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Supplement: Altering the stability of nanoclusters through core-shell supports

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Abstract

This supplement gives detailed information about the preparation of the core-shell supports and provides a control experiement for the influence of the tip on the measurements.

GROWTH OF CORE-SHELL NANOISLANDS

The main manuscript describes the influence of the core-shell supports on the stability of nanoclusters. The shape of these supports can be altered by variation in temperature and nucleation density as described in more detail below.

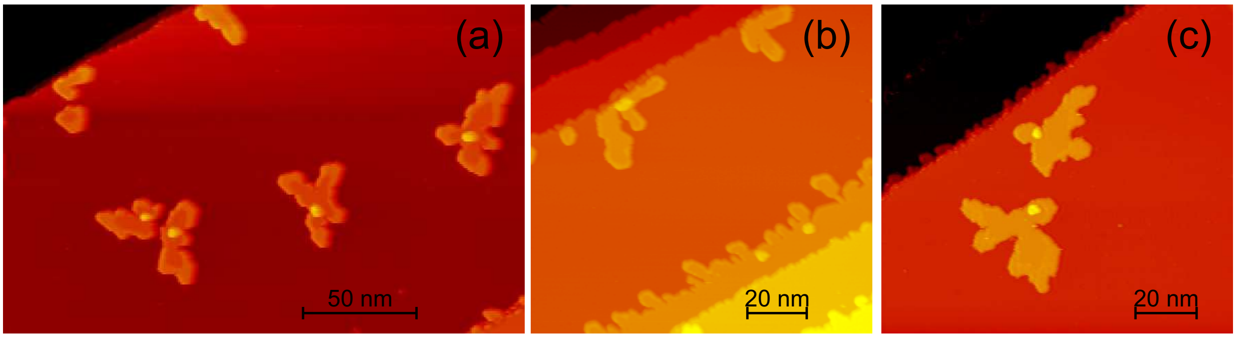

FIG. 1: STM images for low temperature deposition of Ag and Cu, 0.2 ML Cu in 45 s, 0.2 ML Ag in 60 s; Cu depostion at (118 ± 15) K, Ag deposition at (111 ± 18) K, tunneling parameters: (a) 0.66 nA, 884 mV, 118 K (b) 0.76 nA, 372 mV, 115 K (c) 0.82 nA, -884 mV, 109 K.

If both deposition proceed at low temperature, the islands are ramified (Fig. 1), because the diffusion at the border is slow and further atoms arrive at the island before their shape is equilibrated [1]. For fcc(111) faces, where diffusion energies on terraces are usually below 100 meV, but edge diffusion energies are typically of the order of 500 meV this scenario if frequent and leads to ramified islands. The rims of the islands are ragged for the same reason (Fig. 1). This holds not only for islands nucleated on the terraces (Fig. 1a), but also for those nucleated at the lower and the upper step edge (Fig. 1b). Note that second layer nucleation is not necessarily always in the middle of the support (Fig. 1c). The nucleation at the border between Ag and Cu is indicative for a pure Ag island, as this boarder does not exist during Cu growth.

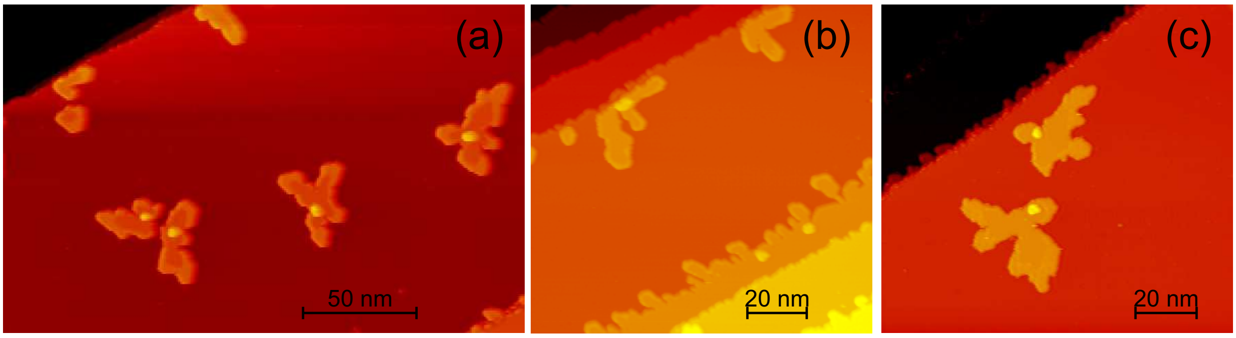

FIG. 2: STM images for deposition of Cu at lower and Ag at higher temperature; Cu 0.2 ML in 115 s at (139$\pm$25) K; Ag: 0.2 ML in 83 s at (134$\pm$21) K; arrows point to pockets in (c,d) tunneling parameters: 884 mV (a) 0.34 nA, 161 K (b) 0.33 nA, 160 K (c) 0.4 nA, 130 K (d) 0.42 nA, 183 K.

