Fabrication of Metallic and Bimetallic Nanostructures by Electron Beam Induced Metallization of Surfactant Stabilized Pd and Pd/Pt Clusters

Manfred T. Reetz* and Martin Winter

Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1, D-45470 Mülheim/Ruhr, Germany

Günter Dumpich, Jens Lohau, and Stefan Friedrichowski

Laboratorium für Experimentelle Tieftemperaturphysik
Gerhard-Mercator-Universität Duisburg, Lotharstrasse 65
D-47048 Duisburg, Germany

Received January 7, 1997

Industrial lithography in microelectronics involves a multistep procedure with formation of micrometer-sized metallic patterns on surfaces.[1] In the quest for writing submicron features for this and other purposes, a variety of different approaches have been developed.[2] The manipulation of individual atoms of xenon or silicon by scanning tunneling microscopy (STM) are spectacular examples[3] but require complicated experimental procedures. STM and AFM (atomic force microscopy) have been utilized in yet other ways to fabricate nanometer-sized surface features such as lines or dots.[2,4] In what appears to be a fairly practical approach, direct writing of metallic features is also possible by irradiating thin films of organometallic materials with electron, ion, or photon beams, the written lines typically being about 100−200 nm wide.[2,5] Similar results are obtained by using organometallic precursors in the gas phase.[6] A new strategy involves the photolysis of thin films of $Cu_2(OH_2)_2(RCO_2)$, which triggers a radical-chain process with formation of copper-containing features having a line width of about 1000 nm.[7]

Here we describe a particularly simple three-step lithographic procedure based on electron beam irradiation of preformed surfactant-stabilized metal or bimetal clusters, the width of the corresponding metallic or bimetallic lines being as small as 30 nm.[8] We have previously shown that nanostructured $R_4N^+X^-$-stabilized metal clusters (e.g., Pd, Pt, Rh, Ru, Co, Ni, Fe, Cu) and related bimetallic clusters (e.g., Pd/Pt, Pd/Ni, Pt/Sn) are accessible in a clean and size-selective manner using electrochemical methods.[9] A monomolecular layer of the surfactant surrounds the metal core and thereby prevents agglomeration with undesired formation of metal powders.[10] We speculated that, following spin-coating of tetrahydrofuran (THF) solutions of such clusters onto GaAs substrates, electron beam irradiation would lead to the physical removal and/or destruction of the organic stabilizer, a process which should result in the agglomerization of the clusters with concominant formation of insoluble metallic features. Removal of the nonexposed soluble cluster-containing areas by simple rinsing was expected to complete the lithographic procedure (Scheme 1).

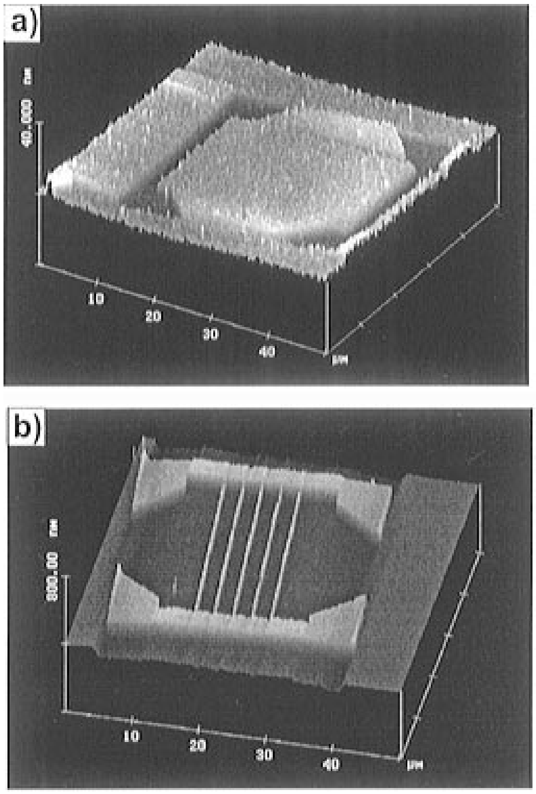
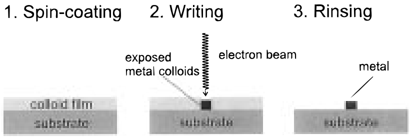


Figure 1. (a) AFM image of the exposed Pd colloid film. (b) AFM image of the exposed Pd colloid film after rinsing with THF.

