Segregation of oxygen impurities in transition metal nitride superlattices

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Abstract

Using a first-principles approach we investigated an effect of oxygen as substitutional impurity on cohesion of three transition metal nitride multilayers. Namely, we studied AlN/VN, AlN/TiN and VN/TiN systems in a rock-salt structure (B1) with (0 0 1) interfaces. Preferred oxygen positions were determined with the help of calculations of free energy that also included vibrational entropy terms. Subsequent calculations of cleavage energy for all possible cleavage planes enabled us to identify the weakest link and to assess the impact of the oxygen impurity on a cohesion of each of the studied multilayers. Supercells of different size were used to estimate possible effect of oxygen concentration. The results indicate that oxygen prefers to replace nitrogen atoms in interfacial planes and that these impurities do not reduce the multilayer cohesion. Moreover, in the case of AlN/TiN system, their presence was found to increase the cleavage energy of the interface.

Introduction

TM nitrides are very hard materials suitable for protective coatings of cutting tools. Although they are hard themselves, new strategies for further enhancement of their hardness are desirable.

Strategies

Exploring new materials
(alloying, doping, ...)

Tuning the microstructure
(multilayer design, rezidual stress design,...)

Example
hardness of TiN ≈ **34 GPa**

Alloying
TiN + Al (metastable solid solution with 0.66% Al fraction)
hardness of ≈ **37 GPa***

Multilayer design
TiN/VN superlattice:
for bi-layer period 5.2 nm,
hardness of ≈ **55 GPa****

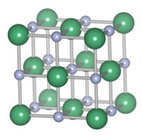
* Mayrhofer et al., Appl. Phys. Lett. 83 (2003) 2049.

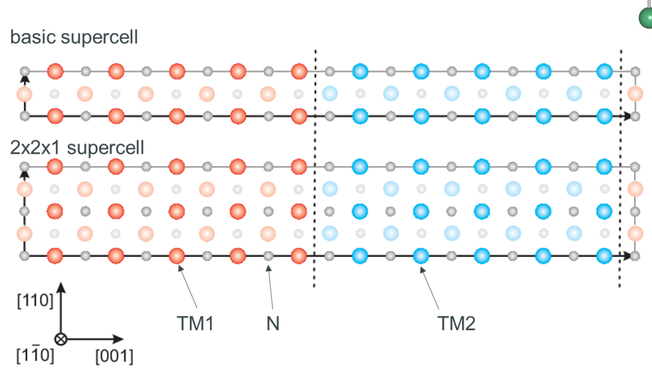
** Helmersson et al., J. Appl. Phys. 62 (1987) 481.

Methods

Computational supercells and code

Transition metal nitrides are considered in the B1 structure.





E_{cut} = 600eV

15x15x1 *k*-points (basic supercell)

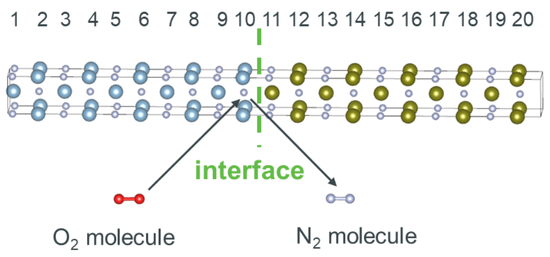
Full relaxation:

F_{max} < 0.0001 eV/A

σ_{max} < 0.02 GPa

Segregation preference

Just a single oxygen substitution is considered in the supercell. Let us define "substitution energy" E_{sub} as



$$E_{\mathrm{sub}} = E_{\mathrm{ml+O}} + 1/2E_{\mathrm{N_2}} - (E_{\mathrm{ml}} + 1/2E_{\mathrm{O_2}}),$$

where E_{ml} ... energy of clean multilayer

E_{ml+O} energy of multilayer with oxygen

E_{N2} energy of nitrogen molecule

E_{O2} eneregy of oxygen molecule

Evaluation of entropy terms

The effect of temperature is taken into account by means of harmonic approximation. The Helmholtz free energy of harmonic phonons is expressed as