At higher deposition temperature, the core is less ramified and the rim encloses large parts of the islands (Fig. 2a,b), because equilibration of the island's shape is possible during growth. Note, however, that in the pockets, the rim is still interrupted (Fig. 2c,d). First, the number of atoms reaching the border of these pockets is smaller per step length. In addition, atoms attaching to another part of the rim would need to diffuse around inner edge sites, where they are bound to more atoms and thus more likely to get trapped there.

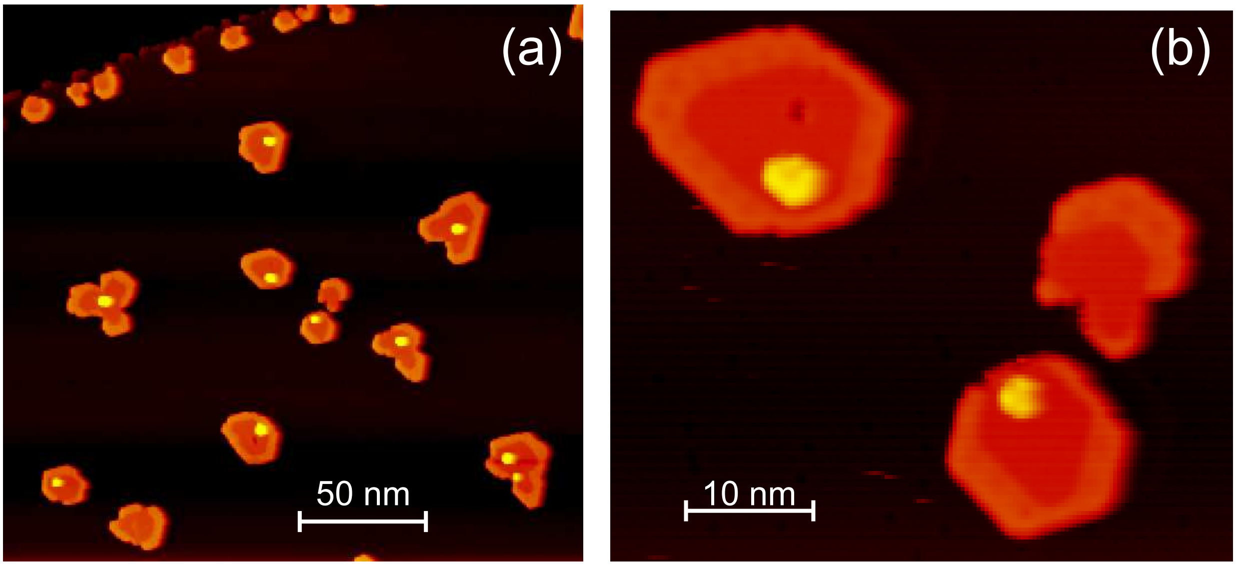

FIG. 3: STM images for deposition of Cu and Ag at same temperature, but after a 1s sputter pulse to provide nucleation centers; Cu 0.2 ML in 50 s, (123 ± 13) K; 0.2 ML in 48 s, (123 ± 13) K: tunneling parameters: all 884 mV (a) 0.28 nA, 180 K (b) 0.36 nA, 180 K.

For creating Cu islands that are more frequent and compact, we used sputter-aided nucleation [2, 3] By providing nucleation centers before Cu deposition, the Cu islands are smaller at same coverage and more compact (Fig. 3a). Consequently, the rim encloses the islands better, in some cases even completely (Fig. 3b, upper island).

