united nations
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international atomic
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the
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international centre for theoretical physics

SMR.1135 - 12

**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)**

"Microstructural and morphological evolution in transition metal nitrides"

**Joseph GREENE
University of Illinois at Urbana-Champaign
Frederic Seitz Materials Research Laboratory
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U.S.A.**

3rd ICTP/IUVSTA Workshop on Thin Film Physics
Trieste, Italy

Microstructural and Morphological Evolution in Transition Metal Nitrides

Joe Greene
University of Illinois

Tuesday, March 23, 8:30 to 10:30

Outline:

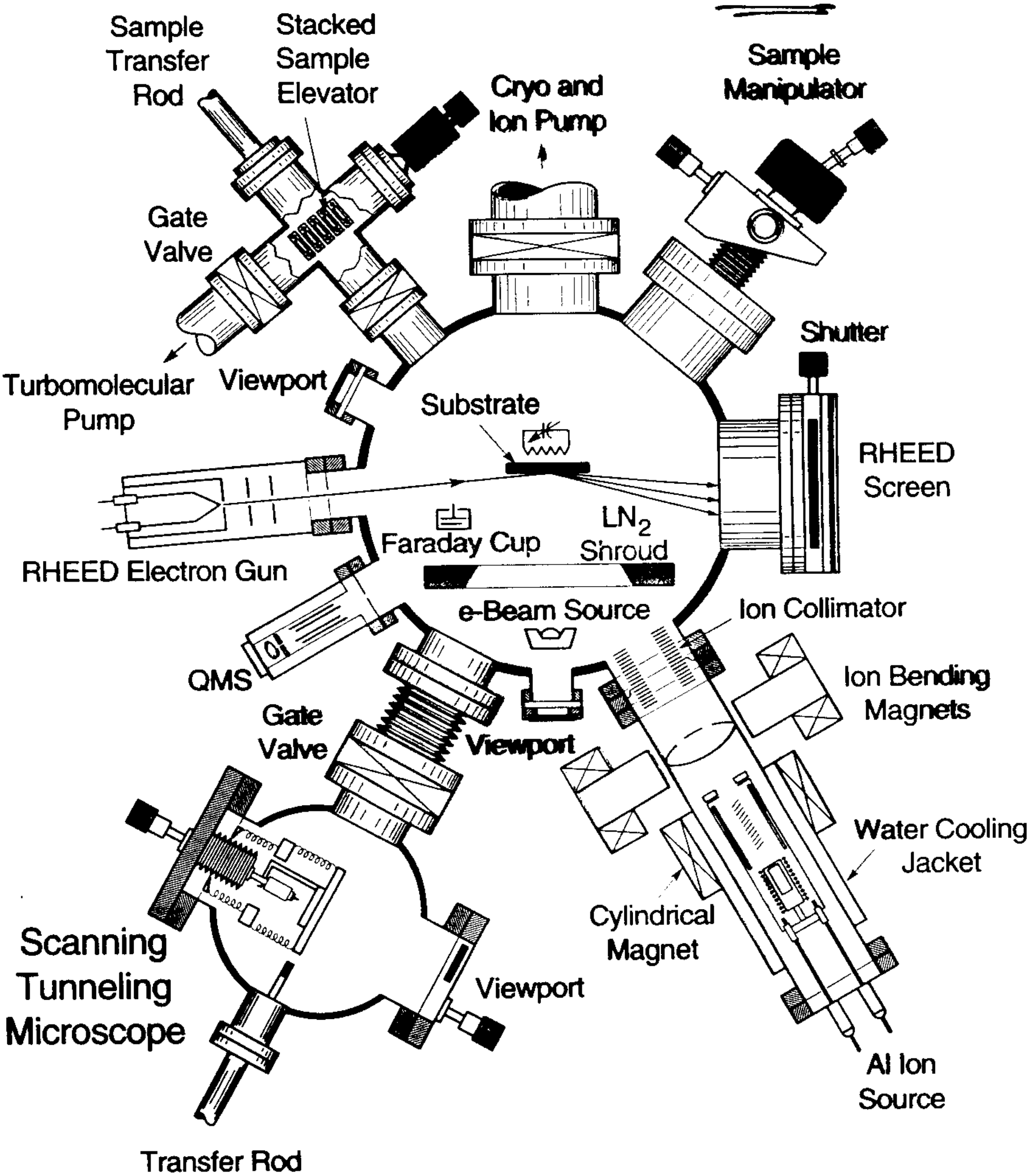
1. Microstructural evolution
   a. Preferred orientation
   b. Density
   c. Role of ion/surface interactions
2. Surface morphological evolution
   a. Kinetic roughening
   b. Layer-by-layer
   c. Role of ion/surface interactions

Microstructural & Surface Morphological Evolution during Film Growth: Role of Low-Energy Ion/Surface Interactions

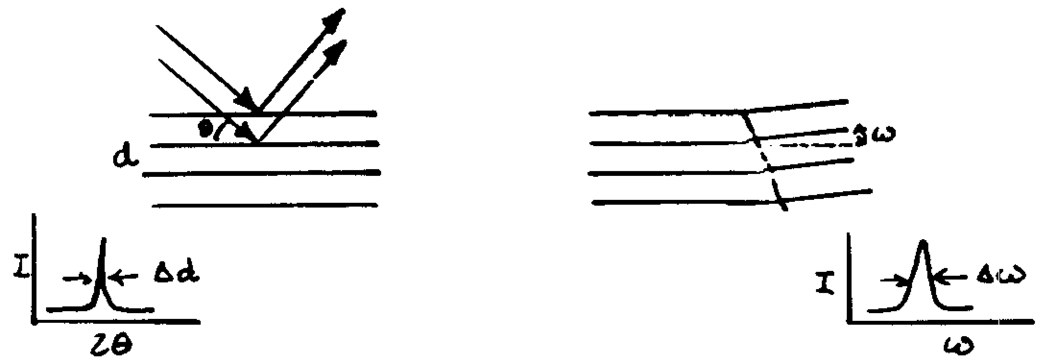
Joe Greene
Univ. Illinois, MRL

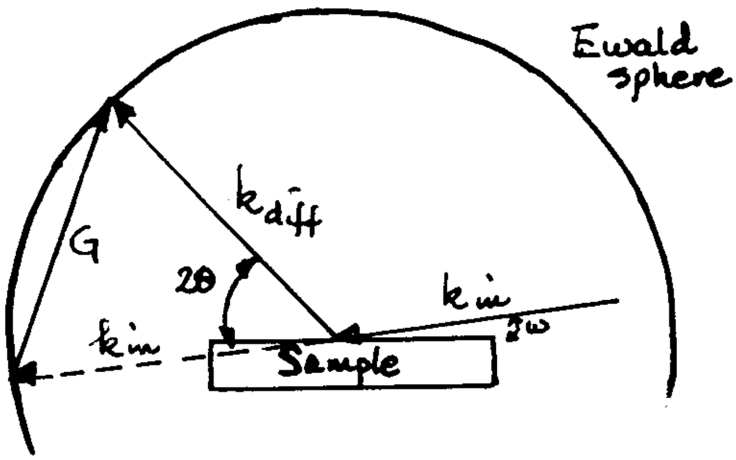
Funding: DOE and NSF/DARPA VIP

PID Al/SiO_2

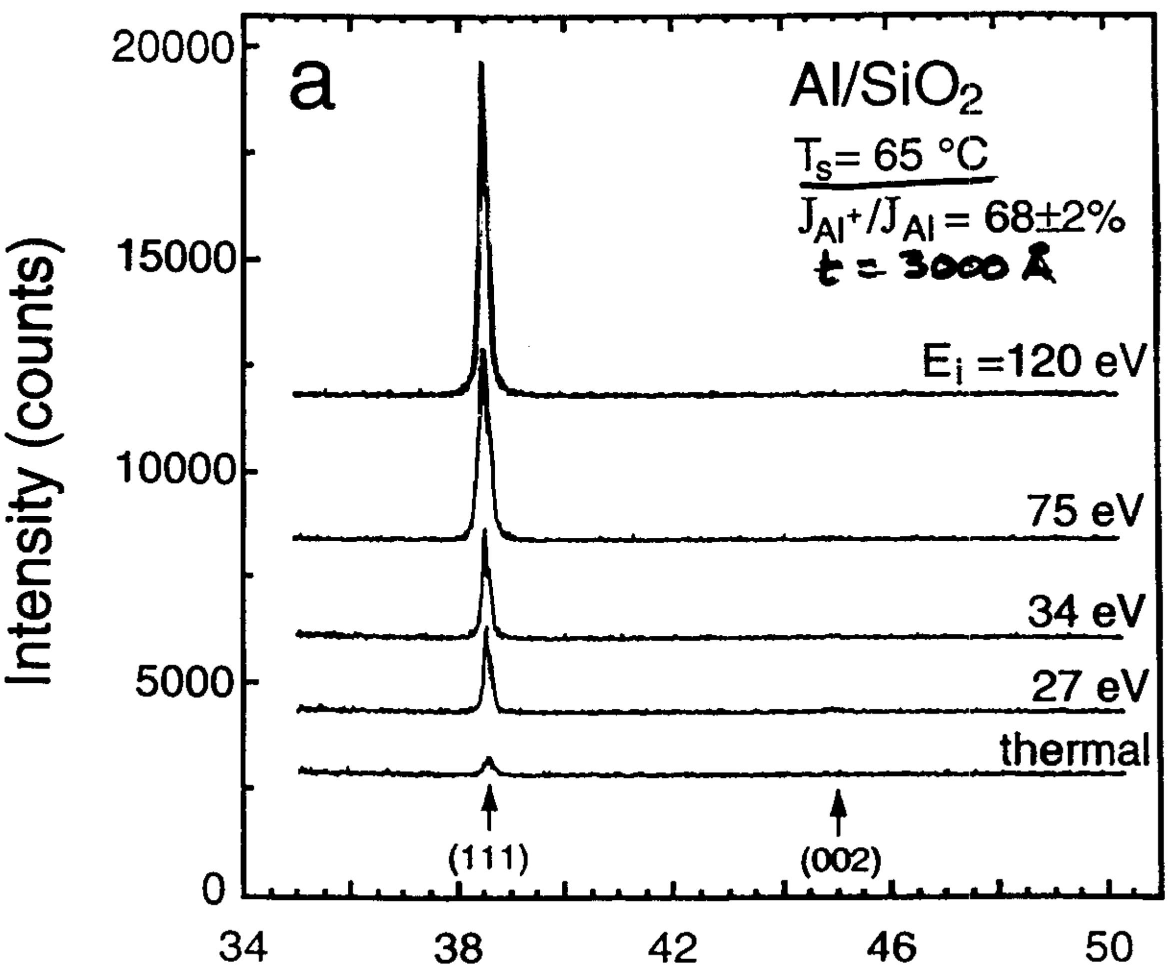


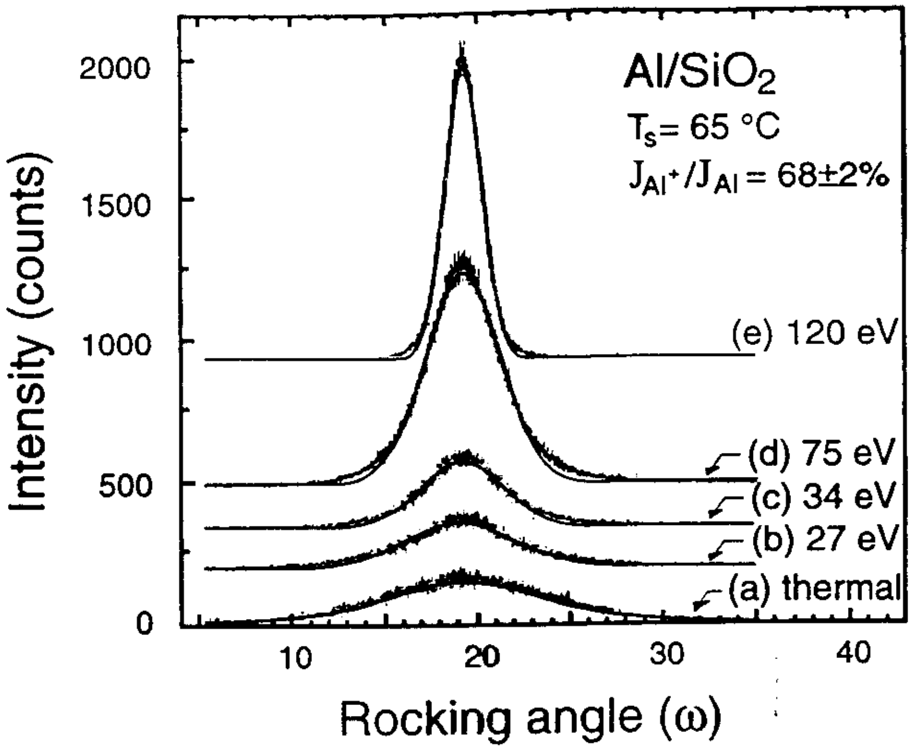
Kim, Petrov, Greene, Rossnagel.
J. Vac. Sci. Technol. A 14, 346



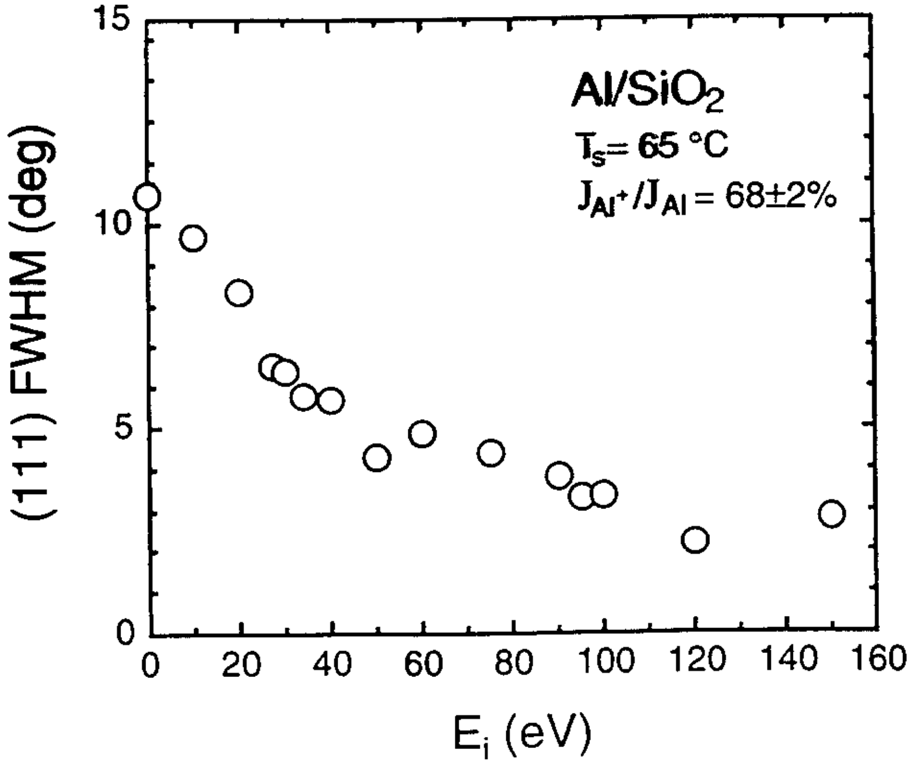


$\bar{k}_{diff} = \bar{k}_{in} + \bar{G}$





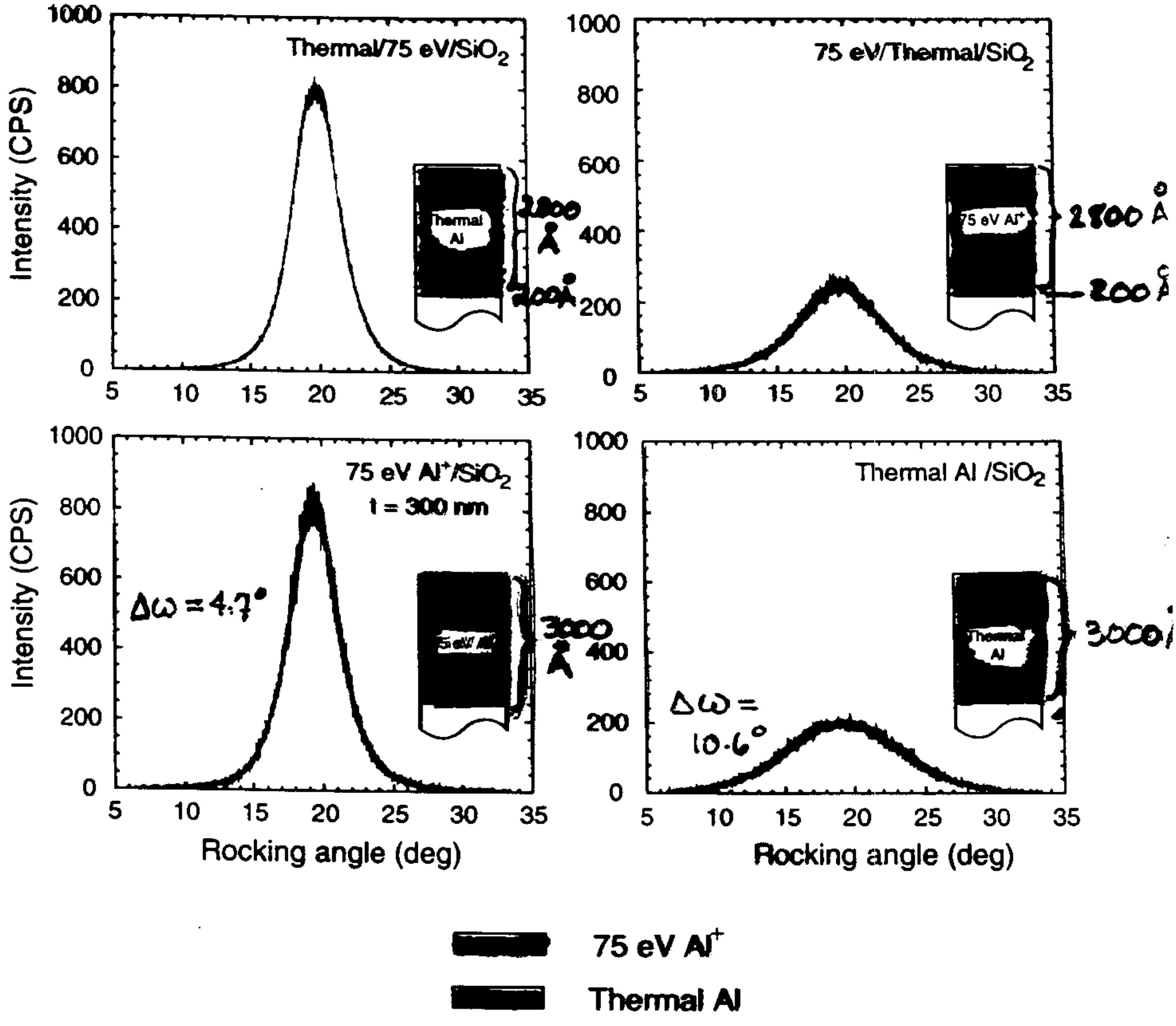
Al/SiO2
Ts= 65 °C
JAl+/JAl = 68±2%
(e) 120 eV
(d) 75 eV
(c) 34 eV
(b) 27 eV
(a) thermal
Intensity (counts)
Rocking angle (ω)



Al/SiO2
Ts= 65 °C
JAl+/JAl = 68±2%
(111) FWHM (deg)
Ei (eV)

