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The formation and stability of Rh nanostructures on TiO_2(1 1 0) surface and TiO_x encapsulation layers

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ABSTRACT

Rh overlayers formed on slightly oxygen deficient TiO_2(1 1 0) single crystals, as well as on ultrathin encapsulation titania layers prepared on Rh multilayers were characterized by AES, LEIS, XPS, TPD and work function (WF) measurements. Rh deposition on TiO_2(1 1 0) below 0.1 monolayer (ML) Rh coverage led to electron transfer from the metal toward the TiO_2(1 1 0) surface. Annealing of Rh multilayers up to 950 K in UHV resulted in the surface diffusion of titanium and oxygen ions into a TiO_x encapsulation layer of definite stoichiometry and a thickness of a few atomic layers. The accompanying 0.3–0.6 eV WF enhancement at Θ_{Rh} = 2–6 ML can be attributed to the smoothing of the Rh overlayer and the formation of a continuous TiO_x dipole layer consisting of positively charged titanium ions at the metal–oxide interface and negative oxygen ions in the topmost layer. De-encapsulation of Rh particles was observed on a TiO_2 sample less reduced in its bulk, revealing the roles of bulk and surface substrate stoichiometry on the decoration process. Increasing the thickness of Rh multilayers supported on the TiO_2(1 1 0) single crystal hampered ion diffusion and consequently, it led to an increase in the temperature characteristic of the completion of the encapsulation. Deposition of additional Rh on the TiO_x encapsulation layers covering Rh multilayers resulted in the growth of Rh particles having a similar height up to 1 ML. LEIS data indicated that the decoration of the second metal layer by titania was hindered. It occurred at a temperature more than 100 K higher than that characteristic of the TiO_2(1 1 0) surface at the same Rh coverage. Aspects of the produced structures in relation to the formation of protective oxide layers, modification of surface work function, catalysis and metal–insulator–metal (MIM) devices are considered.

1. Introduction

The formation of atomically thin metal layers is of fundamental interest in relation to heterogeneous catalysis and preparation of microelectronic devices. Ultrathin oxide films are highly relevant for corrosion protection of metals, magnetic tunnel junctions and dielectric barriers. In heterogeneous catalysis, nanosized metal particles are often supported on oxides of high specific surface area. The properties of well-characterized metal/oxide model systems are documented in excellent reviews [1–3]. The growth of well-defined ultrathin oxide films and their application as template for metal particle growth attracted broad interest and was surveyed in [4–6]. The titania oxide support, being of great practical importance, is one of the most studied materials [7,8]. The variable oxidation state of Ti ions gives the possibility to control the electronic properties (e.g. the electric conductivity and the work function) of titanium oxide easily, thus the catalytic properties of metal particles supported on it can be tuned [9]. Rh is among the catalytically most active materials and its effectiveness is influenced by the particle size [12] besides the particle–support electronic interaction. Since nanosized structures are mostly metastable phases, their stability in practical applications is a critical issue. The stability and reactivity of metal particles can be controlled by an additive such as a second metal [10]. For example, the adhesion of Rh particles to the titania surface can be enhanced by the addition of Mo [11,12]. Moreover, if an atomically thin insulating oxide layer covers one of the metals, an electronic interaction can still be operative due to direct electron tunneling depending on the work function difference between the two metals [6]. This phenomenon can be exploited in heterogeneous catalysis to finely adjust and highly improve the catalytic performance of nanoparticles [5,6,13,14] and also for making nanosized metal–insulator–metal (MIM) rectifiers which are critical components in promising high-efficiency light energy harvesting devices where they are called rectifying antenna, or rectenna [15]. The formation of a stable, atomically thin, homogeneous insulator layer with a constant thickness is a critical issue in the operation of nanosized MIM structures [16]. To prepare a MIM device, oxides similar

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to those used in electrolytic capacitors (e.g. alumina, niobium oxide and tantalum oxide) can be applied as insulators. Although titania has narrower bandgap than these materials, its application in MIM devices is also considered [7,16,17].

Ease of fabrication and structural as well as compositional precision are important factors in the application of nanostructures. They are achieved preferably through some self-limiting process that yields well-defined self-assembled layers. Atomic level control of layer growth can be routinely achieved by several techniques, e.g. atomic layer deposition (ALD), self-limiting oxidation (e.g. oxidation of Al in NiAl(1 1 0) [18]) and chemical vapor deposition (CVD). In addition, self-limited and self-assembling growth of ultrathin oxide layers was observed for metal particles supported by reducible oxides. This is called encapsulation which refers to the decoration of the metal particles by their support material during the catalytic reaction or the annealing in UHV. This phenomenon, termed also as strong metal–support interaction (SMSI) [3], is of great practical importance. It is capable of suppressing the adsorption capacity of metal particles and simultaneously promoting their catalytic activity considerably. SMSI is well-documented for Rh [19] and other platinum metals [3,7] like Pt [20], Pd and Ru on different reducible oxides, but not for gold.

In the present work titania supported Rh was chosen to be investigated, because this reducible oxide can easily form an encapsulation layer through surface diffusion of titanium and oxygen ions on the metal when annealed under UHV conditions. Apart from some new aspects of the encapsulation phenomenon itself, a major focus in this work is on the growth of Rh *on top of* a preformed TiO_x encapsulation layer. Although ultrathin TiO_x overlayers on well-defined metal single crystals have already been used as templates for the preparation of nanosized metal particles [6], here we address the applicability of titania encapsulation layers formed on Rh films.

