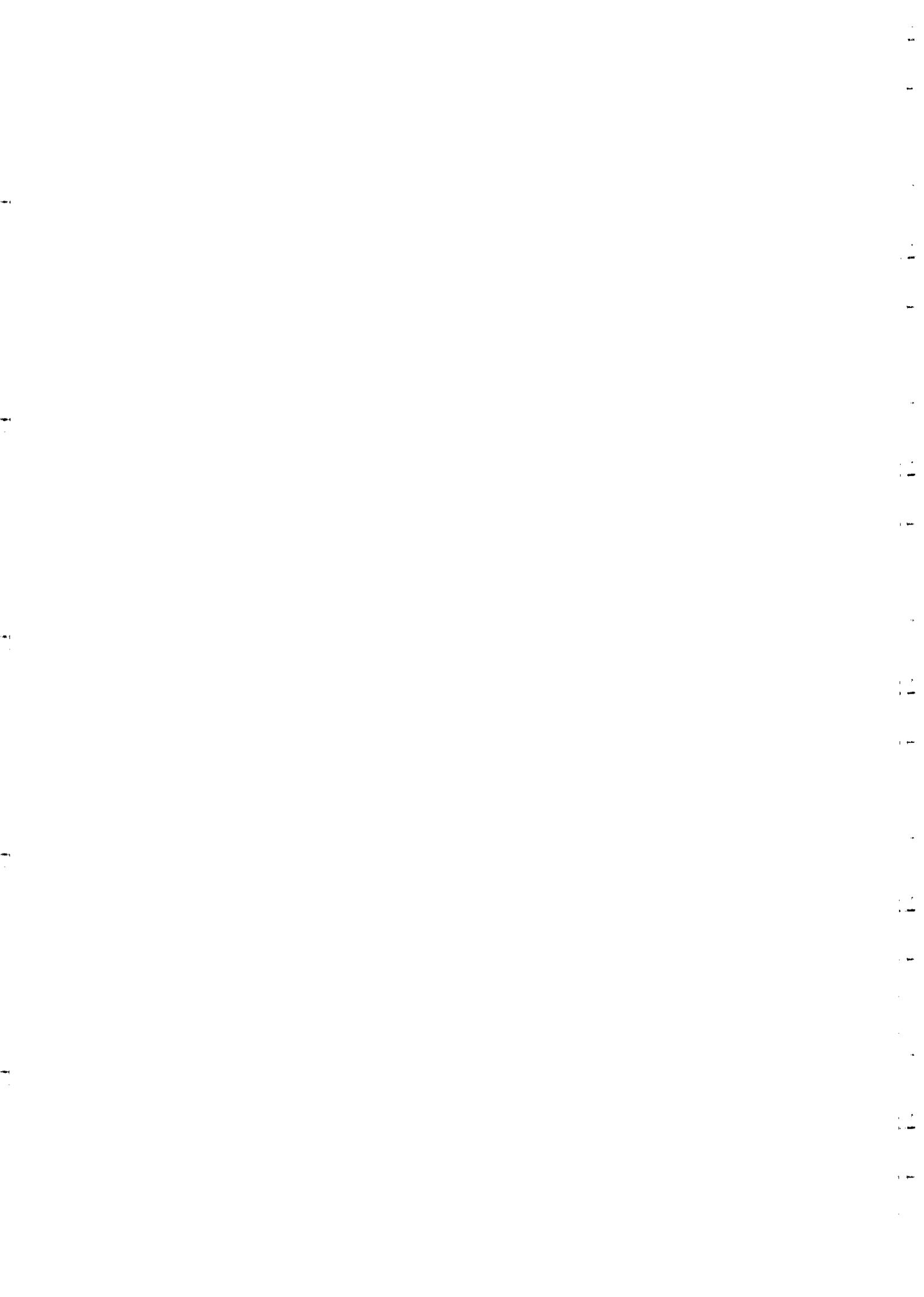


**THIRD WORKSHOP ON
THIN FILMS PHYSICS AND TECHNOLOGY
(8 - 24 MARCH 1999)
including
TOPICAL CONFERENCE ON
MICROSTRUCTURE AND SURFACE MORPHOLOGY
EVOLUTION IN THIN FILMS
(24 - 26 MARCH 1999)**

"Thin film growth by supersonic seeded beams"

**Salvatore IANNOTTA
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Via Sommarive, 18
38050 Povo di Trento
ITALY**



Thin Films Growth From Seeded Supersonic Beams

Salvatore Iannotta



**C.N.R./I.T.C. Research Center
on the Physics of Aggregates
Povo di Trento - ITALY**

(Research Center on the Physics of Aggregates)

- **Gas-Surface Dynamics Dept:**
 - **Senior Researchers:** -S. Iannotta -A. Boschetti
 - **Researchers and Fellowships:** -G. Ciullo -F. Biasioli - M. van Opbergen - T. Toccoli - M. Moratti -M. Malacarne
 - **Technicians:** C. Corradi - M. Mazzola
- *Collaboration with:*
 - **Physics Dept. University of Milan (P. Milani - A. Podestà - P. Piseri -E. Barborini)**
 - **University of Nijmegen (- J. Reuss -A. Parker)**
 - **Max Planck Institute Göttingen (H.G. Rubhan)**
 - **ICM - CNR Milano (W. Porzio)**
 - **University of Aveiro (A. Kharlamov)**
 - **PF MADESSII: ISM - CNR Trieste (M. Pedio), TASC - INFN Trieste (M. Sancrotti), Univ. ROMA III (F. Evangelisti, M. Deseta)**
 - **PF MAT II: TEMPE-CNR - Lecco (A. Tuissi), LAMEL-CNR**

- **Aims**
- **Nozzle versus Knudsen Beams**
 - *Basic Properties*
- **Hyperthermal Seedable Beams of Fullerene**
 - *Synthesis of SiC on Si(111)7x7*
- **PAGACS Source for Refractory Materials**
 - *Growth of SMA films (TiNi)*
- **Seeded Beams of Oligo-Polymers**
 - *Preparation of High Quality Thin Films of Oligo-Thiophenes*

- **High Quality Thin Films by Controlling Precursors by the Beam Parameters:**
 - Kinetic Energy and Momentum
 - State of Aggregation (Clustering)
 - Internal Energy
 - Flux on a large range (up to 10^3 Times than in Knudsen cells)
- **Synthesis of Nanocrystalline Films from Controlled Nanoparticles Building Blocks**
 - Fundamental and Technological Relevance
- **Control Crystalline or Amorphous Character of the Films from the Initial State of the Particles in the Beam**
 - ↳ **Characterization of the Beam**
 - ↳ **Correlation between the properties of the precursors in the beam and of the films**

Supersonic Free Jets ↔ Classical (Knudsen)



λ = mean free path
 d = nozzle diameter
 K_n = Knudsen Number
 h_0 = enthalpy per unit mass
 $\gamma = C_p/C_v$
 $M = \text{Mach Number} = v/V_s$

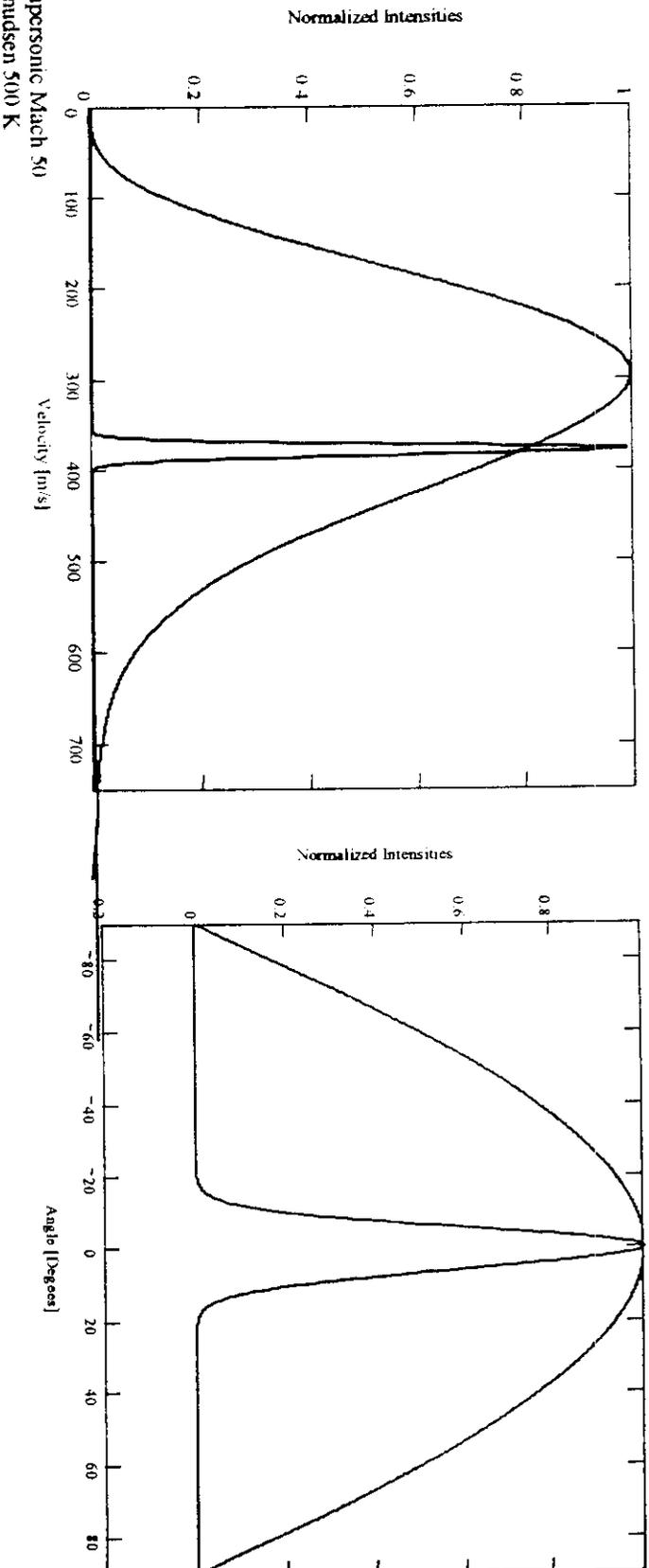
- $K_n = \lambda/d < 1 \iff$ gas is under-expanded
 \iff a large number of collisions still occur
- $T_f \ll T_0 \iff$ Isoentropic Expansion
 $P_f \ll P_0 \iff$ Very High Gradients
 $h_0 = h + v^2/2 \iff v_f \gg v$
 supersonic flow
- $v_f = (2kT_0/m)^{1/2} (\gamma - 1)^{1/2} \quad M \gg 1$
- Narrow Velocity Spreads: $\Delta v/v \approx (2/\gamma)^{1/2}/M$
 $\Delta v/v \approx 1 \div 15 \%$
- Very high forward intensity
- Ro-vibrational cooling (non equilibrium)
- Clustering by constrained nozzles

- $K_n = \lambda/d > 1 \iff$ molecular effusion
 no collision afterwards
- $T_f \approx T_0$
- $v_f \approx v_0$
- Maxwellian velocity distribution
- Cosine-like angular intensity distribution
- No cooling (equilibrium with the oven)
- Clustering by external cooling and gas aggregation

Supersonic Free Jets Classical (Knudsen)

Velocity Distributions

Angular Distributions



$$I_{\text{nozzle}}(v_{\text{mp}}) / I_{\text{knudsen}} = n_{0(\text{nozzle})} f(M, \gamma) / n_{0(\text{Knudsen})} f(M, \gamma) \approx 8-10 \longrightarrow I_{\text{nozzle}}(v_{\text{mp}}) / I_{\text{knudsen}} \approx 10^2-10^3$$

Seeding in Light Gases

$$\Rightarrow E_i \approx (m_i / \langle m \rangle) T_0 \quad \langle m \rangle = \sum_i X_i m_i \quad \text{High dilution} \longrightarrow \text{Aerodynamic Acceleration}$$

example C_{60} in He: $E > 60 \text{ eV}$

Nozzle Sources

- **Vaporization Methods:**
 - Joule Heating
 - Plasma
 - Laser Vaporization
 - Glow and Arc Discharges
- **Regime of Operation:**
 - Continuous
 - Pulsed
- **Type of Nozzles**
 - Sonic (No aggregation)
 - Conical (Converging-Diverging)
 - Campargue



Clustering

Why Seeded (Aerodynamically Accelerated) Supersonic Molecular Beams (HSB) of Fullerenes?

- *Investigate Fullerenes Properties.*
- *Direct Tool to Study Interactions with Atoms, Molecules and Surfaces.*
- *A Very Interesting Range of Kinetic Energies 1-60 eV:*
 - *Gas Surface Energy Transfer:*
 - *from adsorption-desorption to impulsive;*
 - *angular scattering and kinetic energy induced corrugation;*
 - *Molecular Vibrational Excitation:*
 - *important processes which couples directly to the dissociative reaction coordinates.*
 - *Hyper-thermal Surface Chemistry :*
 - *chemical processes in a non equilibrium regime;*
 - *chemistry with a "hammer": scattering from absorbers. One can promote chemisorption, dissociation, surface modifications etc...*
 - *kinetic energy induced chemisorption.*
- *Thin Films Synthesis*

SiC synthesis on Si: Limits and Goals

The Growth Process is Severely Limited by:

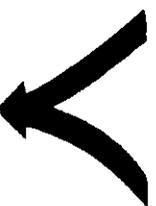
- ❑ *Large Mismatches in Lattice Constants (20%) and Thermal Expansion Coefficients (8%).*
- ❑ *Large Temperatures for the Synthesis (larger than 1000-1300°C) Using CVD and PECVD.*
- ❑ *Formation of Voids at the SiC/Si Interface.*



- ❑ *Control of the Different Steps of the Growth Process and of State and Density of Precursors.*

SiC from C₆₀ as Precursor

- ✿ *Lower Temperature for the Synthesis (850-950 °C).*
(A. V. Hamza et al., *Surf. Sci.* 317 (1994) L1129)
- ✿ *Vapor Pressure Well Controllable by Sublimation.*
- ✿ *Can be Used in Hyperthermal Supersonic Beams (HSB)*
(F. Biasioli et al., *Chem. Phys. Lett.* 270 (1997) 115)



*SiC Synthesis by
Kinetic Energy Activated
Processes*



Impact of Fullerene From Si and H-Si

(K. Beardmore and R. Smith, *Nim B 106 (1995) 74*)

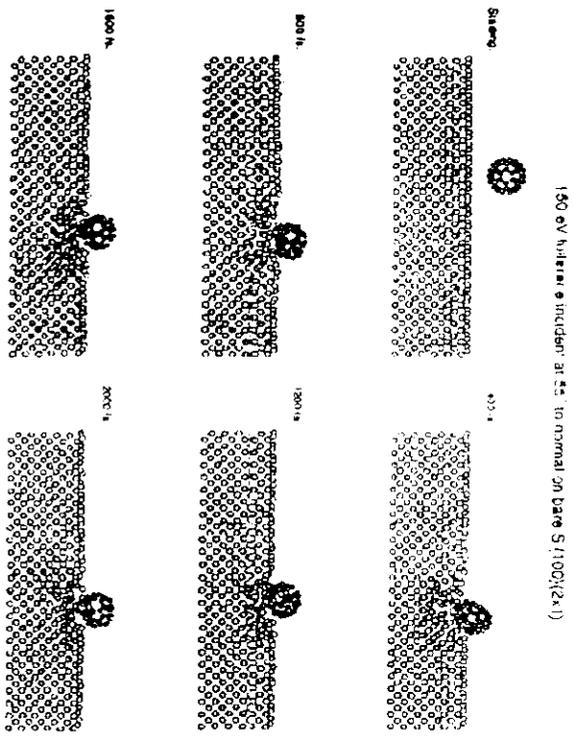


Fig. 2. Atomic positions for a 150 eV C₆₀ molecule incident at 55° to normal on bare Si(100) after various times: 0, 100, 200, and 300 fs. For clarity in Figs 2-4, the atomic positions of only a section of the lattice, 12 Å thick, centred around the impact point are drawn.

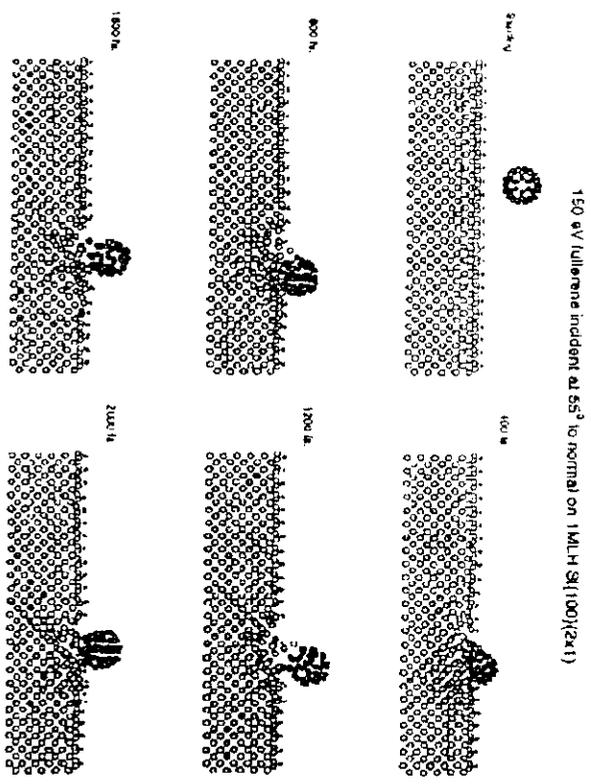
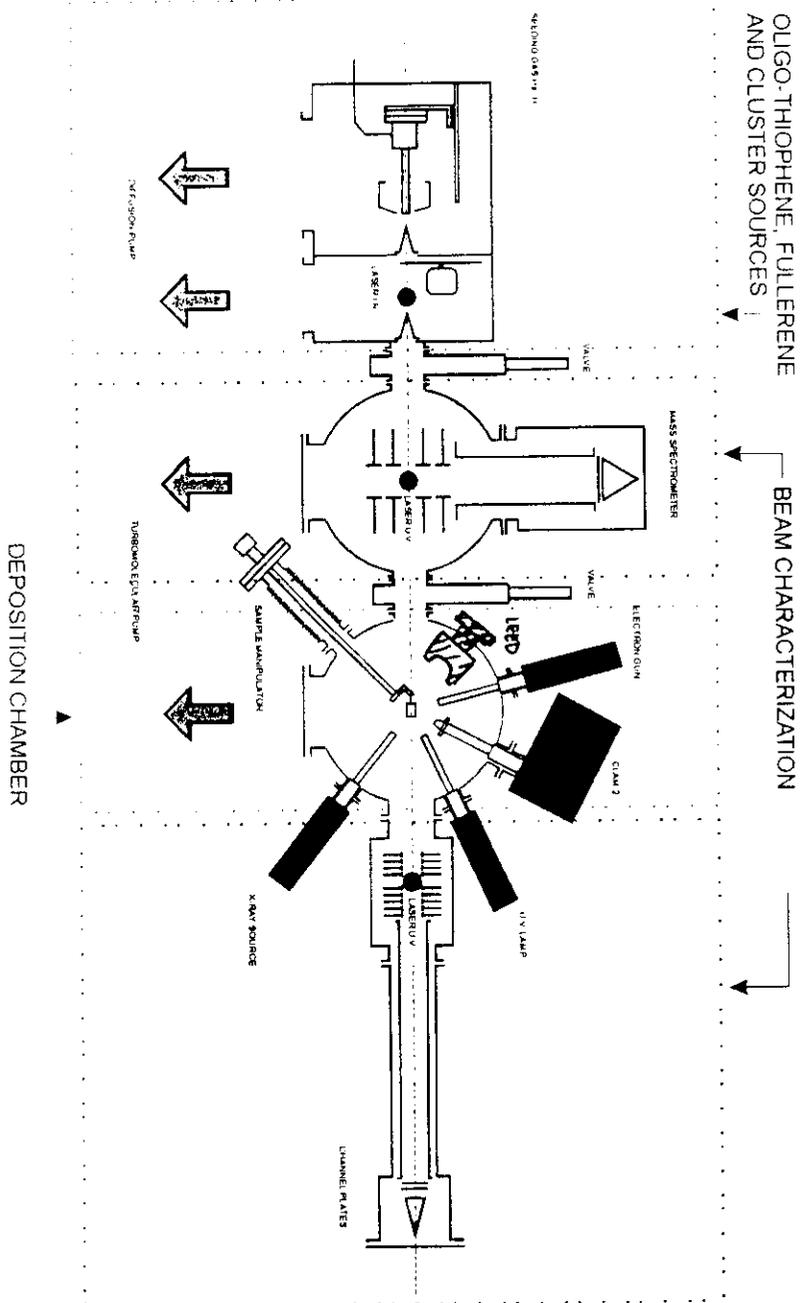
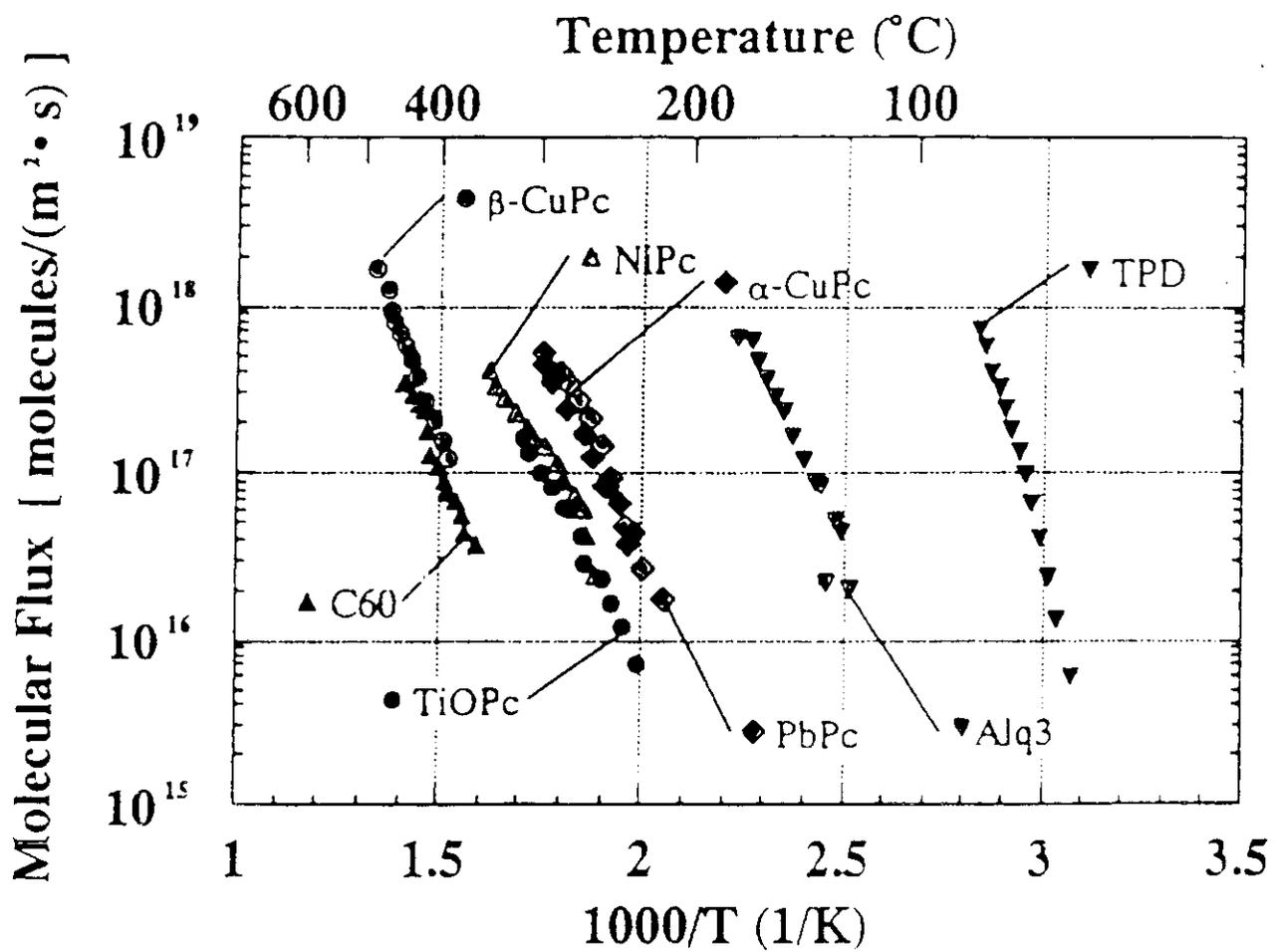


