Self-organisation of CoRh nanoparticles on chemical nanopatterns

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Abstract

First experiments on the combination of nano-imprint lithography and self-assembled nanoparticles deposition are presented. By fabricating chemical nanopatterns of silane molecules on a SiO\textsubscript{2} surface, we aim at directing the self-assembly of CoRh nanoparticles on specific areas. We demonstrate experimentally that a silane monolayer of OTS on a SiO\textsubscript{2} surface modifies drastically the self-assembling process of the nanoparticles. We also present the nano-imprint process which enables us to create nanopatterns of silane for controlling the exact position of the self-assembled nanoparticles on the surface. © 2001 Elsevier Science. All rights reserved

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1. Introduction

The great progress of nanopatterning techniques allows now the study of single nano-objects as carbon nanotubes or nanoparticles (NPs). For systematic studies or nanodevice fabrication, the control of the position and the assembly of these nano-objects is a crucial issue. Vertical [1] and planar [2] devices are developed for investigating magneto-transport mechanisms through a few number of NPs. In this paper, we present an original planar approach for constraining the self-assembly of NPs on specific nanopatterns defined by lithography. This route opens the opportunity to fabricate nanodevices where the active region will be made of a few number of NPs of controlled shape, dimension and spatial arrangement.

2. Experiments and results

Our process consists in the definition of chemical nanopatterns using Nano-Imprint Lithography (NIL) [3] and the subsequent selective deposition of self-assembled NPs on to these selected areas. Thanks to the chemical selectivity between the ligands surrounding the NPs and the surface molecular layer deposited on the nanopatterns, we hope to locate precisely the NPs on the surface and moreover to favour the self-organization of the NPs in these geometrical nanopatterns. After this selective deposition, nanoelectrodes aligned on the nanopatterns will be fabricated by electron beam lithography [4] and magnetotransport measurements will be carried out for probing the behaviour of these regular arrays of NPs. In this paper, we focus our attention on the fabrication of the chemical nanopatterns using NIL and the selective deposition of the NPs. Chemical
nanopatterns are formed on a SiO₂ thin layer obtained by dry oxidation of a Si substrate and silane chemistry is used for depositing a Self-Assembled Monolayer (SAM) of silane molecules on this surface. All the experiments described here have been achieved with Octade cylTrichloroSilane (OTS) as functionalising layer. NPs used in this study are synthesized by decomposition of organometallic precursors leading to well-defined NPs with controlled size, shape and surface state [5]. Once synthesised, particles are coated with the hexadecylamine ligand which allows a long-term stability of the colloidal solution and prevents from further coalescence.

Figure 1 reveals the crucial importance of the surface functionalisation on the self-organisation of CoRh NPs on SiO₂. 100 nm thin membranes of SiO₂ have been microfabricated using photolithography and deep Reactive Ion Etching (RIE) for Scanning Transmission Electron Microscopy (STEM) inspections. CoRh NPs were deposited on these membranes functionalised or not with an OTS SAM. Figure 1. High angle annular dark field STEM images of SiO₂ membranes after NPs deposition. a) untreated surface, b) silanised surface with OTS

Fig.1a reveals that on the bare SiO₂ surface, a high density of NPs (bright spots) are deposited but no evidence of any self-organization effect can be detected. On the opposite, Fig.1b shows that the deposition under the same experimental conditions but on a silanised surface with OTS, exhibits clear self-organization effects of the NPs and a lower density of NPs (all the surface is not covered). We think that the interplay between the ligand molecules of the NPs and the molecules of the functionalisation layer could be adjusted for combining a stable deposition of the NPs with a good surface coverage and self-organization of the NPs. Different couples of ligands and silane layers are under investigation for optimising these two crucial parameters.

Figure 2 presents the silanisation process of a SiO₂ surface inside nanopatterns made by NIL for directing the self-assembly of the NPs in desired locations. The SiO₂ surface covered by PMMA resist and the mold are heated separately at 175°C then brought together applying a force F=1000 N (Fig.2a). The demolding occurs after a cooling down stage. An O₂ RIE step is needed to remove the residual resist layer (Fig.2b). An OTS molecular layer is then deposited by CVD (Fig.2c). Finally, the dissolution of PMMA leaves the SAM of silane molecules in the regions opened in the resist (Fig.2d).

Figure 2. Fabrication process of chemical nanopatterns of silane SAM using NIL

Figure 3 presents an Atomic Force Microscopy (AFM) image in tapping mode of OTS patterns obtained by this process. This one confirms the quality of the patterns, the well defined frontier between the silanised and unsilanised SiO₂ surface and the good coverage of the patterned regions with the silane SAM monolayer. The height of the silane patterns is about 1.8 nm which corresponds to the expected value for a single monolayer of OTS molecules closely packed.

Figure 3. AFM image and cross section of OTS patterns

Nanopatterns of a few tens of nanometers can be obtained using the same process.

3. Conclusion

The crucial role of the OTS functionalisation layer on the self-assembly process of NPs deposited on SiO₂ has been clearly evidenced. We have demonstrated that NIL is an efficient technique for fabricating chemical nanopatterns of OTS molecules on SiO₂. New investigations deal with the influence of the size of these chemical nanopatterns on the self-organization of the NPs.

References: