AB-INITIO STUDY OF SURFACE ENERGIES AND STRUCTURAL INFLUENCE OF VACANCIES IN TITANIUM NITRIDE NANOLAYER

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INTRODUCTION

- Titanium nitride (TiN) has wide range of interesting properties such as high melting point, ultra-hardness, excellent mechanical resistance or good electric and thermal conductivity => largerz applied as coating nanolayer.
- During its phase formation, the occurrence of high-density of N vacancies is very probable => can significantly modify material properties, e.g. change the lattice parameters.
- Other important characteristics: surface energies - play significant role in epitaxial film growth of TiN or in the explanations of particle (e.g. H, O) absorptions on its given surface layer.
- Theoretical predictions of those mentioned properties can provide a meaningful insight to the material behavior or the processes occurring during its modifications.
- ✓ We provide DFT calculations of the mean effects of vacancies on the lattice parameter in rock salt-like structure of TiN and the calculations of its basic surface energies

STUDIED SYSTEM

Material: rock salt-like structure of TiN ($Fm\bar{3}m$, #225)

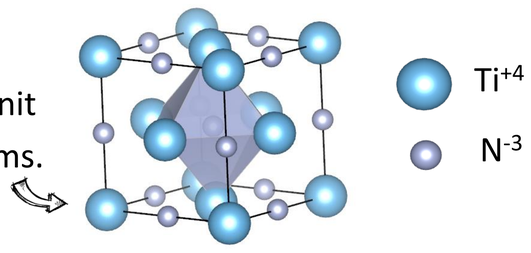

Figure 1 TiN unit cell with 8 atoms.

Characteristics: calculations of:

- ✓ Surfaces energies of 8 crystallographic planes

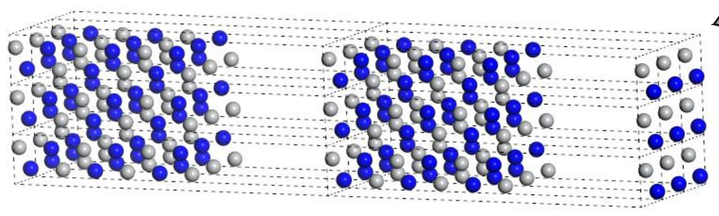

Figure 2 (100) surface with 8 atomic layers in the slab model.

- ✓ Mean effects of vacancies on the lattice parameter of fcc TiN (δ-TiN)
- Supercell with 64 atomic positions (32 Ti and 32 N) for vacancies effects

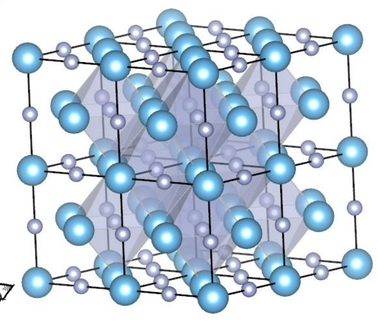

Figure 3 TiN supercell with 64 atoms.

METHODS / SETTINGS

Ab-initio method: Density Functional Theory (DFT) within Cambridge Serial Total Energy Package (CASTEP) code

Exchange-correlation energy functional: generalized gradient approximation functional (GGA) in Perderw, Burke and Ernzerhof (PBE) parametrization.

Energy cut-off: 360 eV (convergence of 0.02 eV per atom).

Monkhorst-Pack k-point grid: 8 × 8 × 8 (convergence of 0.01 eV per atom)

- Calculated energy dependences on lattice parameter were fitted by Birch-Murnaghan equation of state

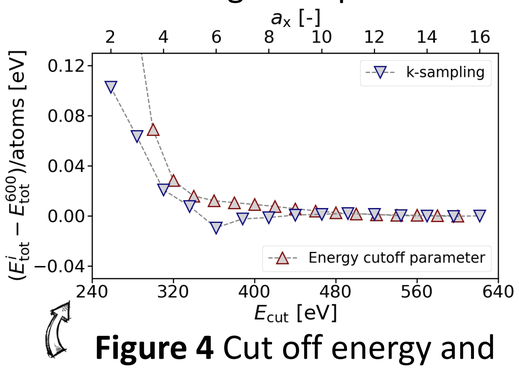

Figure 4 Cut off energy and k-point grid convergence of TiN.

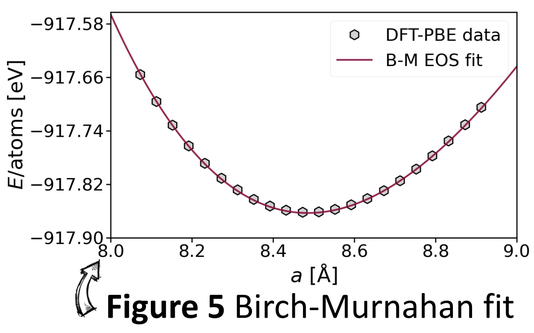

Figure 5 Birch-Murnahan fit quality of DFT data.

