Selective functionalization of Si(111) and Ag(110) surfaces for preparation of Co nanostructures.

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Abstract. Si(111) and Ag(110) surfaces were nano-structured and functionalised in two different ways. Vicinal Si(111), re-arranged into regular terraces and step-bunches, were used as a template for the controlled growth of gold-rich gold-silicide nanodots. Under suitable growth conditions, these nanodots can be aligned along the step-bunches. In contrast to the nanodots, a silicon-rich gold-silicide was formed on the terraces. Different chemical reactivities of the silicides with respect to cobalt are expected and give rise to either magnetic or non-magnetic Co areas. The Ag(110) surface was functionalised with parallel one-dimensional silicon nanowires (NWs) oriented along the [-110] direction of the substrate. The deposition of a sub-monolayer coverage of cobalt at room temperature leads to preferential Co adsorption on the silicon nanowires.

1. Introduction

There is a great technological interest in the controlled preparation of (nano)structured metal- or semiconductor substrates as potential templates for the growth of periodic nanostructures [1]. Many different approaches to structure surfaces have been described in the literature and can be divided into two principal groups. One approach takes exclusively advantage of either surface reconstructions or re-organisations of vicinal surfaces which are both induced through intrinsic properties of the material. These naturally structured substrates are subsequently used to control the growth of adsorbates on the entire surface [2,3]. The formation of regular arrays of nanofeatures, like -dots [4] -wires [5] or – stripes [6] has been observed on so-prepared substrates. Another approach of structuring relies on nanofabrication by scanning probe microscopy [7] and focused ion beam patterning [8]. These latter methods suffer from the limited area (~ 100 nm x 100 nm) which can be structured. Other preparation schemes rely on subsurface stressors, which interfere with the surface through elastic fields [9].

Prepatterned substrates are commonly used to obtain arrays of magnetic nanostructures. The fabrication of magnetic nanostructures, if possible in high density, is one of the open questions in magnetic data storage and has already been addressed by several experimental approaches. Top-down approaches have often been used but have lead to undesired edge effects which dominate the magnetic properties and in particular the magnetization reversal process [10]. An additional challenging topic to handle is the integration of magnetic materials on silicon substrates. The systematic formation of non-
magnetic silicides is observed at the metal-silicon interfaces. The results we present here are based on chemical functionalization of clean Ag(110) and vicinal Si(111) surfaces. We show a new route to self-assemble magnetic nanostructures by passivating silicon surfaces which have before-hand been rearranged into a regular nano-pattern over an extended scale. The second approach described deals with structured Ag(110) surfaces functionalized with Si nanowires. First results of the functionalized Si(111) and Ag(110) substrates and some Co deposition will be presented.

2. Experimental setup
Experiments were carried out in an ultrahigh vacuum chamber (base pressure $\sim 10^{-10}$ mbar) equipped with an Auger Electron Spectrometer (AES), a variable temperature Omicron Scanning Tunneling Microscope (STM), the usual facilities for sample preparation and several evaporation sources. The vicinal Si(111) samples (n-type, resistivity 0.5 – 1 $\Omega$.cm) were disoriented by 1.5° towards the [112] direction. They were prepared by outgassing at 800°C using resistive heating followed by flash-cleaning up to 1250°C. High purity 5N gold was evaporated from a crucible with the Si substrate kept at 370°C. The Ag(110) sample was prepared by repeated cycles of Ar$^+$ ion sputtering and annealing at 400°C by electronic bombardment performed on the rear side. We deposited silicon on Ag(110) substrate at room temperature (RT) from a direct-current heated piece of silicon kept at 1250 °C. The deposition of cobalt was performed using a commercial evaporator. All STM images were obtained at RT and in the constant current mode.

3. Results and discussions
3.1. Au on vicinal Si(111) – a local passivation
Vicinal Si(111) substrates were heat-treated to form regular templates for the subsequent growth of Au-silicides. The created step-bunches were functionalized [11] and locally passivated through the controlled growth of nanometer-sized Au-silicide islands. Fig. 1a shows one STM-image of these Au-silicide islands self-aligned along the step-bunches. A narrow size distribution was obtained by depositing 3.5 ML at $T_s=370°C$. A zoom of one island is given in Fig.1b. The islands are faceted and surface reconstructions were resolved with STM exhibiting a unit cell of 0,6 x 0,6 nm$^2$ as shown in the inset in Fig. 1b.

