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Thin films of nanomaterials made using intense cluster beams†

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Thin films of material containing embedded nanocrystals in the size range from 1.5 to 6 nm have been manufactured using intense cluster beams. A description of the equipment is given, as well as its measured performance. Measurements of the morphology of the material have been made directly using transmission electron microscopy and, indirectly, with SQUID magnetometry. These measurements are consistent with the hypothesis that the material consists of approximately spherical nanocrystals embedded in a matrix. X-ray diffraction measurements have established that the grain size of the matrix material is reduced considerably in these materials. Copyright © 2001 John Wiley & Sons, Ltd.

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INTRODUCTION

Nanomaterials can be made in a variety of ways, but most techniques, apart from self-assembly from atomic deposition, are not suitable for the preparation of thin films. A technique involving the co-deposition of an atomic beam and a cluster beam has been developed[1,2] at the Materialforschungzentrum, Freiburg, and at Daresbury Laboratory.

The next section describes the new machine at Daresbury that is used to prepare these films. Because the clusters are deposited at thermal energies, it is likely that they remain as spherical nanocrystals on deposition. We have carried out a number of experiments that confirm this is true for clusters below about 5 nm diameter when the cluster and matrix materials are mutually insoluble at room temperature. Also, it is likely that embedding a sparse distribution of clusters in a matrix that is normally polycrystalline will cause a significant reduction in the size of the nanocrystal grains. The results described in the final section show that this indeed happens when cobalt clusters are embedded in a copper matrix.

MATERIAL MANUFACTURE

The new machine at Daresbury is capable of producing thin films containing embedded clusters. Whilst some nanomaterials can be made by other techniques, this method is the most versatile and ideally suited to the manufacture of a wide variety of thin nanocomposite films. In this new method an atomic beam is co-deposited with a cluster beam, as shown in the schematic layout of the equipment in Fig. 1.

Standard 2 in magnetrons are used to provide both the cluster beam and the atomic beam. In the former case the clusters are produced by sputtering into a mixture of helium and argon at millibar pressures. Clusters formed by condensation are carried in the gas stream and then skimmed before entering the high-vacuum region where they are deposited, with the atomic beam from the other magnetron, onto a suitable substrate.

Pumping of the skimmed helium is effected by using a $1000\,l\,s^{-1}$ turbomolecular pump and the deposition chamber is pumped using a $1000\,l\,s^{-1}$ diffusion pump. The deposition rates are monitored using a stabilized oscillating-crystal thickness monitor. If mass-separated clusters are required the ionized part of the cluster beam is passed through a wide-aperture quadrupole,[3] downstream of the first sample position (not shown in Fig. 1).

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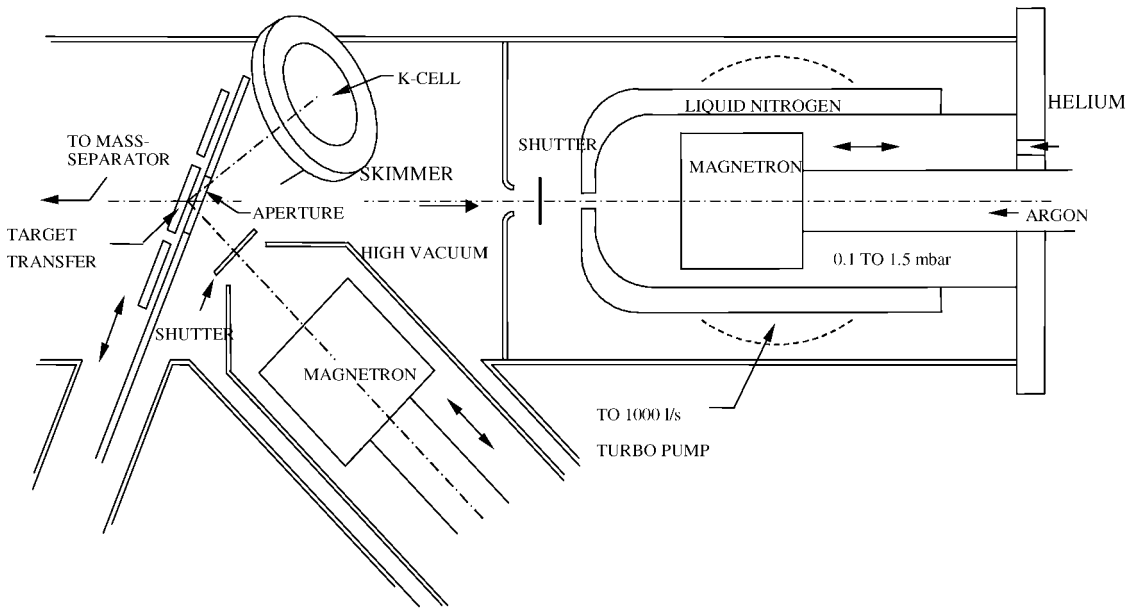

