Available online at www.sciencedirect.com
SCIENCE DIRECT
Surface Science 600 (2006) 497–506
SURFACE SCIENCE
www.elsevier.com/locate/susc

Structure of MgO/V/MgO(001) thin films studied by the combination of X-ray photoemission and ion beam analysis techniques

E. Román [a,*], Y. Huttel [a], M.F. López [a], R. Gago [b], A. Climent-Font [b], A. Muñoz-Martín [c], A. Cebollada [d]

[a] Instituto de Ciencia de Materiales de Madrid (ICMM-CSIC), FIS, Sor Juana Ines de la Cruz 3, 28049 Cantoblanco, Madrid, Spain
[b] Centro de Micro-Análisis de Materiales and Departamento de Física Aplicada, Universidad Autónoma de Madrid, 28049 Cantoblanco, Madrid, Spain
[c] Centro de Micro-Análisis de Materiales and Parque Científico de Madrid, 28049 Cantoblanco, Madrid, Spain
[d] Instituto de Microelectrónica de Madrid—IMM (CNM-CSIC), Isaac Newton 8 (PTM), 28760 Tres Cantos, Madrid, Spain

Received 17 May 2005; accepted for publication 8 November 2005
Available online 5 December 2005

Abstract

The structure of epitaxial 40 Å thick V(001) films grown at room and high temperature (723 K) in MgO/V/MgO(001) model heterostructures is studied in detail by means of X-ray photoemission spectroscopy, Rutherford backscattering spectrometry and elastic recoil detection analysis. The resulting structures of samples grown at both temperatures is very similar, including the eventual contamination by hydrogen in the V layer, and only subtle modifications at the V/MgO(001) interface have been observed. These differences at the very first V layers grown on MgO(001) surface could infer in the growth of the subsequent V layers. The influence of the nature of the V oxides at the V/MgO(001) interface on the properties of the 40 Å thick V(001) films is discussed.

Keywords: Vanadium; X-ray photoelectron spectroscopy; Multilayers; RBS; ERDA

1. Introduction

The study of the properties of ultrathin films and nanostructured films is motivated from both, fundamental reasons and potential technological applications. Subtle modifications of the physical properties of these systems are achieved by tiny changes of the structure that can be induced by different growth conditions and/or adsorption or insertion of doping elements such as H. Vanadium, which is known to act as a strong hydrogen getter [1–4] is the natural prototype element to study the behaviour of H in very thin structures and nanoparticles. Furthermore, V ultrathin films and nanostructured V films are attracting attention for the design of new materials for hydrogen storage for energetic applications. Thus, the hydrogen uptake of extremely thin vanadium (001) layers has been exhaustively studied [5–7]. In those previous investigations, the V layers were grown onto a MgO(001) substrate as (001)-oriented superlattices with Mo or Fe. These systems were chosen because neither Fe nor Mo dissolves hydrogen and, consequently, only the V layers contain hydrogen. On the other hand, very recently, Meded et al. [8] have reported the in-plane resistivity dependence on hydrogen loading of Fe/V and Mo/V superlattices, attributing this dependence to the hydrogen induced V expansion via electronic structure modifications rather than hydrogen atoms acting as point scatterers. In particular, they have shown that the sole physical quantity behind the modification of the resistivity of the multilayer is the vanadium expansion resulting from the incorporation of H.

Even though, most of the studies have been performed on metallic multilayered systems where V layers are in between metallic elements, the growth of V layers in between insulating layers or on insulating surfaces has

* Corresponding author. Tel.: +34 91 334 90 99; fax: +34 91 372 06 23.
E-mail address: eroman@icmm.csic.es (E. Román).

0039-6028/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2005.11.001

gained attention because of potential applications not restricted to catalysis or getter systems. For example, Gutsche et al. focussed their studies on the superconducting properties of V layers on MgO and sapphire substrates [9] and Ikuhara et al. on the epitaxial growth of V films on MgO(0 0 1) [10]. Within the latest purpose, a systematic study on the optimization of the growth of high-quality epitaxial V ultrathin films on MgO(0 0 1) has been recently published by Huttel et al. [11]. The results showed a strong dependence of the V lattice parameters with the growth temperature. In order to explain if the observed behaviour is related to the hydrogen incorporation or the chemical composition of the V layers, we have performed the physico-chemical characterization by means of X-ray photoemission spectroscopy (XPS) depth profiles, Rutherford backscattering spectrometry (RBS) and elastic recoil detection analysis (ERDA).