Al /SiO_2

t = 300 nm T_s = 65 °C

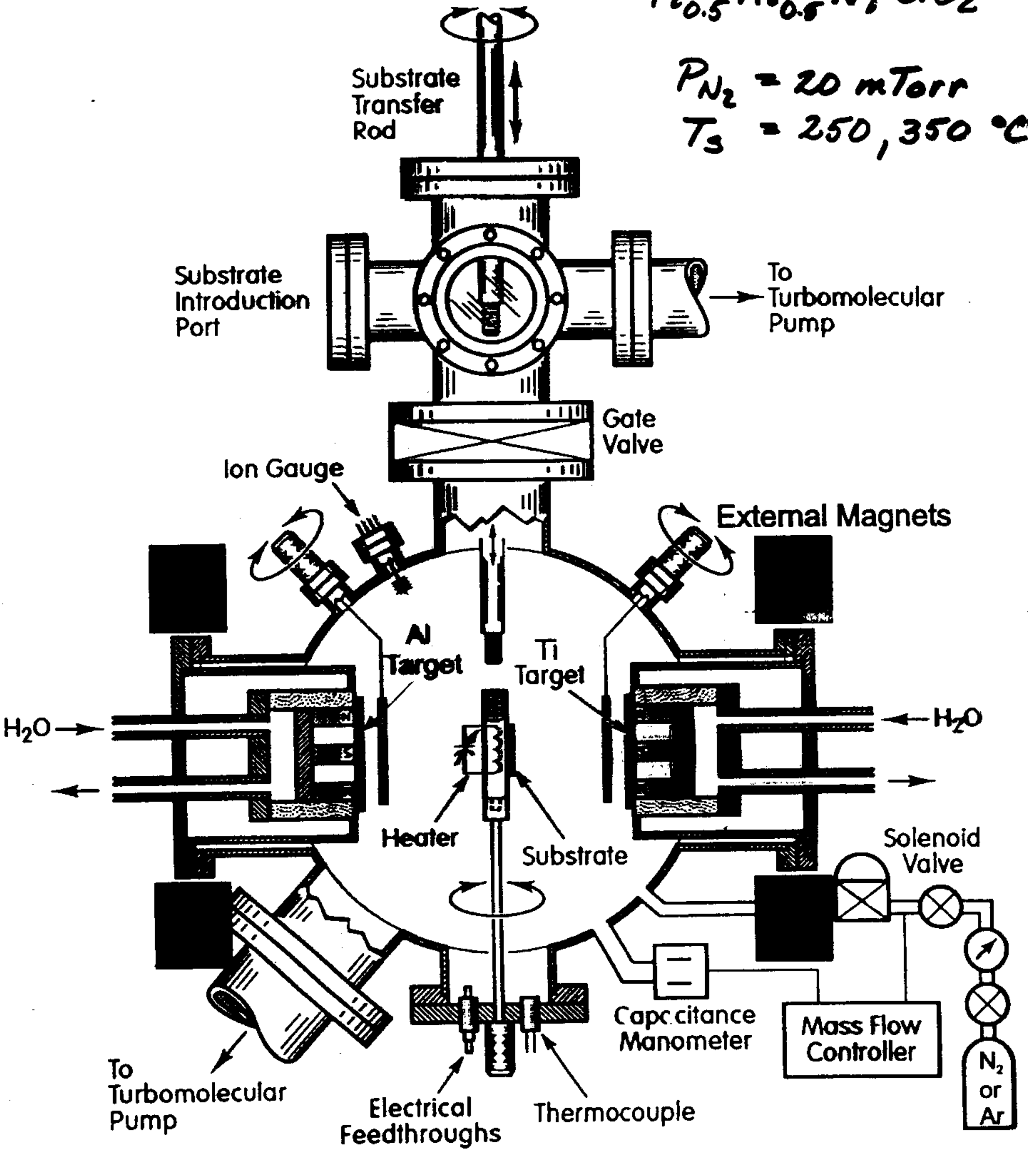


TiN/SiO$_2$

Ti$_{0.5}$Al$_{0.5}$N/SiO$_2$

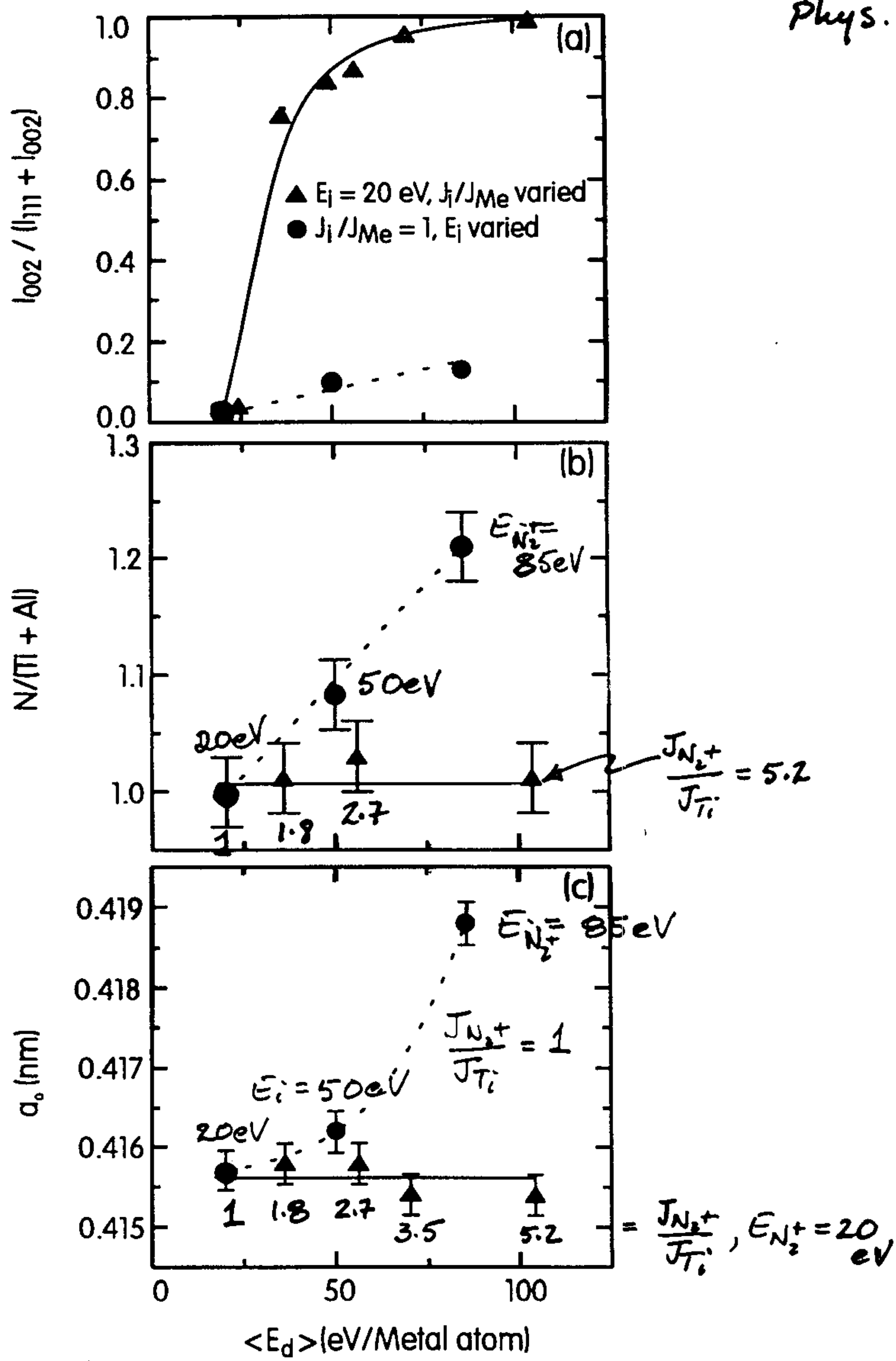
P_{N_2} = 20 mTorr

T_s = 250, 350 °C

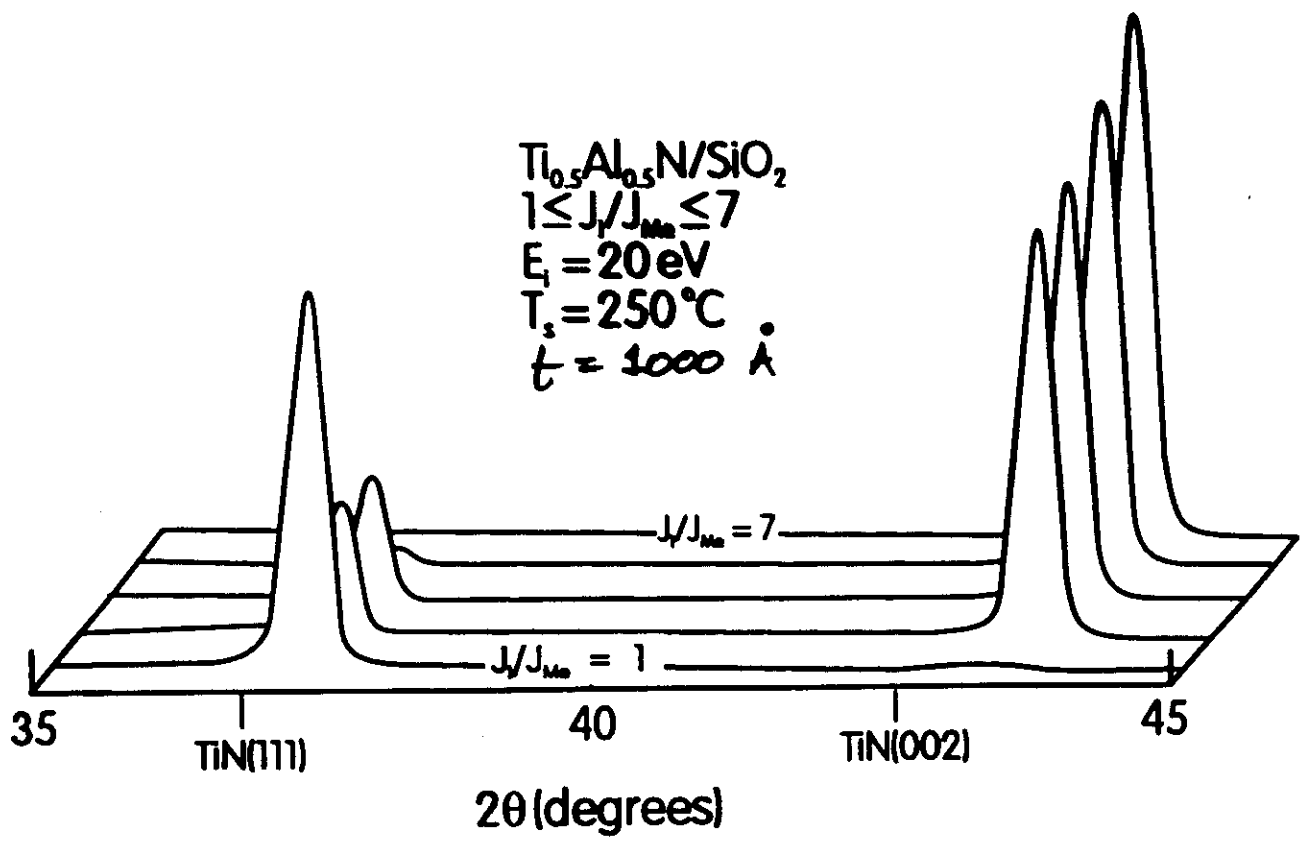


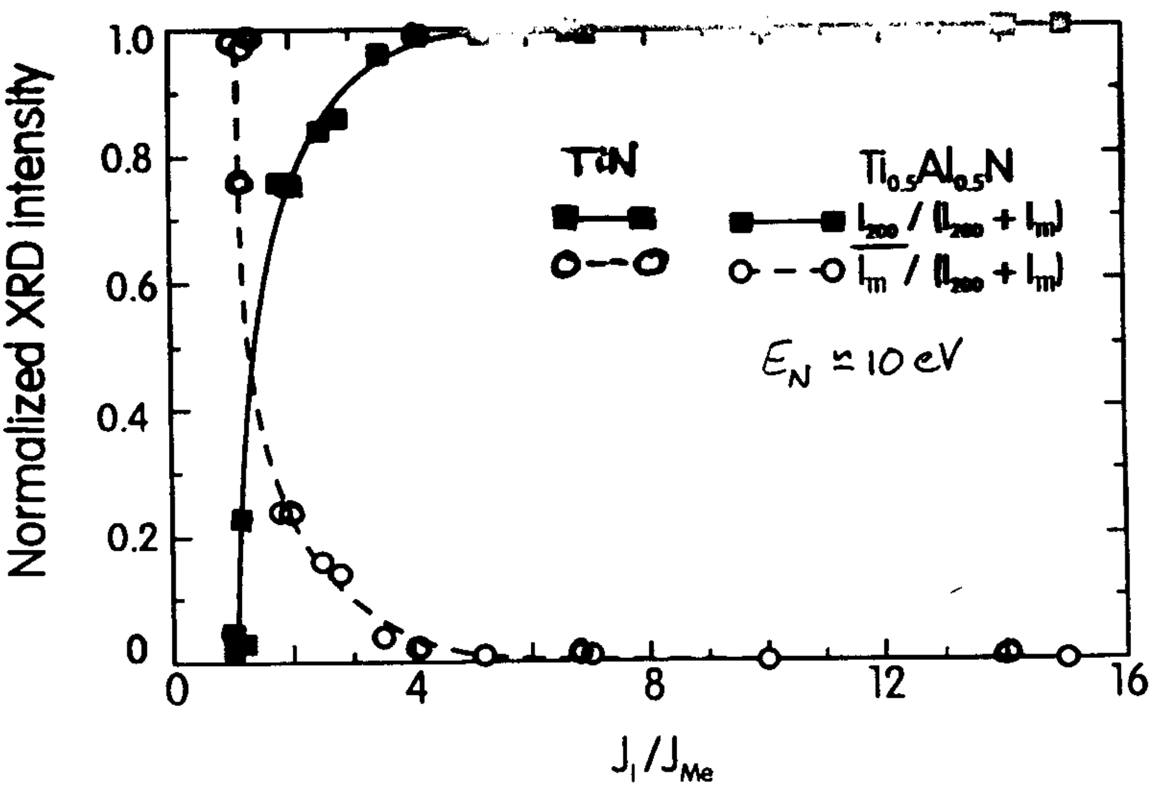
I. Petrov, F. Adibi, J.E. Greene, W.D. Sproul, W-D Münz
JVST A

Greene, Sundgren, Hultman, Petrov, Bergstrom, APL + J. Appl. Phys.

