Superparamagnetic and ferromagnetic CoPt nanoparticles deposited on silicon dioxide

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Abstract. Co₅₀Pt₅₀ nanoparticles were co-deposited on thermally oxidized Si substrates by electron beam evaporation, at a substrate temperature between RT and 750°C. The co-deposition led to formation of nanoparticles which exhibit a mean diameter between 2 and 20 nm depending on the nominal thickness of the layer and on the substrate temperature. Different processing conditions resulted in different structural and morphological properties of the samples, which led to superparamagnetic and ferromagnetic behaviours. The post-annealing treatment of the CoPt nano-grains, performed in-situ soon after the deposition in the crystallization of the L₁₀ ordered phase and consequently in the progressive magnetic hardening of the samples with a maximum coercivity of ~ 7.4 kOe.

1. Introduction

The processing and characterization of magnetic nanoparticles represents, nowadays, frontier research in the field of nanomaterials technology. In particular, the interest on elemental and alloy magnetic nanoparticles is aimed at the engineering of the particle size down to nanoscale level, in order to understand their fundamental properties in the superparamagnetic state and also for technological applications. In this scientific and technological scenario, CoPt nanoparticles are considered to be among the best candidates for high-density recording media and exchange bias nanomagnets [1], as the high anisotropy constant of the tetragonal form [2] enables them to avoid the superparamagnetic behavior, even for particles of few nanometers in diameter [3]. Furthermore, the growth and the investigation of CoPt nanoparticles on SiO₂/Si substrates can be interesting not only in the field of high density recording media but as a possible implementation of CoPt nanoparticles for future integrated circuitry. The aim of the present study is to investigate the relationship between the growth conditions and the nanograin size of CoPt nanoparticles grown on thermally oxidized Si substrates and to investigate their magnetic properties.

2. Experimental

CoPt nanoparticles were prepared by electron beam evaporation at a base pressure of 2×10⁻⁷ mbar by co-deposition. Each sample was grown on a thermally oxidized silicon (100) substrate with a SiO₂ amorphous layer of 90 nm on top. The total nominal thickness of both Co and Pt was measured by a
quartz thickness monitor. The partial deposition rate was ~0.030 and 0.033 nm/s for the Co and the Pt respectively, which led to a Co:Pt atomic ratio ~1. The samples were deposited in a range of substrate temperatures $T_s \sim RT - 750^\circ C$ and at nominal thickness of the layer $f = 0.9 - 8.5$ nm. Table 1 summarizes the main processing parameters of the samples and their mean particle size $D_{ave}$. The samples B were annealed in vacuum for 20 minutes, immediately after the deposition at 750°C.

The structural and morphological properties of the samples were analyzed by X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM). The qualitative chemical characterization of all specimens was performed by Energy Dispersion X-ray (EDX) analysis for Co and Pt. The magnetic properties of the CoPt nano-islands were measured using a Magneto Optical Kerr Effect (maximum field 22 kOe) magnetometer at room temperature. The samples were measured in the perpendicular direction with respect to the plane of the substrate. Corrections for self-demagnetization, to determine the exact internal field of the samples during the magnetic measurements, were not performed.

### Table 1. Main growth parameters ($f$), substrate temperature ($T_s$) and mean diameter of the CoPt nanoparticles ($D_{ave}$).

| ID  | $f$ (nm) | $T_s$ ($^\circ C$) | $D_{ave}$ (nm) | ID  | $f$ (nm) | $T_s$ ($^\circ C$) | $D_{ave}$ (nm) |
|-----|----------|-------------------|----------------|-----|----------|-------------------|----------------|
| A   | 8.5      | 750               | 15.1           | Sample E | 1.7      | 500               | 3              |
| B   | 8.5      | 750*              | 19.5           | Sample F | 1.7      | 300               | 6              |
| C   | 3.5      | 750*              | 5.2            | Sample G | 1.7      | RT                | -              |
| D   | 1.7      | 550               | 4              | Sample H | 0.9      | RT                | 2              |

*Samples B was annealed at 750°C in-situ immediately after deposition, for 20 minutes.

