

Printing of Nanoparticles with Sub-100 nm Resolution

Chad R. Barry, Aaron M. Welle, Jie Gu, Heiko O. Jacobs, and Stephen A. Campbell

Department of Electrical and Computer Engineering, University of Minnesota

Abstract: This article reports on the electrostatic driven self-assembly of nanoparticles onto charged surface areas (receptors) with sub-100 nm resolution from the gas-phase. The charged areas were fabricated using an electric nanocontact printing method that employs a flexible, electrically conductive electrode to pattern electrons and holes in a thin film electret. As electrodes, we used 10 micrometer thick doped silicon wafers carrying a pattern in topography. Areas as large as 1 square centimeter were patterned with charge with 100 nanometer resolution in 10 seconds. A transparent particle assembly module was used to direct and monitor the assembly of organic and inorganic nanoparticles generated from an electrospraying and an evaporative process. Assembly was accomplished with sub-100 nm resolution.

1. Introduction: Nanoparticles can provide a variety of functions and are considered to be the fundamental component of future nanotechnological devices. Nanoparticles are typically created in the gas or liquid-phase. Most well known techniques include metal evaporation, laser ablation, solution vaporization, wire explosion, pyrolysis, colloidal and electrochemical synthesis, and generation from plasmas. Silicon nanoparticles generated by silane pyrolysis or electrochemical reaction of hydrogen-fluoride with hydrogen-peroxide have been used for non-volatile memories^[1], lasers^[2], and biological markers^[3]. Evaporated gold^[4], indium^[5], and ion sputtered aluminum^[6] nanoparticles have been used for single electron transistors; and electron beam evaporated gold and silver particles have been used for plasmonic waveguides^[7]. The ability to position nanoparticles onto specific locations is the key to making these devices. Most actively studied approaches include: i) single particle manipulation^[8], ii) random particle deposition^[5], and iii) parallel particle assembly based on self-assembly^[9-16]. The requirement of high-yield and high-speed assembly makes methods such as single particle manipulation and random particle deposition unsuitable.

As a new direction, we have developed a parallel charge patterning process enabling nanoxerographic printing^[16-19]. The charge patterning technique, referred

to as electric nanocontact printing, generates a charge pattern based on the same physical principles used in scanning probes but forms multiple electric nanocontacts of different size and shape to transfer charge in a single step. With this method, we demonstrated patterning of charge with 100 nm scale resolution and transfer of 50 nm to 20 μm sized particles including silver, gold, indium, iron oxide, graphitized carbon, iron beads, and Xerox toner from a powder, gas, and liquid phase^[16-19]. This article reports on new concepts to position organic and inorganic materials. An increase in resolution is demonstrated using flexible thin silicon electrodes that contain sub-100nm features. An assembly resolution of 60nm was achieved using an evaporative gas-phase process and 200nm resolution was accomplished using an electrospraying process.

2. Experimental: The electric nanocontact printing process to generate charge patterns is illustrated in Figure 1. We developed flexible, thin silicon electrodes to accomplish higher resolution charge transfer than what has been possible with previous methods^[16, 17]. The electrode was made from a 2 inch in diameter, 10 μm thick, n-doped silicon wafer (Virginia Semiconductors) supported on a Au coated flat slab of PDMS. The PDMS support was coated with a 50 nm thick layer of gold by thermal evaporation to provide electrical conductivity to the back side of the thin silicon wafer. The thin silicon electrode is sufficiently conductive and does not require a metal coating on the front side. The topographical features in the thin silicon electrodes were generated using phase-shift photo lithography^[20] and reactive-ion etching. In brief, PDMS stamps with 1 μm wide and 400 nm deep surface relief patterns were placed on the thin silicon surface that was coated with a 500 nm thick Shipley 1805 photoresist. The surface was exposed with ~436 nm UV light for 1.5 seconds (Karl Suss MA-6 aligner) and developed in (1:5) volume-ratio solution of 351 developer and H₂O for 20 seconds. The resulting photoresist features are 100 nm wide lines and rings that are 150 nm high. The features are then transferred into the thin silicon substrate by reactive-ion etching for 45 seconds in a 98% CF₆, 2% O₂ plasma. Due to the

