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Growth and properties of cobalt clusters made by sputtering gas-aggregation

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Abstract. A study of the different operation modes of a sputtering gas-aggregation source is presented. The size distributions of small cobalt clusters shed some light on the first steps of the growth process. Large clusters of 2 to 6 nm diameter with narrow distributions are obtained. Their icosahedral structure is identified by HRTEM observations.

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1 Introduction

The study of clusters is more than ever of strategic importance in order to achieve innovative materials and devices. This is particularly true in the field of spintronics, where the spin-dependent properties of artificial systems with nanometric magnetic elements are very important for new applications for information technologies. In this respect, the use of sputtering gas aggregation source offers the possibility to grow nanometric metallic clusters, with size distributions sometimes quite narrow, relatively easily. However, one drawback is that its operation is somewhat elusive and cannot be explained with simple models.

The growth of clusters can be addressed from a kinetic point of view with the Smoluchowsky rate equations for particle aggregation [1]. Within this formalism, the growth of clusters depends on the collision rate between clusters of sizes N_i and N_j, as well as the capture cross-section when atoms collide with other atoms or clusters. Considering that in our case we have to deal with two types of gases (Ar and He) in addition with the sputtered atoms and growing clusters, all with different drift and diffusion velocities, in an open system with temperature and concentration gradients; considering also the fact that in the source there is a drift velocity and some circulation in addition to diffusion, a solution for the growth equation is not within reach, and efforts to modelize its overall behaviour with simple concepts of clusters growth have failed [2,5], even if simulations can qualitatively reproduce some aspects of the early stages of nucleation [3].

In this paper, we will give a phenomenological description of the operation of the sputtering gas-aggregation source and describe some structural properties of the cobalt clusters we obtained. For one thing, we will show that the size distribution is not unique and that we can identify three regimes, with fairly different sizes and size distributions. These results indicate that there are more than one channel for the growth of clusters. In addition, we will present high resolution transmission microscopy analysis for Co clusters, showing with clear evidence their icosahedral structure.

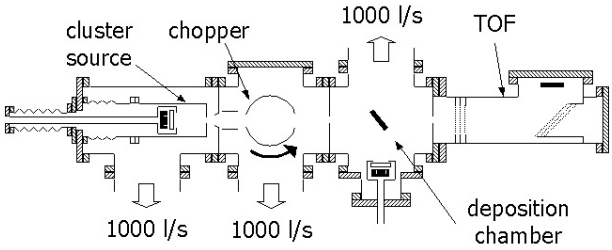

Fig. 1. The sputtering gas-aggregation source.

2 Experimental

The sputtering gas-aggregation source [6] consists of a magnetron sputtering head inserted in a liquid nitrogen cooled tube, which we will call the growth zone (Fig. 1). The length of this growth zone can be modified — from 40 mm to 300 mm — by moving the sputtering head. The sputtered atoms from the target are carried down the tube, where the growth of clusters is initiated by collisions within the sputtered gas, and with argon (injected through the sputtering head) and helium (injected from the back side of the growth zone). The cluster growth is continuously taking place as the gases are drifting to

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a diaphragm, where clusters are expelled in an intermediate chamber, then in the deposition chamber through a skimmer. The three pumping stages allow to keep the pressure in the deposition chamber at 10^{-6} mbar during operation of the source, where the pressure is between 0.1 and 1 mbar. Both Ar and He gases are high purity ($6N$) gases and residual gas analysis indicates impurity levels (O_2, CO, CO_2...) of 10^{-11} mbar in the source chamber (outside the cluster source), compared to 10^{-5} mbar of Ar. Two deflecting plates and a chopper are located in the second chamber. The chopper is used to achieve deposition of very low amount of clusters, when needed, while the deflection plates allow to roughly measure the kinetic energy of the clusters. The deposition chamber is equipped with a quartz crystal monitor for flux measurements. The clusters can be deposited on a retractable sample holder and covered with a protection layer using a second sputtering head. With typical operation conditions the beam size is 25 mm and the deposition rates vary between 0.07 Å/s and 0.4 Å/s, depending on the size of the clusters. In addition, the size distribution can be measured *in situ* with a time of flight spectrometer (TOF) in line with the source. One peculiarity of this system is that up to one third of the clusters are positively or negatively singly charged. For this reason there is no need to ionize the clusters for TOF measurements. Magnetic measurements (not reported here) where made on deposited clusters: they show bulk magnetization, with no magnetic dead layer or exchange coupling with CoO. These are supplementary indications of the purity of the final nanometer-sized clusters.

