The growth of epitaxial VN(111) nanolayer surfaces

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Abstract

Ultrathin films of vanadium nitride (1–20 monolayers = nanolayers) with (111) orientation have been grown on a Pt(111) surface by reactive evaporation of vanadium in NH₃ atmosphere. The VN(111) surfaces have been investigated by X-ray and UV photoelectron spectroscopy, LEED, work function measurements, and ab initio DFT calculations. Nearly stoichiometric, well-ordered VN₀.₉ overlays with their (1 × 1) unit cells rotationally aligned to the high symmetry directions of the Pt substrate have been obtained after annealing the films deposited at 300–500 °C in vacuum. The experimental valence band spectra have been compared to the theoretical density of states for differently terminated VN(111) surfaces, i.e. V and N terminated surfaces, bare and with chemisorbed hydrogen. The comparison suggests that the VN(111) nanolayers are terminated by a hexagonal layer of vanadium atoms, possibly covered with some chemisorbed hydrogen (which may originate from the preparation procedure). The VN nanolayer growth on Pt(111) follows a Stranski–Krastanov layer-plus-island growth mode.

Keywords: Vanadium nitride; Photoelectron spectroscopy; Density functional theory

1. Introduction

Vanadium nitrides are widely used components in multifunctional coatings combining hardness [1], wear and corrosion resistance [2], diffusion barrier [3] and low-friction properties [4]. In all those applications the coating performance is strongly affected by surface roughness and film texture, which not only influence the tribo-mechanical properties but also the chemical behaviour. Oxidation is a key factor during the operation of coated surfaces since the degradation of coatings occurs by a mixture of wear, diffusion and surface oxidation processes [5]. For example, it is believed that a tribological contact region is composed of a mixture of oxidation products of the two base materials in contact with each other, and it has been proposed that the low-friction behaviour of VN containing coatings is due to compounds within the V–O system, with V₂O₅ or defective Magnéli-type structures [6] as the dominant phases [7,8]. However, the type of the oxides formed, the reaction sequences leading to the observed phases and the distribution of oxides across the surface of multicomponent systems is still far from being understood.

In order to disentangle the complexity of materials and thermodynamic variables that conspire during the operation of realistic multifunctional coating systems it is useful to adopt a reductionist approach and to resort to a well-defined, but simpler model system. Here we present a model system to investigate the detailed oxidation behaviour of the vanadium component of multicomponent nitride coating systems, namely VN single crystal surfaces in form of epitaxially grown ultrathin nanolayers on a noble metal surface. In this paper we report the preparation and spectroscopic characterisation of VN(111) nanolayers, epitaxially grown on a Pt(111) single crystal substrate. The

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controlled oxidation of these VN(111) surfaces and the elucidation of the oxidation processes at the atomic level is the subject of subsequent work.

VN nanolayers (1−20 monolayers (ML)) have been grown on Pt(111) by reactive physical vapour deposition under ultrahigh vacuum (UHV) conditions. Specifically, vanadium metal has been evaporated in an NH₃ atmosphere (of the order of 10⁻⁷ mbar) onto the clean Pt substrate at elevated temperature. This preparation procedure has the advantage of reproducible and accurate thickness control of the deposited films (<0.1 ML precision) and of a very low level of contamination. The Pt(111) substrate provides an ordered metallic substrate which is inert towards nitridisation under these conditions. The lattice mismatch between the Pt(111) surface unit cell and VN(111) is ~5%, which should be sufficiently low to allow the formation of epitaxial overlayers. We have used X-ray photoelectron spectroscopy (XPS) to identify the chemical nature of the deposited V nitride films and UV photoelectron spectroscopy (UPS) to probe their valence band structure. The latter method has also been used to follow the evolution of the electronic work function of the growing films. The measured UPS valence band spectra are compared to the density of states (DOS) of differently terminated VN surfaces as calculated by ab initio density functional theory (DFT). The structural order of the VN layers has been investigated by low-energy electron diffraction (LEED).

We find that epitaxial VN(111) nanolayers can indeed be obtained on Pt(111) with a non-reconstructed polar (1×1) surface, which are rotationally aligned along the main symmetry directions of the Pt(111) substrate. The vanadium nitride films are nearly stoichiometric (VN₀·₉) and the spectroscopic data in conjunction with the DFT calculations suggest that the VN(111) surface is terminated by a layer of vanadium atoms.

