P H Y S I C A L   R E V I E W   L E T T E R S

Monodisperse Microisland Formation on Ni/Ru(0001) Monolayers

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The creation of identical microislands consisting of Ni trimers and multiples thereof on Ru(0001) induced by oxygen adsorption has been observed using scanning tunnelling microscopy. The island formation is caused by an oxygen induced expulsion of Ni atoms or trimers out of the moiré-distorted (densified) Ni monolayer. The exceptional stability of the Ni trimers is attributed to oxygen attachment, forming Ni-oxygen composites, as verified by detailed density functional theory calculations. The high density, identical structure, and notable thermal stability of these islands open up new perspectives for the study of the properties of nanostructured surfaces.

Nanostructured substrates can exhibit surprising chemical, mechanical, vibrational, electronic, magnetic, or optical properties that are distinctly different from those of extended flat surfaces [1]. For example, even rather inert materials like gold may turn reactive when reduced to the nm scale [2,3]. The origin of this metamorphosis often lies in an enlarged fraction of atoms with reduced coordination number or the presence of special sites located at the perimeter of the cluster. In addition, quantization conditions may be encountered at small lateral extensions, leading to a reduction in dimensionality of the respective electronic structure. Another dramatic change refers to magnetism: thin films of ferromagnetic materials could become nonmagnetic when evaporated as a thin film (or the other way round), while small 3D cluster often exhibit grossly increased magnetic moments and improved thermal stability [4].

Rather than shaping objects with external tools, the fabrication of nanostructures in the low nm range usually utilizes self-assembly and self-organization (bottom-up approach) to create them, taking advantage of physical properties and preferences of its constituents. One of the major obstacles in ongoing research is that the various procedural methods typically lead to a wide variety of sizes and shapes rather than monodisperse particles in a well-defined environment. Since in the so-called nonscalable regime of particles with less than 100 atoms "every atom counts" [5] as far as their properties are concerned, the identification of correlations between the shape or arrangement of these objects with their features is seriously hampered by the distribution in particle sizes. Thus, one of the major challenges in ongoing material science and research related to nanostructuring of templates is the formation of monodisperse nanoscale objects, along with a characterization and modification of their mechanical and structural properties [6].

In this Letter, morphological changes of Ni monolayers on Ru(0001) induced by oxygen adsorption have been investigated using scanning tunnelling microscopy. Specifically, the creation of identical Ni microislands consisting of 3 Ni atoms (or multiples thereof) is reported and their geometrical structure as well as coordination with respect to the substrate lattice determined. Their formation is attributed to an oxygen induced excessive lateral stress buildup, leading to the expulsion of Ni atoms or trimers out of the Ni monolayer.

Our experimental setup (general description in [7]) comprises a highly stable room temperature STM, with facilities for adsorption and metal deposition at variable T. Excellent temperature control ($T = 100$–700 K) during sample preparation is achieved by utilizing a special all-metal shroud with a thermocouple attached; it is equipped with a directed gas inlet tube and a Ni as well as a Pt evaporator, all of them individually selectable by a special flag. Pressure increase during Ni deposition was of the order of $(1$–$2) \times 10^{-10}$ mbar.

In the submonolayer regime, Ni forms highly strained (tensile), pseudomorphic layers on Ru(0001) as long as the lateral extensions of the Ni areas are not too large, i.e., below about 200 Å [8]. More extended areas tend to densify to yield Ni-Ni distances comparable to Ni(111); due to the resulting misregistry of Ni monolayer and the Ru (0001) substrate, a moiré type of pattern develops [8].

