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Local Current-Activated Growth of Individual Nanostructures with High Aspect Ratios

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The development of vertical nanoelectronics is hindered by limited control over the growth of nanostructures in specific directions. A scanning tunneling microscopy tip was used as a guide to locally consolidate individual nanoparticles and grow metallic nanopillars with high aspect ratios. Consolidation from random agglomerates occurs through electromigration and diffusion in a temperature gradient. The results of this study provide a new avenue for the controlled growth of complex metallic nanostructures for future three-dimensional architectures.

Keywords: Sintering, *In situ* Transmission Electron Microscopy, Nanoparticles, Crystal Growth

Introduction Local directional control of the growth of nanomaterials remains a great challenge faced by the materials community for the development of novel three-dimensional devices with enhanced performance.[1,2] The architecture of complex vertical electronics is difficult to obtain with current methods for manufacturing. Hence, there is a need for new strategies. The growth of one-dimensional nanostructures is one of the most promising fields to achieve these goals.[3–6] Although it is relatively simple to grow nanowires by strategic placement of surface catalysts, the control of their shape and direction during growth remains a major challenge.[7,8] Atom-by-atom deposition is one possibility to synthesize nanowires with designed patterns.[9] However, the time required for high-quality depositions is relatively long, and more robust techniques are desirable.[10] Sintering is an established field for materials densification that has recently been revitalized due to the promising effects of electric fields on decreasing processing temperatures.[11–13] During sintering, particle consolidation is enabled by thermally activated neck formation between individual particles. Necking can, however, also be triggered at lower temperatures through the application of an electrical bias. The mechanisms of enhanced mass transfer in the presence of an electrical field remain

unclear.[14] For electrically conducting materials, local Joule heating of particle contact areas can enhance local diffusion and hence promote neck formation.[14] Morsi et al. have demonstrated local current-activated sintering within compacted powder agglomerates underneath a moving conducting tip.[15] Here, we present a new technique to locally grow one-dimensional structures with a high aspect ratio by using an electrically biased scanning tunneling microscopy (STM) probe to induce directional sintering upon contact with nanoparticles.

Results and Discussion Nickel nanoparticles with an average diameter of 20 nm were drop-casted onto a holey amorphous carbon film on transmission electron microscopy specimen grids. Inside the scanning transmission electron microscope (STEM), a DC electrical bias was directly applied to nickel nanoparticle agglomerates. The electrical circuit was set up such that an STM tip mounted on the transmission electron microscopy (TEM) sample holder acted as the positive electrode while the specimen grid served as the negative electrode connected to the microscope ground (cf. Figure 1(a)). Figure 1(b) shows a bright field STEM image of one of the particle agglomerates. A constant DC voltage of +2.5 V was applied to the STM tip for approximately

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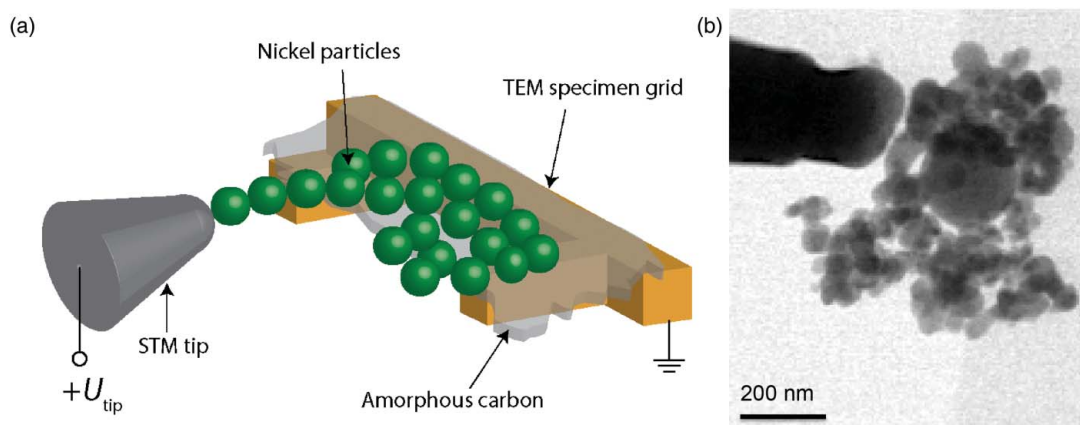


Figure 1. Sketch of the experimental setup. (a) An STM tip mounted on a TEM specimen holder is contacting an agglomerate of nickel nanoparticles mounted on an amorphous carbon support film. The TEM specimen grid serves as a second electrode connected to the microscope ground. (b) STEM bright field image of the nickel agglomerate in close contact to the STM tip.

