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Density-functional study of the elastic properties of titanium nitride layers♣

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Because of their high hardness and strength and a competitive combination of physical and chemical properties, TiN films on different substrates are widely used in a large number of applications. This is why the development of knowledge about their structure and properties is of a great importance. In the present study first principles calculations, based on density functional theory (DFT) with norm-conserving pseudo potentials and a plane-wave wavefunctions base set, were performed to evaluate the elastic properties and their anisotropy in TiN films. The simulations were realised using two exchange-correlation functionals in the form of the local density approximation (LDA) and the generalized gradient approximation (GGA). The used pseudopotentials were generated by the schemes of Hartwigsen-Goedecker-Hutter and Troullier-Martins. The Young's modulus of the TiN films was calculated in the three crystallographic directions <100>, <110> and <111>. For this purpose, the stress response to strain perturbation in a relaxed structure was used. The obtained results were compared with the bulk values for titanium nitride.

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1. Introduction

Titanium nitride is a compound with high hardness, wear and corrosion resistance, and good electrical and thermal conductivity. Because of these superior properties, TiN in the form of surface layers is widely used for applications ranging from hard and protective to decorative coatings and thermal diffusion barriers. A number of technologies have been developed for the application of TiN films on different substrates. However, the number of atomistic studies of TiN films is limited.

The Density Functional Theory (DFT) is a quantum mechanical theory in which the emphasis is on the charge density as the relevant physical quantity [1]. It has proved to be highly successful in describing structural and electronic properties in a great number of materials. This method, which is computationally relatively simple, is suitable for the analysis of different systems, ranging from atoms and molecules to simple crystals. For these reasons DFT is among the most used methods in first-principles calculations available in condensed matter physics, aimed at describing properties of molecular and condensed matter systems.

In the present study, the DFT method is adopted and applied for the estimation of the elastic constants and surface reconstruction of TiN films using different exchange correlation functionals and pseudopotentials.

2. Experimental

The calculations were performed with pseudopotentials and a planewave basis as implemented in the ABINIT computer code [2, 3]. The following density functional approximations were used: the local density approximations (LDA) of Perdew–Wang [4], Teter and co-workers [5] and the generalized gradient approximation (GGA) of Perdew, Burke and M. Ernzerhof (PBE) [6].

The pseudopotentials used with ABINIT were as follows:

- standard norm-conserving pseudopotentials on a numerical grid - Troullier–Martins pseudopotentials [7];
- Hartwigsen and co-workers [8] (HGH) pseudopotentials, whose analytical form is particularly compact;

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The available combinations of exchange-correlation functionals and pseudopotentials were grouped as follows:

- the LDA of Perdew–Wang with the Troullier–Martins pseudopotential, created by the fhi98pp program[9], further referred to as LDA-PW;
- the LDA of Teter and co-workers with the Troullier–Martins pseudopotential, created by ABINIT group, further referred to as LDA-TM;
- the LDA of Teter and co-workers with the Hartwigsen and co-workers pseudopotential, created by ABINIT group, further referred to as LDA-HGH
- the GGA in PBE form with the Troullier–Martins pseudopotential, created by fhi98pp program[9], further referred to as GGA-PBE

The electron density was calculated via the potential-based conjugate gradient algorithm [10]. The wavefunctions at each k-point are represented by the numerical coefficients of a finite set of plane waves, determined by a kinetic energy cut-off. The k-point sets were generated automatically, following the Monkhorst–Pack (MP) scheme [11]. To decrease the number of k-points needed to sample the Brillouin zone, the crystallographic symmetry of TiN was considered. The computation of interatomic forces was performed by the Hellmann–Feynman theorem [12]. The initial calculations started with convergence studies to determine the kinetic energy cut-off and the size of the MP grid. Iterations using self-consistent field (SCF) cycles were performed until the difference of the total energy was less than 2.72×10^{-5} eV. The forces in the unit cell were relaxed using ground state structural optimization via the modified Broyden algorithm [13]. Calculations were performed only for an optimization of the cell volume and the positions of the atoms were selected according to the TiN crystal cell symmetry, described by the Fm3m space group. Each step of the modified Broyden algorithm consists of SCF iterations, which stop when the tolerance of the potential residual was less than 2.72×10^{-17} eV. Modified Broyden algorithm iterations were stopped when the tolerance of the maximal force is less than 5.14×10^{-6} eV/Å. The cell parameter obtained after the end of iterations was used for further calculations. The analysis of the surface properties started with convergence studies with respect to the slab and vacuum thickness. They were performed using the Broyden algorithm, where SCF iterations for each step were stopped when the potential residual was less than 2.72×10^{-17} eV. The elastic constants of crystalline TiN were calculated using the built-in ABINIT feature of the calculation of response functions to strain perturbation [14]. The iterations were performed until the potential residual was less than 2.72×10^{-11} eV. For the slabs, a custom routine was used in order to reduce the computational costs. For the FCC cell of TiN the only symmetry-inequivalent elastic constants are C_{11}, C_{12} , and C_{44} .

3. Results

3.1. Convergence studies and lattice constant

Results from convergence studies showed that the required cut-off energy should be 762 eV. The MP grid with size 4x4x4 is sufficient for determination of the lattice constant with an error less that 1%. The obtained results for the lattice constant are presented in Table 1.