In Fig. 1(a), we have deposited 0.6 ML Ni on Ru(0001) at 373 K. At this coverage, only a fraction of the Ni film has converted to the more dense arrangement. The apparent height of the Ni monolayer amounts to 1.95 Å, as compared to 2.15 Å for Ru steps (see line scan of Fig. 1(c)], allowing an easy identification and discrimination of Ni and Ru surface areas. The periodicity of the warping of the densified Ni monolayer (moiré pattern) is 30–35 Å, in accordance with the dissimilar lattice constants of Ni (2.492 Å) and Ru (2.706 Å). Adsorption of oxygen (about 15 L) at 400 K onto this surface results in dramatic modifications of the surface topography of the Ni monolayer film: The moiré pattern has disappeared completely, and a
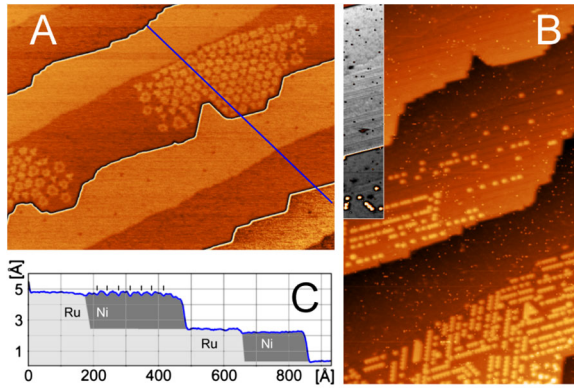
FIG. 1 (color online).   STM images of Ni deposited onto Ru (0001) ($\Theta_{Ni} = 0.6$ ML, $T_{growth} = 373$ K) before (a) and after (b) oxygen has been adsorbed (exposure about 15 L [1 L = 10^{-6} Torr s] at $T_{oxygen} = 400$ K) [25]. A line scan across Ru step edges and deposited Ni, is displayed in (c). In (a), extended areas of the Ni monolayer lead to a loss of the pseudomorphic structure and the formation of a moiré overstructure of the Ni film (periodicity $\delta a \approx 30$–35 Å, as indicated by the markers in (c); corrugation $\delta z \approx 0.3$ Å). The color scheme of image (b) has, in part, been adjusted (inset) to clearly display the uniaxial distortion of the Ni monolayer if oxygen is adsorbed. STM image sizes: (a) 1200 Å × 900 Å; (b) 500 Å × 800 Å.

large number of virtually identical microislands (height approximately 2 Å) covers the Ni film instead [Fig. 1(b)]. Protrusions of that height cannot be ascribed to adsorbed oxygen or caused by some kind of surface relaxation or lattice distortion within the Ni monolayer. As detachment of Ni islands from existing Ni monolayer terraces appears quite remote as well, we suggest that their origin is due to Ni atoms or clusters thereof expelled from the Ni monolayer underneath. A series of experiments at increasing initial Ni coverages confirm that the formation of Ni microislands is directly correlated with the presence of the densified Ni monolayer.

The process of Ni atom expulsion is considered in the following: From studies of oxygen on Ru(0001), we know that oxygen prefers laterally expanded lattice areas [9,10], which, vice versa, can be associated with a tendency of oxygen to expand the underlying Ru substrate laterally. According to theory [10], this trend is not restricted to Ru but should be a quite general one. Our observation of Ni islands expelled from a dense Ni monolayer film therefore represents an extreme case of adsorbate induced expansion of the underlying (surface) lattice. This process very likely is facilitated by the (re)locking of the Ni monolayer into the Ru(0001) substrate lattice.

In Fig. 2, the structural features of the various types of microislands are analyzed in detail. Quite astonishing, we find that, without exception, they contain three Ni atoms or multiples thereof. The vast majority of them come as trimers; occasionally, ringlike hexagons (containing 6 Ni atoms) or starlike arrangements (containing 9 Ni atoms)
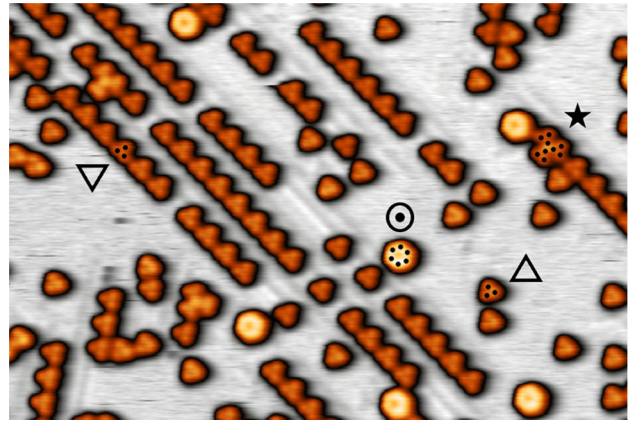

