UN (110) surface properties: ab initio calculations

Dmitry Bocharov[1,2,3], Yuri F. Zhukovskii[2], Denis Gryaznov[2], and Eugene A. Kotomin[2]

[1]Faculty of Computing, University of Latvia, Raina blvd. 19, LV-1586

[2]Institute of Solid State Physics, Kengaraga 8, LV- 1063

[3]Faculty of Physics and Mathematics, University of Latvia, Zellu 8, LV-1002

e-mail of presenting author: bocharov@latnet.lv

Motivation

Application of actinide nitrides as a fuel in the fast transmutation reactor offers potentially enhanced performance as compared to conventional actinide oxide fuels [1,2]. These fuels are receiving renewed attention across the world since the commencement of the Generation IV initiative. Unfortunately, one of the problems with actinide nitrides is their interaction with the oxygen which results in an effective fuel oxidation and degradation. Therefore, it is significant to know more about chemical properties, reactivity and oxidation mechanism of UN surfaces as well as processes occurring on grain boundaries inside the polycrystalline UN. In this work, we compare results obtained for (110) surface with previous results for (001) surface.

Computational method and model

For simulation of pure and defective UN(001) and (110) substrates with empty and oxygen-occupied vacancies, we employ the DFT plane-wave computational package *VASP 4.6* [3], using ultra-soft pseudopotentials combined with the PAW method. We use the Perdew-Wang-91 GGA non-local exchange-correlation functional [3] and the scalar relativistic PAW pseudopotentials representing the core electrons of U (with $6s^26p^66d^25f^27s^2$ valence shell), N ($2s^22p^3$) and O ($2s^22p^4$) atoms (containing 14, 5 and 6 valence electrons, respectively). The cut-off energy is chosen to be 520 eV. We use the Monkhorst-Pack scheme [4] for 4x4x1 and 8x8x1 *k*-point meshes in the Brillouin zone (BZ).

For the UN(001) and (110) substrates, we use 3D slab model consisting of 5-11 atomic layers. The 2D atomic slabs are separated by a vacuum gaps of ~40 Å (Fig 1).

The lattice constant of UN slabs is fixed at 4.87 Å, taken from the lattice relaxation of UN bulk [5]. In all the calculations, we perform the structural optimization within the supercell of fixed linear dimensions. The total spin magnetic moment is also relaxed in all the calculations on the ferromagnetic spin distributions within the uranium sub-lattice.

Fig. 1. Cross-section of 3D UN slabs.

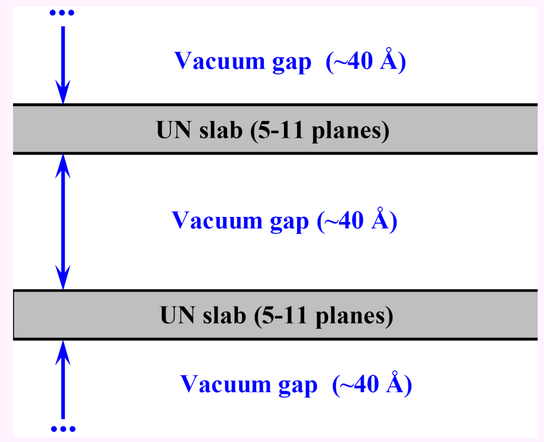

Table 1. Surface energies E_{surf} (J·m^{-2}) and averaged magnetic moments (in μ_B) *per* U atom for the defect-free UN (001) [5, 6] and UN(110) surfaces. ↓

Number of layers	E_{surf} (J/m^2) spin unrelaxed slab (001)	E_{surf} (J/m^2) spin-relaxed slab (001)	$\mu_{av}(\mu_B)$ (001)	E_{surf} (J/m^2) spin-relaxed slab (110)	$\mu_{av}(\mu_B)$ (110)
4	-	-	-	1.981	1.742
5	1.69	1.44	1.57	1.977	1.645
6	-	-	-	1.947	1.543
7	1.70	1.37	1.44	1.928	1.464
8	-	-	-	1.904	1.459
9	1.70	1.29	1.37	1.878	1.417
10	-	-	-	1.853	1.423
11	1.69	1.22	1.33	1.830	1.385

