Growth of One-Dimensional Pd Nanowires on the Terraces of a Reduced $SnO_2(101)$ Surface

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Palladium, vapor-deposited at room temperature on a reduced $SnO_2(101)$ surface, forms one-dimensional islands, one atomic layer high, 5 Å wide, and up to 350 Å long. Scanning tunneling microscopy shows that neighboring islands do not merge. First-principles calculations reveal the atomistic processes that lead to this, for metal oxide substrates unusual, overlayer growth. Formation of 1D islands is mediated by a large anisotropy in surface diffusion, strong Pd-Sn interaction, and the lack of stable binding sites at the sides of the Pd islands. Nucleation is defect mediated, and the initial nucleation site determines the width of the resulting nanocluster.

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The study of (quasi-)one-dimensional (1D) systems, supported on a surface, is a fascinating area of research. Exotic physical properties are predicted for 1D nanowires [1], and 1D conductors at the smallest scale represent important building blocks for nanometer-scale devices [2,3]. In order to engineer self-assembled nanowires with desired properties, it is necessary to fully understand the atomic-scale processes that lead to 1D growth of metal overlayers for different classes of materials.

Step-flow growth on vicinal metal surfaces of refractory metal substrates has been used for templated growth of quasi-1D nanowires with special magnetic properties [2,4]. Stepped Si(111) surfaces are particularly good examples for the tailoring of the properties of 1D metallic structures [3]. On Si(100)-(2 × 1), various metals are known to form perfect 1D dimer rows due to special adsorption sites at the end of the 1D array [5]. The large anisotropy in lattice mismatch leads to the self-assembly of long, 1D rare-earth silicide nanowires on Si(100) [6].

In order to decouple the electronic properties of such nanowires from the support, it is desirable to grow them on wide band-gap insulating substrates. In particular, metal oxides could represent an attractive class of support materials. Reports of 1D growth on a true insulator or wide band-gap semiconductor are rare, however. Most insulating materials have a surface energy that is lower than that of metals, so overlayers do not “wet“ and 3D clusters form. Such clusters can aggregate to 1D structures, for example, at the step edges of NaCl(100) [7], but the resulting features are typically not of atomic-size dimensions. On metal oxides, a 2D-type growth morphology can be stabilized to some extent by kinetic constraints [8] or a strong interaction with defects [9], but generally, 3D growth predominates for late transition metal overlayers that do not react with the substrate and are good candidates for the formation of a structurally and compositionally abrupt interface. One notable exception are some polar oxide surfaces. Because of their inherent instability, a strong hybridization with a metal overlayer and 2D growth by “wetting“ may occur [10]. To our knowledge, no report exists of 1D nanostructures with atomic-size dimensions on a metal oxide surface.

In this Letter we report the growth of 1D Pd structures on the reduced $SnO_2(101)$ surface. Reduced and oxidized $SnO_2(101)$-(1 × 1) surfaces can be prepared by simply occupying and vacating all the bridging oxygen sites [11] [see Fig. 1(a) and 1(b)]. Bulk SnO_2 has a band gap of 3.6 eV. The reduced $SnO_2(101)$ surface is terminated with Sn atoms and has a Sn-5*s*-derived surface state located at the upper edge of the valence band [11], which effectively reduces the (surface) band gap to 2 eV. Under ultrahigh vacuum (UHV) conditions, the reduced surface is inert with respect to molecular adsorption [12]. The completely reversible oxidation or reduction of the $SnO_2(101)$ surface makes this an excellent model system for studying the gas sensing properties of this material [13], and our initial motivation for investigating Pd on SnO_2 came from the

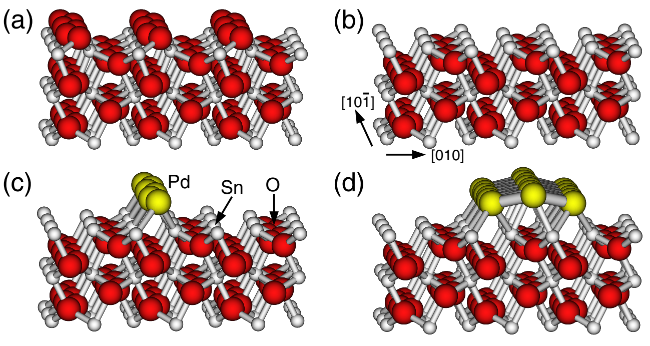

FIG. 1 (color online). Structure of (a) the oxidized, (b) the reduced $SnO_2(101)$ surface, and (c), (d) the reduced surface with one and three atom-wide Pd stripes.

fact that Pd is used as a sensitizer for the detection of both oxidizing and reducing gases [14].