Figure 1 The Daresbury nanomaterials machine.

The performance of the source without mass separation, which is similar to that described in Ref. 2, is as follows.

(1) Cluster sizes are from 1.5 to 7 nm, depending on the source parameters. The source can be moved backwards in the chamber to increase the size of the clusters. Altering the ratio (by volume) of argon to helium within the range from 5 to 50% also affects the size of the clusters. The outer wall of the condensation cell is maintained at liquid-nitrogen temperatures and the helium is pre-cooled before entry into the chamber.

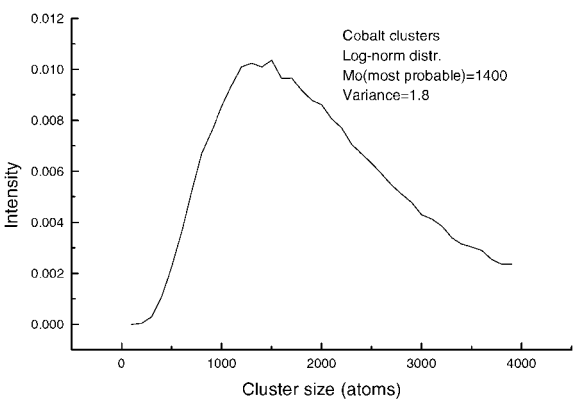

Figure 2 Size distribution of cobalt clusters measured with an analysing magnet.

(2) The distribution of cluster masses (or sizes) can always be fitted to a log-normal function with a spread in cluster sizes (FWHM) of the order of 30% of the average size. Figure 2 shows a typical mass spectrum for 2000 atom cobalt clusters as measured with an analysing magnet downstream from the source.
(3) The deposition rate for clusters depends on the ease at which the element can be sputtered, but it is typically a maximum of a few ångstroms a second. (The ultimate deposition rate is limited only by the atomic sputtering source.)
(4) The maximum deposition rate for mass-separated clusters with a 5% FWHM size spread is about 0.1 $\text{Å}\,\text{s}^{-1}$.
(5) Multilayers, with one layer containing clusters, can be made using a thermal atomic source, as shown in Fig. 1.
(6) The size distribution of the particles can be measured by using an analysing magnet. This can be used to characterize the final material.

All the measurements described in this section are concerned with *material made using clusters directly from the source* (i.e. no mass-separation).

