Domain Shapes and Superlattices Made of 8 nm Cobalt Nanocrystals: Fabrication and Magnetic Properties

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Three-dimensional superlattices forming films oriented along the substrate and dots deposited on a film made of 8 nm cobalt nanocrystals have been fabricated. The magnetic properties of such artificial structures are compared.

Ordered nanoarrays of magnetic materials have received considerable attention both theoretically and experimentally due to their potential application in developing high density magnetic recording media and to their fascinating experimental behavior. Self-assembly is a promising technique for preparing such structures because of its low cost, high yield, and the ability to achieve extremely small features In the past few years, several groups have constructed two-dimensional (2D) and three-dimensional (3D) superlattices with most of the experiments using silver sulfide,[1,2] silver,[3] and gold nanocrystals.[4] It has been quite clearly demonstrated that nanocrystals having a low size distribution are able to self-organize in a very large scale hexagonal network.[1−4] On increasing the nanocrystal concentration, 3D superlattices are obtained. "Supra" crystals are formed.[1]

Very recently, with silver nanocrystals, collective optical properties were observed.[5] Similarly, a marked change in the electron transport properties with the self-organization has been demonstrated.[6]

Like other nanocrystals, cobalt nanocrystals are able to self-organize in 2D hexagonal networks.[7,8] Collective magnetic properties due to dipole−dipole interactions between nanocrystals at a given distance from each other have been pointed out.[7,9]

Conversely to what is observed with silver sulfide and silver nanocrystals having the same size distribution, cobalt nanocrystals do not self-organize in 3D superlattices.[10] A film without any structure is obtained. This is attributed to magnetic interactions between cobalt nanocrystals. To induce organization of these nanocrystals, a magnetic field was applied perpendicular to the substrate. Several organizations, such as dots or labyrinths deposited on a film, both made of cobalt nanocrystals, are observed.[10] These artificial structures can be manipulated to achieve tailored materials for varied applications and for exploration of physical phenomena, since the magnetic properties of this new class of materials differ from both those of individual nanoparticles and bulk materials.[9]

We report here the fabrication of films oriented along the substrate and dots deposited on a film made of 8 nm cobalt nanocrystals and the magnetic properties of these artificial structures.

Cobalt nanocrystals with 8 nm average diameter coated with lauric acid (see appendix) were dispersed in hexane or in powder form.

At room temperature, magnetization curves[11] of cobalt nanocrystals either dispersed in hexane or in powder form show no hysteresis. This is due to the fact that for 8 nm cobalt nanoparticles, the thermal excitation is high enough to overcome the energy barrier related to the magnetic anisotropy. At 3K the thermal excitation vanishes, the magnetization curves of the cobalt nanocrystals dispersed in hexane or collected as a powder show a hysteresis, confirming the ferromagnetic behavior of these nanocrystals. With both samples (dispersed in hexane and in powder form) magnetization saturation, M_s, is not reached. It is deduced from extrapolation and estimated to be 120 emu/g instead of 162 emu/g for the bulk phase for cobalt. Similar behavior has been observed with various magnetic nanocrystals and is attributed to the strong interactions between the lauric acid and cobalt atoms at particle surfaces.[12] The reduced remanences, M_r/M_s, deduced from the magnetization curves of nanocrystals dispersed in hexane and in powder form are 0.51 and 0.45, respectively. This difference is explained in terms of a demagnetizing field. It depends on the demagnetizing factor ($^1/_3$ for spheres) and on the density of nanocrystals. In dilute solution, the density is zero whereas it is not negligible in powder form. The coercive field, H_c, remains unchanged ($H_c = 0.18$ T). The reduced remanence ($M_r/M_s = 0.51$) is above the calculated value for uniaxial anisotropy ($M_r/M_s = 0.50$) and lower than that for cubic anisotropy ($M_r/M_s = 0.81$).[13] With nanocrystals it has been well shown that the calculated limit is never reached,[14] indicating a cubic anisotropy for cobalt nanocrystals, which is consistent with their fcc structure.[7]