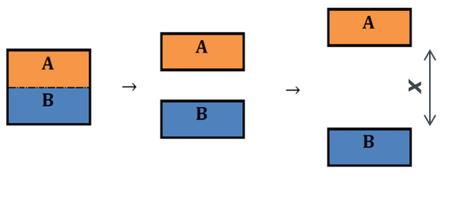
$$F = -k_{\mathrm{B}}T \ln Z$$
$$= \varphi + \frac{1}{2}\sum_{\mathbf{q}\nu}\hbar\omega(\mathbf{q}\nu) + k_{\mathrm{B}}T\sum_{\mathbf{q}\nu}\ln\left[1 - \exp(-\hbar\omega(\mathbf{q}\nu)/k_{\mathrm{B}}T)\right]$$

and the substitution free energy $F_{\mathrm{sub}} = F_{\mathrm{ml+O}} + 1/2F_{\mathrm{N_2}} - (F_{\mathrm{ml}} + 1/2F_{\mathrm{O_2}})$

Cleavage energy

Brittle cleavage is modelled by the rigid block displacement (RBD). The energy can be approximated by the fit

$$E(x) = E_c\left[1 - \left(1 + \frac{x}{l}\right)\exp\left(-\frac{x}{l}\right)\right]$$



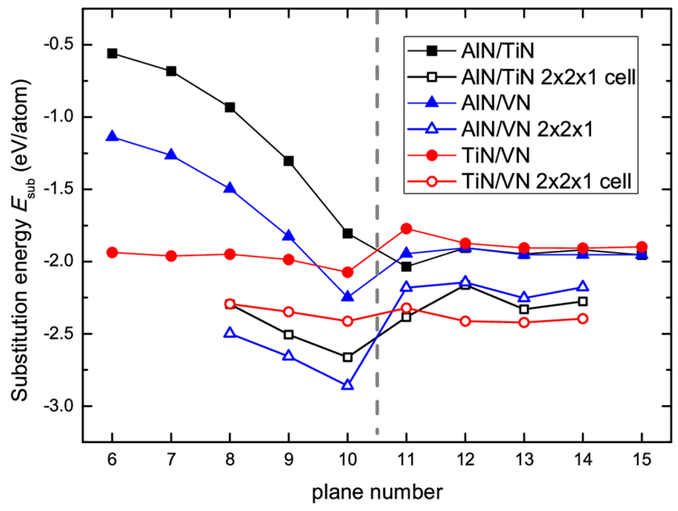
where E_c is the cleavage energy, l is a critical length and x is the displacement of blocks.

J.H. Rose, J.R. Smith and J. Ferrante: *Phys. Rev. B*, 28 (4): 1835, 1983.

Results

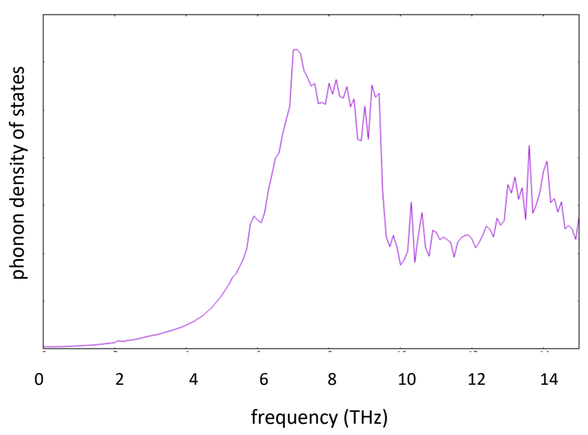
Segregation positions

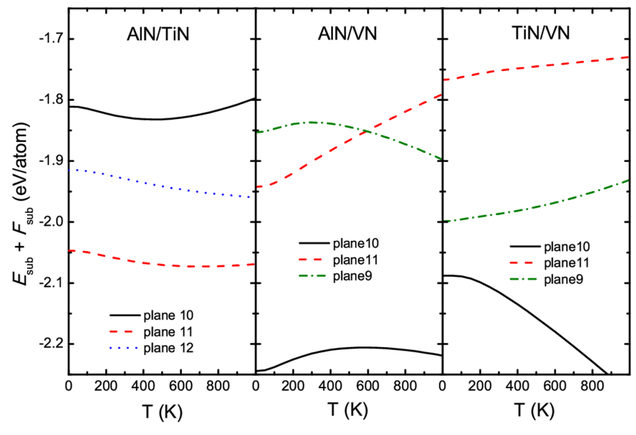
The preferred positions of substitutional oxygen atoms are determined using the substitution energy. One substitution in the basic supercell leads to a monolayer of TM oxide. The 2x2x1 supercell enables us to simulate 1/4 monolayer of substitutional oxygen corresponding to its smaller concentration.



