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Strained c(4 × 2) CoO(100)-like monolayer on Pd(100): Experiment and theory

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ABSTRACT

We report on an interface-stabilized strained c(4 × 2) phase formed by cobalt oxide on Pd(100). The structural details and electronic properties of this oxide monolayer are elucidated by combination of scanning tunneling microscopy data, high resolution electron energy loss spectroscopy measurements and density functional theory. The c(4 × 2) periodicity is shown to arise from a rhombic array of Co vacancies, which form in a pseudomorphic CoO(100) monolayer to partially compensate for the compressive strain associated with the large lattice mismatch (~9.5%) between cobalt monoxide and the substrate. Deviation from the perfect 1:1 stoichiometry thus appears to offer a common and stable mechanism for strain release in Pd(100) supported monolayers of transition metal rocksalt monoxides of the first transition series, as very similar metal-deficient c(4 × 2) structures have been previously found for nickel and manganese oxides on the same substrate.

1. Introduction

The study of ultrathin transition metal oxide (TMO) films gives access to physical and chemical properties substantially different from those observed in the parent bulk oxides, thanks to the reduced dimensionality as well as to substrate induced effects such as charge transfer, epitaxial strain and electronic hybridization. Outstanding examples are the coupling between strain and spin orientation [1], the tuning of the catalytical activity upon selective modulation of the work function [2] and the structural flexibility related to substrate–overlayer matching [3,4]. Notably, metal templates such as Ag(100), Pt(111) and Pd(100) can turn into metallic the otherwise insulating character of TMOs, thus rendering this class of system accessible to fundamental studies based on scanning tunneling microscopy (STM) and electron spectroscopy experiments. Understanding and controlling the physics of these metal supported TMO thin films is crucial for advances in several branches of nanotechnology such as, for example, nanoelectronics, heterogeneous catalysis and high density magnetic data storage.

In a series of recent papers we have investigated the formation of Pd(100)-supported Ni and Mn oxides with special emphasis on the interplay between structural, magnetic and electronic degrees of freedom in the monolayer (ML) regime [4–6]. Here, prompted by the growing interest in Co_xO_y films [1,7–14], we aim to explore the structure on Pd(100) of a Co monolayer in contact with an oxygen atmosphere. The growth of cobalt oxide films has been investigated in details on the metastable Ir(100)-(1 × 1) in a wide range of coverages by Heinz and coworkers [9,11–13]. They have shown that in spite of the square surface unit cell of the substrate, hexagonally arranged thin films develop from the very initial stage (1–2 ML) [9,13]. At higher coverage, (111)-oriented films grow in the form of either spinel Co_3O_4 [11] or rocksalt CoO [12]. Square-like phases have not been yet reported, at variance with the growth on Ag(100), where epitaxial CoO(100) forms [7,8,10,14]. It has been argued that the reasons behind the preferential (111) growth on Ir(100) can be related to the poor matching between the unreconstructed substrate and CoO(100) (~11% lattice mismatch versus ~4% on Ag(100)) [13].

In the present study, we show that the reactive deposition of 0.75 ML Co on Pd(100) yields the formation of a strained metal-deficient CoO(100)-like monolayer. The resulting Co_3O_4 ultrathin film is characterized by a rhombic distribution of Co vacancies with c(4 × 2) periodicity, which partially compensate the relatively high strain in the oxide layer due to the large lattice mismatch of about 9.5%. This specific c(4 × 2) – Co_3O_4/Pd(100) structure resembles very closely the corresponding c(4 × 2) monolayer phases of Ni and Mn oxides on Pd(100) [5,6,15,16], thus pointing to the high versatility of this vacancy-mediated stabilization mechanism for rocksalt TMO oxides on Pd(100). The stability and reproducibility of the c(4 × 2) structure also provide an excellent model system to assess the reliability of density functional theory (DFT) and post-

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DFT approaches applied to TMOs. In fact, it is well known that standard DFT encounters serious difficulties in treating the complex physics of strongly correlated materials due to self-interaction related errors. In particular, DFT describes incorrectly the bulk properties of TMOs (such as MnO, NiO and CoO) leading to a severe underestimation of the bandgap and magnetic moments [17,18]. However, electronic interactions in thin films are expected to differ deeply from those observed in the bulk due to the effects arising from surface and oxide-metal interface proximity. Ultimately, the substrate-induced metallization of the TMO overlayers may results in a substantial weakening of exchange and correlation effects. Therefore, it is not yet universally established which methodology is the most suitable to describe this class of systems.

In this paper, we employ a combined experimental and theoretical approach to get insight into the structural and electronic details of the observed $c(4 \times 2)-Co_3O_4/Pd(100)$ phase. The experimental characterization comprises STM, low energy electron diffraction (LEED) and high resolution electron energy loss spectroscopy (HREELS) measurements, whereas the theoretical description is based on standard and hybrid DFT.

The detailed description of the experimental and theoretical setup is given in Sections 2 and 3, respectively. In Section 4 we present and discuss the results. Finally, in Section 5 we draw the conclusions.