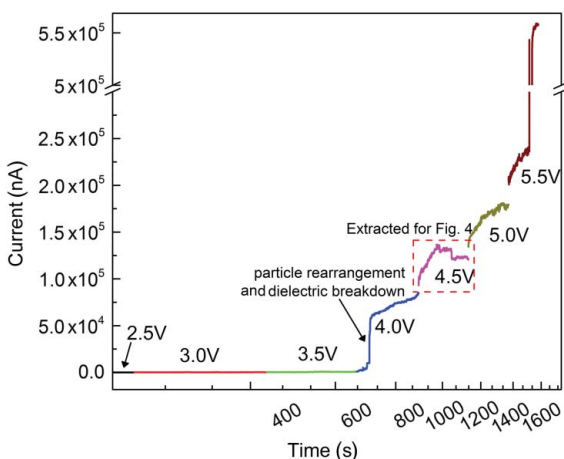


Figure 2. Experimentally observed current versus time for the full duration of the *in situ* TEM experiment. All biasing steps are shown in sequence beginning with +2.5 V. The observed current begins to rise with particle/agglomerate rearrangement at +4.0 V, filament growth at +4.5 V, and rapid consolidation of the Ni filament onto the STM tip at +5.5 V.

200 s. Thereafter, the bias was increased to +5.5 V in increments of 0.5 V every 200 s while the resulting current through the particle agglomerate was recorded as a function of time. No external heating was applied.

Figure 2 shows a plot of the recorded current between the STM tip and the microscope ground as a function of time. Initially, no significant current was observed due to the presence of mostly insulating surface oxide layers that cover the metallic nanoparticles.[16,17] During the holding interval with a constant bias of +4.0 V the observed current abruptly increases to approximately 60 μ A. This observation coincides with some particle rearrangement (see Supplementary online video clip) and is consistent with previously observed dielectric breakdown behavior of surface oxide films covering individual nanoparticles.[16,18] The experimentally observed current continued to increase linearly to approximately

70 μ A albeit at a reduced rate. Once the particle agglomerate became conducting, gradually increasing currents during the holding intervals were observed for each bias setting. Morphological changes of the particle agglomerate were minimal for most bias settings. Dramatic materials transport leading to particle coarsening and longitudinal nanopillar growth was observed at $U_{\text{tip}} = +4.5$ V, while the position of the STM tip relative to the powder agglomerate remained fixed for the duration of the experiment. During the subsequent bias interval at +5.5 V, a sudden current increase was observed coinciding with the consolidation of the remaining particle agglomerate and the already grown pillar into a large and dense sphere. During consolidation, mass is conserved and all the nickel previously making up the as-grown nanopillar and the remaining agglomerate was consumed by the formation of a large sphere attached to the STM tip.

The dynamic growth of the nanopillar and subsequent consolidation was recorded as a video clip of simultaneously acquired annular dark field and bright field STEM images and is attached in the Supplemental online materials. Figure 3 shows a series of STEM micrographs that were extracted from the as-acquired video clip during annealing at +4.5 V. Significant morphological changes of the particle agglomerate are observed in Figure 3(a) and 3(b), followed by unidirectional growth of a nickel nanopillar in the direction parallel to the STM tip (Figure 3(c)–(f)) and subsequent transverse growth (Figure 3(g)–(j)). The encircled area in Figure 3(a) shows a soft agglomerate of nickel particles with a significant open pore volume. Before any growth of the nickel filament is initiated, shrinkage of the agglomerate is observed by elimination of the pore volume (Figure 3(b)). The agglomerate is partly supported by the amorphous carbon film with some particles extending into the vacuum (encircled).

