

11-1-2005

Synthesis and patterning of gold nanostructures on InP and GaAs via galvanic displacement

Mohammad R. Hormozi Nezhad

University of Alberta

Masato Aizawa

University of Alberta

Lon A. Porter Jr.

Wabash College

Alexander E. Ribbe

Purdue University

Jillian M. Buriak

University of Alberta

Follow this and additional works at: <http://docs.lib.purdue.edu/nanodocs>

Hormozi Nezhad, Mohammad R.; Aizawa, Masato; Porter, Lon A. Jr.; Ribbe, Alexander E.; and Buriak, Jillian M., "Synthesis and patterning of gold nanostructures on InP and GaAs via galvanic displacement" (2005). *Other Nanotechnology Publications*. Paper 50. <http://docs.lib.purdue.edu/nanodocs/50>

This document has been made available through Purdue e-Pubs, a service of the Purdue University Libraries. Please contact epubs@purdue.edu for additional information.

DOI: 10.1002/sml.200500121

Synthesis and Patterning of Gold Nanostructures on InP and GaAs via Galvanic Displacement**

Mohammad R. Hormozi Nezhad, Masato Aizawa, Lon A. Porter Jr., Alexander E. Ribbe, and Jillian M. Buriak*

The increasingly challenging technological demands of metallic interconnects on functional semiconductor devices are driving a new area of nanoscience dedicated to building nanoscale metallic features interfaced directly to materials such as silicon, germanium, and compound semiconductors such as gallium arsenide and indium phosphide.^[1] The need for control over metal morphology (both shape and size), and efficient, reliable, and controllable reaction conditions are a few of the requirements that must be addressed. An approach under investigation for its synthetic potential is galvanic displacement, a type of electroless deposition in which metal ions in an aqueous solution are reduced by electrons arising from the semiconductor itself as shown in Scheme 1.^[2]

The room-temperature reactions require only water, semiconductor, metal salt, and possibly a fluoride or acid source to concomitantly dissolve the insulating oxide that forms on the surface of the semiconductor. Galvanic displacement is particularly advantageous because of its amenity to high-throughput processing, the fact that it requires only simple apparatus, generates little waste in contrast to

[*] M. R. Hormozi Nezhad, Dr. M. Aizawa, Prof. J. M. Buriak
Department of Chemistry, University of Alberta
Edmonton, AB T6G 2G2 (Canada)
Fax: (+1) 780-492-8231
E-mail: jhuriak@ualberta.ca

and

National Institute for Nanotechnology (NINT)
National Research Council
Edmonton, AB T6G 2V4 (Canada)

Prof. L. A. Porter Jr.

Department of Chemistry, Wabash College
301 W. Wabash Ave., Crawfordsville, IN 47933 (USA)

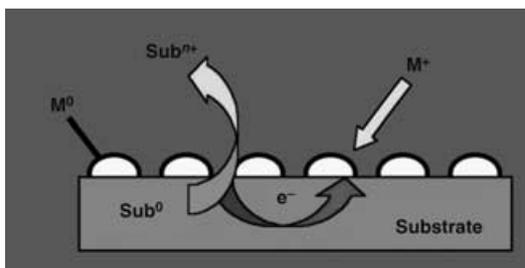
Dr. A. E. Ribbe

Purdue Laboratory for Chemical Nanotechnology
Department of Chemistry, Purdue University
West Lafayette, IN 47907-2084 (USA)

[**] This work has been supported by the National Research Council, the National Institute for Nanotechnology, NSERC, CFI, and the University of Alberta. J.M.B. holds the Canada Research Chair of Inorganic and Nanoscale Materials, M.A. is an NSERC Visiting Fellow, and M.R.H.N. is a visiting graduate student from Shiraz University (Iran). Thanks to Daniel Salamon and Vicki Lui for assistance with SEM.



Supporting information for this article is available on the WWW under <http://www.small-journal.com> or from the author.



