

# The oxidation of metal-capped Co cluster films under ambient conditions

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## Abstract

We report on the unexpected deterioration under ambient conditions of films of Co clusters capped with relatively thick (>100 nm) Cu (or Ti) layers deposited by either thermal evaporation or by radiofrequency sputtering. The magnetic character of the clusters, prepared by gas-phase condensation, allows monitoring the oxidation of the samples through the decay of the saturation magnetization, which takes place on a timescale of days. By contrast, diluted (<10 at.%) cluster-assembled granular Co:Cu films, prepared by co-deposition of the Co clusters with a Cu vapour, are perfectly stable under ambient conditions. We tentatively explain the oxidation of the cluster films as stemming from their very high porosity.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Metallic nanoparticles are crucial building blocks in the ever growing field of nanotechnology, with applications in diverse areas, such as optoelectronics [1], biomedicine [2], and magnetic sensing [3] and data storage [4]. From a fundamental viewpoint, nanoparticles properties are often strikingly far from those of their bulk counterparts, and they can be tailored by tuning their size, concentration, capping shell or surfactant chemistry [1, 5]. Magnetic nanoparticles are a clear example of this, the stability of their magnetic moment strongly depending on all the above parameters, and, in particular, on the possible oxidation of an outer shell [4, 6].

Often, it is tacitly assumed that the capping layers customarily deposited for protection against oxidation onto continuous, conventional thin films are equally efficient when used to cover nanoparticles or cluster films, but this does not seem always the case. For instance, Binns *et al* deposited films of Co clusters and capped them with Ag [7]. They found, however, that the samples presented magnetic features characteristic of partially oxidized Co, namely a clear exchange-bias effect (present in materials where a nanoscaled ferromagnet is in close contact with an antiferromagnet, in this case Co and CoO, respectively). The same applies to the work of Meldrim *et al* in granular Co:Cu and Co:Ag (clusters:matrix) films in the concentration range 10–50% [8].

Recently, Hillenkamp *et al* turned their attention to this subject and explicitly studied this most important question of the possible oxidation of apparently well-capped nanoparticles [9]. They investigated the stability under ambient conditions of Ag clusters prepared in a cluster source and then co-deposited with a silica matrix to form a granular film. Unexpectedly, they found that the plasmon absorption peak associated to metallic Ag disappeared on a timescale of several days, pointing out the progressive oxidation of the nanoparticles.

Cluster-assembly constitutes a flexible strategy to build nanogranular structures, allowing the independent control of particle size and concentration [6]. This technique, employed in the investigations referenced in the above paragraph, uses a relatively high-pressure magnetron sputtering source with a gas-aggregation tube to create a cluster beam. The clusters are then injected in the deposition chamber, where they can build porous films or be combined with another (matrix) material to grow granular films. These two types of samples will be called hereafter 'cluster films' (CF) and 'granular films' (GF), respectively.

In this work, we have taken advantage of the ferromagnetic (F) character of cobalt to shed more light on the often overlooked issue of the adequate oxygen-protection of cluster-assembled films. In spite of the cited previous results, ours are still surprising: relatively thick Cu films (>100 nm), deposited either by sputtering or thermal evaporation, do not prevent Co cluster films from oxidation,

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**Table 1.** Summary of the main characteristics of the cluster films (CF) and granular films (GF) discussed in the text.

Name	Capping/ matrix	Deposition method	Capping layer thickness <sup>a</sup>	Co atomic concentration (%)	$M_S$ reduction (%)
CF1	Cu	rf sputtering	180 nm	—	37
CF2	Ti	rf sputtering	180 nm	—	44
CF3	Cu	Evaporation	120 nm	—	27
CF4	Cu	Evaporation+ rotation	150 nm	—	17 <sup>b</sup>
GF1	Cu	Evaporation	0	$1.8 \pm 0.3$	<0.2
GF2	Cu	Evaporation	0	$4.1 \pm 0.3$	<0.2
GF3	Cu	Evaporation	0	$6.7 \pm 0.6$	<0.2

<sup>a</sup> Approximate values extracted from the deposition rates measured with a quartz crystal monitor.