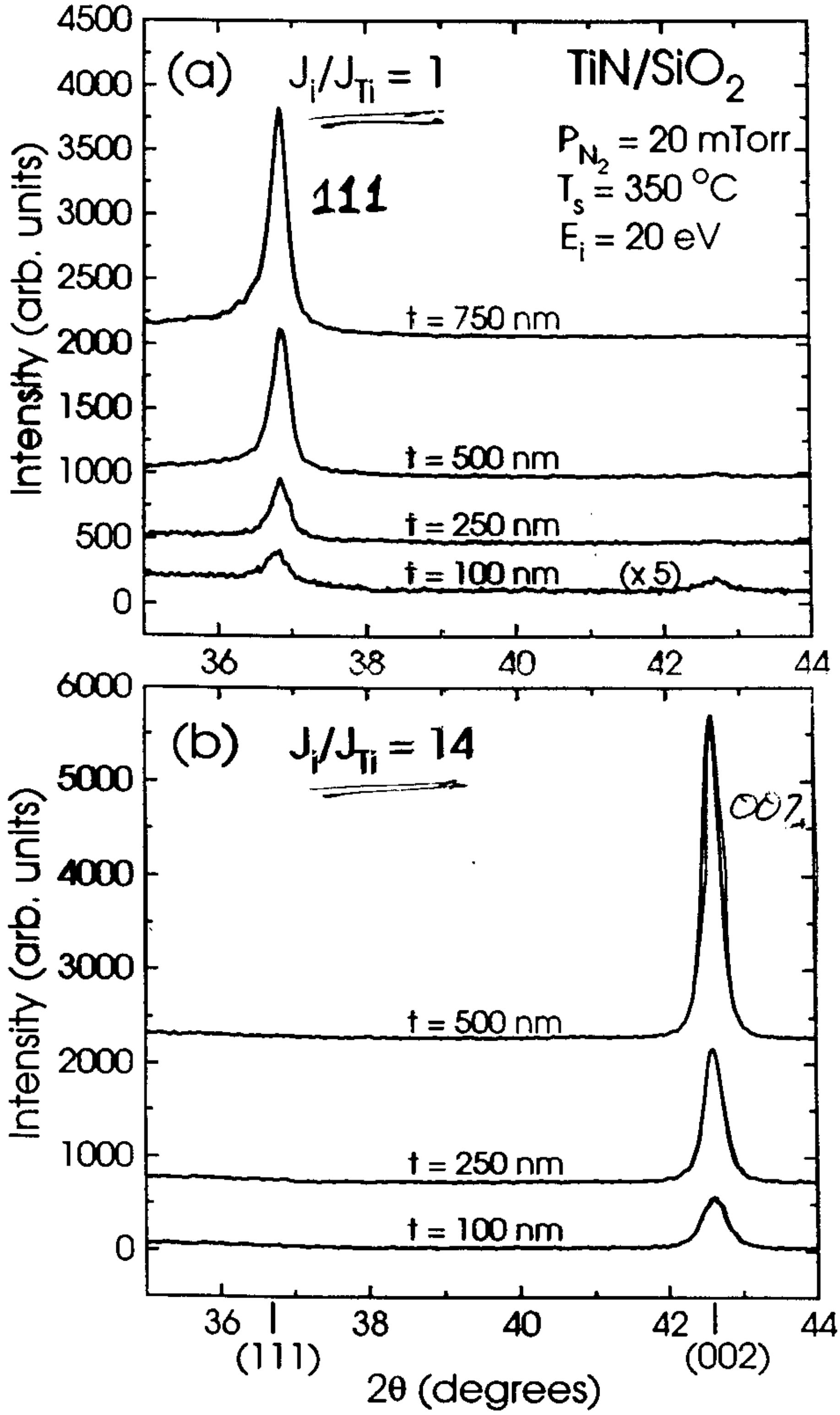


$$\langle E_d \rangle = E_{N_2^+}\left(\frac{J_{N_2^+}}{J_{Ti}}\right)$$

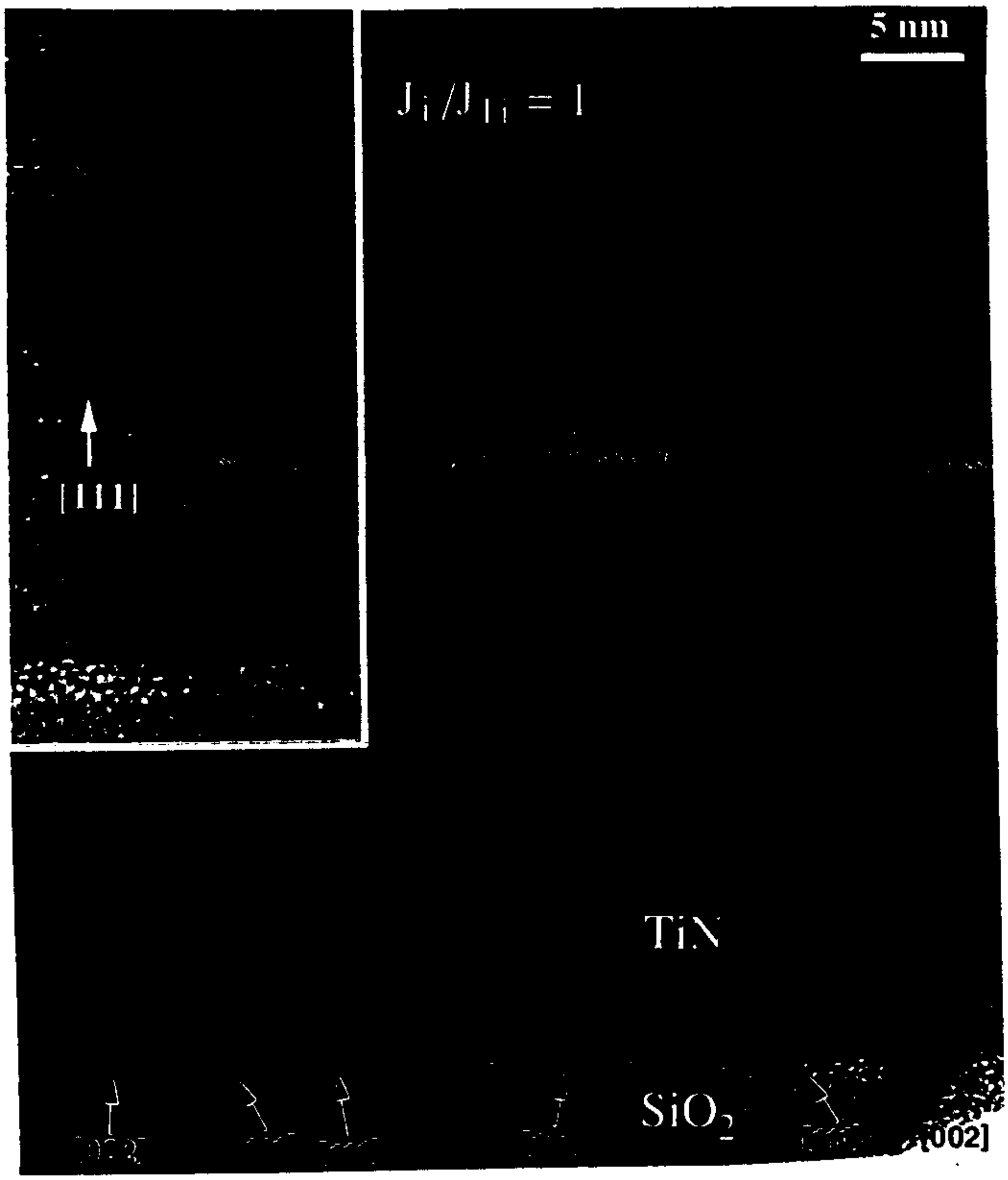




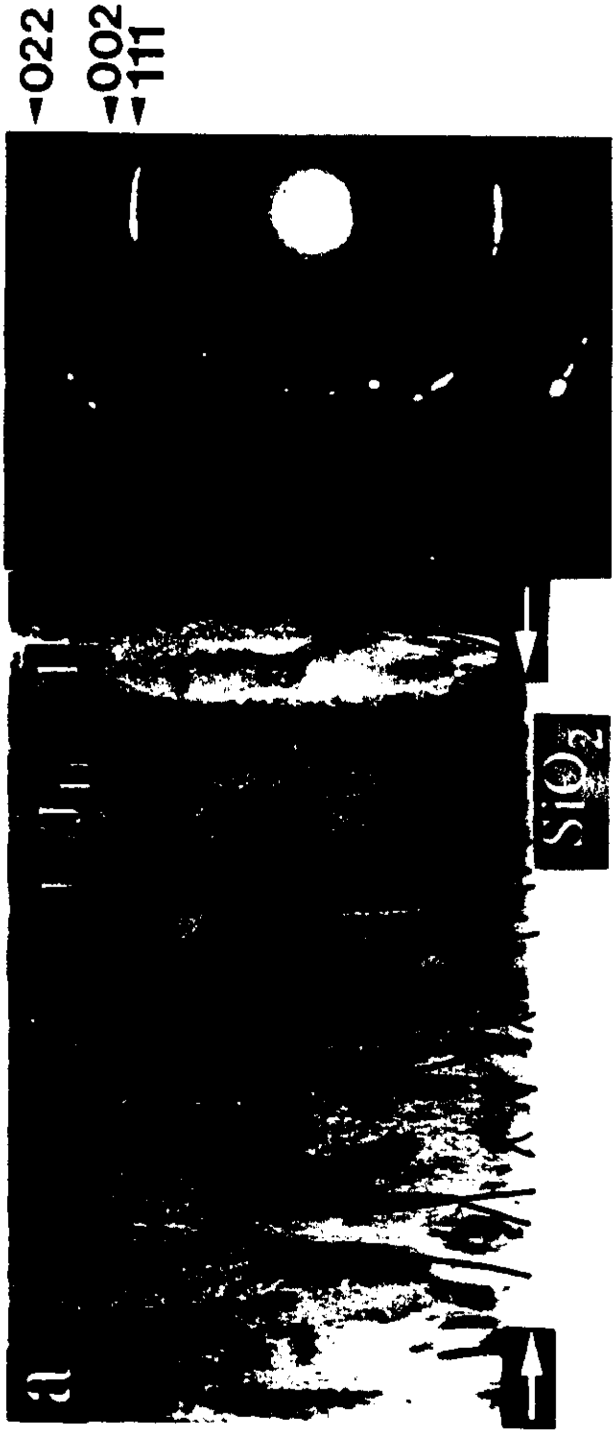
F. Adibi, I. Petrov, J.E. Greene, L. Hultman
J.-E. Sundgren, J. Appl. Phys.



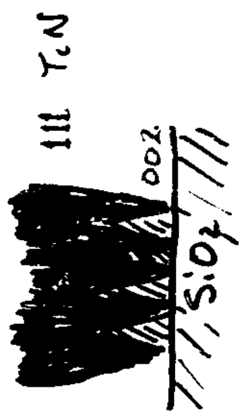
(a) J_i/J_{Ti} = 1
TiN/SiO$_2$
P_{N_2} = 20 mTorr
T_s = 350 °C
E_i = 20 eV
111
t = 750 nm
t = 500 nm
t = 250 nm
t = 100 nm (x 5)
Intensity (arb. units)
(b) J_i/J_{Ti} = 14
002
t = 500 nm
t = 250 nm
t = 100 nm
Intensity (arb. units)
(111)
(002)
2θ (degrees)



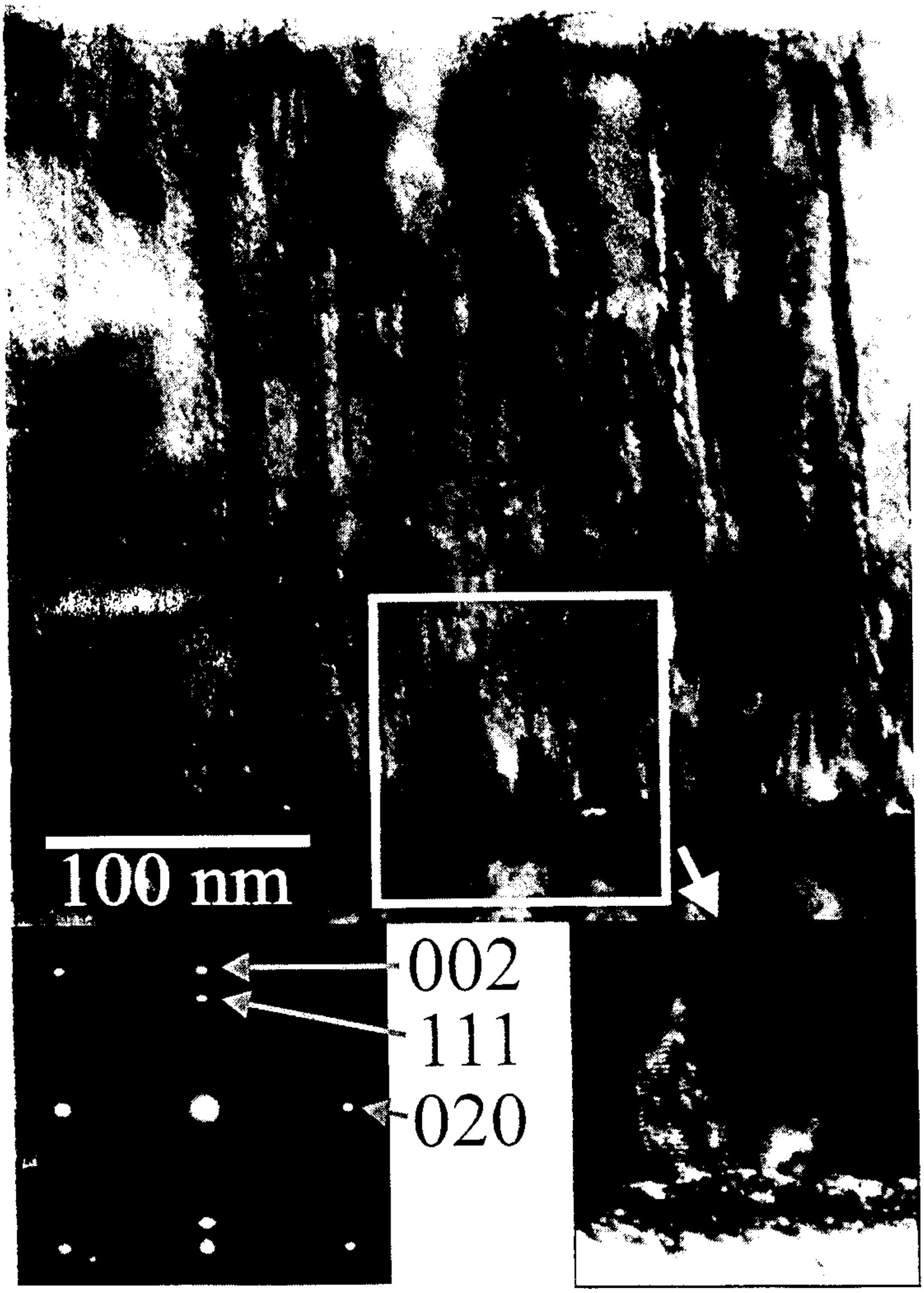
5 nm
TiN
SiO$_2$
[002]



022
002
111
a
SiO2

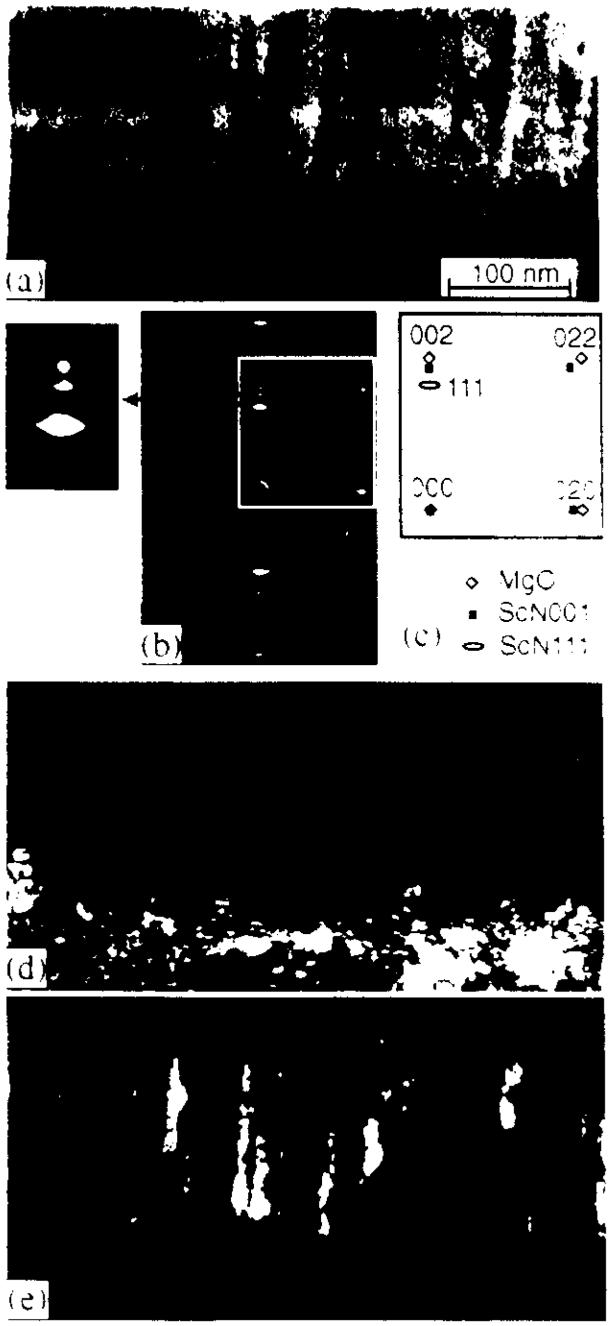


111 TiN
002
SiO2


100 nm
002
111
020

ScN/MgO(001)

T = 750 °C



(001)$_{ScN}$ ∥ (001)$_{MgO}$
[010]$_{ScN}$ ∥ [010]$_{MgO}$

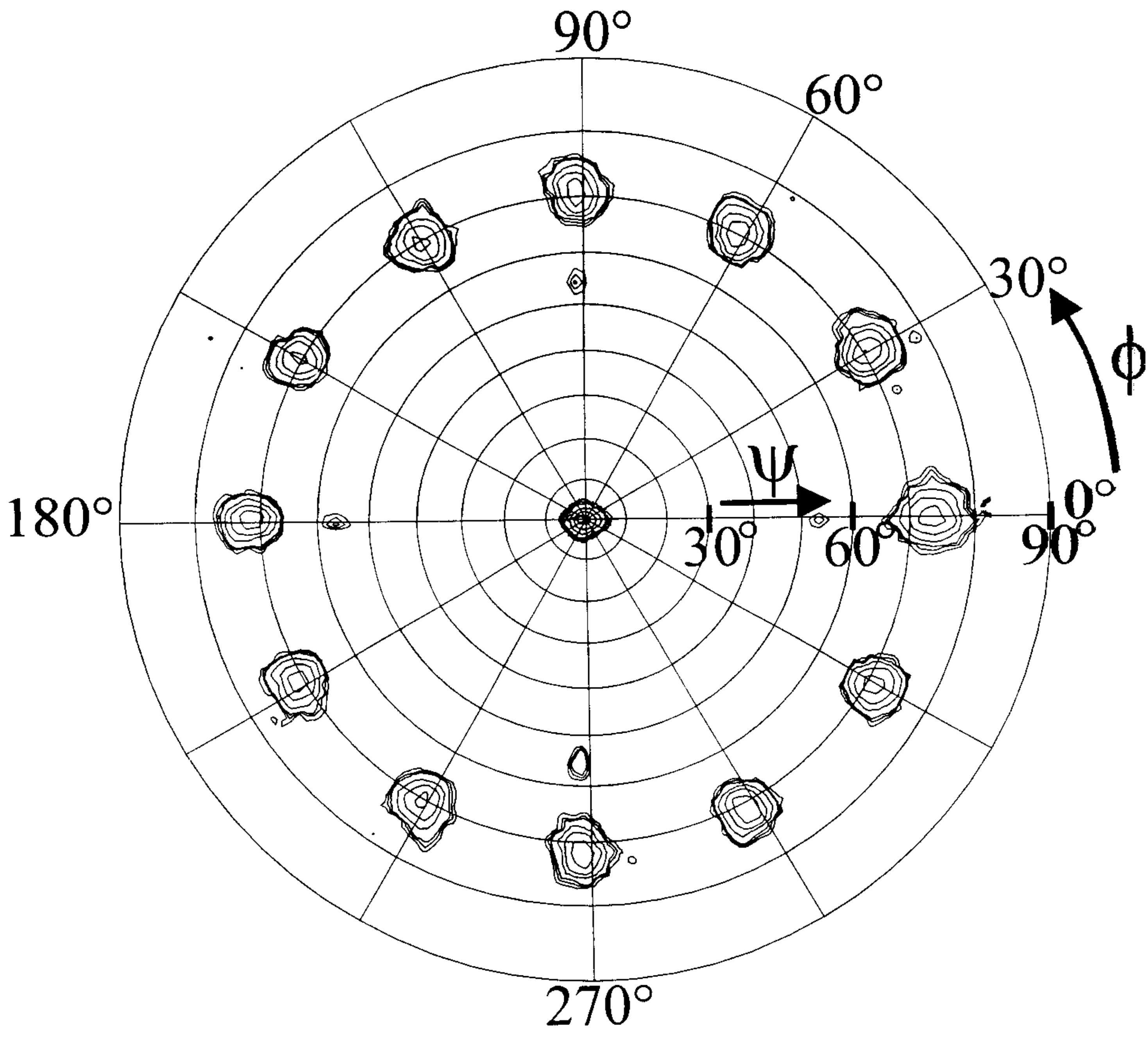
(111)$_{ScN}$ ∥ (001)$_{MgO}$
[11$\bar{2}$]$_{ScN}$ ∥ [110]$_{MgO}$
[1$\bar{1}$0]$_{ScN}$ ∥ [1$\bar{1}$0]$_{MgO}$

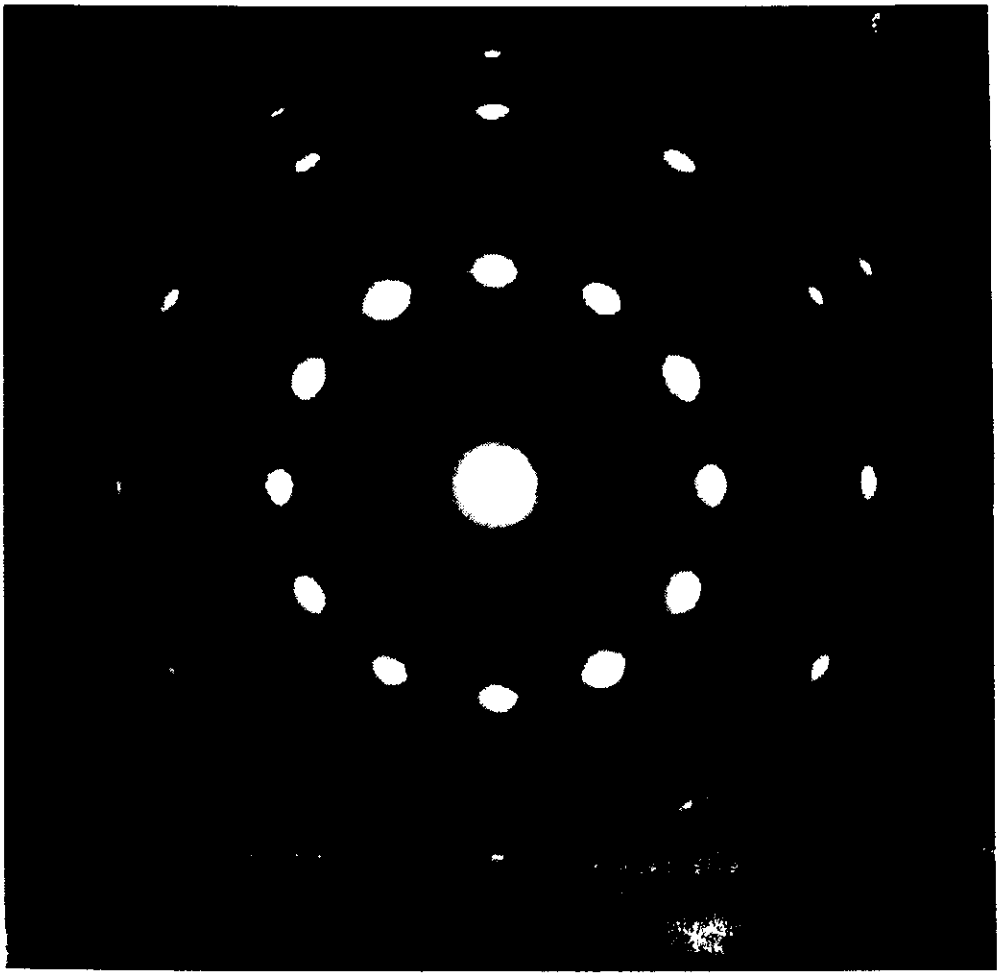
D. Gall, I. Petrov, L.D. Madsen, J.-E. Sundgren, J.E. Greene
J. Vac. Sci. Technol. A 16, 2411 (1998).

