2.703, H-C-C 155.85, the acetylene units are twisted by 15° out of the hypothetical coordination plane.

[12] R. Herges, D. Geuenich, *J. Phys. Chem. A* **2001**, *105*, 3214–3220.

[13] The structures were optimized and checked by harmonic frequency analysis at the B3LYP/6-31 + G* level of theory using the Gaussian 98 suite of programs. Chemical shifts and magnetic susceptibilities are calculated at the same level of theory using the CSGT method implemented in Gaussian98 (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**.

[14] R. Herges, H. Jiao, P. von R. Schleyer, *Angew. Chem.* **1994**, *106*, 1441; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1376–1378.

[15] For a very thorough review on the concept of the ring current see: P. Lazzaretti, *Prog. Nucl. Magn. Reson. Spectrosc.* **2000**, *36*, 1–88.

[16] For a very recent application of current density plots on coronene and corannulene see: E. Steiner, P. W. Fowler, L. W. Jenneskens, *Angew. Chem.* **2001**, *113*, 375–379; *Angew. Chem. Int. Ed.* **2001**, *113*, 362–366.

[17] P. von R. Schleyer, H. Jiao, *Pure Appl. Chem.* **1996**, *68*, 209–218.

[18] W. H. Flygare, *Chem. Rev.* **1974**, *74*, 653.

[19] Experimental ^{61}Ni NMR chemical shifts on tris(ethylene)nickel(0) unfortunately are not known. Because of its large quadrupole moment (0.16×10^{-28} m^2), low natural abundance (1.19 %), and low receptivity the ^{61}Ni NMR chemical shifts of only two trigonal-planar Ni^0 complexes ([Ni(cdt)] (cdt = all-trans-1,5,9-cyclododecatriene) and [Ni(C$_2$H$_4$)$_2$(PMe$_3$)]) have been published: a) R. Benn, A. Rufinska, *Angew. Chem.* **1986**, *98*, 851–871; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 861–881. Further data on tetrahedral, zero-valent complexes: b) K. D. Behringer, J. Blümel, *Magn. Reson. Chem.* **1995**, *33*, 729–733; c) N. Hao, M. J. McGlinchey, B. G. Sayer, G. J. Schrobilgen, *J. Magn. Reson.* **1982**, *46*, 159–162; d) H. Schumann, M. Meißner, H.-J. Kroth, *Z. Naturforsch. B* **1980**, *35*, 639–641; e) R. Benn, A. Rufinska, *Magn. Reson. Chem.* **1988**, *26*, 895–902.

[20] T. A. Keith, R. F. W. Bader, *J. Chem. Phys. A* **1993**, *99*, 3669–3693.

[21] a) K.-R. Pörschke, *Angew. Chem.* **1987**, *99*, 1321–1322; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1288; b) K.-R. Pörschke, *J. Am. Chem. Soc.* **1989**, *111*, 5691–5699; c) T. Takahashi, F.-Y. Tsai, Y. Li, K. Nakajima, M. Kotora, *J. Am. Chem. Soc.* **1999**, *121*, 11 093–11 100.

On the Stability of Electrochemically Generated Nanoclusters—A Computer Simulation**

Mario G. Del Pópolo, Ezequiel P. M. Leiva,* and Wolfgang Schmickler*

The scanning tunneling microscope (STM), operated in an electrochemical environment, offers a precise and cheap way to produce small metal clusters on a foreign substrate. Pioneering work in this area has been performed by Kolb, Ullmann, and Will,[1] who developed the following procedure for the deposition of nanosized copper clusters on single-crystal gold electrodes: The gold electrode is held at a potential a little positive of the deposition potential for copper, while the tip potential is set below this value, so that copper atoms are deposited on the tip surface. The tip is then pressed against the electrode and withdrawn again. As the tip separates from the electrode a metal cluster remains, which typically comprises 20–100 atoms, and is a few monolayers high. This method also works for the generation of palladium clusters on Au(111), but not for copper on Ag(111).[1, 2]

The generation of such metal clusters is of great interest, since they are expected to play a major role in future nanotechnologies. The deposition of copper clusters on the Au(111) surface has been investigated most extensively, and is considered as a prototype for the electrochemical fabrication of nanoclusters. Recently, this process has attracted further attention because the copper clusters are stable at a potential at which bulk copper dissolves. This is surprising because generally clusters tend to be less stable than the corresponding bulk material. Kolb, Engelmann, and Ziegler[3] have speculated that this increased stability is caused by quantum confinement: They propose that the electrons in the cluster are separated from the bulk of the electrode by a potential energy barrier, so that the energy levels in the cluster are discrete and not continuous as in bulk metals. The dissolution