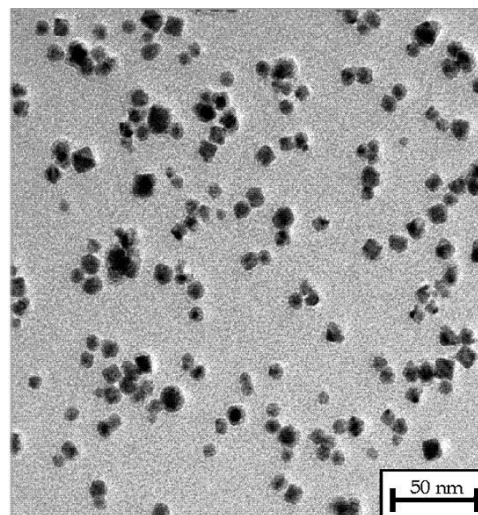
<sup>b</sup> Value extrapolated from a logarithmic fit of the corresponding curve in figure 4.

although evaporation works better. In contrast, Co:Cu granular films with concentrations below 10% at are stable at ambient conditions.

## 2. Experiment

Cobalt clusters were prepared in a commercial cluster source coupled to a chamber equipped with rf sputtering cathodes and a conventional thermal evaporator. The sputtering power in the cluster source was 30 W, and the argon pressure 0.2 mbar, resulting in a particle deposition rate of  $0.2 \text{ \AA s}^{-1}$  and cluster films about 30 nm thick (30 min deposition time). However, this nominal thickness, obtained from a quartz crystal monitor, is an estimate for a compact film that should be multiplied by a presumable high porosity factor (see below). The cluster films were then protected by depositing relatively thick layers of Cu (or Ti) either by rf sputtering (at a rate of  $1.0 \text{ \AA s}^{-1}$ ) or by thermal evaporation (at  $0.8 \text{ \AA s}^{-1}$ ). Table 1 shows the nominal thickness of the deposited capping layers (always above 100 nm, much thicker than those typically used to protect conventional, continuous, thin films). All samples were deposited onto glass substrates (with a very small, time independent diamagnetic response). The substrates were stuck to a plate fixed at an angle of  $45^\circ$  for the samples capped by sputtering, whereas such plate was vertical (perpendicular to the cluster beam), and in rotation for sample CF4, during the deposition of the evaporated capping layers. A few granular samples, where a Cu matrix was evaporated during the deposition of the preformed Co particles, were also prepared. The Co concentration in these films was measured by energy dispersive microanalysis and kept below 10 at.%.

Hysteresis loops were measured in a vibrating sample magnetometer immediately after taking the samples out of the deposition chamber. The films were left at ambient conditions and the hysteresis loop measurement was repeated several times over several days. Transmission electron microscopy (TEM) images of the unprotected particles were taken using a Phillips CM200 microscope, for low particle coverage samples, and a JEM 2100 for cluster films, both in bright field mode. Scanning electron microscopy (SEM) and optical



**Figure 1.** TEM micrograph of the particles used in the cluster films and granular samples discussed in the text. Fitting of the spherical and cubic particles to lognormal distributions yielded, respectively, mean particles diameter of 7.4 and 7.3 nm, and widths of 0.11 and 0.18.

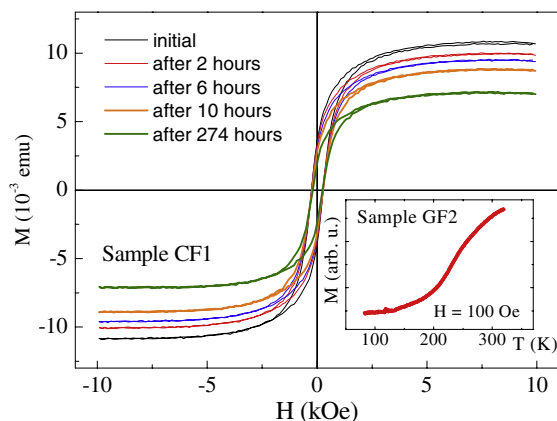
microscopy were also employed. Table 1 summarizes the main characteristics of the seven samples studied in this work: four cluster films (CF) and three granular films (GF).

## 3. Results and discussion

Figure 1 shows a transmission electron micrograph of the same particles used to assemble the films, this time deposited for only one minute onto a carbon-coated Cu grid. A core-shell structure resulting from the oxidation of these unprotected particles can be clearly observed in most of them. The particle size distribution is relatively narrow (bearing in mind that no size filtering whatsoever was performed), with an average particle diameter of about 7.4 nm. It is noteworthy that there are two types of particles, corresponding to roughly spherical and cubic shapes. Both types have very similar size distributions (fitting to a lognormal function yielded the same mean size within the error bar, and distribution widths below 0.2 for both kinds of morphologies). The stark contrast between this observation and those reported in some works on particles prepared in similar cluster sources, where less symmetric morphologies were observed only in relatively large particles [10], should be the matter of further investigation in the future.

