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Growth of self-organized nanosized Co pillars in Au(111) using an alternating deposition process

O. Fruchart*, M. Klaua, J. Barthel, J. Kirschner

MPI für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany

Abstract

Nanosized Co pillars were grown in Au(111) using a novel deposition process. Starting from a self-organized array of Co dots on the Au(111) surface, we alternatively deposit Au (0.9 ML) and Co (0.1 ML). Under appropriate conditions, the newly deposited Co atoms assemble into dots, vertically self-aligned and in direct contact with the Co dots from the previous layers. This way, pillars 8 nm high and with a 2:1 vertical aspect ratio were fabricated. It is argued that the growth process is driven by parameter misfit and surface energy effects, and should thus occur for other pairs of elements than (Co,Au). From the superparamagnetic regime, we deduce that each pillar behaves like a single magnetic entity. The onset of perpendicular remanence occurs around room temperature, instead of 20 K for the initial flat dots. In terms of applications, the main drawbacks of self-assembled and organized nanosized magnetic systems are the small amounts of material contributing to magnetic effects, and the superparamagnetism blocking temperature, generally well below RT. The pillar growth process is a good candidate to solve them simultaneously. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Self-assembly (SA) and self-organization (SO) are appealing low-cost alternative processes to lithography/etching techniques, when the fabrication of high-density assemblies of small dots with a simple arrangement is required (no order, or a simple array).¹ In the field of semiconductors, SA has already been applied to produce assemblies of $In_{r}Ga_{1-r}As/GaAs$ quantum dots with excellent light-emitting characteristics [1]. SA/SO are appealing techniques for magnetic materials as well. The first class of applications is the fabrication of nanostructured materials with specific properties, for instance giant magnetoresistance. The second class of applications is magnetic recording with topological bits, i.e. where each individual dot is used to store one bit of information. With this respect, the so-called SO process yields a poor degree of ordering today, and it seems unrealistic to think that it improves sufficiently in the future for magnetic recording purposes. The solution may come from the combination of lithography (or nanoimprint) and SA techniques [2]. This could surpass each technique taken indepen-

^{*} Corresponding author. Laboratoire Louis Néel (CNRS), BP166-38042 Grenoble, Cedex 9, France. Tel.: +33-476-88-7920; fax: +33-476-88-1191.

E-mail address: fruch@polycnrs-gre.fr (O. Fruchart).

¹We use the term "self-assembled" when the deposited adatoms cluster into disconnected islands, and "self-organized" when the islands form a regular array, at least on the medium range.

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dently: (1) the degree of ordering would be perfect (not possible even for SO) and (2) the UHV-grown dots would be nearly monodisperse and have high-quality interfaces. The latter point is crucial for the monodisperse properties of single bits, and is not met by lithography processes above some tens of Gbit in.⁻² densities.

However, there exists up to now a fundamental obstacle that prevents magnetic SA/SO to be used in nearly any commercial device: as the dots are of small lateral size and generally rather flat, their volume is extremely small, and the dots are superparamagnetic down to very low temperature [3,4]. We present here a new growth mode liable to overcome this obstacle. We use as a starting point the well-known self-organized arrays of Co/Au(111) [5], and deposit sequentially 1 - x ML of Au and x ML of Co, with $x \ll 1$. We show in Section 2 that conditions can be found, under which the deposited Au flattens the surface by filling the space between the Co dots, and the newly deposited Co atoms cluster on top of the existing Co dots, heightening them by 1 ML. By repeating this sequence many times, the sub-ML organized array of flat Co dots is replicated vertically, to form a self-organized array of vertical magnetic columns. This process can be viewed as an extension of the already known 3D-SO of multilayers of dots [6], with an interlayer thickness reduced to zero. Finally, in Section 3, we discuss the growth mechanisms and the quality of the resulting columns. We show that each column acts as a single magnetic entity, whose superparamagnetic temperature is dramatically increased as compared to the flat dots, an effect that is ascribed to the volume increase.