In scanning tunneling microscopy (STM) images [15], the clean, reduced $SnO_2(101)$ surface shows characteristic long and narrow terraces [see Fig. 2(a)] with straight step edges parallel to the crystallographic $[10\bar{1}]$ direction. Surface Sn atoms are imaged as bright features [see inset in Fig. 2(a)]. Very few atomic-size defects are observed; large-scale "bumps" are attributed to spatially extended variations in the electronic structure, possibly caused by subsurface structural defects [11].

At small coverages Pd nucleates on top of the terraces and at step edges along the [010] direction [see Fig. 2(b)]. No nucleation at $[10\bar{1}]$-oriented step edges is observed, indicating either a strongly directional diffusion along $[10\bar{1}]$ or the absence of suitable adsorption sites at these steps. The density of the clusters increases rapidly up to 0.1 ML. Then it grows more slowly and the clusters continue to grow longer. At a Pd coverage of 0.28 ML [see Fig. 2(c)] the surface is covered with long and narrow islands, most of them rather uniform in width. Because of tip convolution effects it is not straightforward to accurately determine the width of these clusters; from comparisons of line profiles taken at the $SnO_2(101)$ step edges, we estimate that the clusters are about 5 Å wide [see Fig. 2(d)] [16]. The length of the clusters appears to be limited by the size of the terraces; they can be several hundred Å long. The clusters are 2.2 Å high, which corresponds to one monolayer of Pd. Interestingly, the 1D clusters grow parallel to each other without merging, separated by a narrow gap, which is estimated to be one unit cell wide. At a coverage of about 0.75 ML [see Fig. 2(e)], a second Pd layer starts to grow on top of the 1D islands.

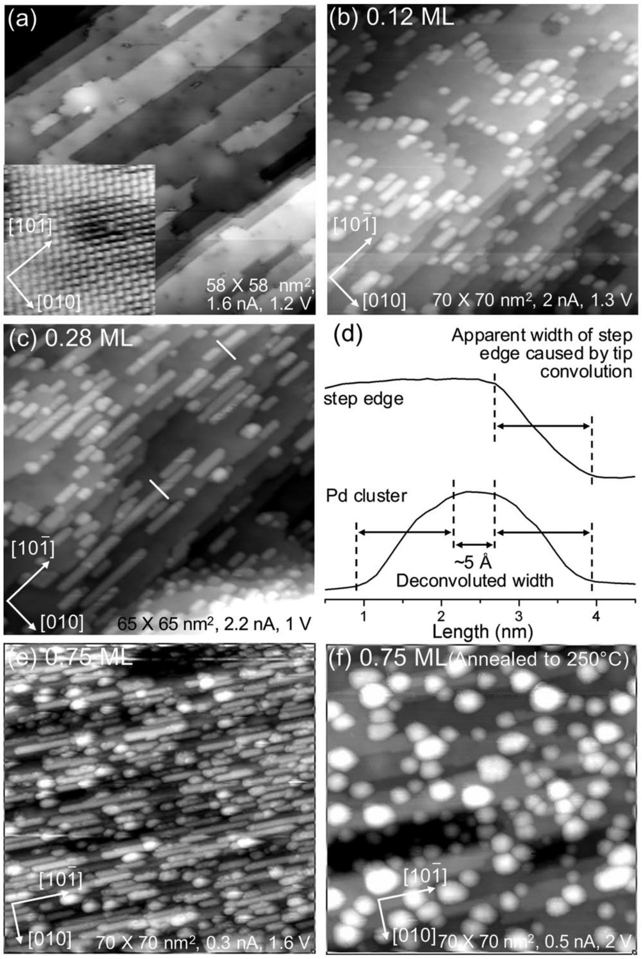

FIG. 2. Empty-states STM images of (a) the clean reduced $SnO_2(101)$ surface (inset 6×6 nm^2) and (b), (c), (e) with increasing coverages of Pd deposited at room temperature. Displayed in (d) are line profiles of a step edge and a Pd cluster taken at the positions of the white lines in (c). (f) shows the surface in (e) after annealing.

The 1D Pd islands are thermally not stable. When a sample with 0.75 ML Pd in the form of mostly 1D clusters was annealed to 250 °C, the clusters became 3D [see Fig. 2(f)]. No indication for Sn-Pd alloy formation was observed in XPS. When Pd was deposited on an oxidized $SnO_2(101)$ surface, nucleation at defects and 3D cluster growth was observed at all coverages.

In order to understand this quite unusual 1D growth mode of a metal on an oxide surface we performed extensive density-functional theory (DFT) calculations [17]. The most favorable adsorption sites of isolated Pd atoms on the reduced, defect-free $SnO_2(101)$ surface are the positions of the missing bridging O atoms [see Fig. 1(b) and 1(c)]. The high binding energy of 2.63 eV points towards a strong interaction between Pd and surface Sn atoms. The lowest-energy structures for Pd stripes (1, 3, 5, and 7 atoms wide) and for a full Pd monolayer were determined. In one atom-wide chains the Pd atoms assume essentially the positions of the missing O rows and form zigzag lines along the $[10\bar{1}]$ direction [see Figs. 1(c) and 3(b)]. In stripes with a width of three and more atoms, neighboring missing O rows are filled and Pd is added above O rows in the second surface layer. The Pd rows become straight and the stripes display a hexagonal symmetry, resembling a Pd(111) layer, albeit with a buckled geometry [see Figs. 1(d) and 3(d)]. The Pd-Pd distances in the stripes are within 1% of the nearest-neighbor distance in bulk Pd. Neighboring Pd stripes are essentially decoupled, even when they are separated by only one missing O row. The formation energy of the Pd stripes increases with their width from 3.12, 3.31, 3.38, 3.41 eV/atom for 1, 3, 5, 7 atom-wide stripes, respectively, to 3.49 eV/atom in the limit for a full Pd(111) monolayer.

This monotonous increase of the formation energy with the width excludes energetic reasons (such as strain-related effects) as the driving force for the growth of islands with a specific and uniform width. Hence, kinetic effects must be responsible for the observed 1D growth. The calculated formation energies of the Pd stripes are less than the Pd bulk cohesion energy of 3.66 eV/atom. Thus, in the limit of high Pd coverage, 3D clusters will be the thermodynamically most stable state. This is consistent with the experiment, where heating transforms the 1D nanowires into 3D clusters.

To study the atomic-scale processes which lead to the observed 1D cluster formation, we have calculated potential energy landscapes for single Pd atoms interacting with surface structures that are representative of successive growth stages (see Fig. 3). A Pd atom was scanned across the substrates, and for each (x, y) position its adsorption energy was evaluated at the height where the vertical force vanishes. (Here, for simplicity, the substrate was kept frozen; all given values for binding energies, local energy minima, and transition barriers, however, are from fully relaxed calculations.) Figure 3(a) shows the resulting potential energy landscape (with an overlay of the top surface atoms) for the clean, reduced $SnO_2(101)$ surface. A strong 1D character is apparent, with a pronounced trough at the missing O rows. The diffusion barrier along (perpendicular to) the rows is 0.11 eV (0.70 eV). Thus, when single Pd atoms hit the surface, they fall into one of the missing O rows where they diffuse back and forth until they are pinned at a nucleation site, such as a defect or an already existing Pd cluster. In this way, a missing O row gets filled, forming a one atom-wide Pd chain.