Scheme 1. Outline of galvanic displacement. A semiconductor substrate in contact with a solution of sufficiently oxidizing metal ions (M^+) will reduce the M^+ to M^0 on the surface of the semiconductor. The semiconductor, in turn, is oxidized.

standard evaporation techniques, and efficiency. Films deposited by galvanic displacement are generally composed of irregular, spherical, or oblate metal structures or particles, some of which are crystalline as determined by TEM and XRD, and others yet undetermined.^[2] Recently, however, hexagonal stacks of crystalline silver nanoplates, termed “nano-inukshuks”, have been prepared on germanium surfaces via galvanic displacement, and these results suggest that size and shape selectivity may be possible by controlling various reaction parameters.^[3] Galvanic displacement to prepare metal–semiconductor structures is still, however, sorely lacking the control and versatility of wet-chemical solution-phase synthesis to prepare isolated anisotropic metal nanoparticles of various shapes and sizes.^[4] There still remain, however, many combinations of technologically important semiconductors and transition-metal ions that should lead to spontaneous reduction of metal films that have not been studied in detail.

In this Communication, we describe the employment of galvanic displacement to prepare nanostructured gold films on single-crystal InP and GaAs. Metal contacts to these materials are important for applications such as next-generation computing platforms, optoelectronics, and LEDs, among others.^[5] While only a smattering of papers have ex-

amined galvanic displacement of noble metals (Au and Pd) on InP and GaAs, alloying or intermetallic formation between the noble metals and these compound semiconductors has been reported.^[6] Galvanic displacement on III–V semiconductors may therefore form the basis for development of a mechanically strong, direct electronic contact between the metal nanoparticle–semiconductor interfaces, important for novel nanoscale metallic interconnects and direct semiconductor–nanoparticle wiring.

Immersion of degreased, native-oxide-capped InP(100) wafer shards in an aqueous HAuCl_4 (1 mM) solution in the presence of dilute acid at room temperature results in rapid deposition of gold nanoparticles on the surface. In the presence of 2% H_2SO_4 as the acid, the surface is decorated with strongly adhering, faceted sub-100 nm-diameter gold nanoparticles within 30 min, as shown in Figure 1. In the center of the wafer, the particles are discrete and separate, but closer to the wafer edges, more metal deposition is noted

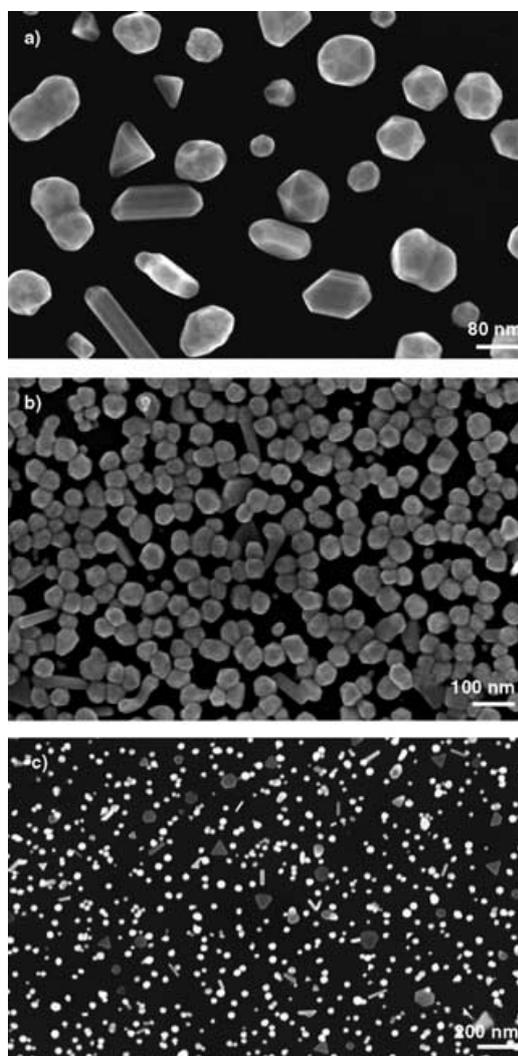


Figure 1. SEM images of gold nanoparticles interfaced with InP(100), produced in the presence of 1 mM HAuCl_4 and 2% H_2SO_4 . a) Center of InP(100) wafer; b) towards the edge of the InP(100) wafer where increasing deposition is observed; c) centre of an InP(100) wafer produced in the presence of 1 mM HAuCl_4 and 0.1% H_2SO_4 .