Figure 3(b)–(e) shows the successive densification of the particle agglomerate and the initiation of

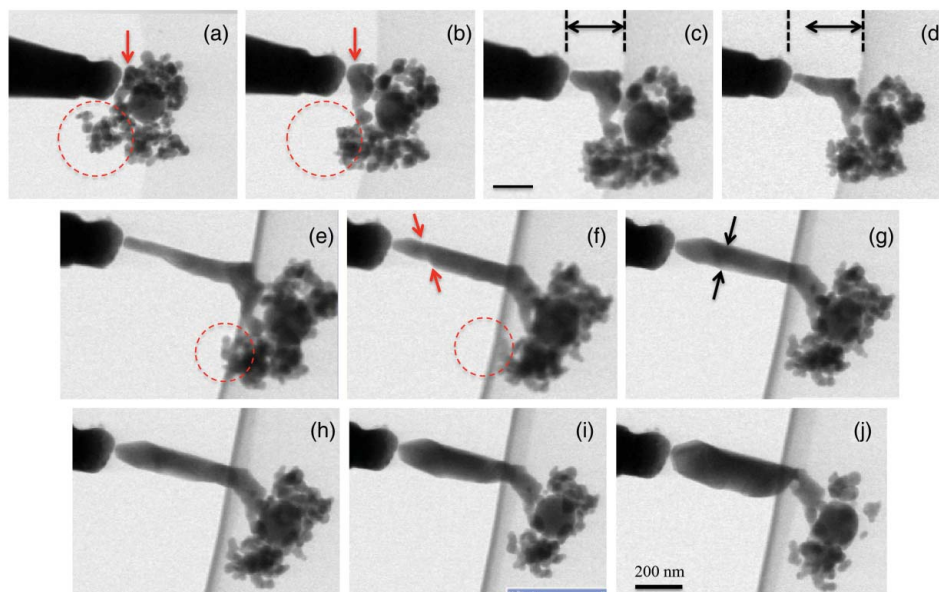


Figure 3. Series of subsequent bright-field STEM images extracted from a video file. The corresponding video clip was recorded during biasing the agglomerate with $U_{\text{tip}} = +4.5$ V. Consolidation of parts of the initial particle agglomerate is observed in (a) and (b) (encircled). Longitudinal growth of the nanopillar occurs in frames (c) through (f). Once a planar growth defect occurs in (f) longitudinal growth ceases and transverse growth is initiated for the remainder of the experiment.

one-directional growth of a nickel pillar. As the length of the filament increases, the carbon support film attached to the opposite side of the nanopillar is elastically pushed away from the STM tip. After 118 s at +4.5 V, the uni-directional growth of the nanopillar ceased (Figure 3(f)). Instead, transverse growth continued for the remainder of the holding interval and results in a significantly increased diameter. The longitudinal growth mode terminates when the encircled nanoparticles in Figure 3(a), 3(b) and 3(e) are fully consumed. Figure 3(f) reveals the introduction of a planar growth defect with an inclination angle of $(56 \pm 2)^\circ$ relative to the growth direction. This angle is in excellent agreement with the angle inclined by $\langle 111 \rangle$ and $\langle 100 \rangle$ directions in cubic metals and suggests the defect to be parallel to the $\langle 111 \rangle$ planes with the nanopillar growing along the $\langle 100 \rangle$ direction. Subsequent Figure 3(g)–(j) indicates further materials transport from the remainder of the particle agglomerate to the nanopillar.

Figure 4 shows the length of and the corresponding growth rate for the nanopillar as a function of time. After a total of 962 s, i.e. approximately 70 s of biasing at +4.5 V, longitudinal growth of the filament is initiated with a growth rate as high as 16 nm/s. Growth continues for roughly 80 s before it terminates with the filament reaching a length around 320 nm. When longitudinal growth stops, the nanopillar continues to grow in the perpendicular direction. During growth, the nanopillar is subject to compressive stress as the STM tip and the TEM grid remained fixed in position. Eventually compressive stress is accommodated by the formation of the planar defect described above, which may represent twinning or a stacking fault. At a bias of +4.5 V, the length of the