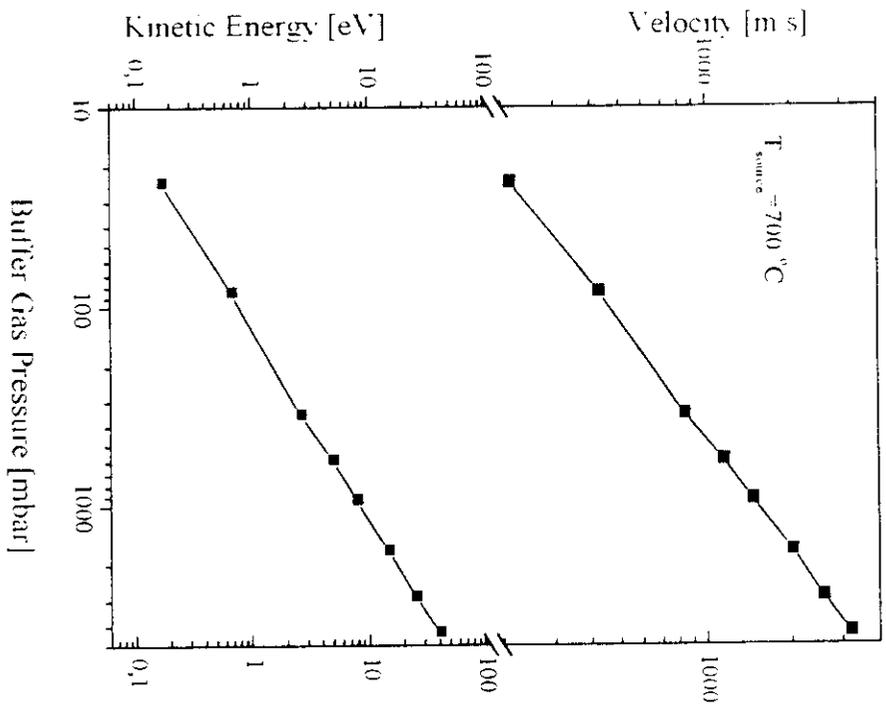
Fig. 3. Atomic positions for a 150 eV C₆₀ molecule incident at 55° to normal on 1MLH Si(100) after various times: 0, 100, 200, 300, 400, 800, 1200, 1600 and 2000 fs.







C_{60} Seeded in He - HSB





C_{60} Beam Characteristics

	Achievable	At Present
Nozzle Diameter	20-2000 μm	60-1500 μm
Seeding gas Pressure	10 Atm	2 Atm
Seeding Dilution	1:10000	1:2000
Energy range	1-60 eV	1-35 eV
Energy Spread	7%	\cong 15%
Intensity	10^{17} s^{-1}	10^{16} s^{-1}
Oven Temperature	>2000 K	1300 K

CHFS A



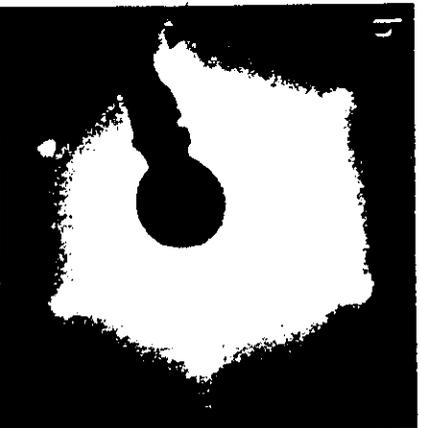
LEED Patterns (Carbonization Processes (C_{60} -Si (111) 7×7))

→ Clean Si(111) 7×7

■ SiC Epilayer (Grown on Si(111) 7×7 . In the following two ways

→ Thermal annealing (870-950 °C) of C_{60} absorbed on the clean surface.

→ Synthesis by Exposing the Hot Si (800 °C) to the C_{60} HSB



Si Spots

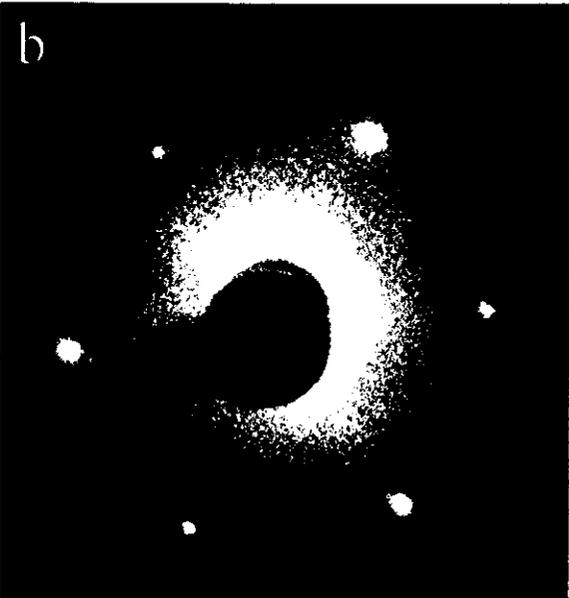
→ Further Growth of SiC by Exposing the Hot (800 °C) Carbided Surface to the C_{60} HSB



Si Spots



CLEAN Si (111) 7x7



SiC EPILAYER ON Si

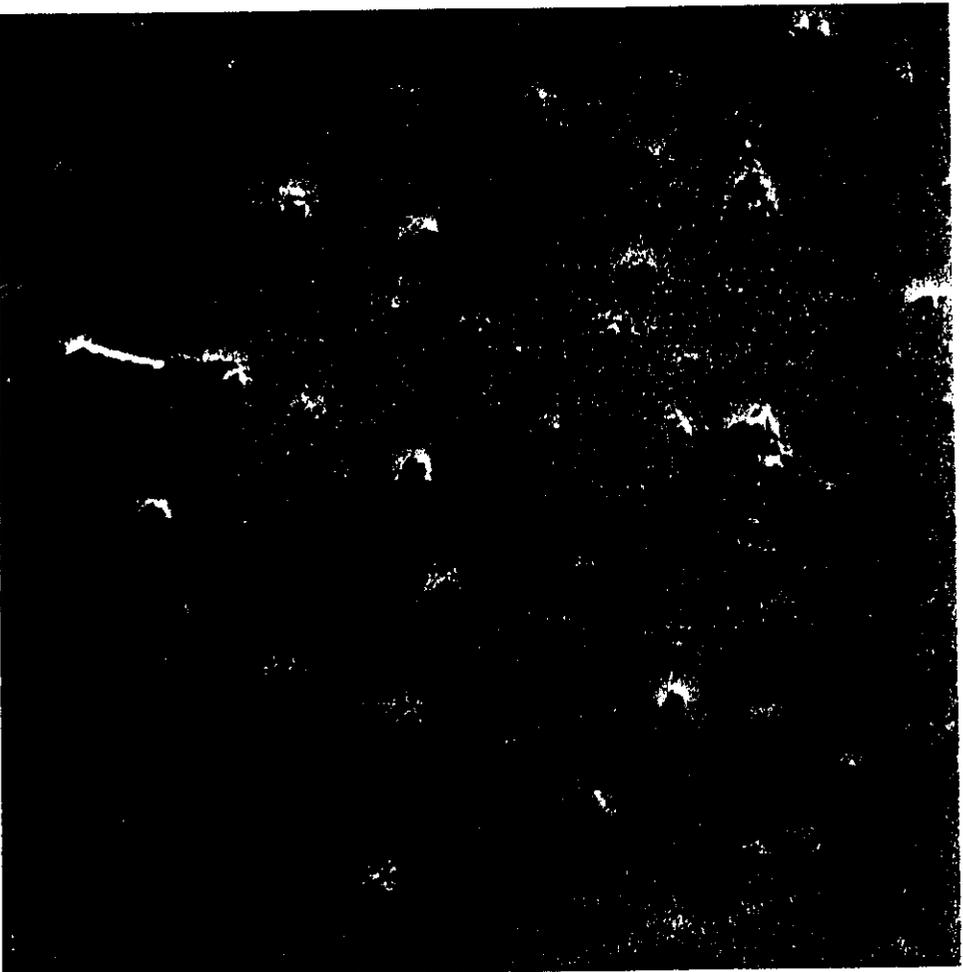
- GROWN BY THERMAL ANNEALING OF A C_{60} ADSORBED FILM ($870-950^{\circ}C$)
- GROWN BY EXPOSING THE HOT Si SURFACE ($800^{\circ}C$) TO THE HSB.



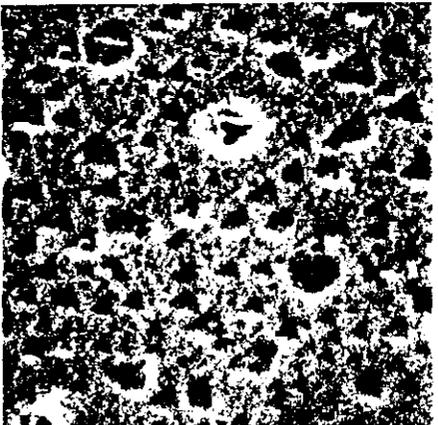
FURTHER GROWTH OF SiC BY EXPOSING THE HOT ($800^{\circ}C$) CARBIDIZED SURFACE



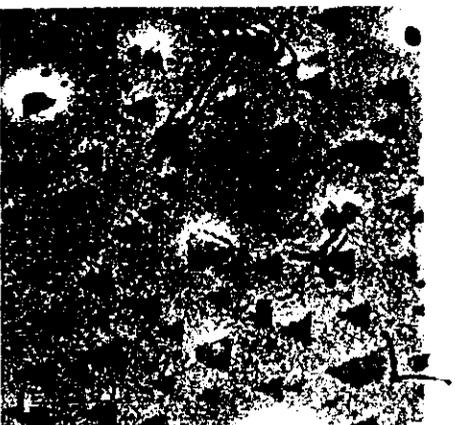
*Typical SEM Micrograph from SiC Directly
Synthesized By Direct Exposure To C₆₀ HSB*



SiC Morphologies at Different Growth Regimes



- High C_{60} Beam Fluxes
- Diffuse Shallow SiC LEED Spots

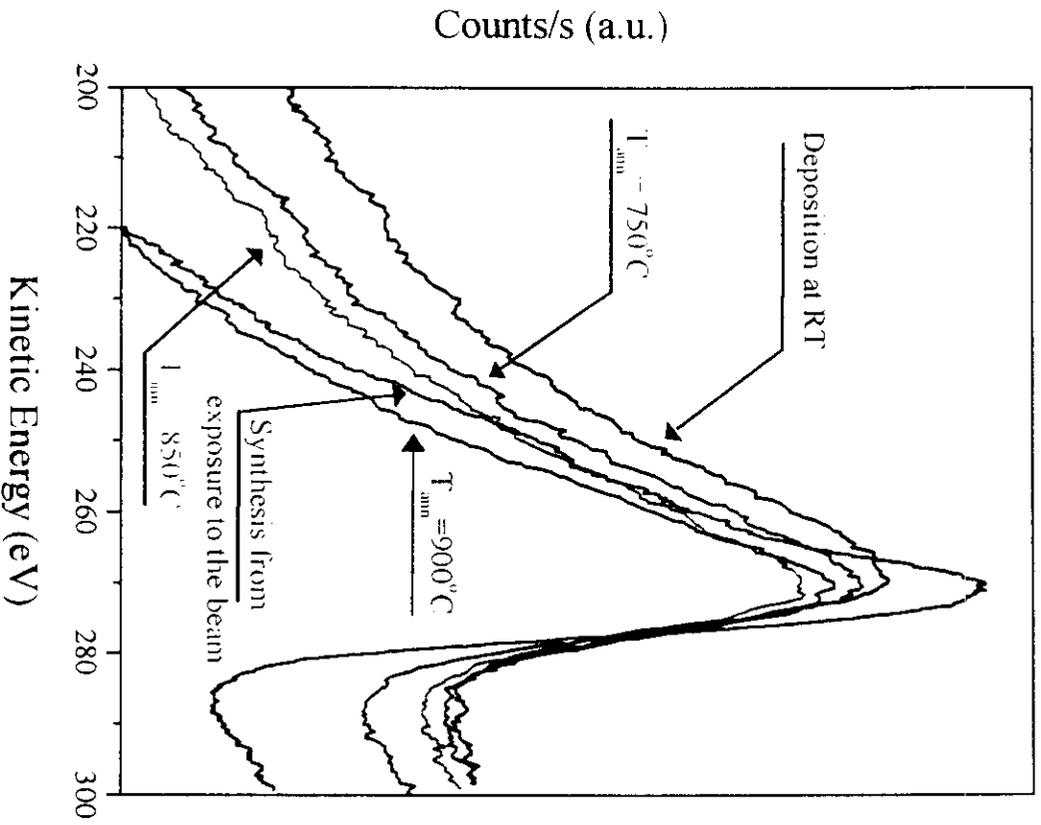


- Medium C_{60} Beam Fluxes
- SiC Sharper LEED Spots



- Low C_{60} Beam Fluxes
- Co-presence of Si and SiC Spots

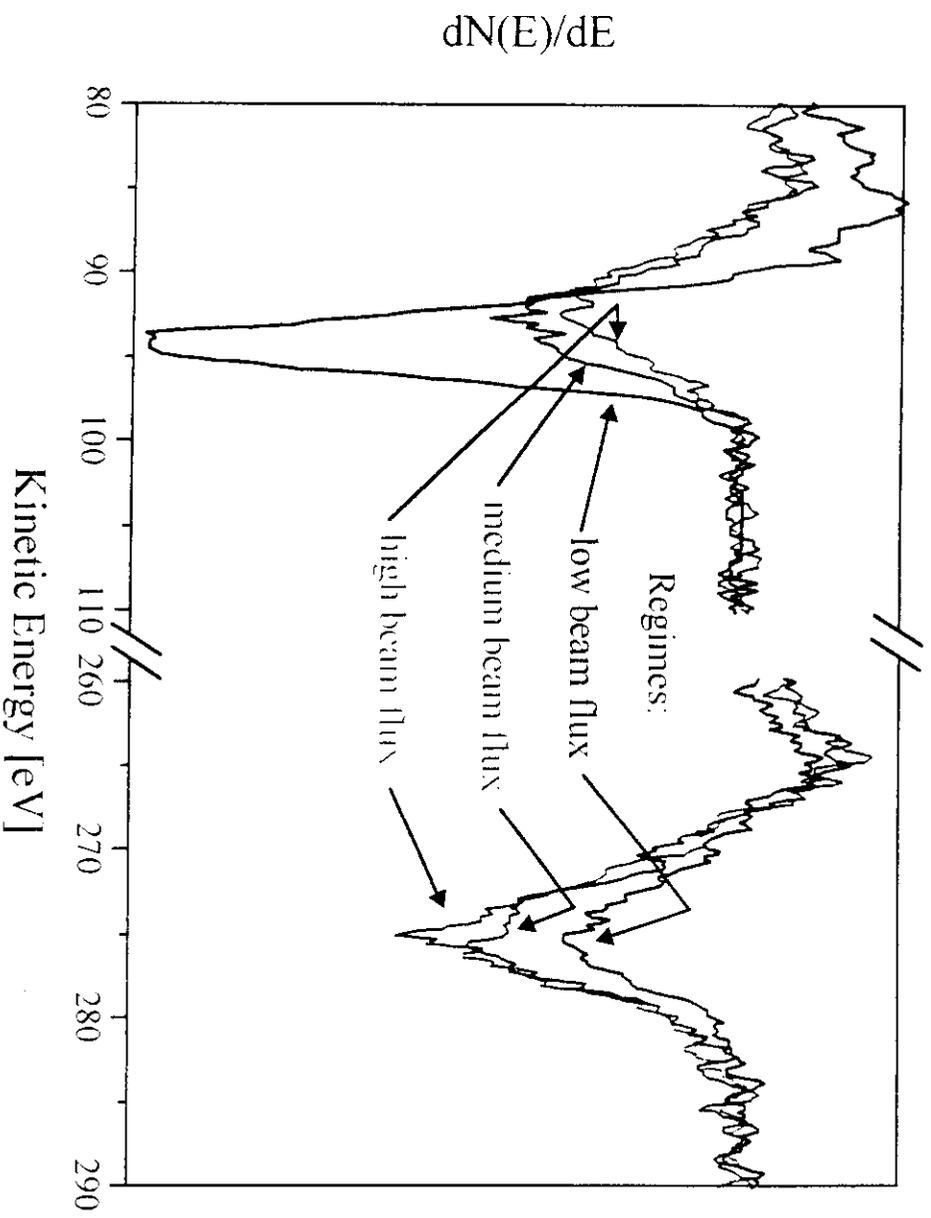
Carbonization Of SiC - Auger Lineshape of C-line