2. Experimental and theoretical procedures

The experiments were carried out in a UHV chamber (base pressure ~1×10⁻¹⁰ mbar) equipped with a hemispherical electron energy analyser (angular acceptance of ±8°), X-ray and UV photon excitation sources, a rear-view LEED optics, an electron beam evaporator and a quartz microbalance for metal deposition and film thickness monitoring, respectively, and the usual facilities for surface manipulation, cleaning and controlled gas introduction [9]. The work function was determined by the low-energy secondary electron cut-off in the UPS spectra excited with He I radiation. The energy resolution in XPS and UPS was set to 1 eV and 0.2 eV, respectively.

The Pt(111) crystal surface was cleaned by cycles of Ar ion sputtering and annealing to 800−900 °C. The initial cleaning of the crystal also involved heating in O₂ at 500−600 °C followed by flashing to 900 °C to remove the carbon segregated to the surface. Surface cleanliness and order were checked routinely by XPS and LEED. Vanadium metal was evaporated from an electron beam evaporator and the evaporation rate was monitored with a quartz microbalance positioned at the location of the sample. Typical evaporation rates were 0.6−1 ML/min in a background pressure of 5×10⁻⁷ mbar of NH₃, with the Pt crystal held at 300 °C. The thickness of the nanolayers is given in monolayers (ML) of deposited V atoms, where one monolayer is defined by the number of surface atoms of the Pt(111) substrate. This monolayer definition also holds approximately for the average thickness of the VN films, because the VN surface unit cell dimension matches that of the Pt unit cell, except for the few percent of lattice mismatch.

First-principles DFT calculations were done by means of the Vienna ab initio simulation Package (VASP) [10], using the projector augmented wave scheme [11] as implemented by Kresse and Joubert [12] and the generalized gradient approximation (GGA) according to Perdew and Wang (PW91) [13]. Repeated slabs consisting of 15 VN units (i.e. 30 layers) with an additional V or N layer to simulate either V or N termination, separated by 15 Å thick vacuum layers, were used. An energy cut-off of 400 eV and a 15×15×1 Γ-centred k-point mesh was sufficiently accurate for the present purposes. The dimensions of the surface unit cell are chosen according to the calculated bulk lattice constant of 4.13 Å. All layers were relaxed until all forces were smaller then 0.01 eV/Å. For the determination of vacancy formation energies calculations were performed for slabs with a 2×2 surface unit cell and seven VN units thickness on a 6×6×1 k-mesh.

3. Results

Fig. 1a shows Mg Kα (hv = 1253.6 eV) XPS spectra of the V 2p core level region as a function of the as-deposited film thickness, whereas Fig. 1b displays the corresponding N 1s spectra. The V 2p spectral region (Fig. 1a) overlaps partly with the emission from the Pt substrate 4p level at ~519.5 eV binding energy, which is particularly apparent for the thin overlayers. The V 2p spectrum contains the 2p₃/2 emission at 513.5 eV and the 2p₁/2 emission at 520.9 eV binding energy, and a broad satellite structure around 516 eV. The V 2p binding energies show no significant energy shifts as a function of overlayer thickness. A small O 1s signal is observed at ~530.5 eV, which is due to a small amount of adventitious oxygen contamination of the films. The oxygen amount was estimated to vary between 5 and 3 at% as the layer thickness was varied between 1 ML and 20 ML. The N 1s emission (see Fig. 1b) is observed at 397.3 eV. The V 2p and N 1s core level binding energies are well within the range of binding energies reported for vanadium nitride in the literature [14,15] and thus specify the chemical identity of the overlayers to VN. The presence of the satellite structure at ~516 eV, which has been ascribed to “poorly screened” core hole states [16], is typical for VN [17] and indicates that the VN formed is nearly stoichiometric [18]. Indeed, the evalu-
ation of the V 2p and N 1s core level intensities using the tabulated atomic sensitivity factors for the different core levels [19] yields a formal stoichiometry of VN$_{0.9}$.