RESULTS

Surface energies:

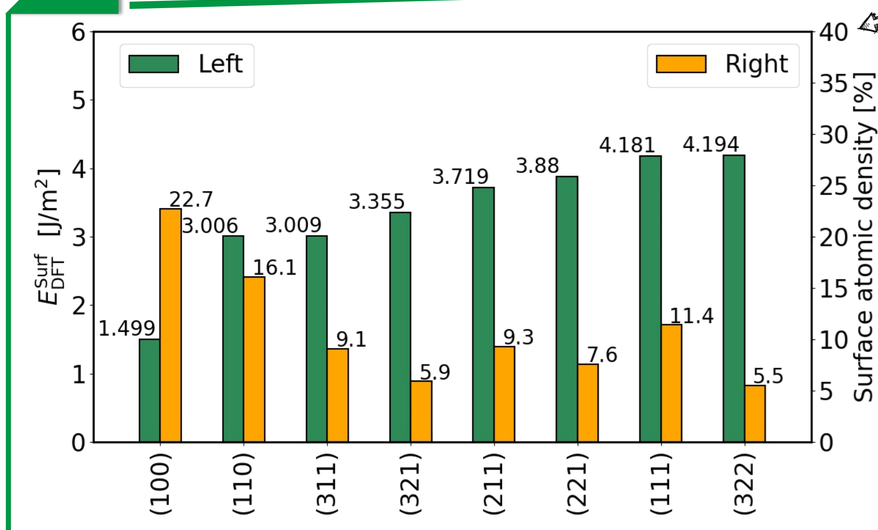

Figure 6 TiN calculated surface energies. Vacuum thickness: 10 Å. 12 atomic layers. Surface relaxations and reconstructions not considered.

Nitrogen vacancies in TiN_{1-x}

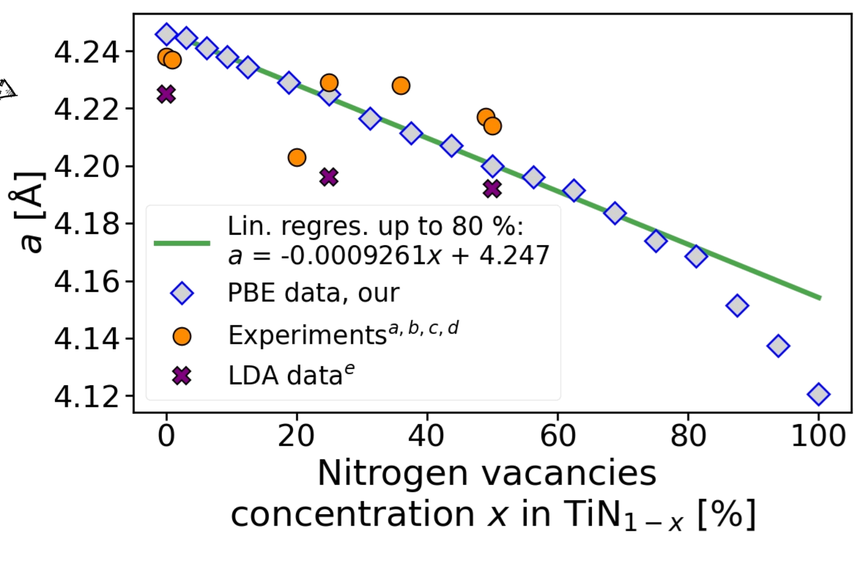

Figure 7 Calculated TiN lattice parameter dependence on N vacancy concentration.

Table 1 Comparison of our calculated TiN_{1-x} lattice parameter dependence on N vacancy concentration x with theoretical and experimental data from available literature.

x in TiN_{1-x} (× 100 %)	a_{ref}, ref. (Å)	a^{PBE}_{our}, linear fit (Å)	$\frac{a^{PBE}_{our} - a_{ref}}{a_{ref}}$ (%)
0.00	4.238[exp, *a*]	4.247	+0.21
0.00	4.225[LDA, *e*]	4.246	+0.52
1.00	4.237[exp, *b*]	4.246	+0.21
20.00	4.203[exp, *b*]	4.228	+0.61
25.00	4.229[exp, *a*]	4.224	-0.12
25.00	4.196[LDA, *e*]	4.224	+0.66
36.00	4.228 [exp, *c*]	4.214	-0.34
49.00	4.217 [exp, *d*]	4.202	-0.36
50.00	4.214[exp, *a*]	4.201	-0.32
50.00	4.192[LDA, *e*]	4.201	+0.21

References: ***a*** - Wriedt, H.A. and Murray, J.L. *Bull. Alloy Phase Diagrams*. 1987, vol. 8, no. 4, pp. 378–388., ***b*** - Höchst, H. *et al. Phys. Rev. B*. 1982, vol. 25, no. 12, pp. 7183–7191. ***c*** - Jiang, C.-C. *et al. J. Alloys Compd.* 1993, vol. 190, no. 2, pp. 197–200., ***d*** - Guemmaz, M. et al. Appl. Phys. A Mater. Sci. Process. 1997, vol. 64, no. 4, pp. 407–415. ***e*** - Guemmaz, M. et al. Int. J. Inorg. Mater. 2001, vol. 3, no. 8, pp. 1319–1321.

CONCLUSION

We determined surface energies of 8 crystallographic planes in TiN by means of the *ab-initio* simulation method of DFT with GGA-PBE exchange-correlation functional. The most stable is (100). Comparing with available published data for (100), (110) and (111) surfaces, our calculations are in very well agreement. Linear decrease of lattice parameter with increasing N vacancy concentration is observed and the linear regression of those data is possible up to 80 % of vacancies presence. From this point, it is reasonable to expect the formation of hexagonal phase of TiN_{1-x}, $x \leq 0.2$. We have reached excellent correspondence with 3 theoretical and 4 experimental published literature data and extended lattice parameter dependence on the full range of nitrogen vacancies with very good linear fit regression.

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