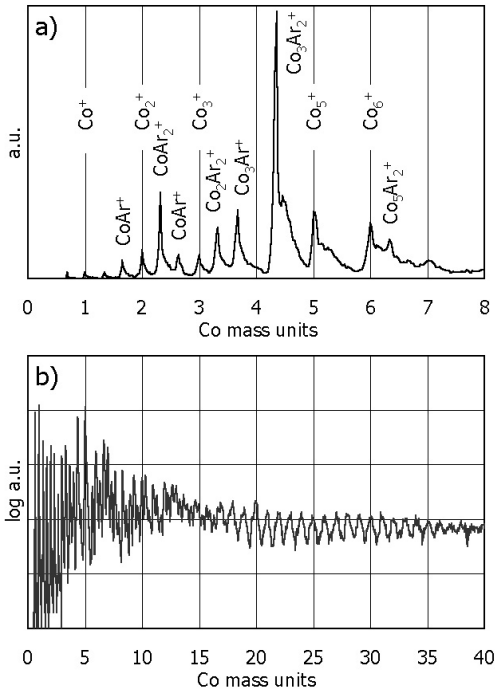

Fig. 2. (a) Size distribution for very small cobalt and argon clusters. The source parameters are the following: Ar 80 sccm; pressure 0.48 mbar; sputtering power 50 W; growth zone length 80 mm. (b) Transition from CoAr clusters to pure Co clusters. Source parameters in this case: Ar 100 sccm; pressure 0.27 mbar; sputtering power 100 W; growth zone length 180 mm.

2.1 Source operation

The control of the cluster source is achieved through the fluxes of argon and helium, the sputtering power, the total pressure in the aggregation tube, and the distance between the sputtering head and the end of the tube. Nevertheless, the size of the clusters primarily depends on the argon partial pressure and on the length of the growth zone, the other parameters being used to tune the shape of the size distribution and the intensity of the beam. Only very small clusters are formed at close distance from the sputtering target, in a zone where the ions have higher energies. At very close distance Co^+ and Ar^+ ions dominate the distribution, while above 50 mm atoms disappear and give place to spectrums similar to the one shown in Figure 2a, where many features are visible. First, the distribution is different below and above Co_5. Below this size all the cobalt clusters with zero, one and two argon atoms are found, except for $Co_4{}^+$ that we have never seen in any condition. Among these small cobalt clusters, the more abundant are always those with two argon atoms. From Co_5 and above the dominant peaks are $Co_n{}^+$, with less abundant Co_nAr^+ and $Co_nAr_2{}^+$. From these results it appears that $Co_5{}^+$ is the stable nucleus from which clusters grow and that the Ar atoms and dimers, that are important in the nucleation process, are expelled from the clusters. This last point is better shown in Figure 2b where cobalt clusters gradually loose their argon atom, up to Co_{17} from where only cobalt is present, as can be seen from the regular spacing of the peaks. The importance of heterogeneous nucleation in gas aggregation sources has been previously observed [4], although not predicted by computer simulation where the growth of clusters mainly proceeds from metal dimers [3]. As the length of the nucleation tube is increased there is only very few modification of the size distribution: clusters in the range 10 to 50 atoms become more abundant, but the maximum of the size distribution remains at Co_5. On the other hand, at a given length, a second population of much bigger clusters in the range 10 000 atoms (5 to 6 nm in diameter) and above emerges (Fig. 3). The size distribution in this range is not regular, with many shoulders and secondary peaks that evolve independently. The flux of these big clusters is very intense right from the point where they appear, of the order of 6×10^9 cluster $cm^{-2}\,s^{-1}$, and they coexist with the small ones with no noticeable depletion in their number. This indicates that they are not the result of the coalescence of the small ones, from which they grow independently. Moreover, although the distribution of the smaller clusters is not very sensitive to the pressure into the nucleation tube, the distance at which the big clusters appear is strictly proportional to the inverse of the argon partial pressure. The other parameters, like the argon flux or the presence or absence of helium, modify the size and the shape of the size distribution but not the point at which they appear. These two populations