![Figure 1](image_url)

**Figure 1.** a) STM image of Au-silicide islands on vicinal Si(111) – b) STM image of one island, inset: zoom into one facet – c) islands covered with Co, inset: structure of Co$_2$Si.

A subsequent Co deposition at 200°C leads to a rough surface on the terraces and the islands. No regular structure was resolved at this stage with STM. Additional annealing to 400°C leads to an atomic rearrangement and the Co$_2$Si silicide structure was observed on the terraces and identified by the typical unit cell of 0.55 x 0.55 nm$^2$ (see inset of Fig. 1c) [12]. Complementary experiments with transmission electron microscopy (not shown here) revealed that all islands are composed of a gold-rich Au-silicides. The magnetic characterization of the samples with SQUID showed no magnetic
signal on substrates that only contained Si-rich gold-silicides whereas on samples with Au-rich gold-silicide islands a magnetic signal was detected which is conform with a fully magnetic Co film on the islands [13].

3.2. Si on Ag(110) – a local functionalization
As already reported [5,14] the submonolayer deposition of silicon on Ag(110) at RT leads to the growth of parallel one-dimensional nanowires (NWs) oriented along the [110] direction of the Ag(110) surface. The upper part of Fig. 2a shows two kinds of silicon NWs, denoted hereafter single NWs and double NWs, varying in their width, which appear as composed of rounded protrusions. We point out that these protrusions are too large to be assimilated to individual atoms. Low energy electron diffraction (LEED) pattern [5,14] reveal a perfect by two periodicity along the [110] direction, i.e. 2 aAg// = 0.578 nm, as illustrated in Fig. 2a. This one dimensional growth is attributed to the strong anisotropy of the Ag(110) surface and to a large difference in strain energy along the [110] and [001] directions. An atomic structural model of these individual NWs, very similar to the Si(100) 2×1 structure, has been proposed by He [15], employing density-functional theory.

Figure 2. a) STM image (20 nm)² of a low coverage of Co deposited at RT on functionalized Ag(110) surface I = 1.3 nA, V = 0.55 V - b) Close view (7.8 nm)² of the area indicated in a) by the square box. - c) Height profile along the transverse line in b)

The initial stages of Co deposition on functionalized Ag(110) covered by individual silicon NWs has been studied by AES and STM. After Co evaporation, the presence of Co atoms has been checked by measuring the Co MNN (53 eV) Auger transition with AES. For very low coverage at RT, the adsorption of Co seems to be preferential on NWs than on bare silver areas. Indeed, only the appearance of additional protrusions on NWs was observed in the STM image displayed in Fig. 2a. These additional protrusions, visible as bright spots, are well-ordered in a row of double protrusions along the [001] direction. We can note that modifications occur mainly on single NWs. When adsorption on double NWs occurs, we observed the formation of a second row of double protrusions, identical and parallel to the row of protrusions on single NWs. A close-up image of the area consisting of one modified NW is shown in Fig. 2b. The periodicity of protrusions along the NWs is 0.43 nm, i.e. 1.5 aAg//. In the perpendicular direction, as the troughs of the bare Ag(110) surface were not resolved in Fig. 2b, the distance between two protrusions can be estimated to be roughly 0.3 nm, i.e. 0.75 aAg// (aAg// = 0.409 nm in the [001] direction). A height profile along the length of the NW, presented in Fig. 2c, shows a height difference between the silicon protrusions and the protrusions observed after deposition of roughly 0.35 Å.
We note that the measured parameters do not correspond to the $((\sqrt{2} \times \sqrt{2}) R 45^\circ)$ surface structure of CoSi$_2$(100) observed after Co deposition on Si(100) surface at high temperature [12]. Previous experimental studies [16] mention that CoSi$_2$ formation does not take place upon condensation on Si(100) at RT, even if Gallego et al [17] report the formation of a spontaneous layer of CoSi$_2$ on Si(100) followed by quasi-layer-by-layer growth of Co with some Si intermixed. Moreover, some studies [18-19] report that, for low coverage, no Co diffusion at RT into the Si substrate occurs, process which is the precursor of silicidation. Our STM images do not allow to resolve the chemical nature of the protrusions observed. Nevertheless, our results, interpreted in the framework of previous studies, are in favor of adsorption of Co on top of Si NWs. Voltage dependent scanning tunneling microscopy or spectroscopic measurements performed on such binary systems is a possible way to identify chemical species at the surface [12].

