Available online at www.sciencedirect.com
ScienceDirect
Surface Science 600 (2006) L274–L280
SURFACE SCIENCE
www.elsevier.com/locate/susc

Surface Science Letters

The self-assembly of metallic nanowires

J. Schoiswohl [a], F. Mittendorfer [b], S. Surnev [a], M.G. Ramsey [a], J.N. Andersen [c], F.P. Netzer [a,*]

[a] *Institute of Physics, Surface and Interface Physics, Karl-Franzens University Graz, A-8010 GRAZ, Austria*
[b] *Institute for Materials Physics, University of Vienna, A-1090 Vienna, Austria*
[c] *Department of Synchrotron Radiation Research, Institute of Physics, Lund University, S-22362 LUND, Sweden*

Received 12 April 2006; accepted for publication 28 July 2006

Abstract

We have demonstrated that nickel adatoms self-assemble into quasi one-dimensional nanowires on vicinal Rh(111) surfaces by decorating their regular monoatomic step arrays, while V adatoms do not. The step decoration process has been followed experimentally by variable-temperature scanning tunnelling microscopy and high-resolution X-ray photoelectron spectroscopy. The physical origin of the different step-assisted self-assembly behaviour of Ni and V adatoms has been elucidated theoretically and is ascribed to different diffusion barriers and trapping capability of Ni and V at Rh steps.

Keywords: Metal nanowires; STM; Density functional theory calculations; Nickel; Rhodium; Stepped surfaces

Linear nanostructures are an intensively studied and actual area of research due to the exceptional physical and chemical properties of low-dimensional systems and their foreseen applications in the field of advanced nanotechnology [1,2]. One-dimensional nanostructures may exhibit very different electronic and magnetic properties as compared to the same materials in more dimensions and at larger length scales, and this different behaviour may be used in designing novel nanoscale devices, sensing units, or new catalysts, where the modified chemical reactivity mirroring these changed physical properties may be exploited to improve and design the selectivity of catalyst systems. A promising route for the fabrication of linear nanostructures in the form of nanowires, constituted by one or several atomic rows, is the self-assembly process on a suitable template surface. Whether this route will be actually realised in future nanotechnology applications will depend to a large extent on the fundamental understanding of the physical and chemical nature of the self-assembly process and on the microscopic control of its driving forces.

Here we explore the feasibility of the formation of metallic nanowires by decorating the monoatomic step structures of a vicinal Rh metal surface by rows of nickel or vanadium metal atoms. The regular array of steps at vicinal surfaces provides a natural template for the growth of low-dimensional systems, if the kinetics and energetics of the deposited adsorbate atoms allow them to self-assemble into (quasi-)one-dimensional stripes along the substrate steps. The so formed metallic nanowires are constituted by the substrate atoms at the step edges and the metal adsorbate atoms that decorate them. In principle, these nanowires have a bimetallic character, because the substrate step atoms and the decorating adsorbate atoms are coupled by electronic and elastic interactions. This gives rise to a modified electronic and geometric structure along the wire direction [3–6] and to associated changes of magnetic effects and in the chemical reactivity behaviour [7].

In this work we have used a combined state-of-the-art experimental and theoretical approach to investigate the physical principles of the step decoration on a vicinal Rh

---

[*] Corresponding author. Tel.: +43 316 380 8553; fax: +43 316 380 9816.
E-mail address: falko.netzer@uni-graz.at (F.P. Netzer).

0039-6028/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2006.07.060

surface by metal adsorbate atoms. In order to obtain insight into the parameters governing the self-assembly process of low-dimensional nanostructures we have studied the deposition and subsequent reorganisation of an early and a late transition metal, viz. vanadium and nickel, on two vicinal Rh(111) surfaces as a function of temperature. We have employed variable-temperature scanning tunneling microscopy (STM) and high-resolution soft X-ray photoelectron spectroscopy (HR-XPS) with use of synchrotron radiation to follow the decoration of steps by V and Ni nanowires on Rh(151513) and Rh(553) surfaces. The energetics of decoration and the hierarchy of adsorption sites has been calculated on the Rh(553) surface by *ab initio* density functional theory (DFT). Both vicinal surfaces expose (111) terraces separated by (111)-type microfacets, the terrace widths being ~33.5 Å and ~10.4 Å for the (151513) and (553) surfaces, respectively. The Rh(151513) surface has been investigated in the STM measurements to obtain stable tunneling conditions on the larger terrace areas, while the Rh(553) surface has been probed in the HR-XPS experiments to enhance the step derived emission intensity in the core level photoelectron spectra. The consistency of the results obtained on the two vicinal surfaces indicates that the same physical processes are relevant and are being probed.