	(001) surface	(110) surface
Size of surface unit cell (ÅxÅ)	3.44 x 3.44 $(\frac{\sqrt{2}}{2}a \times \frac{\sqrt{2}}{2}a)$ or $(\frac{1}{2}a \times a)$	4.87 x 3.44 $(a \times \frac{\sqrt{2}}{2}a)$
Distance between two nearest U and U (or N and N) atoms in *xy* plane (Å)	3.44 $(\frac{\sqrt{2}}{2}a)$ in both directions	4.87 in *x* direction 3.44 in *y* direction
Distance between nearest U and N atoms in *xy* plane (Å)	2.435 $(\frac{a}{2})$	2.435 $(\frac{a}{2})$ in *x* direction not defined in *y* direction
Distance between neighbor layers in z direction (Å)	2.435 $(\frac{a}{2})$	1.72 $(a\frac{\sqrt{2}}{4})$
Distance between nearest atoms in *z* direction (Å)	2.435 $(\frac{a}{2})$, distance between U and N atoms	3.44 $(\frac{\sqrt{2}}{2}a)$, distance between N and N (or U and U) atoms

← Table 2. Comparison of structural properties for the UN(001) and UN(110) surfaces (Fig. 2.)

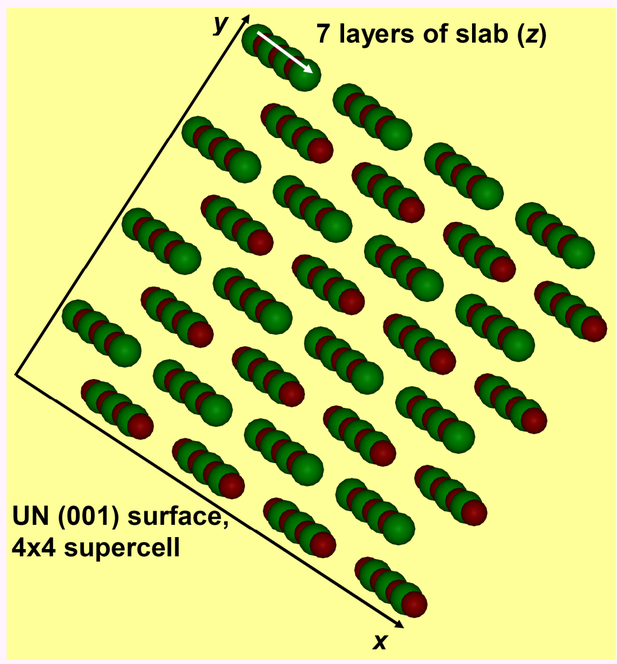

Fig. 2. Structural comparison of (110) and ← (001) surfaces (7-layer slabs) ↓

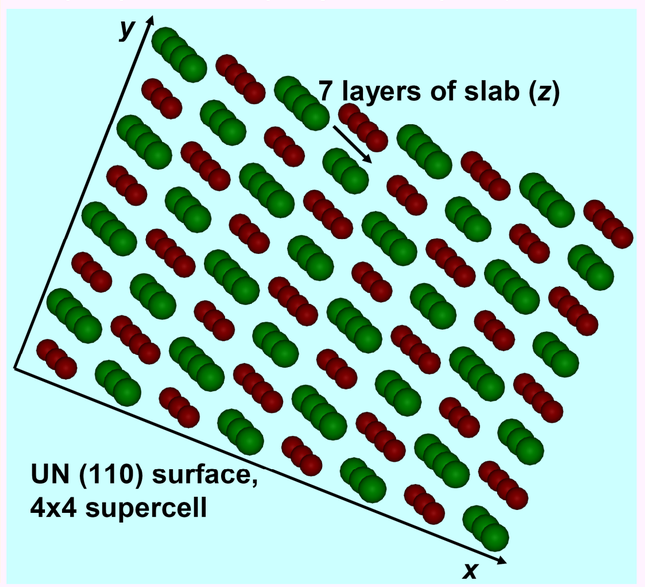

Table 3. Atomic displacements Δz(Å)* for defect-less UN (001) [6] and (110) surfaces.

