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Theoretical Investigation of the Structure and Properties of the VN(111) Monolayer on the MgO(111) Surface

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Abstract—The VN(111) monolayer on the MgO(111) surface has been simulated and optimized in terms of the density functional theory (DFT) calculations. The most favorable arrangement of vanadium nitride on the surface of the magnesium oxide plate has been found. The band structure and densities of states for the VN(111) monolayer have been calculated. It has been concluded based on the densities of states for the VN monolayer on the MgO surface that this structure exhibits properties of a diluted magnetic semiconductor.

1. INTRODUCTION

An increase in volume and rate of information transmission approaches the limit associated with fundamental physical limitations for the further decrease in sizes of active elements. Spintronics is one of the most promising ways to overcome this situation. It opens the possibilities of new in principle solutions in electronics, allowing for the use of not only the electronic charge but also its spin for information storage and transmission. When searching for new materials for spintronics, there is the necessity of their creation based on semiconductors since it is possible to control simultaneously the spin and charge transport in the system only in this case. In connection with this, the diluted magnetic semiconductors, in which the separate spin conduction is observed, have become the subject of growing interest. Similar nano-scale composite materials can be based on compounds of transition metals, particularly their nitrides.

Transition metals form nitrides with predominantly metallic bonding. These substances possess considerable hardness, high electrical conductivity, high melting points, and large enthalpy of formation [1–3]. Vanadium nitride is one of them. Up to 2620 K, this compound has the cubic modification (the NaCl structural type) [4]. It was shown in [5–7] that VN possesses metallic conductivity. Nanocrystalline vanadium nitride can be used in supercapacitors as the charge carrier [8]. Vanadium nitride is synthesized by the reaction of ammonia with $VOCl_3$ upon heating or by passing the gas mixture consisting of nitrogen and vanadium oxyhalogenide vapors over the tungsten,

molybdenum, or rhenium filament heated to 1200–1400°C in the nitrogen atmosphere [9]. Other preparation methods of VN are described in [10–12].

From the viewpoint of magnetic properties, thin films of vanadium nitride are of interest. Uncoupled d electrons of vanadium atoms, which are arranged on the film surface, play an essential role in the electronic structure of these films. The limiting case of a thin film is a monolayer whose structure and properties can substantially differ from those of both the bulk crystal and the film. It is rather difficult to obtain a separate VN monolayer, but the use of the appropriate substrate can substantially simplify this problem.

The VN films are obtained experimentally using MgO or Pt substrates with the (111) surface for both cases [13, 14]. The lattice constant of magnesium oxide is close to that for vanadium nitride (larger by 2%), which makes it possible to grow the film without substantial defects. In addition, both crystal lattices of the (111) surface represent the cell with the hexagonal packing. However, when growing a thin film, small structural relaxations occur, which directly depend on the film size and are caused by the substrate influence. The interaction between MgO and VN plates is described in [14], where the authors simulated the interface of the plates of n MgO(111) layers and n VN(111) layers for n in the range from 1 to 15. The results of the density functional theory (DFT) modeling showed that at various configurations of two MgO and VN plates relative to one another, a stable nanocomposite is formed, in which the favorable configu-

ration is a system with the arrangement of vanadium atoms over the oxygen atoms [14].

Selecting necessary conditions, we could synthesize the VN monolayer on an appropriate MgO substrate. In this case, properties of the monolayer and its nanocomposite with the substrate made of magnesium oxide are of interest in connection with the possibility of manifestation of the properties of a diluted magnetic semiconductor. Thus, the purpose of this work was to perform a theoretical investigation of the structure and properties of the vanadium nitride monolayer and possibilities of its growth on the MgO(111) surface.

2. DETAILS AND METHODS OF CALCULATION

The geometry and electronic structure of the VN monolayer and the nanocomposite "monolayer VN(111) ‖ MgO(111)" were performed in terms of the density functional theory [15, 16] using the Perdew–Burke–Ernzerhof exchange-correlation potential [17]. Calculations were performed in the VASP software package [18–20] using the PAW potential [21]. For all structures, the number of k points in the first Brillouin zone with optimizing the geometry and construction of density of states (DOS) was selected in a form of network $12 \times 12 \times 1$ constructed using the Monkhorst–Pack scheme [22]. When constructing the band structure of compounds, the inverse space was divided into 20 intermediate k points along each symmetric direction. The cutoff energy of plane waves in all calculations was 400 eV. The optimization was performed until the magnitude of forces affecting the atoms became 0.01 eV/Å. In all systems, to prevent the interaction of cell images of plates, the vacuum gap of ~16.5 Å was specified.