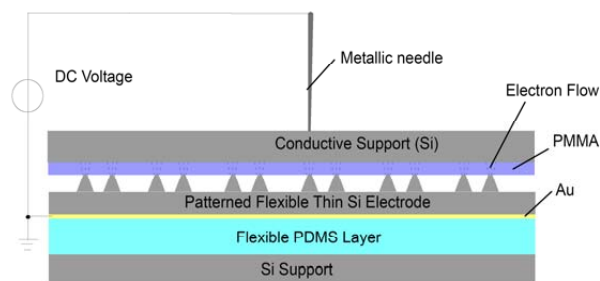


Figure 1: Principle of the electric nanocontact printing process: A silicon chip carrying a thin film electret is placed on top of a thin silicon electrode supported by a flexible PDMS layer on a standard silicon wafer. A needle, attached to a micromanipulator is used to form an electric contact to the backside of the silicon chip. An external voltage is used to transfer a pattern of charge into the electret material at the areas of contact. The silicon chip is removed with the electret carrying a charge pattern.

removal of photoresist from both the top and the sides, the width of the produced pattern on the silicon surface continuously shrinks during the etching and results in tapered silicon structures. The remaining photoresist is stripped off by acetone and reactive ion etching in an oxygen plasma (320 STS etcher) for 120 seconds. The tapered silicon structures were 50 nm wide at the surface and 60 nm tall.

As the charge storage medium, we used a 60 nm thick film of PMMA on <100> silicon wafers. The film was formed by spin coating a 2% solution of 950 K (PMMA) in chlorobenzene (MicroChem Co.) at 5000 rpm and baking it in an oven at 90 °C for 1 hour. The chips were placed on the flexible electrode by hand and contacted from the back with a metallic needle attached to a micromanipulator. The micromanipulator was used to adjust the needle's position and provide pressure to establish contact between the electrode and PMMA thin film. An external voltage of 10V~20V was applied for 30 seconds to generate a constant current of 1mA~5mA. After exposure, we removed and characterized the charge patterns using Kelvin Probe Force Microscopy (KFM).^[21, 22]

The nanoxerographic processes used to direct the assembly of nanoparticles onto the charge patterned chips are illustrated in figure 2. The evaporative gas-phase assembly process uses a tube furnace (Fig. 2A) that generates the nanoparticles by evaporation and condensation. The material to be evaporated is placed inside the quartz tube at the center of the furnace. Ultra pure argon is the carrier gas that flows through the system during operation. The evaporation was carried out at 1100 °C. A vapor containing atoms of the

evaporated material forms within the furnace. The argon carrier gas transports the atoms out of the furnace where they nucleate and condense into particles due to the change in temperature. The gas flow carries the nanoparticles into the particle assembly module through a 1-meter long Tygon tube.

The electrospraying assembly process (Fig. 2C) uses an electrospraying device to produce an aerosol of organic nanoparticles. The electrospraying system will be published separately. In brief, the organic material to be assembled is suspended in buffer solution, ultra pure water, or ethanol depending on the material. A platinum electrode wire, intertwined with a silica capillary, is inserted into the vial after being placed in a sealed chamber of the electrospray apparatus. The chamber pressure is increased to approximately 10psi and a potential of 0-5kV is applied to the platinum electrode. The pressure difference forces the solution up through the capillary and out to the tip. The applied potential is adjusted until a cone jet mode is achieved that releases a stream of <1µm sized droplets. A sheath gas mixture of compressed air and CO₂ carry the electrosprayed material from the capillary tip through a neutralization chamber and into a tube connected to the particle assembly module. The droplets evaporate as they travel through the neutralization chamber and are neutralized by a Polonium 210 alpha source forming an aerosol of organic nanoparticles containing only a few elementary charges.^[23, 24]

The two assembly processes use a particle assembly module (Figs. 2B

,D) to accomplish the directed assembly of nanoparticles. The assembly module consists of a cavity that holds the sample, two electrodes to generate a global electric field that directs incoming charged particles towards the sample surface, and an electrometer to count the charge of the assembled particles.^[18]

To direct the assembly of incoming charged particles we integrated two electrodes into the transparent assembly module. During operation, the electrodes are spaced by 5-7 mm and we apply an external voltage of up to ±1000V to bring charged particles of one polarity into the proximity of the charged sample surface. To monitor the amount of particles that assembled onto the sample under different assembly conditions we implemented a faraday cup in the assembly module. In our faraday cup arrangement, the sample forms the cup electrode and is connected to ground with the electrometer (Keithley 6517A) in between. During assembly, image charges flow from the ground through the electrometer into the sample to the location of assembled, charged particles. As a result, the electrometer measures the accumulated charge of the assembled particles.