To obtain new artificial structures the following procedure is used: a carbon HOPG substrate is immersed in a cell containing 200 μL of cobalt nanoparticles solubilized in hexane (4×10^{-6} M in nanocrystals) and placed between the coils of an electromagnet.[15] A field is applied or not, parallel or perpendicular to the HOPG substrate. The evaporation process, which takes 12 h, occurs under hexane vapor at room temperature and produces a black magnetic film. Addition of a hexane drop to the substrate totally dissolves the various structures described below and the observed TEM picture is the same as that usually obtained by deposition of a drop of the solution. The amount of material deposited on the substrate is around 40% of the initial mass. This is deduced from the optical density at 650 nm of nanocrystals collected from the substrate dispersed in hexane. The structure is observed by SEM[16] on a very large scale (up to 0.02 mm^2).

Whatever the structure of the film described below is, the saturation magnetization reached at 2 T is 120 emu/g.

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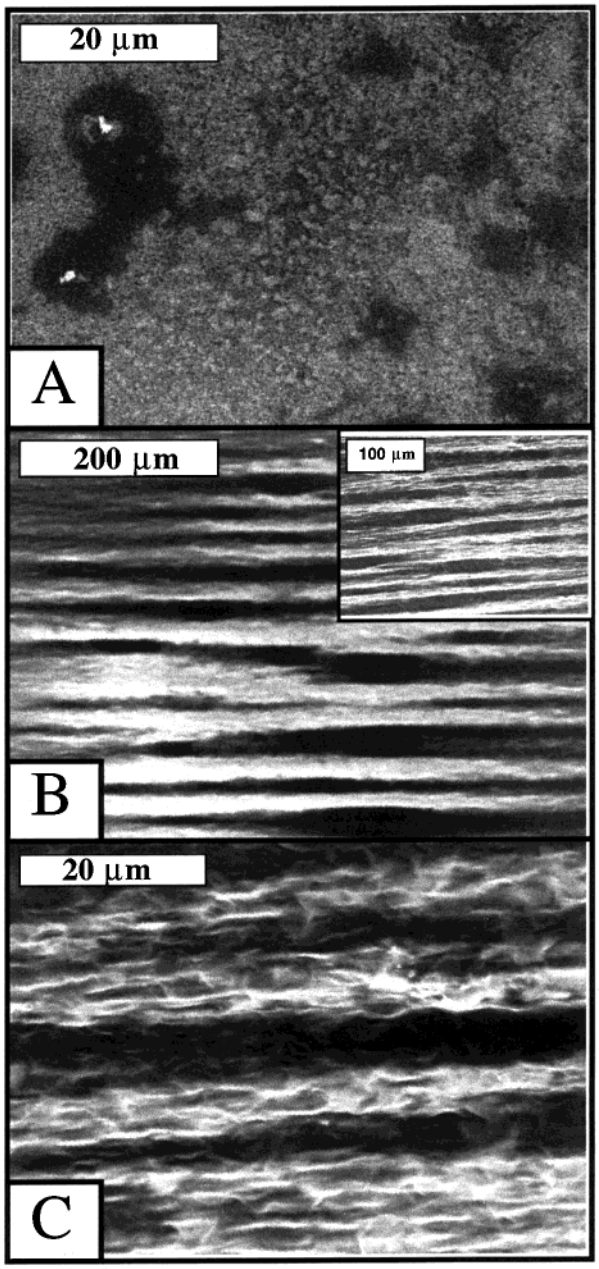

Figure 1. SEM patterns of cobalt superlattices obtained by evaporating 200 μL of a solution of cobalt nanoparticles (4×10^{-6} M in particles) on HOPG substrates. The evaporation time is 12 h. The field is applied parallel to the HOPG substrate. A: deposited without magnetic field. B and C: deposited with a magnetic field ($H = 0.27$ T) parallel to the substrate at various magnification. Inset B: sample tilted at 45°. The deduced height of the film is about 2 μm.

