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Features of adsorption of silicon on TiN(111) compound in presence of substitution impurities Al and Ta: first principle calculations

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Abstract. *We present the results of an ab initio study of silicon adsorption on the (111) surface of TiN with NaCl structure in the presence of substitutional impurities Al and Ta. All possible symmetric non-equivalent positions of the silicon atom on the (111) surface with titanium and nitrogen terminations were considered, and the binding energy of the silicon atom in these positions was calculated. The most energetically favorable positions for adsorption on the considered (111) surface were determined.*

Key words*: titanium nitride, surface, silicon, protective wear-resistant coating, density functional theory.*

Introduction

Many issues related to friction and wear are still relevant today. The increasing demands from modern industry on friction materials are forcing the search for new ways to improve their functional properties. To date, one of the main ways to improve the efficiency and durability of parts and mechanisms has been the application of wear-resistant protective coatings. One of the most promising directions for solving this problem is the use of nanocrystalline multi-component coatings based on the Ti-Al-N solid solution, which have high hardness combined with thermal stability and oxidation resistance [1]. In particular, the simultaneous introduction of tantalum and silicon into the Ti-Al-N nanocrystalline composition allows us to obtain coatings with improved properties characteristic of the $Ti_{1-x-y}Al_xTa_yN$ systems (high resistance to cracking, heat and oxidation [2]) and the $Ti_{1-x-y}Al_xSi_yN$ system (nanocrystalline structure and high hardness [3]). The study of the behaviour of Si atoms on the TiN surface in the presence of Al and Ta substitutional impurities will provide information on the interaction of silicon with both the surface atoms of the system and with the impurity atoms. This will reveal the role of the alloying elements (Al and Ta) in the formation process of the Ti-Al-Ta-Si-N composite.

Research methods

All total energy calculations were performed within the framework of electron density functional theory using the projected augmented plane wave method implemented in the ABINIT software package. The generalised gradient approximation in the Perdue-Burke-Ernzerhof [4] form was used to describe the exchange and correlation effects. The cut-off energy in the expansion of the wave function in terms of the plane wave basis was chosen to be 408 eV. At each iteration of the self-consistency of the electron density of the films, the Hamiltonian eigenvalues were calculated on a 7x7x1 grid of k-points generated using the Monkhorst-Pack scheme.

The adsorption positions of the Si atom on the (111) surfaces with nitrogen and metal terminations of the TiN film with NaCl structure were optimised in the presence of Al or Ta substitutional impurities. The Si binding energy on the surfaces is calculated using

$$E_b = E(\mathrm{Si}) + E(\mathrm{MeN}) - E(\mathrm{MeN\text{-}Si})$$

where E(Si), E(MeN) and E(MeN-Si) are the total energies of the silicon atom, the MeN film and the MeN film with one Si atom adsorbed, respectively, Me is the metal (Ti with Al or Ta substitutional impurities).

To study the interaction between the Si atom and the TiN(111) surface, a 25 % silicon coverage was considered. A 10-layer film was modelled (Figure 1) and the silicon atom was placed in one of

four non-equivalent symmetrical positions on the surface. Aluminium and/or tantalum atoms replaced the titanium atoms closest to the adsorbed silicon atom. In order to analyse the interaction of the Si atom with the studied surfaces, the valence electron density distribution and the Bader charge transfer were calculated and analysed (Table 1).

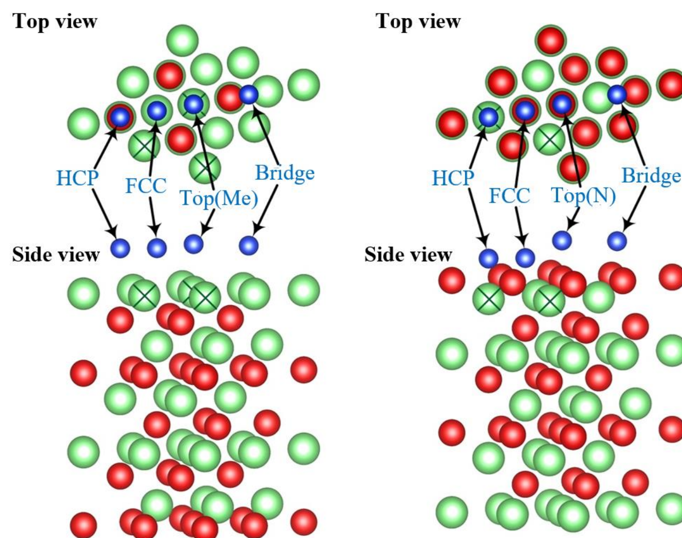

Fig. 1. Adsorption positions of Si atom on TiN(111) surface with metal (left) and nitrogen (right) terminations. Blue balls show the considered adsorption positions of the silicon atom. Green and red balls are metal and nitrogen atoms, respectively. The cross marks the positions of Ti atoms, which were replaced by Al and Ta atoms

