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Self-organized homo-epitaxial growth of (001) vanadium assisted by oxygen surface reconstruction

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ABSTRACT

In this paper the effect of oxygen on the vanadium homoepitaxial growth process is analyzed by using Auger spectroscopy, electron diffraction and scanning tunneling microscopy. As the oxygen induced 1×5 surface structure got a lattice spacing 6% different from the pure V lattice, relaxation is observed by electron diffraction during the growth. The average in-plane lattice spacing is thus shown to be proportional to the oxygen surface concentration. The surface lattice relaxation is observed to exponentially vary with the number of deposited atomic planes. A kinetic model is proposed and allows us to explain these observations. Furthermore, it helps us to distinguish two regimes depending on growth temperature. At high temperature, the oxygen surface concentration during growth is due to oxygen upward diffusion from the underneath V layer. For lower temperature however, this upward diffusion is not efficient and another source of oxygen contamination is evidenced. When the oxygen surface concentration is sufficient, a spectacular self-organization is observed at the surface by surface microscopy. Ribbons shape islands are observed and are tentatively explained as a consequence of oxygen surface concentration and stress induced by the surface reconstruction.

1. Introduction

The understanding of the growth processes involved during thin films epitaxy is of particular interest in order to control the general properties of the synthesized system. The different growth modes, i.e. layer by layer (the Frank–Van der Merwe growth mode), three-dimensional (the 3D Volmer–Weber growth mode), and layer by layer followed by 3D islanding (the Stranski–Krastanov growth mode), have been established a long time ago and were currently observed on many various systems based on semi-conductors, oxides, metals etc. However, if these different growth processes may be justified by using the thermodynamics approach, the introduction of stress into the process is now well-known to be responsible for some peculiar behaviors according to theoretical prediction [1]. For instance, 3D growth was often observed on A/B systems for which a 2D growth was predicted by using thermodynamics consideration. This discrepancy may often be attributed to the occurrence of stress and strain. Self-organization on a surface is also a nice example of using stress to create self-assembled objects [1]. Different theoretical and experimental approaches were proposed to take into account the stress in predicting the growth mode or to use the stress in conceiving new functionalities and new devices (see [2] for a review). Among a large number of epitaxial systems, pure vanadium or vanadium based alloys are very interesting materials:

- V is not magnetic in bulk, but can become magnetic using alloying, stress or nanopatterning due to its 3d valence electrons nature [3–5]
- V is the pure element after Nb that has the highest superconducting temperature (5.4 K) even for ultra-thin films [6]
- vanadium oxides (VO, VO_2, V_2O_3, V_2O_5) show peculiar electronic properties interesting for catalysis [7], or for insulator–metal transition that is not yet fully understood [8]
- V intermixing with other metals takes place at high temperature (850 K with Fe) giving some chance to use it as a robust buffer layer in spintronic devices for instance [9,10].

In this paper, we are interested in strain effect on the homo-epitaxial growth of vanadium. It should be surprising that the strain could play a role during homo-epitaxial growth. However, the vanadium surface is often "contaminated" by oxygen. Up to now, this contamination was attributed to diffusion from the bulk towards the surface during the surface smoothing. Vanadium surfaces free of oxygen are consequently very difficult to prepare [11–14]. This oxygen leads to very nice $1 \times 5 + 5 \times 1$ surface reconstructions (and sometimes $1 \times n$ with $n \neq 5$) as observed by electron diffraction (LEED, RHEED) and Scanning Tunneling Microscopy (STM) [13,15–17]. Moreover, we had clearly established by using RHEED that the Average In-Plane Lattice Spacing

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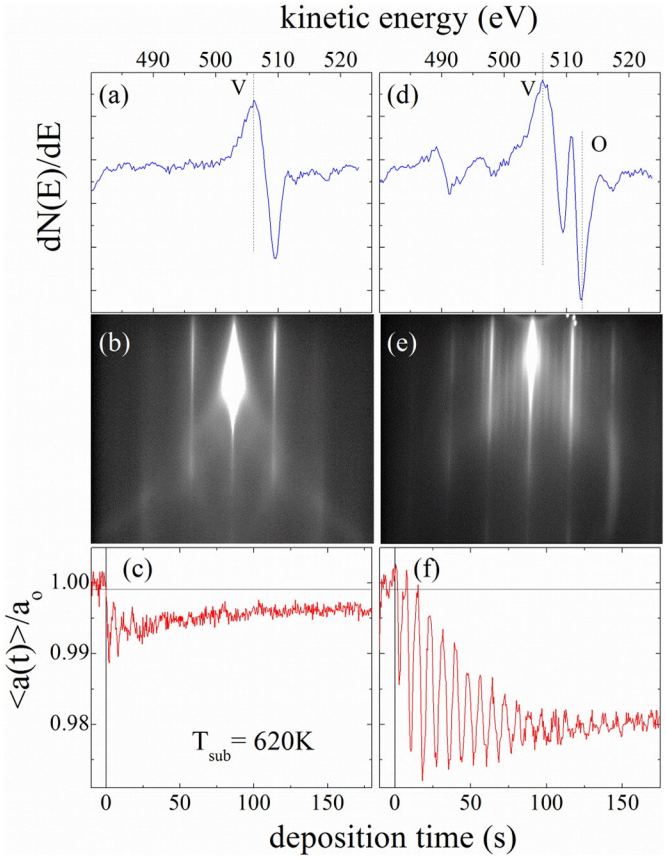

Fig. 1. In-plane lattice spacing variation during growth at Tsub = 620 K depending on the initial oxygen surface coverage. On the left, almost no oxygen was detected by Auger spectroscopy (a) on the initial surface leading to a 1 × 1 RHEED pattern along the [100] direction (b) and small amplitude of the in-plane lattice spacing variations (c). On the right, the Auger initial oxygen coverage (d) leads to a 5 × 1 surface reconstruction as seen by RHEED along the [100] direction (e) and large amplitude of the in-plane lattice spacing variation (f).