In the absence of an applied magnetic field during deposition, a film without structure is observed (Figure 1A). The reduced remanence ($M_r/M_s = 0.50$) is similar to that obtained when the nanocrystals are dispersed in hexane ($M_r/M_s = 0.51$). This is due to the fact the demagnetizing factor is close to zero under both experimental conditions. Conversely, the coercive field drastically increases ($H_c = 0.27$ T) when the nanocrystals are deposited on a substrate compared to that for those isolated in solution ($H_c = 0.18$). This increase could be attributed to small ferromagnetic domains made of several adjacent particles having the same orientation of their magnetic moments. This is supported by the fact that nanocrystals coated with lauric acid are able to self-organize in 2D hexagonal networks.[8] This can be related to what is observed with Fe

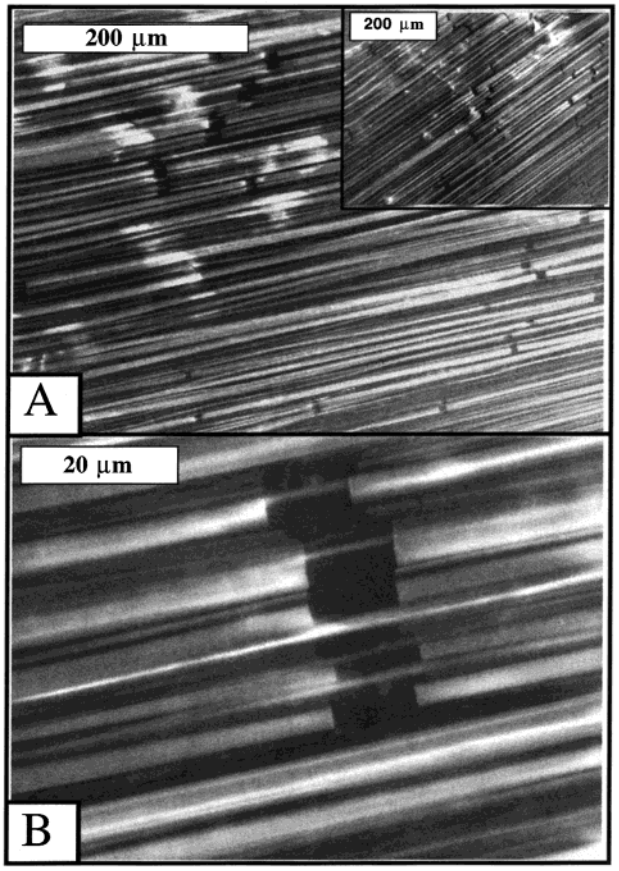

Figure 2. A and B. Various magnifications of SEM patterns of superlattices obtained by deposition on HOPG substrates with a magnetic field parallel to the substrate ($H = 0.56$ T). Inset A: sample tilted at 45 °. The deduced height of the film is about 2 μm.

granular films where the coercive field increases with the particle size.[17]

When the applied magnetic field is parallel to the substrate during the deposition process, the nanocrystals assemble with formation of large linear patterns along the field (Figure 1B,C and Figure 2). The average height of the film, determined by tilting the sample, is 2 μm. The film made of cobalt nanocrystals shows a large extent of corrugation with a quasi-periodic structure in the direction of the applied field. The patterns cover the overall HOPG substrate and the height of the film remains similar for any applied field. However, the corrugation markedly changes with the strength of the applied field. The wavelength of the corrugation is defined as the average distance between two maxima on the film. When the applied field is 0.27 T, there is a rather rough surface with a corrugation wavelength of 38 μm as shown in Figure 1B,C. On increasing the applied magnetic field to 0.56 T, the wavelength shows a large decrease to 7 μm (Figure 2) and the structures are sharper. Thus, the ordering and the compacity of the corrugated film made of cobalt nanocrystals markedly increase with the strength of the applied film.