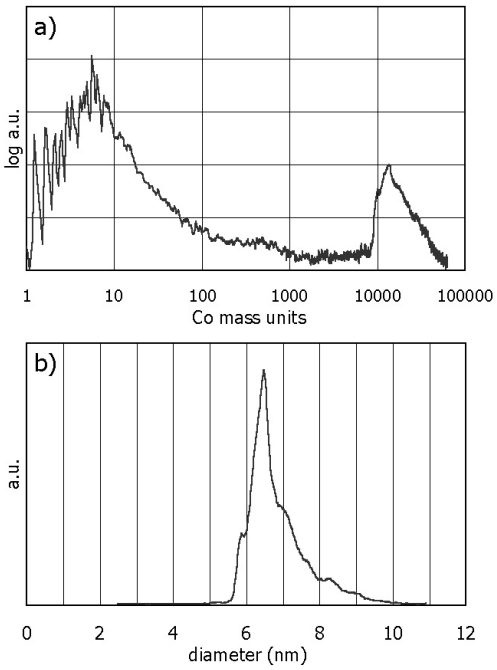

Fig. 3. Mixed regime with two clusters populations. The source parameter are the same as in Figure 2a. (a) Log-log scale, in Co mass units. (b) Close up on the bigger clusters, with linear scale.

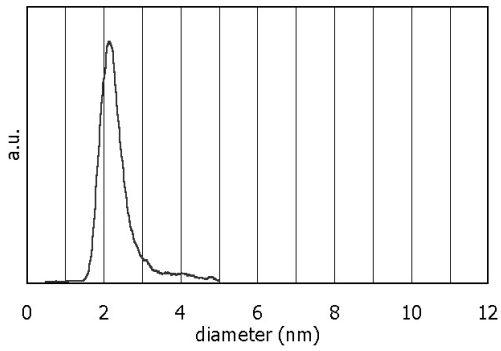

Fig. 4. Third regime of intermediate size clusters. Source parameters for this case: Ar 40 sccm; He 120 sccm; pressure 0.80 mbar; sputtering power 50 W; growth zone length 180 mm.

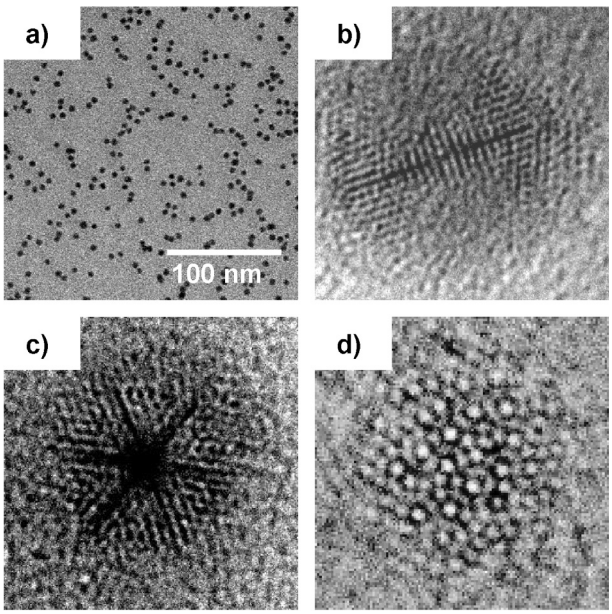

Fig. 5. Cobalt clusters deposited on carbon covered grids. (a) As deposited clusters; (b) 5 nm icosahedral cluster along the twofold axis; (c) 4 nm icosahedral cluster along the threefold axis; (d) 2.7 nm icosahedral cluster along the fivefold axis.