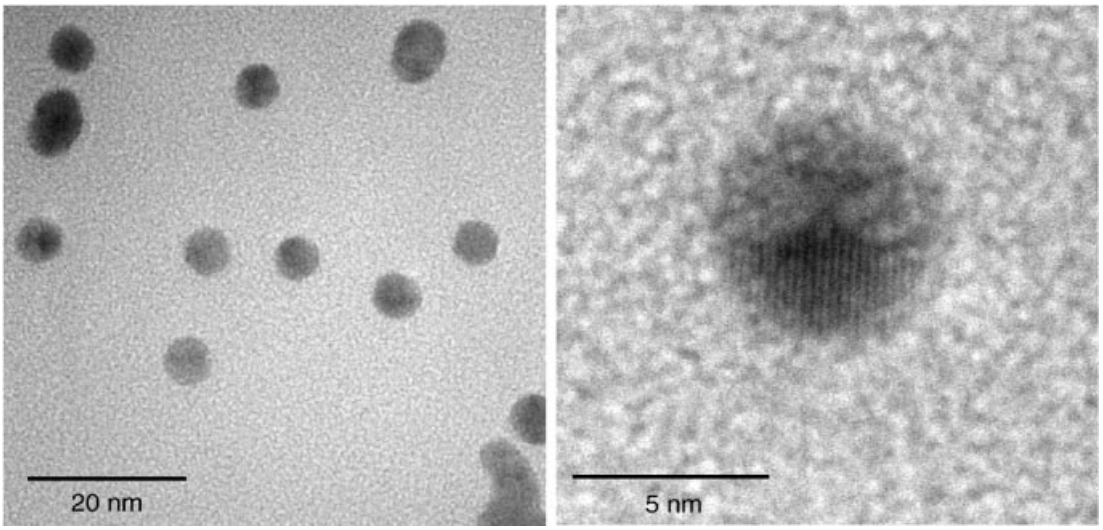

Figure 3 TEM pictures of gold clusters deposited on a carbon grid.

ELECTRON MICROSCOPY MEASUREMENTS

Transmission electron microscopy (TEM) measurements were carried out on gold clusters deposited onto 50 nm carbon foils on 3 mm microscope grids.

A layer of silica was then sputtered to a depth several times the cluster diameter. It was not possible to sputter silica at sufficient intensity to co-deposit at the same time as the gold clusters, so that there are likely to be distinct differences to the mixed-metal systems described later. Fig. 3 shows the images for a sparse covering of 5 nm gold clusters.

From these we infer that clusters deposited at thermal energies retain their shape and crystal nature if the cluster size is below about 5 nm. One effect, which we have found for all experiments where the clusters are deposited directly onto a carbon grid, is that there is a tendency for sintering. This is clearly seen in Fig. 3. Surface migration must take place following deposition even for these relatively large clusters at low energies. Thus nanomaterial made by overcoating a deposited cluster beam will contain sintered particles and the density of these will presumably increase as the surface density of clusters is increased.

One way in which this can be reduced is to co-deposit a matrix material with the cluster beam to ensure that the density of clusters is low, perhaps always less than 10% by volume.

MAGNETOMETRY

Magnetometry measurements have been made on thin-film samples of cobalt clusters embedded in a copper matrix. The aim of these measurements was to measure both the magnetic properties of the cobalt nanocrystals and to understand the final morphology of the deposited material. Cobalt and copper are mutually insoluble at temperatures below about 600 °C and they are, therefore, eminently suitable for the production of well-defined nanomaterials. Samples were produced at 10% volume concentration of cobalt by co-depositing a cobalt cluster beam and a copper atomic beam in a fixed intensity ratio as measured by the thin-film monitor.

The superparamagnetic responses of two typical samples at room temperature are shown in Figs 4 and 5. These have been fitted to the expected superparamagnetic response at room temperature calculated using the deposited cluster size distribution. Thus we take the simple convolution:

$$M/M_s = \frac{\int_0^\infty \rho(N)L(N,H)\ \mathrm{d}N}{\int_0^\infty \rho(N)\ \mathrm{d}N} \qquad (1)$$

where L is the Langevin function, M_s is the saturation magnetization and $\rho(N)$ is the measured size distribution as a function of the number of atoms N. This formula is expected to hold good in