FIG. 2 (color online).   Atomically resolved STM image (200 Å × 135 Å) of Ni microislands created by oxygen adsorption (exposure about 6 L at $T_{oxygen} = 400$ K) on a densified, moiré-distorted Ni monolayer on Ru(0001) ($\Theta_{Ni} = 0.9$ ML, $T_{growth} = 350$ K) [25]. Four types of microislands can be distinguished: upside-down trimers arranged along rows ($\triangledown$); isolated trimers oriented upright ($\triangle$); donut-shaped hexagons consisting of 6 Ni-atoms ($\odot$); starlike arrangements of three trimers ($\star$).

are observed. Ni trimers occur in two different conformations. The one type forms exclusively when arranged in a disordered way (and usually well separated from other trimers); the other one is primarily arranged in an orderly manner along lines with well-defined intertrimer distances of preferably $3d_{Ru-Ru}$. The aligned trimer rows are separated by multiples of $\sqrt{3}/2 \cdot d_{Ru-Ru}$. The star-shaped islands are composed of three trimers, and they usually are part of a trimer row. A close inspection indicates that the interatomic distances within all microislands are equal to or close to d_{Ru-Ru}.

An important question regarding the binding geometry of the trimer islands concerns the sites of the Ni atoms (fcc or hcp hollow sites) and whether the trimer center is located above a hollow site (*B*-type of trimer island) or above a Ni atom of the underlying Ni monolayer (*A*-type of trimer island). In Fig. 3, the locations of Ni islands have been analyzed by overlaying a properly oriented and scaled Ru(0001) substrate lattice [11]. Assuming that for each type of island the Ni atoms occupy a definitive site (fcc, hcp, or bridge site), while precluding the unfavorable on-top sites (see Fig. 3), an unambiguous assignment could be obtained by laterally adjusting the overlay. Our careful analysis of numerous trimer positions then yields: (i) All trimers, either oriented upright, upside-down, or arranged as stars, are positioned around an on-top site of the underlying Ni monolayer; i.e., the trimers are exclusively *A*-type. The two trimer orientations then relate to the occupation of either fcc or hcp hollow sites. (ii) For the hexagons the Ni atoms likewise occupy hollow sites; more precisely, it is the same type of hollow site as found for the single, nonaligned trimers.
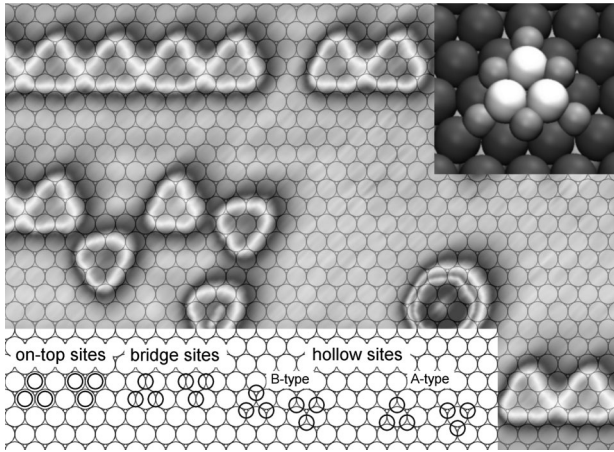
FIG. 3.   Enlarged area of Fig. 2 with overlay of the substrate lattice [25]. For better display, the image has been rotated, so that the substrate atom rows are aligned horizontally. It is apparent that all trimers, oriented either upright or upside-down, are centered around on-top sites, i.e., they represent A-type of islands. In the upper right corner the calculated energy minimum structure of a Ni_3-cluster (bright balls, $d_{Ni-Ni} = 2.53$ Å) on a Ni/Ru substrate surrounded by six oxygen atoms (small gray balls) is displayed. Possible adsorption sites of Ni trimers are depicted at the bottom.