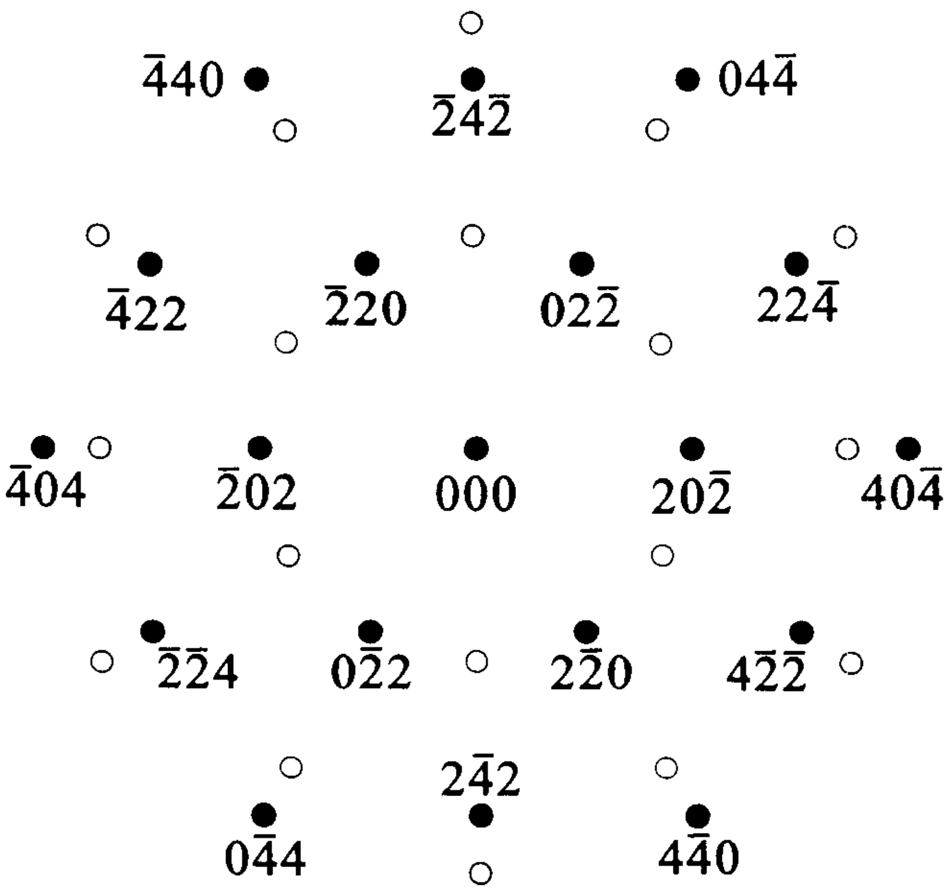
ScN/MgO(001)

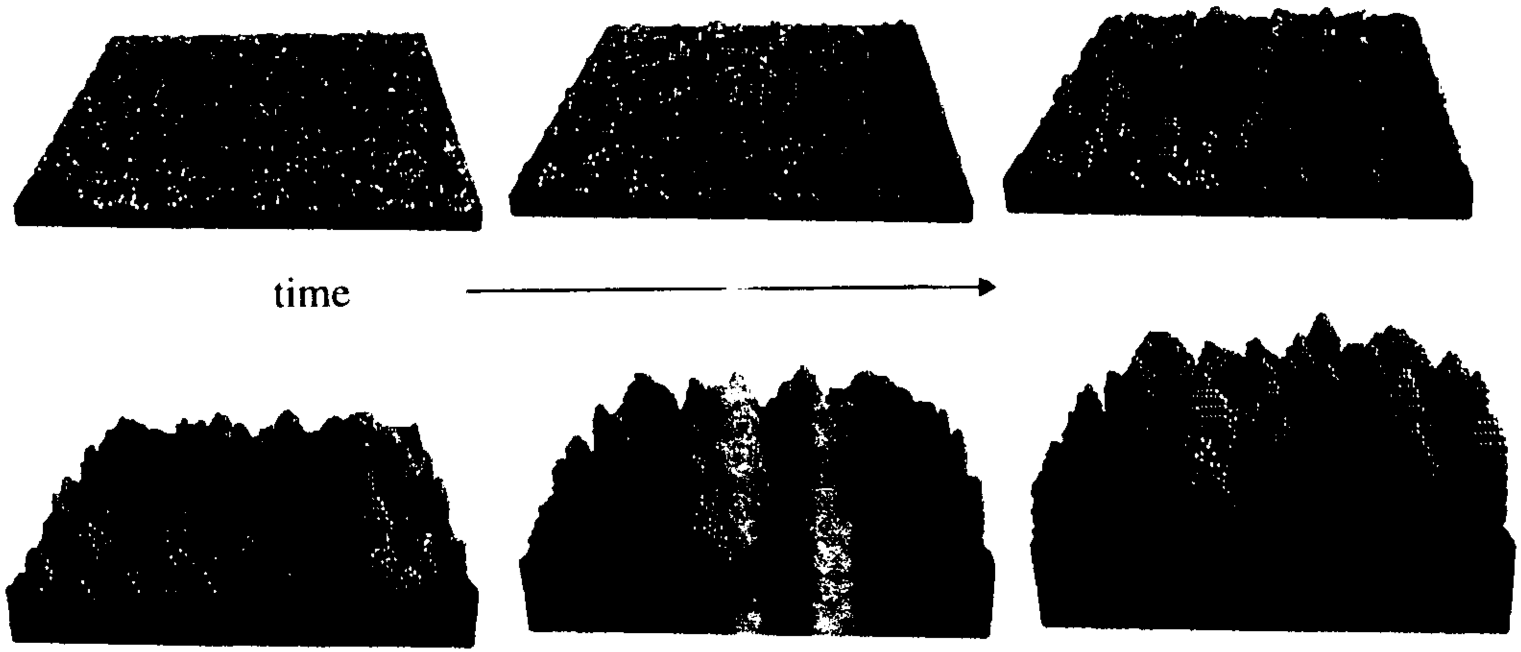
ScN(111) - pole figure

$2\theta = 34.415°$

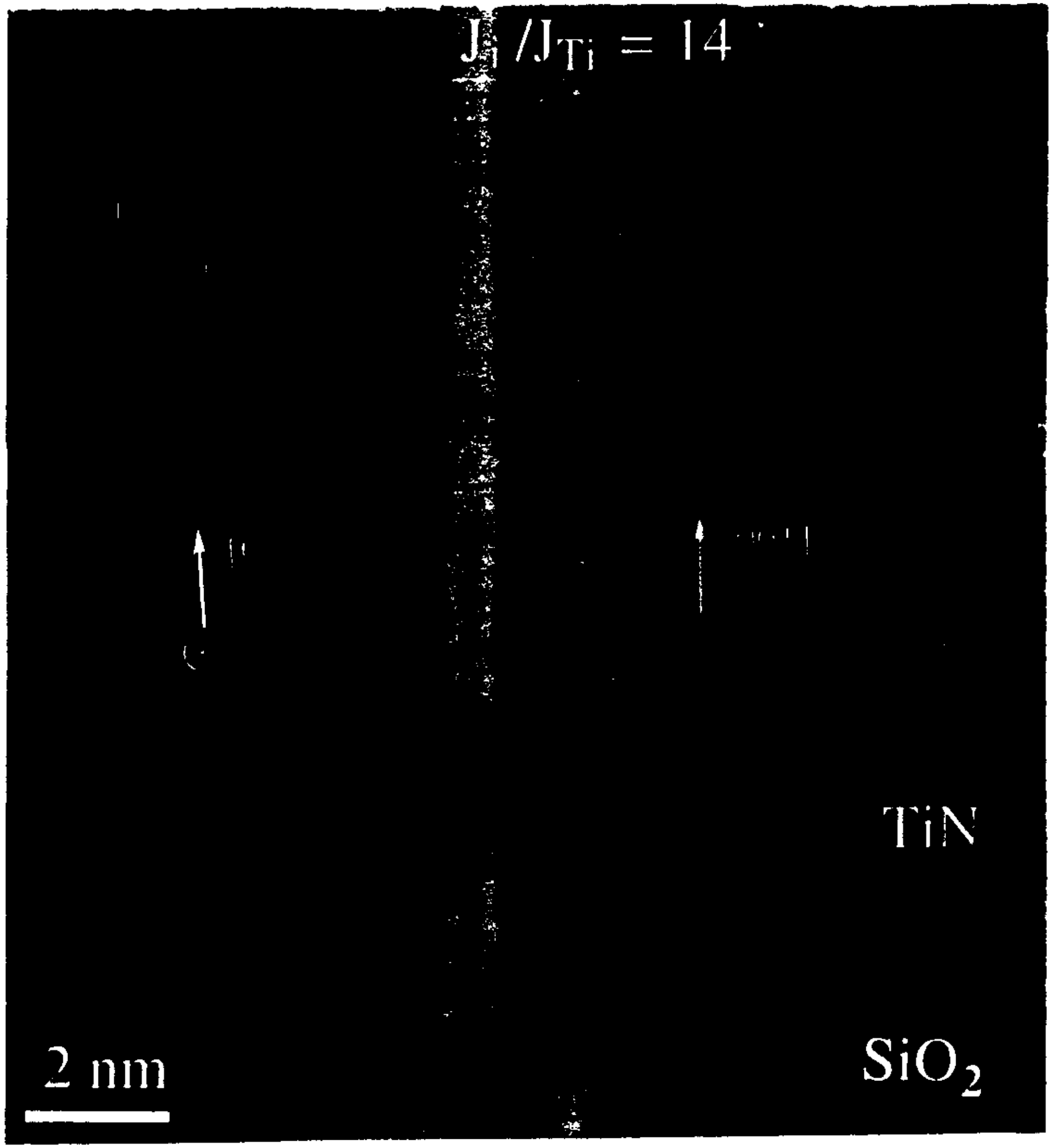


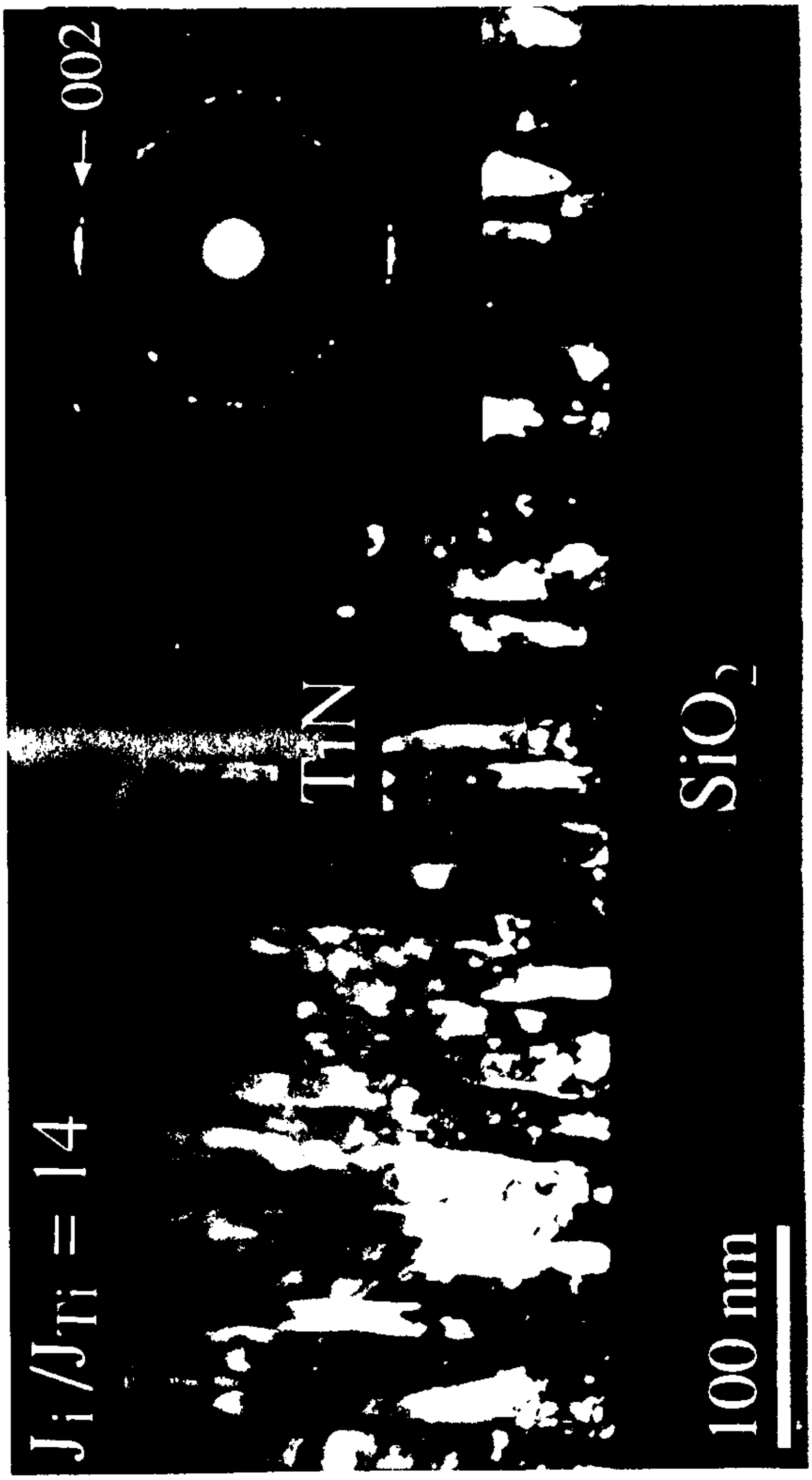



$\bar{4}40$
$\bar{2}4\bar{2}$
$04\bar{4}$
$\bar{4}22$
$\bar{2}20$
$02\bar{2}$
$22\bar{4}$
$\bar{4}04$
$\bar{2}02$
000
$20\bar{2}$
$40\bar{4}$
$\bar{2}\bar{2}4$
$0\bar{2}2$
$2\bar{2}0$
$4\bar{2}\bar{2}$
$2\bar{4}2$
$0\bar{4}4$
$4\bar{4}0$

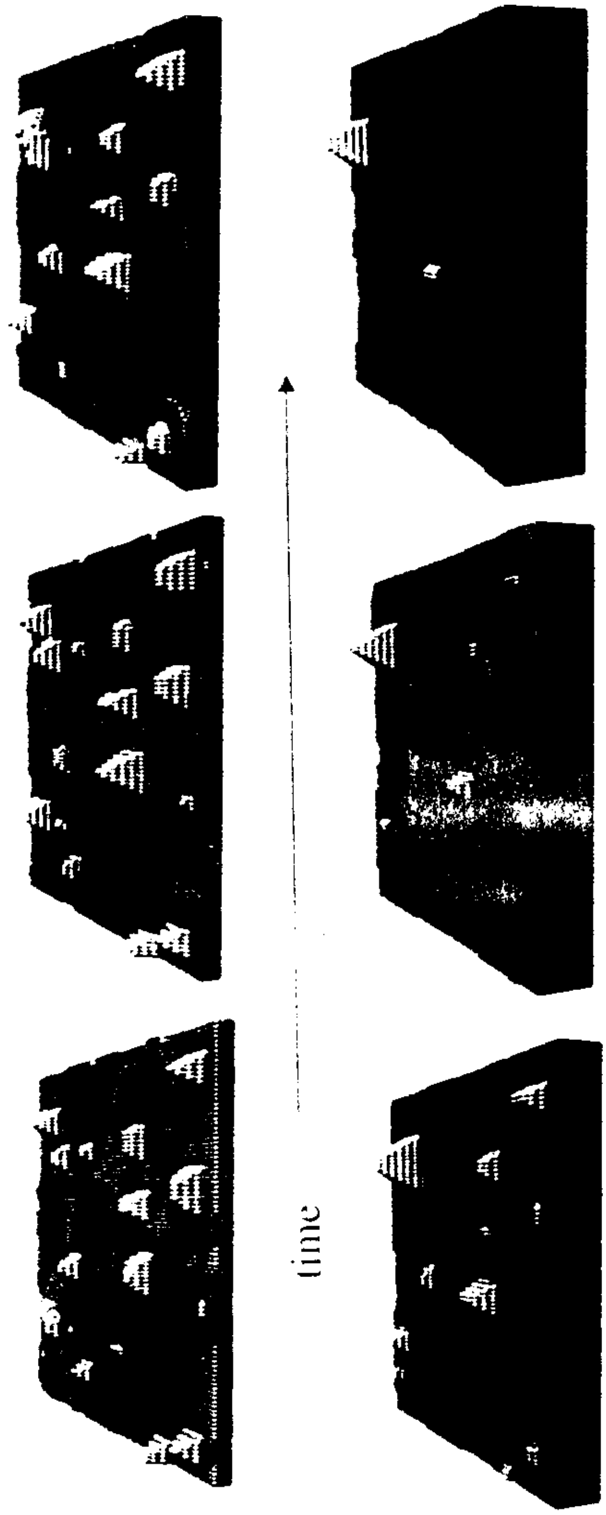


de la Rubia, Gilmore, Greene, Hull, Chopp, Sowers, Sethian
VIP Review, NSF/DARPA, Champaign, IL, Oct, '98


