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Formation of Submicrometer Patterns by Crystallization from Solution

E. W. Kuipers,* C. Doornkamp,
W. Wieldraaijer, and R. E. van den Berg

Koninklijke/Shell-Laboratorium, Amsterdam
Shell Research B.V., Badhuisweg 3
1031 CM Amsterdam, The Netherlands

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Submicrometer features can be either sculptured out of bulk material or built atom by atom from scratch.[1] Since obviously building "atom-up" can be done in a more subtle way than cutting "bulk-down", it is expected that better control at the nanometer level can be attained via the former approach.[2] "Atom-up" techniques are commonly used for the preparation of heterogeneous catalysts, where clusters are crystallized from solution and deposited onto a support. Various techniques have been developed to control the size of these clusters at the nanometer level, but in catalyst preparation the pattern of deposition is not controlled. However, pattern control might be achieved by crystallization on spatially defined foundation sites.[1] Examples of such template-directed processes can be found in biomineralization.[3,4] In the study at hand we have been able to control the pattern of Cu crystallization from solution by a substrate modification using polymers. In this way lines with a width of 0.1 μm can be obtained.

We have studied the deposition of Cu onto flat supports by crystallization of $Cu(NO_3)_2$ from a *n*-butanol solution. At 573 K this $Cu(NO_3)_2$ can be decomposed in air into CuO and subsequently reduced with H_2 to metallic Cu.[5] Polished single-crystalline Si wafers (Si(100)) are used as supports. Since the wafers had not been etched, the outermost atomic layers consisted of amorphous silica.[6] Deposition of copper onto these supports can be achieved by coating the wafer with a $Cu(NO_3)_2$/*n*-butanol solution. The solvent will evaporate, leaving crystals of Cu salt on the support. The particles thus obtained vary widely in size and are unevenly distributed over the wafer. However, monodisperse $Cu(NO_3)_2$ particles that are evenly distributed over the whole wafer, can be obtained if during evaporation of the solvent the wafer is spun.[7] In this case the solvent will form a fixed thin film of uniform thickness within a fraction of a second due to the balance between the shear force and the centrifugal force.[8] This fixed liquid film will slim down within a few seconds by evaporation, leaving the salt behind as monodisperse particles evenly distributed over the support. In Figure 1 an optical dark-field microscopy (DFM) image is shown of a sample made by "spin deposition" from a (0.62 wt %) $Cu(NO_3)_2 \cdot 2.5H_2O$/*n*-butanol solution at 2000 rpm. The particle density and diameter are determined by the rate of concentration increase at the nucleation point. For spin deposition this rate depends on the spinning frequency and the initial concentration of the solution. Since the size of the deposited particles decreases with spinning frequency and increases with the initial concentration, it can be controlled over several orders of magnitude.[7]

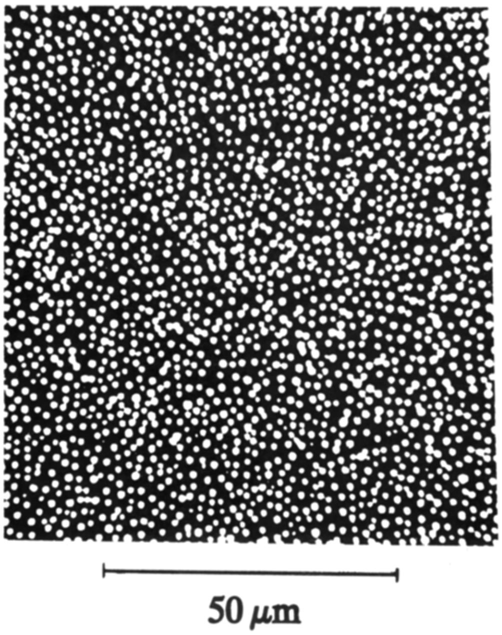

Figure 1. Optical dark-field microscopy image of $Cu(NO_3)_2$ particles spin deposited on Si with a 0.62 wt % solution of $Cu(NO_3)_2 \cdot 2.5H_2O$ in *n*-butanol at 2000 rpm spinning frequency.

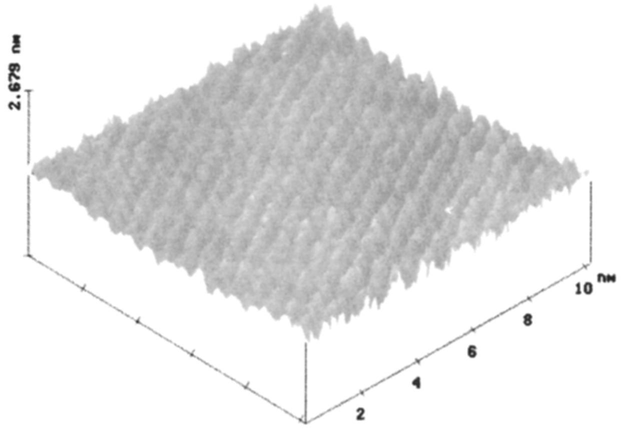

Figure 2. Atomic force microscopy image of a layer of aligned PTFE strings applied on a Si wafer by rubbing with a PTFE rod.

Although particle number density and size can be controlled by spin deposition, we cannot control the deposition pattern in this way. We have tried to obtain a specific nucleation pattern by modifying the support. Prior to deposition the Si wafer was rubbed with a rod of poly(tetrafluoroethylene) (PTFE). When PTFE is drawn across a smooth surface in one direction, the friction produces highly ordered and aligned thin strings of PTFE.[9] The amount of deposited PTFE increases with the temperature and pressure at which the PTFE rod is rubbed along the surface. In Figure 2 an atomic force microscopy (AFM) image of a fully PTFE covered Si surface is shown, revealing polymer strings perfectly aligned along the stroke direction. The string distance is 0.56 nm, in agreement with the spacing observed for bulk crystalline PTFE.[10] A

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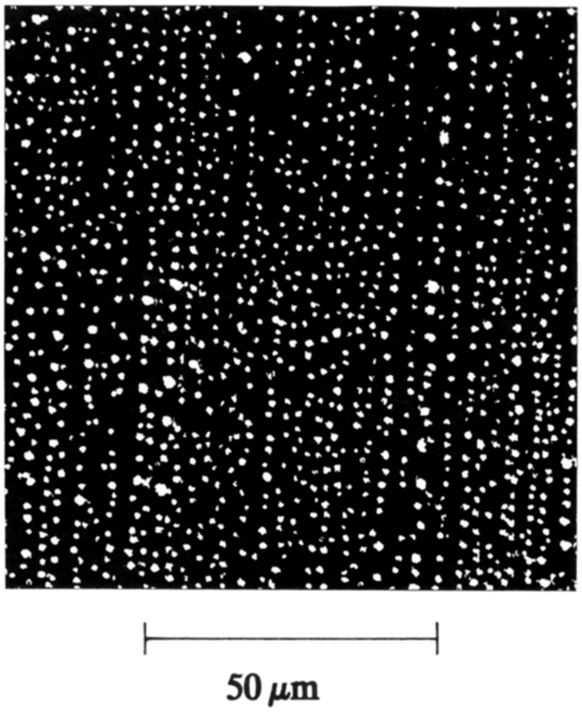

Figure 3. Optical dark field microscopy image of $Cu(NO_3)_2$ particles spin deposited on Si coated with aligned PTFE using a 0.29 wt % solution of $Cu(NO_3)_2{\cdot}2.5H_2O$ in *n*-butanol at 2000 rpm spinning frequency.

similar AFM image has been previously obtained by the group of Hansma.[11] Smith et al. have used such aligned PTFE coatings for the crystallization of polymers and organic compounds.[12] We would like to use such a modified surface to control the deposition pattern of Cu precursor. However we will use not a full but only a low coverage of PTFE obtained by gently rubbing a room-temperature wafer. The coverage is that low, that separated strings will have been applied.[11] We have not been able to trace these isolated strings with AFM. Subsequently, $Cu(NO_3)_2$ was spin-deposited from *n*-butanol solution on such a PTFE-treated wafer. A DFM image of a typical result is shown in Figure 3. In this figure it can be seen that instead of the random distribution of particles obtained on an untreated Si wafer (Figure 1), deposition on the PTFE-coated wafer results in straight rows of particles. The $Cu(NO_3)_2$ particles have apparently decorated the aligned polymers. This is believed to be caused by a reduced nucleation energy barrier at the polymer edges, since at these sites less of the nucleus is exposed to the liquid. Thus, nucleation at the edge between the polymer and the SiO_2 surface occurs at a lower supersaturation than nucleation on the plain SiO_2 surface. After nucleation at some edge between PTFE and SiO_2, the growth of this nucleus will reduce a further concentration increase in its environment, making a second nucleation on the plain SiO_2 surface in its vicinity impossible. Decoration of polymers has previously been observed for deposition of