At the first stage, based on the calculated equilibrium geometry of the unit cell of the periodic vanadium nitride, we modeled the unit cell of the VN(111) monolayer, which is hexagonal-shaped with the translation vector of 3.215 Å and contains one vanadium atom and one nitrogen atom.

Then, we modeled a hexagonal unit cell of the MgO(111) plate with a translation vector of 2.947 Å by the force of translation of the cubic unit cell of magnesium oxide along the crystallographic direction of the (111) surface. The plate was terminated on one side by magnesium atoms and on the other side by oxygen atoms in all cases. When selecting the optimal plate thickness, we selected the surface energy as the comparative criterion. Upon varying the number of the layers from 9 to 10, the difference in the surface energy was less than 0.01 eV/Å², which indicates the sufficient number of atomic layers in the plate necessary for the adequate description of the substrate (in this case, the surface energy is 0.356 eV/Å²). The further simulation

of the VN monolayer was performed for the plate consisting of nine layers of magnesium oxide (111).

Further, we investigated the behavior of the VN monolayer on the MgO surface. For this purpose, the variously oriented VN monolayer was arranged on the surface of magnesium oxide. In some cases, the monolayer was arranged over the surface terminated by magnesium atoms, and in other cases—by oxygen atoms. The bonding energy between the monolayer and the surface was calculated by the formula

$$E = E_{\text{VN/MgO}} - (E_{\text{MgO}} + E_{\text{VN}}), \quad (1)$$

where $E_{\text{VN/MgO}}$ is the total energy of the structure, E_{MgO} is the energy of the MgO plate, and E_{VN} is the energy of the VN monolayer.

3. RESULTS AND DISCUSSION

The VN(111) monolayer, which was formed in the course of geometry optimization, has the plane structure. This can be explained by the tendency of the material to minimize the energy by the force of decreasing the dipole moment of the system, which apparently would appear in the case of the corrugated surface, to the zero value. Smoothening of the corrugated VN(111) surface caused an increase in the translation vector from 2.918 Å for the case of the monolayer obtained from the unit periodic VN cell to 3.215 Å for the plane structure.

Figure 1 shows the band structure and spin densities of states for the VN(111) monolayer. It is seen from Fig. 1 that the monolayer is the diluted magnetic semiconductor since the nonzero density is observed in the density of states for electrons with spin α, while the forbidden band (2.88 eV) is observed for electrons with spin β. However, thin films are in practice synthesized on a substrate, which in turn substantially affects the geometry and, consequently, the electronic structure of the monolayer. Therefore, we further investigated the influence of the assumed magnesium oxide substrate on the VN monolayer film.