Effect of elevated temperature

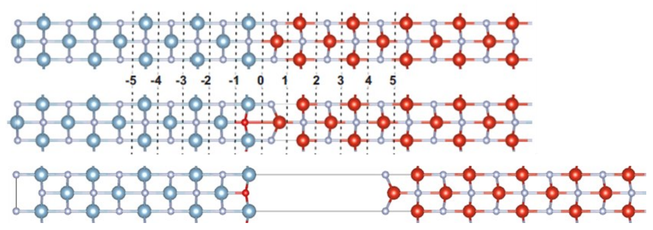
In order to consider possible effect of entropy terms at elevated temperatures, phonon spectra were computed for clean and oxygen segregated multilayers and Helmholtz free energy of harmonic phonons were added to the static lattice energy.



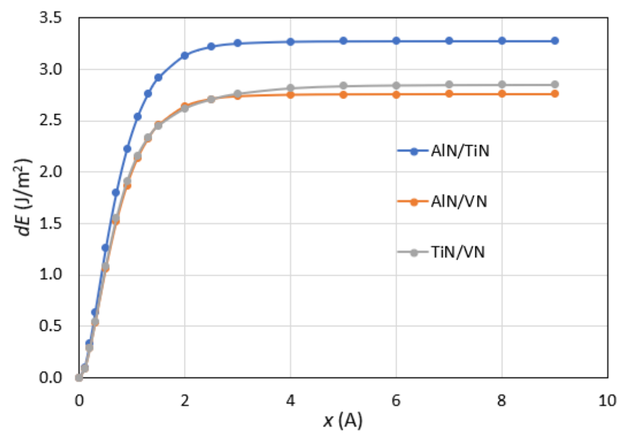


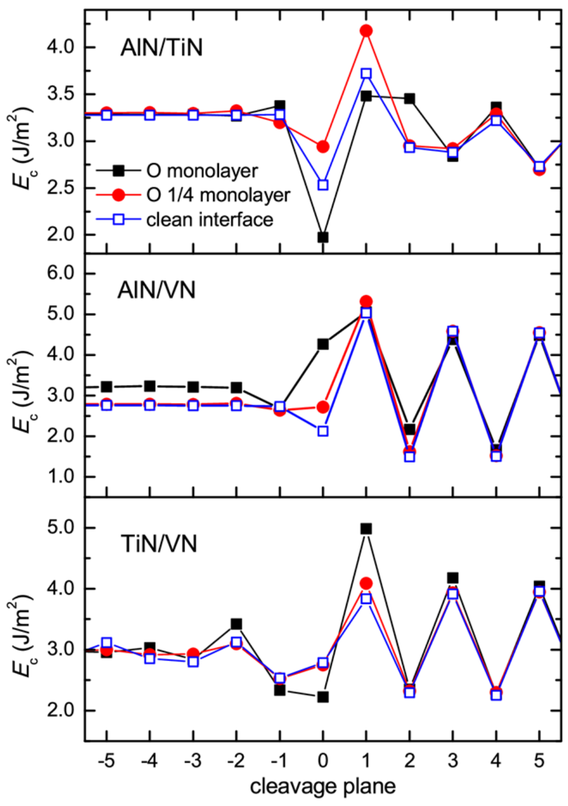
Cohesion of multilayers

The effect of oxygen substitutions is assessed in terms of the cleavage energy E_c.



Results of the RBD calculations for clean interfaces.





Conclusions

- The oxygen substitution preffers to occur at the interface.
- In AlN/TiN superlattice, the segregation preference depends on concentration of oxygen.
- Vibrational entropy terms do not change the segregation preference determined using static lattice calculations.
- Cleavage energy of multilayer interfaces is reduced by the substitutional oxygen only for AlN/TiN and TiN/VN and one monolayer concentration.
- Lower (1/4 monolayer) concentration does not reduce the superlattice cohesion.
- Moreover, for the AlN/TiN system, the oxygen enhances cohesion of the interface and of the whole superlattice.

Acknowledgments

The authors acknowledge the financial support by the Czech Science Foundation (Project No. GA 16-24711S).

The computational resources were provided thank to the support by the Ministry of Education, Youth and Sports of the Czech Republic through the e-INFRA CZ (ID:90140), **OPEN 18-16**.