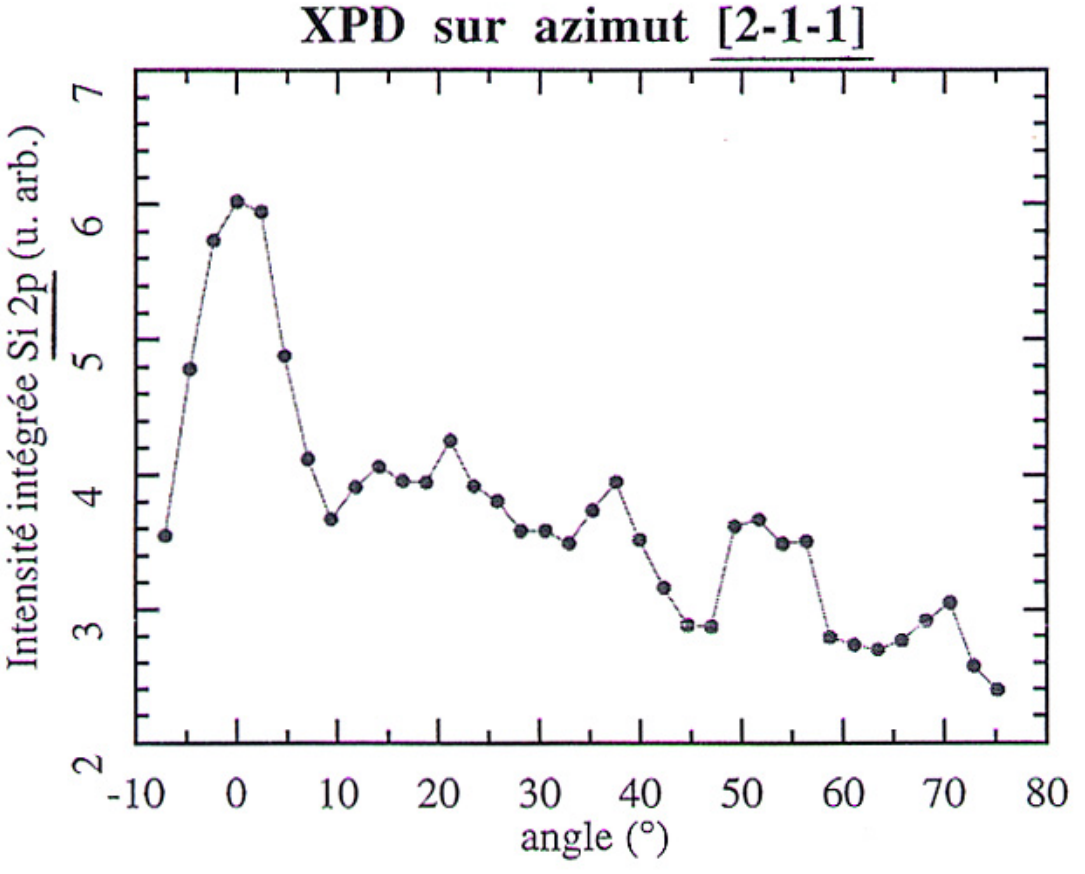
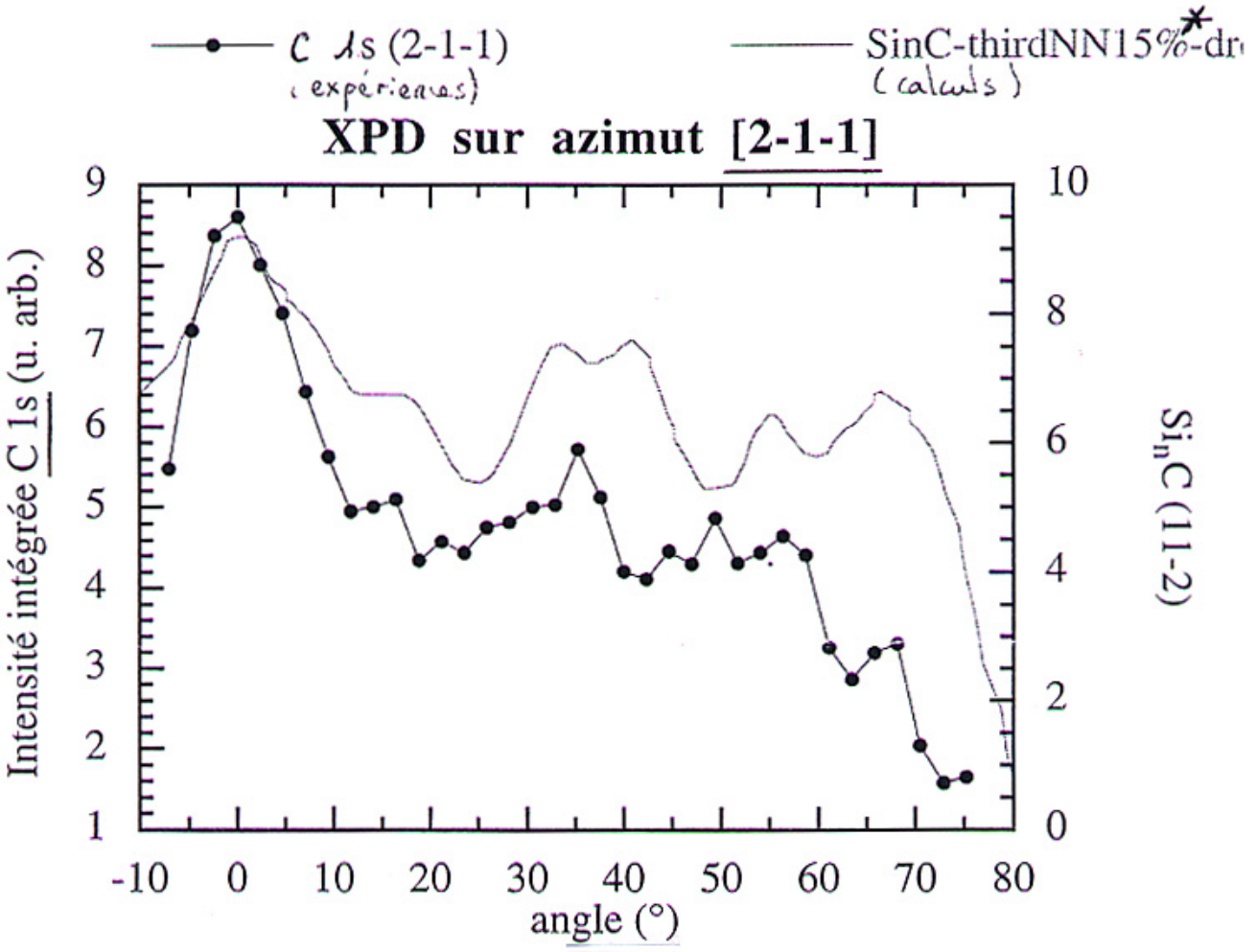


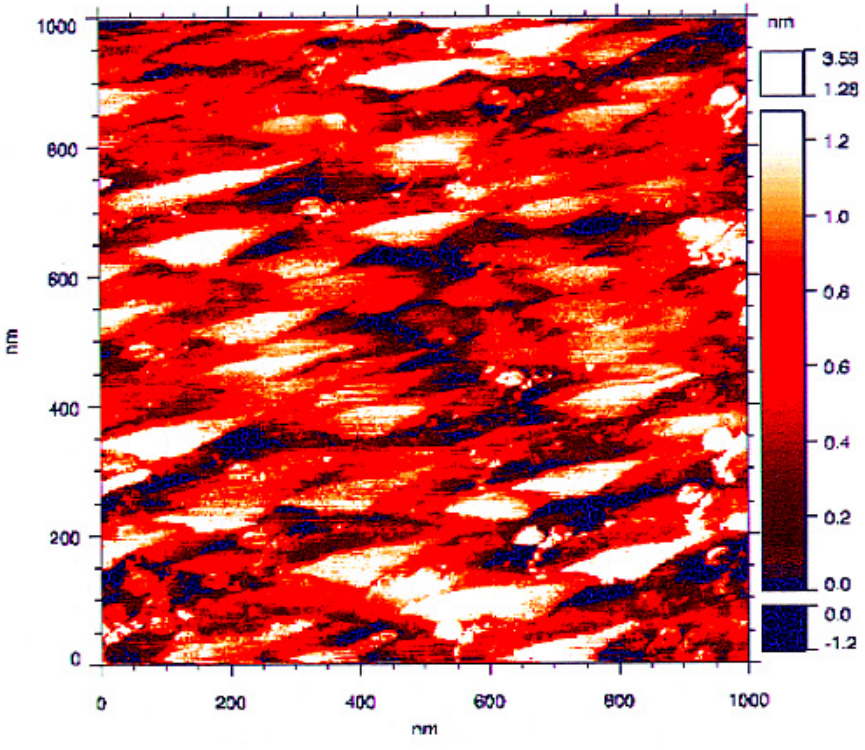
FIG. 4. A schematic picture of a fragment of the structure of a 6.3% C concentration in Si ($Si_{60}C_4$ supercell). Three of the four carbon atoms in the supercell were randomly selected to be second neighbors of each other. (a) The local geometry before relaxation of the atomic coordinates. (b) The zero force final configuration of the fragment. Notice formation of a CSi_3 graphitic structure with the atom C_2 in the center.