also differ in their energy. Clusters in the range 4 to 6 nm are expelled in the deposition chamber with roughly equal velocity, around 70 m/s, which is slightly below that of the gases in the exit diaphragm. On the other hand the voltage needed to deflect the very small clusters out of the TOF indicates that they have essentially equal energy, above that of the big clusters. This is coherent with the picture where the small ones grow in a zone where the energy of the atoms and ions is high, while the big clusters grow in a much colder zone where they are thermalized before being carried down the source by the argon and helium gases.

As the sputtering source is withdrawn from the exit of the source, the very small clusters disappear and the size distribution for the bigger ones slowly moves to smaller sizes while fading away. Then appears a third regime, with a monodisperse size distribution centered on 2 nm and a high flux of 10^{12} cluster $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$ (Fig. 4). This distribution is log-normal with 0.65 nm FWHM. The size distribution in this regime is very narrow and does not change significantly as the length of the growth zone is increased. Another peculiarity of these clusters is that they are only present if helium gas is injected in the source, contrary to the two populations previously described. Once again there is no indication that these clusters are growing at the expense of the two previous populations.

2.2 Microscopy

In order to determine the structure of the clusters, we have deposited them on carbon-coated microscopy grids. Both TEM and HRTEM measurements were made on a Jeol 3010 microscope with 6 and 2 nm unprotected clusters. It turns out that the 6 nm were covered with a thin shell of oxide, with a Co core, while the 2 nm clusters transform completely into cobalt oxide, so their structure is lost.

Figure 5a shows a deposited layer of 6 nm clusters. We verified that their distribution on the surface is Poisson-like, as expected for a random deposition process: the deposited clusters have no tendency to aggregate, which supposes that they is not mobile on the surface. Also, we can verify that touching clusters do not coalesce.

High resolution TEM was made on isolated clusters. In all cases where a structure could be identified, it was that of icosahedral multiply twined crystals as described by Ino [7]. It is made of twenty tetrahedra, sharing one common point at the center and it is bounded by twenty triangular, densely packed faces. The icosahedral structure is easily identified when the clusters are seen from

one of their three principal symmetry axes. Examples are shown in Figures 5b–5d. In Figure 5b the cluster seen from a twofold symmetry axis rests on an edge between two triangular faces. The icosahedral core is 5 nm in diameter, and one can see in the right of the cluster some additional planes with a higher interplanar distance. This shell, about 1 nm thick, is seen around many clusters, and is ascribed to an oxide that forms after deposition around the clusters. In Figure 5c the cluster, with an apparent diameter of 4 nm, is seen from a threefold symmetry axis, which arises when it is resting on one of its faces. Finally, in Figure 5d, we show a cluster very near from a fivefold axis. In this case, because the orientation is not perfect, we must rely on the Fourier transform of the image (not shown) to identify the diffraction pattern expected for this symmetry. Finally, in all the clusters we have imaged, we never found defects (other that the twins) which means that the closure gap, present when building the icosahedra out of twenty fcc tetrahedra, is accommodated *via* elastic deformation.