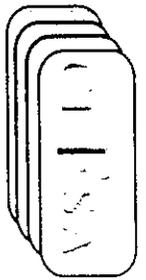




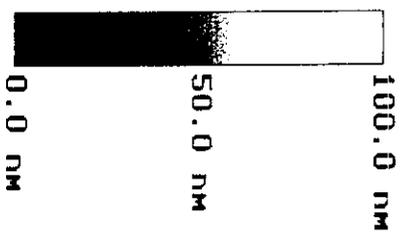
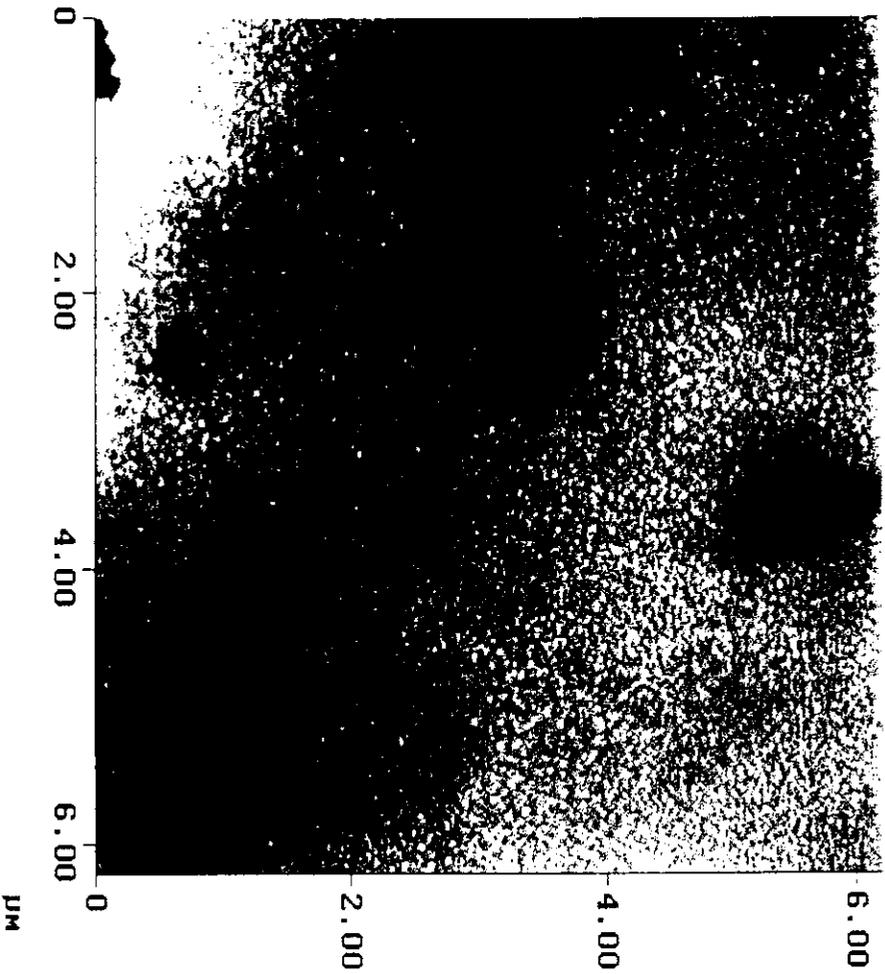
Carbonization Of SiC in Different Beam Regimes

- Auger Lineshape of Si and C





*AFM Image of SiC Synthesized from C₆₀ HSB -
Medium Flux*

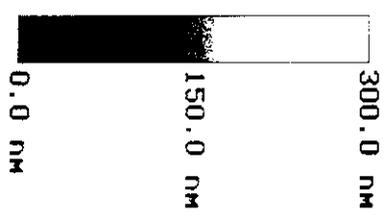
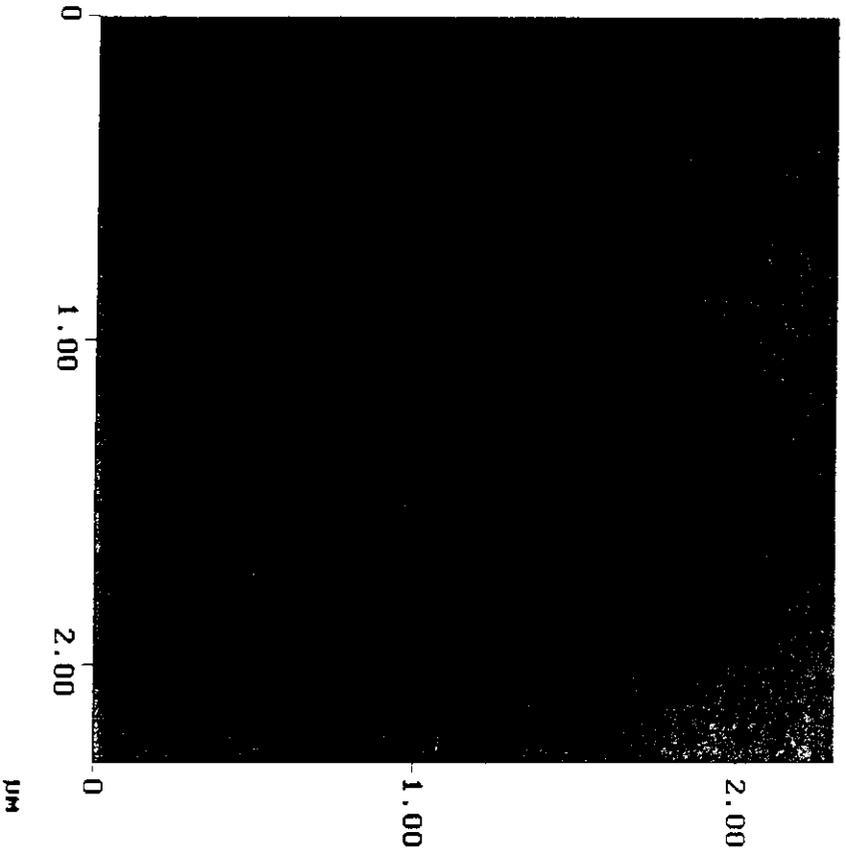


Digital Instruments NanoScope
Scan size 6.221 μm
Scan rate 2.497 Hz
Number of samples 512
Image Data Height
Data scale 100.0 nm

a_zona3.004



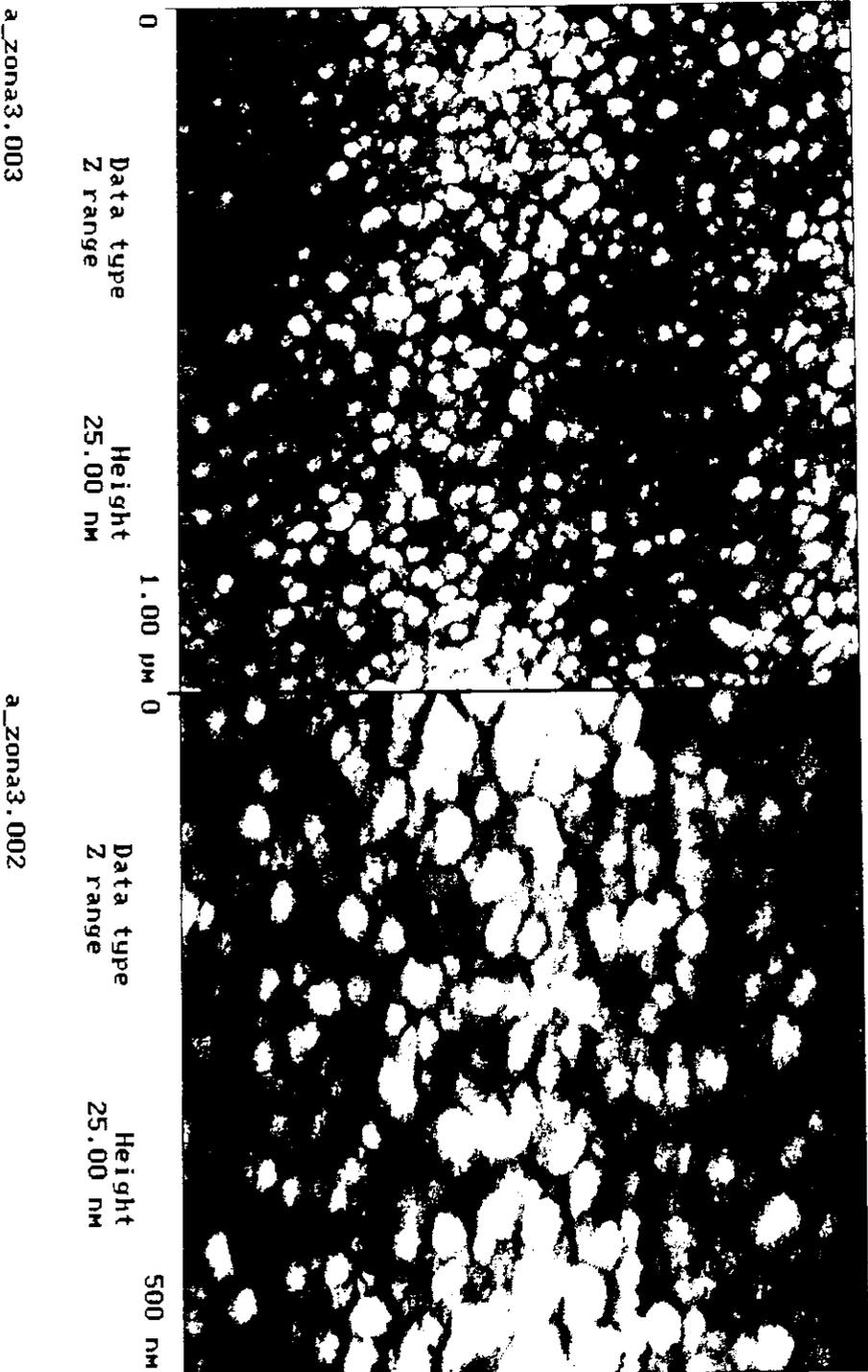
*AFM Image of SiC Synthesized from C_{60} /SSB
Medium Flux*



Digital Instruments NanoScope
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Scan rate 2.497 Hz
Number of samples 512
Image Data Height
Data scale 300.0 nm

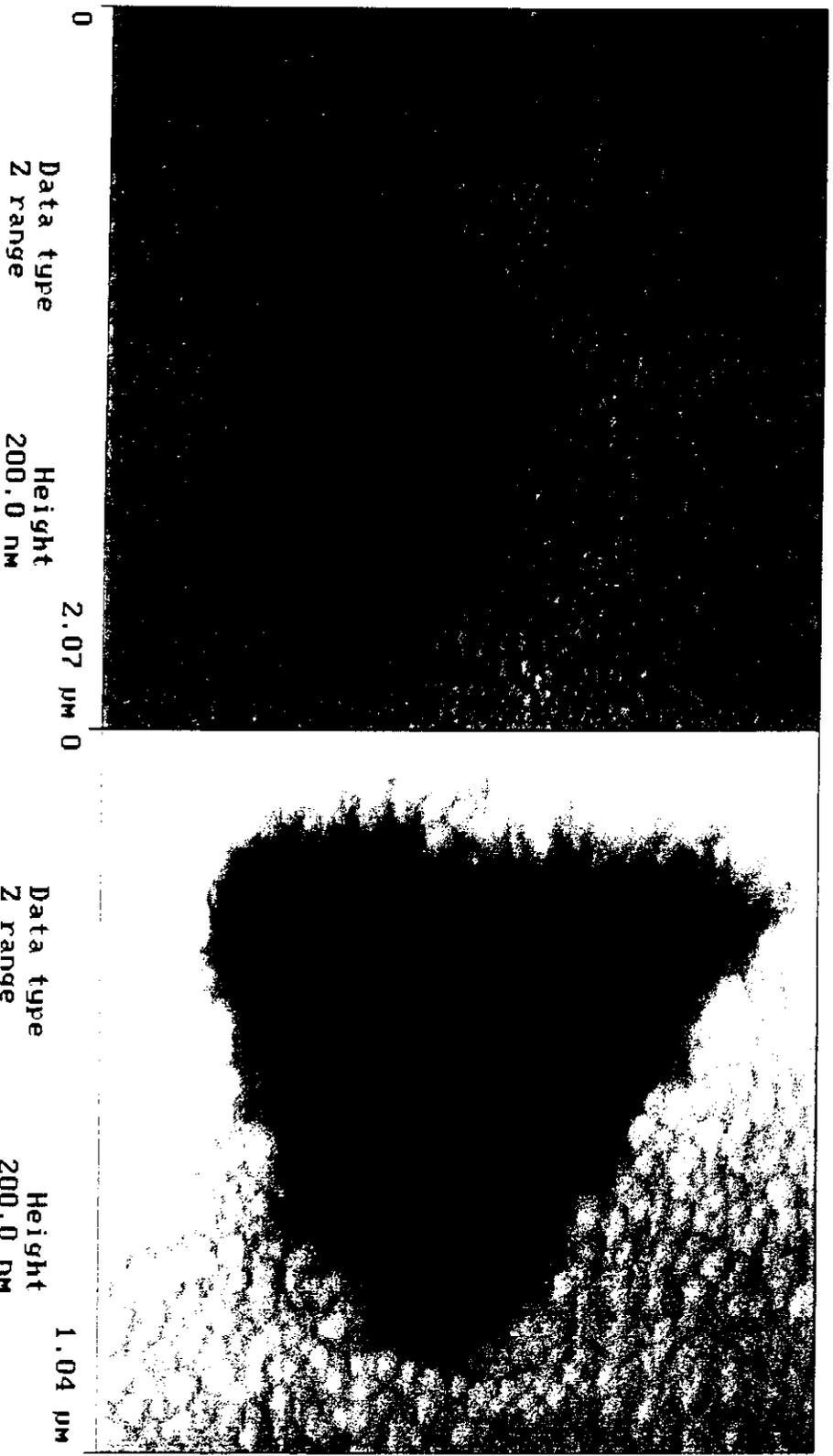


*AFM Image Of SiC Synthesized from C₆₀ / SSP
Medium Flux*





*AFM Image Of SiC Synthesized from CLMISA
Medium Flux*



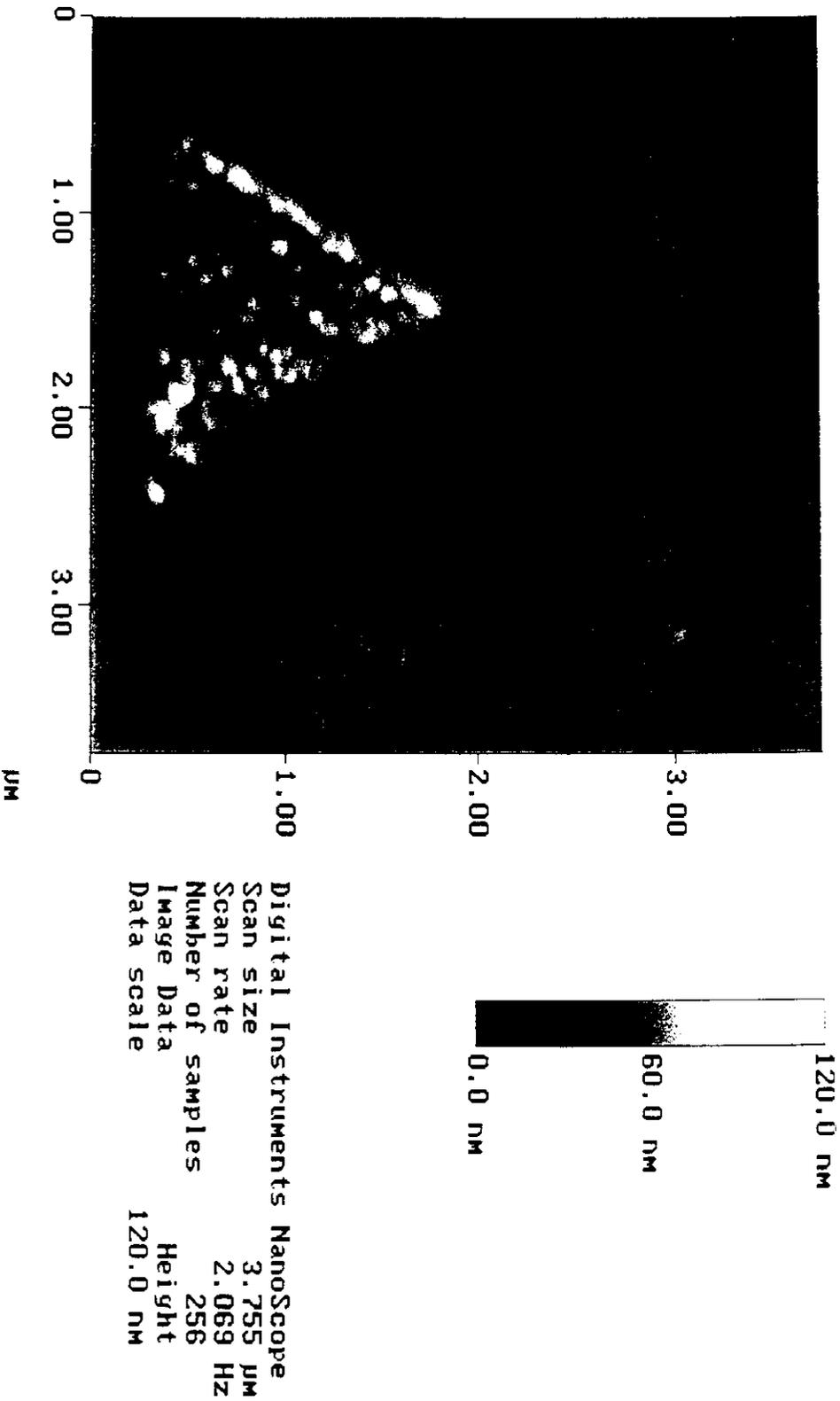
Trueste 99_22

a_zona3.005

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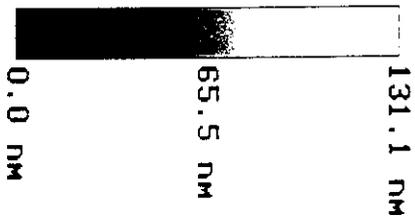
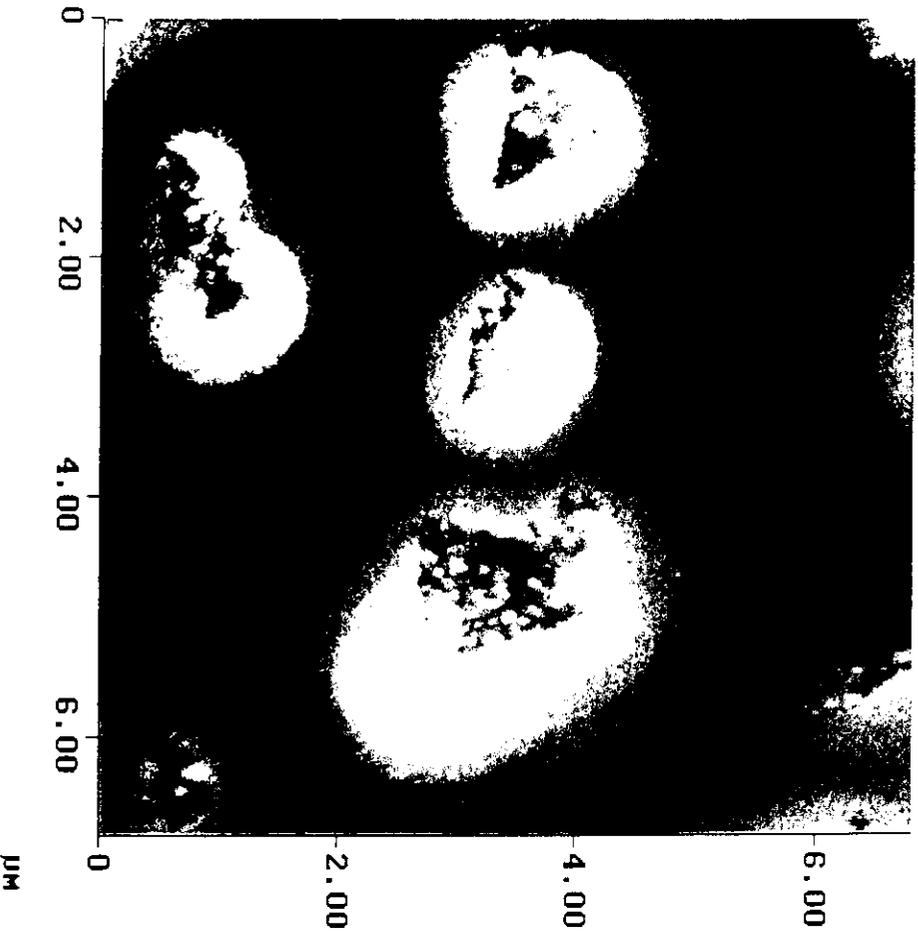