### 3. Results and discussion

Previous studies [4] showed that a perfect mixture of Co and Pt in the particles occurs during e-beam co-evaporation. Figure 1 shows the XRD patterns for the samples A and B ($f = 8.5$ nm, $T_s \sim 750^\circ C$). As can be seen, the XRD pattern for the as-deposited samples (sample A) shows a weak peak in the region between the (111) diffraction lines of the disordered cubic phase (CoPt$_3$) and the ordered tetragonal phase (CoPt), suggesting that the high $T_s$ is not enough to promote a substantial structural ordering of the nanoparticles in the L1$_0$ ordered phase. Consistently with previous results [4, 5], the annealing at 750°C for 20 minutes (figure 1, samples B) led to a satisfactory crystallization of the samples in the L1$_0$ ordered structure and to a (111) texturing. Since (111) is the closest packed plane, the annealing favoured the development of such a texture due to minimization of surface energy for the nanoparticles. Such results were confirmed by plan view TEM diffraction patterns (not shown here). No diffraction spots are observed from the thinner specimens both in XRD and TEM analysis because of the small diffracting volume. Nevertheless, previous studies suggest that the similar

![Figure 1. XRD patterns obtained for the samples A and B.](image-url)
processing conditions performed on samples A and B result in analogous structural transitions on thinner samples [5]. For this reason, since no annealing was performed on the samples with \( f \leq 3.5 \) nm described in the present study (samples C-H), such nanoparticles were expected to be in the cubic phase.

Figure 2(a)-(h) show the in-plane TEM bright field images of the samples A-H respectively. As can be seen comparing figure 2(a) and figure 2(b), the thermal annealing leads to an increase of the mean inter-particle distance \( I_{\text{ave}} \) indicating a typical Ostwald ripening behavior [6], whose extent decreases at lower \( f \) [5]. Comparing figure 2(a) (samples A) and figure 2(c) (samples C), it is observed that the \( D_{\text{ave}} \) decreases with decreasing the nominal film thickness (see table 1). In order to reduce \( D_{\text{ave}} \), the samples were grown at \( f = 1.7 \) nm and \( T_s \sim 550^\circ\text{C} \) (samples D, figure 2(d)). As can be seen \( D_{\text{ave}} \) is significantly smaller. Comparing figure 2(d) - (g) (see also table 1) \( D_{\text{ave}} \) decreases with decreasing \( T_s \) between 550 and 500°C, as expected, and then increases in the range between \( T_s \sim 400^\circ\text{C} \) (the in-plane TEM image of this sample is not shown here) and \( T_s \sim \text{RT} \). Due to the worm-like pattern of sample G it has not been possible to calculate \( D_{\text{ave}} \) (see table 1). The reason for the \( D_{\text{ave}} \) raise for \( T_s \leq 400^\circ\text{C} \) is probably due to the beginning of coalescence between the growing nanoparticles during the deposition at lower \( T_s \) [7]. In order to reduce further \( D_{\text{ave}} \), the samples were deposited with \( f = 0.9 \) nm and at \( T_s \sim \text{RT} \). As can be seen, the samples exhibit a smaller \( D_{\text{ave}} \) of \( \sim 2 \) nm.

Previous studies [8] proposed that a mean interparticles distance \( I_{\text{ave}} > 2-5 \) nm is enough to prevent the occurrence of the exchange and dipolar interactions. For sample A, \( I_{\text{ave}} \) is \( \sim 1 - 2 \) nm, while for all other samples \( I_{\text{ave}} \geq 5 \) nm. This suggests that the dipolar coupling between the nanoparticles is expected only for the samples A.

Figure 3 (a) – (h) shows the perpendicular magnetization curves for the samples A-H respectively. The curves were obtained without demagnetizing corrections; for this reason real magnetization curves with steeper slopes were expected [9]. The as-deposited samples 8.5 nm thick (sample A, figure 3(a)) are ferromagnetically soft. This magnetic behavior is consistent with the incomplete crystallization of such specimens in the tetragonal phase [10]. The thermal annealing at 750°C for 20 minutes (sample B, figure 3(b)) results in a significant increase of \( H_c \) (7.4 kOe) due to the formation of the L1_0 structure [10]. Because of the large inter-grain distance and the \( D_{\text{ave}} \) smaller than the single domain critical size [2], sample B was expected to behave according to the Stoner-Wohlfarth model [9].
The $D_{\text{ave}}$ for thinner samples ($f = 0.9 - 3.5$ nm, see table 1) is smaller than the critical superparamagnetic grain size $D_{\text{cr}}$ for the CoPt$_3$ structure ($\sim 9$ nm). Consistently, samples C - H (figure 3(c) - (h)) exhibit a superparamagnetic behavior, confirmed by the fitting of the experimental data with the Langevin curve.

4. Conclusion
In conclusion, the present study describes the properties of CoPt nanoparticles deposited at $T_s \sim RT - 750^\circ$C. The reduction of the thickness of the samples resulted in smaller $D_{\text{ave}}$, while the formation of the L$_{10}$ phase and the ferromagnetic hardening of the nanoparticles was observed after thermal annealing for the samples deposited with $f = 8.5$ nm. The magnetic properties of the as-deposited samples range from the superparamagnetic behavior for as-deposited samples with $f \leq 3.5$ nm, to ferromagnetism for the samples $8.5$ nm thick with a maximum coercivity of $7.4$ kOe obtained after annealing at $750^\circ$C for 20 minutes.

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