He I ($h\nu = 21.2$ eV) valence band spectra of the clean Pt(111) surface (bottom curve) and after deposition of VN overlayers of varying thickness are presented in Fig. 2. The top curve shows a He II ($h\nu = 40.8$ eV) spectrum of the 20 ML V nitride overlayer. The Pt 5d$6s$ valence band structure with prominent peaks at 1.5 eV and $\sim 4$ eV becomes gradually suppressed with increasing overlayer thickness and is replaced by the triangular-shaped feature at 0–2 eV below $E_F$ and by a broad structure from 3 eV to 8 eV. The latter is due to emission from the hybridised N 2p–V 3d states, which provide the strong bonding framework of the VN compound. There is some fine structure in the N 2p–V 3d spectral structure, which will be addressed further below. Note the high density of states at the Fermi level ($E_F$), which is responsible for the metallic behaviour of VN. The He I valence band signature of the 20 ML VN film of Fig. 2 compares well with the one reported previously in the literature for stoichiometric VN samples [16]. The He II spectrum of the 20 ML VN (top curve) is consistent with the He I spectrum and shows also the triangular-shaped V 3d non-bonding states at 0–2 eV and the N 2p–V 3d structure at 3–8 eV, but less fine structure is resolved in the latter than in the He I spectrum. Significantly, the region between 2 and 3 eV binding energy shows no spectral feature under He II excitation. A vacancy induced spectral structure in this energy region has been predicted theoretically by Marksteiner et al. [20] and has been detected subsequently by angle-resolved photoemission measurements by Lindström et al. [21]; the vacancy derived feature required photon energies $h\nu > 31$ eV to show up with detectable spectral intensity. The absence of spectral structure between 2–3 eV in the He II spectrum (Fig. 2) thus indicates that the VN surfaces prepared here contain no significant concentration of nitrogen vacancies.

The inset of Fig. 2 gives the evolution of the work function as a function of VN overlayer thickness. The work function of Pt(111) decreases upon VN deposition and settles at 4.38 eV $\pm$ 0.02 eV for film thicknesses $> 5$ ML. This measured work function value of 4.4 eV for the VN(111) surface will be discussed in Section 4 in connection with the DFT calculated values.

The VN overlayers prepared by reactive evaporation of vanadium in NH$_3$ at 300 °C substrate temperature showed no ordered LEED pattern after deposition. However, after annealing in vacuum up to 500 °C the structural order of the films was improved and LEED reflections have been observed. Fig. 3a displays the LEED pattern of the clean Pt(111) surface and Fig. 3b the one from a 10 ML VN nanolayer after 3 min annealing at 500 °C. The LEED pattern of Fig. 3c has been obtained from a 1 ML VN surface after annealing at 500 °C; here both Pt and VN reflections are
can be weakly distinguished. The 1 ML VN overlayer is less well-ordered than the thicker films and the spots are weak and diffuse – however, they provide an internal calibration for the overlayer lattice constant. The VN overlayer spots display a hexagonal pattern that is rotationally aligned with the Pt(111) substrate. The lattice constant is derived to 2.89 Å ± 0.02 Å. The comparison with the lattice constant of the VN(111) plane in the bulk (aVN(111) = 2.91 Å) [22] indicates that the VN nanolayers have grown epitaxially with (111) orientation on the Pt(111) surface. The (111) surface of the rock salt structure is the so-called polar surface, which is terminated either by a hexagonal layer of V atoms or a hexagonal layer of N atoms in this case; this question of the surface termination will be addressed in Section 4. The observed (1 × 1) LEED pattern demonstrates, however, that the VN(111) surface is unreconstructed.

The thermal stability of the VN(111) nanolayers on Pt(111) in UHV depends on the overlayer thickness. Whereas the 1 ML film starts to decompose partly already upon annealing at T > 400 °C, the 20 ML VN films are stable beyond 600 °C. Fig. 4 illustrates this point by showing the He I valence band spectra of the 20 ML VN after annealing stepwise up to 600 °C. The 600 °C annealed surface shows a LEED pattern similar to the one displayed in Fig. 3b, and the UPS spectra in Fig. 4 demonstrate that the structural order is reflected in the sharpening of the spectral fine structure of the N 2p–V 3d band: for example, the feature at ~3.5 eV becomes clearly more distinguished in the 600 °C spectrum. The 20 ML VN nanolayer is evidently stable at least up to 600 °C – note that the low-energy secondary electron cut-off at 15–16 eV binding energy and thus the work function remains unchanged.

Angular dependent XPS measurements, i.e. spectra recorded at normal and grazing emission geometry, have been performed to shed light on the morphology and surface composition of the VN nanolayers. Fig. 5a contains the Pt 4f core level spectra of the substrate of the as-deposited 20 ML VN nanolayer recorded at normal emission (NE) and grazing emission geometry (GE = 70° with respect to the surface normal). At NE the Pt 4f7/2 intensity is still ~30% of the clean Pt surface value, but significantly it is completely quenched at grazing emission. This indicates an island-type growth mechanism as discussed below. Fig. 5b compares the V 2p spectra of the 20 ML VN nanolayer, after annealing at 500 °C, at NE and GE. There are

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Fig. 3. LEED patterns of the clean Pt(111) surface (a), of 10 ML VN annealed at 500 °C (b), and of 1 ML VN annealed at 500 °C (c). In (c) Pt and VN reflections are indicated. (electron energy = 58 eV).