$J_i/J_{Ti} = 14$
TiN
SiO_2
2 nm



$J_i / J_{Ti} = 14$
002
TiN
SiO_2
100 nm

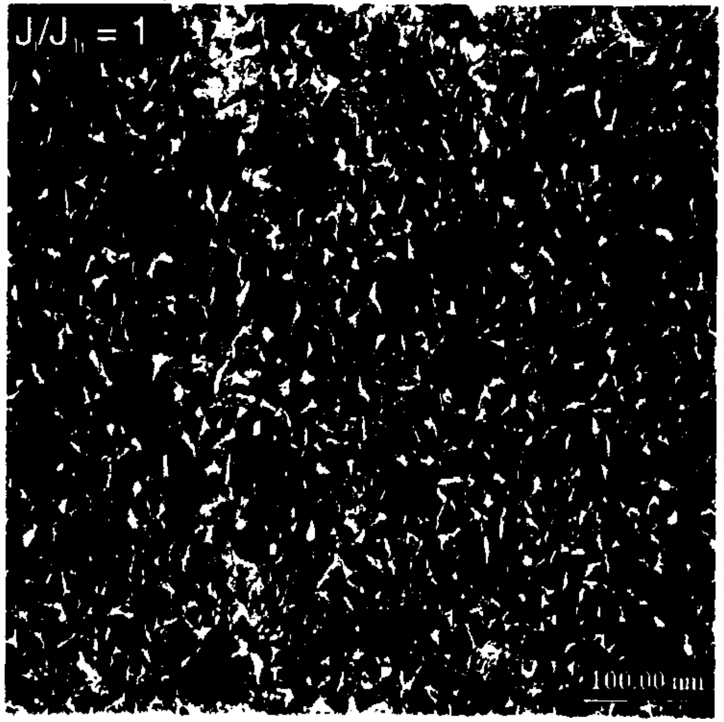

time

TiN/SiO$_2$

T_s = 350°C

$E_{N_2^+}$ = 20 eV

J_i/J_{Ti} = 1



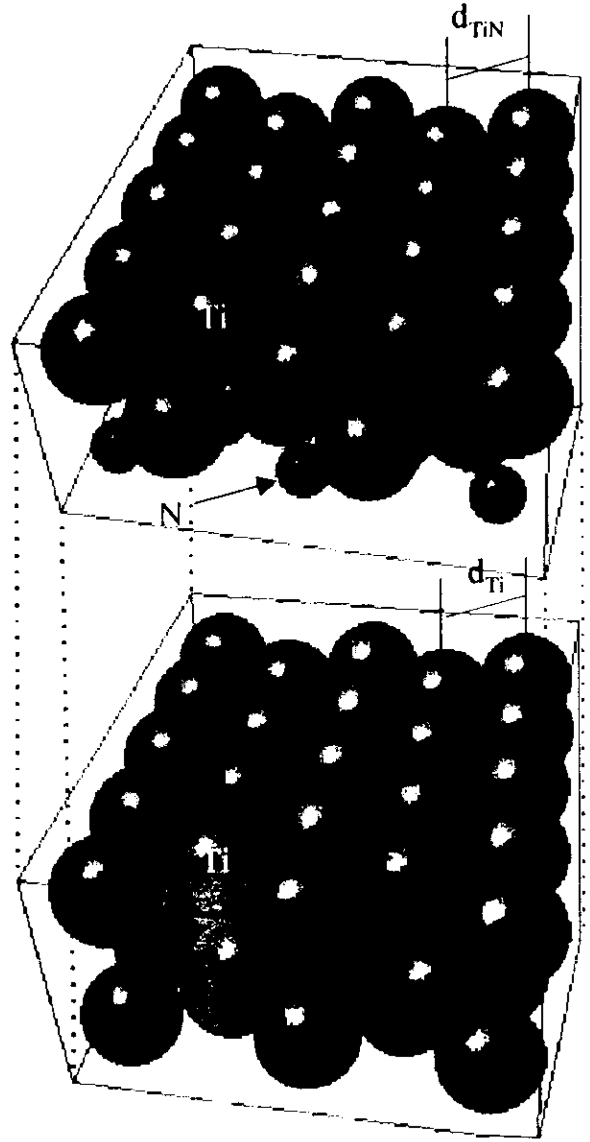
t = 1600 Å

<u>underdense</u>!

intra- and intercolumnar voids

TiN(111)
overlayer

d_{TiN} = 0.29995 nm



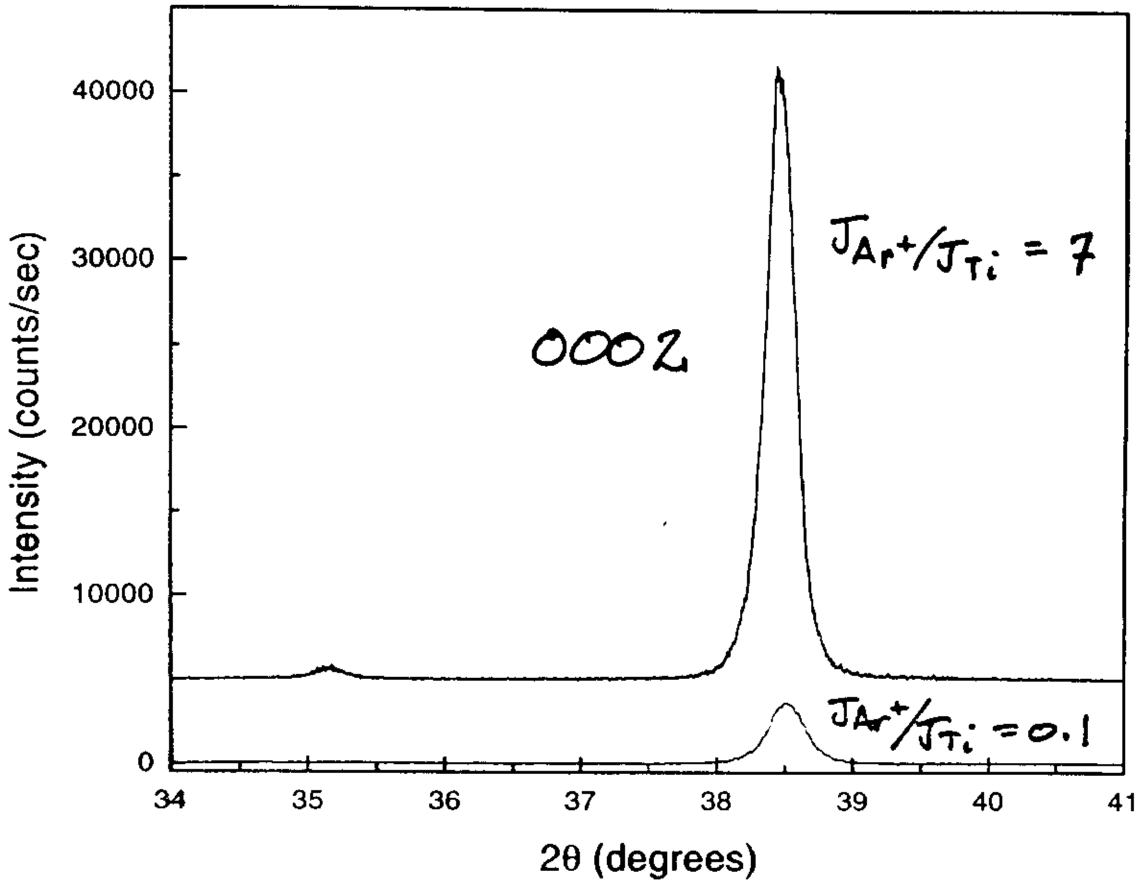
Ti(0002)
crystallographic
template

d_{Ti} = 0.29053 nm

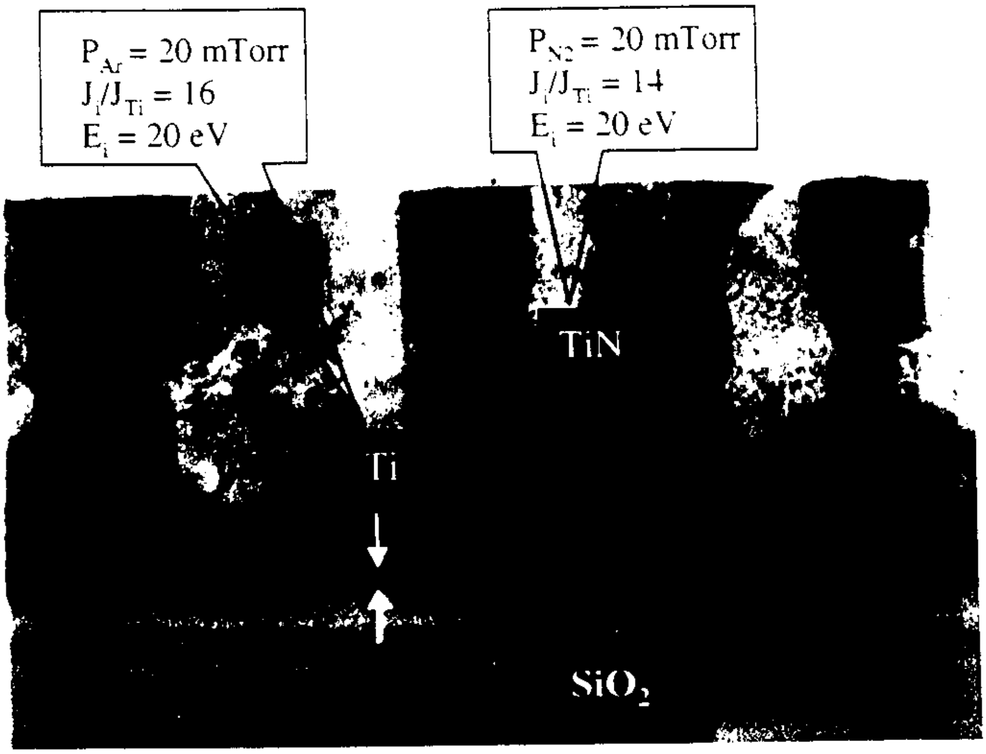
- Ti(0002)/TiN(111) misfit ≅ 1.6 %

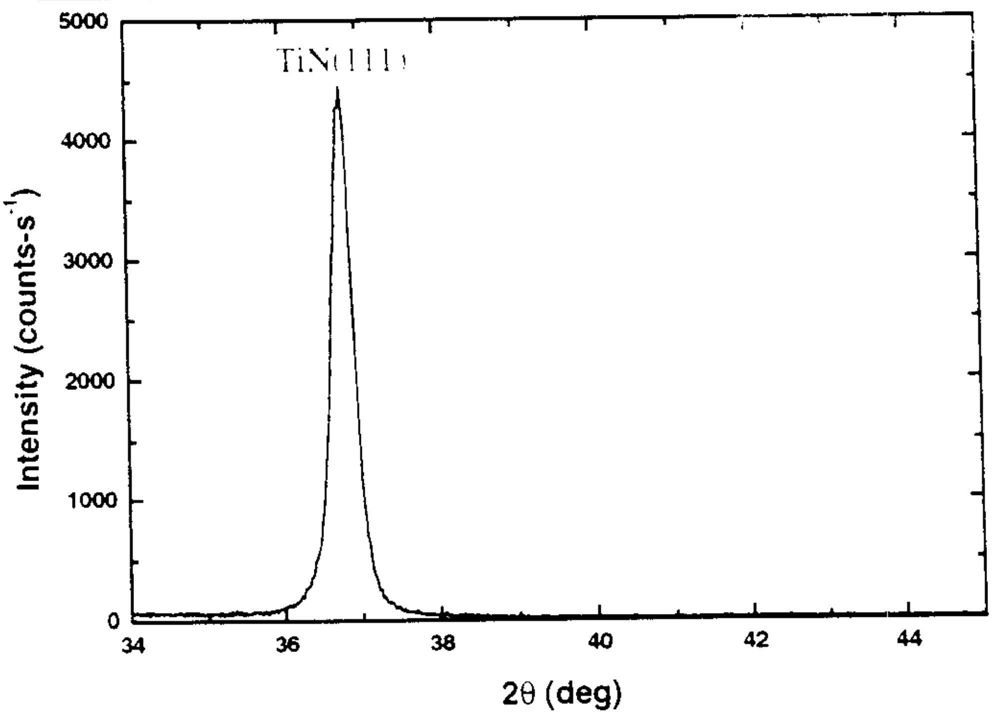
Ti / SiO$_2$

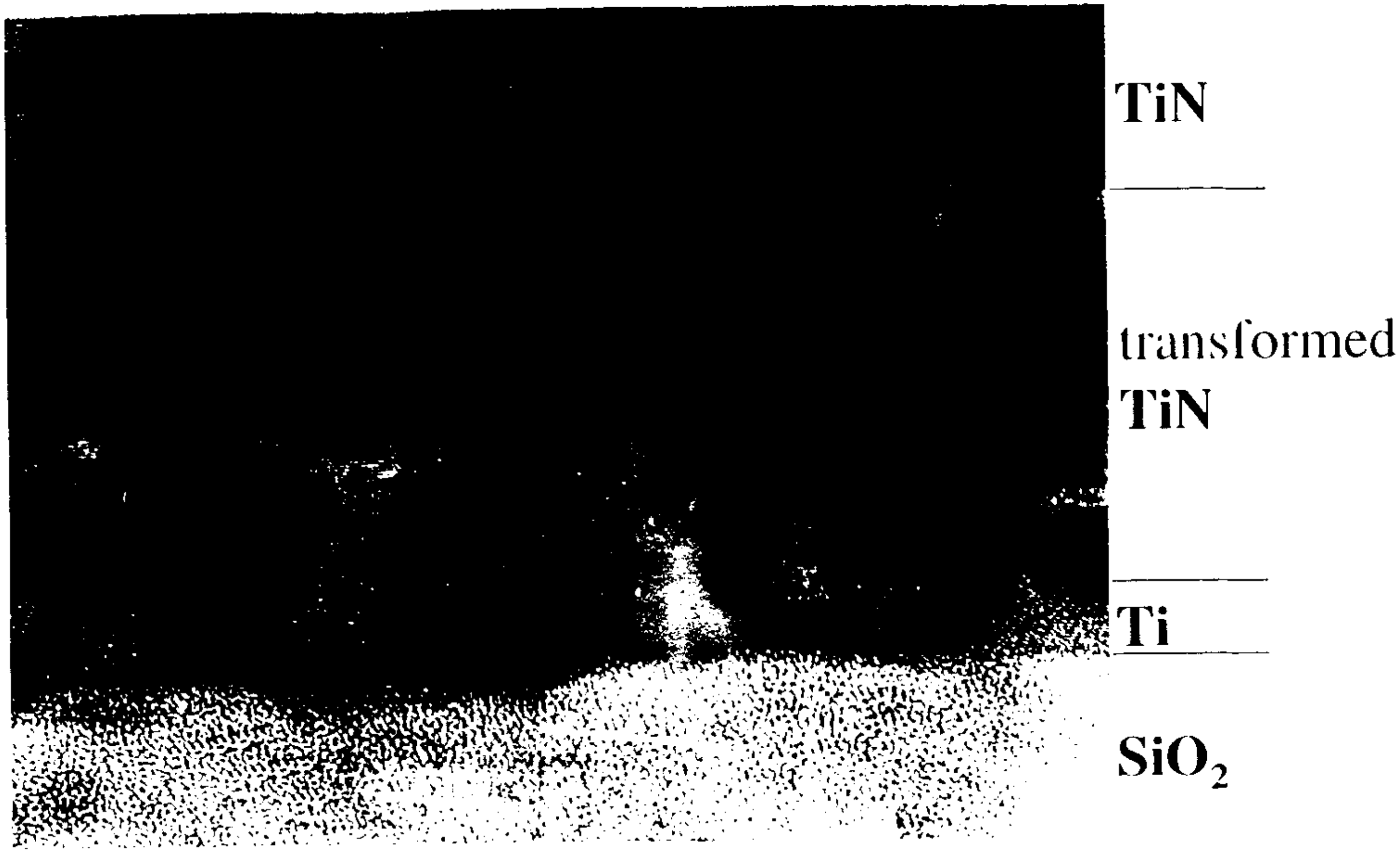
$T_s = 120\,°C$, $P_{Ar} = 20$ mTorr, $t = 0.3\,\mu m$



$E_{Ar^+} = 10$ eV

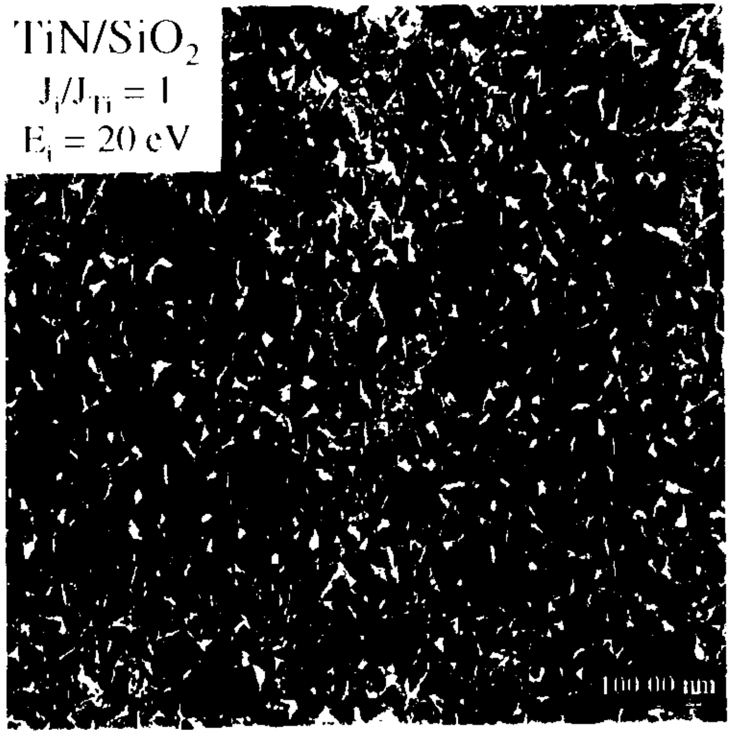

P_{Ar} = 20 mTorr
J_i/J_{Ti} = 16
E_i = 20 eV
P_{N2} = 20 mTorr
J_i/J_{Ti} = 14
E_i = 20 eV
TiN
Ti
SiO_2


TiN(111)
Intensity (counts-s^{-1})
2θ (deg)
0
1000
2000
3000
4000
5000
34
36
38
40
42
44


TiN
transformed TiN
Ti
SiO_2

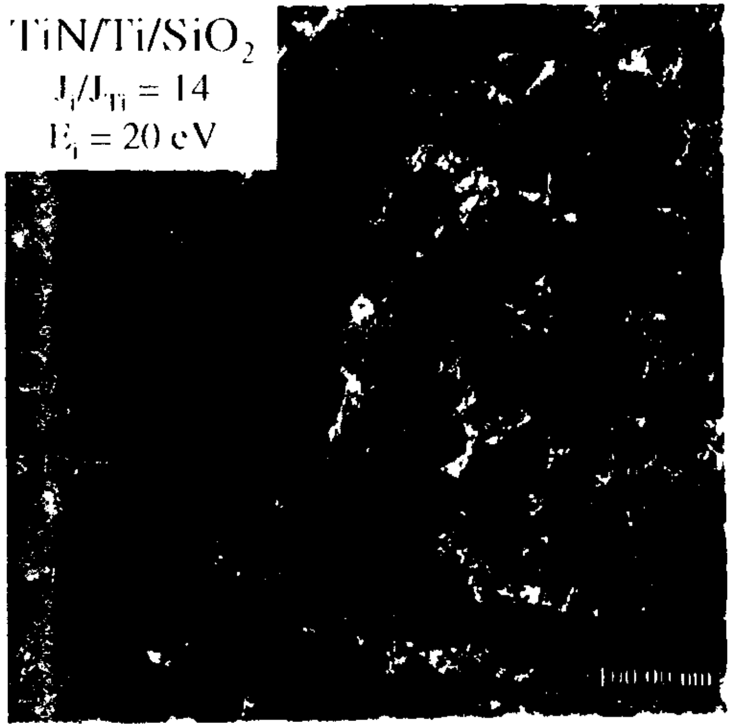
Texture control: TiN/Ti

TiN/SiO$_2$
$J_i/J_{Ti} = 1$
$E_i = 20$ eV



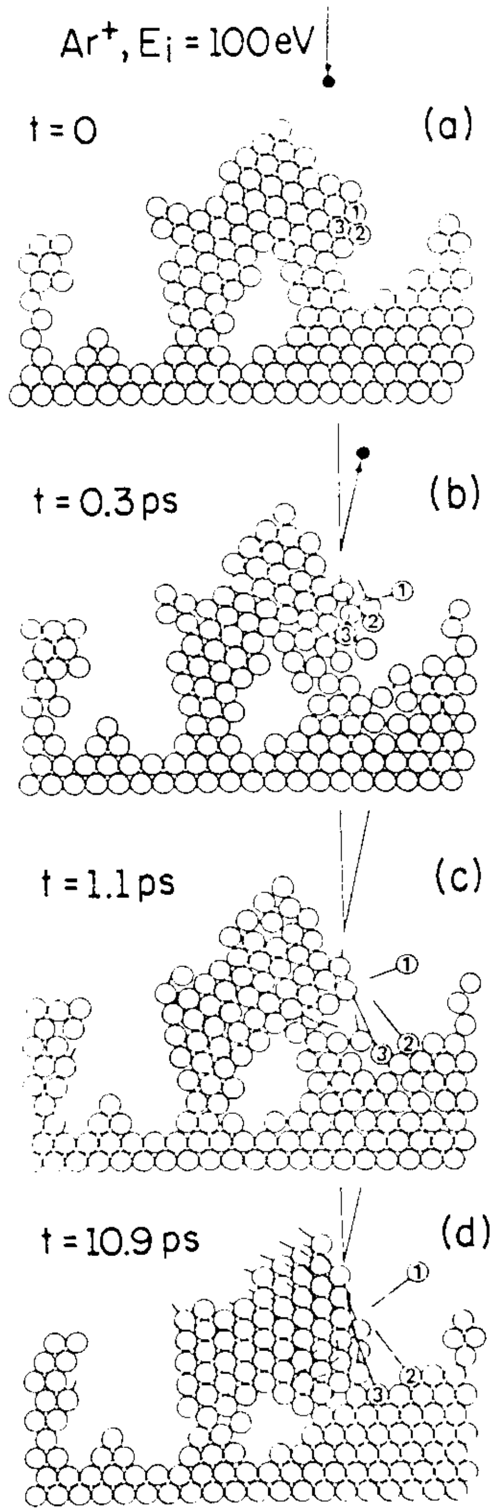
- Underdense 111 TiN
- $\langle d \rangle = 20 \pm 14$ nm