Results

It was found that the binding energy of silicon is positive in all cases considered. On the (111) surface, the highest binding energies are observed when a silicon atom is adsorbed in the FCC sites. It was also revealed that Bridge positions are unstable, causing the silicon atom to leave and move towards the nearest FCC sites on the (111) surface. It was found that replacing a Ti atom with an Al atom in the immediate vicinity of the adsorbed Si atom on the TiN(111) surface reduces the binding energy of silicon with the surface. Conversely, replacing a Ti atom with a Ta atom generally increases the binding energy of silicon to the surface in the majority of cases considered. Exceptions to this rule include configurations where Ta or Al atoms close to a Si atom adsorbed in FCC or HCP sites on the N-terminated (111) surface. These configurations differ from the others in that there is more than one N atom in the first coordination sphere of the adsorbed Si atom. Aluminium enhances the binding of silicon to the surface atoms when more than one Si-N bond is formed. The subsurface layer of the nitrogen termination of surface (111) becomes unstable with the presence of Al or Ta atoms. This instability causes the Si atom to shift from the Top(N) position to the nearest FCC site due to relaxation. Table 1 shows that the substitution of Ti for Al or Ta does not affect the sign of the charge transfer on the Si atom, but only changes its magnitude, i.e. the degree of ionic bonding.

Conclusion

In the present work, the *ab initio* study of the features of the interaction of a Si atom with the (111) surface of TiN compounds in the presence of Al or Ta substitutional impurities was performed within the framework of the density functional formalism. It was revealed that depending on the position of Al and Ta atoms in the surface layers, the binding energy of Si to the surface of the $Ti_{1-x-y}Al_xTa_yN$ system can be higher or lower than its binding energy to the surface of the binary TiN compound. Non-uniform distribution of alloying elements in the surface layers of TiN, at elevated or non-zero temperatures, results in non-uniform distribution of silicon on the surface. As a result, the formation and growth of the Si_zN phase on the $Ti_{1-x-y}Al_xTa_yN(111)$ surface are in the form of islands rather than a continuous layer.

Table 1

The binding energy (in eV) of the Si atom with the TiN(111) surface and the Bader charge transfer in units of electron charge

Adsorption positions	Impurity	Binding energy	Bader charge transfer		
			Si atom	Substitution atom	
				clean surface	with Si adsorption
Metal termination					
Top(Me)	Ti	4.993	0.45	-	-
	Al_S	4.959	0.86	Al: -1.06	Al: -1.62
	Ta_S	5.175	0.08	Ta: -0.55	Ta: -0.33
FCC	Ti	6.043	0.84	-	-
	Al_S	5.682	0.97	Al: -1.06	Al: -1.53
	Ta_S	6.158	0.77	Ta: -0.55	Ta: -0.83
	Al_S+Ta_S	5.773	0.88	Al: 0,01 Ta: -0.86	Al: -1,46 Ta: -0.91
HCP	Ti	5.913	0.87	-	-
	Al_S	5.625	1.02	Al: -1.06	Al: -1.62
	Ta_S	6.037	0.70	Ta: -0.55	Ta: -0.74
	Al_S+Ta_S	5.692	0.88	Al: 0.01 Ta: -0.86	Al: -1.45 Ta: -0.85
Nitrogen termination					
FCC	Ti	7.096	-1.71		-
	Al_{S-1}	7.446	-1.82	Al: -2.31	Al: -2.39
	Ta_{S-1}	6.180	-1.84	Ta: -2.13	Ta: -2.05
	Al_{S-1}+Ta_{S-1}	6.449	-1.77	Al: -2.31 Ta: -2.20	Al: -2.40 Ta: -2.11
HCP	Ti	6.680	-1.84	-	-
	Al_{S-1}	7.171	-1.64	Al: -2.31	Al: -2.38
	Ta_{S-1}	5.349	-1.62	Ta: -2.13	Ta: -1.93
	$(Al_{S-1}+Ta_{S-1})^*$	6.403	-1.62	Al: -2.31 Ta: -2.20	Al: -2.39 Ta: -2.16
	$(Ta_{S-1+} Al_{S-1})^{**}$	5.851	-1.58	Ta: -2.20 Al: -2.31	Ta: -2.00 Al: -2.29

*Примечание. The subscripts S and S-1 for Al and Ta atoms indicate their localisation in the surface and subsurface layers, respectively. The symbols * and ** indicate variants of the position of Al and Ta atoms relative to each other. * Aluminium is located below the nitrogen atom, while the tantalum atom is next to it. ** Tantalum is below the nitrogen atom and the aluminium atom is next to it*

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