The self-assembly of metallic nanowires

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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.

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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
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
autocorrelation analysis of the STM image gives a mean terrace width of \( \sim 33 \, \text{Å} \) which is very close to the theoretical value. Nickel and vanadium adatoms have been deposited by physical vapour deposition from electron beam evaporators, typical evaporation rates were 0.1 monolayers/min as measured by quartz microbalances (one monolayer is defined by the number of surface atoms on the Rh(1 1 1) substrate). Accordingly, the concentration of step atoms on the Rh(15 1 13) and (5 5 3) surfaces correspond to 0.067 ML and 0.2 ML, respectively.

The calculations have been performed using the Vienna \textit{ab initio} Simulations Package (VASP) [10], PAW potentials [11] and generalized gradient corrections (GGA-PW91) as proposed by Perdew et al. [12]. The (5 5 3) surface has been modelled by a slab consisting of six Rh layers parallel to the (1 1 1) terraces with a two-fold periodicity along the step. Only for the calculation of an adsorbed 3-atom cluster a larger \((1 \times 3)\) supercell has been chosen. Still, all adsorption energies are given for a \((1 \times 2)\) unit cell. The Brillouin zone integration has been performed using a \(8 \times 4 \times 1\) Monkhorst-Pack grid. The STM images have been simulated using a simple Tersoff-Hamann [13] approach with a bias voltage of +0.5 eV. All calculations have been performed spin-polarized to take account of possible magnetic effects.

Fig. 1 shows constant-current topographic STM images of the clean Rh(15 1 13) surface (a), after deposition of 0.25 ML Ni on the Rh surface at 150 K (b), after annealing that surface to 520 K (c), and after deposition of 0.25 ML Ni at 420 K. Deposition of 0.25 ML Ni at 150 K results in the formation of two-dimensional Ni islands, which are either attached to step edges (see arrows in Fig. 1(b)) or are situated detached on the terraces areas. After annealing to 520 K the terrace islands have disappeared and the Ni adatoms have moved to the step edges (Fig. 1(c)), decorating them with stripes of one or several atomic rows wide. The best kinetic conditions for the decoration of the Rh step edges by one-dimensional Ni nanostructures have been achieved by deposition of Ni with the substrate held at 420 K. Fig. 1(d) shows straight Rh step edges decorated with the Ni wires, which are distinguished from the Rh surface atoms by the brighter contrast in the STM (see later).

The decoration of Rh step edges by Ni adatoms is also revealed on the Rh(5 5 3) surface by core level photoemission spectroscopy. Fig. 2 displays Rh 3d\(_{5/2}\) HR-XPS spectra of the clean and Ni covered Rh(5 5 3) surface. The clean Rh(5 5 3) surface spectrum (bottom spectrum) has a complex two-peaked shape, which can be separated by decomposition analysis [14] into four spectral components [15]: the two major components B and T are due to emission from Rh atoms in the bulk and on the terrace surface, respectively, whereas the components S and U are related to Rh atoms at the step edges. The component S at 306.4 eV binding energy is clearly visible in the experimental data as a low-energy shoulder and is due to Rh surface atoms at the steps, while the component U is only revealed by the quantitative deconvolution analysis but it is required to obtain a good fit to the data. It has been ascribed to the so-called corner atoms at the lower step edges [15]. Deposition of 0.2 ML Ni at 100 K leads to a reduction of the intensity of the S and T components of the Rh 3d\(_{5/2}\) spectrum by \( \sim 65\% \) and \( \sim 30\% \), respectively, and concomitantly to two new spectral components \( I_S \) and \( I_T \) at higher binding energy (Fig. 2, middle spectrum). The latter two are associated with emission from Rh atoms at steps \( I_S \) and terraces \( I_T \) that are now coordinated to Ni adatoms. The Rh core level spectrum after Ni deposition at 100 K thus confirms that Ni atoms are adsorbed at both step and terrace sites. After flashing to 520 K the emission from free step sites (component S) is completely quenched (Fig. 2, top spectrum) signaling the complete decoration of Rh step sites by Ni adatoms in agreement with STM.