The corresponding potential energy surface for such a one atom-wide Pd chain in Fig. 3(b) shows that the missing O rows to the left and to the right are almost undisturbed. The positions of the energy minima within the missing O rows (marked by diamonds) are only slightly shifted and the diffusion barrier along the rows is almost the same, 0.12 eV. At the positions next to the Pd chain, where new Pd atoms would have to be attached to widen the Pd stripe, two new local energy minima appear (marked with + and ×). However, these new positions are only metastable. They are higher in energy than the minima in the missing O rows by 0.05 and 0.12 eV. More importantly, the barriers for diffusion into the missing O rows are only 0.02 and 0.08 eV; such kinetic barriers can easily be overcome at room temperature. Diffusion of Pd atoms directly along the Pd stripes between the + and × positions is less favorable with a barrier of 0.23 eV. Thus, Pd atoms prefer falling into the neighboring missing O row, where they can diffuse away from the Pd chain, rather than nucleating at the sides of the Pd rows and widening the stripes. This is also true for the sides of broader Pd stripes, see Fig. 3(d).

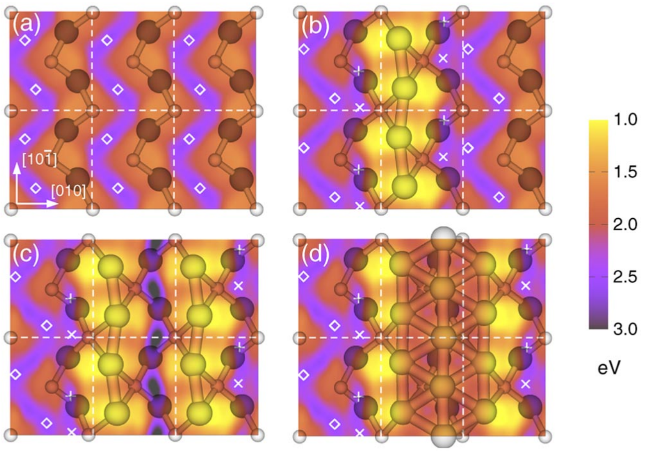

FIG. 3 (color online). Calculated potential energy surfaces for a single Pd atom on different Pd/SnO_2 surface structures (see text). Top Pd, first layer Sn, and second layer O atoms of the Pd/SnO_2 slabs are shown with shaded large gray, small gray, and large dark spheres, respectively. The surface unit cells are indicated by dashed lines. Positions of possible Pd binding sites (taken from fully relaxed calculations) are marked with diamonds (missing O rows), + and ×. The barriers between these binding sites along the deep blue troughs are less than 0.12 eV.

However, if two neighboring missing O rows are filled with Pd [see Fig. 3(c)], the gap between the two Pd rows is easily filled with further Pd atoms and a three atom-wide Pd stripe is formed. Shallow local energy minima at the hollow positions of the Pd hexagons can be seen in Fig. 3(d) on top of the three atom-wide Pd stripes. But again, these positions are only metastable, and the barriers for diffusion along the Pd stripe or for stepping down at either side of the stripe are small. Thus, Pd atoms landing on top of a stripe will either move towards the end, fall down, and make the wire longer, or they drop into a neighboring missing O row where they diffuse away until they hit another island or a nucleation site at another location.

Overall, these calculations predict that once Pd stripes are formed, they will grow longer, but not wider or higher, as it is observed in experiment. According to these results, the width of the stripes should be determined by the initial nucleation site for the Pd stripes. The dominant defects at terraces could consist of a missing surface Sn or subsurface O atom. If these act as a nucleation site for Pd atoms they would affect both neighboring missing O rows. Thus, a strong propensity of forming three atom-wide Pd stripes would be expected, consistent with the observed stripe width of about 5 Å.

To test this hypothesis, Pd was deposited on a SnO_2 surface with purposely created surface defects. A freshly prepared surface was bombarded with 500 eV He^+ ions for 4 min and gently annealed to 300 °C. The He^+ bombarded surface is substantially more defective [compare Fig. 4(a) to Fig. 2(a)]. It contains many holes and small, added hillocks. As predicted, Pd exhibits a pronouncedly different morphology [see Fig. 4(b)] than is seen on the more pristine substrate [see Fig. 2(d)]. The islands are more 2D-like: still 1 ML high, but shorter and wider.