---

[*] Prof. Dr. E. P. M. Leiva, M. G. Del Pópolo
Universidad Nacional de Córdoba
Unidad de Matemática y Física
Facultad de Ciencias Químicas
5000 Córdoba (Argentina)
Fax: (+54) 351-4334189
E-mail: eleiva@fcq.unc.edu.ar

Prof. Dr. W. Schmickler
Abteilung Elektrochemie
Universität Ulm
89069 Ulm (Germany)
Fax: (+49) 731-5025409
E-mail: wolfgang.schmickler@chemie.uni-ulm.de

[**] This work was supported by Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), by Consejo de Investigaciones Científicas y Tecnológicas de la Provincia de Córdoba (CONICOR), by the Secretaría de Ciencia y Técnica de la Universidad Nacional de Córdoba (SeCyT-UNC; program BID 802/OC-AR PICT Nr. 06-04505) and by the Fundación Antorchas (E.P.M.L and M.G.D.) as well as by the Deutsche Forschungsgemeinschaft under the program "Grundlagen der elektrochemischen Nanotechnologie" (W.S.). Some of the calculations were performed on a Digital workstation financed by the Alexander von Humboldt Stiftung.

Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

of a Cu atom to a solvated Cu^{2+} ion would leave two electrons behind, which would have to be accommodated at a level above the Fermi energy. This would be energetically less favorable than the dissolution of bulk copper, for which the remaining electrons stay at the Fermi level, and would thus make the clusters more stable. There are, however, some difficulties with this explanation: There may indeed be a potential energy barrier separating the electrons in a metal cluster from the underlying bulk metal; however, such barriers are small and do not lead to isolated electronic levels in the cluster, but to resonance levels with a lifetime of the order of femtoseconds.[4] Copper dissolution occurs on a much longer timescale, since it involves the solvation of the ion, which takes picoseconds or longer. Therefore there is plenty of time for the dissolving atom to exchange electrons with the substrate. Indeed, the very fact that these clusters can be imaged with an STM shows that there is rapid electron exchange between the cluster and the substrate. Thus the reason for the stability has to lie elsewhere.

To gain further insight into the fabrication and the stability of these copper clusters we have performed extensive molecular-dynamics simulations. The approach of an STM tip to a metal surface in the vacuum has been simulated by the group of Landman;[5] in the cases investigated, it led to an exchange of material between tip and substrate, but did not result in the generation of stable clusters. We have adapted their method to the problem at hand, which has a peculiarity that is often not appreciated: At the potential, at which the copper cluster is formed, the Au(111) surface is already covered by a monolayer of adsorbed copper atoms, a phenomenon that is known as underpotential deposition.

Figure 1 shows a series of snapshots of a typical simulation. The starting configuration (Figure 1 a) shows a platinum STM tip with several layers of deposited copper atoms above the Au(111) surface, which is covered by a copper monolayer; the distance between the surface and the nearest Cu atoms was about 7.6 Å and to the nearest Pt atom about 19.6 Å. The tip was then moved in steps of 0.6 Å towards the surface; after each such step the system was allowed to equilibrate for 300 ps. The "jump-to-contact" process, in which the copper atoms from the tip jump to form a bridge to the substrate, occurred after the tip had been moved by 3.6 Å. This stage is depicted in Figure 1 b; in this instance the bridge consisted of five Cu atoms. The tip was then moved further towards the surface, which began to be deformed. In this particular run the tip was moved another 8.4 Å towards the surface after the jump-to-contact; the closest approach is shown in Figure 1 c. Subsequently the tip was withdrawn from the substrate with the same step size as in the approach. A connective neck began to form, which contained both Cu and Au atoms. After the tip and the substrate have separated, a cluster is left behind on the surface (Figure 1 d). In this particular run the cluster consisted of 26 Cu atoms and 11 Au atoms. Thus the fabricated cluster consists of a mixture of copper and gold, and not of pure copper. In addition, a few Au atoms have been transferred to the tip.