*AFM Image of SiC Synthesized from C₆₀ ISSB
Medium Flux*





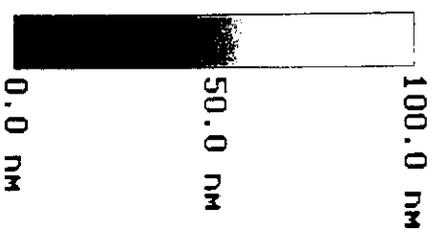
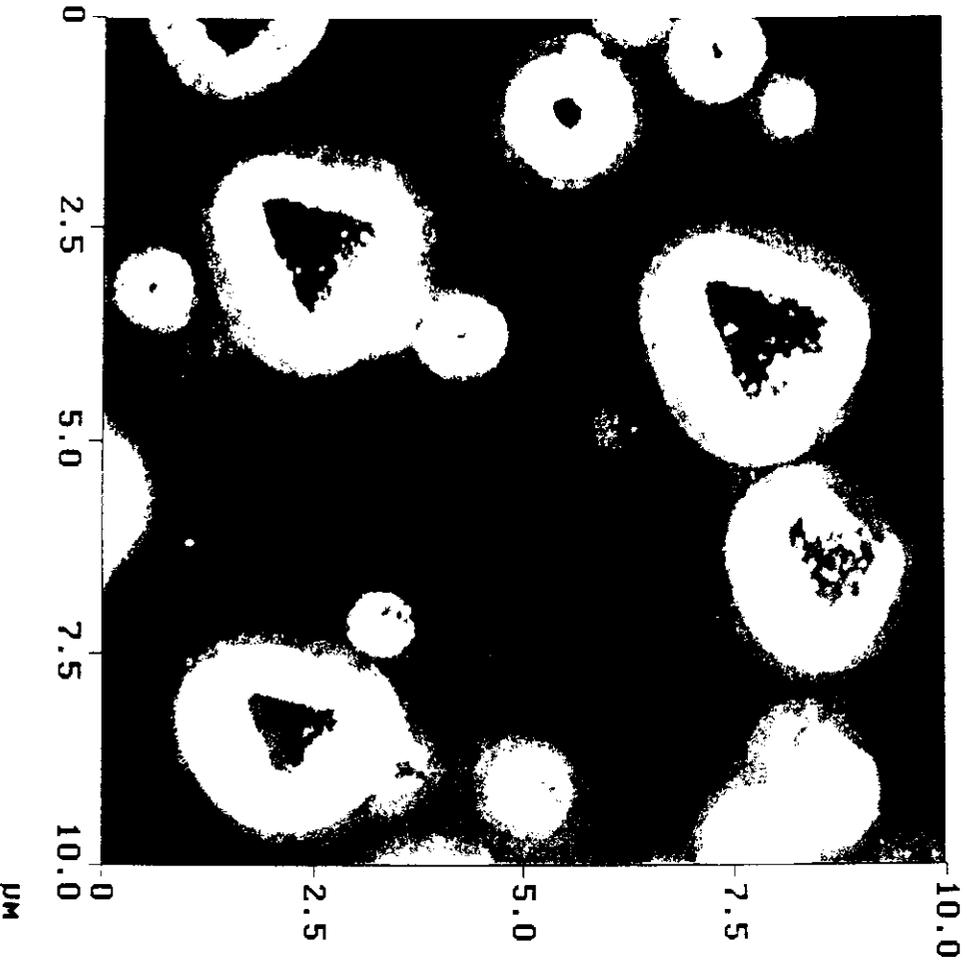
*AFM Image Of SiC Synthesized from C₆₀/HSR
High Flux*



Digital Instruments NanoScope
Scan size 6.832 μm
Scan rate 1.565 Hz
Number of samples 256
Image Data Height
Data scale 131.1 nm



*AFM Image Of SiC Synthesized from C₆₀ HSB
Low Flux*



Digital Instruments NanoScope
Scan size 10.00 μm
Scan rate 2.594 Hz
Number of samples 256
Image Data Height
Data scale 100.0 nm

C_{60} HSB Advantages:

■ *The Synthesis of SiC on Si Could be Achieved at Lower Temperatures by Kinetic Energy Activation.*

■ *Basic Properties of the Films:*

- *Morphology*
- *Density of Voids*
- *Growth rate etc.*

*can be Controlled by Changing
Beam Source Parameters: (Kinetic
Energy
and Flux of the Beam)*



A C_{60} HSB IS A VIABLE AND PROMISING
TOOL TO SYNTHESIZE SiC ON SI.

*Synthesis of
Nano-crystalline
TiNi Thin Films by
Cluster Beam
Deposition*

*E. Barboni, E. Basso, S. Calzavara
E. Cazzulani, E. Fiumani, G. Guidi
and S. Lippini*



*CNR Research Center
on the Physics of Aggregates - TRENTO
ITALY*
in Collaboration with

**Department of Physics University of Milan
**TEMPE-CNR*



CLUSTER Beam Deposition

*(“Synthesis of Nanophase Thin Films
by Cluster Beam Deposition” P. Milani,
S. Iannotta -Springer Verlag Jan. 1999)*

- *Synthesis of Nanostructures by
Assembling Nanoparticles.*
- *Characterization of the
Aggregates Before or During the
Deposition Process*
 - *Cluster Size Distribution*
 - *Cluster Kinetic Energy*
 - *Charge States*
 - *....*
- *Control on Film Properties such
as Grain Size, Crystallinity.
Stoichiometry for SMA alloys ???*

*E. Benvenuto, et al.
Newcastle, Feb. 2004 212-213*

TiNi -SMA- Films

Interests:

- *Actuators or combined Sensor-Actuators in Micro-Electro-Mechanical Systems (MEMS);*
- *Biomedical Systems and BioMEMS;*
- *Micro-Mechanics.*

Advantages over other micro-actuation methods (Piezoelectric, Magnetostrictive or bimetallic effects, etc..):

- *High work output unit volume;*
- *High power / mass ratio;*
- *Capability to be driven by standard logic level signals;*
- *Bio-compatibility;*
- *Scalability.*

Open Questions and Present Limits of Deposition Methods for Good Quality SMA Films

- *High Temperatures (>500-550 °C) of Deposition or Need of Thermal Treatments (Annealing):*
 - *DC and RF Sputtering and laser ablation produce amorphous films at room temperature.*
- *Processes Incompatible with SMA Microsystems Fabrication Directly Integrated with other MEMS Fabrication Technologies.*
- *Poor control on Films Quality due to Growth Environment and Pollutants.*
- *Fine control on Stoichiometry.*
- *Fine Control and Role of Crystallinity and Grain Size.*
- *Interface Film-Substrate*



AIMS

- **Synthesis of Nanocrystalline Materials from Controlled Nanoparticles Building Blocks**
 - *Fundamental and Technological Relevance*
- **Film Growth and Properties Controlled By Cluster Beam Parameters**
 - *Cluster Mass Distribution*
 - *Kinetic Energy and Momentum*
 - *Internal Energy*
 - *Deposition Rate*
- **Crystalline or Amorphous Character of the Particles**

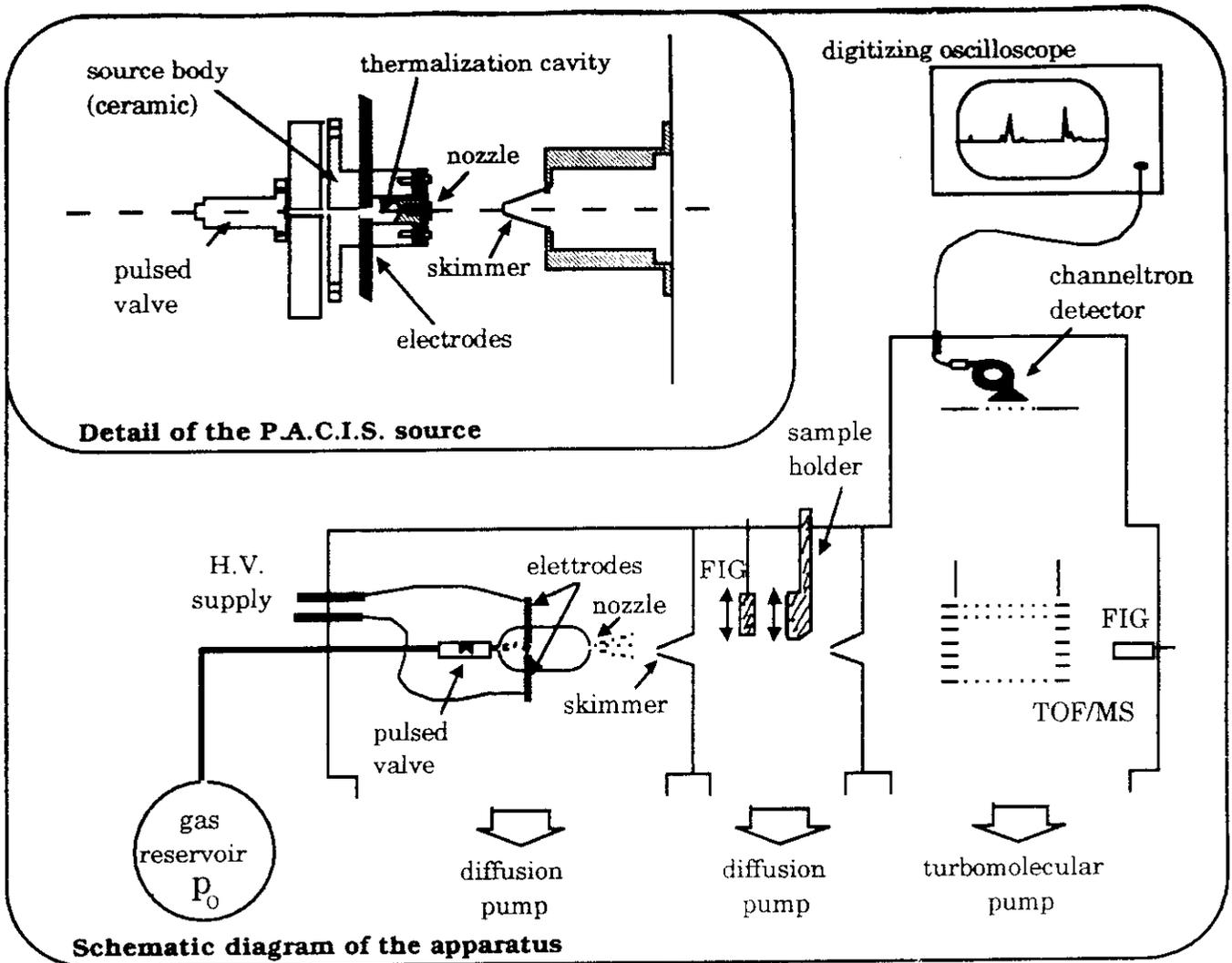


Characterization of the Beam



Correlation between the properties of the nanoparticles and of the films

E. Barbieri et al. Nanostructured Met 10(6) (1998) 1913



Detail of the P.A.C.I.S. source

Schematic diagram of the apparatus

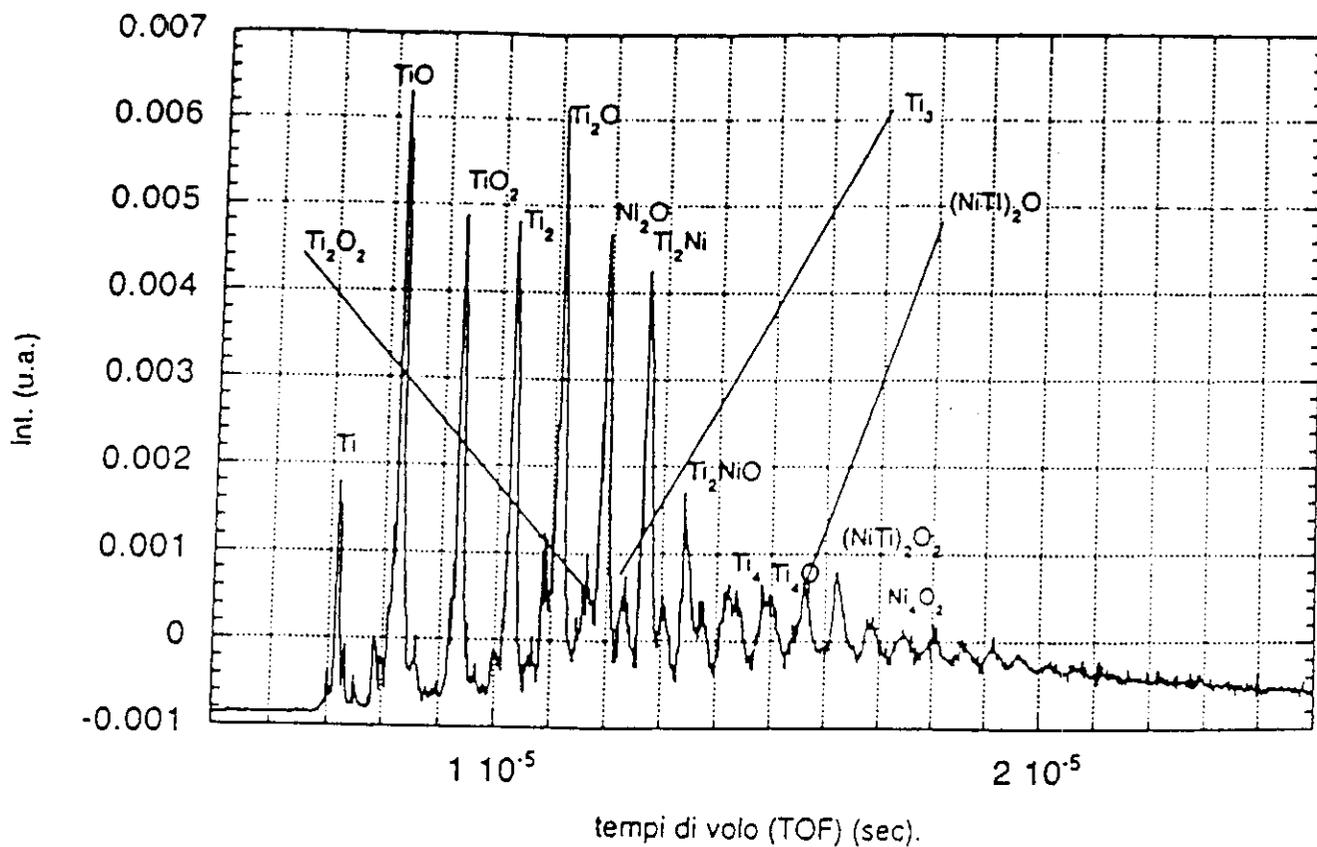
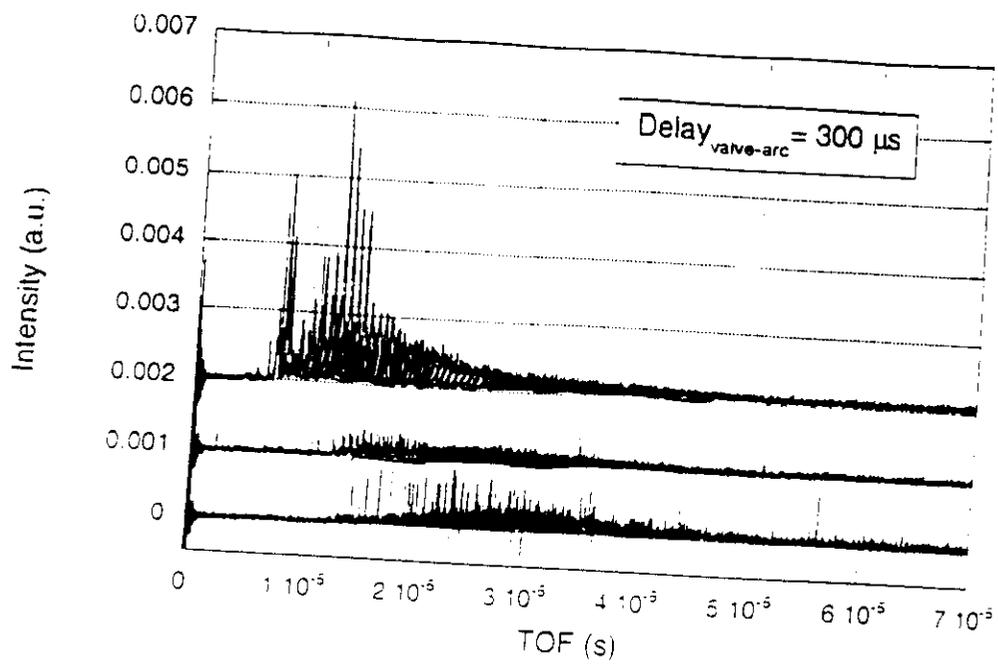
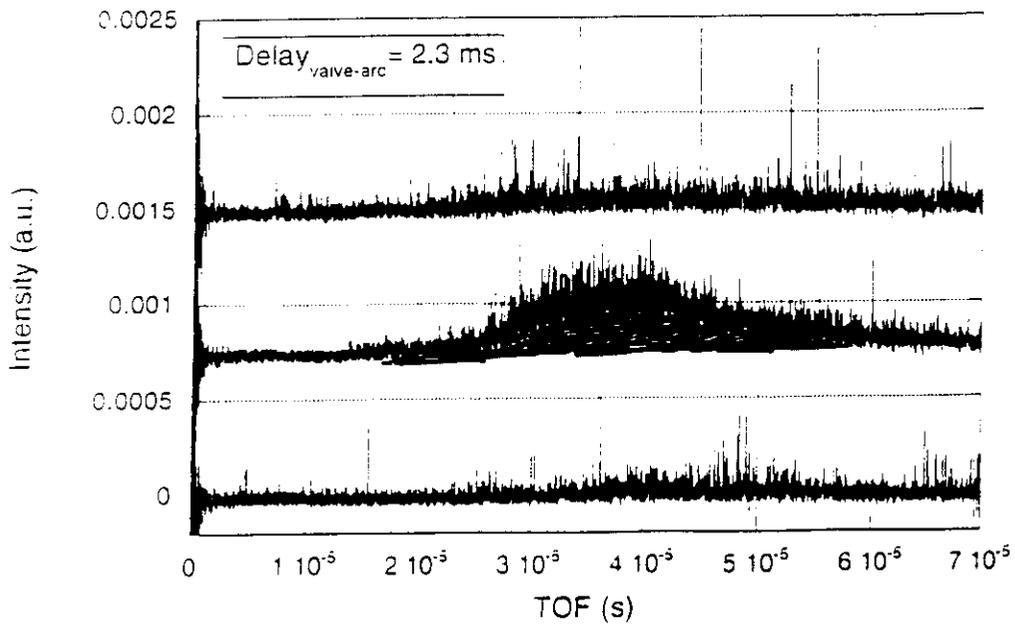
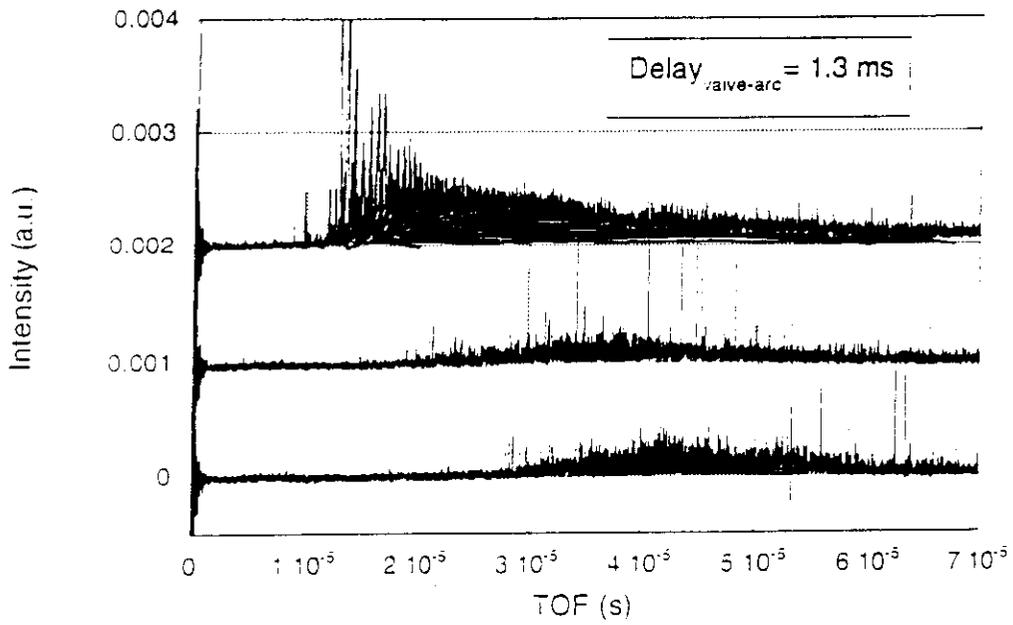
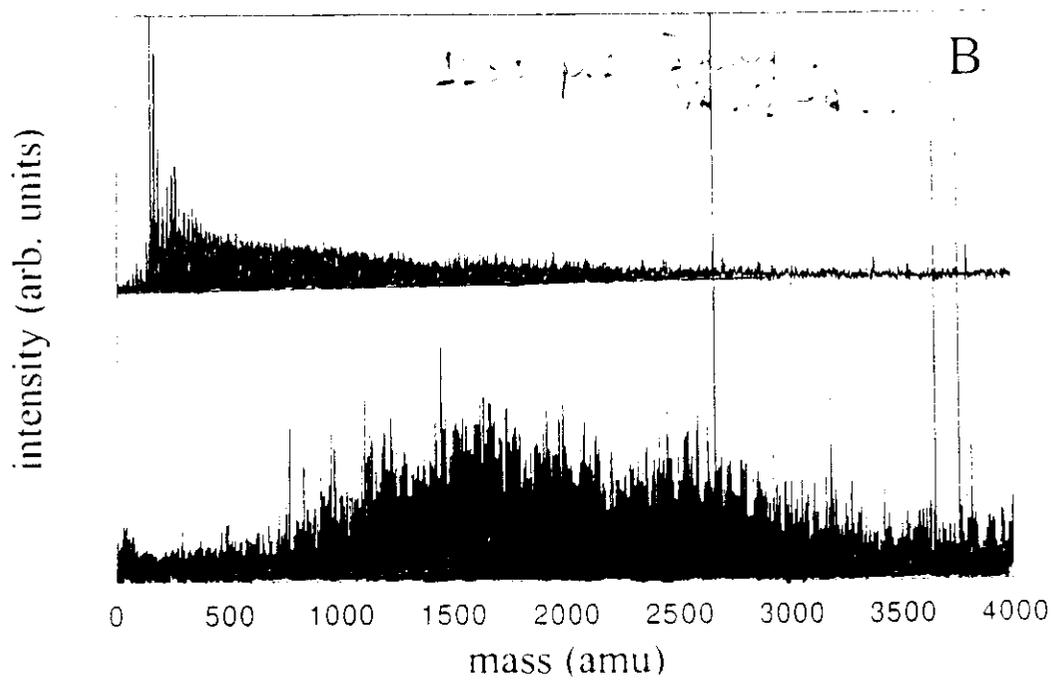
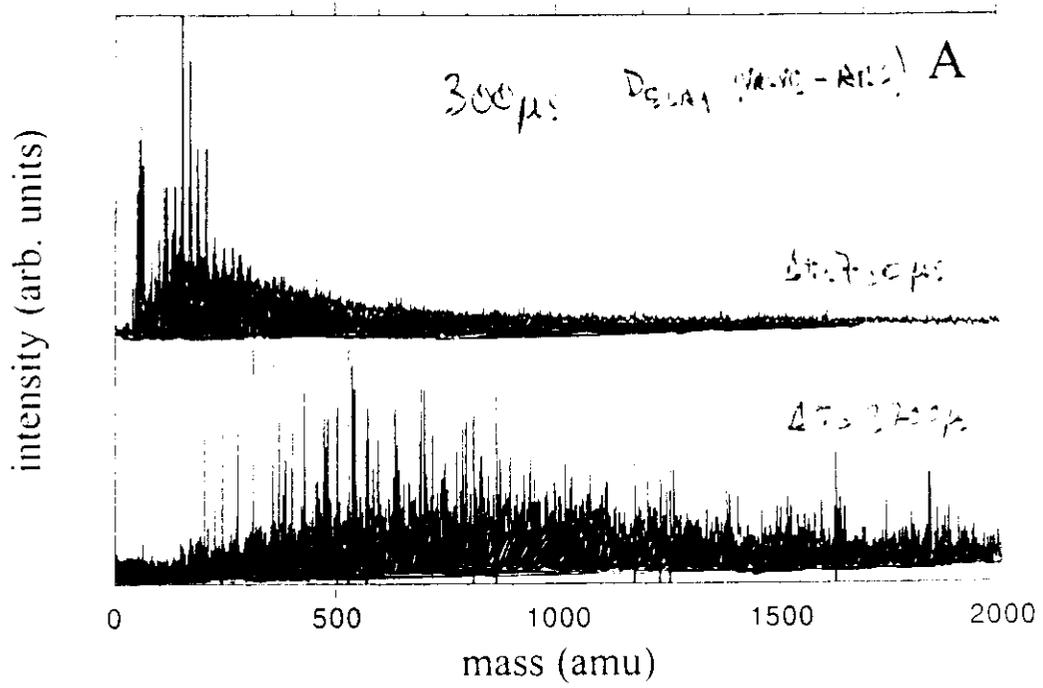