Carbon K edge
30 min C2H2/Si(001)
T=1000°C
RT
HOPG
Ep=500eV
Intensity (arb. units)
280
290
300
Energy loss (eV)

C_2H_2 / Si(111) T=650°C





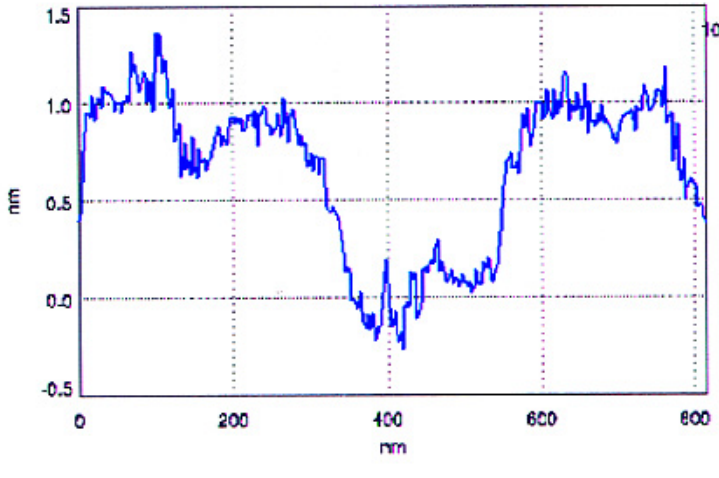


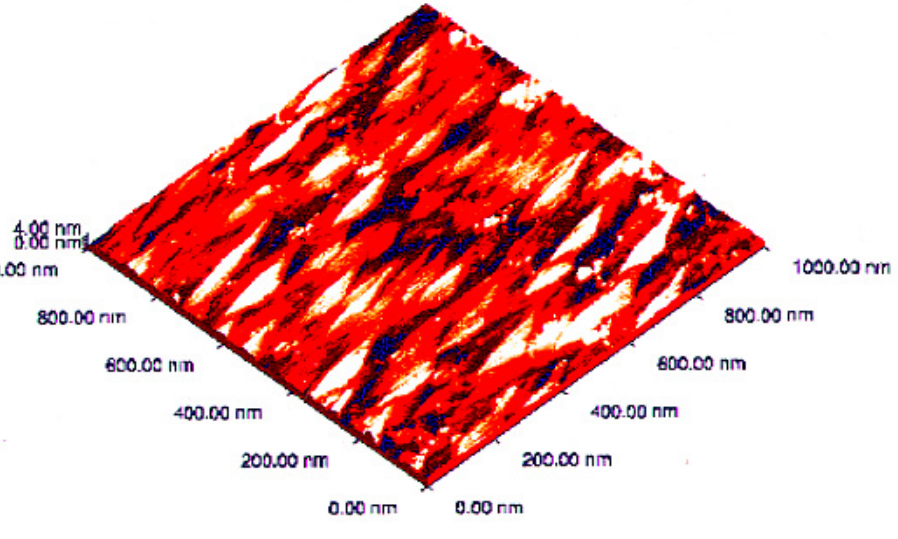
C_2H_2/Si(111)

T=650°C

P=10^{-6} torr

t=30 min

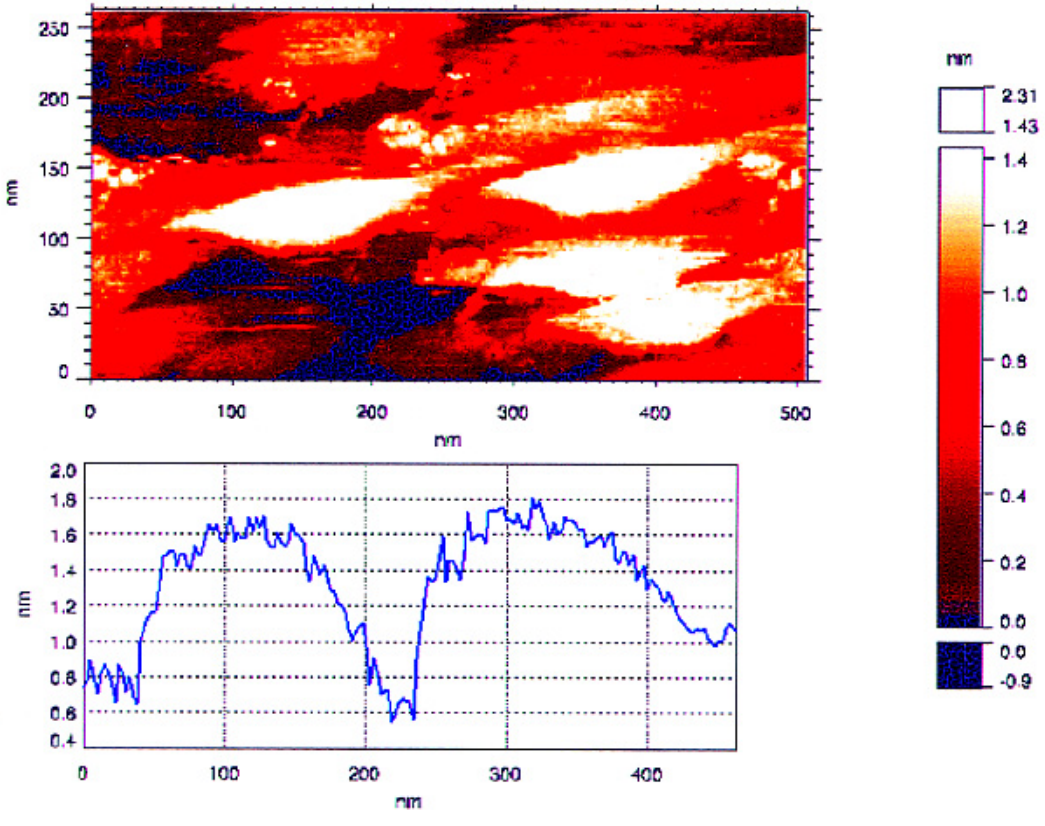




STM images show the formation of flat regions large about 150 nm, high about 1.8 nm and of voids with a depth in the range of 0.5-0.8 nm

C_2H_2/Si(111)

T=650°C
P=10^{-6} torr
t= 30 min



TEM

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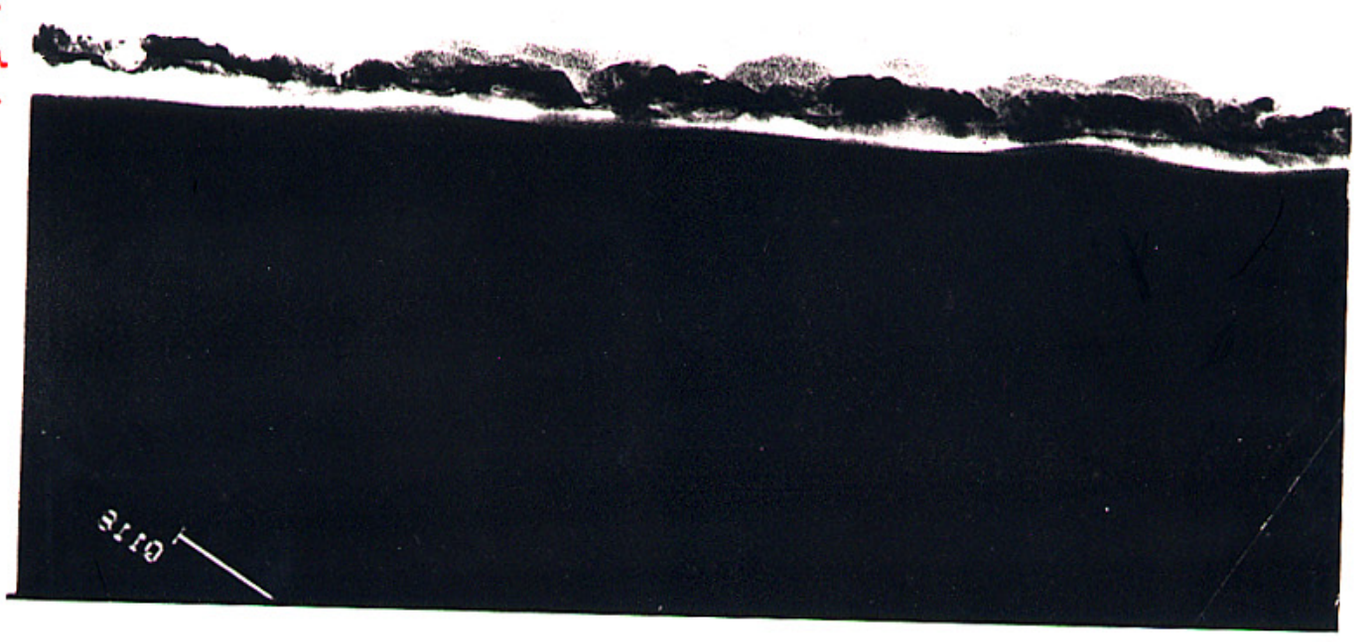
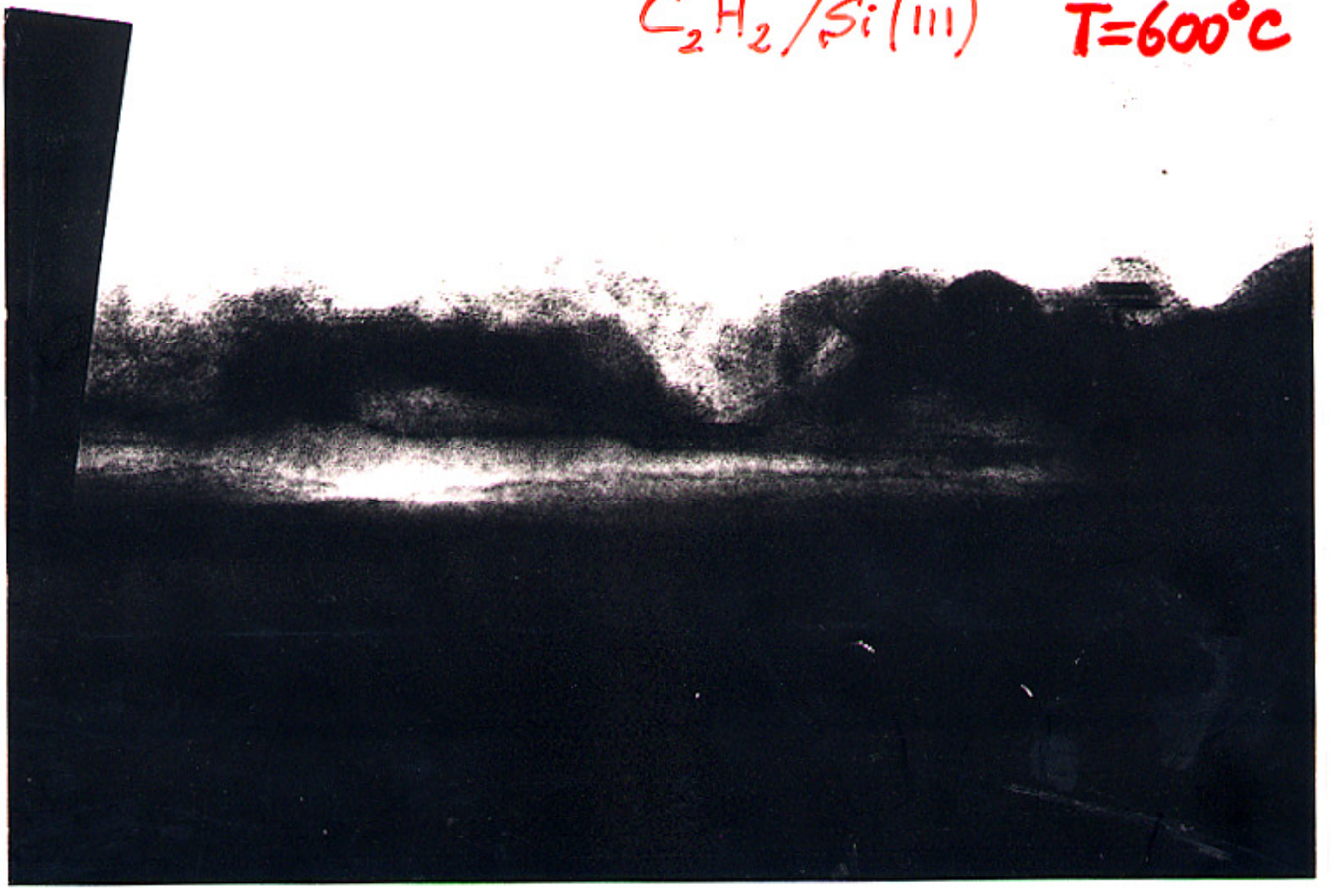


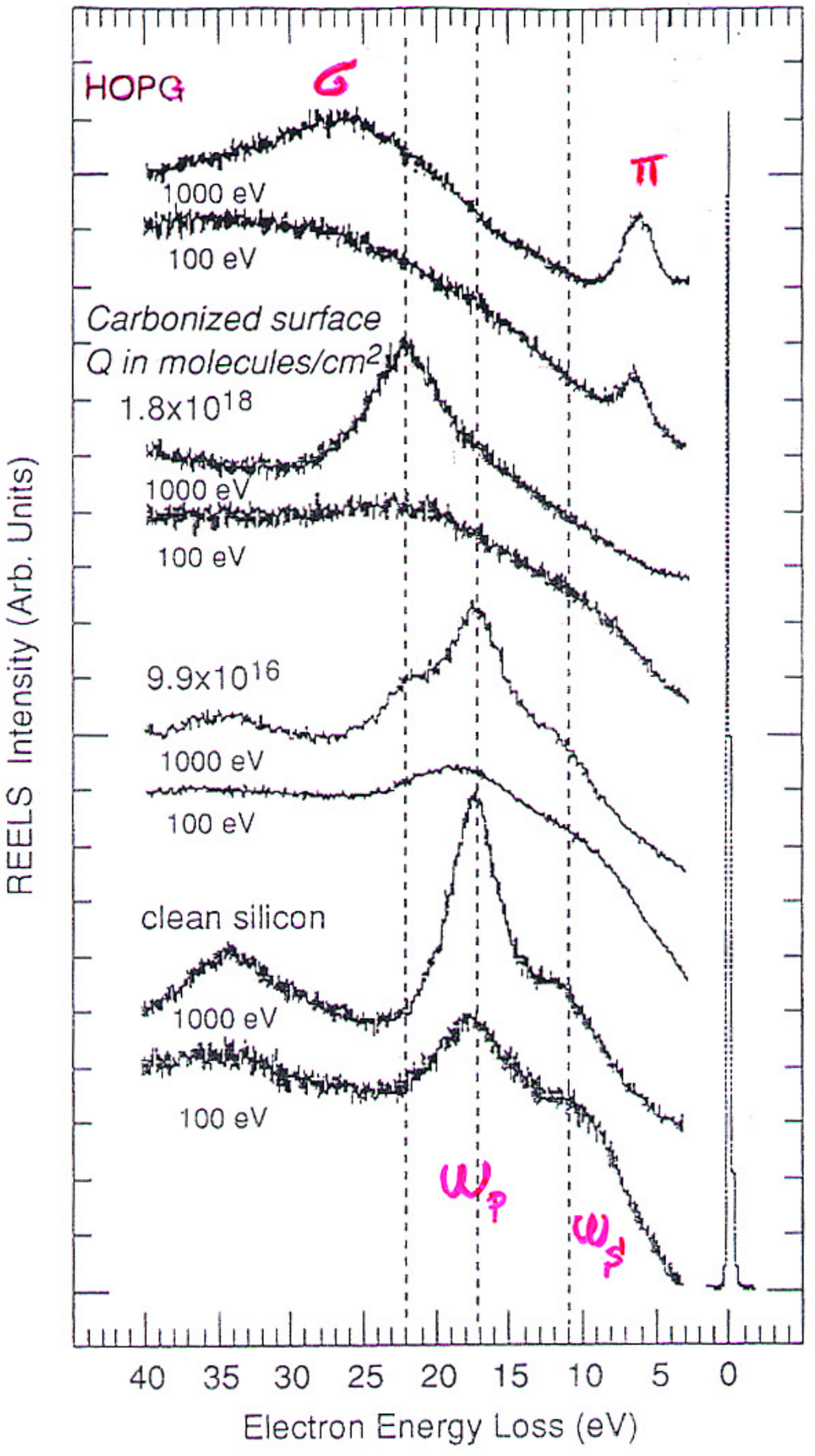
$C_2H_2/Si(111)$ T=600°C



EELS

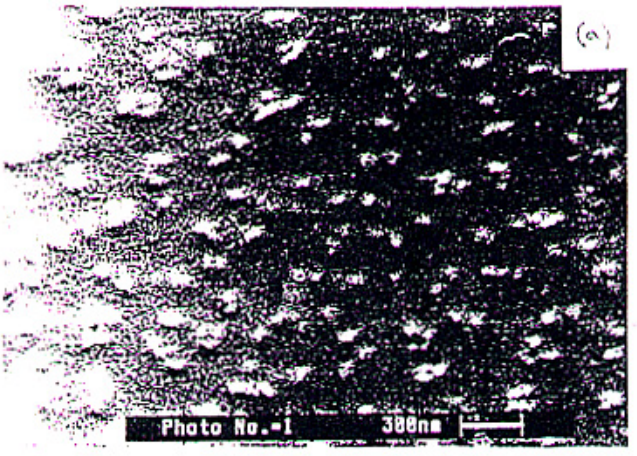
C_2H_2/Si(100)

650°C

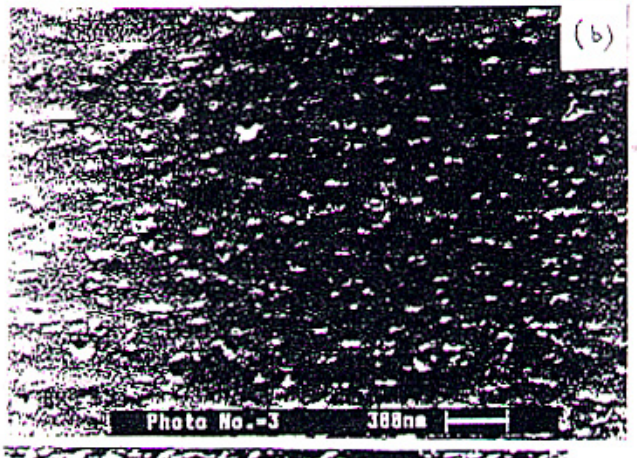


. . . REELS spectra, taken at $E_p = 100$ eV (surface sensitive) and $E_p = 1000$ eV (bulk sensitive), for the clean Si surface, the carbonized surface at two exposures, and a clean HOPG surface. SiC

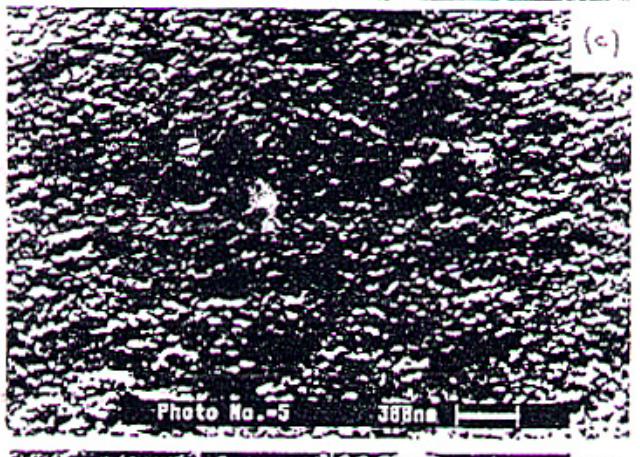
SEM



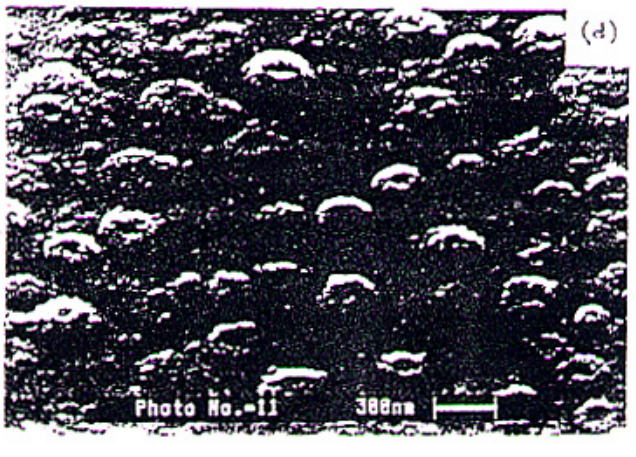
Si(100)
+ C_2H_2
550°C



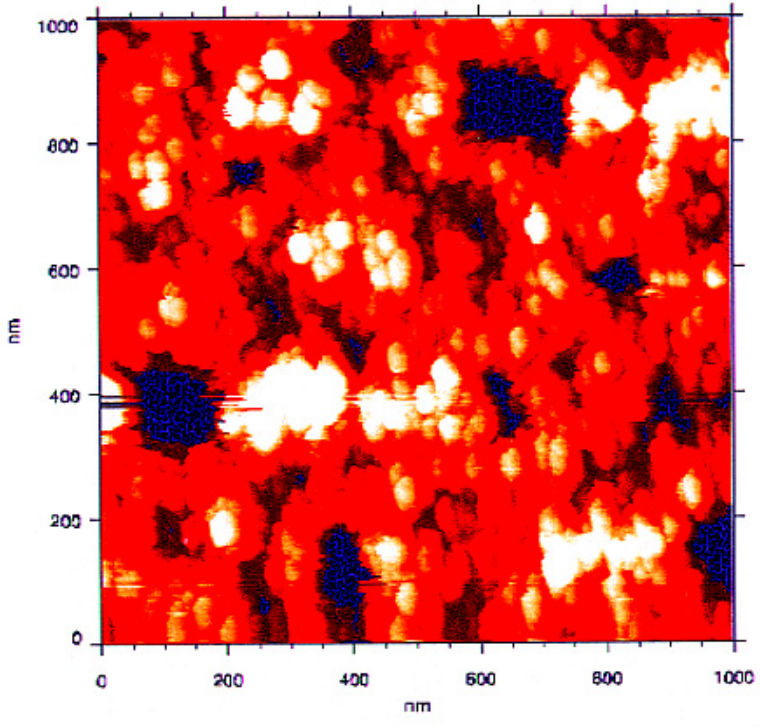
650°C

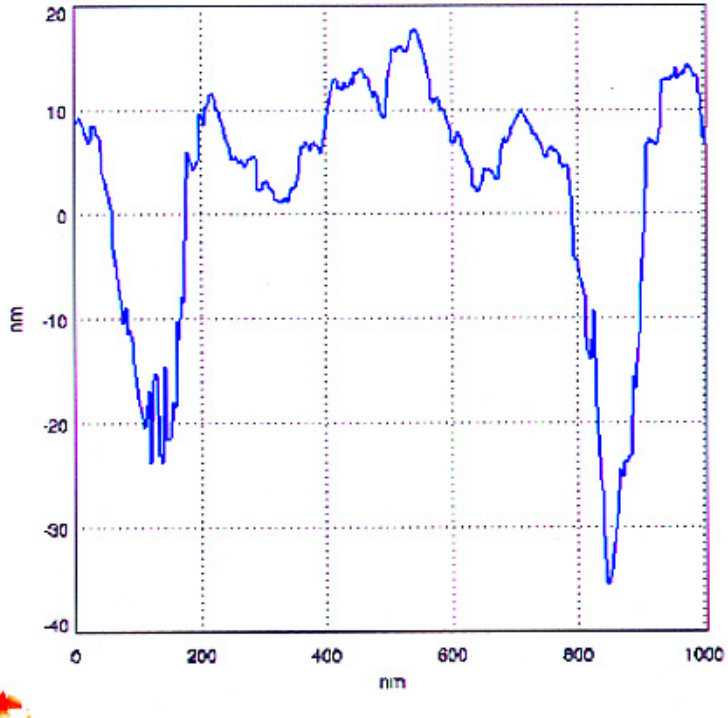


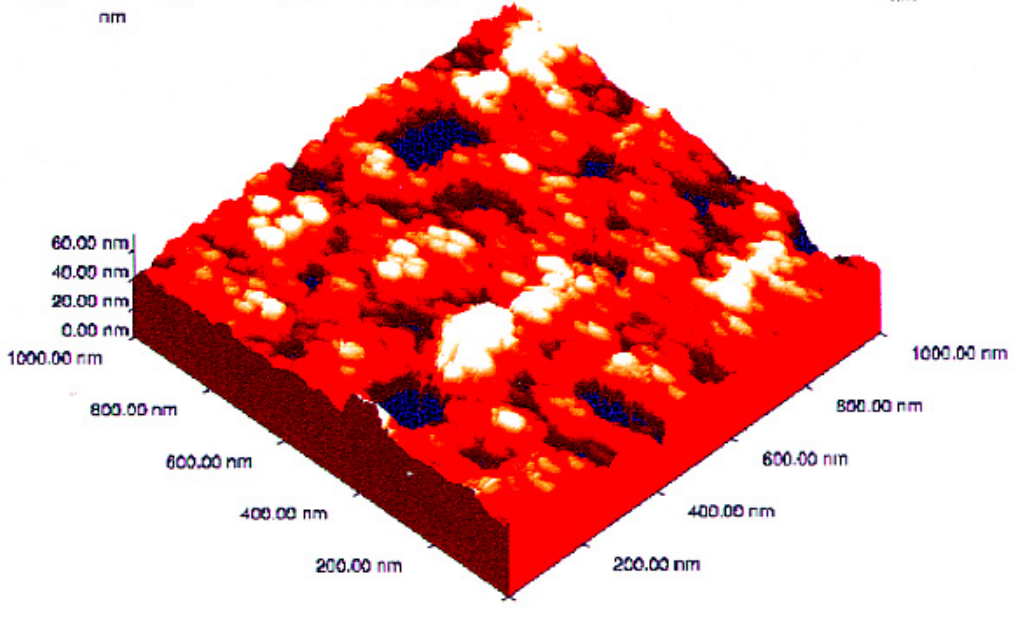
750°C



850°C





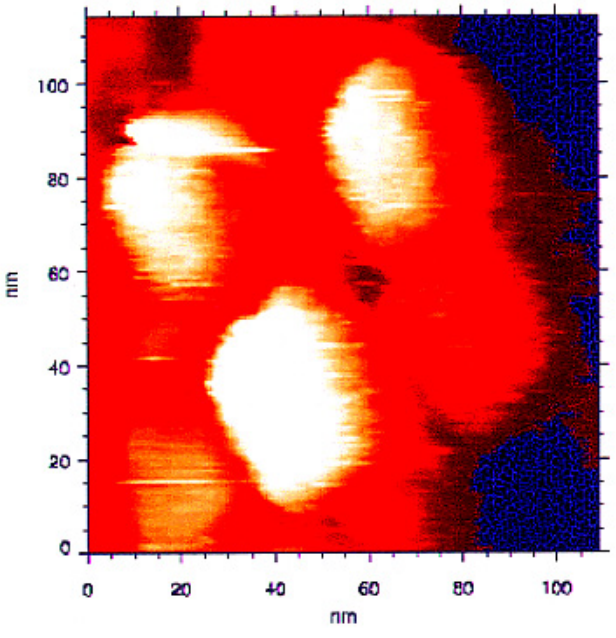


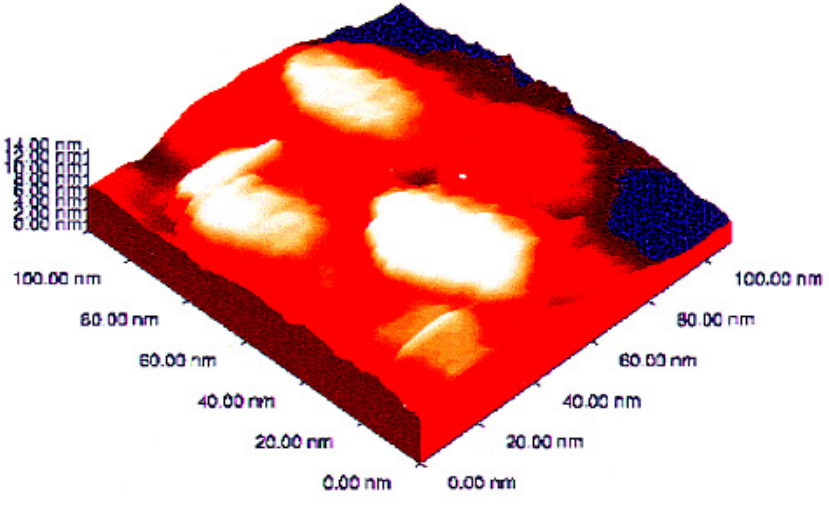
C_2H_2/Si(001)