Scheme 1



In an initial experiment a THF solution of a $(C_8H_{17})_4N^+Br^-$-stabilized 2.0-nm Pd cluster (69% metal content) at a concentration of 150 mg/mL was spin-coated onto a GaAs substrate (3.9 × 3.9 × 0.5 mm) to form a 132-nm-thick film having a surface roughness of about 1 nm. For the electron beam experiments a layout consisting of five lines and broad contact areas necessary for resistivity measurements was chosen. Using a conventional scanning transmission electron microscope (STEM) (operating at an acceleration voltage of 120 kV) equipped with an external computer-driven control system,[11] the film was irradiated with an electron beam at a dosage of 200 000 μC/cm^2. The AFM visualization of the surface shows that the exposed areas are reduced in height by about 5 nm (Figure 1a).

---

(1) (a) Reichmanis, E.; Thompson, L. F. *Chem. Rev.* **1989**, *89*, 1273. (b) Moreau, W. M. *Semiconductor Lithography: Principles, Practices, and Materials*; Plenum Press: New York, 1988.

(2) (a) Avouris, P., Ed. *NATO ASI Ser., Ser. E* **1993**, *239* (Atomic and Nanometer Scale Modification of Materials: Fundamentals and Applications). (b) Gentili, M.; Giovanella, C.; Selci, S., Eds. *NATO ASI Ser., Ser. E*, **1994**, *264* (Nanolithography: A Borderland between STM, EB, IB, and X-Ray Lithographies).

(3) (a) Eigler, D. M.; Schweizer, E. K. *Nature* **1990**, *344*, 524. (b) Lyo, I.-W.; Avouris, P. *Science* **1991**, *253*, 173.

(4) (a) Majumdar, A.; Oden, P. I.; Carrejo, J. P.; Nagahara, L. A.; Graham, J. J.; Alexander, J. *Appl. Phys. Lett*. **1992**, *61*, 2293. (b) Snow, E. S.; Campbell, P. M. *Appl. Phys. Lett.* **1994**, *64*, 1932.

(5) (a) $Pd(OAc)_2$ films: Gross, M. E.; Brown, W. L.; Harriott, L. R.; Cummings, K. D.; Linnros, J.; Funsten, H. *J. Appl. Phys.* **1989**, *66*, 1403. (b) $[Ir_4(CO)_{11}Br][NEt_4]$ films: Hoffmann, P.; van den Bergh, H.; Flicstein, J.; Assayag, G. B.; Gierak, J.; Bresse, J. F. *J. Vac. Sci. Technol., B* **1991**, *9*, 3483. (c) $Au_{55}[P(C_6H_5)_3]_{12}Cl_6$ films: Hoffmann, P.; Assayag, G. B.; Gierak, J.; Flicstein, J.; Maar-Stumm, M.; van den Bergh, H. *J. Appl. Phys.* **1993**, *74*, 7588. (d) Films of gold-containing polymers: Craighead, H. G.; Schiavone, L. M. *Appl. Phys. Lett.* **1986**, *48*, 1748. (e) Goldchloride in sulfurized terpenes: Ohmura, Y.; Shiokawa, T.; Toyoda, K.; Namba, S. *Appl. Phys. Lett*. **1987**, *51*, 1500.