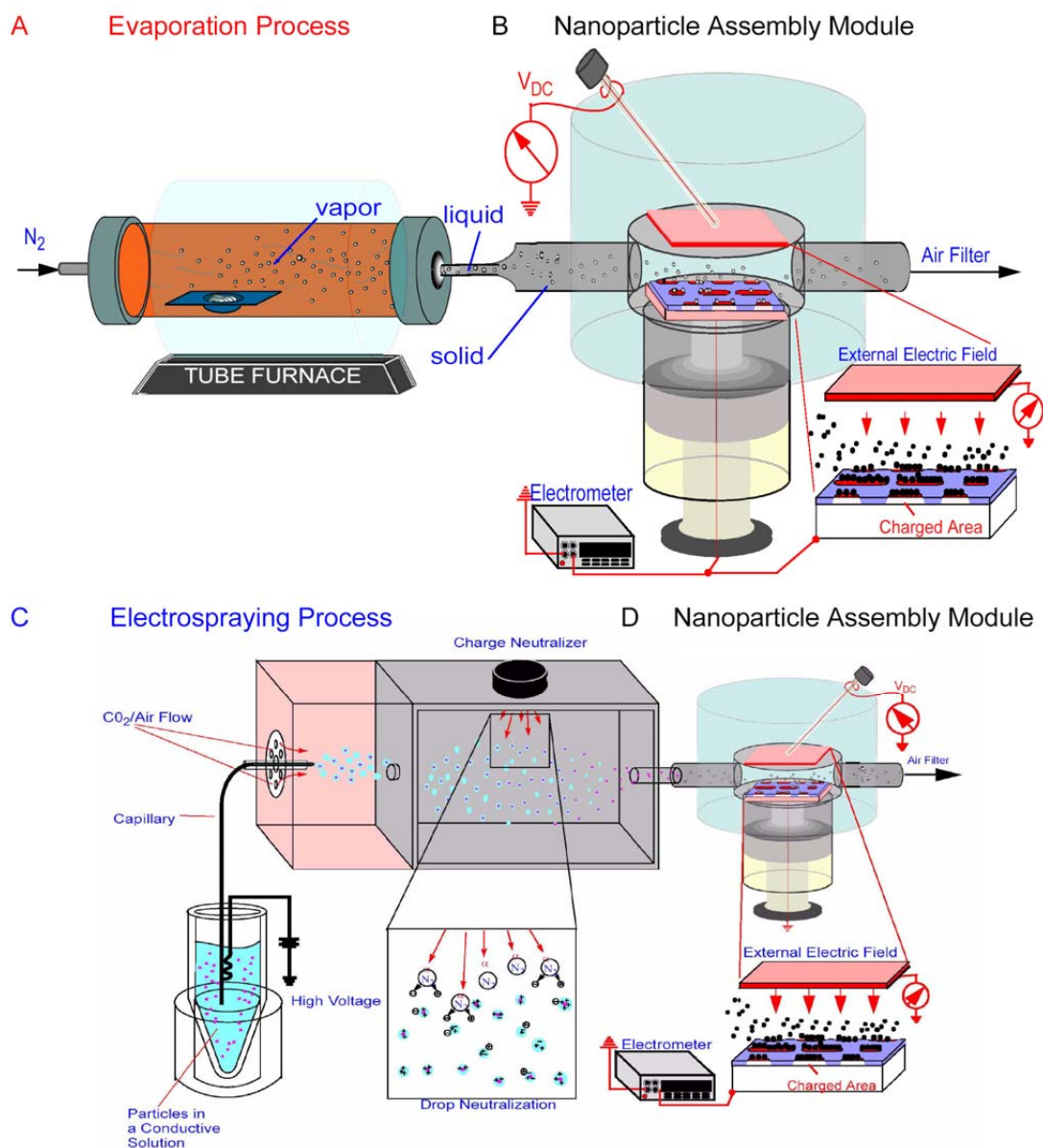


Figure 2: Principle of nanoxerographic printing from the gas phase. (A) *Evaporative Process*: A constant flow of nanoparticles is generated by evaporation of matter in the tube furnace, transport of the atoms to the outlet by the N_2 gas, and condensation. (C) *Electro spraying Process*: An organic solution flows from a vial through a capillary tube into a neutralization chamber by a pressure differential and applied potential. Droplets form, neutralize, evaporate, and then exit the system as an aerosol of nanoparticles. (B,D) *Assembly Module*: The directed assembly of the nanoparticles occurs in the particle assembly module. An external potential, V_{DC} , applied to the top electrode directs incoming nanoparticles to the charged sample surface. The electrometer measures the amount of assembled, charged particles during the assembly process.

