Structure, stress and mechanical properties of Mo-Al-N sputter-deposited thin films: role of point defects

G. Abadias[1], F. Angay[1], D. Eyidi[1], L. Löfler[2], D. Holec[2], P. Djemia[3], F. Tétard[3]

1. Institut Pprime - CNRS – Univ. Poitiers, Chasseneuil-Futuroscope, France
2. Department of Materials Science, Univ. Leoben, Austria
3. LSPM, Univ. Sorbonne Paris Nord, Villetaneuse, France

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Context and motivation

- The aim of the present study is to gain a better understanding on phase formation, defect concentration, and mechanical properties when Al substitutes for Mo in Mo-Al-N coatings.

- We combine thin film growth experiments and density functional theory (DFT) calculations to study the importance of **point defects**

- $Mo_{1-x}Al_xN_y$ thin films with Al fraction x = 0 to 0.5 and nitrogen-to-metal ratio y = 0.78 to 1.38 were deposited by reactive magnetron cosputtering [1].

- Our experimental findings are compared and discussed with previous literature works [2,3].

Experimental procedure

- Base pressure : $p_0 \leq 6 \cdot 10^{-6}$ Pa
- Two separate targets: Mo, Al
- DC power supply
- $Ar+N_2$ plasma discharge with fixed Ar (25 sccm) and N_2 (20 sccm) flow rate
- Working pressure: 0.30 Pa
- Substrate bias voltage: -60 V
- Substrate temperature: 300°C and 500°C
- Film thickness: ~300 nm
- The Al content in $Mo_{1-x}Al_xN_y$ alloy was varied by adjusting the DC power supply of Mo and Al cathodes
- Stress is determined *in situ* using wafer curvature (MOSS technique)

### Deposition
(reactive unbalanced magnetron)

DFT calculations

- VASP code
- Pseudo potential PAW method GGA
- cut-off 600 eV
- Cubic rocksalt structure

- Special Quasirandom Structure (SQS) approach to simulate $Mo_{1-x}Al_xN_y$ solid solutions
- 2×2×2 supercells (64 atoms)
- Elastic constants obtained from strain/stress method [x]
- Polycrystalline Young modulus calculated using the Voigt-Reuss homogenization [x]
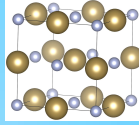
## Microstructural characterization

Elemental composition (WDS)
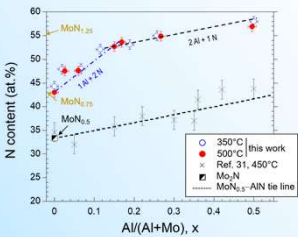
- For x=0, stoichiometry close to $MoN_{0.75}$
- N-deficient films for low Al content (up to x=0.1)
- Increase of N content from 42 at.% to 55 at.% with incorporation of Al content despite constant N_2 flow
- Two distinct regimes evidenced, related to different nitrogen affinity with increasing Al content
- DFT calculations predicts stabilization of cubic structure with increasing Al fraction
- At low Al content (x=0.12), N and Me vacancies are thermodynamically favorable

SEM cross-section views

- Compact microstructure
- Columnar growth evidenced for Al-rich films

XRD patterns
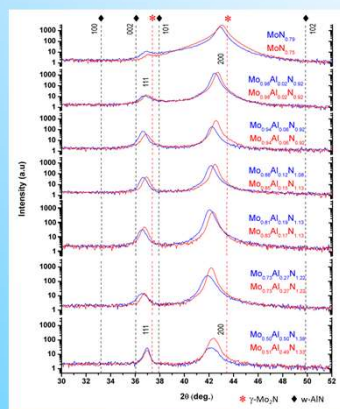
- Cubic rock-salt $Mo_{1-x}Al_xN_y$ alloys with (001) preferred orientation
- Decrease of a_0 lattice parameter with Al content predicted by DFT for defect-free MoAlN
- Expansion of a_0 observed experimentally is contributed to a decrease in N vacancy concentration with increasing x

DFT calculations – Phase stability
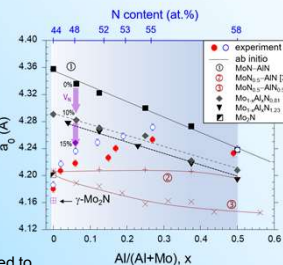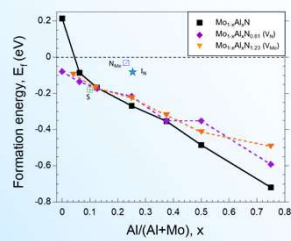
Stress analysis

Sin²ψ plots

In situ wafer curvature
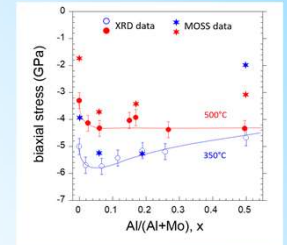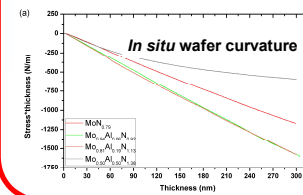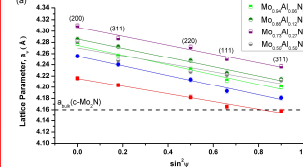

- Compressive stress development due to energetic bombardment during growth
- Lower compressive stress at 500°C
- Non-monotonous evolution with Al content, contribution of tensile stress source for x=0.50 (columnar growth)

Mechanical properties

Nanoindentation tests (XP Nanoindentor MTS) with a Berkovich indenter
Transverse sound velocity measurements from Brillouin Light Scattering [6]
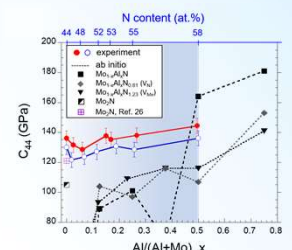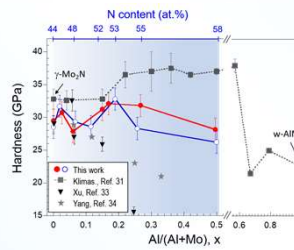
Blackman diagram
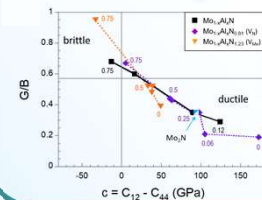
- Non-monotonous variation of hardness and C_{44} elastic constant
- Maximum hardness value of ~33 GPa obtained for $Mo_{0.81}Al_{0.19}N_{1.13}$ film deposited at 350 °C
- Complex dependence of elastic properties of $Mo_{1-x}Al_xN_y$ alloys to point defects
- N vacancies are found to be more beneficial in retaining the ductile properties of Mo-Al-N compared to Me ones.

CONCLUSIONS

- Point defects, especially N vacancies below x = 0.12 and metal vacancies above this value, play a key role in the compositional dependence of the lattice constant, Young modulus, and shear elastic constant of $Mo_{1-x}Al_xN_y$ alloys

- The incorporation of Al into MoN is accompanied by a significant variation in the nitrogen content from 44% (x = 0) to 58% (x = 0.5) despite a constant N_2 partial pressure during deposition

- It is evidenced that ternary $Mo_{1-x}Al_xN_y$ alloys with low Al content (x = 0.02–0.12) tend to stabilize primarily N vacancies in the concentration between 10% and 20%, while the incorporation of a higher Al fraction (up to x = 0.5) results in the formation of less defective films

- Films with larger Al content (x = 0.25 and x = 0.5) exhibit worse mechanical properties (H ~ 27 GPa and elastic modulus ~245 GPa), which could be explained by more covalent bonding

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