Ni cluster on HOPG: Growth Mode and Electronic Properties studied by STM

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Metallic nanoparticles are of growing interest owing to their great potential in applications and therefore, have been extensively investigated during the last two decades. Among others, they are especially useful for catalytic processes, where the total active surface is crucial [1]. Besides the importance of the application of the clusters, such small nanoparticles consisting of only a few atoms up to a several hundreds of atoms represent the crossover between isolated atoms and bulk, and are consequently interesting for fundamental research.

We will present a scanning tunneling microscopy (STM) study on Ni-clusters grown by depositing Ni under UHV condition on highly ordered pyrolytic graphite (HOPG), as reported in [2,3]. It is worth mentioning that a similar method was recently used to grow graphene on individual Ni islands [4], and for the growth of large area single and multilayer graphene on Ni [5]. STM permits the investigation of electronic properties through scanning tunneling spectroscopy (STS) and current imaging tunneling spectroscopy (CITS), in addition to the topographic properties of the nanoparticles, e.g. the size and the shape. All measurements were performed in an UHV-STM at liquid nitrogen temperature.

We investigated the dependence of the size, shape, and distribution of the clusters on the deposition parameters, namely deposition time, deposition rate, as well as, the HOPG mosaic spread and subsequent annealing. After deposition of Ni onto the 'cold' HOPG surface, the formed clusters showed a cloud like shape, as it can be seen in the inset of figure 1a. The shape and size of the cluster did not depend on neither the deposition parameters nor the mosaic spread of the substrate. For low coverage, the clusters grew preferentially along step edges, but appeared randomly distributed on the basal plane. For higher coverage, the Ni-clusters showed the tendency to cluster. However, after annealing, a significant change in the shape and size occurred. A stepwise procedure was used to study the details of the annealing process, where the temperature was raised in 100K steps up to 870K. Already the first annealing step at approximately 450K led to the formation of single crystalline clusters. This single crystalline structure was furthermore observed for all other used annealing temperatures, an example is shown in the inset of figure 2a. While the width of the clusters was not affected by the annealing, their height continuously increased for temperature higher than 550K. We ascribe this behavior to diffusion, which can be divided into two different regimes: First, at low annealing temperature mainly an atomic rearrangement takes place. Second, for higher temperature, whole clusters can diffuse on the HOPG surface. On the other hand, we found a reproducible way for picking-up individual clusters from the surface for both kind, as grown and annealed ones. So far we were not able to inverse the process, which means we are able to 'clean' the surface but can not fully manipulate the clusters.

Besides this topographic characterization, we carried out measurements of the electronic properties of the clusters by the means of current-voltage measurements in a CITS experiments on individual clusters. The differential conductance was then derived by numerically differentiation of the current-voltage signal. The overall shape of the current vs. voltage curve indicates a metallic behavior of the cluster. But we found a pronounced minimum in the differential conductance at the Fermi-edge for again both, non-annealed and annealed clusters. The averaged signals for various squares on the HOPG background (black) and the Ni-clusters (blue) are shown in figures 1a and 2a. Furthermore, all clusters display an enhanced signal at roughly 400mV along the edge of the cluster. The resulting CITS maps for selected voltages are displayed in figures 1b and 2b.

References

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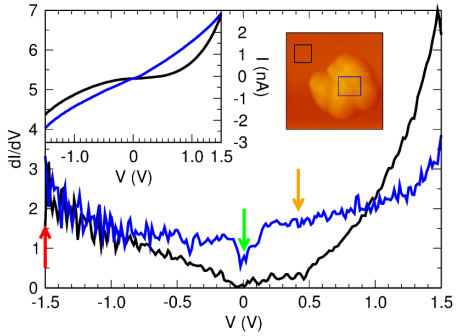
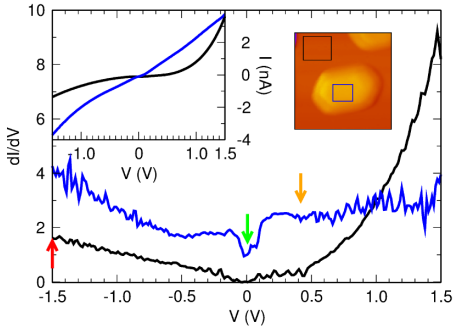
Figures

(1a) non-annealed cluster

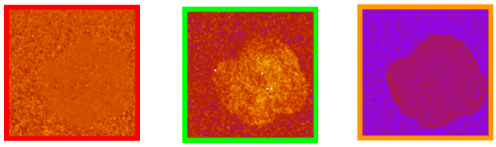


(2a) annealed cluster



Electronic properties of (left) non-annealed and (right) annealed cluster derived from CITS measurements. The dI/dV graphs are calculated by numerical differentiation of the current-voltage curves that have been averaged over the rectangular areas marked in the topography image. For completeness the averaged current vs. voltage results are also given as inset. The measurements obtained on the HOPG substrate are plotted in black and display the typical spectra of HOPG. The results measured on the Ni-clusters are shown in blue. For both, as grown and annealed clusters a significant minimum at the Fermi level can be found.

(1b) selected CITS maps at constant bias as marked in (1a)



(2b) selected CITS maps at constant bias as marked in (2a)