2. Experimental

The experiments were performed in two different ultrahigh vacuum (UHV) chambers (base pressure $< 5 \times 10^{-8}$ Pa). The first one was equipped with facilities for Auger electron spectroscopy (AES), temperature programmed desorption (TPD) and reflection absorption infrared spectroscopy (RAIRS). AES measurements were performed using a Physical Electronics coaxial-gun single pass cylindrical mirror analyzer (CMA), while mass spectrometric and TPD data were collected by a QMS 200 (Balzers) quadrupole mass spectrometer. In the second chamber AES, low energy ion scattering spectroscopy (LEIS) and X-ray photoelectron spectroscopy (XPS) techniques were used. AES was performed in differential mode with 2.5 keV primary electron energy, 3 V modulation and 1–2 μA beam current. AES data were evaluated by plotting either the absolute peak-to-peak heights of main peaks (Rh: 302 eV, Ti: 387 eV, O: 503 eV, C: 272 eV) or the Auger ratios calculated against the Ti(387 eV) peak. A SPECS IQE 12/38 ion source was used for LEIS. He^+ ions of 800 eV kinetic energy were applied at a low ion flux equal to 0.03 $\mu A/cm^2$. The incident and detection angles were 50° (with respect to the surface normal) while the scattering angle was 95°. LEIS spectra were obtained using a Leybold hemispherical analyzer. Note that the information depth of LEIS is predominantly restricted to the outermost atomic layer when performed with noble gases, due to the high tendency of neutralization of noble gas ions in solid materials.

The TiO_2(1 1 0) single-crystals were products of PI-KEM. The samples were attached to a Ta plate with an oxide glue (AREMCO, ceramobond 571), and could be heated with a W filament placed behind the Ta plate. The sample temperature was measured by a chromel–alumel thermocouple, attached to the side of the sample with the same adhesive material. The heating and cooling rates during cleaning and all measurements presented here were always less than 2 K/s and were regulated by a computer-controlled circuit. The duration of annealing in stepwise heating experiments was equal to or less than 5 min.

The typical cleaning procedure of titania consisted of Ar^+ ion bombardment (1–1.5 keV, 3×10^{-6} A cm^{-2}, 300 K, 30 min) and annealing at 950 K for 30 min. The absence of oxygen-treatments resulted in a blue-colored, slightly defective crystal. It is noteworthy that after this procedure the contribution of Ti^{3+} and Ti^{2+} signals to the Ti 2p photoemission feature was found to be below 3%, according to XPS. The above treatment ensured the appropriate electrical conductivity for electron spectroscopy and high enough defect-density to observe 2D-like growth of Rh-particles in an extended coverage range. It is known from previous STM investigations that similar treatments result basically in (1×1) bulk terminated registry, although the presence of 1–2% of defect sites (0D dots and 1D strings of Ti_2O_3 stoichiometry) cannot be excluded [21]. This surface will be referred to as a nearly stoichiometric one.

An EGN4 e-beam evaporator from Oxford Applied Research was used for the deposition of Rh by Physical Vapor Deposition (PVD) at sample temperatures of 300–330 K and 500 K. The two similar TiO_2(1 1 0) samples were cleaned and exposed to Rh vapor in the same way in the two UHV chambers. Special attention was paid to the thorough calibration of the Rh coverages in the two chambers by means of uptake-curves taken with AES. In the XPS-LEIS chamber the coverage was also checked by XPS and LEIS [22,23].

Work function (WF) measurements were made by recording the cutoff energy of inelastic secondary electrons excited by the AES beam. The sample bias was −19 V and the changes in WF values were determined from the shifts of the inflexion points of current vs. voltage curves [24] by an accuracy of around 0.1 eV.

3. Results and discussion

3.1. Rh deposition on the titania surface and formation of TiO_x encapsulation layer

As a first step toward preparing a Rh—TiO_x—Rh structure, we study the effect of different parameters on the formation of Rh clusters, Rh multilayers and TiO_x overlayers. Although the decoration of Rh by titania is well-documented [3,19], this process is sensitive to sample pretreatment. The effect of substrate temperature and different surface treatments on the growth of Rh layers on TiO_2(1 1 0) surfaces was previously monitored in our laboratory by LEIS [22,23], AES and TPD [11] measurements, and 2D-like particle growth was found up to 0.2–0.35 ML Rh coverage on a nearly stoichiometric sample. It is widely accepted that the coverage range of 2D particle growth can be extended by enhancing the kinetic hindrance for the particle growth [1] by reducing (i.e. generating oxygen-deficiency) and roughening the surface by extended Ar^+-ion sputtering before Rh-deposition. In our case, the coverage range of 2D-like growth was substantially enhanced as demonstrated in Fig. 1A. By comparing the position of the breakpoint (R) of the Rh AES signal to that of (S) (characteristic of reduced and nearly stoichiometric supports) a factor of 1.5× increase can be estimated for the 2D-like growth range on oxygen deficient surfaces. This suggests a strong metal–substrate bond at the surface defect sites and indicates that a defective TiO_x surface can serve as a template for Rh particle growth just like for other metals, e.g. Au [13] and Fe [6].

Work function data depicted in Fig. 1B were collected to identify the charge transfer processes resulting from Rh-deposition. The WF of bare TiO_2(1 1 0) surface depends sensitively on the surface structure and composition of the oxide. The WF of a stoichiometric