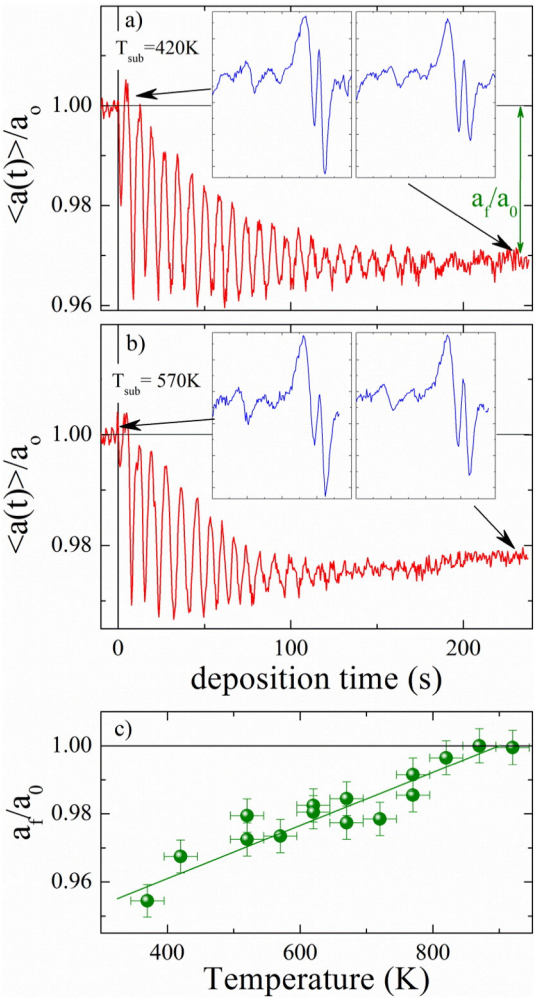

Fig. 2. Evolution of the oxygen quantity during V growth at 420 K (a) and 570 K (b) and link with the final relaxed in-plane lattice spacing (c). The oxygen quantity was measured before the growth and at the end of the growth by Auger spectroscopy (insert in a) and b), same scale as in Fig. 1). The final values of the in-plane lattice spacing observed after 30 ML thick are plotted versus growth temperature in c).

(noted AIPLS in the following) of this reconstructed surface is very different from the V bulk lattice spacing. Indeed, when growing pure V on top of such surfaces, some spectacular in-plane lattice relaxation was observed [12]. This large effect was attributed to the large mismatch between the lattice spacing of pure V and of the oxidized surface. This mismatch was estimated to be around 6%. The O and V atomic arrangement and distances was analyzed by Koller et al. [13] and Kralj et al. [17] by using STM, and the expansion of the average lattice spacing from bulk V to 1 × 5 oxygen induced reconstruction was confirmed.

Consequently, speaking of homo-epitaxy of V on an oxygen induced (001) vanadium reconstructed surface is not pertinent. However, this mismatch obtained during the "homo"-epitaxial growth is a chance to analyze the growth by varying the temperature on a system with a large mismatch. Indeed, this analysis is often not possible in the case of a hetero-epitaxial metallic system since intermixing takes place when increasing the temperature. We thus examined the relaxation process of a growing V layer by electron diffraction varying the substrate temperature (noted T_{sub} in the figures) in the range 300–1020 K. The corresponding surface morphology is observed by using STM after initiating the growth for different deposition temperatures. The growing islands shape was observed to be strongly anisotropic, which was tentatively explained by taking into account the strain induced by oxygen. The paper is divided in 4 parts. In the first part, the experimental details on the strain measurements, chemical analysis and STM analysis are reported. The strain experimental results are shown in the second part and the STM analysis in the third part. Finally, the original surface morphology observed by STM is discussed in the fourth part according to the strain observations.

2. Experimental details

The vanadium buffer layers are grown by Molecular Beam Epitaxy (MBE) on (001) MgO substrates. The static pressure in the chamber was $7 \cdot 10^{-11}$ Torr and decreased when cooling the cryogenic panels with liquid nitrogen. Vanadium was evaporated from a 99.5% nominal purity target by using an electron gun, the pressure rising up to $4 \cdot 10^{-9}$ Torr during the process. The (001) bcc V epitaxy takes place on (001) MgO even at room temperature with the epitaxial relationship [110] (001) MgO // [100] (001) V. In the following, the crystallographic directions are given in the BCC vanadium lattice. To get flat V surfaces, an annealing was performed up to 1000 K. In these conditions, several surface superstructures may be observed, like the 1 × 1 (clean surface), and the pseudo 1 × 1, 5 × 1 and 6 × 1 [11,13,15,17]. These surface arrangements were now clearly attributed to the presence of oxygen. Indeed, even if the oxygen contamination is very small during the growth process, this oxygen present in the bulk layer diffused towards the surface during the high temperature annealing (at least 1000 K) necessary to smooth the surface. This is the reason why oxygen free (001) V surface are very difficult to obtain even after several ion bombardment cycles (see [16] and ref. therein). However, we managed to