Editorial Advisory Board Member

Jillian Buriak is a Professor of Chemistry at the University of Alberta, holder of the Canada Research Chair of Inorganic and Nanoscale Materials, and Group Leader of the Materials and Interfacial Chemistry Group at the National Institute for Nanotechnology of the National Research Council. She was born in Toronto, Canada in 1967, and completed her AB at Harvard University and her PhD at the Université Louis Pasteur (Strasbourg, France). She followed up with a post-doc

at The Scripps Research Institute and took up her first independent position of assistant professor in the Department of Chemistry at Purdue University (USA) in 1997. She was promoted to associate professor in 2001, and moved to her present position in 2003. Recent awards include the Rutherford Medal, the ACS Pure Chemistry Award, and the Dreyfus Teacher-Scholar Award.

and the nanoparticles are in contact (Figure 1 b).^[3] Fivefold twinning appears prevalent based on the observation of many nanoparticles with pseudo-pentagonal shapes and icosahedra (Figure 2).^[7] Other forms noted include truncated tetrahedra, hexagonal and triangular plates, rods, and other polyhedra, shapes routinely observed via solution-phase syntheses.^[4a,b] As shown in Figure 2 g, particles with spherical or twinned (fivefold axes visible, including icosahedra) structures predominate, and hexagonal and triangular plates, rods, and other semi-regular shapes such as truncated