Table 1. TiN lattice constant calculated in this study and in JCPDS *and Ref. [15]*

Experiment/ Used functional	Lattice constant, Å	Deviation from the JCPDS value, %
Experiment (X-Ray JCPDS No 38-1420)	4.241	
GGA-PBE	4.386	3.4
GGA [15]	4.237	0.1
LDA-PW	4.169	1.7
LDA-HGH	4.182	1.4
LDA-TM	4.432	4.5
LDA [15]	4.175	1.6

The most accurate result is obtained by the LDA-HGH functional, which is comparable to the other LDA reference data. The LDA-TM set gives the most inaccurate value. This could be due to the application of ultrasoft pseudopotentials and the equation of state method in [15]. It is obvious that the type of pseudopotential plays a crucial role in the performed calculations. The differences between the calculated and experimental values could be related to the particularities of the used pseudopotentials which do not take into account the outer core states (semi-core) of Ti. This, in the presence of a strongly electronegative N atom makes the “frozen core” approximation less accurate.

3.2. Surface geometry

The film surfaces were studied by constructing a supercell containing TiN layers and vacuum space. The thickness of the vacuum region was calculated from the convergence studies performed until the error was less than 1% for the (110) and (111) surfaces and less than 2% for the (100) surface. In the last case the accuracy could not be improved due to the failure of the electron density minimization procedure. The analysis of the atom positions after surface relaxation was been performed considering the fact that the (100) and (110) planes contain Ti and N atoms, while the (111) planes are built only by Ti or N atoms [16]. The relative change of the atoms' positions in % from the lattice parameter along the [100] and [110] directions for five film layers and along [111] for six layers is presented in Table 2. The minus sign indicates the outward direction.

Table 2. Relative shift of atoms on the (100) and (110) surface and (111) Ti and N terminated surfaces, with respect to the surface normal in %

Surface	GGA-PBE	LDA-PW	LDA-HGH	LDA-TM
(100)Ti	4	4	4	
(100)N	-1	0	-1	
(110)Ti	4	4	5	3
(110)N	3	3	3	1
(111)Ti	5	4	6	5
(111)N	6	6	5	5

For the (100) and (110) planes, in addition to the inward relaxation the titanium atoms go further inside the surface than the nitrogen atoms. For the (100) surface the N atoms outward shift is more pronounced for LDA-HGH and GGA-PBE, while the Ti atoms inward relative shift is equal. In the case of the (110) surface the N atoms relax inward which is less pronounced for the LDA-TM. This is also valid for the Ti atoms, whose shift is most pronounced for the LDA-HGH. In the case of the (111) orientation, the N-terminated surface relaxes inwards more strongly than the Ti-terminated surface, which is more pronounced for the GGA-PBE and LDA-PW and less for the LDA-TM. These results are in a qualitative agreement with [15].

2.4. Elastic constants

The calculation of the response functions did not converge to the desired values – the residual potential was about $1x10^{-9}$ eV. The estimated error due to the k-point sampling of the 10x10x10 MP grid for the elastic constants was less than 1% for GGA-PBE and LDA-PW and about 15% for LDA-HGH and LDA-TM. The results for the elastic constants are presented in Table 3.

Table 3. Elastic constants in GPa, calculated by the ABINIT program, compared to results from Refs. [15, 17].

Functional	C_{11}	C_{12}	C_{44}
Exp. [17]	625	165	163
GGA-PBE	422	135	104
GGA [15]	598	118	159
LDA-PW	634	134	124
LDA-HGH	783	144	136
LDA-TM	527	128	114
LDA [15]	704	125	168

There is an obvious trend for the GGA to decrease the elastic constants, while LDA increases them. The values strongly depend on the type of pseudopotential and on the exchange correlation as does the lattice constant. The most accurate results for the C_{11}, compared to the experimental data, gives the LDA-PW and for the C_{12} and C_{44} – the LDA-HGH. The differences from the reference data could be due to the lack of convergence during the calculation of the response function. This may be caused by the selected model of occupation of electron energy levels, which in this case is semiconductor type.

Table 4. Young's modulus in GPa for the bulk and thin film of TiN

Surface	GGA-PBE	LDA-PW	LDA-HGH	LDA-TM
[100] bulk	285	460	576	376
[100] thin film	307	484	301	385
[110] bulk	240	318	364	281
[110] thin film	227	352	296	271
[111] bulk	228	288	324	259
[111] thin film	231	256	236	236

The values for the bulk TiN are calculated using the elastic constants from Table 3. It can be seen that for the TiN film in [100], the Young's modulus has a greater value than the corresponding one for the bulk material, except for the LDA-HGH. For the [110] direction, no clear dependence between the bulk and the film values of Young's modulus obtained by the different sets is evident. For the [111] direction, the film values are lower than the bulk ones.

3. Conclusions

1. By the DFT method the lattice parameter, elastic constants and Young's modulus in the [100], [110] and [111] directions of bulk and thin film of TiN have been evaluated. In addition, the topography of the thin film surfaces has been characterised.
2. The lattice constant is strongly dependent on the type of the pseudopotential used. The highest accuracy is achieved by the most advanced HGH in spite of the LDA, inferior to GGA. The accuracy of results could be

increased by introduction of semi-core states and the use of GGA.

3. For the evaluation of the elastic constants the GGA-PBE and LDA-PW should be used.

4. The Young's modulus of TiN in the [100] direction of the thin film are higher than the bulk ones, while for [111] the trend is the opposite. For the [110] direction, no clear relationship between the film and bulk values is observed.

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