Lecture 4:

Fundamentals of Nucleation and Growth; Control of microstructure evolution


Atomic-scale phenomena affecting N&G

Second part of lecture

Fast Ions & Neutrals (and sometimes electrons)
- Create preferential nucleation sites
- Disrupt small clusters
- Increase effective adatom mobilities
- Heat the surface

1st part of lecture

Thermal Species
- Adsorb
- Diffuse
- Desorb
- Coalesce into clusters
- Cluster growth

Substrate
Zone Structure Models

Concept of Homologuous Temperature: $\frac{T_{\text{substrate}}}{T_{\text{melting}}}$
(to account for differences in activation barriers for different materials)
Nucleation and Growth

- Deposition flux [cm\(^{-2}\)s\(^{-1}\)]
- A step edge acts as an infinite size nucleus.
- Transfer among nuclei; ripening
- Stable clusters
- Metastable clusters
- Adatom diffusion
- Surface vacancy

The critical radius \(r^*\)

The nucleation energy barrier, \(E^*\)

Cluster Energy (Arbitrary Units)

Cluster Size (atoms)
Thermodynamics of Nucleation

Energy cost to form a new surface (spherical particle): $4pr^2\gamma$
Energy gain to form a stable phase: $4/3 (pr^3) \Delta G_V$

(1) $\Delta G_{Tot.} = 4pr^2\gamma - 4/3 (pr^3) \Delta G_V$

Where: $\gamma$ = surface energy per unit area
$\Delta G_V$ = free energy of nuclei per unit volume
$\Delta G_{Tot.}$ = the total change in free energy

Set $d(\Delta G_V)/dr = 0$ and solve for critical cluster size:

(2) $r^* = 2\gamma / \Delta G_V$

(3) $\Delta G^*_{Tot.} = 16 p \gamma^3 / 3 (\Delta G_V)^2$

(4) $\Delta G^*_{Het.} = \Delta G^*_{Tot.} S(\Theta)$

(5) $S(\Theta) = (2 + \cos\Theta)(1 - \cos\Theta)^2/4$

$\Theta = 10^\circ \Rightarrow S(\Theta) \approx 10^{-4}$

The critical cluster size
Homogeneous nucleation barrier
Heterogeneous nucl. Barrier

$\gamma$: surface and interfacial energies

$\gamma_s$, $\gamma_i$, $\gamma_f$:

\[ \gamma_s + \gamma_i = \gamma_f \]

Cluster Energy (a.u.) vs. Cluster Size (atoms)
Growth processes controlling microstructure evolution

- condensation of atom, surface diffusion
- nucleation of isolated islands
- island growth
- impingement and coalescence of islands
- formation of polycrystalline islands and channels
- development of continuous film
- local epitaxy on grains&columns
- competitive column growth and grain coarsening
- (Renucleation)

Case of pure elemental materials
P. Barna: In-situ TEM: indium evaporation on amorphous carbon

\[ T_s = 90 \degree C \]
\[ T_s/T_m = 0.85 \]
\[ R = 5 \text{ Å/s} \]
\[ p = 5.10^{-7} \text{ Torr} \]
P. Barna: In-situ TEM: indium evaporation on amorphous carbon

$T_s = 75 \degree C$

$T_s/T_m = 0.81$

$R = 5 \text{ Å/s}$

$p = 5 \times 10^{-7} \text{ Torr}$
P. Barna: In-situ TEM: indium evaporation on amorphous carbon

$T_s = -150 \, ^\circ C$
$T_s/T_m = 0.29$
$R = 2.5 \, \text{Å/s}$
$p = 2 \cdot 10^{-7} \, \text{Torr}$
Phase diagram of In islands on a-C
Growth processes controlling microstructure evolution

- condensation of atom, surface diffusion
- nucleation of isolated islands
- island growth
- impingement and coalescence of islands
- formation of polycrystalline islands and channels
- development of continuous film
- local epitaxy on grains & columns
- competitive column growth and grain coarsening
- (Renucleation)

Case of pure elemental materials
Zone Structure Models

Concept of *Homologous Temperature*: $T_{\text{substrate}}/T_{\text{melting}}$

(to account for differences in activation barriers for different materials)

SZMs systematically categorize self-organized structural evolution during PVD (*similar or related diagrams can be formulated for CVD and electrodeposition*) as a function of deposition parameters.