2. Description of growth

The growth, structural and magnetic characterizations were performed in situ in a group of interconnected UHV chambers, equipped with Ar ion gun, thermal evaporation, RHEED, LEED, STM and a variable temperature MOKE setup (65–300 K). The (111) surface of a Au single crystal was prepared by cycles of Ar ion sputtering, and annealing at 800 K. Au was evaporated from a crucible at a rate of 0.5 ML min⁻¹. Co was evaporated by electron bombardment of a rod, at a rate of 0.02 ML min⁻¹. The base pressure of the evaporation chamber is below 5×10^{-11} mbar. The STM images were recorded in a separate chamber 30 min after deposition, to allow the crystal to cool down. Finally, the temperature is estimated using a thermocouple attached to the sample holder. As the thermocouple is not in direct contact with the crystal, and is away from the furnace, the temperatures given in the present paper must be considered as a lower bound of the temperature of the Au crystal.

The Au(111) surface is very peculiar in the sense that it undergoes a surface reconstruction with a large period, in the 10-nm-length scale [7]. In short, the topmost Au ML floats on the bulk (111) crystal. with some areas with fcc termination (bulk like) and other areas with hcp termination. These two types of areas alternate periodically, and are separated by linear partial dislocation lines where the atoms of the floating layer coherently pass the atomic saddle-point between an fcc and an hcp site. This periodic displacement results in a surface compression of about 4% as compared to the bulk lattice parameter, a mechanism that allows the surface stress to be reduced perpendicularly to the lines. Finally, a nearly isotropic surface stress decrease is achieved by the periodic alternating $+120^{\circ}$ bending of the partial dislocation lines. The dimensions of the rectangular cell of the resulting reconstruction pattern is about $7.5 \text{ nm} \times 13 \text{ nm}$ [7].

We now turn to the description of our work. As a first step, we deposit 0.2 ML of Co on Au(111) at 300 K. A regular 7.5 nm \times 13 nm array of Co dots is formed, due to the preferential nucleation at the periodic \pm 120° kinks of the Au reconstruction (Fig. 1a). Cross-sections of the STM images reveal that the dots are 0.4 nm high, i.e. are bilayers of Co. This step was already known from the literature [5].

As a second step, we deposit the exact amount of Au needed to fill the space between the Co dots, and complete up to the fourth atomic layer above the Au substrate (Fig. 1b). The temperature is raised from 425 to 475 K during the deposition. As a Co atomic layer is slightly thinner than a Au atomic layer (by approximately 0.03 nm), the buried array of dots now appears as an array of hollows (approximately 0.06 nm deep). This hollow effect had been noticed by other authors [8]. Some hollows are decorated by another Au ML (0.23 nm higher than the hollows).

The new part of the process starts here. As a third step, 0.2 ML of Co is deposited at 500 K. The surface displays a regular array made of both hollows and dots (Fig. 1c). The hollows are 0.12 nm deep, i.e. four times the height difference between a





Co ML and a Au ML. This suggests that a doublelayer place-exchange mechanism took place, i.e. that the incoming Co atoms expelled the Au atoms covering the buried dots. Besides, the dots are 0.23 nm higher than the hollows, suggesting that a fifth ML of Au atoms is to be found somewhere in the dot.

As a fourth step, the amount of Au necessary to smoothly complete the fifth layer above the substrate is deposited at 500 K. The surface morphology is similar to that after step 2, but with 0.12 nm deep hollows.

Starting from this point and remaining at 500 K. we repeat the following sequence many times: 0.1 ML of Co. plus 0.9 ML of Au. STM images recorded after each deposition reveal that at each step, the incoming Co atoms expel the Au atoms via a singlelaver place-exchange mechanism, so that the existing Co dots are heightened by 1 ML. Fig. 1d shows the surface after 16 such steps, i.e. presumably after 20 ML of Co have been piled up. More defects are present than after step 1, and the dots' lateral size is more distributed, but the organization in a regular array is preserved. This suggests that the artificial alternating process resulted in the fabrication of vertical pillars of nearly pure Co, with a 2:1 vertical aspect ratio, namely 5.5 nm high and 3 nm in diameter on the average.