The system "monolayer VN(111) ‖ MgO(111)" was simulated with six various positions of the VN monolayer (top, hcp, and fcc) relative to the MgO substrate (Fig. 2). In addition, the monolayer was alternately arranged on both sides of the plate substrate. For example, for the surface terminated by oxygen atoms (Fig. 2): position top means the arrangement of vanadium or nitrogen above the first oxygen layer, hcp—above the second layer with magnesium atoms, and fcc—above the third layer with oxygen atoms. For the surface terminated by the magnesium atoms: top—above magnesium, hcp—above oxygen, and fcc—above the third layer, which consists of magnesium atoms, respectively. The values of the bonding energy of the VN monolayer with the MgO surface as well as the average deviation of nitrogen and vanadium
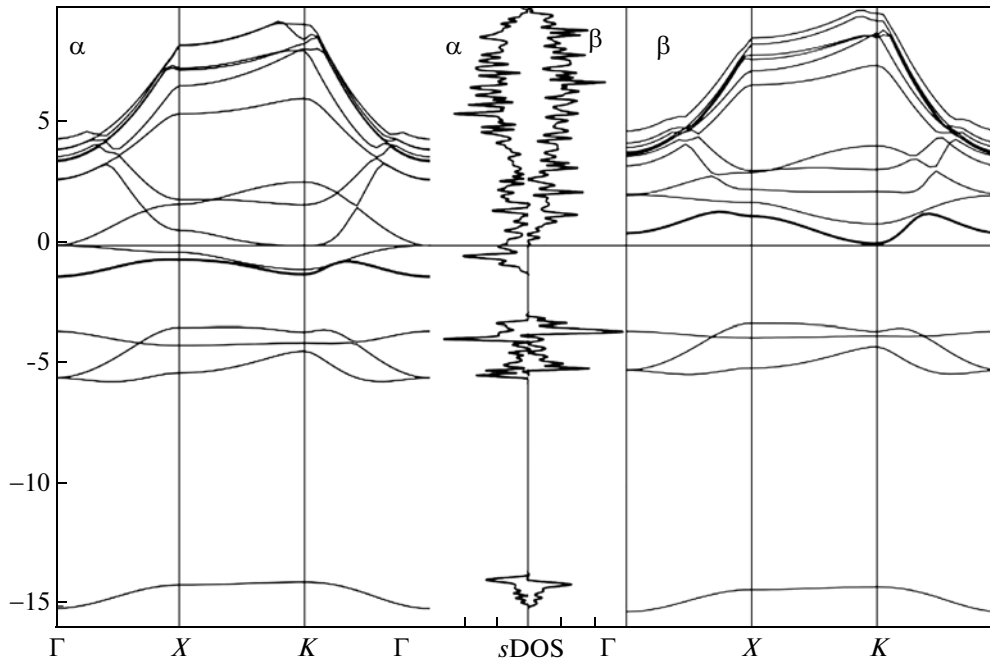
Fig. 1. Band structure for subsystems of α and β electrons and spin densities of states of the VN(111) monolayer.

atoms from the monolayer plane are presented on the table.

Starting from the tabulated data, we can conclude that the arrangement above the surface terminated by oxygen atoms is most stable. The configuration, in which the V atom is arranged immediately above the O atom (the $V_{top}-N_{fcc}$ configuration) is most favorable. Due to this, the V–O chemical bond is formed (1.8 Å). It is characteristic of both structures that the nitrogen atom should be distanced sufficiently far from the oxygen atom in the most energetically favorable arrangements because of the partial negative charge at both atoms.

It is noteworthy that when growing the VN thin films, their structure will tend to take on the shape of the substrate surface, which is indicated by the average deviation of the atom from the plane (Δ) of the monolayer after the DFT optimization presented in the table. A substantial distortion is observed for all most favorable arrangements of the monolayer, namely, it becomes corrugated, which should be reflected in its properties.

To investigate the electronic structure of the nanocomposite, we calculated the total density of states for the most favorable configuration ($N_{hcp}-V_{fcc}$) of the system "monolayer VN(111) ‖ MgO(111)" (Fig. 3a) as well as separately of the magnesium oxide plate (Fig. 3b).

The nonzero value of the density of states at the Fermi level indicates that the electronic structure of the nanocomposite "monolayer VN(111) ‖ MgO(111)"

possesses the conductor property for both electronic subsystems with the same direction of the spin projection. However, when calculating the density of states of nanocomposite, the atoms of a free MgO surface not bound with VN can introduce the essential contri-

Bonding energy of the VN(111) monolayer with the MgO(111) surface and the average deviation of the V and N atoms from the monolayer plane

Configuration	E, eV	Δ, Å
Surface terminated with magnesium atoms		
$N_{top}-V_{hcp}$	−0.8979	0.339
$N_{top}-V_{fcc}$	0.0419	0.103
$V_{top}-N_{hcp}$	0.5801	0.119
$V_{top}-N_{fcc}$	0.6304	0.109
$N_{chp}-V_{fcc}$	0.1075	0.104
$N_{fcc}-V_{hcp}$	0.5157	0.108
Surface terminated with oxygen atoms		
$N_{top}-V_{hcp}$	0.7383	0.157
$N_{top}-V_{fcc}$	0.1016	0.157
$V_{top}-N_{hcp}$	−3.4329	0.358
$V_{top}-N_{fcc}$	−4.1295	0.360
$N_{chp}-V_{fcc}$	−4.0746	0.380
$N_{fcc}-V_{hcp}$	−3.6547	0.379