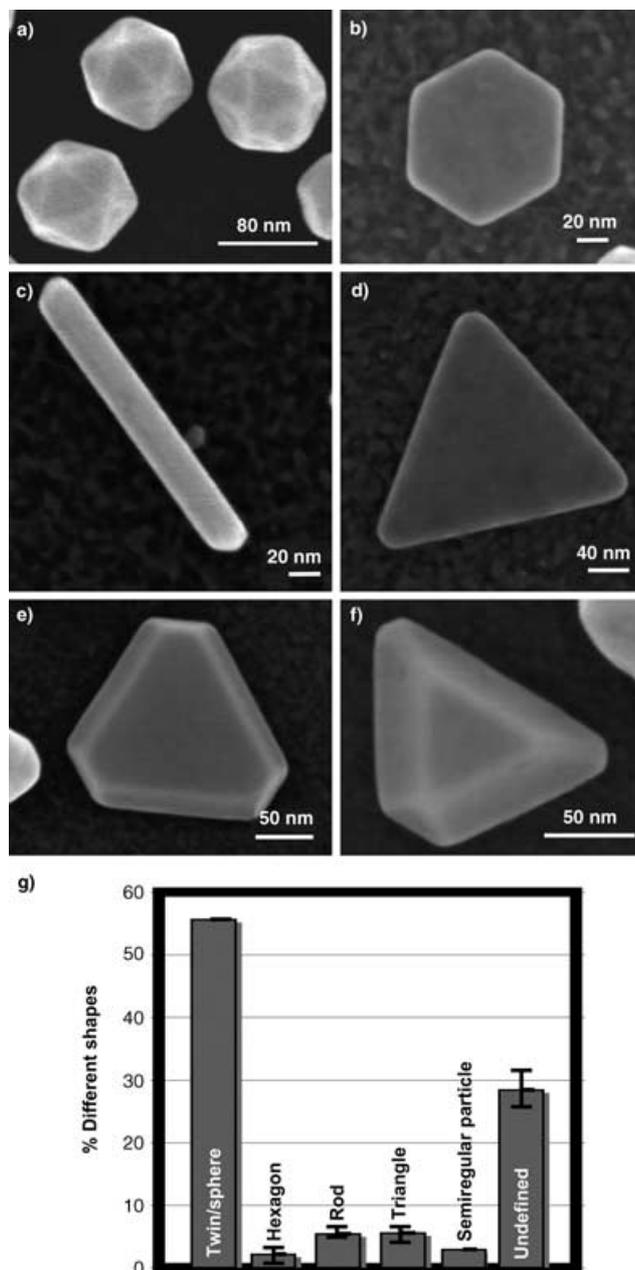


Figure 2. Different nanoparticle shapes observed on InP(100): a) icosahedra; b) hexagonal plates; c) rods; d) triangle plates; e, f) truncated tetrahedra. g) Distribution of different shapes observed at 2% H_2SO_4 and 1 mM HAuCl_4 . The distribution was determined by SEM image analysis, based on an average of three different samples, with 160–400 particles per sample.

tetrahedra (Figure 2 e and f) make up a small fraction of the gold nanoparticles, on the order of 10–15%. XRD clearly indicates that the structures are crystalline gold (see Supporting Information), as would be expected based on the obvious faceting. The gold nanoparticles resist sonication in methanol, although thicker layers of gold, visible to the naked eye, can be removed with scotch tape. Reducing the sulfuric acid concentration to 0.1% appears to slow down the rate of deposition, and renders it more uniform across the face of the InP(100) wafer. Statistical analysis of the breakdown of nanoparticle shapes reveals, that within experimental error, the distribution at 0.1% H_2SO_4 is similar to that of 2% H_2SO_4 (Figure 2 g). Leaving the InP(100) immersed for longer than 2 h in 0.1% or higher of sulfuric acid/1 mM HAuCl_4 results in roughening of the indium phosphide surface between the nanoparticles, followed by continued growth and coalescence of the nanoparticles to form an almost continuous film across the face of the wafer that is visible to the naked eye. Deposition of HAuCl_4 (in aqueous solution) in the absence of an external acid source produces scattered sub-100 nm gold nanoparticles on the surface, but nucleation and growth cease after 30 min, as determined by AFM.

Shape-selective syntheses of gold nanoparticles in solution generally require a structure-directing agent such as cetyltrimethylammonium bromide (CTAB) or poly(vinyl pyrrolidone) (PVP).^[4a–c] Since these additives are absent in this system, the effects of the acid counteranion were investigated for their possible role in gold structure development and selection. HF, HCl, HBr, and H_3PO_4 were examined, the last being of particular interest to mimic possible soluble phosphorous oxidation products of InP(100) corrosion. Surprisingly, only subtle counteranion effects were noted in the gold galvanic displacement products. HF results in a more rapid deposition and thicker nanoparticulate films, and dilute (2%) HCl and HBr reactions were similar to 0.1% sulfuric acid, although HBr deposition was somewhat slower. Nanoparticles formed in the presence of H_3PO_4 appeared less well defined, although similar hexagonal and triangular plates, and fivefold twin structures were noted. The rates of initial nucleation and reduction of gold in the presence of HF, H_2SO_4 , and H_3PO_4 on InP(100) were determined by open-cell potential experiments, and are identical, taking place within the first 100 s of immersion (see Supporting Information), as has been noted previously for Ni^{2+} and Ag^+ deposition on silicon and germanium, respectively.^[2a,3] Following the initial stage of nucleation, only particle growth occurs, explaining the relative similarities of the average particle size, both intra- and inter-sample.

The mixture of shapes observed on the InP(100) surface is very similar to that observed in seeded systems with, for instance, CTAB surfactant mixtures on surfaces.^[8] The reasons for this are not obvious. While superficially these galvanic displacement reactions appear very simple, requiring only water, salt, wafer, and usually an acid source, the systems become complex due to the formation of soluble and insoluble species via galvanic displacement, including oxides of phosphorous and indium, and chloride ions (from the HAuCl_4 precursor), as well as a concentration of metal salt

that is continually decreasing. It is possible that one or more of the solution-phase components acts as a directing agent. In addition, since the underlying material on which this deposition is occurring is a semiconductor, electrochemical Ostwald ripening may be playing a role in the growth of larger particles, at the expense of smaller ones, although this remains to be determined.^[9] In situ AFM studies are presently underway to better understand nucleation and growth.