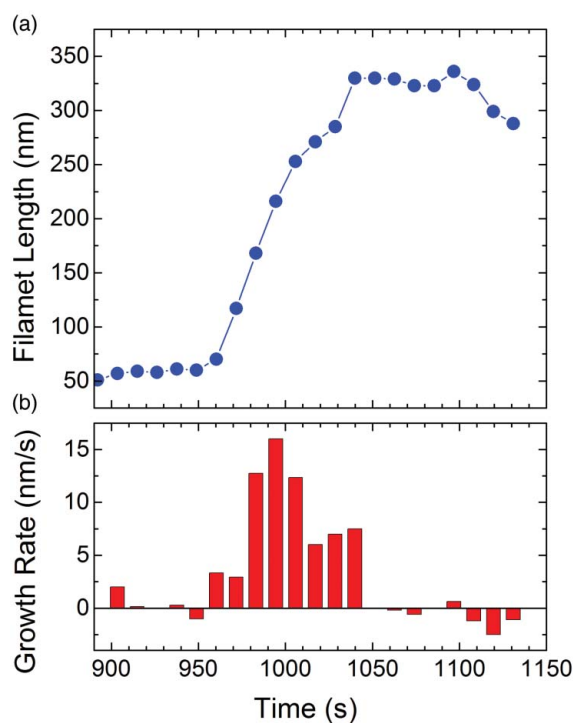


Figure 4. Length and growth rate of the evolving nanostructure. (a) Shows the length of the evolving nanopillar in the direction of current flow as a function of relative time while a bias of $U_{\text{tip}} = +4.5$ V is applied to the STEM tip. The plot shows that the nickel nanopillar grows to a length of 320 nm with a maximal growth rate as high as 16 nm/s (b).

nanostructure starts shrinking as indicated in Figure 4. After a total time of approximately 1,500 s rapid consolidation into a large sphere was observed.

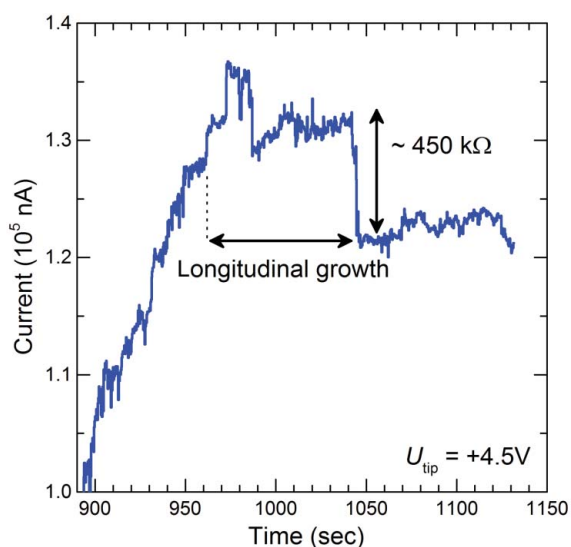


Figure 5. Experimentally determined current as a function of time for $U_{\text{tip}} = +4.5$ V. The observed current gradually increases to a maximum value before an abrupt decrease marks the initiation of the longitudinal growth mode. At a relative time of approximately 1,040 s, the current abruptly decreases due to the formation of a planar growth defect with an ohmic resistance of approximately 450 k Ω . Thereafter, transverse growth of the nanopillar is observed.

The electrical current through the particle agglomerate for the time interval during which longitudinal growth is observed ($U_{\text{tip}} = +4.5$ V) is plotted in Figure 5. The current gradually increases with time similar to all other holding intervals (cf. Figure 2). However, when longitudinal growth is initiated after 962 s the current abruptly increases in two steps for approximately 25 s before returning to its original value (Figure 5). During that time the particle agglomerate reveals significant re-arrangement of particles and coarsening (see arrow in Figure 3(b)). The observed current continues to slightly increase due to small increases in diameter of the growing nanopillar. It is thus concluded that particle-rearrangement enables the formation of low-resistivity pathways for electrical current through the agglomerate, which, in turn, promotes materials flow to the STM tip. This behavior is consistent with earlier observations of neck formation and growth between individual particles.[19] During growth, the current density through the contact area between the growing filament and the STM tip increases from roughly 1×10^{11} A/m ^{2} at the onset of growth to about 7×10^{11} A/m ^{2} when longitudinal growth ceases. At this time the planar defect is incorporated into the filament and the current drops abruptly by approximately 10 μ A. For a constant bias of +4.5 V, the sudden drop of electrical current corresponds to an overall change in ohmic resistance of approximately 450 k Ω . The change in resistance is, however, orders of magnitude higher than expected for extended twinned regions or stacking faults.[20]