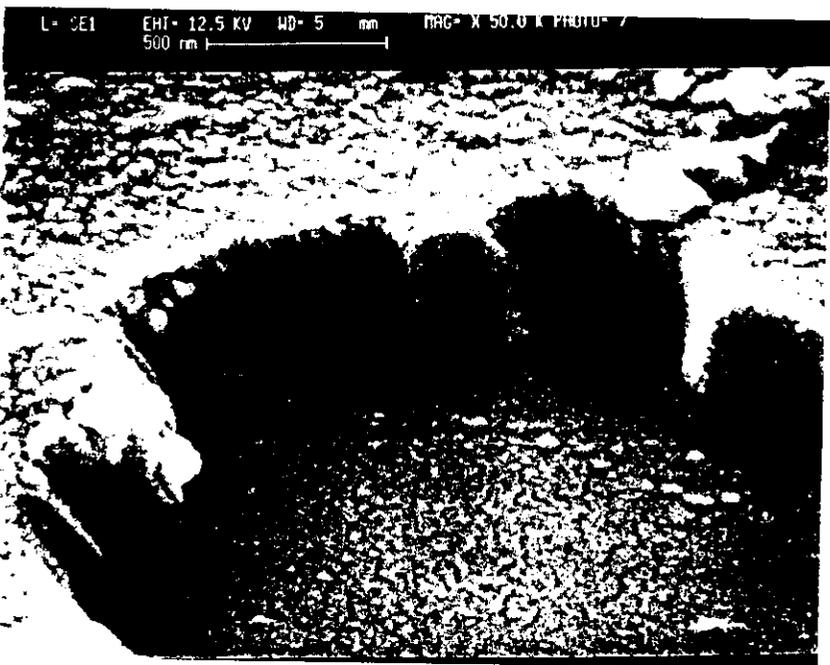
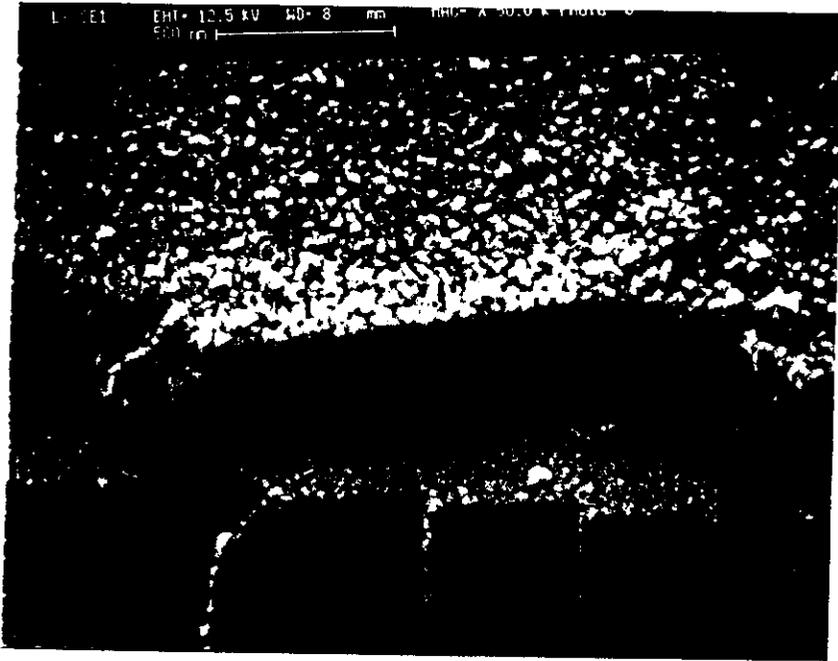
Figura 6.7 Spettro di massa raccolto con ritardo valvola-scarica di 1200 μ sec e ritardo scarica-spettrometro di 800 μ sec. Ai picchi più intensi é stata assegnata una massa.



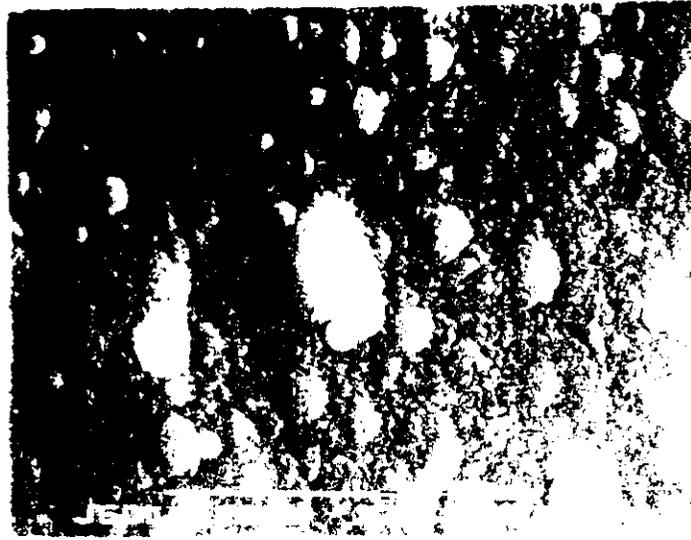
Nickel-Titanium





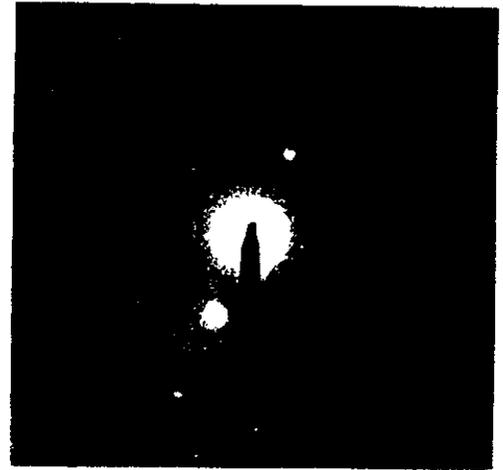
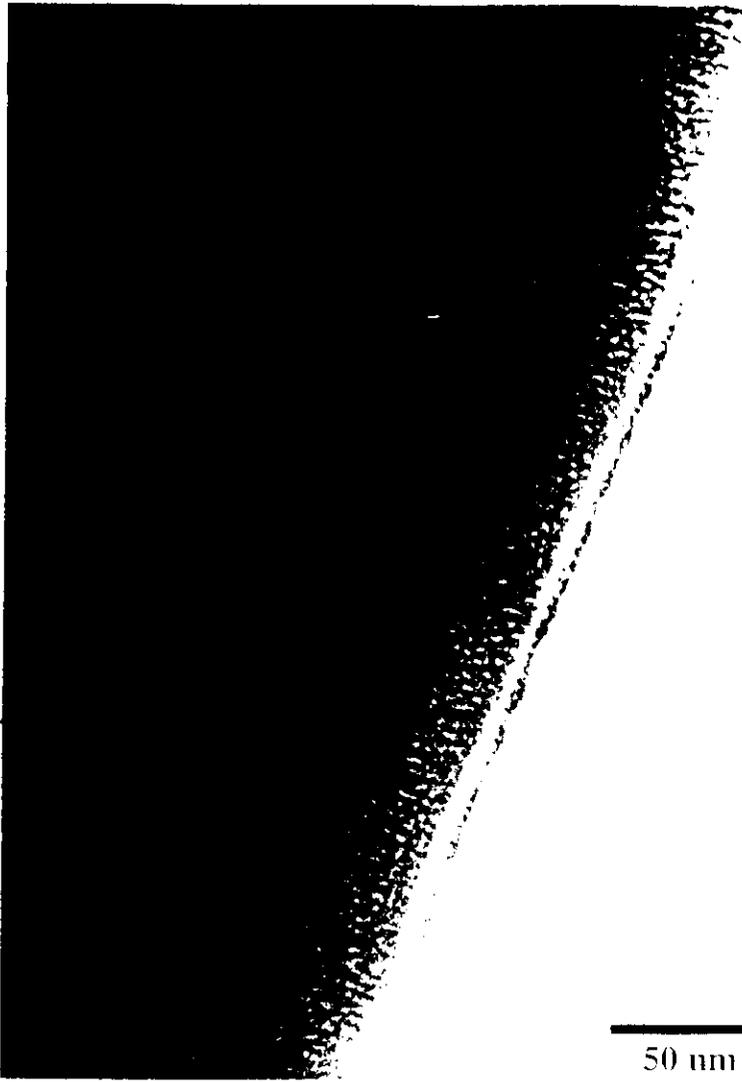


A



B

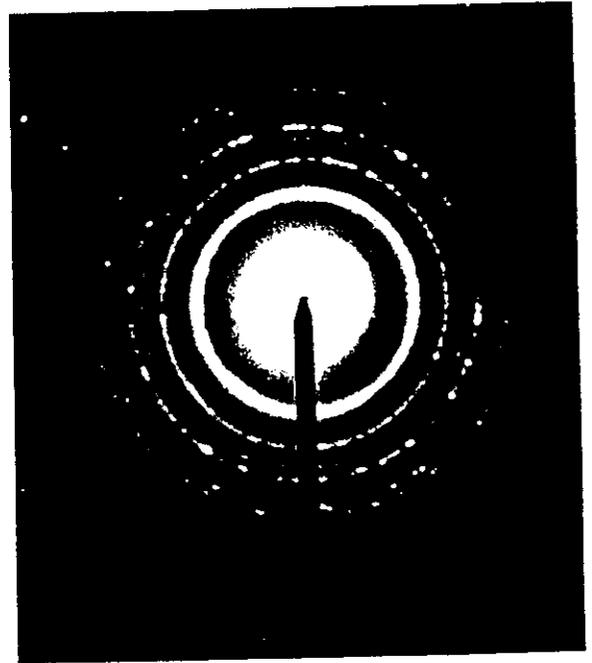
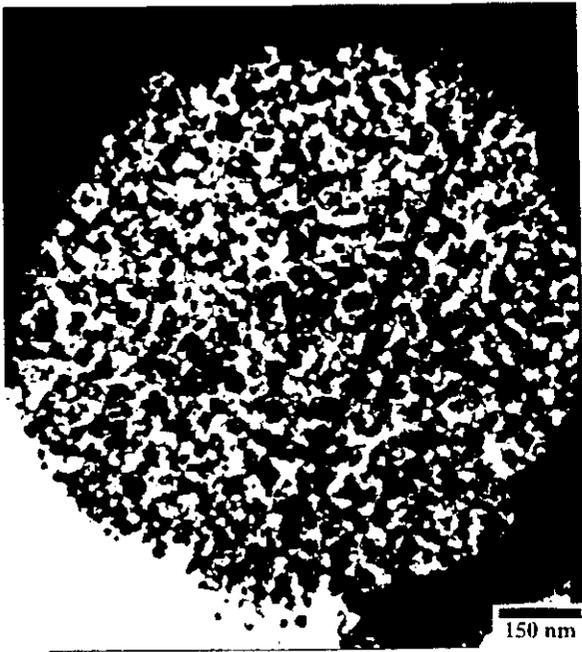




-CROSS SECTION MICROGRAPH OF A FILM
GROWN FROM BEAMS MADE OF ATOMS
AND SMALL CLUSTERS -

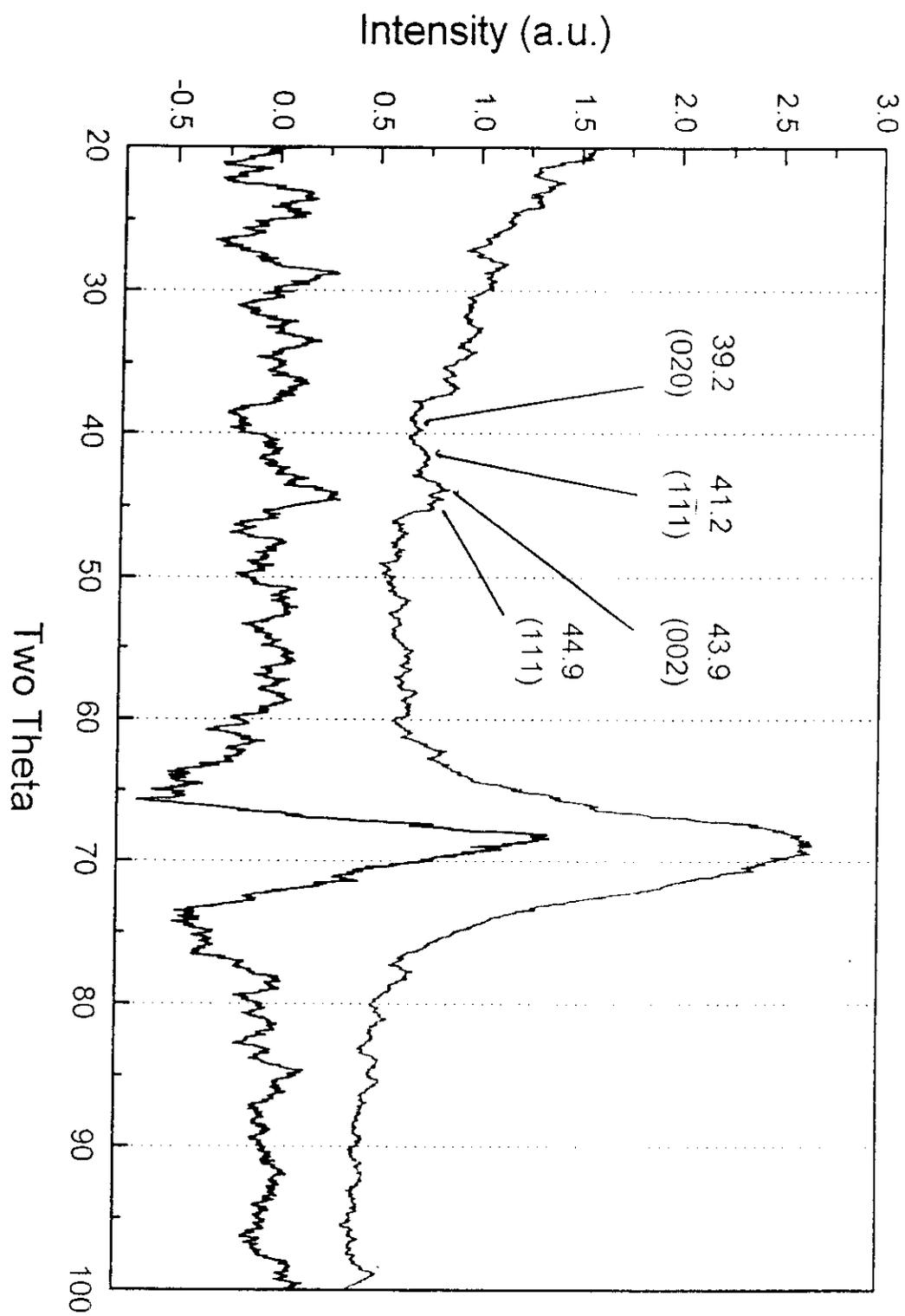
FILMS TYPE E

TYPICAL AMORPHOUS CHARACTER



50 nm

- MICROGRAPHS OR FILMS MADE WITH BEAMS WITH LARGER CLUSTERS - FILMS TYPE A
- NANOCRYSTALS ARE CLEARLY VISIBLE.