More magnetic studies are planned on the different substrates. The magnetic properties of small quantities of Co deposited on isolated Si nanowires and on Si nanowire arrays will be studied in the near future.

[1] Z. Zhang et M. Lagally, Editors, Morphological Organization In Epitaxial Growth and Removal, Series on Directions in Condensed Matter Physics, Vol. 14, World Scientific 1998.
[2] S. Padovani, F. Scheurer, I. Chado and J. P. Bucher, Phys. Rev. B 61, 72 (2000).
[3] V. Repain, J.M. Berroir, S. Roussel and J. Lecoeur, Surf. Sci. 447, L152 (2000).
[4] N. Weiss, T. Cren, M. Epple, S. Rusponi, G. Baudot, S. Rohart, A. Tejeda, V. Repain, S. Roussel, P. Ohrresser, F. Scheurer, P. Bencok, H. Brune, Phys. Rev. Lett. 95, 157204-1 (2005).
[5] H. Sahaf, L. Masson, C. Léandri, F. Ronci, B. Aufray, G. Le Lay, Appl. Phys. Lett. 90, 263110 (2007).
[6] K. Kern, H. Niehus, A. Schatz, P. Zeppenfeld, J. George, G. Comsa, Phys. Rev. Lett. 67, 855 (1991).
[7] G.E. Engelmann, J.C. Ziegler and D.M. Kolb, Surf. Sci. 401, L420 (1998).
[8] M. Koh, S. Sawara, T. Shinada, T. Goto, Y. Ando and I. Ohdomari, Appl. Surf. Sci. 162-163, 599 (2000).
[9] A. E. Romanov, P. M. Petroff and J. S. Speck, Appl. Phys. Lett. 74 2280 (1999), F. Leroy, J. Eymery, P. Gentile, F. Fournel, Surf. Sci. 545, 211 (2003).
[10] A. Moser, K. Takano, D.T. Margulies, M. Albrecht, Y. Sonobe, Y. Ikeda, S.H. Sun, E.E. Fullerton, J. Phys. D – Appl. Phys. 35, R157 (2002).
[11] A. Rota, A. Martinez-Gil, G. Agnus, E. Moyen, T. Maroutian B. Bartenlian, R. Mégy, M. Hanbücken, P. Beauvillain, Surf. Sci. 600, 1207 (2006).
[12] B. Voigtländer, V. Scheuch, H.P. Bonzel, S. Heinze, S. Blügel, Phys. Rev. B 55, 13444 (1997).
[13] A. Fleurence, G. Agnus, T. Maroutian, B. Bartenlian, P. Beauvillain, E. Moyen, M. Hanbücken, Appl. Surf. Sci., submitted (2007).
[14] C. Léandri, G. Le Lay, B. Aufray, C. Girardeaux, J. Avila, M. E. Davila, M.C. Asensio, C. Ottaviani, A. Cricenti, Surf. Sci. 574, L9 (2005).
[15] Guo-min He, Phys. Rev. B 73 35311 (2006).
[16] G. Rangelov, P. Augustin, J. Stober, Th. Fauster, Phys. Rev. B 49, 7535 (1994).
[17] J.M. Gallego, R. Miranda, S. Molodtsov, C. Laubschat, G. Kaindl, Surf. Sci. 239, 203 (1990).
[18] H. L. Meyerheim, U. Döbler, A. Puschmann, Phys. Rev. B 44, 5738 (1991).
[19] W.S. Cho, J.Y. Kim, N.G. Park, I.W. Lyo, K. Jeong, S.S. Kim, D.S. Choi, C.N. Whang, K.H. Chae, Surf. Sci. 453, L309 (2000).