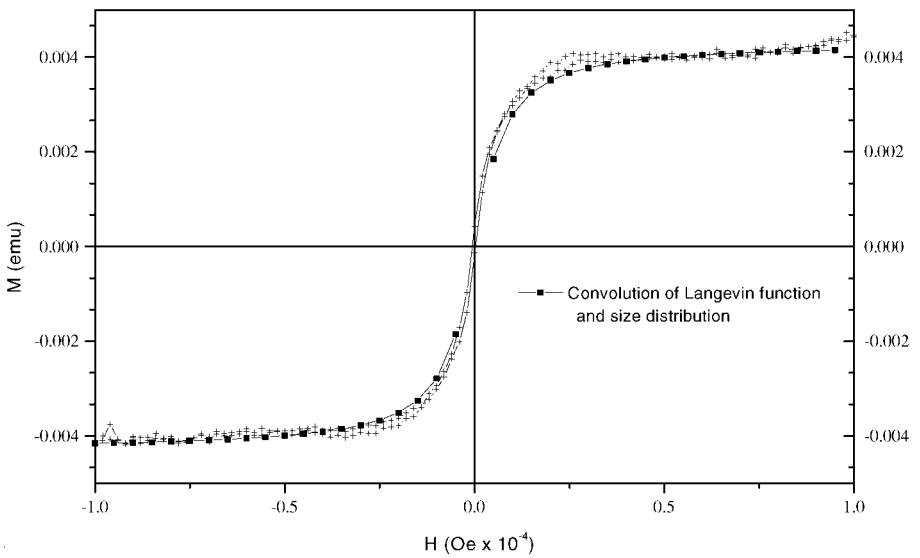

Figure 4 Magnetization loop for 8000 atom sample compared with superparamagnetism prediction.

the regime where the thermal energy (kT) and the magnetic dipole energy (μH) are comparable and where both are much greater than the magnetic anisotropy energy. It is clear that the samples can be fitted reasonably well with the deposited size distributions. In both cases we have used a dipole moment equal to $1.7N\,\mu_B$ since the moment per atom in the bulk, and for free clusters, is $1.7\,\mu_B$.

The small deviations at low fields may be due to some sintering. (This will increase the heavier masses and will therefore cause a higher value at lower fields in line with the deviations shown.) Alternatively, the effects may be due to cluster–cluster interactions with strengths comparable to the cluster dipole energy in the field.

Measurements have also been made of the residual magnetism at low temperatures. In these experiments[4] the sample was cooled (in zero field) and a hysteresis curve recorded at fields up to 1 T. From these hysteresis curves one could then extract the magnetization at zero field. A curve of M_R/M_S, where M_R is the residual magnetism and M_S is the saturation magnetization obtained from the room temperature response, is shown in Fig. 6 for the sample with the cluster size distribution shown in

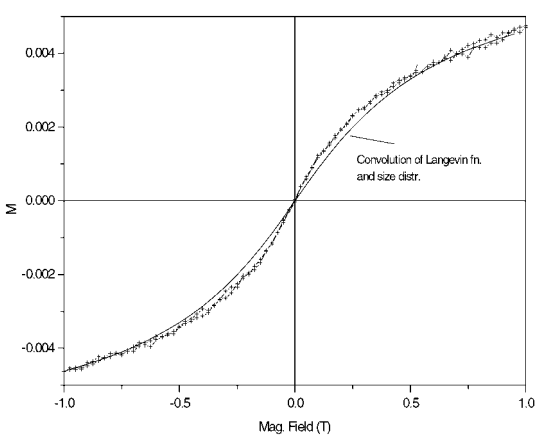

Figure 5 Magnetization for 1000 atom clusters compared with convolution using size distribution.

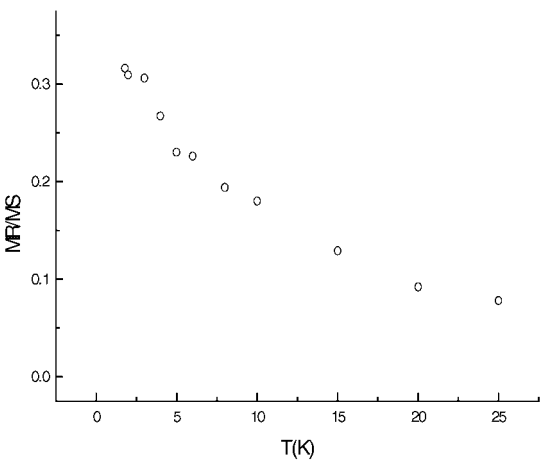

Figure 6 Residual magnetization normalized to the saturation value for 2000 atom clusters.