- *PAGACS Sources can be efficiently used to synthesize TiNi -SMA alloys.*
- *Amorphous and Crystalline thin films are produced with different cluster size distributions in the beam.*
- *Nanocrystalline films are obtained on room temperate substrates without any need of thermal treatments.*
- *Cluster beam deposition preserves stoichiometry of the original alloy used.*
- *The sources are scalable and compatible with ultra clean environment and processing.*
- *The cluster size distribution of the beam can be efficiently controlled by source parameters and skimmer selection (segregation).*
- *TOF mass spectrometry can be efficiently used to characterize cluster beam distribution and ionic structure of the particles.*
- *The preparation of high quality, grain size controlled, SMA films is envisaged.*

Seeded Supersonic Beams of Thiophene-Based Oligomers

A tool:

- *to study the properties of the isolated aggregates.*
- *to grow high quality thin films.*



*CeFSA - CNR Research Center
On the Physics of Aggregates
Povo di Trento - ITALY*

Open Questions and Present Limits in films Growth

- *Control on Quality and Crystallinity of Thin films;*
- *Interaction with substrates and interface properties and correlation with devices design and fabrication;*
- *Functionalization to tailor the electronic and optical properties;*
- *Better understanding of correlation between structural, morphological , electronic and optical properties.*

Growth Methods:

- *Chemical*
 - *Spinning*
 - *Langmuir Bludgett*
- *Physical*
 - *OMBE (Organic Molecular Beam Epitaxy)*
 - *SuMBE (Supersonic Seeded Molecular Beam Epitaxy)*





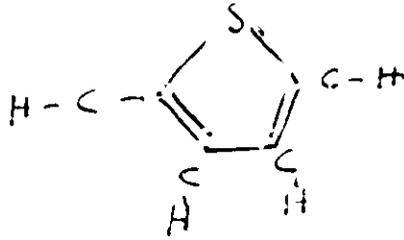
Oligo-thiophenes: Interests

- *Prototype π -conjugated organic molecule:
Basic and Fundamental Interest.*

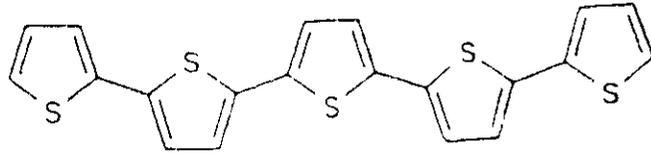
- *Technological interests:*
 - *organic electronics (FETs: R.Hajlaoui et al. Adv. Mat., 9 (1997) 389, G. Horowitz Adv. Mat. 10(1998) 365).*
 - *LEDs and other electro-optical devices (H. Mauch E.Gumlich Springer Verlag 1996)*
 - *NLO applications (M.G. Harrison et al. Synth. Met. 67 (1994) 215; D. Fischou et al. Adv. Mater. 6 (1994) 64)*
 - *Photovoltaic cells (J. Simon, Molecular Semiconductor, Spinger Verlag (1985)).*

A PROTOTYPICAL CONJUGATED MOLECULAR SYSTEM

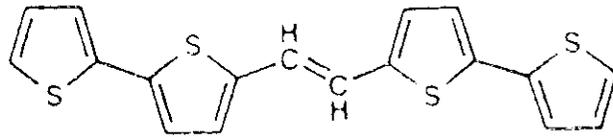
THIOPHENE



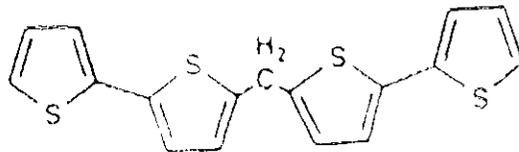
T₅



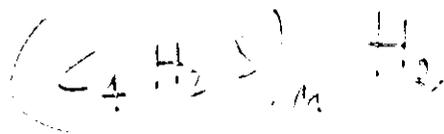
T₂VT₂



T₂MT₂



OLIGO-THIOPHENE



SYNTHESIS OF ORGANIC FUNCTIONAL MATERIALS:

- LANGMUIR-BLUDGETT (SELF-ASSEMBLY)
- SPINNING
- OMBE (ORGANIC MOLECULAR BEAMS)



?

- HSB (HYPERFINE SUPERLUMINESCENT BEAMS)

T4 Possible Crystal Structures

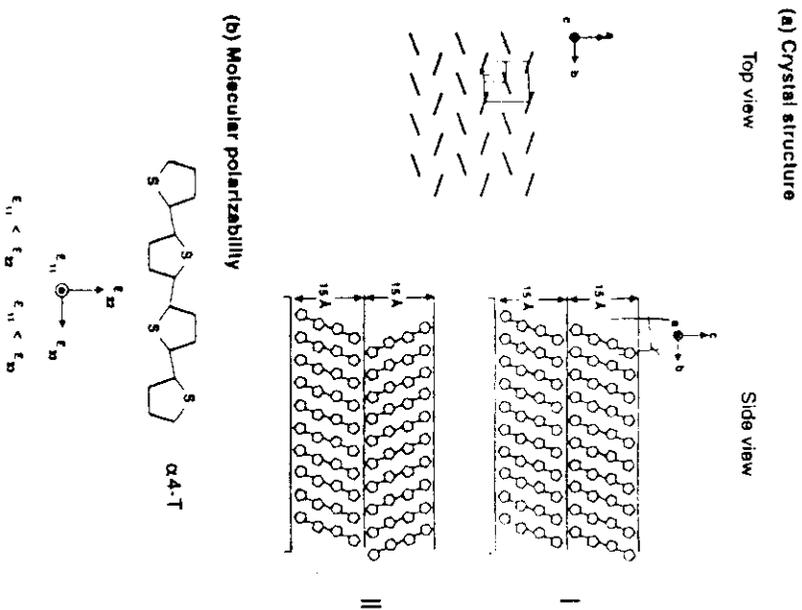


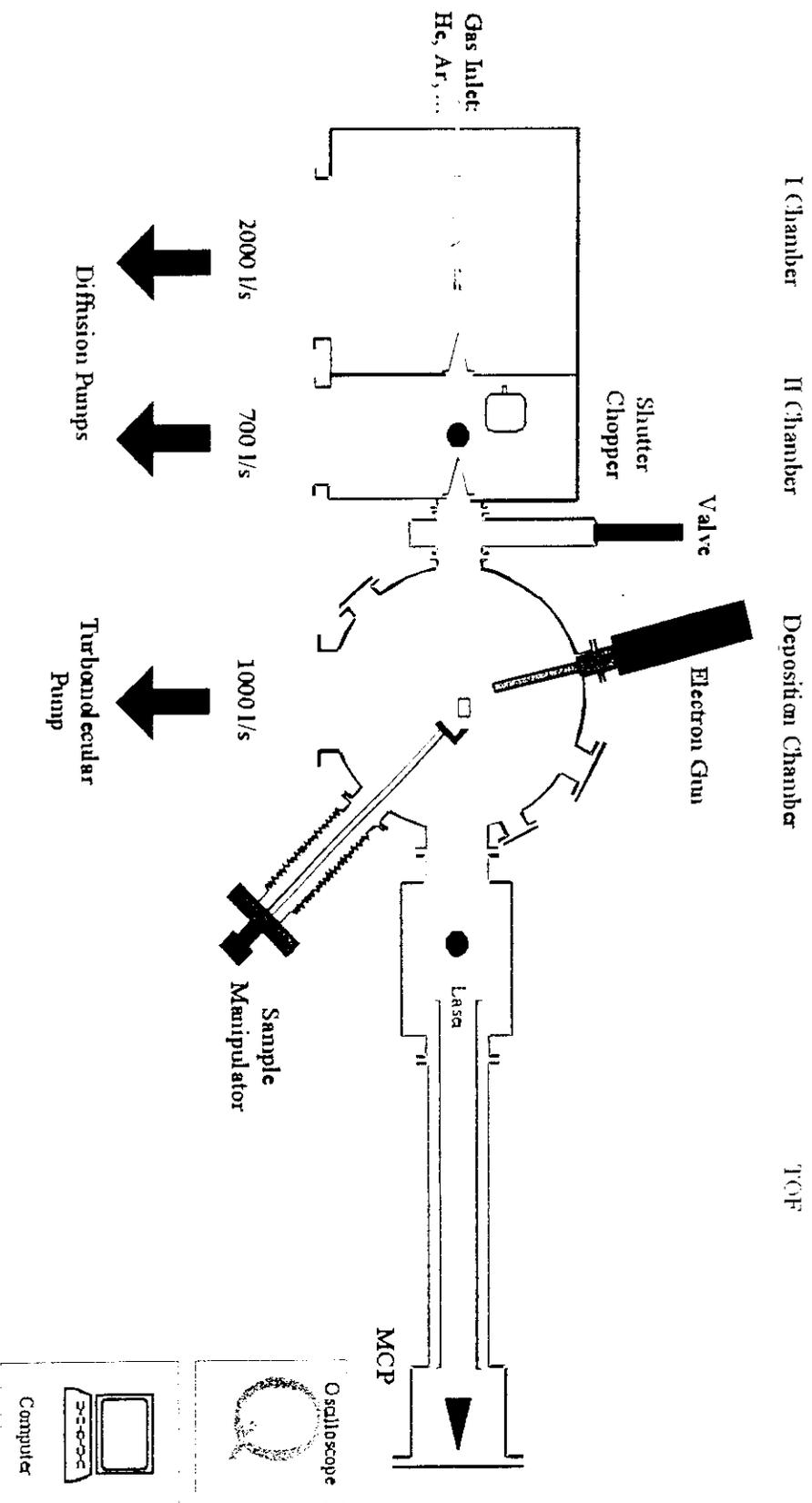
FIG. 2. (a) Possible crystal structures of evaporated quaterthiophenes consistent with the layering found from $\Theta - 2\Theta$ x-ray data on evaporated films (I) has been proposed on the basis of powder diffraction data [Porzio]. (II) is the structure which has been proposed for α -3T [Bohnis] and dimethyl-substituted quaterthiophene[Hotta]. (b) Polarizability of a single α -4T molecule. The polarizability $\epsilon_{crystal}$ of the crystal is approximated by taking the average of the molecular polarizabilities in the unit cell.



T4 Crystal Data

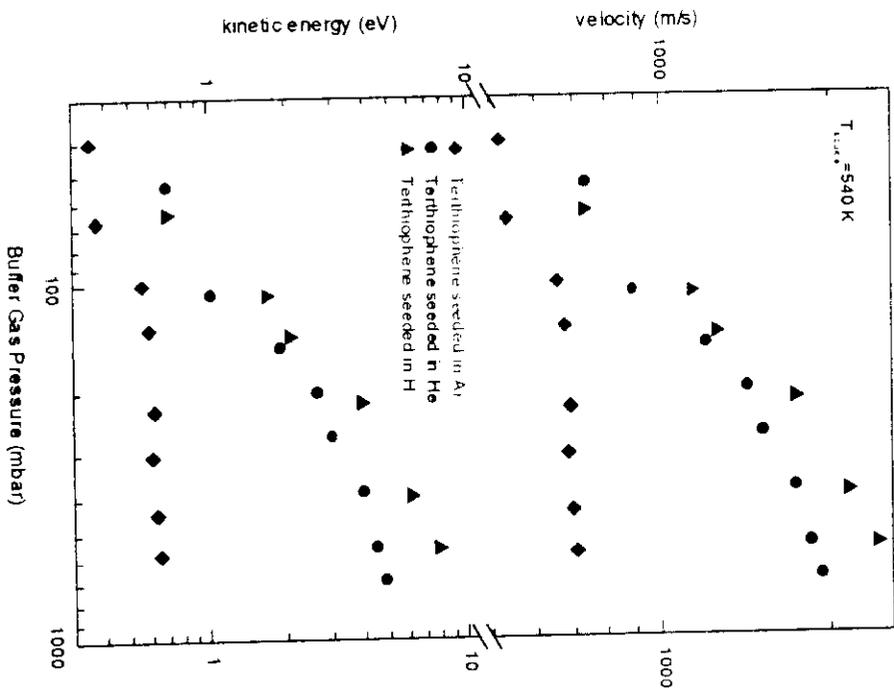
Table 1. Crystal data and structure refinement for 2,2':5',2M':5M':2M' quaterthiophene.

Identification code	4T
Empirical formula	$C_{16}H_{10}S_4$
Formula weight	330.48
Temperature	293(2) K
Wavelength	0.71069 Å
Crystal system	Monoclinic
Space group	$P2_1/a$
Unit cell dimensions	$a = 8.936(3)$ Å $b = 5.7504(9)$ Å $c = 14.341(3)$ Å $\beta = 97.22(2)^\circ$ $731.1(3)$ Å ³
Volume	2
Z	2
Density (calculated)	1.501 Mg/m ³
Absorption coefficient	0.634 mm ⁻¹
$F(000)$	340
Crystal size	$0.40 \times 0.30 \times 0.05$ mm ³
θ range for data collection	2.86 to 27.99°
Index ranges	$-1 \leq h \leq 11, -1 \leq k \leq 7, -18 \leq l \leq 18$
Reflections collected	2282
Independent reflections	1644 [$R(\text{int}) = 0.0487$]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1644 / 0 / 104
Goodness-of-fit on F^2	1.098
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0431, wR_2 = 0.1417$
R indices (all data)	$R_1 = 0.0556, wR_2 = 0.1484$
Largest diff. peak and hole	0.488 and -0.396 e. Å ⁻³