TiN/Ti/SiO$_2$
$J_i/J_{Ti} = 14$
$E_i = 20$ eV

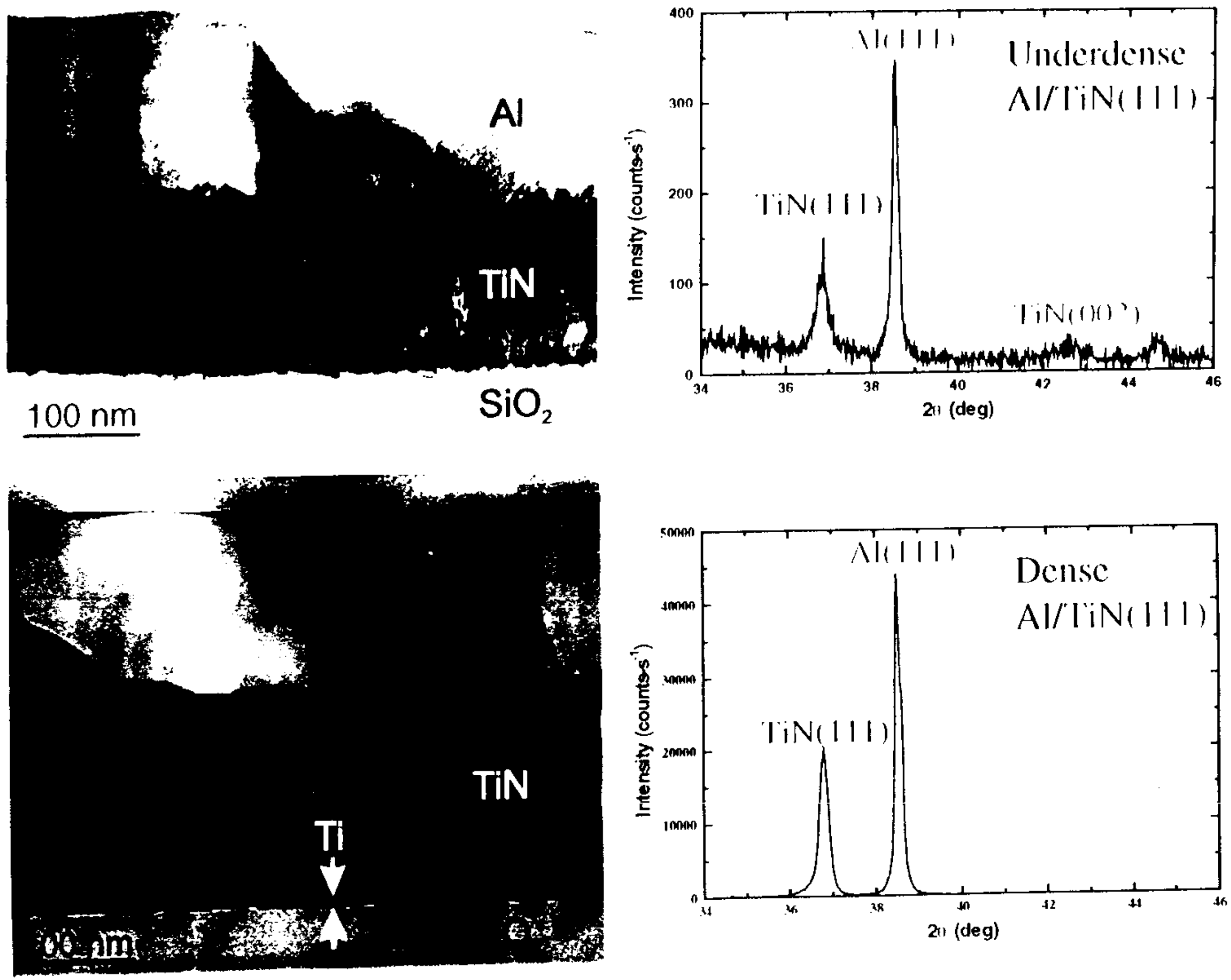


- Dense 111 TiN
- $\langle d \rangle = 43 \pm 30$ nm

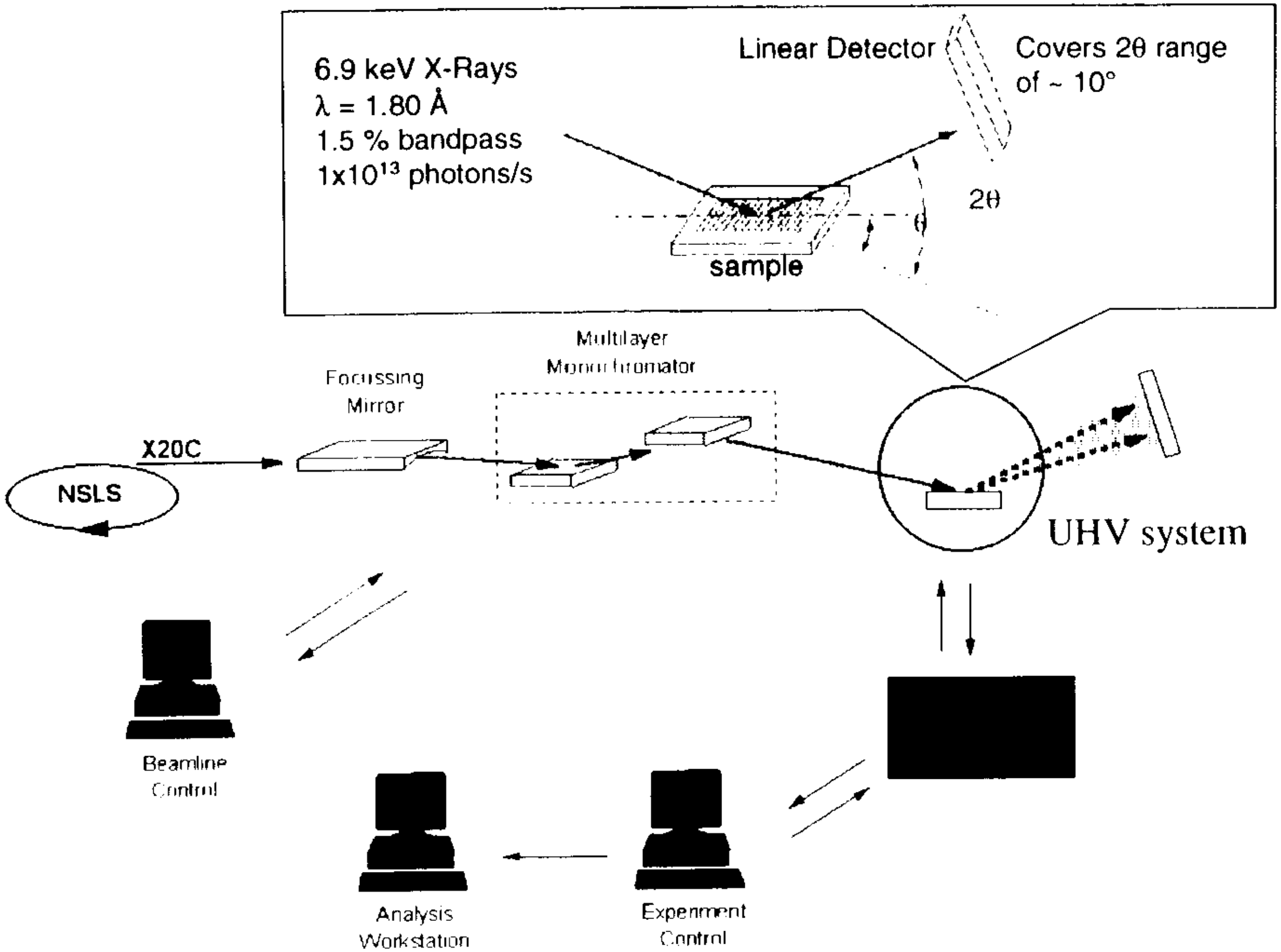
Density control: $J_i/J_{Ti} = 14$



Ar+, Ei = 100eV
t = 0
(a)
t = 0.3 ps
(b)
t = 1.1 ps
(c)
t = 10.9 ps
(d)


Al
TiN
SiO$_2$
100 nm
Underdense
Al/TiN(111)
Al(111)
TiN(111)
TiN(002)
Intensity (counts-s^{-1})
2θ (deg)
TiN
Ti
Dense
Al/TiN(111)
Al(111)
TiN(111)
Intensity (counts-s^{-1})
2θ (deg)

In-situ Synchrotron XRD during RTA



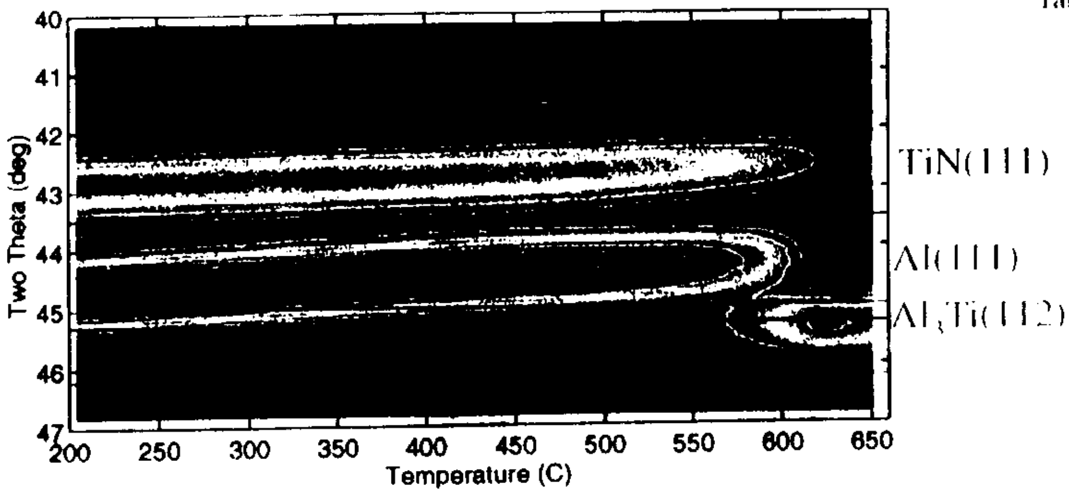
University of Illinois

Diffusion barrier lifetime (Synchrotron XRD)

$T_{ramp\ rate} = 3\ °C\text{-}s^{-1}$

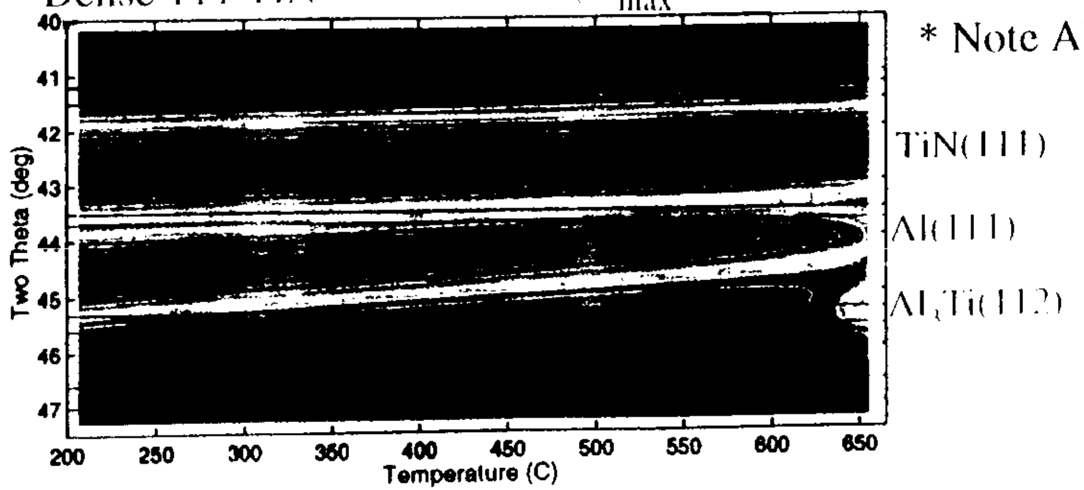
Color	Intensity
blue	low
↓	↓
red	high

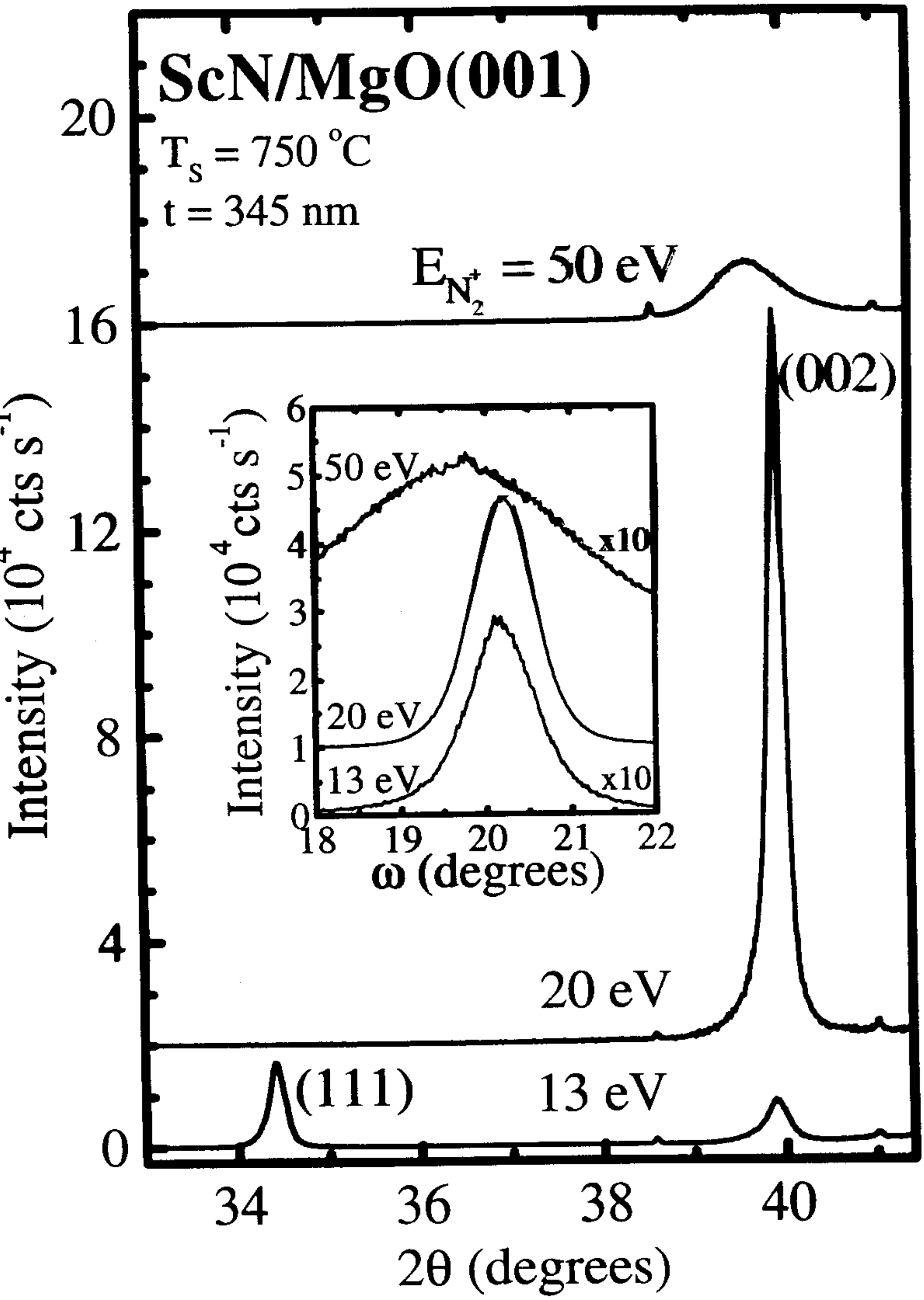
- Underdense 111 TiN ($T_{max} = 450\ °C$)