Galvanic displacement of HAuCl_4 on GaAs(100) is much less structured than on InP(100), and does not require an external acid source. Dendritic growth occurs rapidly on the edges of the wafer, and is accompanied by irregular gold deposits on the front face of the wafer with scattered 1- μm -diameter flat hexagonal and triangular plates (see Supporting Information). Open-cell potential experiments also indicate rapid nucleation of gold on the surface, followed by an equilibrium metal-deposition regime. Deposition in dilute H_2SO_4 (0.1%) with 1 mM HAuCl_4 results in almost complete coverage of the GaAs(100) surface with gold within 1 h of deposition (see Supporting Information).

The galvanic displacement reaction is not particularly site-selective, and to demonstrate that this chemistry is amenable to surface patterning, we continued with an approach developed in our group based on static plowing microscopy using an atomic force microscope (AFM).^[10] Using a diamond-coated AFM tip, the oxide coating layer of InP or GaAs could be selectively removed through mechanical abrasion, thus exposing the underlying substrate. Scribing through the native oxide of InP(100) with the diamond AFM tip with a force of 6 μN , followed (within seconds) by dipping in an aqueous 0.1 mM HAuCl_4 solution for 10 min results in rapid deposition of gold exclusively in the scribed areas, as shown in Figure 3, with a small number of defects visible. Because galvanic displacement of gold occurs rapidly on GaAs(100) without acid, a 5-nm-thick thermal oxide was prepared, and the sample scribed to yield a 4-nm-deep trench on the surface. Rapid immersion in a 0.1 mM HAuCl_4 solution again