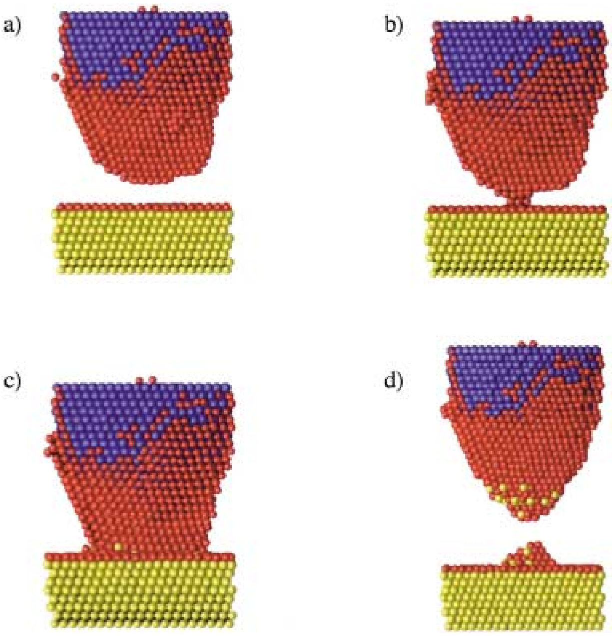

Figure 1. Snapshots of four stages in the fabrication of a metal cluster on Au(111). Yellow spheres: gold atoms; red spheres: copper atoms; blue spheres: platinum atoms.

Until now, we have performed 12 such simulations with various distances of approach. In some simulations the tip was withdrawn in a steady instead of a stepwise manner. Whenever a cluster of more than monomolecular height was formed, it contained both Au and Cu atoms, the gold content varying between 8 and 40 %.

We note in passing that a monolayer of copper deposited on gold has a tendency to form a surface alloy after several hours;[6] this is further evidence for the ease with which these two metals form alloys in an electrochemical environment, even without the impact of a tip.

As a measure of the hardness with which the tip approaches the surface we may use the distance over which the tip is moved towards the surface after the jump-to-contact process.[5] This distance was varied between 2.4 to 8.4 Å. The size of the clusters ranged from 10 to 60 atoms, and their height between two and four monolayers. There was little systematic variation between the distance of furthest approach and the size of the clusters, except that the gentlest approach always produced the smallest clusters. Experimentally, the height of the clusters has been found to increase with the distance of approach,[2] and to reach an average height of about three to fours layers, the same as in our simulations. The experimentally produced clusters seem to contain more atoms than ours, typically about one hundred, but this difference can be attributed to the ideal tip shape in the simulations, and to the small system size. Overall our simulations reproduce the cluster heights and sizes of the experiments quite well.

During the formation of the cluster, Au atoms are moved from the substrate to the cluster and also to the tip. Therefore the surface shows some damage both in the Cu monolayer and in the gold substrate (Figure 2), which typically extends over one to two layers of the substrate. The experimental evidence for such damage is controversial: While Kolb et al.[3] claim that the substrate is left intact, others[7] have observed holes after cluster formation. In any case we would expect such damage to heal rapidly on the timescale on which the experiments are performed, which is seconds to minutes,

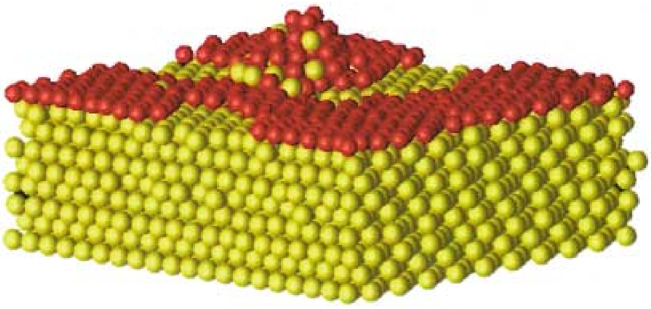

Figure 2. Final stage of the cluster formation.

while our simulations last only a few nanoseconds. The corrugation of the Au(111) surface is small and surface transport fast.

Copper and gold are known to form stable alloys, so we expected our clusters to be more stable than pure copper clusters. To test this hypothesis, we removed the tip from our system and let the cluster and substrate relax to equilibrium. We then determined the cluster atom whose removal requires the least change in energy—obviously, this is always a surface atom. This atom was removed, and the system was again equilibrated. This process was repeated till the cluster had disappeared. This simulation was then repeated for a cluster in which all the gold atoms have been replaced by copper. The sequence of energy increments associated with the removal of the atoms was used along with the master equation for a one-dimensional single-step process to obtain the number of atoms and the cluster height as a function of the chemical potential μ. The cohesive energy of bulk copper is $E_c = -3.54$ eV, so a pure copper cluster would be completely dissolved at chemical potentials below this value.