From an understanding of film formation follows the possibility for microstructural and nanostructural engineering in order to design a material for specific technological applications.


2.1 ORIENTED, EPITAXIAL CRYSTALS ARE GROWING ON THE MoS$_2$
WHEREAS ON THE NEIGHBOURING CARBON SUBSTRATE THE LIQUID PHASE APPEARS

$T_S = +100^\circ C$  \( P = 1.5 \cdot 10^{-8} \text{ TORR} \)
$E = 3 \text{ A}/\text{S}$  \( M = 20000 \times \)

0.2 $\mu$  27
2.3 THE EFFECT OF THE THICK LAYER IS STRIKING WHEN ONLY ONE PART OF THE INVESTIGATED SURFACE IS COVERED BY IT

$T_s = +95^\circ C$  $p = 1 \cdot 10^{-8}$ TORR

$E = 3 \, \text{Å}/\text{S}$  $M = 20 \, 000 \, X$

$0.2 \, \mu$
P. Barna: In-situ TEM: indium evaporation on amorphous carbon

\[ T_s = 75 \, ^\circ \text{C} \]
\[ T_s/T_m = 0.81 \]
\[ R = 5 \, \text{Å/s} \]
\[ p = 5 \times 10^{-6} \, \text{Torr} \]

\[ P_{\text{total}} = 5 \times 10^{-6} \, \text{TORR \ WITHOUT \ COOLING \ TRAP} \]

\[ E = 5 \, \text{Å/s} \]
\[ N = 14000 \times \]

0.5 μm
Reactive deposition

Effects of additives: alloying elements; dopants; contaminants

Indium on a-C; $T_s = 75 ^\circ C$, $R = 5 \text{ Å/s}$, $p = 5 \times 10^{-6}$ Torr

Segregation of co-deposited C results in the formation of a “tissue phase” covering the In crystals, causing renucleation
Reactive Deposition
the Al-O system

O has low solubility in Al:
- segregates to surfaces and grain boundaries
- forms oxide layers or "tissue phases"
- interrupts the local epitaxial growth
- causes renucleation

⇒ control of grain size.

Equiaxed nanograins with random orientation

P.B. Barna, in J deSegovia (ed) Proc. 9th IVC Madrid 1983
P.B. Barna et al, Phys. Stat Sol (a) 146 (1994) 31
Superhard and supertough nanocomposites
thermal segregation and renucleation

TiC/DLC and YSZ/Au nanocomposites
Voevodin, Zabinski

TiN/SiNx, W₂N/Si₃N₄, VN/Si₃N₄, Vepřek et al.
TiC/SiC/aCH, J. Patscheider
ZrN/Cu, AlN/Cu, CrN/Ni, Musil et al.
TiN/TiB₂, TiC/TiB₂, Mitterrer, Mayrhofer et al.
and others
Materials physics interest stems from:

- TM Nitrides are extremely anisotropic
  - preferred orientation is important
- all major uses require $T_s \leq 450 \, ^\circ\text{C}$ ($T_s/T_m \approx 0.2$)
  - adatom mobilities are relatively low
- highly kinetically limited; underdense rough films with 111 PO