The VT-STM experiments have been performed in a custom-designed variable-temperature STM system as described previously [8]. HR-XPS spectra have been measured at beamline I311 in the Swedish synchrotron radiation laboratory MAX-lab, Lund; the beamline and the electron spectrometer end station have been specified in Ref. [9], the total energy resolution employed in the present experiments was ~100 meV. The vicinal Rh surfaces have been cleaned by heating in oxygen and by cycles of Ar ion bombardment and annealing. The preparation of a well-ordered Rh(151513) surface with a regular step array is difficult, because the interaction between steps across the wide terraces, which provides the basis for the regular step arrangement, is weak. A typical STM image of the clean Rh(151513) surface, obtained at room temperature, is shown in Fig. 1(a): the step edges display some frizziness and the terraces some variation of widths. However, an

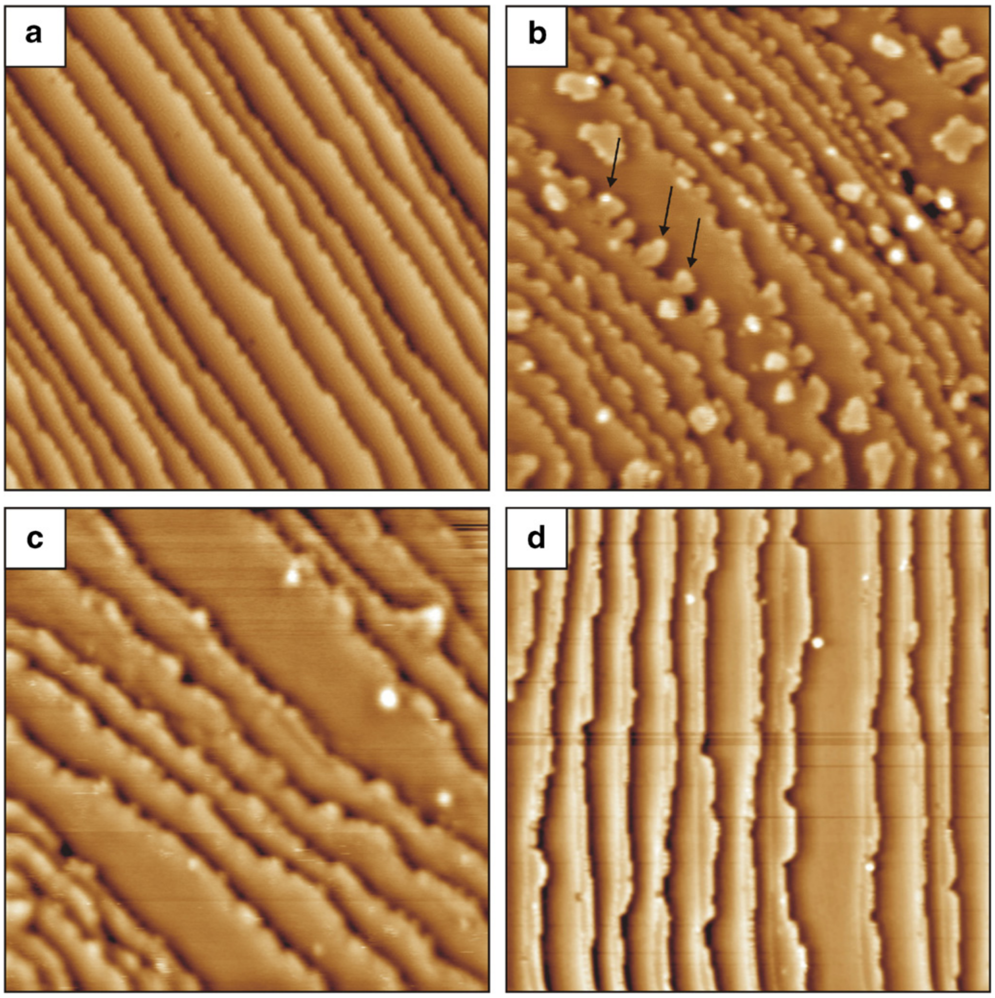

Fig. 1. STM images of the clean Rh(151513) surface (a: 540 × 540 Å^2), after deposition of 0.25 ML Ni at 150 K (b: 400 × 400 Å^2), after annealing the surface of (b) to 520 K (c: 300 × 300 Å^2), and after deposition of 0.25 ML Ni at 420 K (d: 500 × 500 Å^2). (Tunneling conditions: (a) +2 V sample bias, 0.3 nA tunnelling current; (b) +3 V, 0.1 nA; (c) +3 V, 0.1 nA; (d) +0.75 V, 0.2 nA.)