To simplify the text, the samples obtained by applying zero (Figure 1A), 0.27T (Figure 1B,C) and 0.56 T fields (Figure 2) are called A, B, and C, respectively. The hysteresis loops are recorded when the applied magnetic field is parallel to the substrate, i.e., parallel to the film direction. Under these experimental conditions, the nanocrystals form a film and the demagnetizing factor is close to zero. Figure 3 shows a change in the hysteresis loop with the sample used. The hysteresis loop of sample A is inside that of sample B. Similarly it is straighter

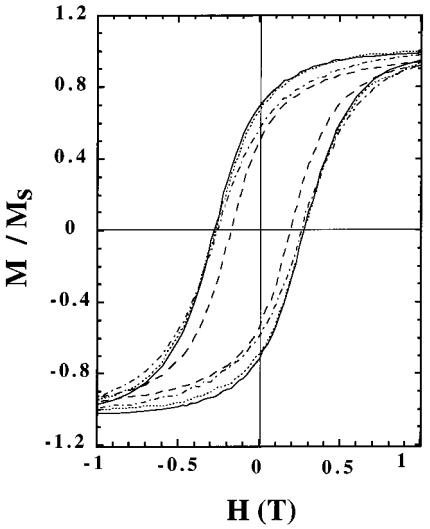

Figure 3. Hysteresis magnetization loops obtained at 3 K for samples A, B and C. In all cases the measured field is along the plane of the substrate. In A (— —) and B (— — —), the field is parallel to the cobalt film. For sample C, the field is either parallel (—) or perpendicular (— - —) to the linear patterns.

for sample C than B. The reduced remanences are 0.50, 0.57, and 0.70 for A, B, and C, respectively. The coercive field is 0.27 T for A and B and 0.30 T for C. The increase in the reduced remanence when a magnetic field is applied to the sample during the deposition process cannot be attributed to a change in the macroscopic shape as this remains the same for both B and C. Such behavior could be attributed to a partial orientation of the easy axes involving a rotation of the nanocrystals. With cubic anisotropy it is quite difficult to distinguish from hysteresis loop if the easy axes are oriented. As a matter of fact rotation of the sample by 90° along the plane of the substrate induce a theoretical change of the reduced remanence from 1 to 0.90 if all the easy axes are oriented. This cannot be observed experimentally. However, the increase in the reduced remanence with the strength of the applied field during the evaporation process is rather large. To explain such increase, formation of a ferromagnetic domain induced by strong dipolar interactions is assumed. During the deposition process in a magnetic field, the magnetic moments of the nanocrystals are oriented and ferromagnetic domains appear in the film. Their size increases with the strength of the applied magnetic field and they remain stable when the magnetic field is turned off. The stability of the ferromagnetic domain is controlled by the dipolar interactions between adjacent particles in the 3D structures. The increase in the ordering and the compacity of the film (i.e., by increasing the strength of the magnetic field applied during the deposition process) favors formation of ferromagnetic domains. Their size increases with increasing the magnetic field applied during deposition. Simulations developed in our laboratory for nanocrystals organized in 2D on hexagonal networks having a large coupling constant indicate formation of ferromagnetic domains. The presence of a ferromagnetic domain, at zero field, induced by dipole−dipole interactions has been demonstrated.[18] In our previous paper,[9] we showed that cobalt nanocrystals are characterized by a low coupling constant ($\alpha_d = 0.05$) whereas such ferromagnetic domains appear at zero field for a coupling constant greater than 0.2. However the simulations were done at zero field for a 2D superlattice organized in a hexagonal network and not for a 3D film composed of several layers of cobalt nanocrystals deposited under a field. Formation of ferromagnetic domains is also supported by an increase in the coercive field with increasing the strength of the magnetic field applied during the nanocrystals deposition.