2. Experimental setup

The STM experiments were conducted in a custom designed ultra-high vacuum system operating at a base pressure of 8×10^{-11} mbar and equipped with typical facilities for sample cleaning, heating and cooling and for physical vapor deposition. The system comprises a variable-temperature STM (Oxford Instruments), a cylindrical mirror analyzer for Auger electron spectroscopy (AES) and LEED optics [19]. The STM was operated at room temperature (RT) in constant current mode, employing electrochemically etched tungsten tips cleaned *in situ* by electron bombardment. The HREELS measurements were performed in a separate system described previously [20], using an Erlangen EELS (ErEELS) spectrometer in specular reflection geometry at an incident angle of 60° and a primary energy of 6.5 eV. A resolution better than 6 meV was typically ensured, as measured at the full width at half maximum of the reflected primary peak. The homogeneity of the surface structure was carefully checked by LEED and by recording the phonon spectra at several different positions on the sample. The crystal was always kept at RT during acquisition of the HREELS spectra.

The Pd(100) crystal surface was cleaned by a standard procedure comprising alternate cycles of 1 keV Ar^+-ion bombardment and annealing at 1000 K. Further annealing for five minutes in O_2 atmosphere (2×10^{-7} mbar) at 570 K, followed by a brief flash to 950 K in UHV, was also used to remove contamination of residual atomic carbon. The optimal strategy to prepare the $c(4 \times 2)$ Co oxide phase consists in the reactive deposition of 0.75–0.8 ML of cobalt from an electron beam evaporator in 1×10^{-6} mbar O_2 partial pressure with the substrate kept at RT, followed by 5–10 min annealing at 570 K at the same oxygen pressure. The evaporation rate employed was $\sim$0.5 ML Co min^{-1}, as measured by a quartz crystal microbalance. The metal coverage is referred to the density of surface atoms in Pd(100), 1 ML containing 1.32×10^{15} Co atoms/cm^2.

3. Computational details

The computational method adopted in all calculations relies on the density functional theory (DFT) within the generalized gradient spin density approximation parameterization scheme proposed by Perdew–Burke–Ernzerhof (PBE) [21]. In addition to standard (i.e. Kohn–Sham based) DFT we have also applied a hybrid approach based on a proper mixing between exact Hartree–Fock (HF) and PBE exchange following the recipe of Heyd–Scuseria–Ernzerhof (HSE03) [22,23]. The resulting many body exchange (x) and correlation (c) functional reads:

$$E_{xc}^{\mathrm{HSE003}} = \frac{1}{4}E_x^{\mathrm{HF,sr},\mu} + \frac{3}{4}E_x^{\mathrm{PBE,sr},\mu} + E_x^{\mathrm{PBE,lr},\mu} + E_c^{\mathrm{PBE}}, \tag{1}$$

with (sr) and (lr) indicating the short- and long-range parts of the respective electron–electron exchange interactions. The range separation is controlled by the parameter μ, related to a characteristic distance, $(2/\mu)$, at which the short-range interactions become negligible. According to the HSE03 instructions, we have used $\mu = 0.3$ Å^{-1}.

The computational cell consists of an asymmetric slab constituted by a four-layer thick Pd(100) substrate on top of which lies a Co-deficient CoO(100) single layer. The PBE-optimized Pd lattice constant (2.79 Å) defines the dimension of the $c(4 \times 2)$ unit cell. Depending on the lateral registry and on the imposed magnetic configurations, the details of which are discussed in the next section, we have explored nine different structural models. Each of these has been fully relaxed at PBE level by means of a damped molecular dynamics strategy and keeping the two bottommost Pd layers fixed to the corresponding bulk positions. The HSE calculations were performed adopting the optimized PBE geometry unless otherwise stated. A Γ-centered 10×10 Monkhorst-Pack [24] k-point mesh for Brillouin zone integrations and an energy cutoff of about 300 meV guarantee well converged results.

The relative stability of the models considered was determined by comparing the computed generalized adsorption energy γ, defined as:

$$\gamma = (E_{\mathrm{slab}} - E_{\mathrm{Pd(100)}} - n_{\mathrm{Co}}\mu_{\mathrm{Co}} - n_{\mathrm{O}}\mu_{\mathrm{O}}), \tag{2}$$

where E_{slab} and $E_{Pd(100)}$ indicate the DFT energy of the $c(4 \times 2)-Co_3O_4/Pd(100)$ slab and the clean Pd(100) system, respectively, while n_{Co} and n_O are the number of Co and O atoms. According to our previous study [25], we set μ_{Co} and μ_O to the energy of bulk Co (hexagonal close-packed) and half of the free O_2 dimer energy, respectively.

4. Results and discussion

Fig. 1a reports a large scale experimental STM image of the surface resulting from deposition of 0.8 ML Co on Pd(100) at the conditions specified above. The surface is uniformly and almost entirely covered by large CoO monolayer islands, which have rectangular-like shape and edges running along the $\langle 011 \rangle$ directions of the Pd substrate. The remaining portion of uncovered Pd amounts to <10% and only very sparse second layer islands decorate the oxide wetting layer. Two large terraces separated by a monoatomic step are shown in Fig. 1b: they are atomically flat and display only few isolated defects. The high resolution STM images as the one reported in Fig. 1c clearly indicate a very well-ordered $c(4 \times 2)$ periodicity, with the latter also confirmed by the LEED pattern presented in panel (d).

A striking similarity between these STM and LEED results and those for the corresponding Ni oxide [5] and Mn oxide [4] $c(4 \times 2)$ phases on Pd(100) is evident and facilitates the structural search, providing a straightforward model for the computational investigation. This structural model consists of a CoO(100) monolayer, pseudomorphic to Pd(100) and therefore compressed with respect to bulk CoO(100), where the $c(4 \times 2)$ periodicity arises from one missing Co atom out of every four, thus leading to an