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Epitaxial MoO_x nanostructures on $TiO_2(1\,1\,0)$ obtained using thermal decomposition of $Mo(CO)_6$

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Abstract

Stoichiometric and highly-defective $TiO_2(1\,1\,0)$ surfaces (called as *yellow* and *blue*, respectively) were exposed to $Mo(CO)_6$ vapours in UHV and in a reactive O_2 atmosphere. In the case of *yellow*-TiO_2, an O_2 reactive atmosphere was necessary to obtain the $Mo(CO)_6$ decomposition at 450 °C with deposition of MoO_x nanostructures where, according to core level photoemission data, the Mo^{+4} state is predominant. In the case of *blue*-TiO_2 it was possible to obtain Mo deposition both in UHV and in an O_2 atmosphere. A high dose of $Mo(CO)_6$ in UHV on *blue*-TiO_2 allowed the deposition of a thick metallic Mo layer. An air treatment of this sample at 580 °C led to the elimination of Mo as MoO_3 and to the formation of a transformed layer of stoichiometry of $Ti_{(1-x)}Mo_xO_2$ (where x is close to 0.1) which, according to photoelectron diffraction data, can be described as a substitutional near-surface alloy, where Mo^{+4} ions are embedded into the titania lattice. This embedding procedure results in a stabilization of the Mo^{+4} ions, which are capable to survive to air exposure for a rather long period of time. After exposure of the *blue*-$TiO_2(1\,1\,0)$ substrate to $Mo(CO)_6$ vapours at 450 °C in an O_2 atmosphere it was possible to obtain a MoO_2 epitaxial ultrathin layer, whose photoelectron diffraction data demonstrate that is pseudomorphic to the substrate.

Keywords: MoOx nanostructures on $TiO_2(1\,1\,0)$; Photoelectron diffraction; XPS; Ultrathin epitaxial MoO_2; Near-surface $Ti_{(1-x)}Mo_xO_2$

1. Introduction

Oxygen deficient MoO_x/TiO_2 structures are of great interest for their catalytic properties, which could also result potentially useful to accelerate and discriminate surface reactions of relevance in the field of gas sensing. From a fundamental point of view studying the MoO_x/TiO_2 is interesting also, in order to compare the results with the rich collection of data so far reported for similar M/TiO_2 and MO_x/TiO_2 systems [1], where M is both a non-transition and transition metal. In particular, much interest is attached to the test of the possibility that ordered nanostructures (nanoparticles or ultrathin films) could be obtained when adopting a single crystalline $TiO_2(1\,1\,0)$ substrate.

It has been already observed that when Mo is evaporated at low coverages on a $TiO_2(1\,1\,0)$ surface, there is a reaction between the metal and the substrate that leads to the formation of MoO_x nanostructures at the interface [2,3]. This behaviour is comparable to that of other transition metals, e.g. the case of V. Actually, it was observed that a stepwise deposition of metallic vanadium, each step being followed by a post-oxidation treatment at 150 °C in 2×10^{-6} mbar of O_2, leads to the formation of a $VO_2(1\,1\,0)$ ultrathin film pseudomorphic to the substrate [4]. If the post-oxidation treatments, following the V deposition steps, are performed by annealing the sample in UHV rather than in an oxygen atmosphere, instead of producing a long range ordered epitaxial VO_2 film, a short range ordered VO(1 0 0) layer is obtained [5].

However, in the case of Mo a rather peculiar behaviour is observed: it is possible to obtain MoO_x particles depend-

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ing on the status of the substrate and on the annealing conditions [2]. If the substrate is a perfectly stoichiometric $TiO_2(1\,1\,0)$ sample (i.e. a new substrate single crystal, hereafter called *yellow*-TiO_2) it was observed that a thermal treatment in UHV of a 3 eq ML Mo deposit leads to the formation of MoO_x species, where the oxidation state of Mo varies depending on the annealing temperature. At temperatures higher than 500 °C, Mo is present on the surface as Mo^{+4}, but the Mo/Ti ratio quickly approaches zero as the temperature increases, because a large part of the metal is oxidised to MoO_3 which is very volatile [6]. On the other hand, if a highly-defective $TiO_2(1\,1\,0)$ sample is used as substrate (i.e. a crystal which was subjected to several sputtering and annealing cycles, hereafter called *blue*-TiO_2), a thermal treatment in UHV allows the formation of MoO_x structures only at very low coverages (below 0.5 eq ML), while at higher coverages the very strong Mo–Mo interaction always leads to the formation of a Mo(1 0 0) epitaxial film [7]. Since MoO_2 has a distorted rutile structure similar to VO_2 [8], it is quite likely that the formation of MoO_x particles at the interface could evolve toward the formation of an epitaxial MoO_2 layer. Actually, very recently a scanning tunnelling microscopy (STM) investigation on Mo deposits on *blue*-$TiO_2(1\,1\,0)$ surfaces has been reported [9] which indicates the formation of pseudomorphic MoO_x islands (stripes elongated along the [0 0 1] orientation).