- Dense 111 TiN ($T_{max} = 610\ °C$)*

* Note Al m.p. = 660 °C

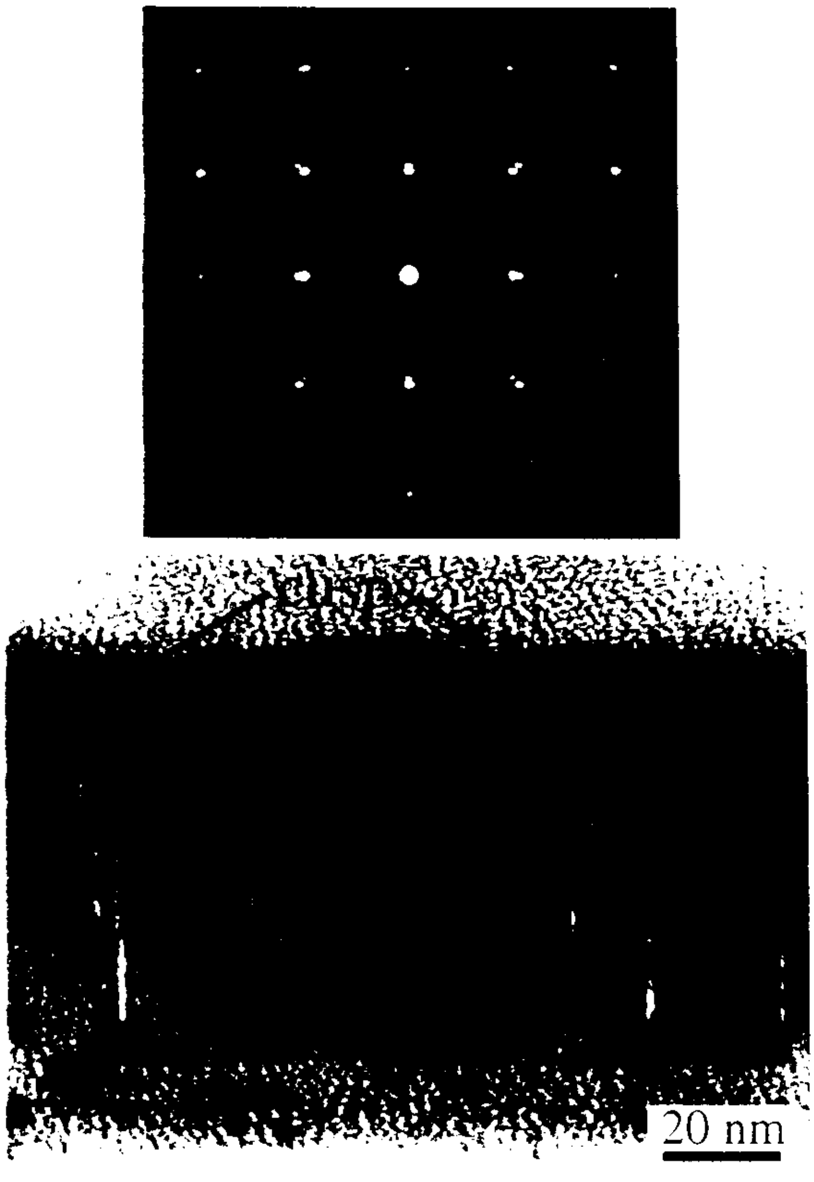


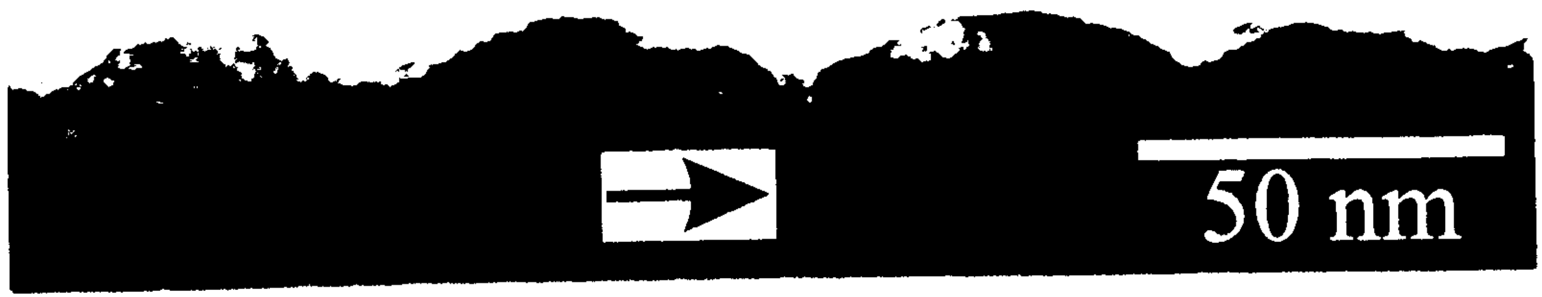


ScN/MgO(001)
T_s = 750 °C
t = 345 nm
$E_{N_2^+}$ = 50 eV
(002)
20 eV
(111)
13 eV
Intensity (10^4 cts s^{-1})
2θ (degrees)
34
36
38
40
0
4
8
12
16
20
50 eV
x10
20 eV
13 eV
x10
ω (degrees)
18
19
20
21
22
0
1
2
3
4
5
6

Epitaxial ScN

T = 800 °C



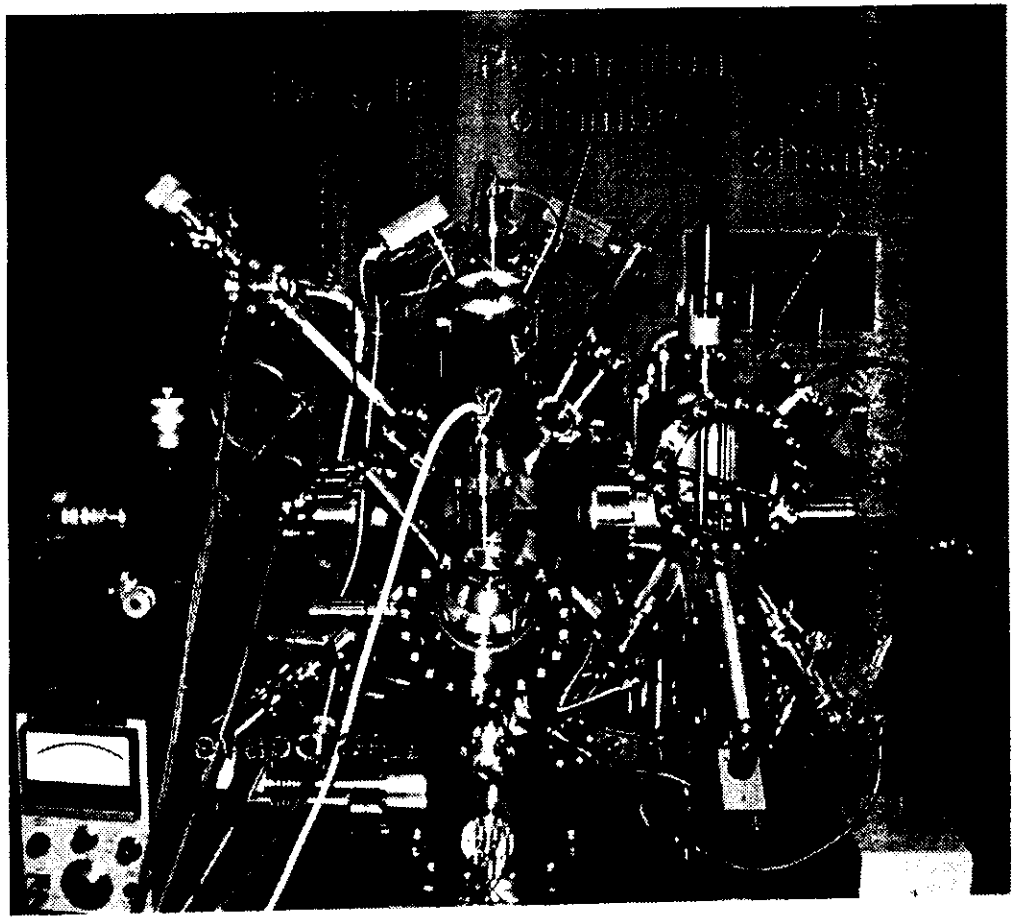


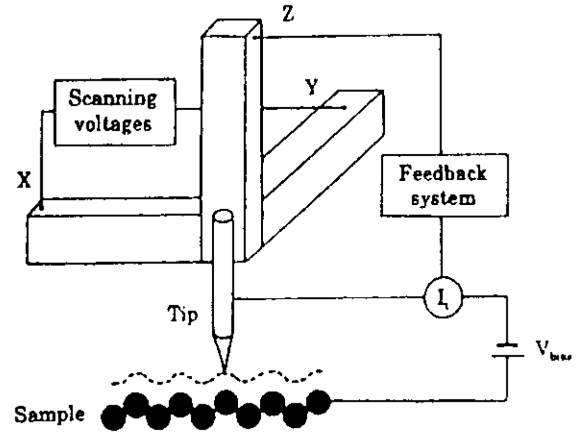
ScN/MgO(001) 1×1

$T_s = 750°C$

D. Gall, I. Petrov, N. Hellgren, L. Hultman, J.-E Sundgren, J.E. Greene, J. Appl. Phys. 84, 6034 (1998).

4



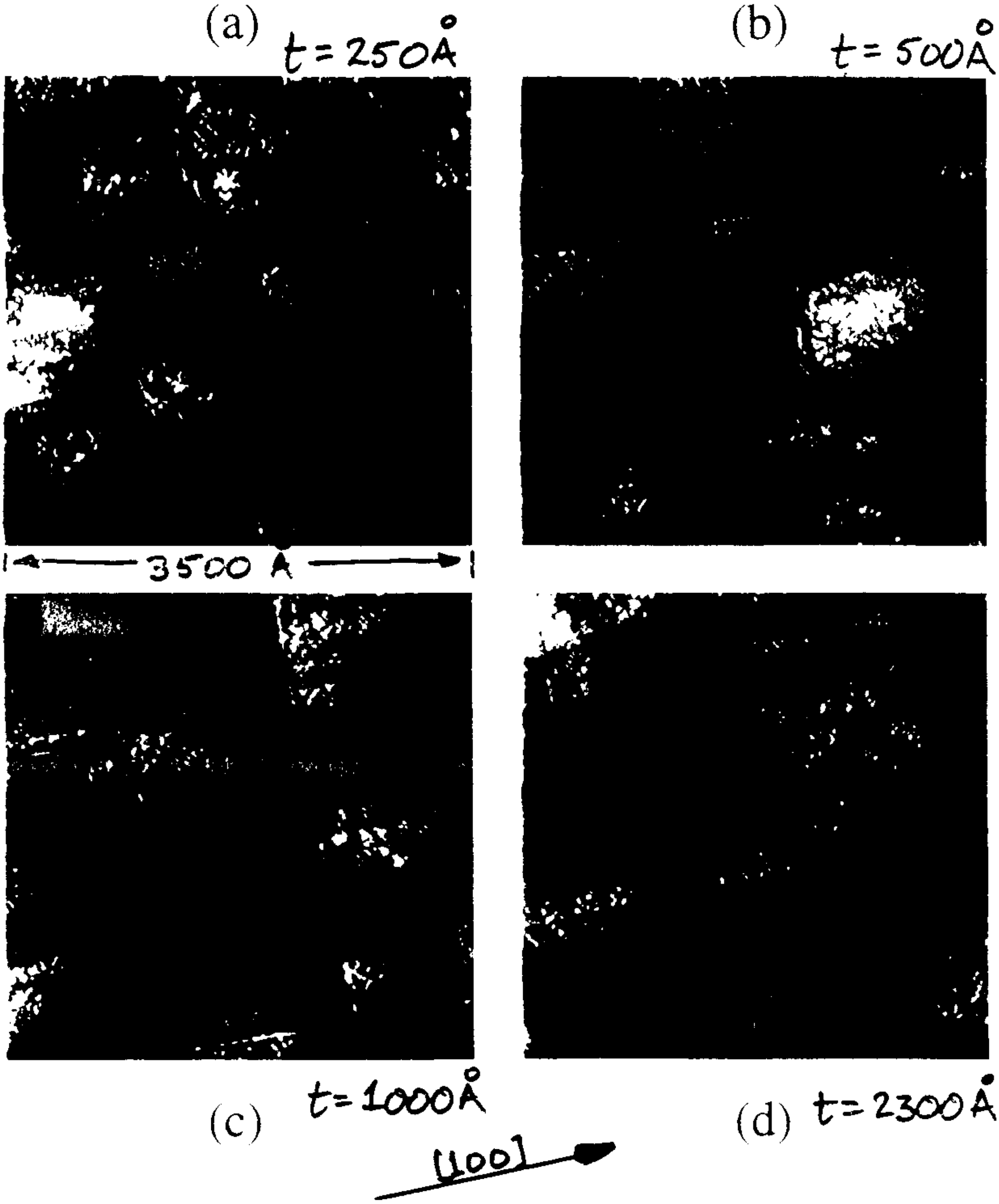


UHV variable-temperature scanning tunneling microscope

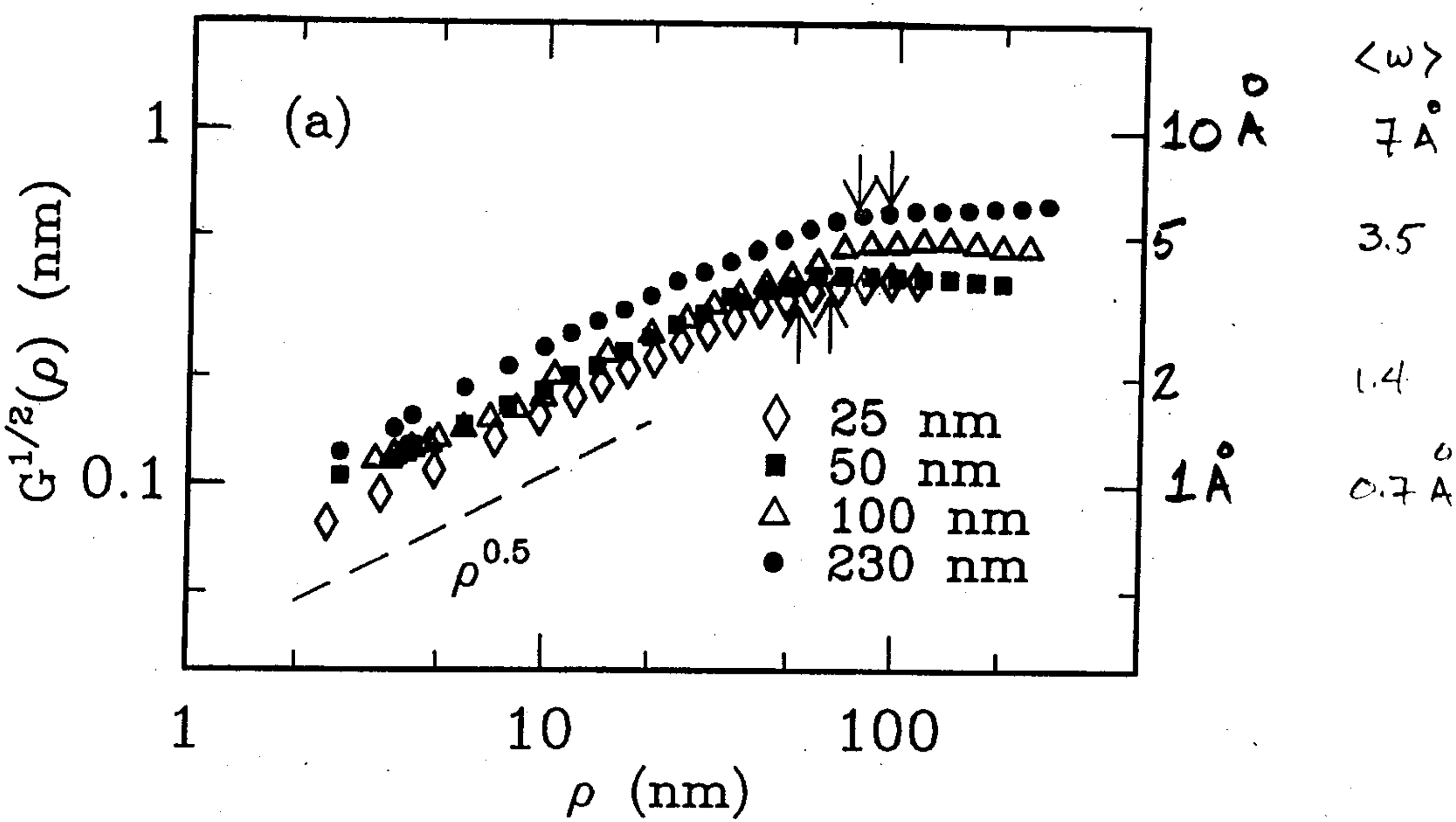
TiN / MgO(001) 1×1

$T_s = 750°C$

$\Delta a / a = 0.006$



Karr, Petrov, Cahill, Greene, Appl. Phys. Lett.



(a)
1
0.1
$G^{1/2}(\rho)$ (nm)
1
10
100
ρ (nm)
$\rho^{0.5}$
25 nm
50 nm
100 nm
230 nm
10 Å
5
2
1 Å
⟨ω⟩
7 Å
3.5
1.4
0.7 Å

Note: $\frac{[G(d/2)]^{1/2}}{d} = \underline{\underline{0.006}}$!!