The atomic structure of the Ni nanowires is addressed in the STM images of Fig. 3, which display the Ni stripes at the Rh (15 1 13) step edges at greater detail (Fig. 3(a–c)). Note that the Ni wires and in particular their edges are imaged with enhanced contrast in the STM. Images (a) and (b) show that the kinks of the Ni stripes include angles \( \alpha \)
of 120°, and that the width differences of stripes separated by kinks are multiples of $d = (d_1 - d_2) = 2.3 \text{ Å}$, which corresponds to the distance between two Rh [1 1 0] rows. This indicates the pseudomorphic growth of the Ni wires on Rh as illustrated by the model of Fig. 3(d) and by the STM image of Fig. 3(c). The latter shows 7–8 atomic rows wide Ni stripes with atomic resolution, confirming the pseudomorphic growth behaviour. Fig. 3(e) and (f) are a simulated

Fig. 3. (a – c) High-resolution STM images of the Rh(151513) surface with steps decorated by Ni nanowire stripes a: $(82 \times 82 \text{ Å}^2)$, +0.75 V, 0.2 nA; b: $(90 \times 90 \text{ Å}^2)$, +0.75 V, 0.2 nA; c: $(48 \times 48 \text{ Å}^2)$, +0.005 V, 10 nA. Panel (d) shows a model of the Ni nanowires indicating their pseudomorphic growth. Panel (e) displays a DFT simulated STM image (bias +0.5 V) of a Rh(553) surface with steps decorated by 2-atom wide Ni stripes; note that the Ni adatoms display the bright contrast. Panel (f) shows the corresponding DFT derived model of the Rh(553) surface with steps decorated by 2-atom wide Ni stripes (bright circles: Rh terrace atoms; dark circles: Ni adatoms).

Fig. 4. Model geometries treated in the DFT calculations (bright spheres: Rh atoms; dark spheres: Ni atoms).
STM image of 0.4 ML Ni/Rh(553) using a bias voltage of +0.5 eV and a corresponding model based on the DFT calculations of Ni wires on Rh(553); accordingly, the Ni covered region is imaged with a brighter contrast due to the large spillover of charge from the Rh substrate.

The DFT calculations have been performed on a number of different model geometries and at different coverages of Ni adatoms on Rh(553) to clarify the physical mechanism of the decoration process. In the low-coverage case of single Ni adatoms, a systematic scan of the potential energy surface displays the distinct influence of the step edge. Adsorption sites in the vicinity of the step are energetically favoured, but in contrast to adsorbates like oxygen [16] only an adsorption directly on the step facets (Fig. 4(a)) leads to a significant increase of the adsorption energy of 0.7 eV with respect to adsorption at the terrace. Therefore the Ni atoms display a clear preference for high-coordinated sites. Although doping 4d metals with magnetic impurities, like Co/Rh(111), has been predicted to induce new magnetic features [17], the magnetic moment of Ni is completely quenched upon adsorption. With an increasing Ni coverage of 0.2 ML the calculations predict a line-wise growth of the Ni structures (Fig. 4(b)). In comparison with this reference structure, neither the adsorption of separated Ni atoms (Fig. 4(c), ΔE = +1.43 eV) nor the formation of surface alloys (Fig. 4(d), ΔE = +0.16 eV) is energetically favourable. Although the Ni nanowires are expanded by 9% compared to the Ni bulk distance, also a stress reduction via the formation of local clusters (Fig. 4(e)) is unstable (ΔE = +0.23 eV). With an increasing coverage the stripe-wise growth is predicted to continue (Fig. 4(f)), leading to the experimentally observed formation of pseudo-morphic nanowires.