**TiN & TaN**: Model systems for low-temperature ion-assisted growth

$\text{TiN, Ti}_{1-x}\text{Al}_x\text{N, Ti}_{1-x}\text{W}_x\text{N, TiN/VN SL, CrN, Cr}_{1-x}\text{Ti}_x\text{N, TaN, V}_N, ScN, Sc_{1-x}\text{Ti}_x\text{N, CeN, Ti}_{1-x}\text{Ce}_x\text{N, VN}}$
Random Nucleation; 111 texture dominates in a kinetically limited competitive column growth
111 TiN texture evolution at low-$T_s$

random orientation
porous structure
2D mean-field kinetic MC “SOS” simulation

BC: $E_s^{111} > E_s^{001}; E_b^{111} > E_b^{001}$

The lower surface adatom mobility on polar 111-surfaces (with three backbonds) results in a higher adatom incorporation probability on 111-grains which finally overgrow the non-polar 002-grains (one backbond).
3D-Kinetic Monte Carlo Simulation of low-Ts (100 K)
Competitive Al 002 Al texture evolution

- Initial equal distribution of 111 and 002 islands.
- With adatoms desorption rates negligible anisotropies in surface diffusivity becomes decisive.
- Average adatom residence time is higher at lattice sites of low diffusivity (low potential energy) 002 surfaces vs high diffusivity (high potential) 111 surfaces.
- Adatoms, which are stochastically deposited near grain boundaries and, through surface diffusion, sample sites on both...
Structure-zone diagrams

Movchan: evaporation

\[ J_n, E_n \sim 0.2 \text{ eV} \]

Thornton: sputtering

\[ J_n, E_n \sim 2-20 \text{ eV} \]

\[ J_i, E_i \sim e(U_{\text{plasma}} - U_{\text{bias}}) \text{ eV} \]

\[ J_i \sim 1, E_i \sim 100-500 \text{ eV} \]

\[ J_i \sim 5-20, E_i \sim 20 \text{ eV} \]
The grain size, initially small, increases with thickness while column boundaries become increasing more open. The Zone T structure forms through random nucleation, limited coarsening during coalescence, and competitive column growth. The column tops are faceted due to kinetic roughening, which in combination with atomic shadowing results in deep cusps between columns and open column boundaries. The individual columns, however, are dense indicating sufficient adatom surface mobility to sustain local crystal growth.
Effects of Increasing $E_i$ with $J_i/J_{Me} \leq 1$

XTEM image from the middle portion of a TiN layer grown by reactive magnetron sputter deposition at 300 °C with a total pressure $P_t = 5.6$ mTorr. The ion-to-Ti flux ratio $J_i/J_{Ti}$ incident at the film surface was < 1 while the ion energy $E_i$ was varied in steps of 40 eV.

Mechanisms of Ion-Irradiation Induced Densification;

100 eV Ar⁺ on Ni

The impact of energetic ions on a surface collapses protruding areas and shrinks trapped void volume.

Shown are results of a *molecular dynamics simulation* of an ion impact on a surface.

- Forward sputtering
- Recoil Events
- Lattice relaxation

Figure from Karl-Heinz Müller, Surf. Sci. Lett. (1987)
Effects of ion energy

\[ E_i \approx 100 \text{ eV}, \frac{J_i}{J_{Me}} = 0.5 \]

TiN/SiO₂
\( T_s = 350 \, ^\circ\text{C} \)

Effects of Increasing $E_i$ with $J_i/J_Me \leq 1$, cont.

The densification obtained in the high-energy ($\geq 100$ eV) ion bombardment regime comes at a steep price:
- Lattice defects
- Compressive stresses
- Discharge gas incorporation

XTEM images of TiAlN films grown by reactive magnetron sputtering onto steel substrates at 450 °C with $p = 5.6$ mTorr and $J_i/J_Me = 1$. 