Fig. 4. He I valence band spectra of a 20 ML VN nanolayer as a function of annealing temperature.
no changes in the main lines between the two emission geometries, but the shake-up satellite (Sat.) at \( \sim 516 \text{ eV} \) carries more spectral weight at GE. The (N 1s/V 2p) peak intensity ratio increases by \( \sim 50\% \) when going from NE to GE. Taken together, these data suggest that the surface region is nitrogen enriched as compared to the volume of the film and that it contains less nitrogen vacancies.

**4. Discussion**

The polar (111)-type surfaces of ionic compounds with the rock salt structure have raised considerable scientific interest, because they are inherently unstable in bulk samples on electrostatic grounds [23,24], but it has been predicted recently that they can be fabricated in the form of nanoscopic thin films [25]. The situation is somewhat different for the cubic VN because of the strong covalent character of the bonding, but the (111) surface is still polar, i.e. it supports a dipole moment perpendicular to the surface, and the stability of the different surface terminations, i.e. nitrogen versus vanadium, is of interest. In particular, since it is expected that the surface reactivity is strongly dependent on the terminating atom layer. We have calculated therefore by DFT theory the electronic DOS of nitrogen and vanadium terminated VN(111) surfaces and the results are shown in Fig. 6. The DOS have been resolved into surface, subsurface and bulk contributions and have been projected onto V and N sites. Figs. 6a and b simulate the situation in the VN bulk: panel a is for stoichiometric VN (VN1), whereas panel b is for VN with 25\% of N vacancies (V4N3). We note that the N vacancies introduce vacancy-derived peaks in the V 3d states at around \( -0.75 \text{ eV} \) and \( -1.75 \text{ eV} \). Panels c and d display the DOS of the V (c) and N (d) terminated VN(111) surfaces. The V-terminated surface is distinguished by a DOS peak at \( -1 \text{ eV} \), whereas the N-terminated surface has a significant DOS structure at \( -3 \text{ eV} \), which is absent on the V-terminated surface. The two panels at the bottom of Fig. 6 show the DOS of V (e) and N (f) terminated VN(111) surfaces covered by a monolayer of chemisorbed hydrogen. Since hydrogen is present from the decomposition of NH\(_3\) during VN film growth, the presence of hydrogen at the VN surfaces is possible and may be of relevance.

The DOS structures in Fig. 6 are all characterised by the high DOS of the non-bonding V 3d states in the region from the Fermi energy (\( E = 0 \text{ eV} \)) to \( -2 \text{ eV} \) and by the N 2p–V 3d bonding states at \( 4-8 \text{ eV} \). As mentioned above, the V-terminated surface has a V 3d derived surface state split off the bulk states at \( 1-1.5 \text{ eV} \) below \( E_F \), which is not apparent on the N-terminated surface. Conversely, on the N-terminated surface the N 2p–V 3d bonding states at the surface are split off from the corresponding bulk band and are shifted towards lower binding energy forming a well-separated surface state peak at \( -3 \text{ eV} \), while on the V-terminated surface and bulk states are intimately mixed in the region \( 4-8 \text{ eV} \). Upon hydrogen chemisorption on the V-terminated surface (panel e) the V 3d derived surface state at \( -1.5 \text{ eV} \) is quenched and shifted to lower binding energy: there is some redistribution of DOS in the N 2p–V 3d bonding band with a new structure around \( -3.5 \text{ eV} \). Hydrogen adsorption on the N-terminated surface produces little change in the V 3d band but new N–H bonding states between 6 and 8 eV.

Comparing the calculated DOS structures of Fig. 6 with the experimental valence band UPS spectrum of the annealed 20 ML VN(111) surface of Fig. 4 we note that the tail of the V 3d non-bonding states between 1 and 2 eV below \( E_F \) is smooth showing little signs of a feature due to the split off V 3d surface states of the V-terminated surface. Also, there is no clear signature of the distinct surface state of the N-terminated surface at \( -3 \text{ eV} \) in the experimental spectrum. However, the experimental feature at \( -3.5 \text{ eV} \) may be tentatively associated with the split off V–H bonding states of the H covered V-terminated surface. The features between 4 and 8 eV in the experimental spectrum reflect the structure of the hybridised N 2p–V 3d DOS, containing surface and bulk contributions, but they do not allow a distinction between different surface terminations.
The angle-resolved XPS measurements have indicated that the surface region is N enriched. Moreover, the observation of the satellite structure in the V 2p core level spectra showing increased spectral weight at grazing emission geometry (Fig. 5b) suggests that the surface region contains a smaller concentration of N vacancies than the bulk. However, this does not necessarily imply an N surface termination. Theory has compared the relative stability of N vacancies in the bulk vs. that at the surface. From the DFT calculations, simulating 25% N vacancies in a particular layer in a seven VN units thick film, one learns that the penalty for forming N vacancies in the layer below a V-terminated VN(111) is rather high (0.7 eV) as compared to the bulk, confirming that forming N vacancies on both sides of a V layer (the vacuum can be considered as a “vacancy”) is rather unlikely. On the contrary, in the case of an N-terminated surface, the formation of vacancies below the surface is enhanced by 0.5 eV. From these results an N-terminated VN(111) seems less likely as compared to a V-terminated surface with an enhanced N content in the sub-surface region.