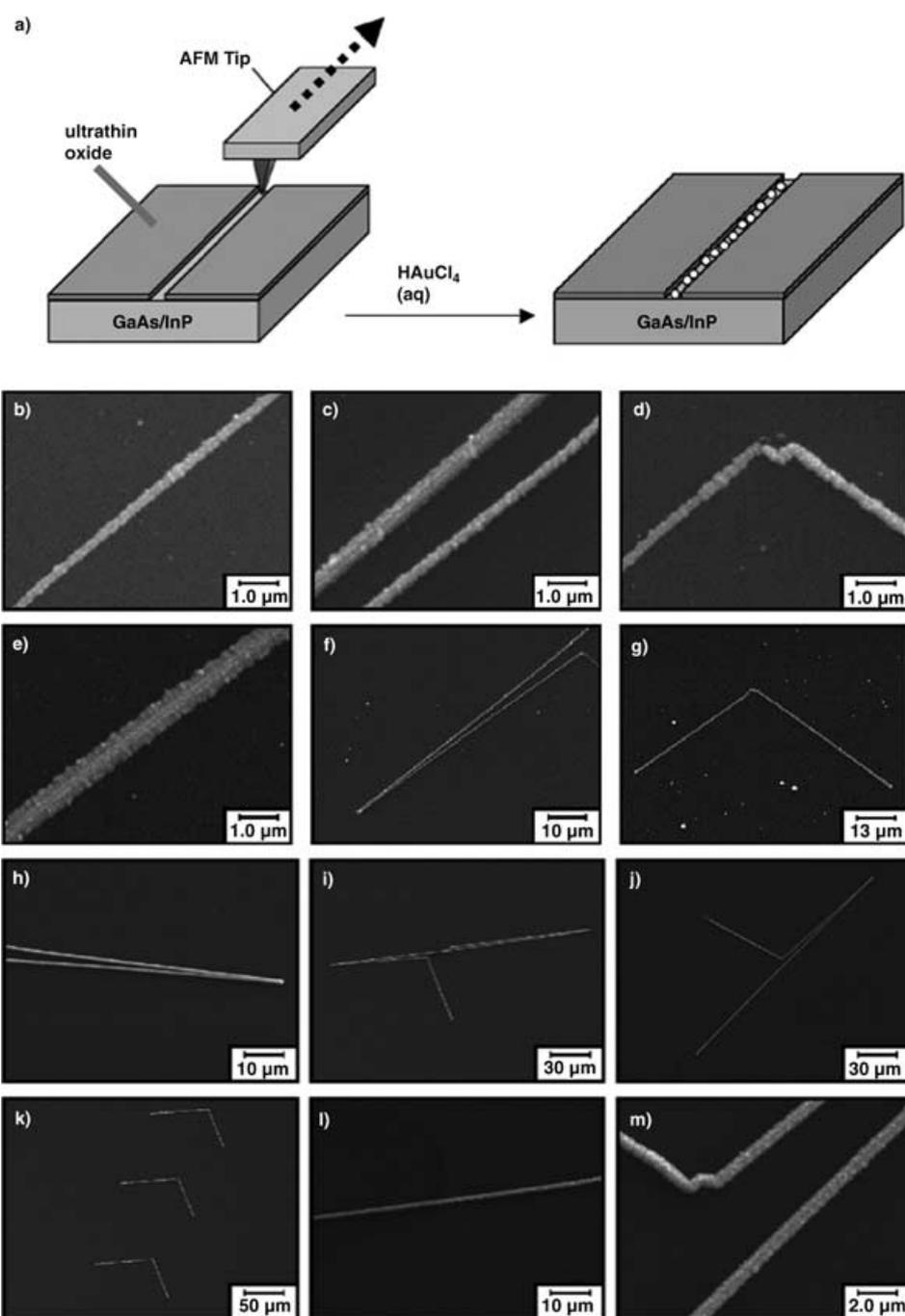


Figure 3. Scanning plowing lithography on InP(100) and GaAs(100). a) Outline of the procedure: plowing with a diamond-coated AFM tip through the oxide exposes the underlying semiconductor. b–g) SEM images of gold deposited on InP(100) formed by scribing through the native oxide, followed by galvanic displacement. h–m) SEM images of gold deposited on GaAs(100) formed by scribing through the thermal oxide, followed by galvanic displacement.

results in exclusive metal deposition in the scribed areas, with no pinhole defect deposition; the thermal oxide is sufficiently thick and insulating to prevent large-scale gold deposition in the unscribed areas within this time frame. Detailed studies of feature width and control over the rate of deposition are presently underway.

To conclude, galvanic displacement of gold on InP results in crystalline nanoparticles of various shapes such as

icosahedra, triangular and hexagonal plates, and other structures, in the absence of any obvious structure-directing agent. Galvanic displacement of gold on GaAs also proceeds, but up to this point, has led to unstructured gold films. This technique is very promising due to its simplicity and high efficiency. The influence of additives is presently under investigation in order to generate greater shape selectivity, as well as detailed electrochemical studies of the nanoparticle–semiconductor interfaces themselves. Through nanolithography based on scribing through surface oxide, the galvanic displacement reaction can be patterned on the surface of both InP and GaAs, and detailed studies of control over the feature sizes, shapes and other parameters are underway.

Experimental Section

InP(100) n-type wafers (resistivity = 0.001 Ω cm) were purchased from CRYSTACOMM. An n-type InP(100) wafer shard was sonicated in acetone and methanol for 10 min each and then dried with a N_2 flux. The InP wafer shard was placed in 100 mL of 1:1 49% HF (aq) and 18 M Ω (Barnstead) water for 10 min.^[11] The wafer was then dipped for 2 min each into five beakers containing 18 M Ω water and then dried with a N_2 stream.

GaAs(100) n-type wafers (resistivity = 0.001 Ω cm) were purchased from ITME. An n-type GaAs(100) wafer shard was sonicated in acetone and methanol for 10 min each and then dried with a N_2 flux. The GaAs wafer shard was placed in H_2SO_4 : H_2O_2 : H_2O (4:1:100) solution for 2 min then HCl: H_2O (1:3) for 2 min and 18 M Ω (Barnstead) water for 10 min. The wafer was then dipped for 2 min each into five beakers containing 18 M Ω water and then dried with a N_2 stream.

To carry out galvanic displacement, the InP or GaAs sample was placed in a 10 mL mixture of $H AuCl_4$ (Aldrich) and acid solution in a glass vial and kept in the dark for the required length of time. The InP wafer was then removed from the solution and dipped in water and then methanol and dried under a nitrogen stream.