$V_s = 0$ V

$V_s = 150$ V
Independent control of ion flux and ion energy

\[ E_i = e(V_{\text{plasma}} - V_{\text{bias}}) \]

\[ J_i = f(B_{\text{ext}}) \]

Comparison of the effects of ion flux and ion energy

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

$T_s = 350 \degree C$

- $E_i = 20 \text{ eV}, J_i/J_{\text{Me}}$ varied
- $J_i/J_{\text{Me}} = 1, E_i$ varied

At low energies, $E_i \sim 10\text{-}20 \text{ eV}$, (below the bulk lattice displacement threshold) there are distinctly different mechanistic pathways leading to microstructural evolution and texture development depending upon whether in $E_i$ is varied at constant $J_i/J_{\text{Me}}$ or $J_i/J_{\text{Me}}$ is varied at constant $E_i$.

Preferred orientation of $\delta$-TaN$_x$/SiO$_2$

- $E_i = 20$ eV, $x = 1.13$
- $J_i/J_{Ta} = 10.7$
- $002$-pole
- $J_i/J_{Ta} = 1.3$
- $111$-pole

$I = I_{111} + I_{002} + I_{022} + I_{113}$

$T_s = 350$°C
$t = 500$ nm
$E_i = 13.6\pm .2$ eV
$J_i/J_{Ta} = 6.0\pm .5$

Normalized XRD intensities

$\varphi = 30^\circ$
$60^\circ$

$f_{N_2} = 0.15$
Preferred orientation
effects of ion flux and nitrogen partial pressure

$\delta$-TaN$_x$/SiO$_2$

- $T_s = 350$ °C
- $t = 500$ nm
- $E_i = 20$ eV
- $J_{Ni} = 0.15$

Normalized XRD intensities

$I_{111}/I_\Sigma$

$I_{002}/I_\Sigma$

$I_\Sigma = I_{111} + I_{002} + I_{022} + I_{113}$

Normalized XRD peak intensity

$J_i/J_{Ta}$

$J_{Ni}/J_{Me}$

I$_{002}$/I$_{111}$ in TiN

I$_{002}$/I$_{111}$ in TiAlN

I$_{111}$/I$_{111}$ in TiN

I$_{111}$/I$_{111}$ in TiAlN

$T_s = 350$ °C

$t = 1 \mu$m, 20 mTorr N$_2$

TiN$_x$/SiO$_2$

Normalized XRD intensities

$I_{111}/I_\Sigma$

$I_{002}/I_\Sigma$

Normalized XRD peak intensity

$J_{Ni}/J_{Me}$

$J_i/J_{Ta}$

$J_{Ni}/J_{Me}$

TiN/SiO$_2$

T$_s = 350$ °C

$t = 1 \mu$m

$J_{Ni}/J_{Ti} = 14$

$I_{002}/I_{111} + I_{002}$ in TiN

$I_{002}/I_{111} + I_{002}$ in TiAlN

$I_{111}/I_{111} + I_{002}$ in TiN

$I_{111}/I_{111} + I_{002}$ in TiAlN

$J_{Ni}/J_{Me}$

$J_i/J_{Ta}$

Normalized XRD peak intensity

$J_{Ni}/J_{Me}$

$J_i/J_{Ta}$

$T_s = 350$ °C

$t = 1 \mu$m, 20 mTorr N$_2$
TaN/ SiO$_2$

$J_{i}/J_{Ta} = 10.7$

$f_{N2/Ar} = 0.15$

$E_i = 10$ eV

$T_s = 350$ °C

Competitive growth 002 win over 111

Atomic-Scale Surface Processes Controlling the Growth of Cubic Transition-metal Nitrides: TiN, CrN, ScN, and TaN

Density functional calculations & scanning tunneling microscopy

Competitive grain growth

- Momentum transfer to surface ↑.
- \( \theta_N \) on (002) ↑ due to collisionally-induced dissociative chemisorption of \( \text{N}_2^+ \).