The work functions of the clean N-terminated and V-terminated VN(111) surfaces have been calculated to 6.06 eV and 4.83 eV, respectively, as shown in Table 1. The effects of H chemisorption have also been included. None of the values for the clean surfaces are in good agreement with the experimentally determined work function of 4.38 eV ± 0.02 eV, even if the shortcomings of a local DFT-approximation are considered with a usual deviation of ±0.2 eV. However, test calculations have shown that the presence of chemisorbed hydrogen has a significant influence in lowering the work function, in particular on the N-terminated surface, where the adsorbed H forms a very stable amine-like N–H bond thereby reducing

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<tr>
<th>$\phi$ (eV)</th>
<th>Clean</th>
<th>0.5 ML $\text{H}_2$</th>
<th>1 ML $\text{H}_2$</th>
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<tr>
<td>V-terminated</td>
<td>4.83</td>
<td>4.83</td>
<td>4.42</td>
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<tr>
<td>N-terminated</td>
<td>6.07</td>
<td>2.46</td>
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the stability of a terminating N layer. This is best seen for the 1 ML case where the N layer is on the verge of being lifted off from the V layer below. On the other hand, the chemisorption of hydrogen on a V-terminated surface according to DFT also lowers the work function to a value close to the experimental one. The presence of chemisorbed hydrogen at the VN surface is possible, considering the present growth conditions in a reactive NH3 atmosphere, even after annealing in UHV to 500–600 °C. Chemisorbed hydrogen is difficult to detect directly with the methodology employed in the present work, but it is noted that the DOS of the H covered V-terminated surface is in reasonably good agreement with the experimentally observed valence band spectrum. It should be mentioned parenthetically here that the calculated work functions refer to ideal surface geometries, whereas the film surfaces prepared experimentally have a degree of roughness and must have a significant number of undercoordinated atoms at island boundaries (see the following paragraph). The latter will reduce the experimental work function values.

Finally, we wish to address the growth mode of the VN nanolayers on Pt(111). The XPS intensities of the Pt substrate 4f core levels become attenuated upon VN overlayer growth (not shown here), but after deposition of 20 ML VN the Pt 4f intensity is still ~33% of the clean surface value in normal emission (Fig. 5a). However, in grazing emission geometry the Pt 4f intensity is vanished. The Pt valence band features in UPS have also disappeared completely for coverages >5 ML VN (Fig. 2). Furthermore, the Pt(111) LEED spots vanish after deposition of 1–2 ML VN. Taken together and considering the different surface sensitivities in the different experiments a Stranski–Krastanov layer-plus-island growth mode. The VN nanolayers grow on Pt(111) according to a Stranski–Krastanov layer-plus-island growth mode.

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References


5. Summary

Epitaxial, nearly stoichiometric VN0.9 nanolayers with (111) orientation and a (1 × 1) surface structure have been grown on a Pt(111) single crystal surface by reactive evaporation of vanadium in NH3 atmosphere. The surfaces have been characterised experimentally by LEED, X-ray and UV photoelectron spectroscopy, and work function measurements and theoretically by ab initio DFT calculations. The VN (1 × 1) unit cells are rotationally aligned to the high symmetry directions of the Pt(111) substrate. The experimental valence band spectra have been compared to the theoretical DOS of V- and N-terminated VN(111) surfaces, with and without chemisorbed hydrogen. The comparison suggests a vanadium terminated surface, containing possibly chemisorbed hydrogen, with an N enriched sub-surface layer; this is consistent with the angle-dependent XPS core level measurements. A hexagonal nitrogen surface layer termination is less likely according to the DFT calculations. The VN nanolayers grow on Pt(111) according to a Stranski–Krastanov layer-plus-island growth mode.