Modelling thin film growth of transition metal nitrides

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Introduction:

Reactive magnetron sputter deposition of TiN

Mechanical properties
Optical coating
Diffusion barrier for Al or Cu interconnects
Biocompatible overlayer

all influenced by the crystallographic orientation
General trends in out-of-plane orientation:

- Influence of *film thickness*: \([200] \rightarrow [111]\) often explained by the “minimisation of overall energy” model e.g. Pelleg, Oh, Je...

Abadias and Tse, JAP 95 (2004)
General trends in out-of-plane orientation:

- Influence of *film thickness*: [200] => [111] often explained by the “minimisation of overall energy” model e.g. Pelleg, Oh, Je...

- Influence of the *ion-to-atom ratio*: [111] => [200] often explained by “kinetics” or “diffusion rates” e.g. Greene, Hultmann, Gall,...

Hultman, JAP 78 (1995)
General trends in out-of-plane orientation:

- Influence of film thickness: [200] => [111] often explained by the “minimisation of overall energy” model e.g. Pelleg, Oh, Je...

- Influence of the ion-to-atom ratio: [111] => [200] often explained by “kinetics” or “diffusion rates” e.g. Greene, Hultmann, Gall,...

- Influence of the N₂-flow: random => [111] => [200]

Mahieu, PhD. Thesis

=> Extended Structure Zone Model
Thin film growth:

Microstructure as a function of mobility: Structure Zone Model

Movchan-Demchishin 1969
Thornton 1974

Messier et. al 1984
Grovenor et. al 1984
Thin film growth:

Microstructure as a function of mobility: Extended Structure Zone Model

Zone Ia & b
Zone Ic
Zone T
Zone II
ESZM
Conclusions
More results
Energy flux
Diffusion rate
Diffusion length
Conclusions

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Transition:

Schematic structure:

Zone: Characteristics

Zone Ia
Zone Ic
Zone T
Zone II

Hit & stick
no mobility
amorphous

Thin film growth:

Microstructure as a function of mobility: Extended Structure Zone Model

Transition:

Schematic structure:

Zone: Characteristics:

Zone Ia
- no preferential orientation

Zone Ib
- preferential orientation: fastest growth direction

Zone II
- preferential orientation: lowest surface energy

=> Nucleation of crystalline islands

=> faceting occurs due to growth rate anisotropy of crystallographic planes

=> Nucleation of crystalline islands

Plane with lowest perpendicular growth rate survive

Substrate

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Zone Ic: growth rate anisotropy

1: sticking coefficient \( S_c \)

Hartman-Perdok theory:\(^1\)

\[ (1-S_c) \]

Perpendicular growth rate
\[ \approx \text{sticking coefficient } S_c \]

High mobility

Number of nearest neighbours influenced by
- adparticle Ti or TiN
- reactive gas: N or N\(_2\)

2: high adparticle mobility

\[ \Rightarrow \text{high lateral growth rate} \]

\[ \Rightarrow \text{low perpendicular growth rate} \]

Huang:\(^2\)

\[ \text{adparticle mobility } \approx \]

\[ \text{number of nearest neighbours} \]

\[ \text{between adparticle and growing plane} \]

1: e.g. P. Hartman and W.G. Perdok: Acta. Cryst. 8 (1955)

Zone Ic: growth rate anisotropy

crystallographic plane with lowest perpendicular growth rate = lowest number of nearest neighbours

<table>
<thead>
<tr>
<th>adparticles</th>
<th>state of the reactive gas</th>
<th>number of nearest neighbours on the plane:</th>
<th>faceting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>N₂</td>
<td>1</td>
<td>{100}</td>
</tr>
<tr>
<td>Ti</td>
<td>N</td>
<td>5</td>
<td>{111}</td>
</tr>
<tr>
<td>TiN</td>
<td>N₂</td>
<td>2</td>
<td>{100}</td>
</tr>
<tr>
<td>TiN</td>
<td>N</td>
<td>5</td>
<td>{111}</td>
</tr>
</tbody>
</table>

⇒ {100} or {111} faceting due to growth rate anisotropy
**Zone Ic:** no adparticle diffusion from one grain to another

**Schematic structure:**
- **Zone Ia & Ib**: Hit & stick, no mobility, amorphous
- **Zone Ic**: no preferential orientation
- **Zone T**: preferential orientation: fastest growth direction
- **Zone II**: preferential orientation: lowest surface energy

**Transition:**
- Kinetic energy → Thermal energy

**Not allowed:**
- No interaction between different grains + immobile grain boundaries ⇒ straight and facetted columns of random out-of-plane orientation
**Zone T:** adparticle diffusion from one grain to another

**Transition:**

- Thermal energy
- Kinetic energy

**Schematic structure:**

- **Zone Ia & Ic:**
  - Hit & stick
  - No mobility
  - Amorphous
  - No preferential orientation
- **Zone T:**
  - Preferential orientation: fastest growth direction
  - Preferential orientation: lowest surface energy

**Allowed interaction/competition between different grains**

**Evolution of grain boundaries with increasing film thickness**
Zone T: overgrowth

Grain with most tilted facet slowly envelops and thus overgrows other grain.

This corresponds to grains with geometric fastest growing direction perpendicular to substrate.