Low \( \frac{J_i}{J_{\text{Ta}}} \) or \( f_{\text{N}_2} \):
- \( D_{111} < D_{002} \) → 111 texture

High \( \frac{J_i}{J_{\text{Ta}}} \) or \( f_{\text{N}_2} \):
- \( D_{111} > D_{002} \) → 002 texture
2D mean-field kinetic MC “SOS” simulation

BC: $E_s^{111} > E_s^{001}; E_b^{111} > E_b^{001}$

$J$ (atoms/cm$^2$-s)
Effects of Increasing $J_i/J_{Me}$ with $E_i \sim 20$ eV

Case of TaN

XRD $\omega$-20 scans from 500-nm-thick $\delta$-TaN layers grown by reactive magnetron sputter deposition on amorphous SiO$_2$ at 350 °C as a function of $J_i/J_{Ta}$ with $E_i = 20$ eV. C.-S. Shin, D. Gall, Y.-W. Kim, N. Hellgren, I. Petrov, and J. E. Greene, J. Appl. Phys. 92 5084 (2002)

Incident N2 ions are collisionally dissociated
⇒ source of atomic N that chemisorbs on 001 grains (not on polar N-terminated 111-grains).
⇒ The increasing ion flux raises the N-coverage on 100 grains to form TaN admolecules which are more strongly bonded to the surface than Ta adatoms, and therefore has lower surface mobility.
∴ the net flux of cations from 002 to 111 oriented grains is reversed under high-flux conditions, resulting in the development of 200 texture.
TiN initial stages of growth

TiN/SiO$_2$, $T_S=350^\circ$C, $P_{N_2}=20$ mTorr
Effects of ion flux

TiN/SiO₂

\( \frac{J_i}{J_{Ti}} = 14 \)

\( E_i = 20 \text{ eV} \)

\( T_s = 350^\circ C \)

002 texture dominates from the earlier stages of growth

3D kinetic MC simulation of 002 TiN texture evolution at high $T_s$

Texture inheritance at low ion energies

Once texture has developed, low-energy ion irradiation controls film density but preferred orientation persists through local epitaxy.
Atomic arrangement in 0002 Ti and polar 111 TiN

TiN(111) overlayer
\[ d_{\text{TiN}} = 0.29995 \text{ nm} \]

Ti(0002) crystallographic template
\[ d_{\text{Ti}} = 0.29053 \text{ nm} \]

Ti(0002)/TiN(111) misfit \( \cong 1.6\% \)
Highly 0002-textured Ti template

Ti/SiO$_2$
$T_s = 80\,^\circ\,C$
$x_{Ti} = 25\,\text{nm}$
$P_{Ar} = 20\,\text{mTorr}$
$J_i/J_{Ti} = 2$
$E_i = 11\,\text{eV}$

Dense microstructure.
$\langle d \rangle = 26\pm21\,\text{nm}$.
Highly 111-textured TiN/Ti(0002)

55 nm

Gas | Ar | N₂
---|----|----
P (mTorr) | 20 | 20
J_i/J_Ti | 2 | 14
E_i (eV) | 11 | 20

\[ \Gamma_\omega = 1.9^\circ \]
Microstructure comparison

Density control: $J_i/J_T = 14$

Texture control: TiN/Ti

- (111) texture.
- $\langle d \rangle = 20 \pm 14$ nm.
- underdense grain structure.

- (002) texture.
- $\langle d \rangle = 18 \pm 12$ nm.
- dense grain structure.

- (111) texture.
- $\langle d \rangle = 43 \pm 30$ nm.
- dense grain structure.
Texture and density control in $\delta$-TaN

- Underdense 111
- Dense 001
- Dense 111

Intensity (x10$^4$ cps)

- $\delta$-TaN/SiO$_2$
  - $J_i/J_{Ta} = 1.3$
  - $\Gamma_\omega = 16.7$

- $\delta$-TaN/Ti/SiO$_2$
  - $J_i/J_{Ta} = 10.6$
  - $\Gamma_\omega = 9.3$

- $\delta$-TaN/Ti/SiO$_2$
  - $J_i/J_{Ta} = 10.6$
  - $\Gamma_\omega = 5.4$

Graph showing the intensity (x10$^4$ cps) and $\omega$ (deg) for different orientations and materials.