(6) See for example: (a) Harriott, L. R.; Vasile, M. J. *J. Vac. Sci. Technol., B* **1988**, *6*, 1035. (b) Tao, T.; Ro, J. S.; Melngailis, J.; Xue, Z.; Kaesz, H. *J. Vac. Sci. Technol., B* **1990**, *8*, 1826. (c) Kunz, R. R.; Mayer, T. M. *Appl. Phys. Lett.* **1987**, *50*, 962.

(7) Avey, A. A.; Hill, R. H. *J. Am. Chem. Soc*. **1996**, *118*, 237.

(8) Reetz, M. T.; et al. Patent application DE-A-19618447.9, 1996.

(9) Reetz, M. T.; Quaiser, S. A. *Angew. Chem.* **1995**, *107*, 2461; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2240.

(10) Reetz, M. T.; Helbig, W.; Quaiser, S. A.; Stimming, U.; Breuer, N.; Vogel, R. *Science* **1995**, *267*, 367.

(11) An STEM instrument of the type CM12 (Philips) was used in combination with an electronic control element consisting of a computer, a digital signal processing board and two digital analog converters (SIETEC).

S0002-7863(97)00054-1 CCC: $14.00

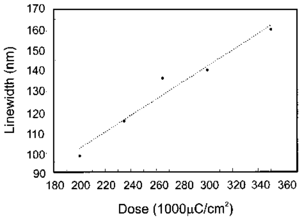


Figure 2. Correlation between the electron beam dosage and the line widths of a 180-nm-thick film of $(C_8H_{17})_4N^+Br^-$-stabilized Pd colloids.

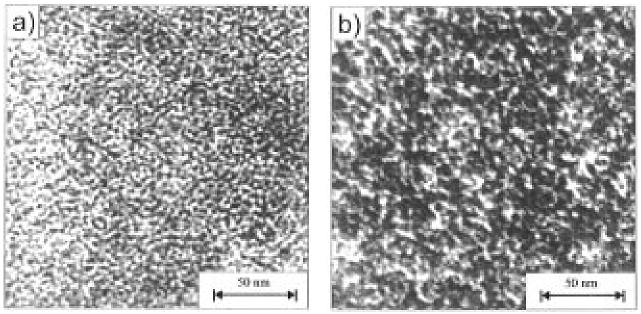


Figure 3. (a) TEM image of a part of a Pd line showing the granular structure with cluster agglomerates in the range 4−5 nm. (b) TEM image of a part of a Pd line after annealing (180 °C, 10 min) showing cluster agglomerates in the range 8−10 nm.

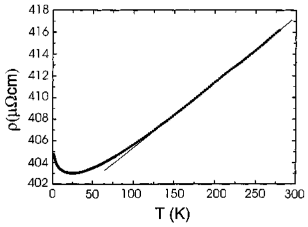


Figure 4. Temperature dependence of the resistivity of a Pd nanostructure.

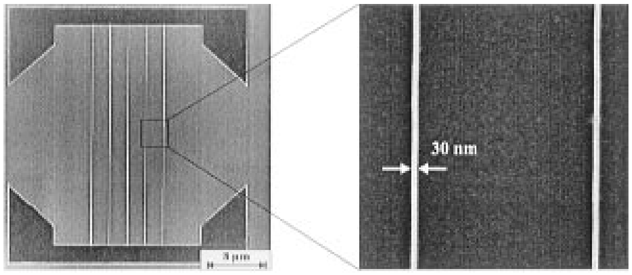


Figure 5. SEM image of a bimetallic Pd/Pt nanostructure.

The surface was then rinsed with THF and examined once more with AFM (Figure 1b). The five-line pattern is clearly visible, the height of the lines being 95 nm, i.e., 72% of the original film thickness. The SEM visualization shows fairly sharp lines which are 50 nm in width. Upon annealing of the sample (180 °C; $P = 1$ mbar; 2 h), the width of the written features remained more or less constant but the height was reduced to 67 nm.