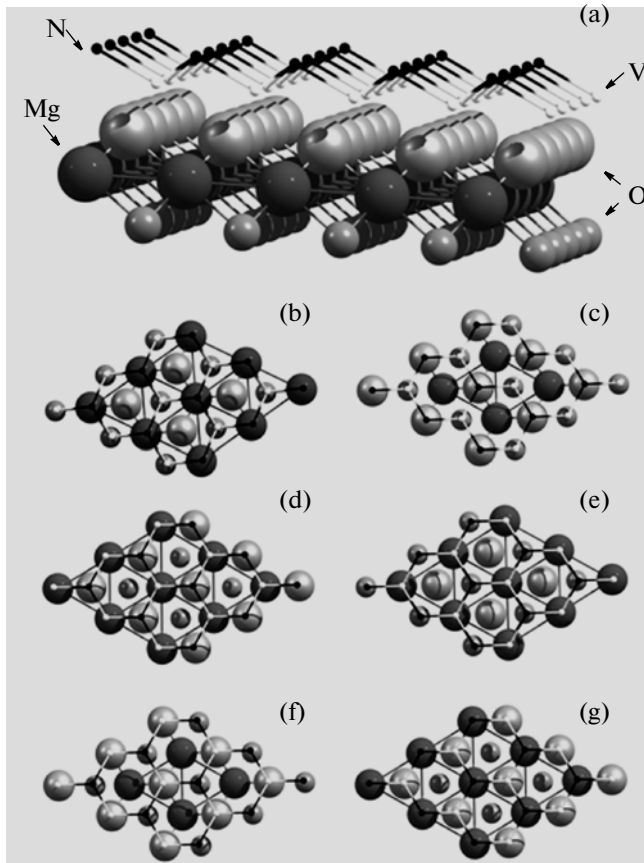**Fig. 2.** Arrangement of the VN monolayer relative to the MgO substrate with the O-terminated surface: (a) general view of the structure, (b) $N_{hcp}-V_{fcc}$ position, (c) $N_{top}-V_{fcc}$ position, (d) $N_{top}-V_{hcp}$ position, (e) $N_{fcc}-V_{hcp}$ position, (f) $N_{top}-V_{fcc}$ position, and (g) $N_{top}-V_{hcp}$ position.
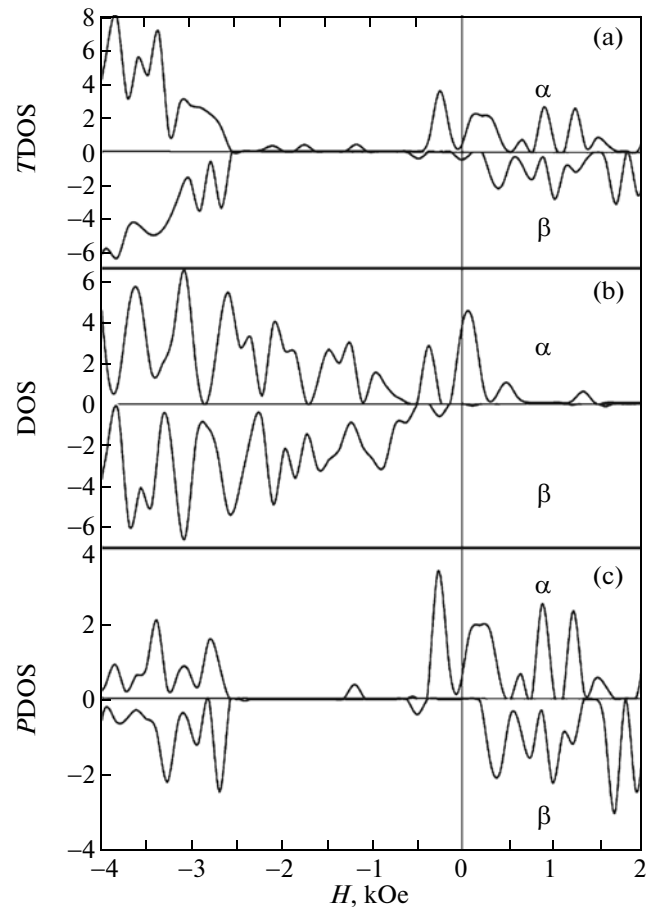

Fig. 3. Densities of states: (a) the whole structure, (b) MgO plate, and (c) four upper layers of the plate with the VN monolayer.

bution, which is arranged near the Fermi level. We can confirm this statement when analyzing the density-of-states of the MgO plate (Fig. 3b). Despite the fact that periodic magnesium oxide is dielectric, the peaks at the Fermi level are present in the density-of-states pattern for the plate consisting of nine MgO layers, which indicates the presence of the surface conduction in the plate.

