Density-functional study of the crystallographic structure of chromium nitride films

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Abstract. First principles calculations within the framework of the density functional theory with ultrasoft pseudopotentials and plane-wave wavefunctions basis set were performed to investigate the electronic and crystallographic structure of chromium nitride. Different types of antiferromagnetic orderings were considered in the calculations. Three crystallographic planes, namely \{100\}, \{110\} and \{111\}, most commonly observed during the growth process of CrN layers, were investigated assuming AFM\(_{1[110]}\) magnetic ordering. The corresponding surface energies and magnetic structures were simulated.

1. Introduction
Over the last decades, hard and corrosion resistant coatings have frequently been used to protect machine parts and tools and to extend their service life. Transition metal nitrides and among them chromium nitride (CrN) are among the most common materials for these applications. CrN is a hard coating material with excellent wear, corrosion and oxidation resistance. The coatings with potential for industrial applications are mainly deposited by magnetron sputtering. In view of optimizing the technologies and extending the practical applications, the CrN films have been widely analyzed by the existing and by newly developed modern techniques.

The Density Functional Theory (DFT) [1] has recently been implemented in relatively simple computational codes which may help in the characterization of structure formation processes on an atomic level and of important coating parameters. These codes have widely been used for the first-principles calculations of surface reconstruction and surface parameters which may significantly influence the properties [2].

In the present study a method based on the quantum mechanical DFT was developed and applied to the evaluation of surface energies of CrN films as a function of their crystallographic orientations.

2. Theoretical background
The atomic arrangement in perfect crystals can be described by a periodically repeated unit cell, represented in the DFT by periodic boundary conditions. However, in many physical systems, the perfect periodicity is violated and the system is either approximately periodic or periodic only in one
or two directions. Examples of such systems include surfaces, point defects in crystals, substitutional alloys, heterostructures, liquid crystals, etc. These systems may be successfully simulated by a periodically repeated fictitious supercell with a shape and size depending on the system studied. In the case of solid surfaces, a crystal slab alternated with a slab of empty space is used. Both slabs are large enough to ensure that the bulk behavior is recovered inside the crystal slab. The surface behavior should be unaffected by the presence of the periodical boundary conditions. Due to the absence of an abrupt termination, the supercell approach is usually more convenient than the simulation of an extended system by taking a finite piece of the material. During the study of the slab, a structural relaxation should be performed in order to reflect the effects of surface reconstruction due to the abrupt change of the density on the surface. This process corresponds to a convergence towards the atomic configuration with a minimum energy. The lowest-energy structure produced with the aid of DFT will be the equilibrium structure at zero temperature and zero pressure.

In our earlier analyses of CrN with DFT [3], we found that in order to obtain a stable crystallographic structure, antiferromagnetic ordering along the [110] crystallographic direction should be introduced. The NaCl type crystallographic structure of CrN observed at room temperature can be successfully reproduced by a number of antiferromagnetic layers with the same spin orientation, which alternate their spin every next layer [3]. This spin arrangement is known as AFM1_{110} and was used in the present study.

3. Computational procedure
The calculations were performed using ultrasoft pseudopotentials and a plane wave basis as implemented in the Quantum Espresso (QE) integrated suite of computer codes [4]. The generalized gradient approximation (GGA) of Perdew, Burke and M. Ernzerhof (PBE) [5] was used. The applied pseudopotentials with QE were ultrasoft, generated by the Vanderbilt scheme [6] and taken from the QE distribution [4]. The wave functions 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 [7]. To decrease the number of k-points needed to sample the Brillouin zone, the crystallographic symmetry of the samples was considered. The computation of interatomic forces was performed by the Hellmann Feynman theorem [8]. 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 10^{-5} eV. The forces in the unit cell and the lattice vectors were relaxed using ground state structural optimization via the Broyden algorithm as implemented in the QE. Calculations were performed until the interatomic force became less than 7x10^{-3} eV/Å and the cell pressure (for the lattice constant calculations) was less than 0.05 kbar.

The film surfaces were simulated with a supercell containing CrN layers and vacuum space using the calculated relaxed lattice constant. The characterization of the surface properties started with convergence studies with respect to the slab and vacuum thickness. The latter was calculated from the convergence studies performed until the error became less than 0.1% for the cases when \{100\}, \{110\} or \{111\} crystallographic planes are lying in the surfaces. During the calculations, the angle between the [110] direction, along which the spins are aligned, and the directions of the surface normals \{100\}, \{110\} and \{111\} respectively, were taken into account. For the case of the \{100\} lying on the surface, the possible angles are 45° (supercell system noted as {100}a) and 90° (supercell system noted as \{100\}b). When the crystallographic orientation of the surface is \{110\} the angles are 0° (supercell system noted as \{110\}a), 90° (supercell system noted as \{110\}b) and 60° (supercell system noted as \{110\}c). For the case of \{111\} the possible angles are 90° (supercell system noted as \{111\}a) and 32.27° (supercell system noted as \{111\}b). The numerical experiments were performed both for spin orientation fixed along [110] and with non-collinear relaxation to estimate the changes of the magnetic structure due to surface effects. Because of the requirements for the accommodation of the magnetic structure, the calculations for all surface orientations were limited to six layers only.
4. Results and discussion