In the next section, we examine in more detail the growth process, and give magnetic evidence of the continuity of the pillars.

3. Discussion

3.1. Growth mechanism

Let us briefly recall the present understanding of the regular nucleation of Co on the bare Au(111) surface, before examining the case of pillar growth.

Fig. 1. Illustration of the pillar growth process: (a) 300×300 STM image after deposition of 0.2 ML of Co at 300 K on Au(111) (step 1 in the text), (b) after deposition of Au up to the fourth ML, performed while raising the temperature from 425 to 475 K (step 2 in the text), (c) after another deposition of 0.2 ML of Co at 500 K (step 3 in the text), (d) 300×300 STM image after 0.2 ML of Co have been piled one on top of the other (see text). For steps a to c, the frame displays STM and schematic cross-sections, whose vertical scale has been enhanced for clarity.

Meyer et al. [9] studied the deposition of different metals on the Au(111) reconstructed surface, and observed preferential nucleation at the kinks of the reconstruction only for those metals with a surface energy higher than that of Au (Ni, Co, Fe). The microscopic origin of this criterion was unveiled taking nickel as an example: during the very first stages of growth, the Ni adatoms do not cluster into dots, but instead are integrated into the Au surface via a place-exchange mechanism, which happens to be the most efficient in the vicinity of the kinks.

We come back to the present work. Concerning the second deposition of Co (step 3), it can immediately be ruled out that the Au reconstructions are responsible for the clustering of the newly deposited Co adatoms atop the buried Co dots. As a matter of fact, at step 2 and for all subsequent steps, the regions made out of Au are still reconstructed into fcc-and hcp-termination areas, but the partial dislocation lines are no longer regular and their kinks are often displaced off the dots (see STM picture in Fig. 1b and c). Therefore, the reason why the new Co adatoms can nucleate on top of the previous Co dots must be that it is energetically more favorable for these atoms to be in direct contact with Co and embedded into the surface, rather than wander on the bare surface. Two parameters are liable to play a role in this phenomenon. The first parameter is the high surface energy of Co as compared to Au, which favors the clustering of pure Co entities. The second parameter is stress minimization. Indeed, the in-plane lattice parameter in the initial 2-ML-high dots has already relaxed close to its bulk value [10], so that the elastic energy of the incoming atoms is minimized if they cluster atop a nearly relaxed area rather than somewhere else on a pure Au area [the in-plane misfit between the Co bulk parameter and the Au surface parameter is 10%, taking into account the surface parameter of Au(111)]. This suggests that pillar growth might occur for other elements than Co and Au, provided that a sufficient difference of surface energy and/or lattice parameter mismatch exists. It should, however, be noted, that a prerequisite for pillar growth to happen, might be that the two elements have no tendency to intermix or form alloys, either of a bulk or interface nature.

The above discussion suggests why nucleation can occur atop the existing Co dots, but does not tell us why nucleation does not occur simultaneously at the reconstruction kinks, which are known to be potential nucleation sites. We present additional experiments to answer this question.

The first experiment is to deposit the second Co layer at room temperature (RT), instead of 500 K in the optimized process described in Section 2. For RT deposition, the Co adatoms cluster into dots and the organization is lost (Fig. 2a and b). A close examination of STM images reveals that Co adatoms nucleate simultaneously atop the buried Co dots, and at special spots of the Au reconstructions, like kinks and crossings of the partial dislocation lines.

The activity of the Au nucleation centers was also checked by an experiment performed directly at 500 K. At the end of step 3 (second layer of Co dots), the 0.2 ML of deposited Co has essentially contributed to expel the equivalent of 0.2 ML of Au, and heighten the existing Co dots by 2 ML. If another 0.1 ML of Co is further deposited, then nucleation also occurs at some kinks and crossing of the Au reconstructions (Fig. 2c).