In this work we present a detailed investigation on the structure of thin V films [40 Å thick ≈ 25 monolayers (25 ML)] deposited on MgO(0 0 1) substrates and covered by a 80 Å MgO capping layer. The combination of the above-mentioned techniques provides us a complete vision of the composition and structure of the samples; in particular we show that the relative hydrogen content in samples grown at different temperatures cannot explain the observed changes in the resistivity of the V thin layers [12] and that some differences between samples grown at different temperatures are observed at the V/MgO(0 0 1) interface. The paper is organized as follows: in Section 2 we give the experimental details; in Section 3 we present the qualitative RBS, ERDA and XPS results while Section 4 is devoted to the discussion of the quantitative results. Conclusions are given in Section 5.

2. Experimental details

The samples were grown in an ultrahigh vacuum system with base pressure in the low 10^{-9} mbar with both triode sputtering and laser ablation facilities. The ultrathin V films (40 Å thick) were deposited by triode sputtering either at room temperature (RT) or at high temperature (HT), namely at 793 K (HT) on MgO(0 0 1) single crystals. Prior to V deposition, a 100 Å MgO buffer layer was grown by laser ablation at 720 K on the substrate to planarize the surface. After the V deposition, a thick MgO capping layer between 50 and 80 Å was deposited by laser ablation and at RT to protect the V layers from oxidation. Complete samples crystallographic structure was measured ex situ by X-ray diffraction and is reported in detail elsewhere [11].

The X-ray photoelectron spectroscopy (XPS) spectra and depth profiles have been recorded in a separated ultrahigh vacuum chamber with a base pressure in the low 10^{-10} mbar. The samples have been etched using 1 KeV energy Ar^+ ions at an incidence angle with respect to the normal of the sample of 42°. The ion energy was chosen in order to minimize ion implantation induced phenomena. The corresponding etching rate was 0.18 Å/μA min [13], which corresponds here to approximately 0.06 Å/min. The MgKα X-ray emission (1253.6 eV) was used for all the measurements and the angle between the hemispherical analyzer (Specs, PHOIBOS 100) and the normal of the surface was kept at 30°. The quantitative analysis was performed by the evolution of the photoemission integrated intensities of O 1s, Mg 2s, V $2p_{1/2}$ and V $2p_{3/2}$ transitions for each sample. In all cases, the same Shirley type background was removed as well as the satellites peaks and the quantitative XPS analysis was performed by using the program Specslab1.

The RBS and ERDA measurements were performed at the Centro de Micro-Análisis de Materiales (CMAM) at Universidad Autónoma de Madrid, Spain [14]. RBS and ERDA experiments were done simultaneously with a 2 MeV He^+ beam at an incidence angle of 75° with respect to the sample surface normal. The RBS and ERDA spectra were acquired with silicon surface barrier detectors located at a scattering angle of 170° and 30°, respectively. In front of the detector located at the forward scattering angle, a 13 μm thick mylar foil was placed to filter the H recoils from the He scattered particles. The RBS and ERDA spectra have been fitted using the SIMNRA code [15] and considering, in both cases, the same film structure. The cross section for the $^1H(\alpha,p)^4He$ process given by Quillet et al. was used for quantification of the ERDA data [16].

3. Qualitative results

3.1. RBS and ERDA results

Fig. 1a compares the RBS spectra measured on MgO/V/MgO(0 0 1) structures for V grown at room temperature (RT) and high temperature (HT). The first qualitative observation is that both spectra are almost identical, indicating that only slight differences in the sample structure are to be expected. The main features that can be observed in the spectra are related to scattered He ions from O, Mg and V atoms. For each target element, the maximum possible energy of the scattered projectiles is given by the kinematic factor of a classical collision and would correspond to a collision event at the target surface. A lower energy value would be obtained for collisions at a certain depth in the target, which would reflect in counts at lower energy channels of the detector (the depth derived from the energy calibration of the detector and the energy loss of the projectile in the solid). In addition, the final yield at each energy channel provides information about the concentration of the element at the corresponding depth. The broad features related to Mg and O indicate a thick layer since the signal comes mainly from the MgO(0 0 1) substrate. The well defined peak corresponding to V indicates a very thin layer. Minor features above the V peak energy are also observed and correspond to the presence of small concentrations of impurities that will be discussed below. Note that the Mg signal at the V/MgO(0 0 1) substrate interface (around channel 370) shows small differences for the RT and HT