The repeated measurement of the hysteresis loop for the CF samples described in table 1 yielded the surprising result that the saturation magnetic moment ( $M_S$ ) always decreases significantly over a time span of a few days (figure 2 shows the data measured in sample CF1). The time dependence of the saturation moment decay is roughly logarithmical (see below).

It must be noticed that the particles are magnetically blocked at room temperature, as evidenced by the considerable coercive field ( $>200 \text{ Oe}$ ) exhibited by the loops. Although the bulk value of the anisotropy constant for fcc Co (usually the stable phase for small particles) yields a critical size

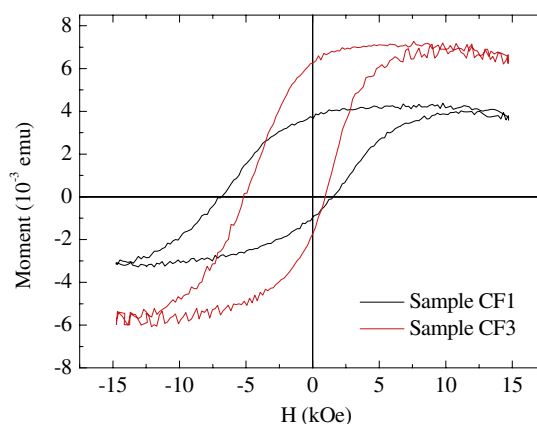


**Figure 2.** Hysteresis loops, measured at ambient conditions after different times, of a Co cluster film capped sputtered Cu (sample CF1). The inset shows the temperature dependence of the zero-field-cooled magnetization of a sample with similar nanoparticles dispersed in a Cu matrix (sample GF2).

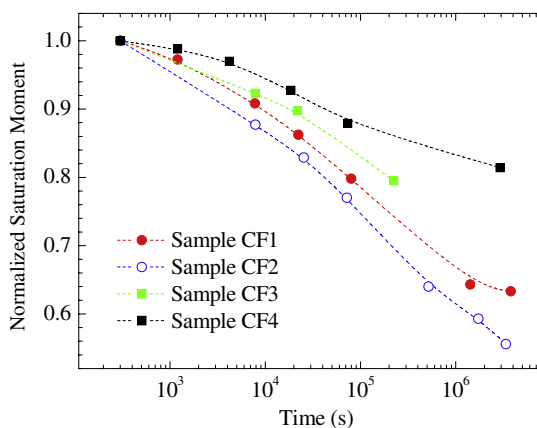
for superparamagnetism at room temperature close to 9 nm (larger than our particles), it must be taken into account that: (i) the effective anisotropy depends heavily on the particle size, structure, shape and surface details (see [11] and references therein), and (ii) the strong dipolar—and even direct exchange-coupling between the particles in the cluster films will stabilize them up to temperatures higher than their blocking temperature in isolated conditions [12]. Nonetheless, we have measured the zero-field-cooled (ZFC) magnetization curve (in a field of 100 Oe) of one of the granular films (GF2) and observed, indeed, that the curve maximum (average blocking temperature) is above room temperature (see inset of figure 2). Consequently, the magnetic particles considered in this work are stable at room temperature even when they are dispersed at a relatively low concentration (as in sample GF2).

Since incomplete oxidation of Co nanoregions typically results in the formation of CoO [13, 14], an antiferromagnetic (AF) compound contributing a negligible moment, the reduction of the saturation moment can be most simply interpreted as due to the progressive oxidation of the Co clusters. This interpretation is confirmed by the appearance of a strong exchange-bias effect, as figure 3 exemplifies for the same sample of figure 2 (black curve) after it had reached a stable magnetization (2 weeks). The sample was cooled in a field of 10 kOe down to 80 K prior to registering the magnetization upon field cycling. The unidirectional exchange coupling between the AF CoO and the ferromagnetic Co regions yields a shift of the hysteresis loop by a large exchange-bias field of 2.7 kOe and a significantly enhanced coercive field. Keeping the sample under vacuum prevented the sample from losing saturation moment, confirming that the cause for such losses is oxidation under ambient conditions. Note that in Co films exposed to ambient conditions the topmost 2.5 nm will oxidize forming a passivating oxide layer [15], i.e., spherical particles of 7.4 nm diameter would be expected to oxidize almost completely if they were left unprotected.

Several variations in the nature of the capping layer were tried in an attempt to reduce the oxidation of the underlying Co cluster film (see figure 4). To begin with, the capping

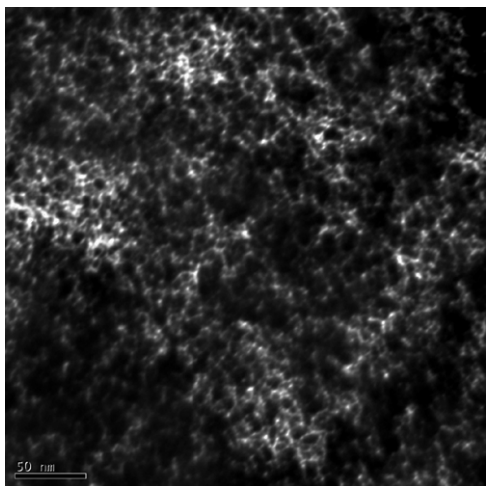


**Figure 3.** Hysteresis loops, measured at 80 K after field cooling in 10 kOe, corresponding to samples CF1 and CF3 after they had reached a stable magnetization.



**Figure 4.** Time evolution (under ambient conditions) of the saturation magnetization of differently capped Co cluster films. Lines are guides to the eye.

material was changed to titanium (sample CF2), which resulted in no improvement whatsoever with respect to the Cu capping layer of a similar thickness (CF1). Evaporating the capping layer (Cu) instead of sputtering it (sample CF3) did lead to a reduction of the cluster film oxidation, although about one fourth of the Co atoms still oxidized after a few days. This reduction might be tentatively attributed to the less directional character of the Cu vapour, i.e., sputtered materials are more prone to form columnar structures which could facilitate the diffusion of oxygen. This tendency is well known to be even stronger for oblique sputtering [16], as it is the case in samples CF1 and CF2. The last effort to reduce the oxidation consisted in rotating the samples during the evaporation of the Cu capping layer (sample CF4), which also resulted in some improvement (from 27% to 17%). In figure 3 it can be seen how one of this less oxidized samples (CF3) exhibits, apart from a higher saturation moment, a lower exchange-bias field compared with sample CF1 (with a reduction of 0.7 kOe). A higher degree of cluster oxidation, assuming a core-shell Co-CoO picture, would lead to a reduced ferromagnetic core size, and therefore, as observed, to a larger exchange-bias field (it must be recalled that  $H_E \propto 1/t_{FM}$  as a consequence of the surface

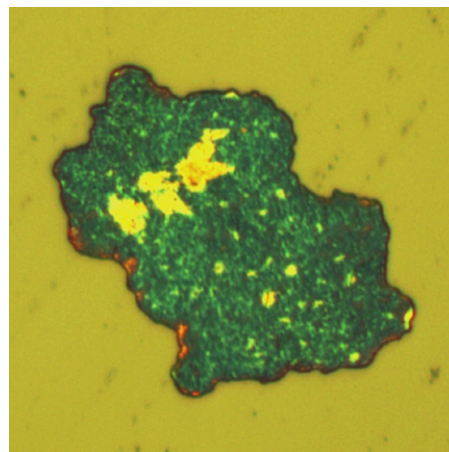


**Figure 5.** TEM micrograph of a cluster film, deposited over 30 min, showing a high degree of porosity. The scale bar at the bottom left corner is 50 nm.

nature of exchange coupling, where the effective ferromagnetic thickness  $t_{FM}$  is related here to the core diameter) [17]. It must be remarked that we have not observed any loop with a two-phase nature, as reported by Meldrim *et al* in partially oxidized Co:Cu dense granular films [8], i.e., the oxidation of the films reported here seem to have affected in a similar fashion to all, or most, of the Co particles, whereas Meldrim *et al* detected a non-biased phase (centred component) and a biased one (shifted component).

Recently, Koch *et al* prepared Co cluster films capped with Ag (of unreported thickness) and found shifted hysteresis loops at low temperature. They comment that ‘it is not clear whether the oxide shell formed within the deposition source or through imperfections in the capping layer’. The results reported above seem to indicate the latter.