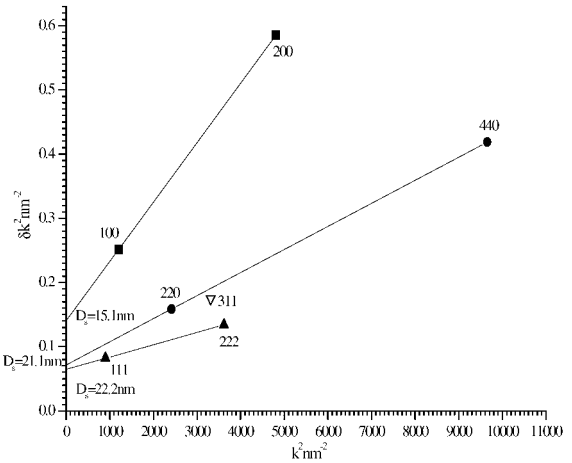

Figure 7 Scherrer plot (copper lines) for 1000 atom Co clusters at 2.5% concentration in copper.

Fig. 2. The curve indicates that the transition to ferromagnetism only takes place at extremely low temperatures. Preliminary calculations based on a simple model,[5,6] assuming that the magnetism is due only to magnetic anisotropy (i.e. with no cluster–cluster interactions), have been made. These show that the curve is best fitted with very low values for the magnetic anisotropy energy barriers in the range 1.0–2.0 μe V atom^{-1}. This is an order of magnitude smaller than bulk (hcp) cobalt and is reasonably explained if the cobalt is in fcc form. A low value like this is also consistent with the hypothesis that the material consists of a majority of spherical nanocrystals, since departures from spherical symmetry would produce considerably larger energy barriers arising from uniaxial shape anisotropy. The residual magnetism, therefore, provides some extra confirmation of the morphology of the material.

MORPHOLOGY OF THE MATRIX

It is well known[7] that for metal clusters in a metal matrix the matrix is polycrystalline. We have studied the structure of the matrix for cobalt clusters embedded in a copper matrix using powder X-ray diffraction at the Daresbury synchrotron. The widths of the fcc copper lines have been used to determine the size of the matrix nanocrystals. Figure 7 shows a typical Scherrer plot for the line widths as a function of the crystal directions.

These plots can then be used to determine[8] the nanocrystal sizes, and for this case there is a significant reduction in the grain size of the copper matrix. It is clear from these data that the nanocrystal size is reduced from about 60 nm when there are no clusters, to about 17.5 nm when the density of cobalt clusters is approximately 2.5%. This is to be expected, since the clusters cause mismatching of the lattice and, therefore, prevent the matrix nanocrystals from growing. This technique also shows that the copper nanocrystals are non-spherical, with the shortest dimension (see Fig. 7) along the 100 direction.

CONCLUSIONS

Nanomaterial thin films have been made by co-depositing a cluster beam and an atomic beam. The cluster beam was generated using a gas-aggregation source with a magnetron used to sputter the cluster material. A conventional magnetron was used to sputter the matrix material. A number of studies have been carried out on the material to establish its morphology. These indicate strongly that the clusters retain their crystallinity and shape within the matrix. (This is probably only true for immiscible elements.) As expected, the grain size of the matrix can be altered by adjusting the density of clusters deposited.

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REFERENCES

1. Eastham DA, Qiang Y, Maddock TH, Kraft J, Schille J-P, Thompson GS, Haberland H. *J. Phys: Condens. Matter* 1997; **9**: L497.
2. Haberland H, Mall M, Moseler M, Qiang Y, Reiners T, Tghurner Y. *J. Vac. Sci. Technol. A* 1994; **122**: 925.
3. Denby PM, Eastham DA. *Nucl. Instrum. Methods Phys. Res.,* 2000; **A441**: 588.
4. Eastham DA, Whittaker G, Harrison A. In preparation.
5. Walker M, Mayo PI, O'Grady K, Charles SW, Chantrell RW. *J. Phys.: Condens. Matter* 1993; **5**: 2779.
6. Walker M, Mayo PI, O'Grady K, Charles SW, Chantrell RW. *J. Phys.: Condens. Matter* 1993; **5**: 2793.
7. Edelstein AS, Cammarata RC (Eds). *Nanomaterials*. IOP Publishing: Bristol, 1996; 350 *et seq*.
8. Edelstein AS, Cammarata RC (Eds). *Nanomaterials*. IOP Publishing: Bristol, 1996; Chapter 10.