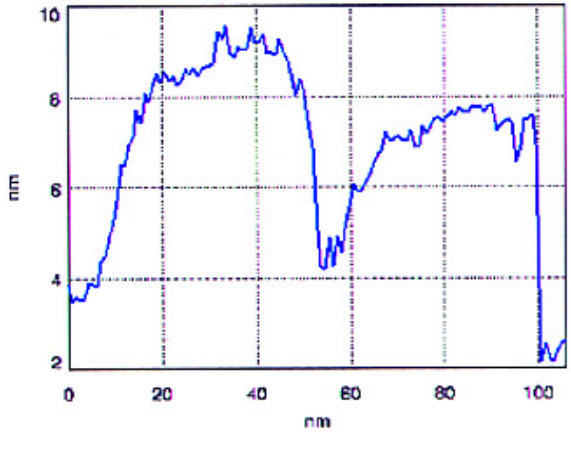
T=650°C

P=10^{-6} torr

t=10 min







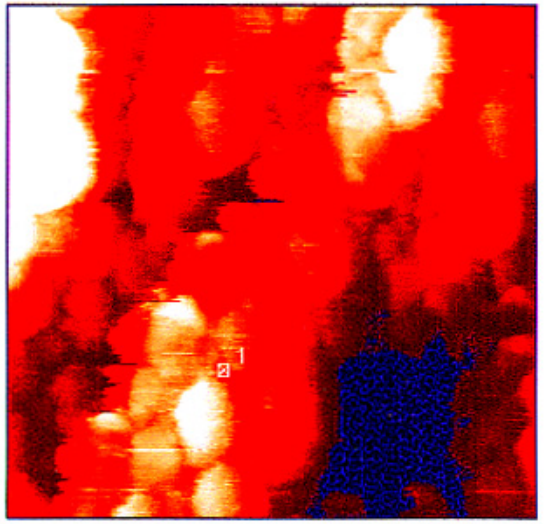
C_2H_2/Si(001)

T=650°C

P=10^{-6} torr

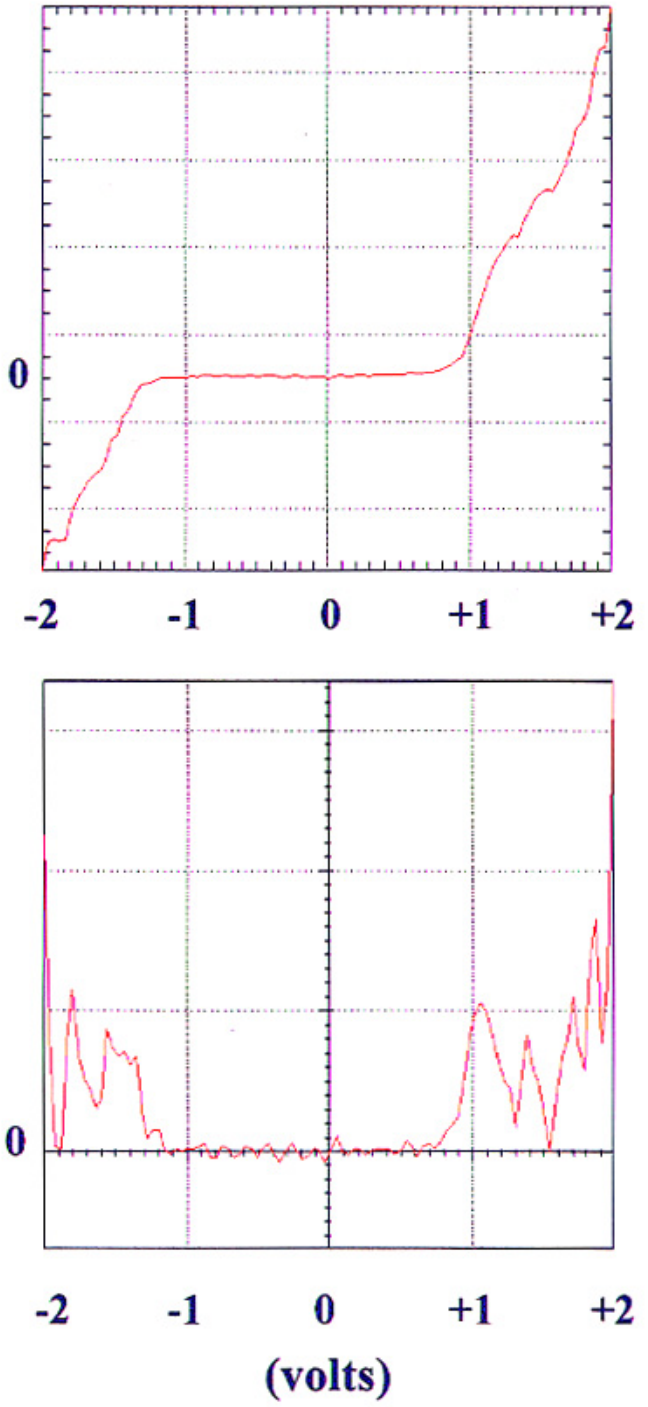
t=10 min

I-V spectroscopy



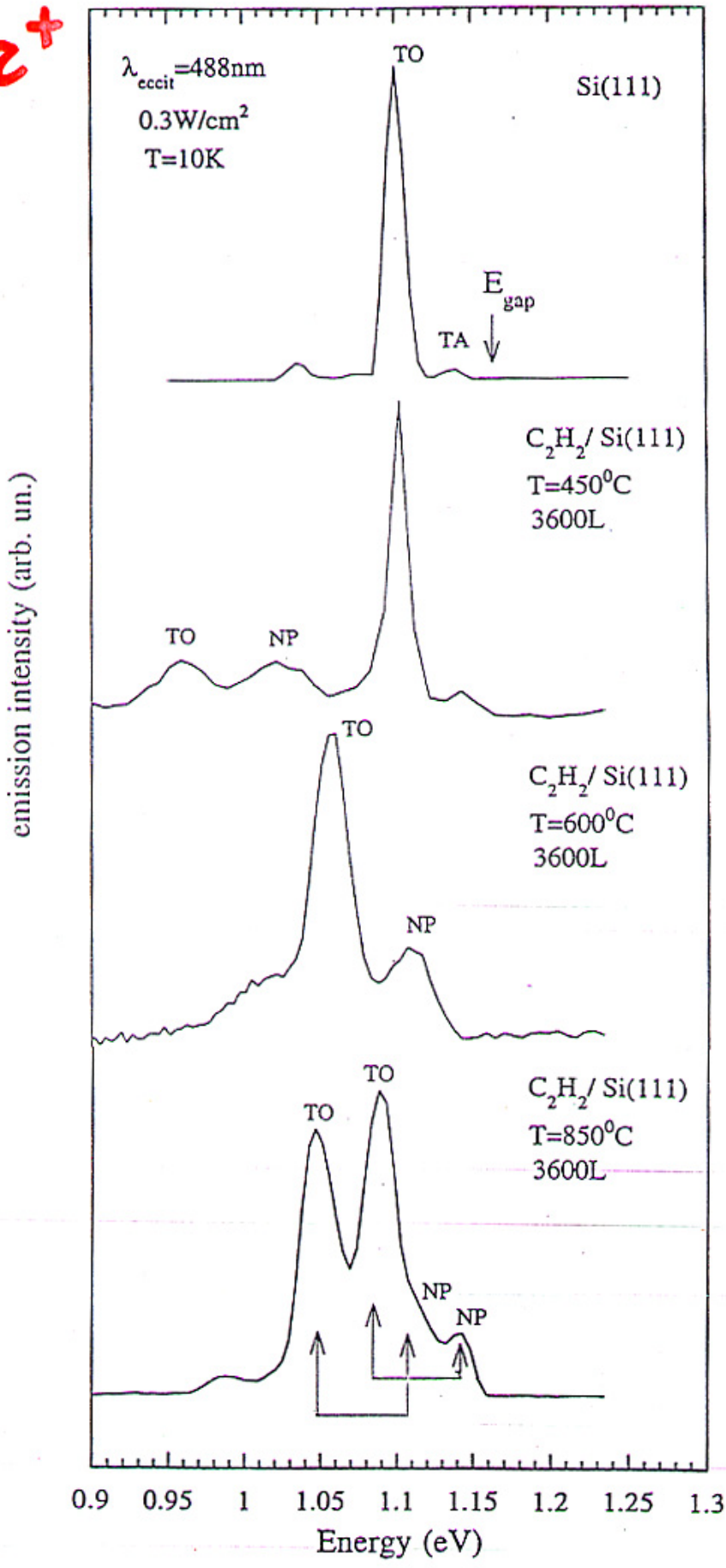
$C_2H_2/Si(001)$

T = 650 °C
P = 10^{-6} torr
t = 10 min



LUMINESCENCE

Ar^+



$Si_{(1-x)}C_x$

$C = 2.5\%$

$C = 1.5\%$

$C_1 = 1.5\%$

$C_2 = 1.0\%$

K. Brunner, K. Eberl and W. Winter, PRL 76, 303 (1996)

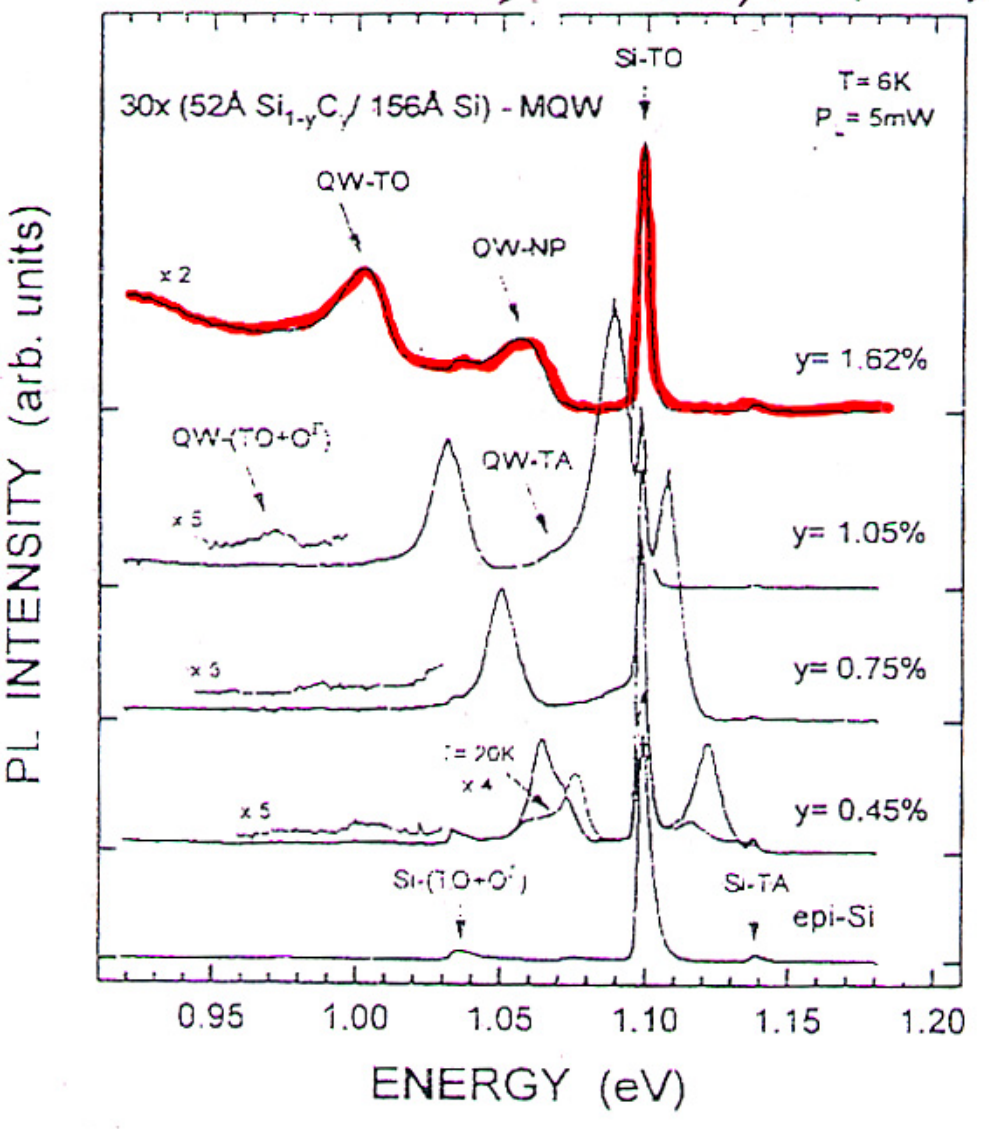
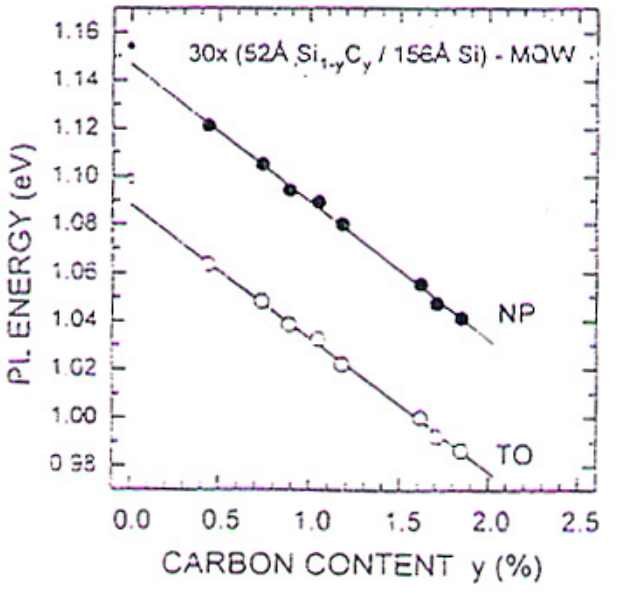
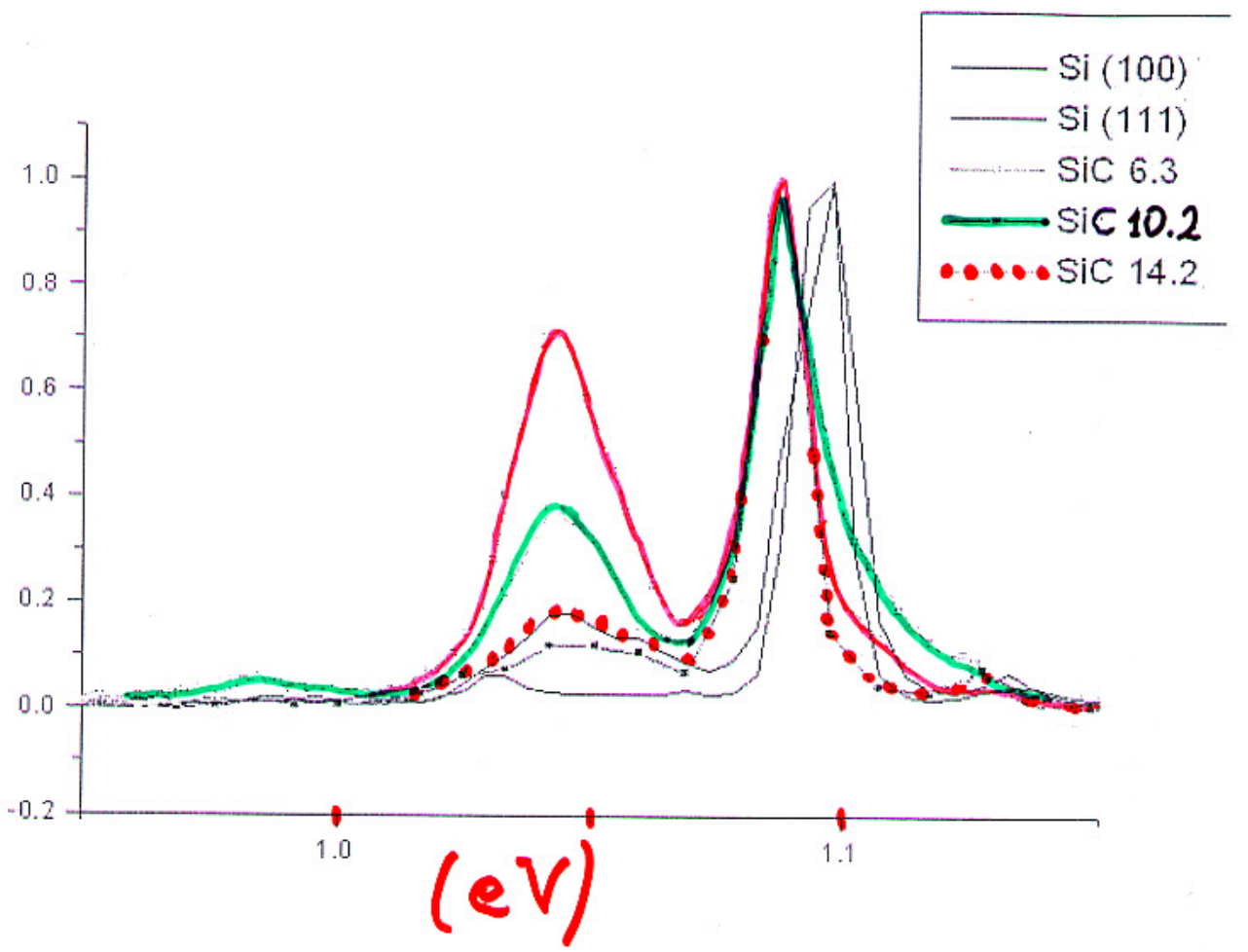


FIG. 2. PL spectra of 52 Å $Si_{1-y}C_y$/156 Å Si MQW structures with different C content y. The samples were excited by a 476 nm Kr^+ laser beam at $T = 6$ K.




