Relation between energy and momentum flux towards the substrate and the hardness of TiN.

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setup:

Unbalanced magnetron type II
Metallic Ti target
reactive gas: \( N_2 \)

Film: 1 µm TiN on polycrystalline stainless steel

Metallic Ti target

Total flow: 60 sccm, total pressure: 0.55 Pa, \( I_d \): 0.9 A, grounded substrate

\( d_{T-S} \): 7-9-11-13-15 cm
\( N_2 \) flow: 3-6-9-12-15-18 sccm

Variation in microstructure, orientation, and hardness. Why?
Hardness as a function of T-S distance and N\textsubscript{2}-flow

Tendency:
- Increasing hardness with increasing N\textsubscript{2}-flow
- Increasing hardness with decreasing d\textsubscript{T\textendash}S

<table>
<thead>
<tr>
<th>d\textsubscript{T\textendash}S (cm)</th>
<th>Hardness (GPa)</th>
<th>orientation</th>
<th>Column diam. (nm)</th>
<th>Density (% of bulk TiN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>11.3 ± 0.5</td>
<td>[111]</td>
<td>102 ± 10</td>
<td>103</td>
</tr>
<tr>
<td>11</td>
<td>9.8 ± 0.6</td>
<td>[111]</td>
<td>99 ± 14</td>
<td>103</td>
</tr>
<tr>
<td>13</td>
<td>9.1 ± 0.9</td>
<td>[111]</td>
<td>99 ± 14</td>
<td>75</td>
</tr>
<tr>
<td>15</td>
<td>5.56 ± 0.3</td>
<td>[111]</td>
<td>98 ± 12</td>
<td>77</td>
</tr>
</tbody>
</table>

Reason? Determine energy and momentum flux towards the substrate!
fluxes:

- Energy flux:
  - plasma radiation
  - kinetic energy sputtered particles
  - kinetic energy refl. particles
  - condensation energy
  - ions
  - electrons
  - recombination energy
  - gas heating

- Momentum flux:
  - kinetic energy sputtered particles
  - kinetic energy refl. particles
  - ions

=> Langmuir probe

Energy resolved mass spectrometry
Microbalance/ QC measurements
MC simulations of transport through gas phase

Ti+1/2N₂ ⇒ TiN

=⇒ Ar⁺⁺e⁻ ⇒ Ar⁺ + 2e⁻
energy flux: condensation energy/Ti

\[ \text{Ti} + \frac{1}{2} \text{N}_2 \Rightarrow \text{TiN} \]

\[ E_{\text{cond}} = 8.4 \text{ eV} \]

\[ E_{\text{cond}} = 8.4 eV \frac{N_{Ti}}{N_{Ti} + N_{TiN}} \]

\( N_i = \text{number of ions measured with mass spectrometer} \)

- condensation energy
- plasma radiation
- \( E_{\text{kin}} \) sp. particles
- \( E_{\text{kin}} \) refl. particles
- electrons
- ions
- recombination energy
- gas heating

Graph showing the relationship between \( E_{\text{cond}} \) and \( \text{N}_2 \)-flow (sccm) for different distances from target to sample (d_T-S: 7 cm, 9 cm, 11 cm, 13 cm, 15 cm, 18 cm).
energy flux: plasma radiation energy/Ti

- condensation energy
- plasma radiation
- $E_{\text{kin sp. particles}}$
- $E_{\text{kin refl. particles}}$
- electrons
- ions
- recombination energy
- gas heating

Ti target

$E_{pl} = \frac{14eV}{4\pi(d_{T-S} - 0.2)^2} \times \frac{1}{Y_{Ar}F_{sp,Ar}}$

Average energy loss during ionization:
Excess of:

Radiation in all directions: ~30eV [1-3]
Ionization energy of Ar: 15.76eV

Total plasma radiation energy/Ti: ~3 eV/Ti

energy flux: $E_{\text{kin sputtered particle/Ti}}$

Ti target

- condensation energy
- plasma radiation
- $E_{\text{kin sp. particles}}$
- $E_{\text{kin refl. particles}}$
- electrons
- ions
- recombination energy
- gas heating

$E_{sp} = (E_{sp,Ar} \times F_{Ar}) + (E_{sp,N} \times F_{N})$

Average energy of Ti arriving at substrate
(MC simulations)

Fraction of Ti particles sputter ejected due to Ar or N

$F_i = \frac{f_i \times Y_i \times F_{sp,i}}{\sum_{i} f_i \times Y_i \times F_{sp,i}}$
energy flux: $E_{\text{kin}}$ reflected particle/Ti

- condensation energy
- plasma radiation
- $E_{\text{kin}}$ sp. particles
- $E_{\text{kin}}$ refl. particles
- electrons
- ions
- recombination energy
- gas heating

$$E_{\text{refl}} = E_{\text{refl},i} \times f_i \times \frac{B_i \times F_{\text{refl},i}}{Y_i \times F_{\text{sp},i}} \quad i = Ar, N$$

[Graph showing the relationship between $E_{\text{refl}}$ and $N_2$-flow (sccm) with different target distances ($d_{T-S}$): 7 cm, 9 cm, 11 cm, 13 cm, 15 cm]
energy flux: electron energy/Ti

\[ E_{el} = \frac{f \times E_{ave,el} \times \Theta_{el}}{\Theta_{Ti}} \]

- condensation energy
- plasma radiation
- \( E_{\text{kin}} \) sp. particles
- \( E_{\text{kin}} \) refl. particles
- **electrons**
- ions
- recombination energy
- gas heating

**Electron Energy Distribution**

- N\(_2\)-flow (sccm)
- energy (eV)

**Conditions**

- Red: d\(_{\text{T-S}}\) = 7 cm
- Green: d\(_{\text{T-S}}\) = 9 cm
- Blue: d\(_{\text{T-S}}\) = 11 cm
- Black: d\(_{\text{T-S}}\) = 13 cm
- Brown: d\(_{\text{T-S}}\) = 15 cm

**Obtained from Langmuir probe**
energy flux:

Energy flux due to ions and recombination of ions with electrons:

One needs flux of ions towards grounded substrate!

Not yet measured, but can be neglected [1-4]

Energy flux due to gas heating:

Can be neglected (0.9 A and 0.55 Pa) [5-6]

Total energy flux/Ti:

Tendency:
- Increasing energy flux/Ti with increasing $N_2$-flow
- Increasing energy flux/Ti with increasing $d_{T-S}$
Total momentum flux/Ti:

- $E_{\text{kin}}$ sp. particles: mass, amount and energy known
- $E_{\text{kin}}$ refl. particles: mass, amount and energy known
- ions: neglected
Total momentum flux/Ti:

Tendency:
- Increasing momentum flux/Ti with increasing \( N_2 \)-flow
- Increasing momentum flux/Ti with decreasing \( d_{T-S} \)
relation with hardness:

Hardness is:
- not related to energy flux/Ti
  but
- can be related to momentum flux/Ti

Further or ongoing research: 1) contribution of ions 2) influence of pressure and magnetic configuration 3) influence of sputter gas
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