3 Discussion

The growth of clusters is divided into three regimes, according to the length of the growth zone. In the first regime very small Co_nAr_m clusters are formed, and we can follow their nucleation and their growth. At a given distance, inversely proportional to the Ar partial pressure, a second population of much bigger clusters appears. Their size distribution is most of the time ill-defined and its evolution, when varying the source parameters, is not simple. Moreover, the flux of these big clusters is always maximum at the moment when they appear, and decreases regularly when the growth zone length is increased. Finally, at relatively long growth length, a third population of intermediate size clusters with sharply peaked size distribution emerges. Contrary to the two other regimes, this one is seen only when helium gas is injected in the source.

The first regime, very close to the sputtering head, can be understood considering that: (1) the temperature and the energies of the atoms and ions are higher; (2) there is less helium (in the case where it is present) to cool the mixture of Ar and Co. In these conditions, the cooling is not sufficient to reach a regime where the coalescence of clusters can give rise to large size clusters.

The second regime arises from argon and cobalt atoms that diffuse radially when leaving the target, in a region where the cooling is more efficient and where the vapor is quenched as it mixes with the helium gas. This quenching effect is probably very sudden, because the apparition of the second regime is very abrupt and the size distribution does not vary significantly when the length of the growth zone is increased. These clusters are carried by the gases and they are expelled from the source at a velocity that is a fraction of the drift velocity of the gas in the exit diaphragm.

The population of clusters in the third regime, probably the most interesting because of its very peaked size distribution, is more puzzling. It appears only at rather long distances, after the two previous regimes have fade away, and is only found when helium gas is present. By analogy with what is found when clusters grow in a flame [10], we can speculate that these clusters grow from atoms that have escaped from the zones where the clusters from the two previous regimes grow. They enter a colder zone, which promotes nucleation, but also with lower density of cobalt atoms, which explains why they are smaller.

From these results it is obvious that no simple model for the nucleation and growth of clusters from a gas phase can describe the overall behavior of the gas aggregation source. There is more than one channel for the growth of clusters, giving rise to clearly separated regimes that have to be depicted individually.

Regarding the structure of the clusters, cobalt icosahedra have been reported previously from photoionization measurements on free Co clusters, obtained by laser vaporization, for sizes up to 2.3 nm [8]. Also, Kitakami *et al.* [9] conclude from electron diffraction that deposited Co clusters are multiply twined icosahedra below 20 nm. The results we obtain confirm these findings, which are coherent with calculations based on the competition between surface and strain energy that indicate a transition at 6 nm [9] or 9–10 nm [7] from icosahedra to fcc Wulff polyhedra. Furthermore we observe that in the conditions of our experiment the icosahedral structure resists both the landing of the clusters and their partial oxidation.

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References

1. J.A. Venables, G.D.T. Spiller, M. Handücken, Rep. Prog. Phys. **47**, 399 (1984)
2. S. Yamamuro, K. Sumiyama, K. Suzuki, J. Appl. Phys. **85**, 483 (1999)
3. B. Briehl, H.M. Urbassek, J. Vac. Sci. Technol. A **17**, 256 (1999)
4. Y. Qiang, Doktorarbeit, Albert-Ludwigs-Universität, Freiburg im Bresgau, 1997
5. C.K. Chung, I. Arai, S.M. Lee, Trans. Mat. Res. Soc. Jap. **25**, 955 (2000)
6. H. Haberland, M. Mall, M. Moseler, Y. Qiang, T. Reiners, Y. Thurner, J. Vac. Sci. Technol. A **12**, 2925 (1994)
7. S. Ino, J. Phys. Soc. Jpn **27**, 941 (1969)
8. M. Pellarin, B. Baguenard, J.L. Vialle, J. Lermé, M. Broyer, J. Miller, A. Perez, Chem. Phys. Lett. **217**, 349 (1994)
9. O. Kitakami, H. Sato, Y. Shimada, F. Sato, M. Tanaka, Phys. Rev. B **56**, 13849 (1997)
10. T. Hayashi, T. Ohno, S. Yatsuya, R. Uyeda, Jap. J. Appl. Phys. **16**, 705 (1977)