From these results we extract the following key factors that lead to the formation of 1D metal islands on a metal oxide substrate and speculate how such 1D nanostructures could be utilized in other systems or devices. First, a strong interaction between the overlayer metal and the surface is

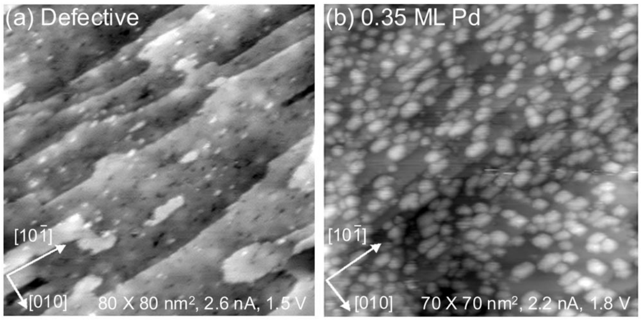

FIG. 4. Constant current STM images of (a) a $SnO_2(101)$ surface slightly damaged by He^+ sputtering and (b) after deposition of 0.35 ML of Pd.

critical. Adsorption sites have to exist to which the metal atoms bind more strongly than to already-formed metal islands. Otherwise, 3D cluster growth predominates, as it is the case for most metal oxide materials [including the oxidized $SnO_2(101)$ surface]. The reduced Sn-terminated $SnO_2(101)$ surface is special in this regard, as it can be prepared with an exclusively cation-terminated surface. Although no alloy formation was observed in our experiment, the fact that Pd and Sn are miscible in the bulk could indicate that materials that also show alloy formation with Sn (e.g., Pt, Ni, Al) could be good candidates for metal overlayers with such a desired strong interaction. Second, an anisotropic distribution of the metal atom adsorption sites which leads to both a strongly 1D diffusion and a strong anisotropy in sticking is critical for the formation of 1D structures (Fig. 3). In our case, along the 1D diffusion path (the missing O rows) the separation of the metal atom adsorption sites is close to the nearest-neighbor distance in the bulk metal, so that stable metal atom chains can form. The missing O rows, however, are separated by rows with underlying O atoms in the second surface layer where Pd atoms are much more weakly bound. Thus, the sides of already-formed Pd stripes represent shallow energy minima which prevents a growth of the islands in two dimensions. Third, heterogeneous nucleation is critical for the width of the resulting 1D islands (see Fig. 4). As an interesting implication, it should be possible to grow 1D structures with a predetermined width by "seeding" with purposely created defects. For example, widely dispersed sites of strongly interacting adsorbates that reside in the "troughs" of the missing O rows could initiate the formation of one atom-wide chains at room temperature.

Such nanowires with a uniform predetermined width on a wide band-gap insulator would provide an interesting playing field for studying electronic properties of 1D structures. Such structures could potentially lend themselves to surface functionalization. The $SnO_2(101)$ surface itself is quite inert with respect to molecular adsorption [12]. For example, we find that formic acid adsorbs strongly at the 1D Pd islands at room temperature, but does not stick to the substrate. Hence molecules with appropriate end groups could be arranged in a 1D-type array or could connect neighboring wires. Since SnO_2 is optically transparent, one could envision this system being a good template for the engineering of interesting 1D molecular devices.

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[15] Sample preparation and characterization is described in Ref. [11]. Pd was deposited with an *e*-beam evaporator (~0.25 Å/ min) and empty-states STM were taken in the constant current mode, both at room temperature.

[16] Attempts to obtain atomically resolved STM images of 1D Pd clusters were not successful. High resolution STM requires increasing the tunneling current, which caused a shape transformation to 3D clusters.

[17] The PBE functional, together with norm-conserving pseudopotentials and a mixed-basis of plane waves (16 Ry cutoff energy) and localized atomic orbitals, were used of the periodic slab calculations. The slabs were three SnO_2 triple-layers thick, and *k*-point sampling was done with a (4, 4, 1) Monkhorst-Pack mesh.