{100} faceting: [111] orientation, {111} faceting: [100] orientation
Zone II: recrystallization during grain growth

**Transition:**
- Thermal energy
- Kinetic energy

**Schematic Structure:**
- Zone Ia
- Zone Ib
- Zone Ic
- Zone T
- Zone II

**Zone Ia:**
- Hit & stick
- No mobility
- Amorphous

**Zone Ib:**
- No preferential orientation

**Zone Ic:**
- Preferential orientation: fastest growth direction

**Zone T:**
- Preferential orientation: lowest surface energy

**Zone II:**
- Recrystallization during grain growth

**Conclusions:**

**More Results:**

**Energy Flux:**

**Diffusion Rate:**

**Diffusion Length:**

**Conclusions:**
Zone II: recrystallization during grain growth

Transition:

Schematic structure:

Zone: Characteristics:

Zone Ia: Hit & stick
- no mobility
- amorphous

Zone Ib: island diffusion

Zone Ic: ripening
- no preferential orientation

Zone T: grain boundary migration
- preferential orientation: fastest growth direction
- preferential orientation: lowest surface energy

⇒ generally aim for lowest surface energy
ESZM overview: influence of $N_2$-flow

Transition:

Schematic structure:

Zone:

**Zone Ic**
- no preferential orientation

**Zone Ib**
- no preferential orientation

**Zone Ia**
- no preferential orientation

Conclusions

Energy flux
Diffusion rate
Diffusion length

Zone T
- preferential orientation: fastest growth direction
  - [111] $N_2$
  - [100] $N$

Zone II
- preferential orientation: lowest surface energy
  - [100]

ESZM overview: influence of film thickness

**Transition:**
- Thermal energy
- Kinetic energy
- Thermal energy
- Thermal energy

**Schematic structure:**
- Zone Ia
- Zone Ib
- Zone Ic
- Zone T
- Zone II

**Zone Ia** - no preferential orientation

**Zone Ib** - no preferential orientation

**Zone Ic** - no preferential orientation

**Zone T** - preferential orientation:
- Fastest growth direction: [111] N₂
- Lowest surface energy: [111] N

**Zone II** - preferential orientation:
- Energy flux: [100] N

**Energy flux**
- Diffusion rate
- Diffusion length

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- More results
- Energy flux
- Diffusion rate
- Diffusion length

**Abadias and Tse, JAP 95 (2004)**

**S. Mahieu et al.: TSF 515 (2006) 1229-1249**
ESZM overview: influence of ion-to-atom ratio

Transition:

Schematic structure:

Zone: Zone 1a Zone 1b Zone 1c Zone T Zone II

N-atoms due to plasma dissociation and collisional dissociation of N₂⁺ ions

Hultman, JAP 78 (1995)

Conclusion out-of-plane orientation

Microstructure and out-of-plane orientation understood after

- calculation of energy flux towards growing film (mobility)
- measurement of plasma composition (atomic/molecular reactive gas)
More results: influence of T-S distance and N₂-flow on orientation

Out-of-plane orientation changes between random, [111], [200]

Relation with energy flux per Ti particle $\Theta$?
Modeling energy flux towards substrate

- Condensation energy: \( Ti\ (s) + \frac{1}{2} N_2\ (g) \rightarrow TiN\ (s) \)
- Kinetic energy of sputtered Ti particles: binary collision
  Monte Carlo simulation + SRIM + PPM
- Kinetic energy of reflected and neutralized ions: binary collision
  Monte Carlo simulation + SRIM + PPM
- Energy of electrons: Langmuir probe measurements
- Energy from plasma contribution
- Metallic flux of Ti: PPM + quartz crystal oscillator

Detailed measurement and calculation method in
S. Mahieu et al: in preparation
Energy flux: influence of T-S distance and N$_2$-flow

Energy flux per deposited Ti particle ($\Theta$) increases with N$_2$-flow and with T-S distance.

Energy flux:

Diffusion rate of adparticles

\[ D \approx e^{-\frac{E_b}{kT}} \approx e^{-\frac{1}{\Theta}} \]

with $E_b$ the barrier needed to allow:
- intergrain diffusion (zone Ic$\rightarrow$ zone T) $E_b = E_{gb}$
- recrystallization during grain growth (zone T$\rightarrow$ zone II) $E_b = E_{recyst}$

Detailed measurement and calculation method in S. Mahieu et al: in preparation
**Diffusion rate**: influence of T-S distance and $N_2$-flow

*Intergrain diffusion:*

*Recrystallization during grain growth:*

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<table>
<thead>
<tr>
<th>$N_2$-flow (sccm)</th>
<th>3</th>
<th>6</th>
<th>9</th>
<th>12</th>
<th>15</th>
<th>18</th>
</tr>
</thead>
<tbody>
<tr>
<td>diffusion rate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- random
- [111]
- [200]
- 50%[111], 50%[200]
Diffusion length: influence of T-S distance and N₂-flow

Diffusion length $L$: $L \approx \sqrt{(D \ast t)} \approx \sqrt{e^{\left(-\frac{E_g}{eT}\right)}}/R_d$

Difussion length $L$ too short

Substrate

$\Lambda < L$  $E > E_{gb}$

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Transitions Zone Ic/zone T/zone II

- high diffusion length \((L > \Lambda)\)
- high diffusion rate \((E > E_{gb})\)

Recrystallization during grain growth

Intergrain diffusion

Energy flux
Diffusion rate
Diffusion length

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Transitions Zone Ic/zone T/zone II

- high diffusion rate ($E > E_{\text{recryst}}$)
- recrystallization by grain boundary migration

**Diffusion rate**

$$r = \text{exp}\left(\frac{1}{Q}\right)$$

**Diffusion length**

$$L = \sqrt{\text{exp}\left(-\frac{1}{Q}\right)}$$

**Energy flux**

$[111]$, $[200]$

**N$_2$-flow** (sccm)

- random
- $50\% [111], 50\% [200]$
Conclusions:

Development of microstructure understood if:

- Diffusion rate and length are calculated from energy flux $\Theta$
- In zone T: plasma composition is known
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