3. Results and Discussion: Representative patterns of localized charge in PMMA, patterned using thin silicon electrodes and recorded by KFM are illustrated in Figure 3. Fig. (3A) shows the recorded surface potential distribution for a surface that was patterned with hollow

squares made from 230 nm (FWHM) wide lines. Fig. (3B) shows 300 nm wide parallel lines.

The resolution of the charge pattern that is obtained in Kelvin probe depends heavily on the AFM tip geometry and tip condition. Over the course of this investigation we have observed that the minimal width

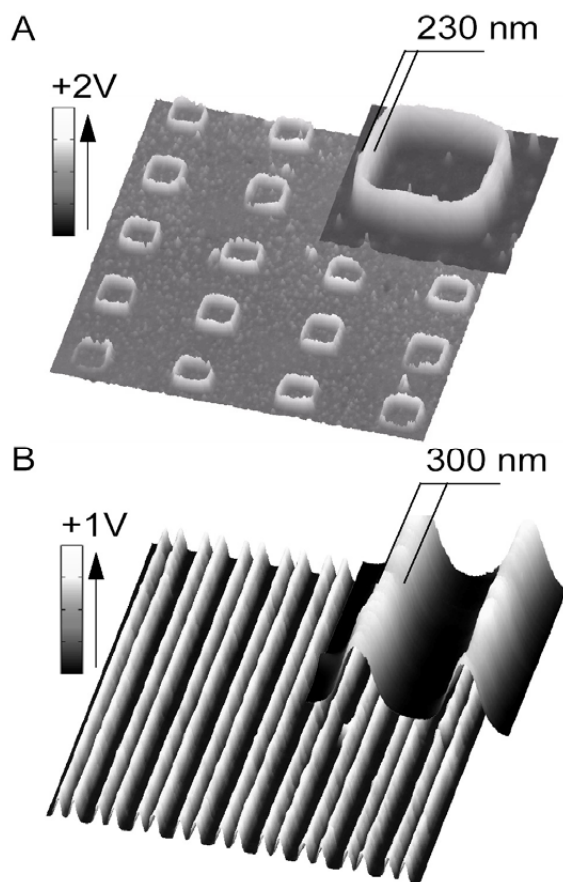


Figure 3: (A) Kelvin probe force microscopy image of 300 nm (FWHM) positively charged parallel lines generated using a thin silicon electrode. (B) Scanning electron microscopy image of 50 nm wide lines extending from the surface of a thin silicon electrode.

of the recorded charge patterns is not limited by the feature size of the electrode but by the AFM tip itself. For similar charge patterns we have observed feature sizes that range from 150 nm to 300 nm with different AFM probes. In general the resolution of the recorded potential image is larger than the resolution of the actual electrode structure, charge pattern, and the particle assembly result. An explanation for this can be found by investigating the influence of AFM tip geometry on the potential distribution. We have calculated the influence of the tip geometry on the potential distribution.^[15] The measured distribution is a two dimensional convolution of the actual surface potential distribution with the transfer function of the tip. Commercially available tips currently limit the resolution to be larger than 100 nm. Even a single elementary charge will show up as a bell curve that is

50-100 nm wide.^[15] Nanoparticles might be the best probe to reveal the actual surface charge resolution.

This hypothesis is confirmed in Fig. 4, where nanoparticles have been assembled at a resolution equal to that of the fabricated thin silicon electrodes. Fig. (4A) is a scanning electron microscope (SEM) image of a thin silicon electrode containing 50 nm wide lines extending from the surface. Fig. (4B) shows a representative image of nanoxerographic printing of nanoparticles from the gas-phase by the evaporative method. The image contains 60 nm wide lines of silver nanoparticles trapped at areas patterned with charge using the thin silicon electrode shown in Fig. (4A).