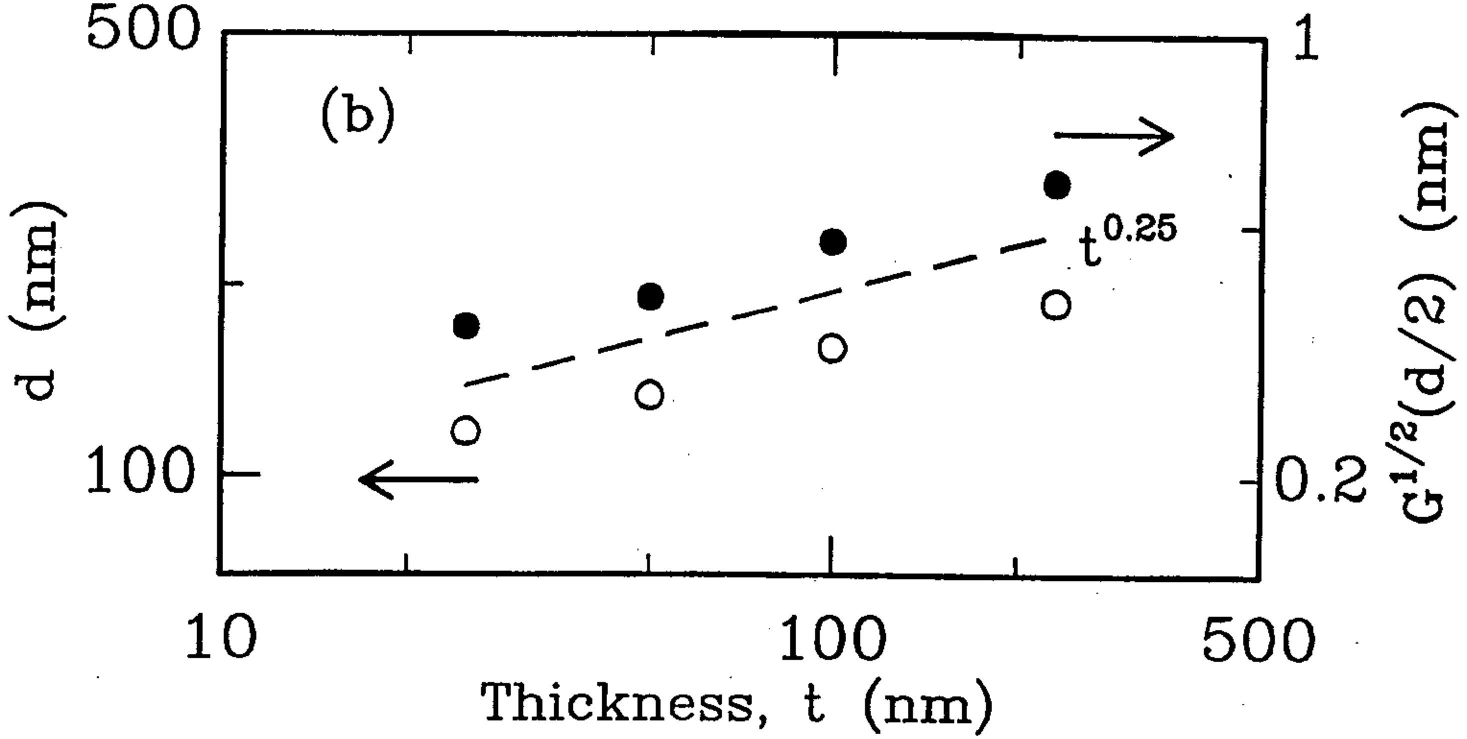


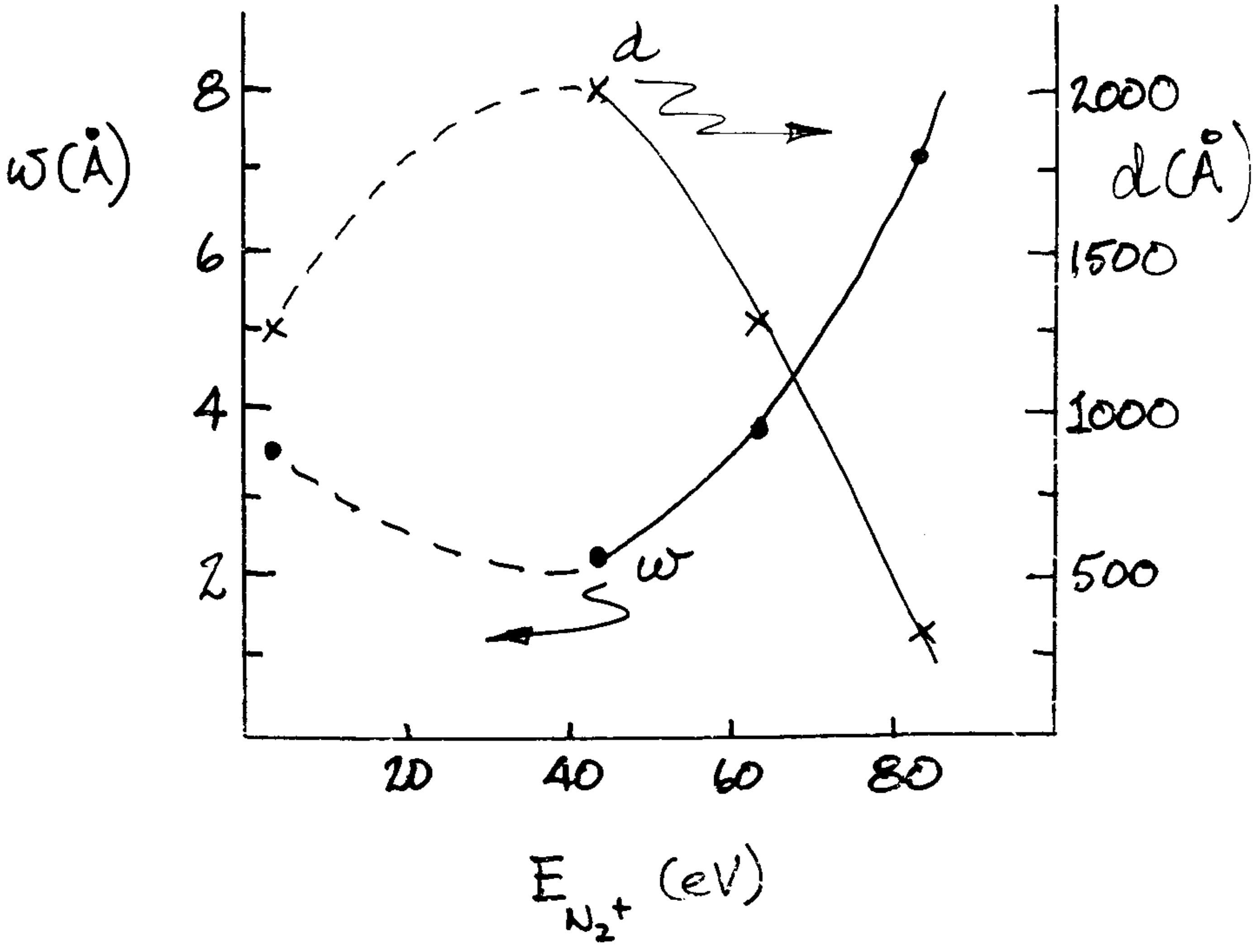
Fig 2

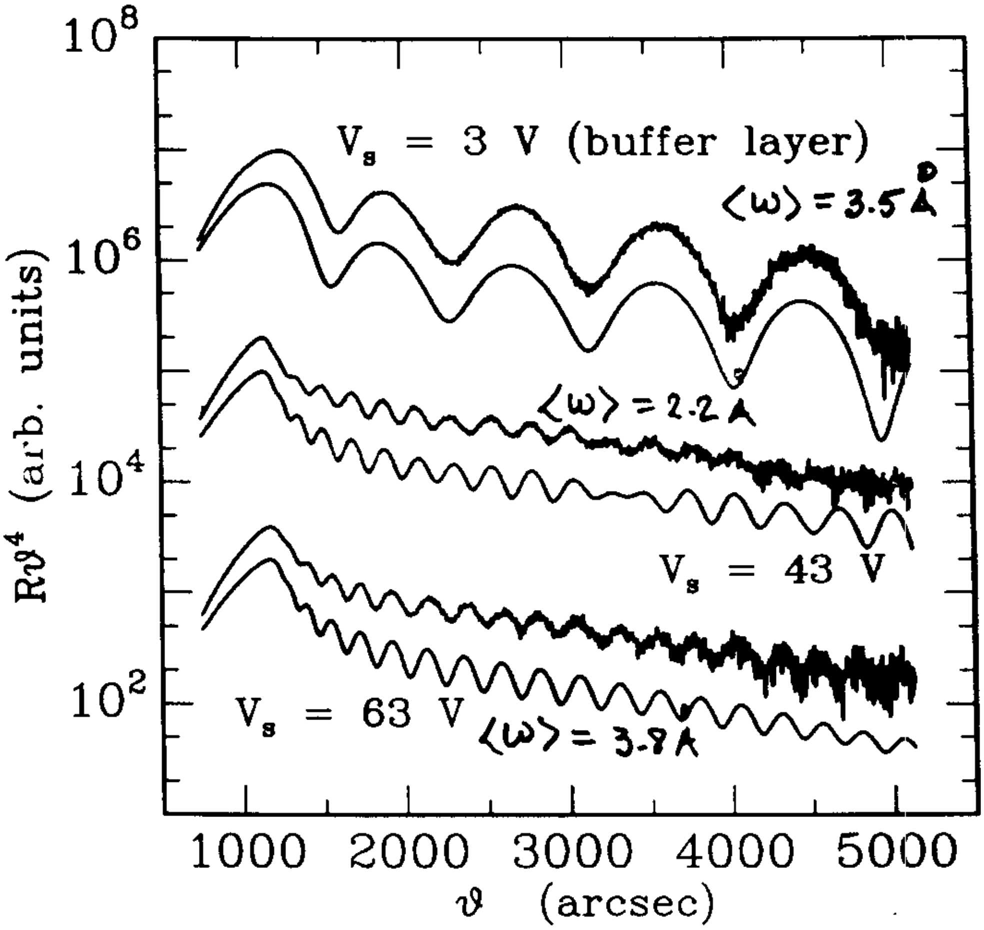
$E_{N_2^+} = 43$ eV $E_{N_2^+} = 63$ eV

TiN / MgO (001) 1x1

$T_s = 750$ °C

$t = 600$ Å

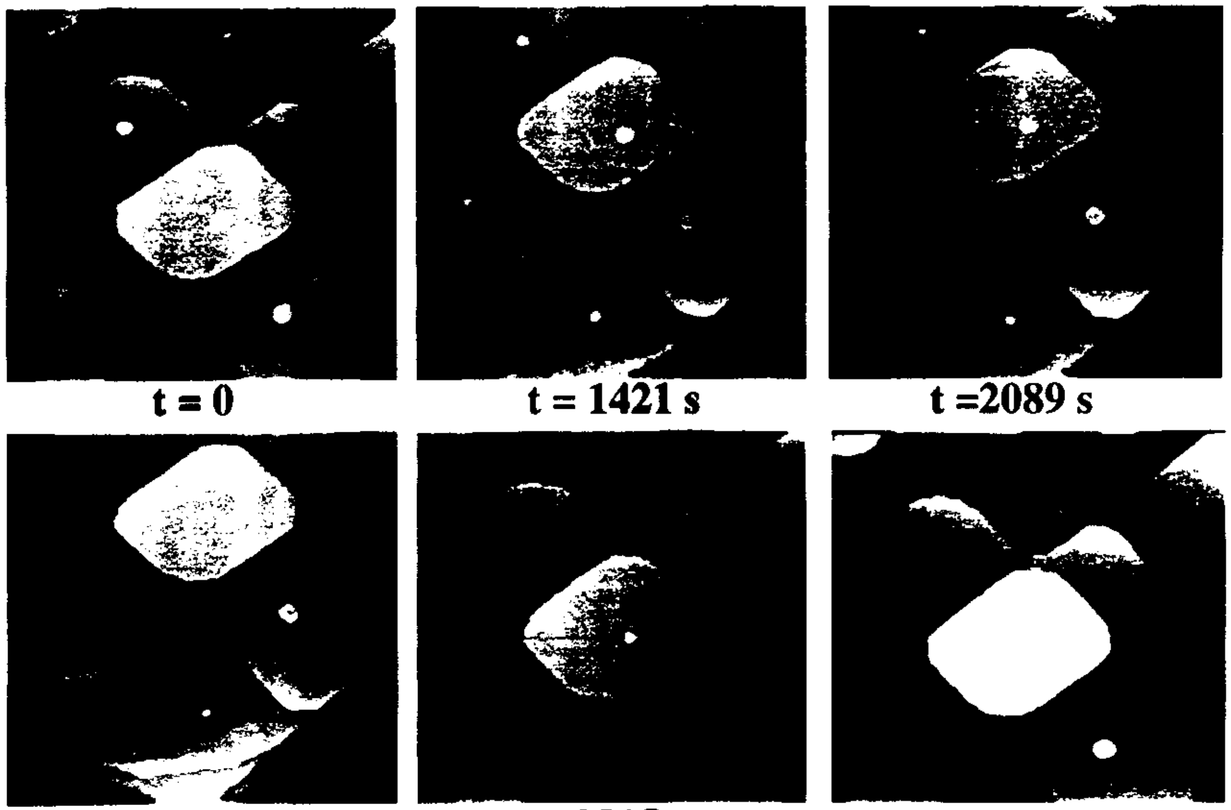

w(Å)
d(Å)
d
w
8
6
4
2
2000
1500
1000
500
20
40
60
80
$E_{N_2^+}$ (eV)



TiN/MgO(001)
T_s = 750 °C
t = 600 Å

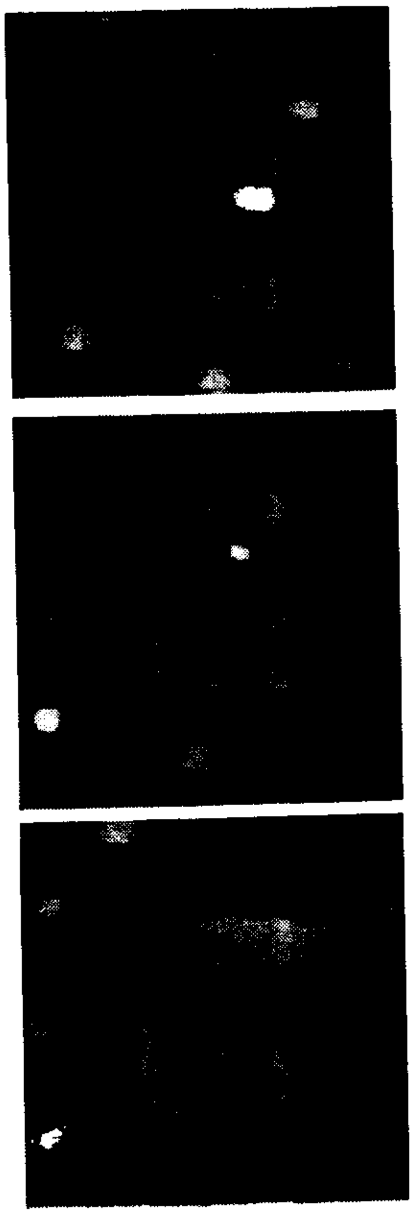
TiN(002) : T_a = 900 °C

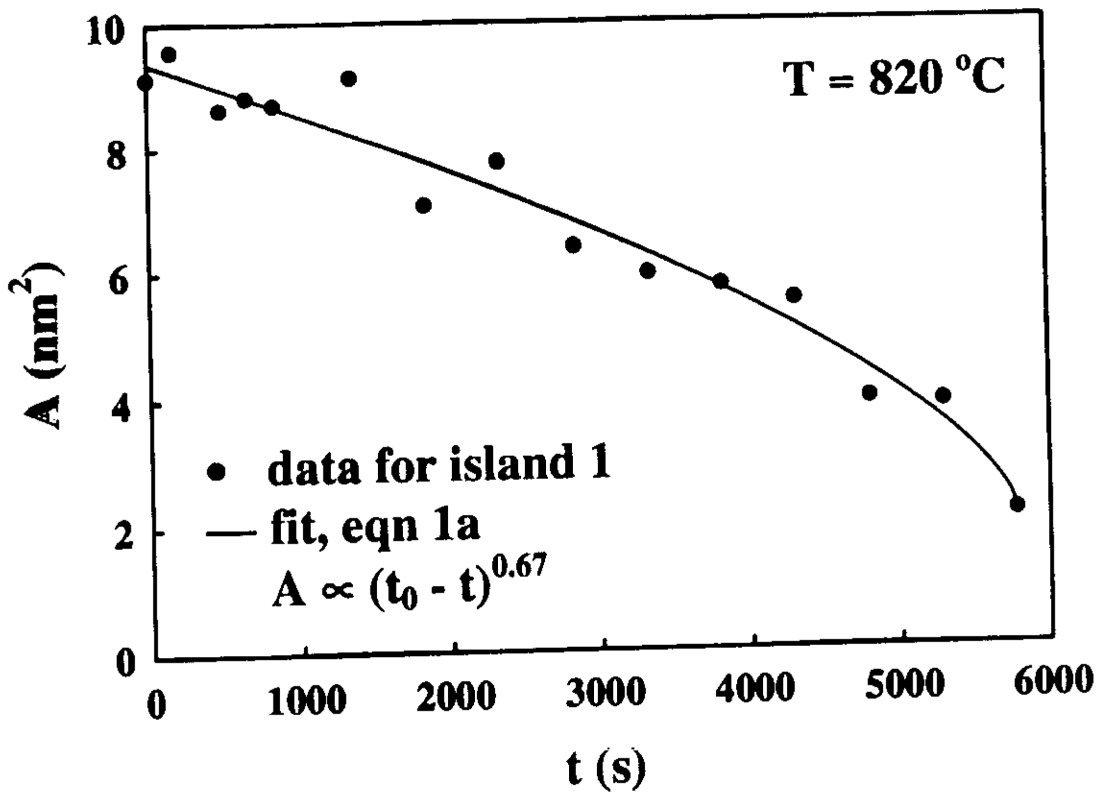
Scale : 800 x 800 Å



t = 0 | t = 1421 s | t =2089 s | t = 2414 s | t = 2815 s | t = 3419 s

TiN / TiN(002), θ = 0.2

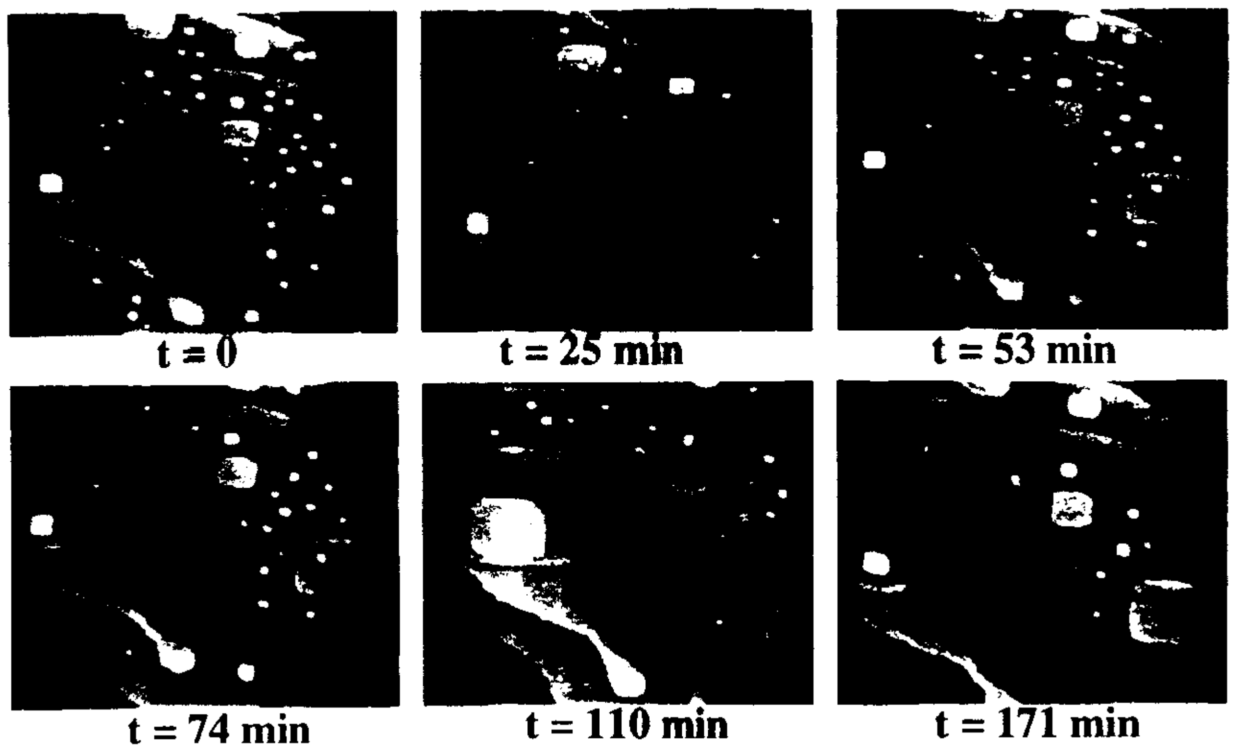




STM images showing single island dissolution to descending step edge. Decay is diffusion limited with a rate exponent n = 0.67.

TiN(002) : $T_a = 820\ ^oC$, $\Theta = 0.2$ ML

Scale : 1000 x 830 Å



Finally, the airbag quit!! Question is, did we learn anything? Answer: probably not, but you might consider the following.

- Low E_i (< bulk displacement energy) with high J_i/J_{Me} *during* film growth
  - * enhances "local" adatom mobilities
  - * selects low surface-energy PO
  - * densifies microstructure by minimizing atomic shadowing
  - * minimizes lattice strain
  - * *Note*: "average-energy/deposited-atom" model not scalable to low E_i

- High potential-energy, high diffusivity, 002 TM-nitride planes are favored by high adatom mobility due to rapid island spreading (ie: low adatom concentrations → low 2D nucleation rates)
  - * low E_i, high J_i/J_{Me} ion irradiation selects this P.O. *upon growth initiation* by minimizing and dissolving 111 islands

- Kinetically-limited development of 111 P.O. in TM nitrides
  - * due, in absence of large strain, to anisotropy in surface diffusion rates
  - * occurs under conditions of low adatom mobility
  - * favors low potential energy, low diffusivity planes due to high island nucleation rates and large cross-section for intercepting incident flux
  - * ∴ *must* occur gradually through competitive growth

- Surface morphological evolution in TM nitrides at $T_s \leq 750$ °C controlled by kinetic roughening
  - * aspect ratio lower than for metals, semiconductors
  - * large in-plane correlation lengths
  - * low edge-atom mobilities → dendritic islands