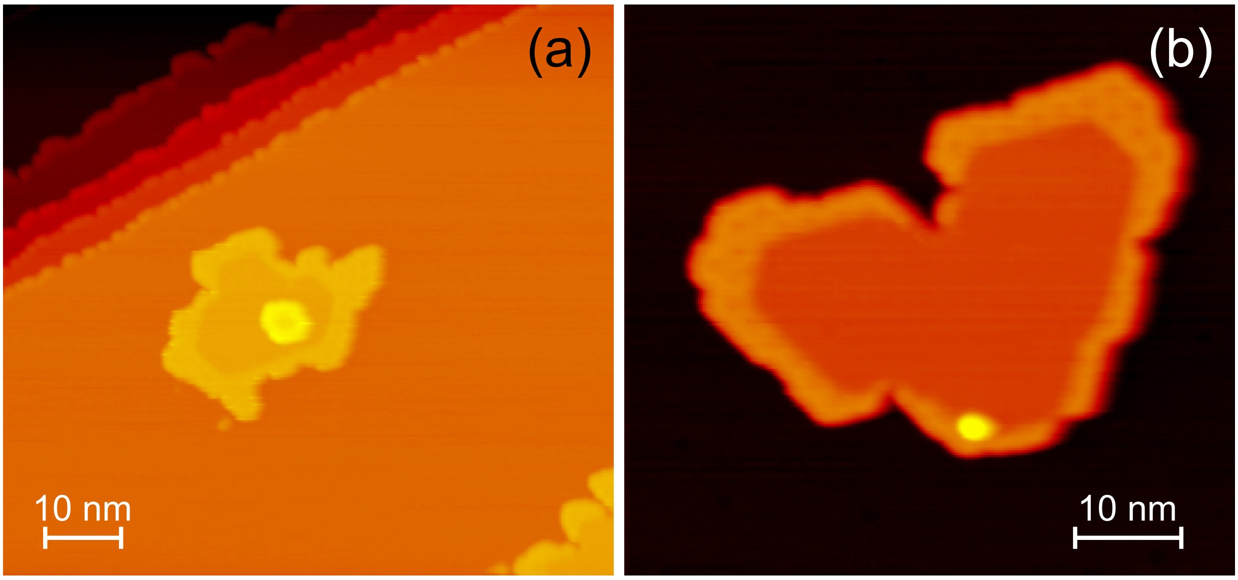

FIG. 4: STM images of individual islands for deposition of Cu at higher temperature and Ag at lower temperature; Cu, 0.2 ML in 110 s at (126 ± 26) K; Ag, 0.2 ML in 50 s at (113 ± 13) K; tunneling parameters: (a) 0.41 nA, 884 mV, 115 K (b) 0.45 nA, 884 mV, 143 K.

Larger compact islands are provided at higher deposition temperature for Cu, at which the diffusion rate along the island border is substantial (Fig. 4). If the deposition temperature of the rim is then lower than that during growth of the core, the rim is more ragged due to the lower diffusion rates (Fig. 4). In this case, the non-centric position of the island at the border between the lower imaged Cu and the higher imaged Ag identifies it as a pure Ag island that nucleated heterogeneously at this rim. Its uniform height is in clear contrast to the height of the island in the middle of the support shown in Fig. 1 of the main manuscript, which thus consists of a Cu core and a Ag shell.

Thus, the ramification of the islands depends on the deposition temperature of the core, here Cu, while the deposition temperature of the shell, here Ag, determines the smoothness of the rim.

INFLUENCE OF TIP ON DECAY

In order to control whether the observed decay of the 2nd layer island was tip induced, we imaged a larger region after their complete decay. On none of the other supports, any 2nd layer island was left (Fig. 5). This proves that the islands also decay without the presence

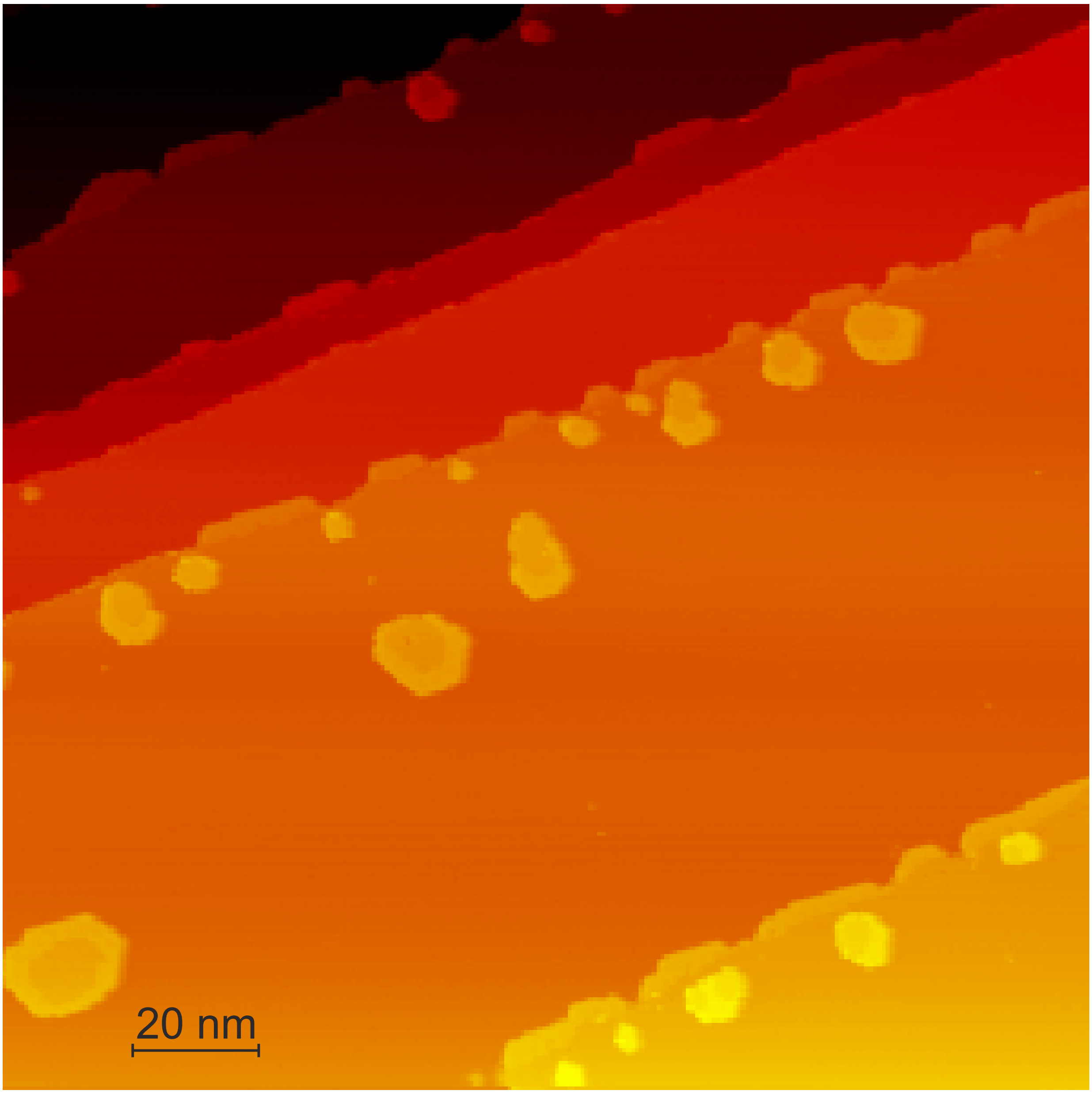

FIG. 5: STM image after movie of two central islands, 0.4nA, 883 mV.

of the tip.

INFLUENCE OF SHAPE OF SUPPORT ON VALIDITY OF LSW THEORY

The shape of the border at R may influence the LSW theory in two respects. On the one hand, it determines the adatom density close to the sink of the adatoms. In case of a circular border, this is proportional to $1/R$. For a ramified shape, R should be replaced by an effective radius; a radius that corresponds to an island that produces the same adatom density as a circular island of radius R_{eff}. In the derivation of the two limiting cases, the exponential term for the outer barrier is linearized. This corresponds of a border of infinite radius, i.e. a straight step. On the other hand, the distance between the island's borders is shape dependent. Though this distance is irrelevant in the interface-limited case, it is relevant in the diffusion limited case, where the prefactor of the differential equation is proportional to $1/ln(R/r)$. For the derivation of the limited cases, this size dependence of prefactor is neglected by defining a constant decay length. Thus, the deviation of the support from a circular shape should not alter the decay exponents of the limiting cases.

This reasoning is corroborated by the fact, that diffusion limited decay in ensembles of Ag islands on Ag(111) has been successfully described by LSW theory [4]. In such an ensemble case, the outer adatom sink consists of several islands that encircle the decaying islands These islands have even the opposite curvature from the assumed circular outer border.

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