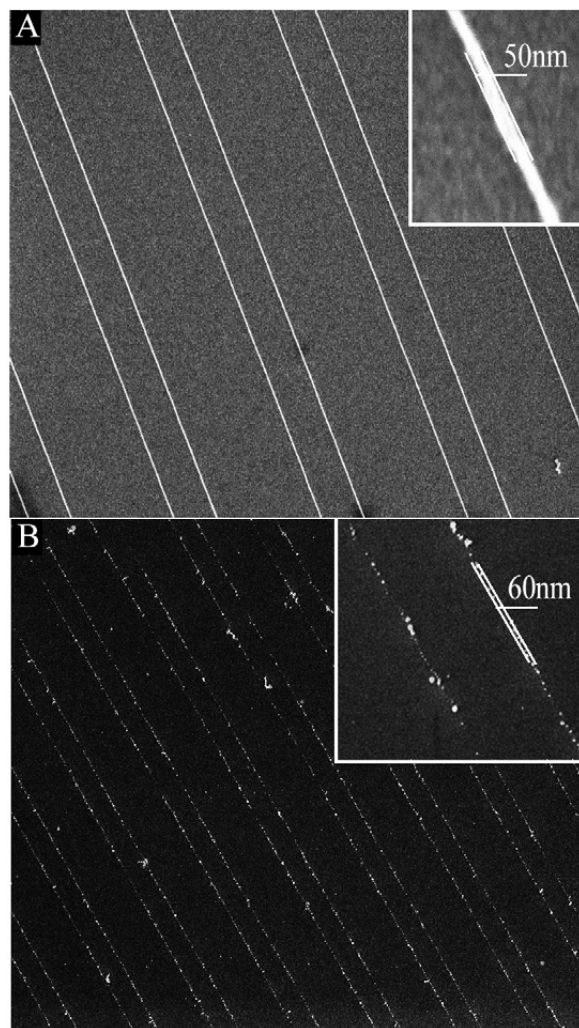


Figure 4: (A) An SEM image of a thin silicon electrode containing 50nm wide lines extending from the surface. (B) An SEM image of 60 nm wide lines of silver nanoparticles assembled using the evaporation system.

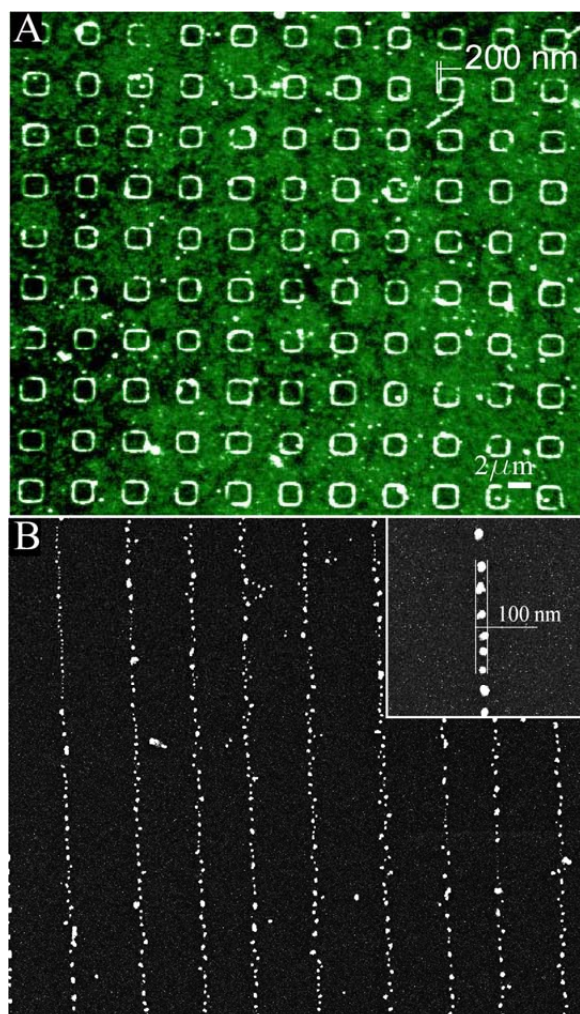


Figure 5: Images of organic materials assembled using the electrospraying system. (A) A fluorescence microscope image of $2\ \mu\text{m}$ squares made from 200 nm wide protein coated lines. (B) An SEM image of 100 nm wide lines of protein coated colloidal gold nanoparticles.

Organic materials were also assembled onto patterns generated with the thin silicon electrodes. Fig. 5 shows the assembly of organic materials from the gas-phase by the electrospraying method. The fluorescence microscope image shown in Fig. (5A) depicts $2\ \mu\text{m}$ squares made up of 200 nm wide protein coated lines. Fig. (5B) is an SEM image of protein coated colloidal gold nanoparticles assembled onto 100 nm wide lines of charge.