According to theoretical studies, the compact trimer and hexagon arrangements represent the most stable geometries of the respective cluster sizes [12–14]. However, these islands are unstable with respect to attachment of additional adatoms. Kinetic barriers which occasionally surround microislands are usually low [6,15] and are inefficient in preventing continued island growth at noncryogenic temperatures, e.g., at $T \approx 300$ K. Therefore, tetramers, etc., should be present if atom-by-atom assembly is operative [6]. Their total absence could mean that the units expelled from the Ni monolayer are Ni trimers rather than single Ni atoms.

There are still open questions with respect to the nature of the observed microislands, i.e., whether they are all-metal or Ni-oxygen composites. We strongly favor stabilization of the microislands by oxygen atoms attached to the Ni clusters, since (i) oxygen is readily available, and (ii) recombination of neighboring islands should be fast and efficient, should they be composed of Ni atoms only; this would clearly contradict our observation of rather stable units. A similar stabilization of a trimer island (3 Cu atoms with 3 sulfur atoms attached) has been theoretically investigated by Feibelman [16] to explain S-enhanced Cu transport on Cu(111). Stable V_6O_{12} clusters have been experimentally observed on Rh(111) [17]. These circular units detach from extended oxide areas upon continued oxidation at elevated T. Because of a pronounced reactivity towards oxygen, the V-atoms are both terminated and interlinked by O, leading to a rather weak substrate bond of these "oxide molecules."

In order to substantiate our model, we performed density functional theory (DFT) calculations using the VASP code [18] within the generalized gradient approximation (GGA) [19] to describe exchange-correlation effects. The ionic cores were represented by projector augmented wave (PAW) potentials [20,21]. The surface was represented by a slab of three layers of Ru, covered by a pseudomorphic overlayer of Ni atoms onto which different Ni clusters were deposited. The results were obtained for an energy cutoff of 350 eV and $4 \times 4 \times 1$ k-points for the used 4×4 surface unit cell which is sufficiently large to prevent any interaction between the considered Ni clusters [22]. A Methfessel-Paxton smearing of $\sigma = 0.2$ eV was applied to speed up the convergence of the calculations, and the results were then extrapolated to $\sigma \to 0$ eV.

We find that oxygen atoms generally bind rather strongly to all Ni clusters considered in our calculations. For all structures, the binding energies are larger than 2 eV per oxygen atom with respect to the free O_2 molecule. Using the concept of *ab initio* thermodynamics [23], this means that the Ni clusters are indeed covered by oxygen atoms under the conditions of the experiment. The most stable structure of a Ni_3 cluster positioned on a pseudomorphic Ni/Ru overlayer is surrounded by six oxygen atoms (see Fig. 3). According to our calculations, A-type trimers are more stable than B-type by more than 1 eV per cluster, confirming the experimental observation. Furthermore, we find those A-type trimers above hcp sites to be 132 meV more stable per cluster than those above fcc sites which is consistent with the experimentally found preference for one particular trimer orientation.

In our calculations, we did not find any significant energetic preference for Ni_3 clusters compared to Ni_4 that would ban the existence of this larger cluster size. However, for the energy minimum configuration of the Ni_3O_6 cluster, any possible binding sites for additional Ni atoms are blocked by oxygen atoms. It is thus suggested that the stability of the Ni_3 clusters with respect to addition of further Ni atoms is caused by their passivation through attached oxygen.