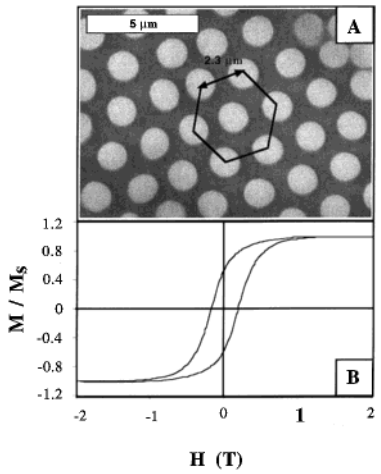

Figure 4. A-SEM patterns of dots obtained by deposited cobalt nanoparticles on HOPG under 0.27 T magnetic field applied perpendicular to the substrate. B: Hysteresis loop recorded at 3 K of the dot patterns. The sample is along the magnetic field of the SQUID.

Previously we reported formation of dots sitting on a thick film (2 μm) made of cobalt nanocrystals.[10] To get such dots the procedure is similar to that described above for films. The major difference is that the applied magnetic field is perpendicular to the substrate instead of parallel. The strength of the applied field is 0.27T. The SEM patterns observed at the end of the evaporation process show formation of microscopic dots (Figure 4A). They are organized in a well-defined hexagonal network deposited on a dense film made of cobalt nanocrystals. The average dot diameter is 1.75 μm with a size distribution of 5.3%, and the interdot distance is 2.4 mm (core to core). The height of the dots estimated by tilting the sample is 0.5 μm and they are on a 2 μm high film of cobalt nanocrystals.

The magnetic behavior is recorded under an applied magnetic field parallel to the substrate. The reduced remanence and the coercive field are 0.63 and 0.27 T, respectively. This indicates no drastic change in the magnetization with formation of dots on a film made of nanocrystals. However, the reduced remanence is higher (0.63) than that observed for nanocrystals when the nanocrystals are aligned (0.57). Under both experimental conditions the strength of the magnetic field applied during deposition remains at 0.27 T. These differences in the reduced remanence can be attributed to a shape anisotropy of the artificial structure.

In the present paper we demonstrate that it is possible to obtain 3D superlattices of cobalt nanocrystals. Aligned nanocrystals are observed when a magnetic field is applied parallel to the substrate during the deposition process. The increase in the reduced remanence is attributed to formation of ferromagnetic domains induced by the magnetic field applied during the deposition process. By applying, during the deposition process, a magnetic field perpendicular to the substrate, dots deposited on a film, both made of cobalt nanocrystals, are observed. The magnetization data can be explained by a change in the shape of the artificial structure.

Appendix

Reverse micelles, which are water in oil droplets stabilized by a monolayer of surfactant (e.g., cobalt bis(2-ethyl-hexyl)-sulfosuccinate, usually called $Co(AOT)_2$), are characterized by an average diameter of 12 nm. The water content, defined as *w*

= $[H_2O]/[AOT]$, is fixed at 40. The cobalt counterions are reduced with sodium tetrahydroboride, $NaBH_4$. In a typical experiment, 200 μL of a 1 M $NaBH_4$ aqueous solution are added to 3 cm^3 of a micellar solution of 0.1 M $Co(AOT)_2$ containing water. Immediately after borohydride addition, the micellar solution color turns from pink to black, indicating the formation of colloidal particles. They are extracted from reverse micelles, under anaerobic conditions, by covalent attachment of lauric acid $C_{12}H_{25}COOH$. Addition of ethanol in excess induces the precipitation of the lauric acid coated particles. The solution is washed and centrifuged several times with ethanol to remove all the surfactant and then a black powder is recovered which is easily redispersed in toluene. This chemical surface treatment highly improves the stability of cobalt exposed to air. Thus, cobalt nanoparticles can be stored without aggregation or oxidation for at least 1 week. Cobalt nanocrystals have been characterized by EXAFS.[8] No oxide is detected. The average diameter and size distribution are 8 nm and 14%, respectively.

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