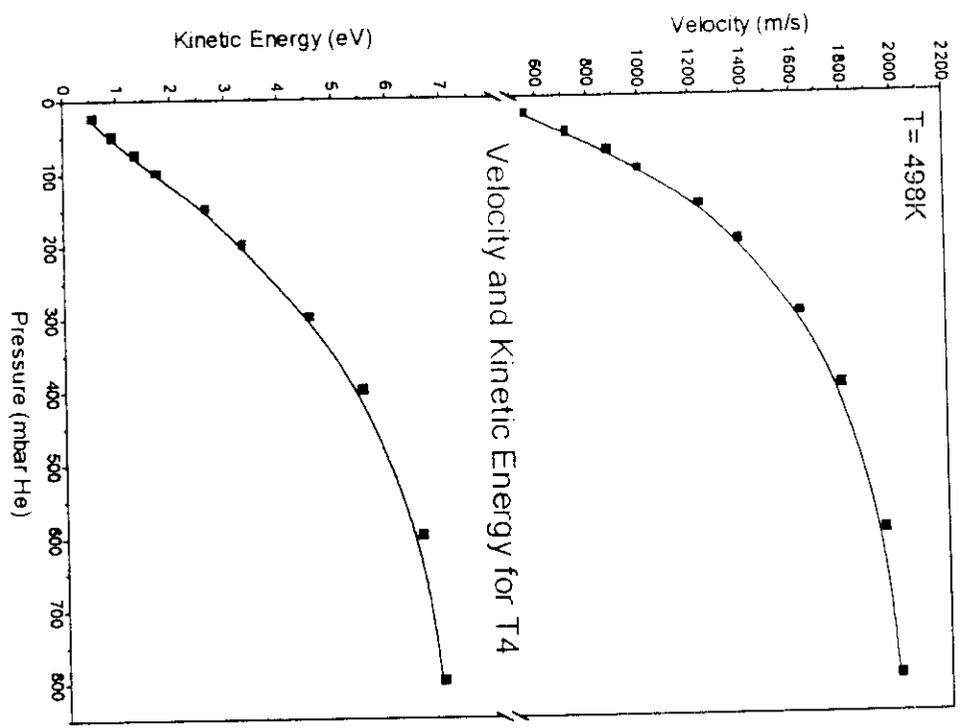
Experimental Apparatus

T3 HSB - Energy and Velocity as a Function of He, Ar and H2 Seedings

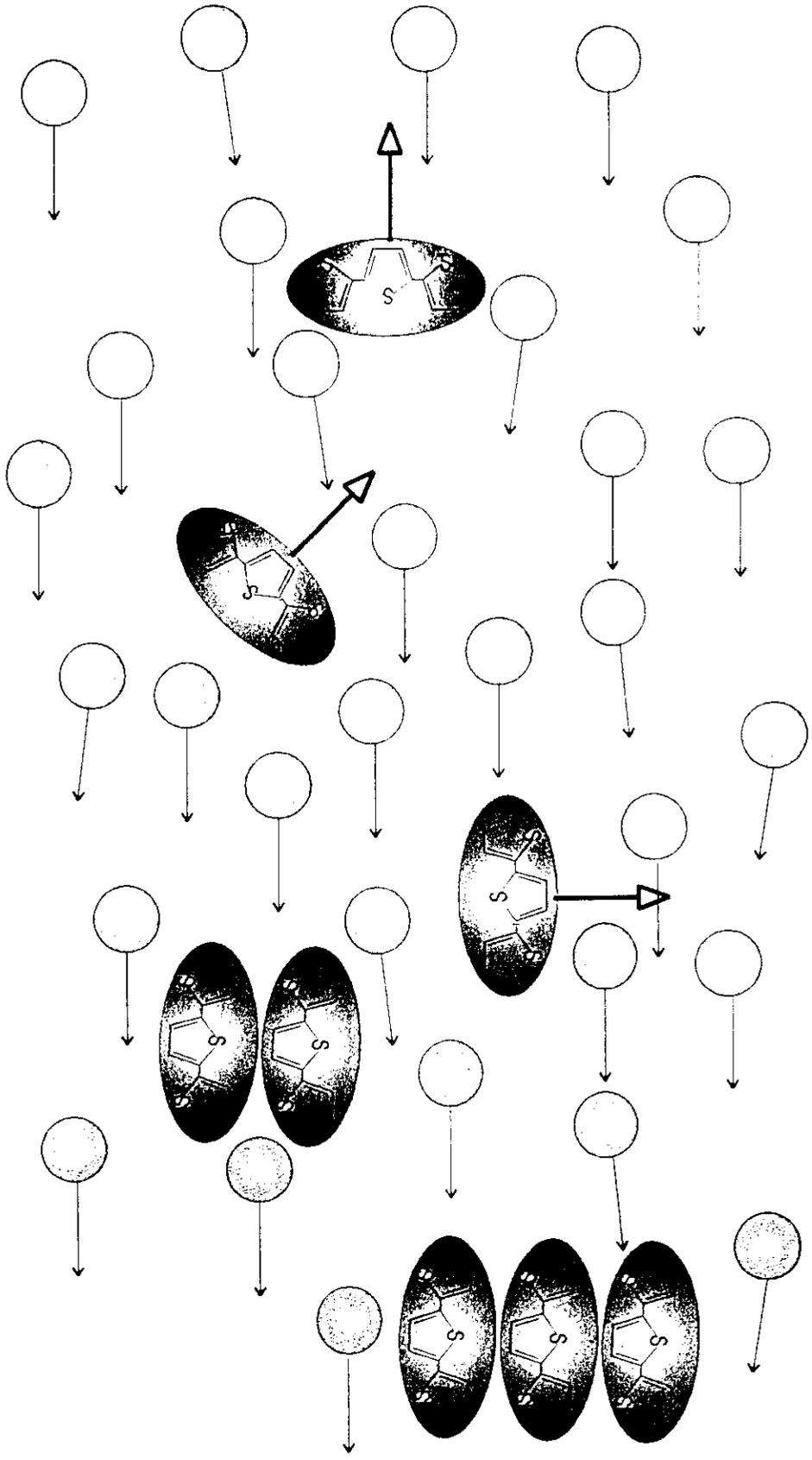




T4 - HSB seeded in He

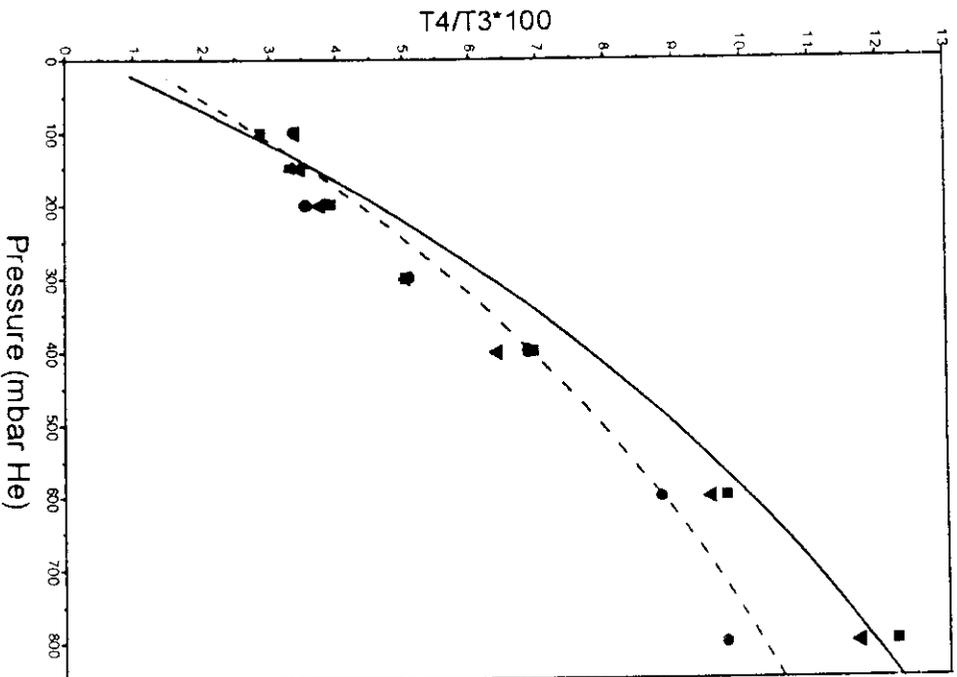


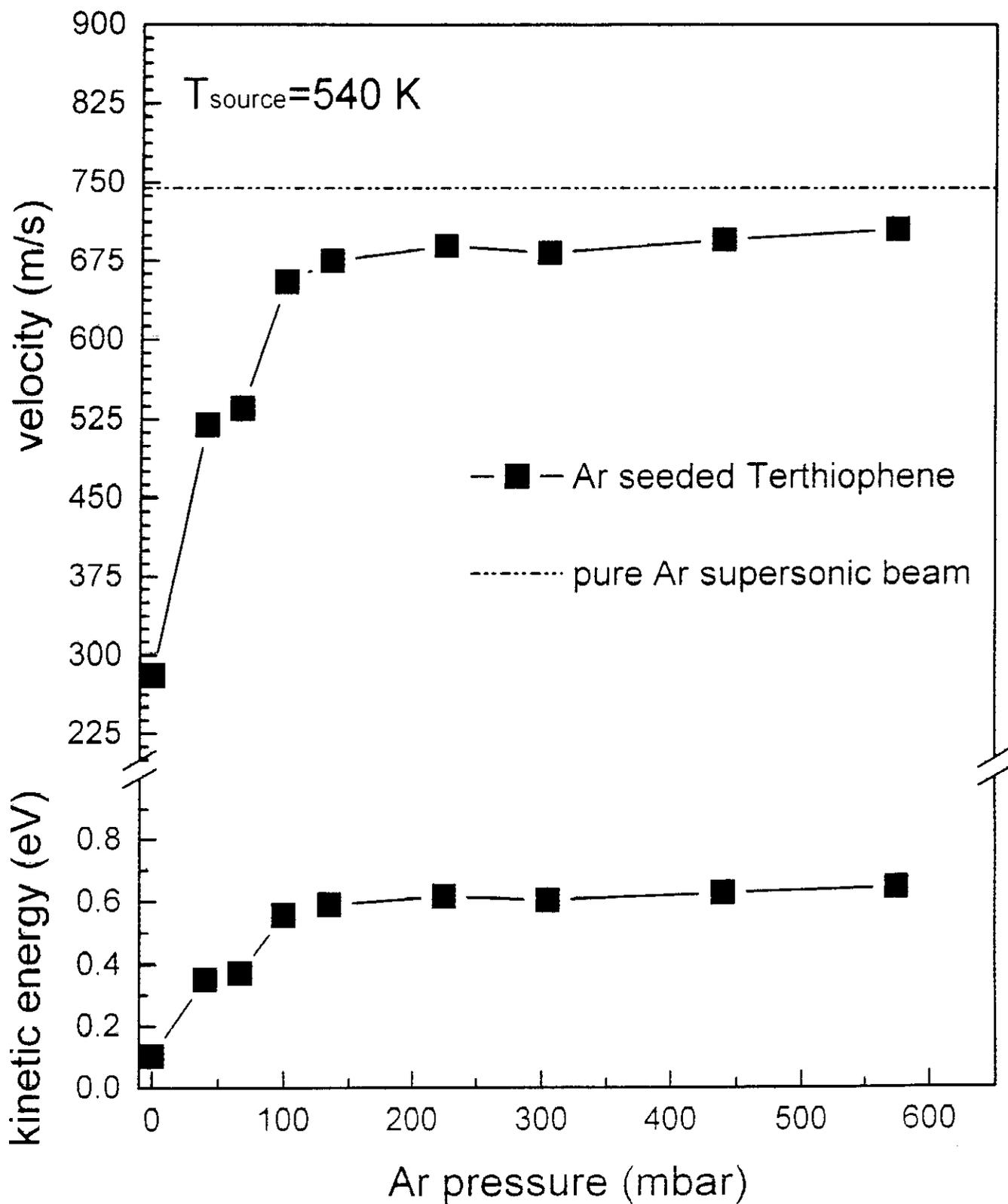
Expansion
axis

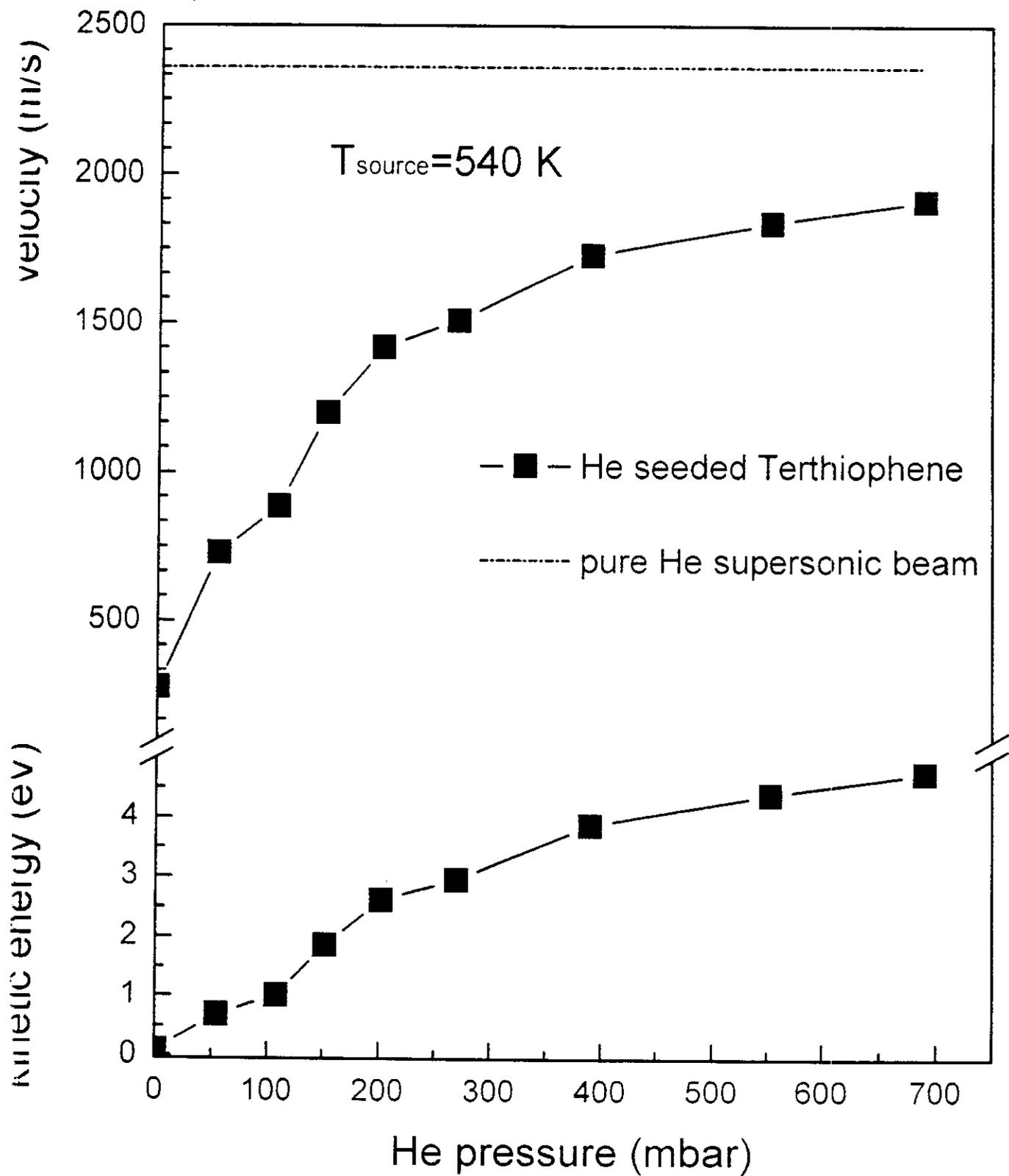




T4/T3 Abundance Increased By the Segregation in the HSB

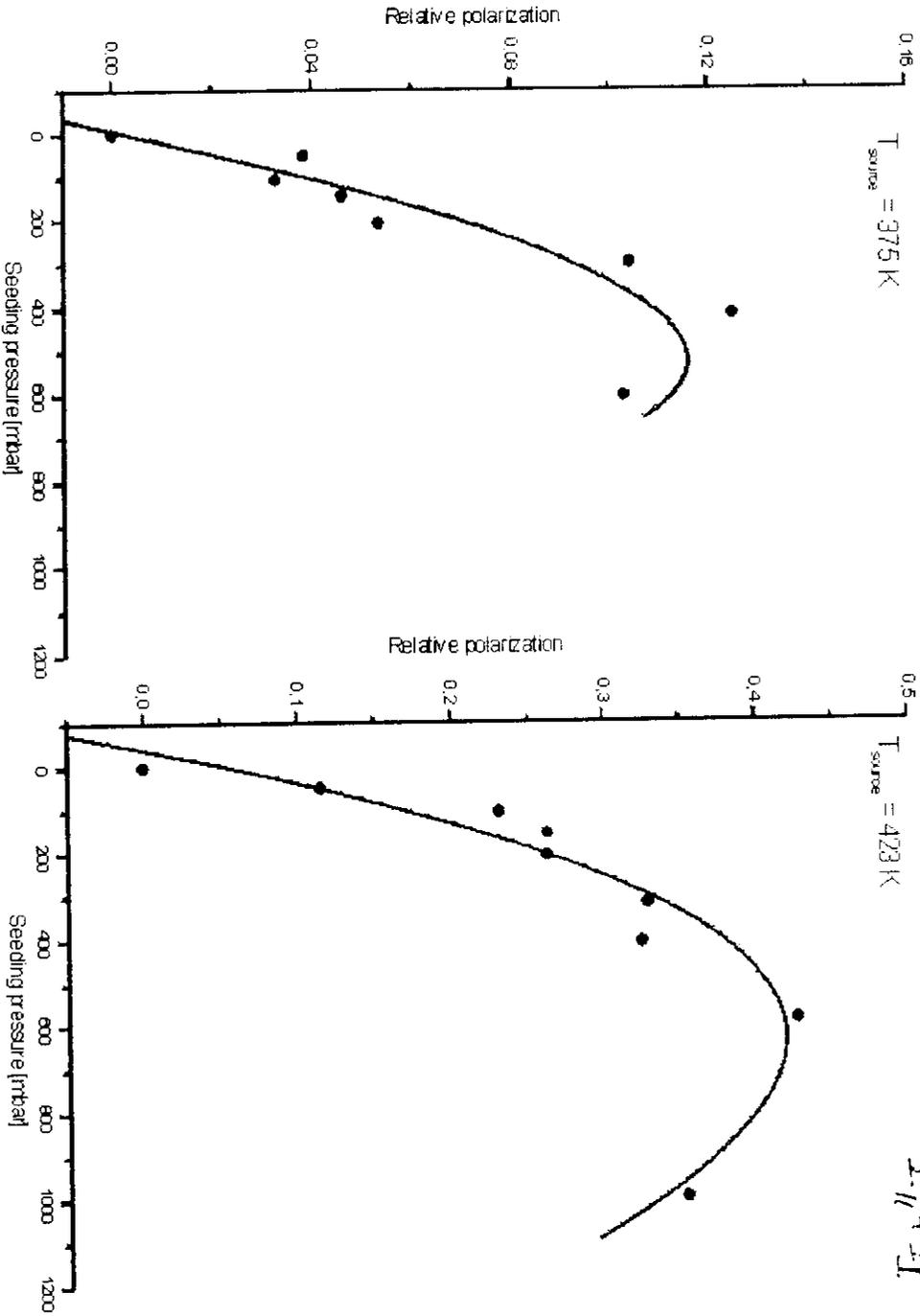




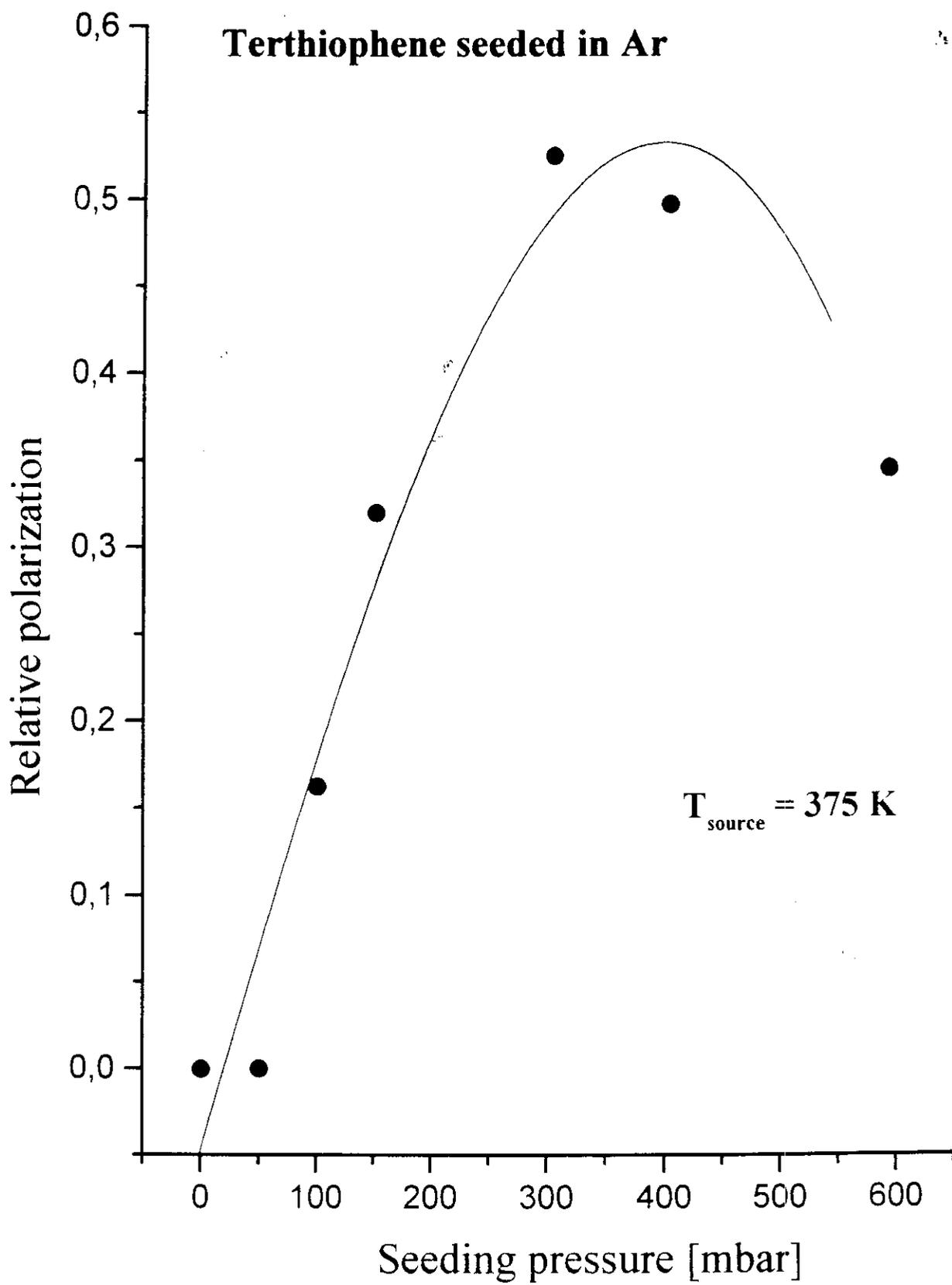




$$\frac{I_{||} - I_{\perp}}{I_{||} + I_{\perp}}$$

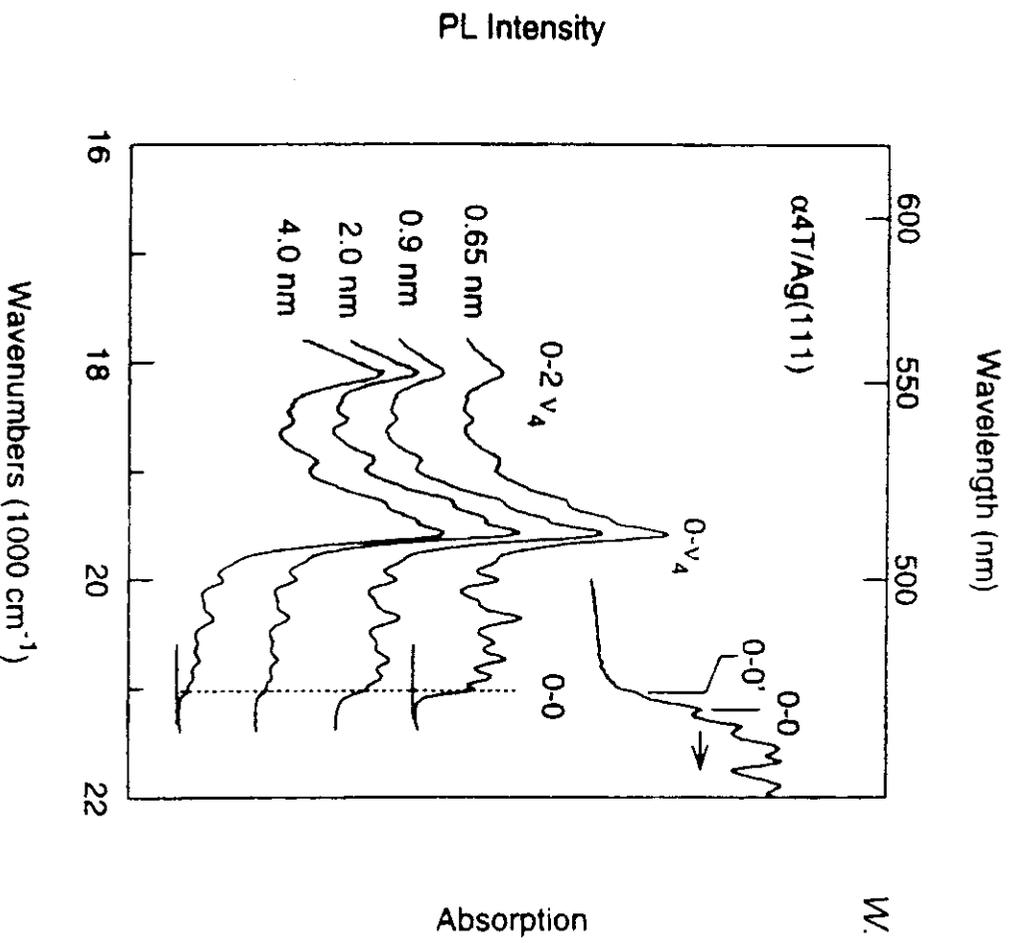


Terthiophene seeded in He



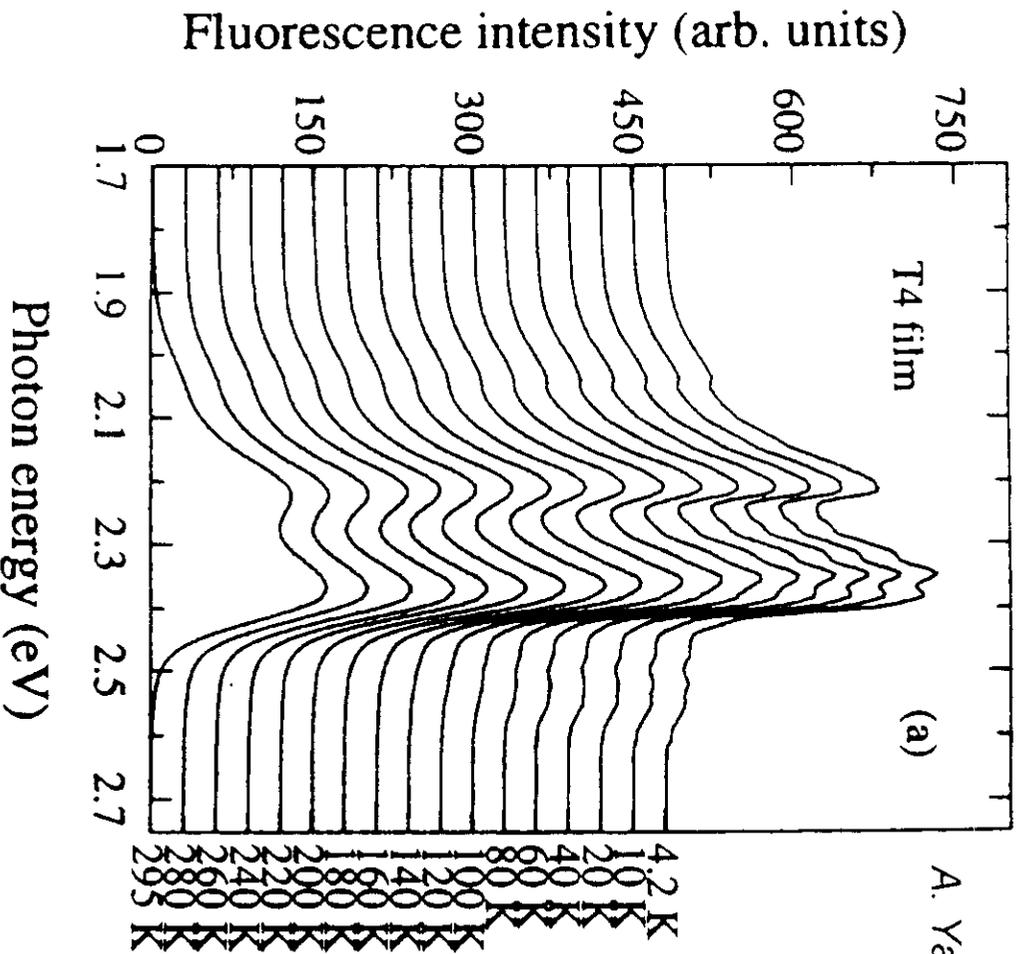


T4 Grown from Standard Vacuum Deposition: Fluorescence as a Function of Thickness