However, during the synthesis, the monolayer will be arranged on a sufficiently thick substrate, which excludes the influence of the lower plate layer. In order to exclude the contribution of the atoms of the free MgO surface, we constructed the partial density of states of four upper layers of the MgO(111) plate with the deposited VN(111) monolayer (Fig. 3c).

After the exclusion of the contribution of the free surface, the nonzero density of states will be observed in the electronic structure of this system for electrons with spin α, while the forbidden band (0.85 eV) is present for electrons with spin β. Thus, the electronic

subsystem of the nanocomposite "monolayer VN(111) ∥ MgO(111)" with spin α will manifest the conductor properties, while that one with spin β—the semiconductor properties. This means that this system will behave as the diluted magnetic semiconductor. In this case, the spin density of the system is arranged at vanadium atoms (Fig. 4).

The VN monolayer exhibits properties of a diluted magnetic semiconductor only if it is the cut of the (111) surface. In the context of the investigation, we also considered the VN(100) and VN(110) monolayers. The results of our calculations show that the forbidden band is absent in the electronic structure of these monolayers. For comparison, the authors of [23] investigated ultrathin films and the TiN(100) monolayer on the MgO(100) substrate by the quantum-chemical methods. The result of calculations showed that the formed interface has a metallic character with the absence of the separate spin conductivity. Despite this fact, we can present studies [24–26] as an example for the comparison. Their authors showed the BN monolayer with absorbed atoms of the transition metal, graphene on the MnO substrate, and the MoS_2
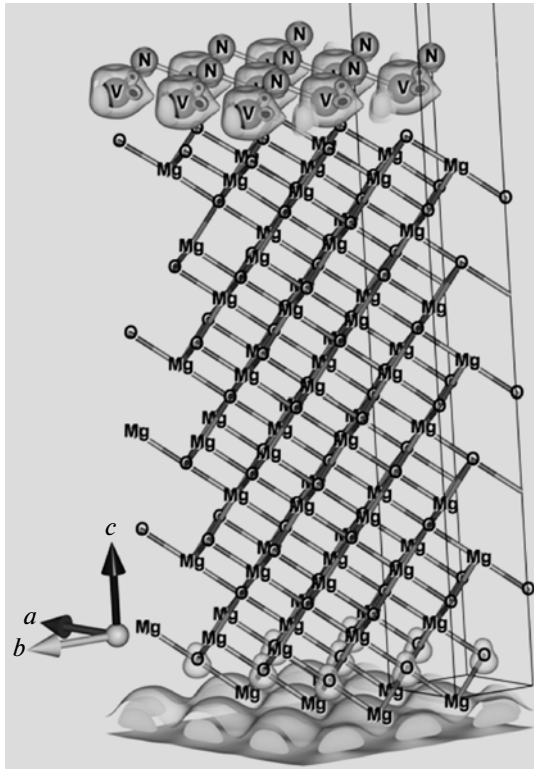
Fig. 4. Spatial distribution of the spin density in the "monolayer VN(111) ‖ MgO(111)" system.

monolayer modified with manganese. The formed structures of monolayers have spin-dependent properties. In addition, the authors of [27] considered nitrides of aluminum, gallium, and indium doped with vanadium. They showed that the addition of vanadium into the above-mentioned compounds add them the properties of the diluted magnetic semiconductor. Comparing the presented examples, we can judge on the adequacy of our results.

We also verified the influence of an increase in the number of the VN layers on the magnetic properties of the interface. Calculations showed that with the subsequent increase in the number of the VN layers in the film, the property of the diluted magnetic semiconductor will be lost. For example, the vanadium nitride film consisting already of two layers will be conductor according to our calculations.

4. CONCLUSIONS

We for the first time calculated the electronic structure of the system "monolayer VN(111) ‖ MgO(111)". It is shown that the structure of thin VN films tends to take on the shape of the substrate surface. The distribution of the density of states upon the deposition of the VN(111) monolayer on the MgO(111) surface characterizes this structure as a diluted magnetic

semiconductor. This allows us to consider this material as promising for using in spintronics.

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