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The growth of epitaxial VN(1 1 1) nanolayer surfaces

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Abstract

Ultrathin films of vanadium nitride (1–20 monolayers = nanolayers) with (1 1 1) orientation have been grown on a Pt(1 1 1) surface by reactive evaporation of vanadium in NH_3 atmosphere. The VN(1 1 1) surfaces have been investigated by X-ray and UV photoelectron spectroscopy, LEED, work function measurements, and ab initio DFT calculations. Nearly stoichiometric, well-ordered $VN_{0.9}$ overlayers 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(1 1 1) surfaces, i.e. V and N terminated surfaces, bare and with chemisorbed hydrogen. The comparison suggests that the VN(1 1 1) 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(1 1 1) 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 V_2O_5 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(1 1 1) nanolayers, epitaxially grown on a Pt(1 1 1) single crystal substrate. The

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controlled oxidation of these VN(1 1 1) 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(1 1 1) by reactive physical vapour deposition under ultrahigh vacuum (UHV) conditions. Specifically, vanadium metal has been evaporated in an NH_3 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(1 1 1) substrate provides an ordered metallic substrate which is inert towards nitridisation under these conditions. The lattice mismatch between the Pt(1 1 1) surface unit cell and VN(1 1 1) 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(1 1 1) nanolayers can indeed be obtained on Pt(1 1 1) with a non-reconstructed polar (1×1) surface, which are rotationally aligned along the main symmetry directions of the Pt(1 1 1) substrate. The vanadium nitride films are nearly stoichiometric ($VN_{\sim 0.9}$) and the spectroscopic data in conjunction with the DFT calculations suggest that the VN(1 1 1) 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 $\sim 1 \times 10^{-10}$ 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(1 1 1) 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 O_2 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 mircobalance 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 NH_3, 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(1 1 1) 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 $15 \times 15 \times 1$ 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 $6 \times 6 \times 1$ k-mesh.

3. Results

Fig. 1a shows Mg Kα ($h\nu = 1253.6$ 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 $2p_{3/2}$ emission at 513.5 eV and the $2p_{1/2}$ emission at 520.9 eV binding energy, and a broad satellite structure at 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 adventitous 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-