In contrast to nickel, vanadium adatom decoration of the steps of vicinal Rh surfaces is incomplete and the formation of extended V nanowires is not observed. The STM image of Fig. 5(a), recorded after deposition of 0.2 ML V onto Rh(151513) at 150 K, shows V island structures distributed both over terrace areas and at step edges as in the case of Ni (see Fig. 1(b)), but after flashing the surface to 520 K the island distribution is not much altered (Fig. 5(b)). This is confirmed by the Rh 3d core level spectrum (Fig. 6(a), middle spectrum), where the spectral component associated with non-coordinated free step atoms (S) is still significant after annealing at 520 K. After heating to 670 K the STM image (Fig. 5(c)) shows brighter contrast lines at the step edges and no V islands are apparent anymore on the surface, but areas with darker contrast on the terraces are also seen. The latter are reminiscent of etch pits and are interpreted in terms of vacancy islands in the Rh substrate, which have been formed by V-Rh exchange processes and V adatoms penetrating into subsurface positions. This is supported by the Rh 3d and V 2p core level spectra. The Rh 3d_{5/2} spectrum (Fig. 6(a), top spectrum) recorded after annealing to 870 K shows the population of a new core level component, I_{TA} with a binding energy of 306.8 eV, which is attributed to the emission...
from terrace Rh atoms, coordinated to subsurface V atoms – thus signalling the onset of surface alloy formation. Fig. 6(b) presents a plot of the V surface coverage, derived from the V 2p core level intensities, versus temperature: the V surface coverage decreases rapidly with temperature as a result of the penetration of V adatoms into the Rh bulk. In contrast, the surface concentration of Ni, which is also given in Fig. 6(b), remains almost constant up to 900 K.

The analysis of the potential energy surface of an adsorbed V atom corroborates these observations. Fig. 7 illustrates the energy profile for the diffusion of Ni and V adatoms in the direction perpendicular to the step edges. For both cases the adsorption in the 3-fold hollow terrace site (site 9 in Fig. 7) was taken as a reference energy. In comparison two major differences between the diffusion of Ni (black line) and V (red line) can be found: for the diffusion of the Ni atoms all barriers are smaller than 0.15 eV; on the other hand, the diffusion of V is restricted by barriers of up to 0.40 eV. Therefore, the thermal diffusion of V is limited to much higher temperatures. A second crucial point is the observation that the energy gain for adsorption sites in the vicinity of the step (site 1) is much more pronounced in the case of Ni (−0.70 eV) than in the case of V (−0.38 eV). Consequently, the Ni adatoms experience a significantly higher thermodynamic driving force and are also trapped to a higher degree in the vicinity of the steps.

Finally, the different behaviour of Ni and V on vicinal Rh surfaces is also explained by the propensity of V to form V–Rh alloys. While the formation of a surface alloy is energetically unfavourable for adsorbed Ni atoms (ΔE = +0.27 eV), the same structure (Fig. 4(d)) becomes thermodynamically stable in the case of V (ΔE = −0.82 eV). Although the initial formation of this alloy is hindered by kinetic limitations, it provides a limit for increasing the diffusion rate. Indeed, as found experimentally the diffusion cannot be further enhanced by higher surface temperatures because of the dominance of the alloying process at T > 570 K.

The comparison of the adsorption and diffusion of an early transition metal, like vanadium, and a late transition metal, like Ni, allows us to draw some general conclusions about the specific conditions that have to be met for the step-assisted self-assembly of metallic nanowires. Although

![Fig. 6.](image1.png) (a) HR-XPS Rh 3d<sub>5/2</sub> core level spectra of the clean Rh(553) surface (bottom spectrum), after deposition of 0.2 ML V at 100 K followed by annealing to 520 K (middle), and after annealing that surface to 870 K (top). The labelled spectral components are discussed in the text. (b) Plot of the Ni and V surface coverage, derived from Ni and V 2p XPS peak intensities, versus temperature.

![Fig. 7.](image2.png) Energy profiles for the diffusion of Ni and V adatoms on Rh(553) in the direction perpendicular to the steps. The top panel illustrates the diffusion pathways. The bottom panel gives the relative energies of the different sites indicated by the numbers as referred to the 3-fold hollow terrace site 9 (Ni: black line; V: red line). (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)
the qualitative shape of the potential energy surface is similar for both metals, that is both metals show a preference for high coordination sites, the different interaction strength has drastic consequences. The stronger hybridisation between vanadium and rhodium does not only lead to higher diffusion barriers, but also to an increased stability of the surface alloy. Therefore, the higher surface temperatures needed to overcome the diffusion barriers also decrease the kinetic stabilisation of the V step decoration with respect to the formation of a surface alloy. On the other hand, the weaker hybridisation between nickel and rhodium facilitates the diffusion of the adsorbates, and thus facilitates the trapping of the adatoms in the vicinity of the step edge. These conditions are a prerequisite for the formation of the quasi-one-dimensional wires.

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