Si (100)
Si (111)
SiC 6.3
SiC 10.2
SiC 14.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
1.0
1.1
(eV)

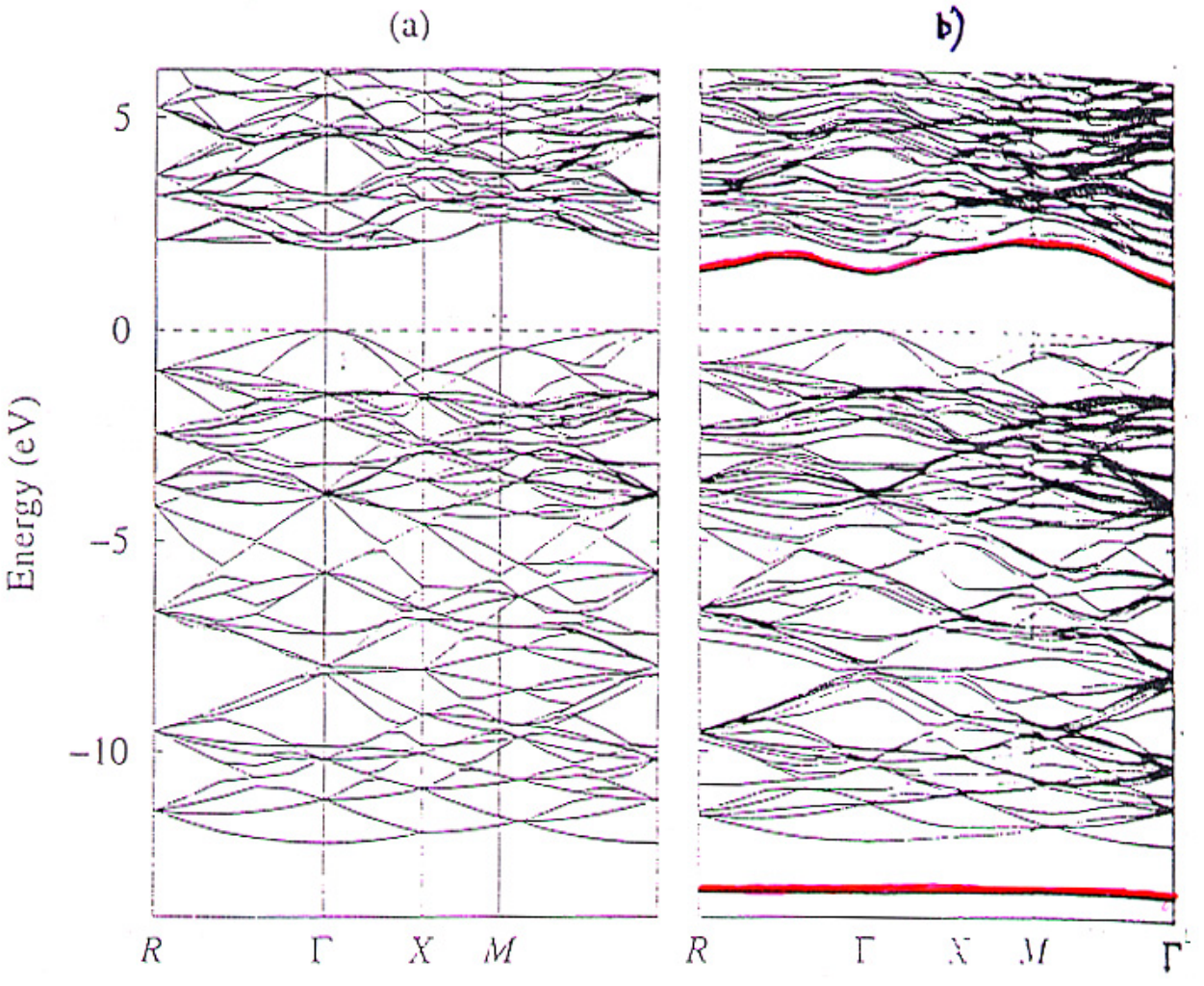
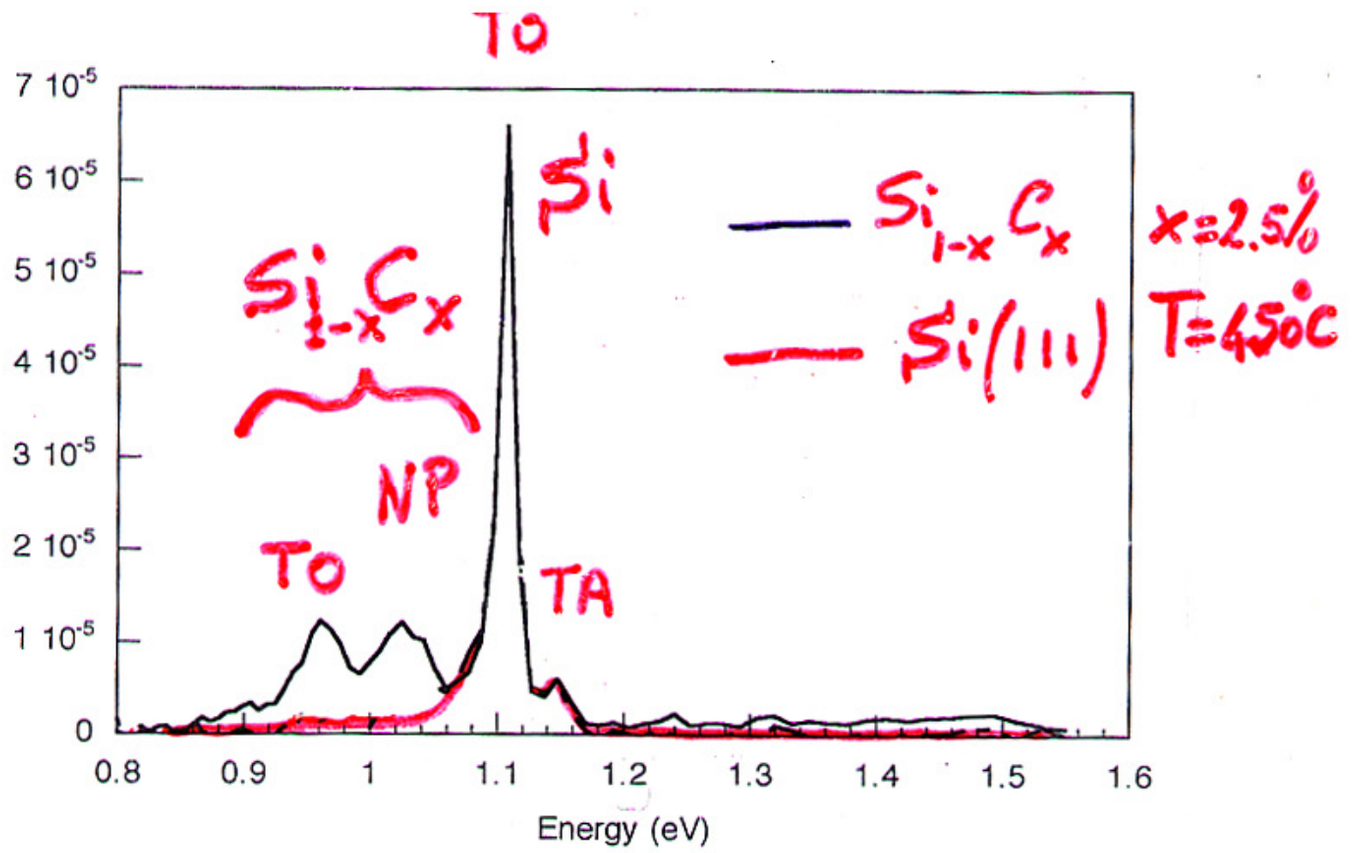
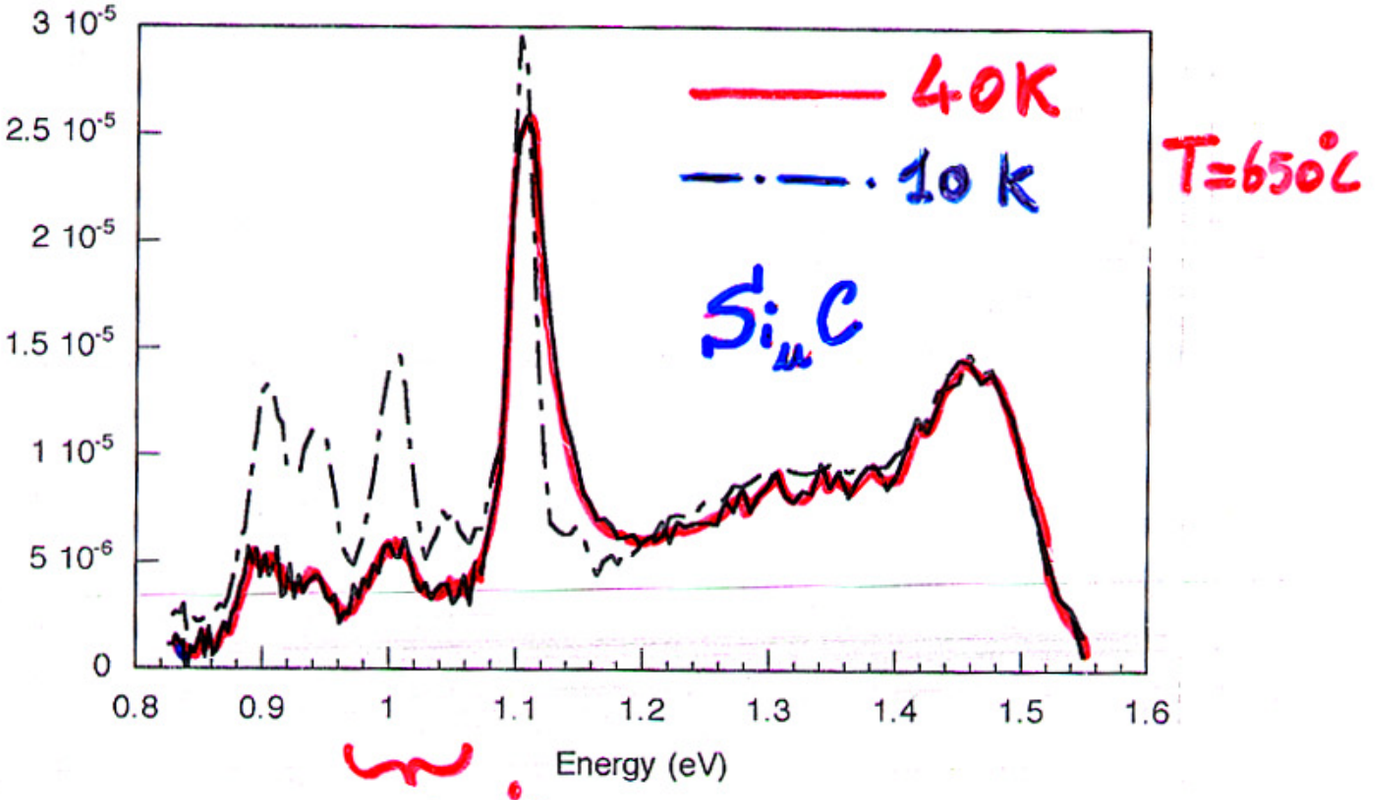