The convergence studies showed that the required cut-off energy for CrN is 748 eV. To reflect the metallic band structure of CrN, electron level smearing via the scheme of Methfessel-Paxton (MP) [9] with smearing width of 0.27 eV was introduced. The MP grid with size $6 \times 6 \times 6$ is sufficient for determination of the lattice constant with a relative error of less than 1%. The calculated value of the CrN lattice constant is 4.140 Å, which is equal to the experimental data taken from the X-Ray JCPDS No 11-0065 data file. In order to reflect the unit cell size and the vacuum layer, the MP grid used for the surfaces with different crystallographic orientations were as follows: for $\{100\}_a$ – $14 \times 1 \times 14$ and $\{100\}_b$ – $1 \times 1 \times 10$; for $\{110\}_a$ – $14 \times 10 \times 1$, $\{110\}_b$ – $1 \times 10 \times 14$ and $\{110\}_c$ – $7 \times 1 \times 10$; for $\{111\}_a$ – $7 \times 7 \times 1$, and for $\{111\}_b$ – $7 \times 7 \times 1$. The thickness of the vacuum slab was calculated from the convergence studies performed until the error was less than 0.1% and thus it was defined to be 12 Å. In the two layers in the middle of the CrN slab the atoms are kept fixed, while the others was allowed to relax free until the force acting on them was minimized below the given threshold. The analysis of the atom positions after surface relaxation was performed considering the fact that the $\{100\}$ and $\{110\}$ planes contain both Cr and N atoms, while the $\{111\}$ planes are built of Cr or N atoms only [10]. The surface energy of the layers was calculated by subtracting the energy of the slab from the energy of the bulk (supercell without vacuum slab) for the same number of atoms and dividing the result by 2 to reflect the fact that each supercell has two surfaces of the same kind.

The results from the non-collinear calculations showed no change in the spin direction, so it can be concluded that for all the cases the spins stay collinear with the $[110]$ direction. This was used in further calculations assuming a collinear magnetization. The results obtained are given in the table 1.

|                | $\{100\}_a$ | $\{100\}_b$ | $\{110\}_a$ | $\{110\}_b$ | $\{110\}_c$ | $\{111\}_a$ | $\{111\}_b$ |
|----------------|------------|------------|------------|------------|------------|------------|------------|
| Cr             | 2.96       | 0.92       | 2.92       | 2.92       | 3.12       | 1.71       | 1.70       |
| N              | -1.04*     | -0.2       | 0.85       | 0.84       | 0.43       | 2.99       | 3.07       |
| Surface energy:|            |            |            |            |            |            |            |
| relaxed        | 1.09       | 1.26       | 2.16       | 2.16       | 2.17       | 2.52       | 2.52       |
| non relaxed    | 1.30       | 1.32       | 2.53       | 2.53       | 2.49       | 3.88       | 3.88       |

* The minus sign indicates outward displacement.

The results show that for both relaxed and non relaxed structures the surface energies in CrN are maximum for the $\{111\}$ crystallographic orientation of the surface while for the $\{100\}$ orientation they are minimal. For the two types of the $\{111\}$ surface orientations there is no difference in the surface energy values but it is not so for the different types of $\{100\}$ and $\{110\}$ orientations. From a thermodynamic point of view, it can be expected that the orientations with a lower energy will be more stable.

The relaxation leading to a decrease of the surface energy is accompanied with an inward and outward displacement of the surface atoms. According to the results in the Table 1, the inward displacement is predominating while the outward displacement is observed only for the N atoms placed in $\{100\}$ planes. The displacements are the highest for the Cr atoms lying in the $\{110\}$ and for N atoms lying in the $\{111\}$ surface planes. These results correlate with the higher degree of relaxation of the surface energy observed in these orientations in comparison with $\{100\}$. Thus, for the discussed $\{111\}$ surface orientations, the decrease of the surface energy due to relaxation is 35%, while for the $\{110\}$ and $\{100\}$ it varies from 13% to 15% and from 5% to 16%, respectively. The results discussed are in a qualitative agreement with the data in [2] obtained by similar analyses performed on TiN surfaces.
5. Conclusions
Computer simulations based on the DFT method made it possible to analyze CrN solid surfaces with \{100\}, \{110\} and \{100\} crystallographic orientations.

Successful simulation of the crystallographic structure of CrN films needs antiferromagnetic ordering of the spins along [110] direction.

The surface energies depend on the type of crystallographic planes and their orientation with respect to the direction of antiferromagnetic ordering. They were evaluated and the relaxation processes accompanied with surface atoms displacements and surface energy decrease were analyzed: the relaxation is the most pronounced for CrN surfaces with \{111\} orientation which has the highest initial energy and the lowest one for the \{100\} surfaces with the minimal initial surface energy. After the relaxation, the energy of the \{111\} surfaces is preserved maximal, while the \{100\} stays minimal.

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