The nanopillar grows through transport of nickel atoms from the particle agglomerate towards its contact with the stationary STM tip, as indicated by Figure 3. The direction for longitudinal growth is parallel to the direction of the electric current, and electromigration is, therefore, one possible transport mechanism. This hypothesis was confirmed by subsequent experiments during which the applied bias and, hence, the current direction, was reversed. Instead of consolidating onto the STM tip, the nanoparticles broke free of the tip and consolidated on the carbon support. Material transport was only observed towards the negative electrode. As the observed currents are of the order of 100 μ A, with current densities in excess of 10^{11} A m $^{-2}$, significant Joule heating of the growing nanopillar, the amorphous carbon, and the remaining particle agglomerate occurred during the *in situ* experiments. An estimation of the sample temperature based on Joule heating and thermal conduction revealed unphysical results of more than 10^4 K, indicating that radiative heat losses inside the TEM vacuum chamber must have been significant. However, Figure 3(d)–(h) reveals diffraction contrast indicating crystallinity of the growing nanopillar. Figure 3(f) reveals the formation of a planar growth defect for a current of approximately 1.3×10^5 nA. It is, therefore, concluded that the local temperature remained below 1,455°C, i.e. the melting point for bulk Ni. However, the current density is the highest at the contact between the growing nanostructure and the STM tip, and local melting in this area or during the final rapid consolidation cannot be neglected. TEM analysis before and after the *in situ* experiment revealed that the total volume of Ni was conserved, i.e. evaporation of Ni under ultra-high vacuum conditions did not occur. The electron beam of the TEM was not found to have any significant influence on the observed morphological changes as beam current densities during STEM imaging remained 4 and 5 orders of magnitude lower than those created by *in situ* biasing.

Thermally activated diffusion must contribute as a growth mechanism. For the experimental setup reported in this study, the STM tip serves as a heat sink due to its large thermal mass compared with the amorphous carbon film, and enables the observed mass flow from the particle agglomerate on the amorphous carbon support to the relatively colder STM tip.

The encircled area in Figure 3(a) shows an agglomerate of nickel particles with significant open pore volume extending into the vacuum. Before any growth is initiated, shrinkage of the agglomerate is observed by the elimination of the pore volume indicating thermally activated mass transfer rather than electromigration. During subsequent filament growth, the same agglomerate further reduces in volume indicating that it serves as a materials source for the growth process. The particle agglomerates located on the amorphous carbon remain

comparatively unchanged during the longitudinal growth (Figure 3(c)–(f)), with minor changes in their shape and some particle coarsening due to Ostwald ripening. More significant neck formation and Ostwald ripening are observed at a later stage (Figure 3(h)–(j)). It is, therefore, concluded that the driving force for the observed growth behavior is the reduction of free surface energy for the nickel agglomerate, which is facilitated by both electromigration and thermal diffusion. Furthermore, it is energetically more favorable for nickel to support filament growth in the absence of the carbon film, while the presence of the amorphous carbon film stabilizes the Ni agglomerate and hinders coarsening. Strong adhesion of Ni to carbon is consistent with previously observed wetting of Ni nanoparticles by graphene layers at elevated temperatures during *in situ* TEM experiments.[21,22]

Termination of the longitudinal growth coincides with the introduction of the planar growth defect into the filament, after which transverse growth is initiated. The ohmic resistance associated with the defect structure scatters the conducting electrons and, thus, causes local heating, i.e. a local barrier for further thermal diffusion and longitudinal growth. Transverse growth of the nanopillar is initiated due to a reduced thermal gradient and limited current density, hence leading to a reduction of the nanopillar aspect ratio (Figure 3(d)–(j)). Eventually, the metal filament and remaining metal particle agglomerates consolidate rapidly and form a large spherical volume on the STM tip. Since the position of the STM tip remained constant for the duration of the experiment compressive stress within the nanopillar created by the longitudinal growth has likely induced the formation of the observed planar growth defect.

Conclusion In summary, we report the longitudinal growth of a nickel nanopillar guided by the STM tip. Growth occurs through two complementary mechanisms: electromigration and diffusion in a thermal gradient. The length of the growing pillar is determined by incorporated growth defects that limit the thermal diffusion to the growth front. The reported study provides an avenue for the growth of metallic nanostructures with high aspect ratios. Arbitrary shapes may be obtained by moving the STM tip. Such utilization of a nanoscale pen may be suitable for three-dimensional printing of nanostructured electrodes and complex wiring assemblies.

Supplementary online material More detailed information on experiments is available at <http://dx.doi.org/10.1080/21663831.2013.855272>.

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