In further experiments it was shown that the line width can be controlled by the electron beam dosage, which in turn can be adjusted by variation of the exposure time. All writing was performed using single exposures (Figure 2). With higher electron beam dosages (>350 000 µC/cm²) we obtained features having larger width and inaccurate lines due to the proximity effect. With very low electron beam dosages (<200 000 µC/cm²) the features were completely removed by the rinsing process. Under routine conditions (e.g., 132-nm-thick films, 200 000 µC/cm² dosage) line widths of about 50 nm are generally obtained.

To shed some light on the chemical and morphological changes that occur upon electron beam treatment and annealing, a surface feature produced by electron beam irradiation of a film composed of 2.5-nm $(C_8H_{17})_4N^+Br^-$-stabilized Pd clusters (79% metal content) was studied by transmission electron microscopy (TEM). To carry out such experiments, a different surface had to be used, namely carbon on sodium chloride. After spin-coating, irradiation, and rinsing, the NaCl was removed by dissolving in water and the feature-carrying carbon film was placed on a standard TEM grid. Following TEM analysis, the same sample was annealed in situ (180 °C, 10 min). The results show that electron beam exposure causes the original 2.5-nm clusters to agglomerate to larger entities in the range 4−5 nm (Figure 3a). TEM visualization of the annealed sample reveals that further agglomeration with formation of particles in the range 8−10 nm has occurred (Figure 3b).

To test the metallic character of the written lines, the electrical conductivity was measured using a four-point probe. The specific resistivity ρ of a nanostructure of a type shown in Figure 1 turned out to be 1928.5 $\mu\Omega$ cm at room temperature, which is about 2 orders of magnitude higher than that of bulk Pd. It is thus likely that the nanostructures are porous and contain organic material. Indeed, after annealing, the specific resistivity at room temperature was reduced by a factor of 10 ($\rho = 181$ $\mu\Omega$ cm). Although the material probably still contains carbon, the nanostructures are clearly metallic in nature. The temperature dependence of the specific resistivity was determined using a low-quality sample containing Pd lines having a *high* ρ-value at room temperature ($\rho = 417$ $\mu\Omega$ cm after annealing). Accordingly, above 125 K, resistivity increases linearly with increasing temperature, a clear indication that even this particular contaminated sample has metallic character (Figure 4).

The written Pd features, which can also be fabricated using halogen-free ammonium salt stabilized clusters,[9,12] offer the possibility of nanoscale coating with copper using electroless plating. A different and general strategy for writing bimetallic lines is possible by using bimetallic clusters[9] in the present electron beam lithography. For example, a $(C_8H_{17})_4N^+Br^-$-stabilized Pd/Pt bimetallic cluster (2.5 nm; Pd: 27%; Pt: 18%) was used in an analogous manner, leading to bimetallic lines having a width of 30 nm (Figure 5).

In summary, the use of preformed metallic and bimetallic $R_4N^+X^-$-stabilized clusters in electron beam induced metallization constitutes a simple nanoscale lithographic procedure which circumvents the need for metal vaporization. The advantages include simplicity, variability concerning the nature of the metal, and easy fabrication of bimetallic features, line widths as small as 30 nm currently being routine. In addition to potential applications in conventional areas, the written metallic features described herein may be useful as masters in replica molding,[13] i.e., in the mass production of nanostructures.[13,14]

JA970054H

---

(12) Reetz, M. T.; Helbig, W.; Quaiser, S. A. In *Active Metals: Preparation, Characterization, Applications*; Fürstner, A., Ed.; VCH: Weinheim, 1996; pp 279−297.

(13) Xia, Y.; McClelland, J. J.; Gupta, R.; Qin, D.; Zhao, X.-M.; Sohn, L. L.; Celotta, R. J.; Whitesides, G. M. *Adv. Mater.* **1997**, *9*, 147.

(14) Chou, S. Y.; Krauss, P. R.; Renstrom, P. J. *Science* **1996**, *272*, 85.