4. Conclusion: In conclusion, we have demonstrated the use of electric nanocontact printing for the purpose of high resolution self-assembly of nanoparticles. A

resolution of 60 nm has been achieved using the thin silicon electrodes as a patterning tool. We have also introduced a new method to print organic materials by electrospraying. To enable the fabrication of novel devices such as nanoparticle transistors and LEDs we need to increase the control of the amount of particles that are being deposited. We are confident that this control is possible by adjusting the charge on the particles.

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REFERENCES

- [1] M. L. Ostraat, J. W. De Blauwe, M. L. Green, L. D. Bell, M. L. Brongersma, J. Caspersen, R. C. Flagan, H. A. Atwater, *Applied Physics Letters* **2001**, 79, 433.
- [2] M. H. Nayfeh, S. Rao, N. Barry, J. Therrien, G. Belomoin, A. Smith, S. Chaieb, *Applied Physics Letters* **2002**, 80, 121.
- [3] G. Belomoin, J. Therrien, A. Smith, S. Rao, R. Twesten, S. Chaieb, M. H. Nayfeh, L. Wagner, L. Mitas, *Applied Physics Letters* **2002**, 80, 841.
- [4] C. Thelander, M. H. Magnusson, K. Deppert, L. Samuelson, P. R. Poulsen, J. Nygard, J. Borggreen, *Applied Physics Letters* **2001**, 79, 2106.
- [5] T. Junno, M. H. Magnusson, S.-B. Carlsson, K. Deppert, J.-O. Malm, L. Montelius, L. Samuelson, *Microelectronic Engineering* **1999**, 47, 179.
- [6] T. W. Kim, D. C. Choo, J. H. Shim, S. O. Kang, *Applied Physics Letters* **2002**, 80, 2168.
- [7] S. A. Maier, M. L. Brongersma, P. G. Kik, S. Meltzer, A. A. G. Requicha, H. A. Atwater, *Advanced Materials (Weinheim, Germany)* **2001**, 13, 1501.
- [8] C. Baur, A. Bugacov, B. E. Koel, A. Madhukar, N. Montoya, T. R. Ramachandran, A. A. G. Requicha, R.

- Resch, P. Will, *Nanotechnology* **1998**, 9, 360.
- [9] W. A. Lopes, H. M. Jaeger, *Nature* **2001**, 414, 735.
- [10] J. Janin, *Progress in Biophysics & Molecular Biology* **1995**, 64, 2.
- [11] C. M. Niemeyer, B. Ceyhan, S. Gao, L. Chi, S. Peschel, U. Simon, *Colloid & Polymer Science* **2001**, 279, 68.
- [12] P. D. Yang, A. H. Rizvi, B. Messer, B. F. Chmelka, G. M. Whitesides, G. D. Stucky, *Advanced Materials* **2001**, 13, 427.
- [13] C. Petit, A. Taleb, M. P. Pileni, *Advanced Materials* **1998**, 10, 259 ff.
- [14] W. M. D. Wright, D. G. Chetwynd, *Nanotechnology* **1998**, 9, 133.
- [15] H. O. Jacobs, A. Stemmer, *Surface & Interface Analysis* **1999**, 27, 361.
- [16] H. O. Jacobs, G. M. Whitesides, *Science* **2001**, 291, 1763.
- [17] H. O. Jacobs, S. A. Campbell, M. G. Steward, *Advanced Materials* **2002**, 14, 1553.
- [18] C. R. Barry, N. Z. Lwin, W. Zheng, H. O. Jacobs, *Applied Physics Letters* **2003**, 83, 5527.
- [19] C. R. Barry, M. G. Steward, N. Z. Lwin, H. O. Jacobs, *Nanotechnology* **2003**, 14, 1057.
- [20] T. W. Odom, J. C. Love, D. B. Wolfe, K. E. Paul, G. M. Whitesides, *Langmuir* **2002**, 18, 5314.
- [21] H. O. Jacobs, H. F. Knapp, S. Muller, A. Stemmer, *Ultramicroscopy* **1997**, 69, 39.
- [22] H. O. Jacobs, P. Leuchtman, O. J. Homan, A. Stemmer, *Journal of Applied Physics* **1998**, 84, 1168.
- [23] B. Y. H. Liu, D. Y. H. Pui, B. Y. Lin, *Particle Characterization* **1986**, 3, 111.
- [24] D. Covert, A. Wiedensohler, L. Russell, *Aerosol Science and Technology* **1997**, 27, 206.