Number of atomic planes	U atom displacements				N atom displacements			
	(001) surface		(110) surface		(001) surface		(110) surface	
	Surface	Sub-surface	Surface	Sub-surface	Surface	Sub-surface	Surface	Sub-surface
5	-0.050	-0.012	-0.053	-0.005	0.023	0.023	-0.279	0.068
7	-0.046	-0.009	-0.038	-0.009	0.024	0.028	-0.272	0.092
8	-	-	-0.027	-0.010	-	-	-0.273	0.108
9	-0.047	-0.011	-0.042	-0.014	0.024	0.028	-0.279	0.091
10	-	-	-0.010	0.008	-	-	-0.255	0.120
11	-0.047	-0.011	-0.015	0.015	0.025	0.031	-0.252	0.118

* negative sign means an inward atomic displacement towards the slab center

Table 4. Atomic Bader charges on defect-less (001) and (110) surfaces of UN

Atom	Number of UN (001) slab atomic layers				Number of UN (110) slab atomic layers			
	5	7	9	11	5	7	9	11
Surface U	1.68	1.74	1.68	1.72	1.46	1.48	1.49	1.48
Sub-surface U	1.67	1.63	1.63	1.67	1.88	1.85	1.83	1.84
U in central (mirror) plane	1.69	1.72	1.65	1.66	1.60	1.74	1.64	1.70
Surface N	-1.65	-1.67	-1.67	-1.68	-1.55	-1.55	-1.55	-1.55
Sub-surface N	-1.68	-1.70	-1.70	-1.67	-1.75	-1.73	-1.75	-1.73
N in central (mirror) plane	-1.74	-1.65	-1.65	- 1.63	- 1.70	-1.71	-1.75	-1.74

Table 5. Nitrogen vacancy formation energies (in eV) as well as averaged magnetic moment μ_{av} *per* U atom for UN (001) [6] and (110) slabs (2x2 supercell).

Number of layers	N-vac E_{form} on (001) surface	$\mu_{av}(\mu_B)$ (001)	N-vac E_{form} on (110) surface	$\mu_{av}(\mu_B)$ (110)
5	3.700	1.702	3.075	1.818
7	3.706	1.548	3.028	1.585
9	3.708	1.452	3.036	1.512
11	3.712	1.392	3.026	1.453

$$E_{form}^{N\_vac} = \frac{1}{2}\left(E_{def}^{UN} + 2E^{N} - E^{UN}\right)$$

Table 6. Incorporation (*I*), solution (*S*) energies in eV, average spin magnetic moments of U atoms and effective charge of O atoms in e^- for O incorporation into N vacancy on UN (001) [7] and (110) surfaces. The reference states for calculating the incorporation and solution energies are the chemical potentials of O, N and U calculated for O_2, N_2 molecules and α-U, respectively (2x2 supercell).

Number of layers	(001) surface				(110) surface			
	I (eV)	*S* (eV)	$\mu_{av}^{U}(\mu_B)$	$q_{eff}(e^-)$	*I* (eV)	*S* (eV)	$\mu_{av}^{U}(\mu_B)$	$q_{eff}(e^-)$
5	-6.173	-2.473	1.647	-1.36	-5.853	-2.778	1.736	-1.27
7	-6.181	-2.476	1.495	-1.36	-5.822	-2.794	1.516	-1.29
9	-6.186	-2.479	1.412	-1.36	-5.820	-2.784	1.472	-1.29
11	-6.195	-2.483	1.365	-1.35	-5.817	-2.791	1.416	-1.29

$$I = \frac{1}{2}(E_{O\_inc}^{UN} - E_{vac}^{UN} - 2E_O) \qquad S = I + E_{form}^{N\_vac}$$

Conclusions

1. Depending on slab thickness, the surface energies are ~0.5-0.7 J·m^{-2} larger for UN(110) surface (Table 1). It means that the UN(001) surface [5] is energetically more favorable.
2. Energies of the nitrogen vacancy formation on the uranium mononitride surface are also larger for (110) surfaces, by ~0.7 eV irrespectively of slab thickness.
3. Effective charges on N and U atoms of both perfect and defective UN(110) surface are slightly smaller than those for UN(001) surface.
4. Averaged magnetic moment μ_{av} is slightly larger on both regular and defective UN(110) surface.

Acknowledgements

This study was partly supported by the European Commission FP7 project *F*-BRIDGE and ESF project No. 2009/0216/1DP/1.1.1.2.0/09/APIA/VIAA/044. and. The authors kindly thank R.A. Evarestov, A. Kuzmin, P. Van Uffelen and V. Kashcheyevs for a numerous fruitful discussions. The technical assistance of A. Gopejenko and S. Piskunov was the most valuable.

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