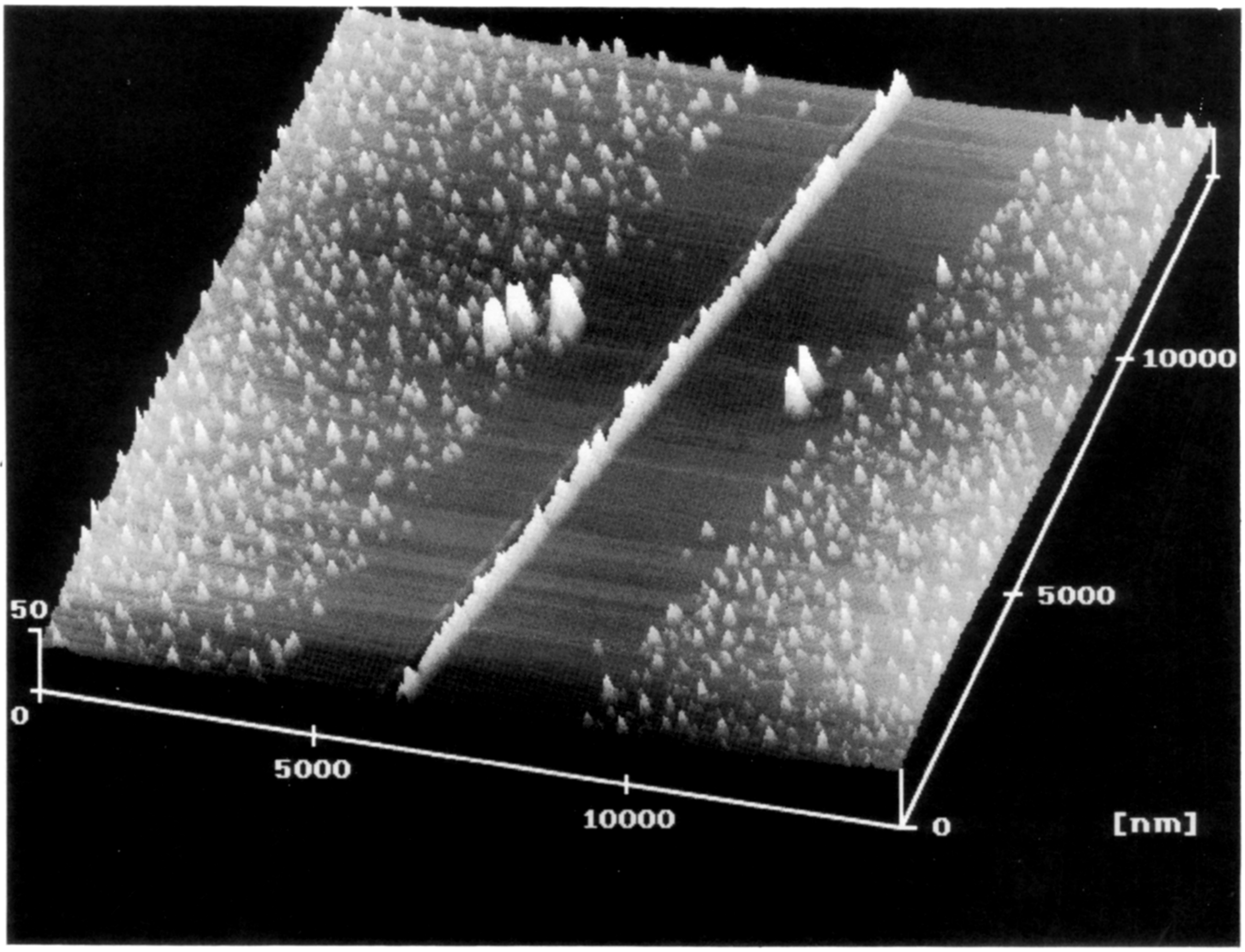

Figure 4. Atomic force microscopy image of a Cu line obtained by spin deposition of a 0.1 wt % solution of $Cu(NO_3)_2{\cdot}2.5H_2O$ in *n*-butanol at 4000 rpm spinning frequency on a PTFE coated Si wafer; the $Cu(NO_3)_2$ is subsequently decomposed in air at 573 K and reduced to copper in a H_2 flow at 573 K.

various metals from the vapor phase. This phenomenon has even been utilized in electron microscopy to make steps of a few angstroms observable.[13]

On the sample shown in Figure 3 separate particles can be distinguished. If, however, the nucleation density at the polymer edge could be increased, one would expect that during growth eventually the particles would coalesce and form a continuous line. As stated before, with spin deposition the nucleation density can be easily increased by either an increase of spinning frequency or a decrease of the initial concentration.[7] In an attempt to obtain a higher nucleation density than in the previous samples, we have spin deposited a 0.1 wt % solution on a PTFE-treated Si wafer at 4000 rpm. An AFM image of a sample thus obtained is shown in Figure 4. Here one can see that indeed a continuous straight line has been formed and that it is made up of many small particles which are merged together. The lines extend over several mm's and, depending on the nucleation density, can have widths of less than 0.1 μm. It should be mentioned, however, that there are strong fluctuations in the width and quality of the lines. This is believed to be caused by a poor control of the morphology of the polymer strings.

As stated earlier, in the vicinity of the strings all of the Cu precursor is deposited alongside the polymer. The depletion of precursor along the polymer is believed to cause denuded zones at both sides of the line. Further away, the particles will be deposited randomly on the plain surface, as usual. Both features are clearly observable in Figure 4.

In summary, site-specific deposition of a dissolved Cu salt can be achieved by a modification of the support with polymers. In this way pattern control at the submicrometer level is possible and Cu lines with a width of 0.1 μm can be formed.

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