W. Gebauer et al. Chem. Phys. 227 (1998) 33

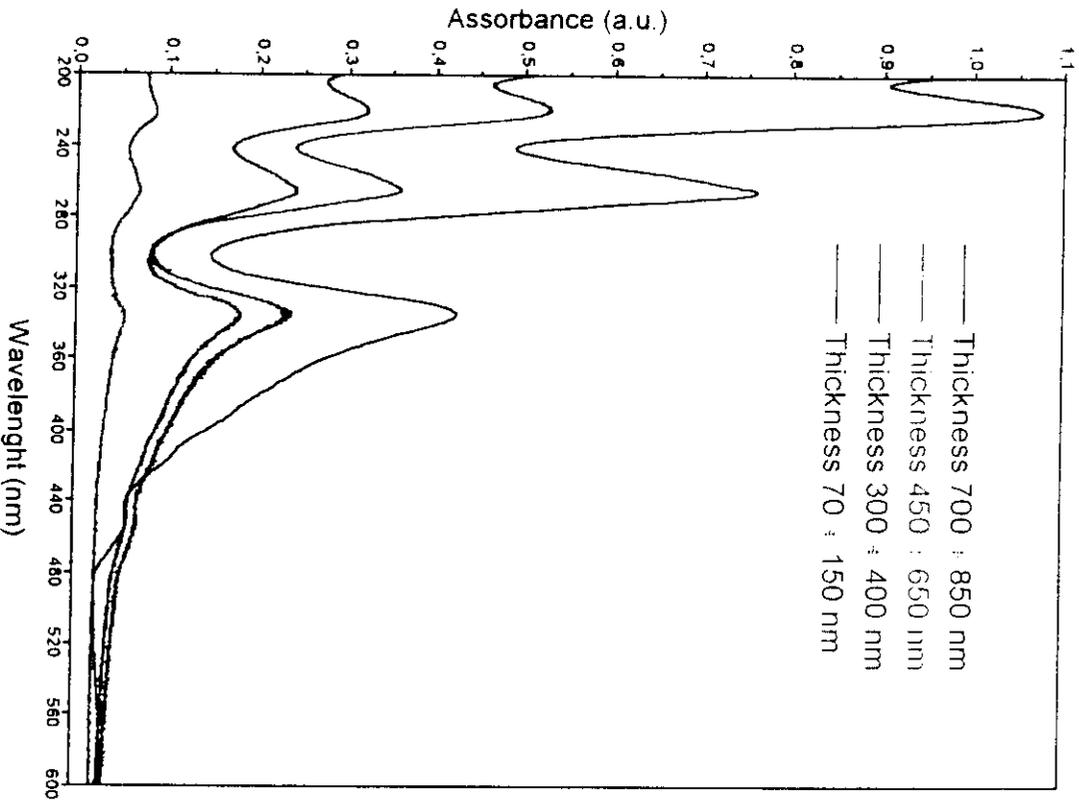
*T4 Fluorescence Spectra (3.26 eV excitation) of
Vacuum Deposited Films (375 nm)*



A. Yang et al. *J. Chem Phys.* 109 (1998) 8442

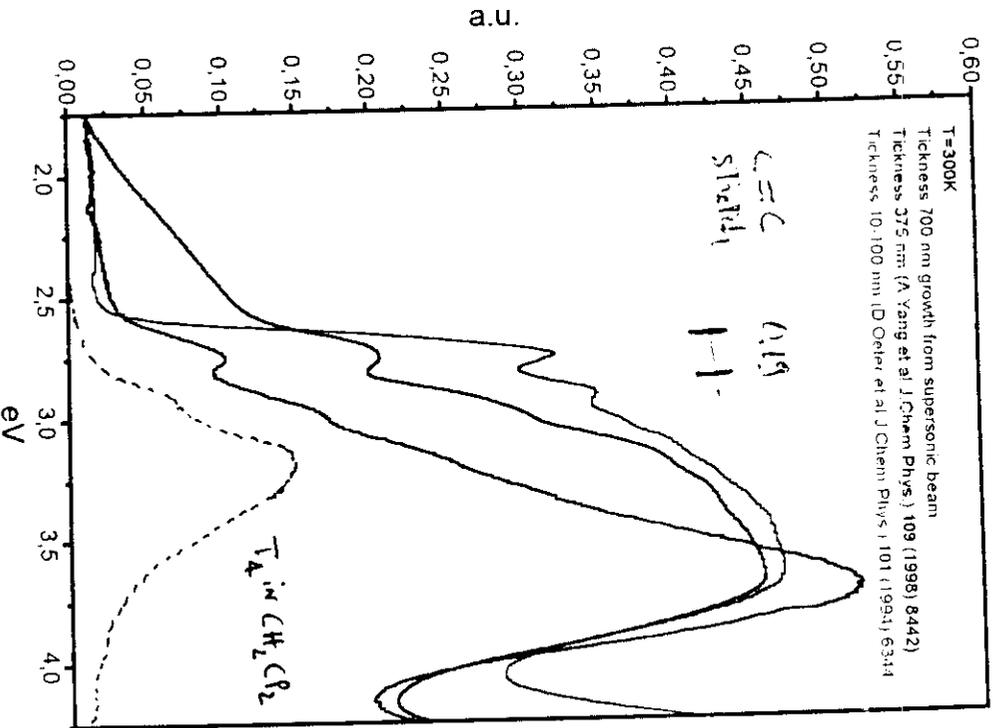


T4 - Grown from He seeded HSB - Absorbance for Films with different thickness



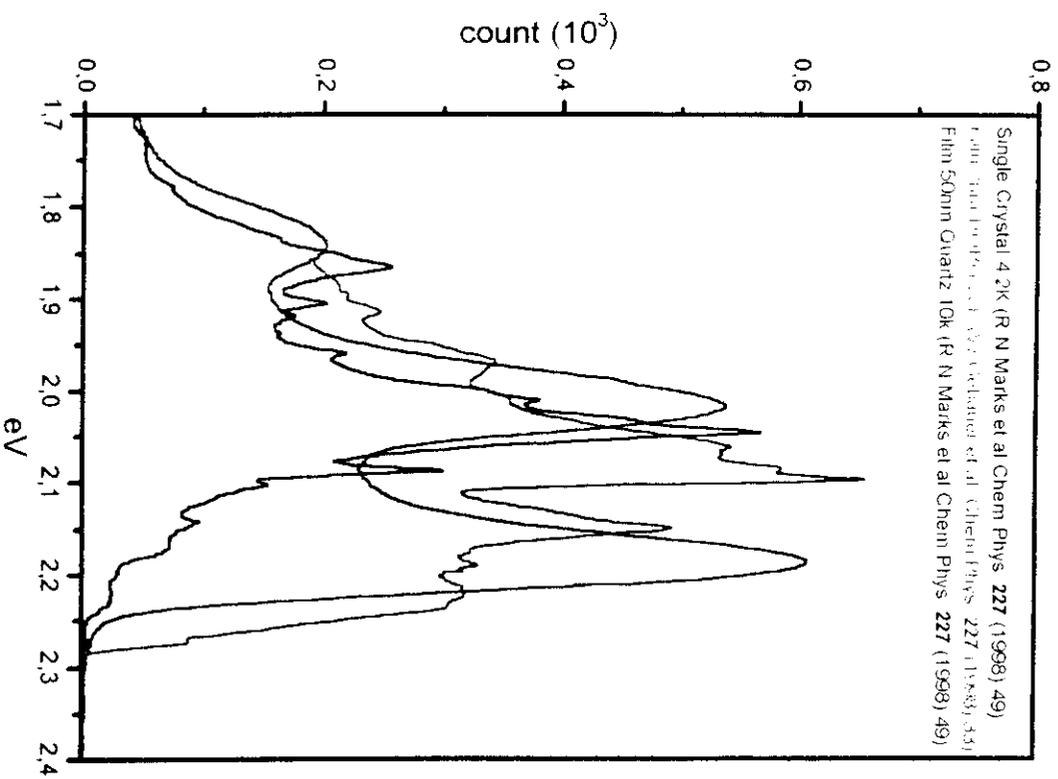


Comparison Between Films Grown from T4-HSB and Conventional Vacuum Deposition: Absorbance



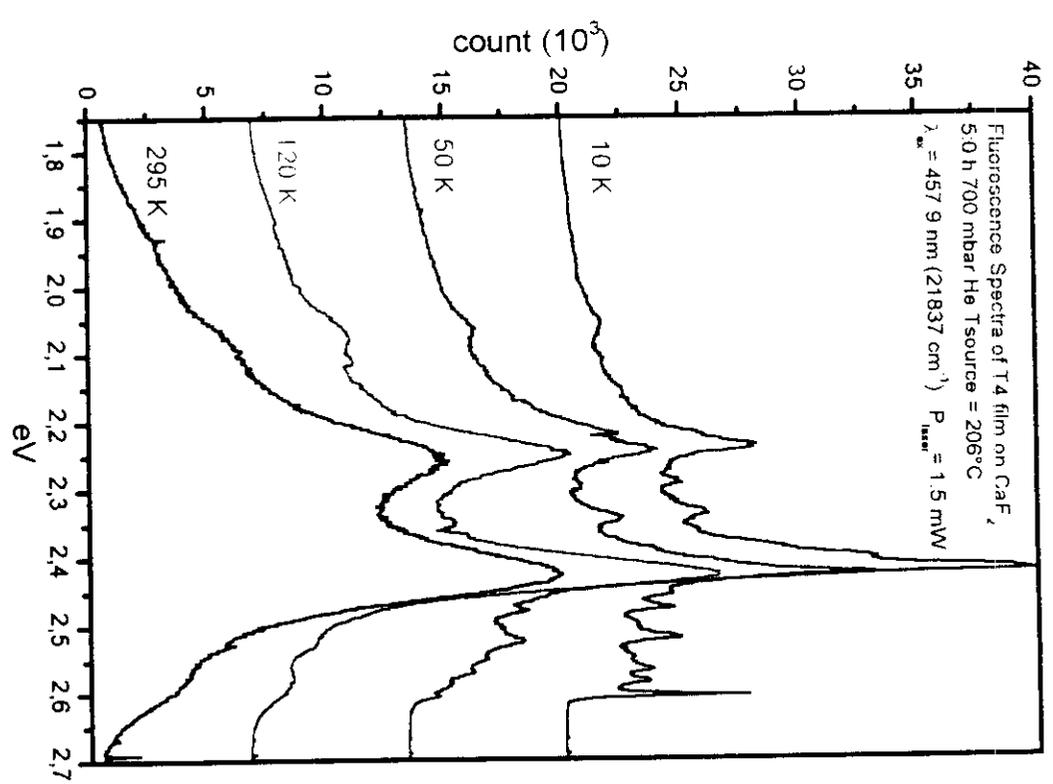


*Available PL data From 6T from Thin Films
and Single Crystal*



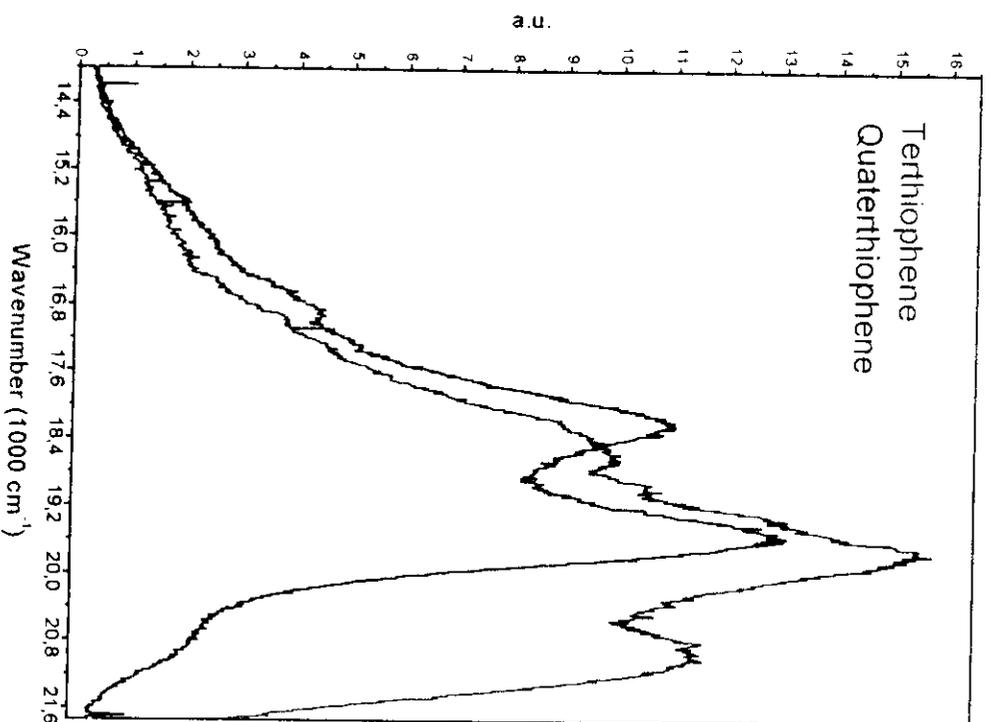


HSB Grown films: Fluorescence from T4 as a Function of Temperature



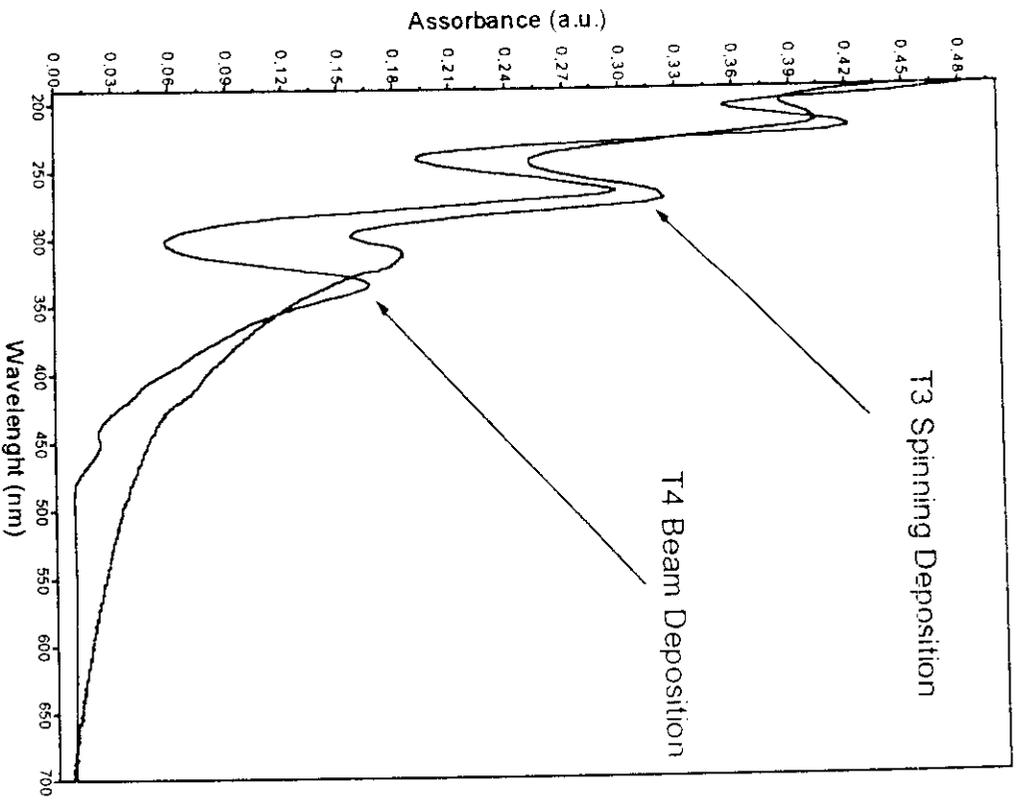


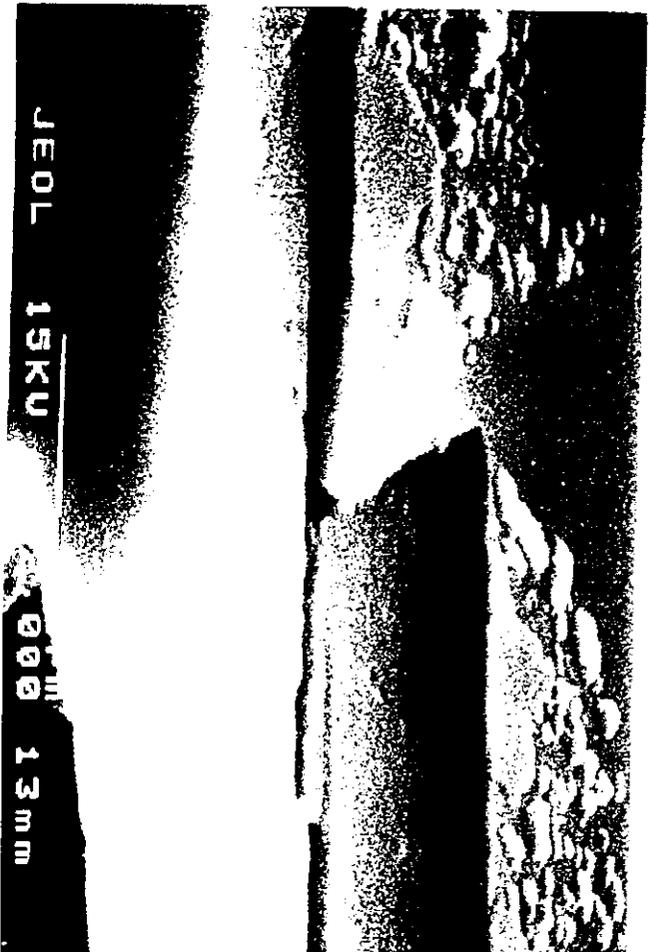
T3 versus T4 Fluorescence
-The T4 film is Obtained from HSB
- The T3 from Spinning





T3 versus T4 Absorbance





*SEM Micrograph of Films
of T4 grown by HSB:
seeding in He*



*Thin T4 Film with Island
Formation Grown by HSB
(low Pressure Source)*



Conclusions and Perspectives

- We have built an highly efficient and reliable source for hyperthermal supersonic beams for Fullerene and oligo-polymers.
- The fullerene source produces the beam of neutrals in the ground electronic state with the highest achievable kinetic energy: very promising applications.
- The processes involving vibrational cooling and acceleration of super-hot clusters can be studied directly.
- The Synthesis of films of oligo-polymers can be studied in well defined conditions with full control of the molecular degrees of freedom.
- An UHV apparatus combining PACIS and HSB sources will allow to study co-deposition and funtionalization processes.

Es: - OLIGO-TNIPHENES + C₆₀ → ELECTRON TRANSFER
+ NLO
PHOTOVOLTAIC ...
- ORGANIC + METAL CLUSTERS → "PHYSICAL" FUNCTIONALIZATION