In the view of these two experiments, our understanding of the nucleation process is the following. During the second and further Co depositions, two types of nucleation sites compete: one type is on Au



Fig. 2. Second Co layer deposited under different conditions. (a) 0.2 ML of Co at 300 K and (b) corresponding location of the buried dots (dark) and of the new nucleation sites (white). The small dark stripe at the lower left corner is an area with unfilled fourth Au layer. (c) 0.3 ML at 500 K. (d) 0.2 ML at 575 K.

reconstructions, the other type is atop the buried Co dots. The latter sites are energetically more favorable. At RT, thermal activation is limited, so that the place-exchange mechanism is not activated. The surface thermodynamic equilibrium is not reached, and both types of sites are populated (Fig. 2a). At 500 K, thermal activation is sufficient to reach the *surface* thermodynamic equilibrium, which means that only the most energetically favorable site is populated, i.e. the site atop the buried Co dots (Fig. 1c). Finally, thermal activation becomes efficient in the *volume* when step 3 proceeds at 575 K, as illustrated in Fig. 2d. It can be inferred from STM cross-sections of this image that the dots with the smaller diameter are those whose height difference with an integral number of Au MLs is the most important. This indicates that these dots clustered towards a more spherical shape, burying more Co planes below the surface, at the expense of their lateral size. This is coherent with the observation, upon annealing, of the self-burrowing of initially flat Co dots [11].

Finally, we discuss the role of a third potential type of nucleation mechanism, that occurring at atomic step edges. It is known that during the first



Fig. 3. Each arrow indicates a buried pillar that pins the step edge. Here, the pillars are about 4.2 nm in diameter, and 15 ML of Co have been piled up. Note that for clarity, the gray scale has been split as indicated on the right panel, so that the step edge appears as a thin curve. Inset: to the contrary, during the first Co deposition, nucleation also takes at the step edges (same scale).

Co deposition (step 1), nucleation also proceeds at step edges, giving rise to ill-defined elongated islands (see the inset at the top left of Fig. 3). In the present case, it is observed after each Co deposition at 500 K (steps 3 and further) that no nucleation occurred at the step edges (Fig. 3). These are the results from the combination of two effects:

(1) At the end of each Au deposition, the Au step edges are pinned by some existing Co dots (see white arrows on Fig. 3).

(2) During subsequent Co deposition at 500 K, the atomic mobility of Co atoms along a step is sufficient for their reaching a buried Co dot pinning the step edge, before meeting another 1D-adsorbed Co atom. The Co atoms adsorbed on a step edge therefore contribute to the heightening of an existing Co dot, not to the nucleation of new ill-defined elongated islands.

This observation is of prime importance, because the organization would have rapidly decayed if new ill-defined elongated islands had nucleated at each step of the process. Nonetheless, step edges may have a slight influence on growth. It is still unclear whether they may stabilize or destabilize SO.

3.2. Magnetic measurements

The purpose of this section is to deliver to the reader some magnetic basics. A detailed study will be reported elsewhere. Polar and longitudinal MOKE hysteresis loops were obtained in situ in the field range ± 0.8 T. The magnetization of the assembly of pillars is essentially perpendicular and we focus on perpendicular loops in the following.

Fig. 4 shows temperature-dependent hysteresis loops of the pillars whose growth is depicted in Fig. 1. These pillars are roughly 3 nm in diameter and 5.5 nm high. We first analyse the superparamagnetic regime. Each pillar can be viewed as a macrospin with a mostly uniform magnetization state, because the pillars' dimensions are below all magnetic characteristic length scales. Besides, as the anisotropy is strongly perpendicular, each macrospin can be in two states only (up or down, i.e. it can be treated as an Ising macrospin). Accordingly, the superparamagnetic loops of Fig. 4a were fitted using a Brillouin 1/2 function (see for instance Ref. [12]). Besides, the inter-pillar dipolar fields were taken into account