In electrochemistry the (electro)chemical potential of the copper atoms varies with the electrode potential. Therefore, the scale of chemical potentials for copper can be converted to the electrode potential ϕ according to Equation (1) where the standard equilibrium potential for the copper deposition and dissolution reaction has been taken as zero; the division by two is due to the fact that copper dissolves as a divalent ion.

$$\phi = (E_c - \mu)/2 \tag{1}$$

Figure 3 shows the number of atoms n and the cluster height h both for a typical copper–gold cluster and for a pure copper cluster as a function of the electrode potential. The pure copper cluster dissolves at a potential below the dissolution potential for pure cluster, since its large surface area makes it less stable. In contrast, the copper–gold cluster has still about a third of its original size at a potential of $\phi = 0.05$ V (Figure 3a), and only gradually dissolves at higher values. Interestingly, our simulations reflect the experimental observation by Kolb et al. that the dissolution of the cluster is layer by layer.[2]

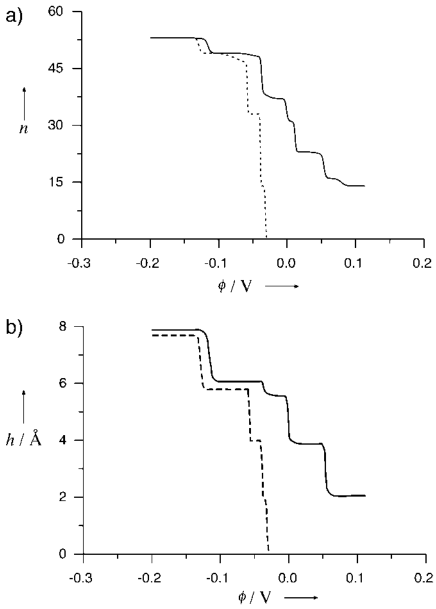

Figure 3. Number of atoms n (a) and cluster height h (b) as a function of electrode potential ϕ; the zero of the potential scale correponds to the dissolution potential for bulk copper. Full lines: Cu–Au cluster, broken line: pure Cu cluster.

Thus our simulations suggest that the stability of the clusters is caused by the formation of a Cu–Au alloy. This hypothesis also explains why copper does not form stable clusters on silver: Copper and silver are immiscible at temperatures below 600 K, and do therefore not form stable Cu–Ag clusters. Indeed, a few test simulations for the deposition of copper on Ag(111) that we have performed never resulted in clusters. In contrast, palladium and gold do mix at room temperature,[8] so the formation of clusters on Au(111) when palladium is deposited with an STM is in line with our arguments; we surmise, that these clusters consist of both palladium and gold atoms.

Therefore it seems that in general this electrochemical technique only results in stable clusters if the substrate and the deposited metal form a stable alloy. Indeed, it is difficult to see how it could be otherwise: At potentials above the equilibrium potential of the deposited metal a pure cluster should either dissolve or relax into an island one monolayer high; at lower potentials the cluster should continue to grow. Only an alloy can remain stable above the dissolution potential for the pure metal.

Received: July 23, 2001 [Z17566]

[1] D. M. Kolb, R. Ullmann, T. Will, *Science* **1997**, *275*, 1097.
[2] D. M. Kolb, R. Ullmann, J. C. Ziegler, *Electrochim. Acta* **1998**, *43*, 2751.
[3] D. M. Kolb, G. E. Engelmann, J. C. Ziegler, *Angew. Chem.* **2000**, *112*, 1166; *Angew. Chem. Int. Ed.* **2000**, *39*, 1123.
[4] R. Otero, A. L. Vazquez de Parga, Rodolfo Miranda, *Surf. Sci.* **2000**, *447*, 143.
[5] "Consequences of Tip-Sample Interactions": U. Landman, W. D. Luedtke in *Scanning Tunneling Microscopy III* (Eds.: R. Wiesendanger, H. J. Güntherodt), Springer, Berlin, **1993**; U. Landman, W. D. Luedtke, N. A. Burnham, R. J. Colton, *Science* **1990**, *248*, 454.
[6] E. Budevski, G. Staikov, W. J. Lorenz, *Electrochemical Phase Formation and Growth*, Wiley-VCH, Weinheim, **1996**, p. 128 ff.
[7] S. Maupai, Ph.D. thesis, Technical University of Erlangen, **2001**.
[8] R. Hultgren, P. D. Desai, D. T. Hawkin, M. Gleiser, K. K. Kelly, *Selected values of the thermodynamic properties of binary alloys*, American Society for Metals, Metals Park, OH, **1973**.