FIG. 4. Theoretical band structure of (a) Si_{64} and (b) $Si_{63}C_1$. Because of the use of a supercell, the band structure for pure Si is folded with the conduction-band minimum—which is close to the X point of the primitive BZ—being folded back to approximately the Γ point. The thick lines denote the deep and hyperdeep band of the $Si_{63}C_1$ system. The deep band is within the gap region of pure silicon which results in a smaller gap for $Si_{63}C_1$.

– W. Windl, O.F. Sankey, J. Menendez
Phys. Rev. B 57, 2431 (1998)


TO
7 10-5
6 10-5
5 10-5
4 10-5
3 10-5
2 10-5
1 10-5
0
0.8
0.9
1
1.1
1.2
1.3
1.4
1.5
1.6
Energy (eV)
Si
Si1-xCx
NP
TO
TA
Si1-xCx
Si(111)
x=2.5%
T=450°C


3 10-5
2.5 10-5
2 10-5
1.5 10-5
1 10-5
5 10-6
0
0.8
0.9
1
1.1
1.2
1.3
1.4
1.5
1.6
Energy (eV)
4.0K
10 K
SiμC
T=650°C
x=2.0%
x=3.7%

A. Demkov and O. Sankey, Phys. Rev. B48, 2207(93)

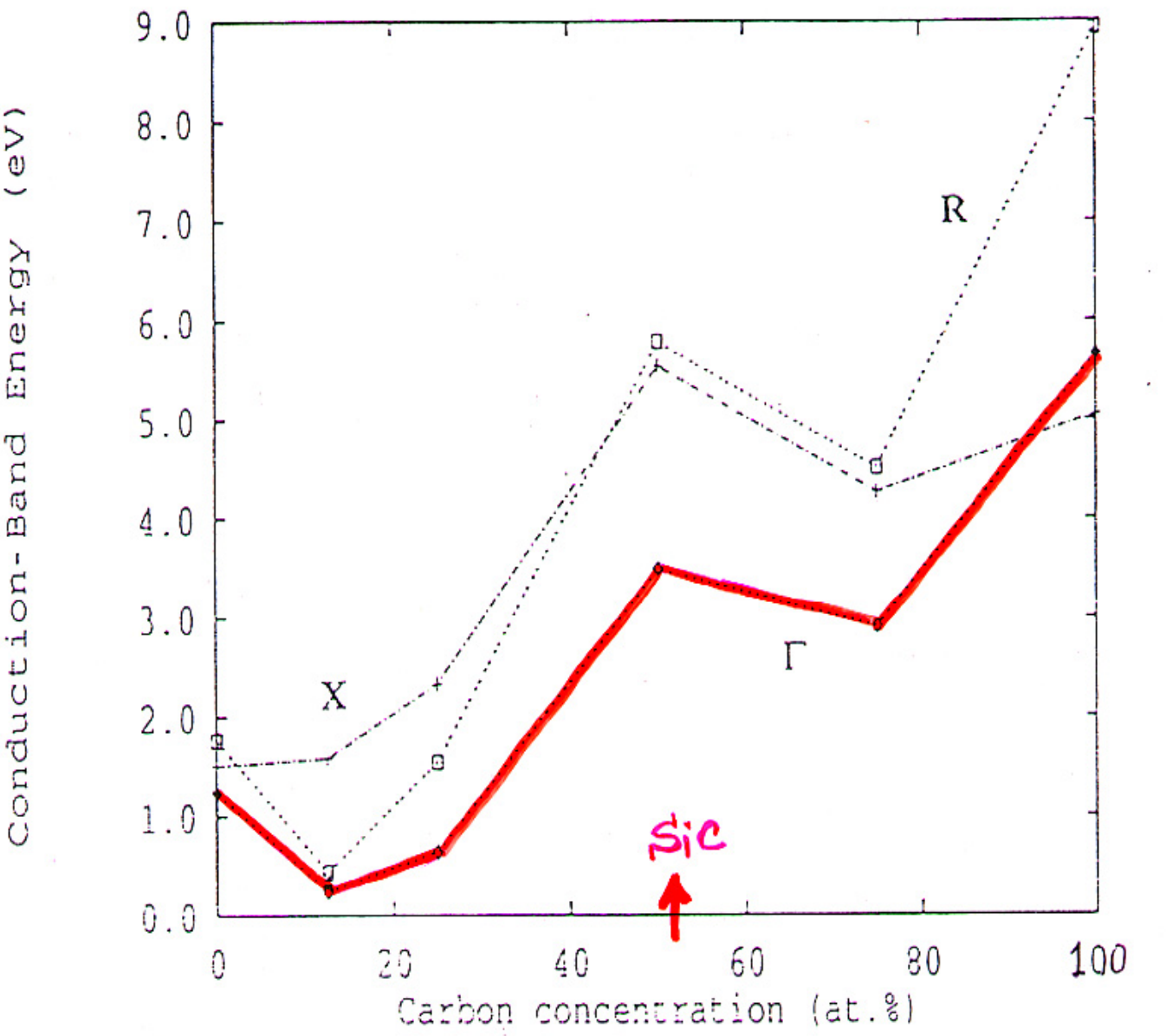


FIG. 1 . Conduction-band eigenenergies at the Γ, *R*, and *X* points of the Brillouin zone vs carbon concentration computed for 8-atom cells using the plane-wave method and the Harris energy functional. All cells are unrelaxed (perfect tetrahedral bonding) with a lattice constant determined by Vegard's rule.

Conclusions

- The carbonization process of a Si(111) and Si(100) clean surfaces exposed to acetylene molecules has benn investigated by several UHV techniques, including STM, to follow the surface reaction and chemisorption as a function of different doses and temperatures of the substrates.

- C_2H_2 chemisorbs at RT on Si(111) surface forming an ordered arrangement with adatoms and restatoms of the 7x7 reconstruction.

- We found that the best growth condition occurs at very low temperature (around 600-650°C) exposing the substrate to 10^{-5} Torr of C_2H_2 for the Si(111) surface orientation. In this case, LEED patterns are good and the STM images show the presence of flat, large nanostructures of about 150 nm. Besides, the study of the Carbon CVV lineshape, of the near carbon K-edge EELS profile and the EELFS features clearly indicate the formation of a single 3c-SiC phase.

- Conversely, for the Si(100) substrate no LEED images have been observed and the STM images show large volcanoes-shaped holes due to the interaction of silicon atoms with acetylene giving rise to the SiC compound. The resulting SiC layer appears fully nanostructured and formed by agglomerated bubbles whose medium size has been found to be in the range of 2.5-4.0 nm.

- Infrared photoluminescence spectra evidence of the formation of a $Si_{(1-x)}\ C_{(x)}$ alloy with x of about 1%

- The exposure to acetylene is an highly efficient method to change in a continuous way the near-infrared optical properties of clean silicon surfaces in the spectral range 0.8-1.5 eV.