Sputter deposited transition metal nitrides as back electrode for CIGS solar cells

W.P. Leroy, S. Mahieu, D. Depla

Research Group DRAFT, Ghent University
The bigger picture

Why Renewable Energy?
• Renewables are unlimited
• Environmentally friendly
• Relatively low maintenance
• ...

Pictures: EMRS, Groen! & EPIA
Potential of renewables

Abundantly available:

On average, each m² on Earth can generate 1700kWh/year, using the current technology

Source: EPIA
Why Thin Film Solar Cells?

- Less material usage
  => lower energy pay-back time & lower production cost

- Flexible substrates
  => roll-to-roll techniques

- Lightweight
  => more applications
Flexible Thin Film PV cells

Metal foils (Cu, Stainless Steel, Ti) as flexible substrates:
+ combine good availability with low cost
+ no degradation of substrate at high production temperatures
- Metal impurity diffusion into absorber layer
- No beneficial Na indiffusion

Thin absorber layer:
+ less material
- low efficiency due to more absorption losses

Transition Metal Nitrides:
+ good barrier properties
+ high thermal stability
+ high optical reflection in the red and near-infrared region
Framework

External parameters
Pressure, (reactive) gas flow, T-S distance, power, magnetron design, …

Substrate fluxes
Metallic Flux
Ion Flux
Energy Flux
Reactive species

Control Growth Process:
ESZM [1]

Intrinsic properties
Density, Composition, Microstructure, Orientation

- Slow
  + Configuration independent
  + Insight in the process

Functional Properties
Reflectivity, Adhesion, Hardness,…

T&E
+ Fast
- Configuration dependent

A case study using TiN

**Typical conditions:**
- Total flow: 60 sccm
- total pressure: 0.3 – 0.8 Pa
- $I_d$: 0.9 A, grounded substrate
- $N_2$ flow: 3-6-9-12-15-18 sccm
- $d_{T-S}$: 7-9-11-13-15 cm

**Unbalanced magnetron type II**

**Metallic Ti target**

**Film:**
1 µm TiN on Si (or SS) substrates
Example Growth process – intrinsic property

Microstructure and orientation versus diffusion length:

- random/zone Ic
- [111]/zone T
- [200]/zone T
- [111]+[200]/zone II
- [200]/zone II

8x10^-8

zone II
zone T
zone Ic

Direct relation between Microstructure/orientation and diffusion length

N₂ flow (sccm)

3 6 9 12 15 18


Reactively (Ar+N₂) sputtered TiN
How about a functional property?

Correlation between reflection and diffusion length?

Ar series
Kr series

Reactively (Ar+N₂) or (Kr+N₂) sputtered TiN
Maybe the intrinsic property?

Correlation between density and diffusion length?

Reactively (Ar+N\textsubscript{2}) or (Kr+N\textsubscript{2}) sputtered TiN
Density and Reflection are correlated \cite{1}:

Both properties are influenced in a similar way!

\cite{1} A. Rizzo et al. TSF 2001, 384, p.215
The ion-to-atom ratio?

Previously evidenced: NO correlation between Ion-to-atom ratio and thin film texture!

So don’t expect a correlation to a property like e.g. hardness!

But what is the idea behind this choice?

Ions, reflected particles and sputtered particles contribute not only in energy, but also in momentum.
Total energy vs Momentum

The total energy flux per deposited particle originates from different processes (condensation, electrons, ions, neutrals, radiation, ..)

and is a thermal energy which is dissipated to the growing film as heat.

=> controls the mobility/growth

Momentum is the local transfer of kinetic energy to the underlying atoms and can locally change the structure, resulting in a change of some thin film properties.

=> minimum kinetic energy to cause kinetically induced processes\[^{[1]}\]

Momentum

Experimental measurement of the total momentum flux:

\[ M_{tot} = M_{sp} + M_{refl} + M_{ion} \]

Calculation\(^{[2]}\) of the separate contributions of
- ions
- neutralized & reflected particles
- sputtered particles

The correlation is already much better!
Relation density – total momentum

![Diagram showing the relationship between relative density and \( M_{tot}/Ti \) (kgm/s), with data points for Ar and Kr series.](image)
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The total momentum is defined by ions, sputtered particles and reflected atoms.

The energy of the ions is IN OUR CASE very low (below 5 eV).

Momentum of the Sputtered and Reflected particles

A very Nice correlation!
A slow, but more general approach allows to gain insights in the fundamental relations governing the functional properties.

Total Energy Flux arriving at the substrate controls mobility/growth.
To remember:

Not everything scales with total energy, momentum can also be the key parameter.

A clear relation is found between the reflection of the transition metal nitride thin films and the momentum of sputtered and reflected particles.
Outlook:

- TiN: make the best reflecting coatings & metal diffusion measurements
- ZrN: similar research track, as it should give even better reflection\(^1\), probably due to even more reflected neutrals!

\(^1\) S. Schleussner, T. Kubart et al. TSF 2009, 517 p.5548

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Read the details in:
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