Scanning probe nanolithography was carried out in the following manner. A diamond-coated silicon tip (Veeco Instruments, ULNC-DCBO, 17 Nm⁻¹ spring constant) was employed to plow through the thermal oxide layers, thereby exposing the underlying bulk semiconductor. While these specialty tips were more cost-prohibitive, the economical oxide-sharpened silicon tips (MikroMasch, NSC-15) were found to lack the strength required for plowing a continuous furrow through the inorganic oxide layers. Static plowing was accomplished in contact-mode operation, where the tip was scanned across the sample surface with a constant force ($\approx 6 \mu$ N). This set-point proved sufficient to plow through the thermal oxide, thereby exposing the GaAs(100) or InP(100) surface as scanning progressed. Continuous furrows were reproducibly obtained at scanning speeds of 10–100 μ m s⁻¹ with lengths in hundreds of micrometers, restricted only by the range of the available AFM scanner. Vector scan operation allows for the AFM tip to be driven along paths of arbitrary length scales at predefined angles, while also providing for control over z-axis displacement and applied force. Utilizing the NanoScriptä software (Veeco Instruments), a general program-

ming script provided access to a diverse set of customized scan profiles. As a consequence of an open-loop instrument, such as the Nanoscope III, some drift was observed in the resist furrows. Furrows were imaged employing oxide-sharpened silicon tips (MikroMasch, NSC-15), operating in intermittent (tapping) mode.

Keywords:

galvanic displacement • gold • nanolithography • nanoparticles • semiconductors

- [1] a) H. Zhang, R. C. Jin, C. A. Mirkin, *Nano Lett.* **2004**, *4*, 1493; b) L. A. Porter, H. C. Choi, A. E. Ribbe, J. M. Buriak, *Nano Lett.* **2002**, *2*, 1067; c) F. Karadas, G. Ertas, E. Ozkaraoglu, S. Suzer, *Langmuir* **2005**, *21*, 437. M. Aizawa, J. M. Buriak, *J. Am. Chem. Soc.* **2005**, *127*, 8932.
- [2] a) D. Niwa, T. Homma, T. Osaka, *J. Phys. Chem. B* **2004**, *108*, 9900; b) L. Magagnin, R. Maboudian, C. Carraro, *J. Phys. Chem. B* **2002**, *106*, 401; c) T. Zambelli, M. L. Munford, F. Pillier, M.-C. Bernard, P. Allongue, *J. Electrochem. Soc.* **2001**, *148*, C614; d) G. Oskam, J. G. Long, A. Natarajan, P. C. Searson, *J. Phys. D* **1998**, *31*, 1927; e) F. A. Harraz, T. Tsuboi, J. Sasano, T. Sakka, Y. H. Ogata, *J. Electrochem. Soc.* **2002**, *149*, C456; f) P. Gorostiza, M. A. Kulandainathan, R. Díaz, F. Sanz, P. Allongue, J. R. Morante, *J. Electrochem. Soc.* **2000**, *147*, 1026; g) X.-H. Sun, N.-B. Wong, C.-P. Li, S.-T. Lee, P.-S. G. Kim, T.-K. Sham, *Chem. Mater.* **2004**, *16*, 1143; h) N. Takano, D. Niwa, T. Yamada, T. Osaka, *Electrochim. Acta* **2000**, *45*, 3263; i) G. V. Kuznetsov, V. A. Skryshevsky, T. A. Vdovenkova, A. I. Tsyganova, P. Gorostiza, F. Sanz, *J. Electrochem. Soc.* **2001**, *148*, C528; j) C. Carraro, L. Magagnin, R. Maboudian, *Electrochim. Acta* **2002**, *47*, 2583; k) C. Kim, Y. Oikawa, J. Shin, H. Ozaki, *Microelectron. J.* **2003**, *34*, 607; l) P. Gorostiza, P. Allongue, R. Díaz, J. R. Morante, F. Sanz, *J. Phys. Chem. B* **2003**, *107*, 6454.
- [3] M. Aizawa, A. F. Cooper, M. Malac, J. M. Buriak, *Nano Lett.* **2005**, *5*, 815.
- [4] a) T. K. Sau, C. J. Murphy, *J. Am. Chem. Soc.* **2004**, *126*, 8648; b) F. Kim, S. Connor, H. Song, T. Kuykendall, P. Yang, *Angew. Chem.* **2004**, *116*, 3759; *Angew. Chem. Int. Ed.* **2004**, *43*, 3673; c) Z. Wei, F. P. Zamborini, *Langmuir* **2004**, *20*, 11301–11304; d) M. A. El-Sayed, *Acc. Chem. Res.* **2004**, *37*, 326; e) Y. D. Yin, R. M. Rioux, C. K. Erdonmez, S. Hughes, G. A. Somorjai, A. P. Alivisatos, *Science* **2004**, *304*, 711; f) M. A. El-Sayed, *Acc. Chem. Res.* **2001**, *34*, 257; g) Y. Yin, R. M. Rioux, C. K. Erdonmez, S. Hughes, G. A. Somorjai, A. P. Alivisatos, *Science* **2004**, *304*, 711; h) V. F. Puentes, D. Zanchet, C. K. Erdonmez, A. P. Alivisatos, *J. Am. Chem. Soc.* **2002**, *124*, 12874; i) E. Prodan, C. Radloff, N. J. Halas, P. Nordlander, *Science* **2003**, *302*, 419; j) S. Chen, Z. L. Wang, J. Ballato, S. H. Foulger, D. L. Carroll, *J. Am. Chem. Soc.* **2003**, *125*, 13186; k) C. Charnay, A. Lee, S.-Q. Man, C. E. Moran, C. Radloff, R. K. Bradley, N. J. Halas, *J. Phys. Chem. B* **2003**, *107*, 7327; l) T. K. Sau, C. J. Murphy, *Langmuir* **2004**, *20*, 6414; m) R. Jin, Y. Cao, C. A. Mirkin, K. L. Kelly, G. C. Schatz, J. G. Zheng, *Science* **2001**, *294*, 1901; n) Y. Sun, Y. Xia, *Science* **2002**, *298*, 2176; o) K. K. Caswell, C. M. Bender, C. J. Murphy, *Nano Lett.* **2003**, *3*, 667; p) V. Germain, J. Li, D. Ingert, Z. L. Wang, M. P. Pileni, *J. Phys. Chem. A* **2003**, *107*, 8717; q) C. Xue, Z. Li, C. A. Mirkin, *Small* **2005**, *1*, 513.
- [5] a) I. Yagi, S. Idojiri, T. Awatani, K. Uosaki, *J. Phys. Chem. A* **2005**, *109*, 5021; b) C. H. Wu, S. M. Liao, K. C. Chang, *Mater. Sci. Eng. B* **2005**, *117*, 205; c) W. P. Giziewicz, C. G. Fonstad, *J. Vac. Sci. Technol. A* **2002**, *20*, 1052; d) H. I. Chen, C. K. Hsiung, Y. I. Chou, *Semicond. Sci. Technol.* **2003**, *18*, 620.

- [6] L. A. D'Asaro, S. Nakahara, Y. Okinaka, *J. Electrochem. Soc.* **1980**, *127*, 1935.
- [7] J. A. Asencio, M. Pérez, M. José-Yacamán, *Surf. Sci.* **2000**, *447*, 73.
- [8] A. J. Mieszawska, F. P. Zamborini, *Chem. Mater.* **2005**, *17*, 3415.
- [9] P. L. Redmond, A. J. Hallock, L. E. Brus, *Nano Lett.* **2005**, *5*, 131.
- [10] L. A. Porter, A. E. Ribbe, J. M. Buriak, *Nano Lett.* **2003**, *3*, 1043.
- [11] H. Lim, C. Carraro, R. Maboudian, M. W. Pruessner, R. Ghodssi, *Langmuir* **2004**, *20*, 743.

Received: April 12, 2005

Published online on August 25, 2005