The calculated magnetic moment (per atom) of the all-metal Ni_3 cluster ($\sim 0.8 \mu_B$) is significantly larger than found for the Ni atoms of the pseudomorphic overlayer on Ru ($0.4 \mu_B$), and also larger than the Ni bulk value of $0.6 \mu_B$. Such a behavior is not unexpected [4]: low-dimensional systems often exhibit an enhanced magnetism because of their reduced band width. Note, however, that in the case of Ni trimers passivated by oxygen atoms, the magnetic moments are strongly quenched to average values of less than $0.2 \mu_B$ per Ni atom.

In Fig. 4, a Ni monolayer on Ru(0001) has been exposed to increasing amounts of oxygen at $T = 400$ K. Thereby, disordered trimers form first, with a $\approx 95\%$ preference for one orientation, only after elevated oxygen doses the trimers arrange along lines. We note that oxygen exposures
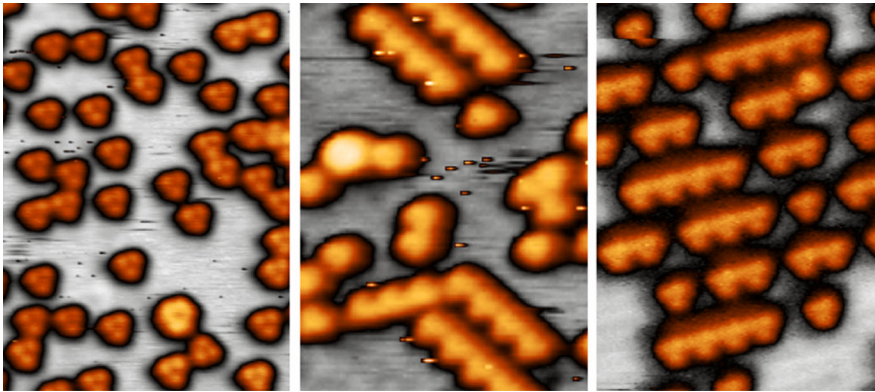
FIG. 4 (color online). STM images (70 Å × 100 Å each) of Ni deposited onto Ru(0001) (Θ_{Ni} = 0.9 ML, T_{growth} = 400 K) which has been exposed to increasing amounts of oxygen at T_{oxygen} = 400 K [25]: (left) oxygen exposure 1 L; (center) additional oxygen exposure 2 L; (right) additional oxygen exposure 10 L. In between of the gas exposures, the sample has been recooled to room temperature for STM imaging.

at lower $T \approx 300$ K yields a 70:30 ratio of the two trimer orientations. This means that the strong preference for the one orientation after annealing to 400 K is due to thermodynamics. A close examination of the substrate surface structure reveals that the lining up of the Ni trimers is directly correlated with an uniaxial lattice distortion of the underlying Ni monolayer (ridges protruding about 0.15 Å). This oxygen induced reconstruction occurs independently of the presence of Ni trimers, i.e., it is found on the pseudomorphic Ni monolayer as well [see Fig. 1(b), inset]. In between these stripes, a (2×2) periodicity is discernible which is in accordance with the observation of a $p(2 \times 2)$ overstructure of oxygen adsorbed on Ni(111) and the formation of antiphase domains at coverages beyond 0.25 ML [24].

To conclude, the formation of well-defined and uniform microislands consisting of three (95% relative fraction), six (3%) or nine Ni atoms (2%) is reported. Their formation is associated with the expulsion of Ni atoms or trimers from a densified, moiré-distorted Ni monolayer on Ru(0001); occasionally, these recombine to form larger entities, i.e., donut-shaped hexagons (6 Ni atoms) or starlike arrangements (9 Ni atoms). The process of expulsion is induced by the negative surface stress imposed on the densified Ni monolayer after oxygen adsorption. The exceptional stability of the microislands is ascribed to oxygen attached to the islands, thereby forming (metallic) Ni-oxygen composites. We suspect that similar treatments applied to other material combinations might well exhibit a similar behavior. The remarkable surface density, identical structure, and notable thermal stability of clusters thus prepared thereby allow investigations using nonmicroscopic tools and methods, paving the way to a wide range of spectroscopic and catalytic studies.

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