A few granular samples (Co:Cu), with Co atomic concentrations ranging from 1 to 7 %, were also grown in order to check their possible deterioration under ambient conditions (see table 1) and shed light on the possible reasons for the oxidation of the cluster films. We found that they did not lose any saturation magnetization, at least on the timescale of days. This result is in agreement with the observations of Meldrim *et al*, who found several indications of the presence of CoO in granular Co:Cu and Co:Ag with volume concentrations of 30 and 50%, but not in the 10% concentrated samples [8]. They argued that granular samples with sputtered matrices become more porous (due to shadowing from the clusters) with increasing concentration, and this porous matrices allow for slow air diffusion. The observed reduction in magnetization loss when the matrix is evaporated (CF3) instead of sputtered (CF1) supports this hypothesis, as discussed above. Both our and Meldrim *et al*’s results on the stability of *diluted* granular samples are in contrast with the remarkable observations of Hillenkamp *et al*, who recently found an ageing behaviour in highly diluted (below 1 at.%) Ag:SiO<sub>2</sub> granular samples prepared by cluster-assembly (evaporating the silica matrix) or by annealing a co-deposited silica–silver film [9]. The oxidation of the silver clusters was attributed to diffusion of



**Figure 6.** Fragment of the CF4 film as seen from the cluster film side after a 30 min ultrasonic bath. The cluster film has been fully removed in the yellow areas, where the bottom of the Cu capping layer can be clearly observed. The picture lateral size is 250  $\mu\text{m}$ .

atmospheric oxygen through pores in the silica matrix and ‘even through the amorphous silica network’. It is certainly hard to think of a different mechanism to account for such slow oxidation processes, but it is still rather unexpected to have such a porous nature (with a network of interconnected pores to allow for oxygen penetration) in metallic capping layers about 200 nm thick. Nonetheless, and given that much thinner capping layers suffice to protect conventional thin films, it may be tentatively argued that the extremely high porosity of the cluster films, as can be seen in figure 5 (which reproduces a micrograph of a cluster film of similar thickness and formed by clusters of similar size to those studied here [18]), somewhat propagates up into the cover layer. A detailed cross-sectional HRTEM study would be needed to confirm this hypothesis.

Once assumed that oxygen will penetrate through the capping layer, the oxidation of the Co particles is facilitated by the lack of chemical bonding between them and the Cu capping layer. This statement is based on the following simple experiment. Some bits of sample CF4 (the least oxidized of the four cluster films in table 1) were peeled off from the glass substrates and submitted to an ultrasonic ethanol bath for 30 min, after which the solid material was filtered and dried. After the film lifting, both fresh surfaces had a dark colour characteristic of the Co–CoO particles (by comparison with unprotected Co films), although it was only a slight overtone in the glass side. The bath had two effects on the sample bits: (i) they were fragmented into submillimetre pieces, i.e., the films were very fragile (this could be related, in turn, to the presence of imperfections, which could also facilitate oxygen diffusion), and (ii) the cluster film was partially removed, leaving large exposed regions of the bottom side of the Cu capping layer (as observed using an optical metallographic microscope, see figure 6), i.e., the bonding between the two layers is so weak that a conventional cleaning procedure is enough to separate them. As a final note, it must be remarked that the samples sides were well covered by the capping layers, which were observed by scanning electron microscopy to spill down the substrate sidewalls, and, therefore, oxygen penetration through

the sides of the films cannot be held responsible for the observed oxidation.

In the granular films, the simultaneous deposition of the particles and the matrix yields a completely different scenario, with the particles much better protected inasmuch as they are fully surrounded by copper. This is so even if there is not chemical bonding, a question that we will try to ascertain in projected spectroscopic studies (XPS and EXAFS) in granular films comprising smaller Co particles than those studied in this work (in order to have a larger fraction of Co atoms at the Cu interface).

#### 4. Conclusions

In conclusion, by investigating Co clusters capped by Cu (and Ti) under different conditions we have emphasized and generalized the word of caution recently expressed by Hillenkamp *et al*: small metallic clusters are extremely susceptible to oxidation and conventional protection layers, effective for continuous thin films, may not be enough to guarantee their stability at ambient conditions. A double check of the ambient stability is, thus, in order before performing any sort of studies in cluster-based nanostructures, even if they have been capped with relatively thick cover layers. This word of caution applies too to recently developed bimetallic core-shell nanoparticles [19], very promising for biomedicine applications due to, among other reasons, their presumable chemical stability.

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