Nucleation and growth of magnetic nanoclusters on graphene moiré

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Arrays of magnetic nanoclusters can have important technological implications, such as magnetic recording media for the new generation high-density data storage applications. In a search for an appropriate non-magnetic template for cluster arrays, van-der-Waals surfaces are a promising alternative to the reconstructed noble-metal surfaces. Recently, a new two-dimensional form of boronnitride was discovered [1]: highly regular structure of hexagonal boron nitride with a 3 nm periodicity and a 2 nm hole size can be formed by self-assembly on Rh(111). Graphene was also shown to form Moiré superstructures, with a periodicity of about 3 nm as a result of lattice mismatch, on Ir(111) [2] and Rh(111) [3] surfaces. This regular graphene nanostructure can serve as a template for the preparation of monodisperse nanocluster arrays [2], e.g., magnetic nanoclusters (NCs) [3]. On the other hand magnetic materials in contact with graphene are of interest for spintronic applications such as spin filter e.g. [4]. In this work, we use a graphene moiré grown on Rh(111) or Ir(111) as a template. Submonolayers of ferromagnetic metals including Ni, Fe and Co are deposited on the graphene moiré template at room temperature and at low temperature around 150 K and are investigated by scanning tunneling microscopy (STM) and by x-ray magnetic circular dichroism (XMCD). Additionally, we study the process of intercalation of ferromagnetic materials underneath the graphene layer.

In the first step a graphene layer is prepared on the metallic surface by thermal decomposition of hydrocarbons. Subsequently ferromagnetic metals are deposited on the graphene surface. Fig. 1 (a) shows STM topographs of a small amount of Ni deposited on graphene/Rh(111) at 150 K. Large terraces and steps of graphene/Rh(111) covered with Ni nanoclusters (NCs) can be clearly distinguished. The NCs show mostly hemispherical shapes with at least some cluster edges which appear to be oriented along the in-plane < 1-10 > direction. The apparent height of the clusters was measured to be 0.85 ± 0.1 nm which roughly corresponds to four fcc (111) planes of Ni. The diameter distribution of the clusters is very narrow with the average cluster diameter being 3.1 nm. Most of the Ni clusters were found to be located on the regular grid showing a quite high unit cell occupation probability for the deposited amount. However, the nucleation of NCs obviously occurs at two different regions within the moiré unit cell (top-fcc and top-hcp). The randomized occupation can be attributed to the fact that the deposition temperature of 150 K is below the optimum temperature. Upon increasing Ni coverage no visible order of the cluster arrangement can be realized. At higher coverage Ni clusters exhibit a distinctly different size distribution compared with that at lower coverage. The lateral size of the clusters is more spread.

Ni deposited at room temperature exhibits a completely different growth mode compared with deposition at 150 K. Instead of small compact NCs, Ni forms triangular-shaped islands with their edges roughly aligned with the close packed < 1-10 > directions of the Rh(111) substrate as shown in Fig. 1 (b). The existence of large islands nucleated at terraces indicates that Ni atoms are highly mobile on the graphene surface at room temperature. On the other hand, it is remarkable that, in spite of the weak bonding strength between Ni and the graphene surface, the moiré structure imposes registration and orientation on the Ni nanostructures. The average apparent height of the islands is 1.8 nm and the size defined by the length of the edges is ranging from about 5 nm to about 18 nm.

Deposition on graphene on Rh(111) at room temperature shows significant differences in the growth mode for Ni compared to Fe and Co [compare Fig. 1 (b) and (c)]. Whereas Ni preferentially forms flat triangles with alignment to the moiré structure of the graphene template, the growth of Fe clusters shows only little faceting. In the case of Ni/Gr/Rh(111) the clusters are of order 20 nm in size and show

a broad size distribution. For Fe/Gr/Rh(111) the clusters are slightly smaller, around 8 nm. XMCD measurements on the Ni clusters are currently in progress to study the impacts of the different geometries on the spin and orbital moments and on magnetic anisotropies.

Partial intercalation of the room temperature grown Ni and Fe clusters can occur upon soft annealing and yields mono-atomically thick epitaxial islands incorporated between substrate and graphene layer. The moiré structure of the graphene layer is preserved on top of the intercalated clusters. In the intercalated state both materials show a strong alignment of the borders to the moiré structure.

References

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Figures



Fig. 1 (a) STM topograph (40 nm x 40 nm; U=1.03 V; I=0.13 nA) of Ni nanoclusters deposited at 150 K on Gr/Rh(111) (b) STM topograph (60 nm x 60 nm; U=1.54 V; I=1.14 nA) of Ni clusters deposited at room temperature on Gr/Rh(111) (c) STM topograph (33 nm x 33 nm; U=1.11 V; I=0.49 nA) of Fe clusters deposited at room temperature on Gr/Rh(111)