There are few examples in literature on the growth of epitaxial MoO_2 films. The first study reports about the growth of epitaxial MoO_2 on a Mo(1 1 0) substrate [10], where the growth was obtained by a thermal treatment in O_2 (2×10^{-6} Torr) at 850 °C. In other cases the Mo(1 1 2) surface was used as substrate for the growth of $MoO_2(0\,1\,0)$ [11] or $MoO_2(1\,0\,0)$ epitaxial layers [12]. However, there is no evidence in literature for an epitaxial MoO_2 ultrathin film pseudomorphic to the $TiO_2(1\,1\,0)$ substrate in analogy with the VO_2 case. On the other hand it is evident, from the arguments above reported, that the obtainment of a MoO_2 film by annealing in UHV a thin Mo deposit or by post-oxidation treatments in an O_2 atmosphere are not convenient routes (formation of volatile MoO_3 and consequent Mo loss).

For these reasons we have decided to explore the possibility to use $Mo(CO)_6$ as an alternative source to obtain the deposition of MoO_x species and epitaxial MoO_2 ultrathin films on $TiO_2(1\,1\,0)$. Actually, in our laboratory we have accumulated much experience on the use of metal carbonyls as alternative sources of transition metals for the deposition of metals or oxides in UHV conditions. A first example was the decomposition of $Ru_3(CO)_{12}$ in a O_2 reactive atmosphere that allowed the deposition of epitaxial RuO_2 on $TiO_2(1\,1\,0)$ [13,14]. In that case also post-annealing treatments in O_2 of $Ru_3(CO)_{12}$ saturated surfaces led to the formation of oxide islands. In the case of $Mn_2(CO)_{10}$ an exposure to the carbonyl vapours in a reactive H_2O atmosphere allowed the obtainment of epitaxial MnO(1 1 1) on a Pt(1 1 1) surface [15]. On the other hand, $Mo(CO)_6$ has been already used for the deposition of MoO_x clusters on Au(1 1 1): the authors found that the Mo nanoparticle obtained by dissociation of $Mo(CO)_6$ at 500 K were inactive toward oxygen [16]. However these nanoparticles could be oxidised by reaction with NO_2 at 500 K to form Mo oxides, i.e. MoO_2 and MoO_3.

In this paper we will show how $Mo(CO)_6$ can be effectively used for the deposition of epitaxial MoO_x nanostructures on $TiO_2(1\,1\,0)$ by using a reactive O_2 atmosphere. The experiments were carried out using two different TiO_2 substrates, i.e. a new *yellow*-TiO_2 crystal and a *blue*-TiO_2 crystal.

2. Experimental

For both *blue*-TiO_2 and *yellow*-TiO_2 substrates it was possible to obtain a sharp Low Energy Electron Diffraction (LEED) pattern and no carbon or other contaminants (as deduced by X-ray Photoelectron Spectroscopy, XPS, measurements) after a few cycles of sputtering (2.0 kV, 10 μA/cm^2) and annealing (UHV at 650 °C for 5–10 min). Prior to each deposition the same procedure was always repeated. The experiments were performed in two different UHV systems. One is a custom made UHV system operating at a base pressure of 6×10^{-8} Pa. The analysis chamber is equipped with a sputter gun, LEED and XPS (all of them from Omicron). The sample is mounted on a two-axis goniometer which allows to move the sample in the polar direction θ (with respect to surface normal) and in the azimuthal direction ϕ (full 360° rotations) so allowing to collect angle scanned X-ray photoelectron diffraction (XPD) and angle-resolved X-ray photoemission spectroscopy (ARXPS) data. Angular accuracy is always better than ±1° in both directions. All the XPS, XPD and ARXPS data were acquired by using a Mg K_α radiation. The second UHV apparatus is a modified VG-ESCALAB MkII system, used to acquire automatically 2π XPD plots, where the centre of the plot corresponds to the surface normal, a radial section represents a polar scan, a circular section is an azimuthal scan and the photoelectron intensity is given by the colour scale. In this case an Al K_α excitation source was used. The manipulator has similar performances as those reported above for the previous apparatus.

The carbonyl was introduced in the UHV preparation chambers (isolated from the analysis chambers by a gate valve) by opening a gate valve connected to a small volume containing the carbonyl wrapped in a Ta foil (hereafter Ta-pocket) where small holes were created. Several attempts were needed in order to optimise the size and number of holes to the needed deposition rate. While dosing the carbonyl the sample was kept at 400–450 °C. The experiments were performed in UHV and in an O_2 atmosphere (see below).

3. Results

3.1. Yellow-$TiO_2(1\,1\,0)$ substrate

In the case of the *yellow*-TiO_2 substrate only traces of Mo were present on the surface (as determined by XPS)