Fig. 4. Normalized polar hysteresis loops of an assembly of dots 3 nm in diameter and 5.5 nm high. Inset: inter-pillar dipolar fields are demagnetizing in the present case of perpendicular magnetization. (b) Temperature dependence of the inverse zero field susceptibility.

as an effective field, and estimated in the mean field approximation. In these conditions, the inverse zerofield susceptibility is expected to rise linearly with temperature:

$$\frac{1}{\chi} = \frac{d(\mu_0 H)}{dm} = \mu_0 H_{dip} + \frac{k}{\mu_0 \mu_{Co} N} T.$$
 (1)

H is the external applied field, *m* the perpendicular magnetization normalized to 1, H_{dip} the inter-pillar dipolar field, μ_{Co} the magnetic moment per Co atom (set to the bulk value in first approximation), *N* the average number of Co atoms per pillar, and *T* the temperature. The experimental variation is indeed

linear (Fig. 4b). The intersection with the *y*-axis yields directly $H_{dip} = -42$ mT, and the slope yields N = 2800 atoms. These figures are in good agreement with those estimated from the size and geometry of the pillars observed by STM: $H_{dip}^{STM} = -32$ mT and N = 3300 atoms. This good agreement suggests that each pillar behaves like a single magnetic entity, and confirms the continuity of the pillars that had been suggested in the view of the STM images. Besides this good *quantitative* agreement, the fact that the superparamagnetic curves saturate rapidly and are closely fitted by Brillouin functions for any temperature, is an indication of a moderate volume distribution of the pillars.

We finally discuss the magnetic remanence observed at low temperature. Let us recall that the pillar growth process of magnetic materials was motivated by the search of a high superparamagnetic blocking temperature $T_{\rm B}$, as compared to flat dots. As each pillar is mostly single domain, its magnetic relaxation can be described by the Brown theory of thermal activation, which predicts that $T_{\rm B}$ is roughly proportional to the anisotropy times the volume of the pillar [13]. Therefore, fluctuations of $T_{\rm B}$ are expected from one pillar to another, because of differences of volume or anisotropy. The temperature for the onset of remanence shall therefore be interpreted as the largest $T_{\rm B}$ available in the assembly of pillar. For pillars of diameter 3 nm and height 5.5 nm, we deduce from Fig. 4 that the upper bound of $T_{\rm B}$ is around 90 K, whereas the $T_{\rm B}$ of flat dots with identical areal density and lateral size is about 20 K [4]. This dramatic increase is ascribed to the large volume of the pillars as compared to the flat dots. Following this idea, we checked that $T_{\rm B}$ increases when the pillars' volume is increased. For pillars of average diameter 4.2 nm and height 8 nm, the onset of remanence occurs at $T_{\rm B} = 300$ K (see Fig. 5), i.e. 15 times higher than in flat dots. However, the increase of remanence with the decrease of temperature is moderate in the assembly of pillars, whereas the increase should be rapid in the case of an isolated single pillar with a given $T_{\rm B}$. It is still unclear whether this effect is the consequence of a wide distribution of $T_{\rm B}$ in the sample, or is caused by the inter-pillar dipolar fields that favor a ground state with antiparallel alignment of neighboring spins (it shall be noted that these pillars have a larger volume,



Fig. 5. For pillars of diameter 4.2 nm and height 8 nm: perpendicular remanence, measured by hysteresis loops performed at different temperatures.

but the same packing density as the pillars examined in Fig. 4, so that now the strength of inter-pillar dipolar fields is larger). Further characterization is needed to clarify this point.

4. Conclusion

We have demonstrated with the system Co/Au(111) a novel thin film growth process based on alternating Co and Au depositions, which allows the submonolayer-range flat pattern of Co dots to be replicated vertically. This way, we have fabricated self-organized arrays of nanosized vertical pillars with perpendicular magnetization, embedded in a nonmagnetic Au matrix. Magnetic measurements suggest that this process might be the key to rise dramatically the superparamagnetic blocking temperature of high-density self-assembled/self-organised systems (20–300 K in the present case), while keeping the lateral packing density unchanged.

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