Composition and Structure of AgCo nanoparticles

M. Spasova, M. Farle, T. Radetic*, U. Dahmen*, N. Sobal†, M. Hilgendorff†, and M. Giersig†

*NCEM, Lawrence Berkeley Lab. USA
†Hahn-Meitner-Institut Berlin, Germany

Future magnetic storage media will require bit structures on the nm scale. Magnetic nanocrystals with large intrinsic magnetic anisotropy may present one route to achieve such ultrahigh storage densities. It is known that the magnetic properties of single element magnetic particles and their chemical stability can be improved by adding other metals. For example, CoPt\textsuperscript{1} and FePt\textsuperscript{2} nanocrystals show higher magnetocrystalline anisotropy and, hence, higher blocking temperatures than pure Co and Fe particles of similar size. Here, we report on the synthesis, crystal structure and chemical composition of AgCo nanoparticles. The later results were obtained by a detailed transmission electron microscopy (TEM) investigation. High-temperature solution-phase synthesis provides a method for the preparation of nanoparticles which are uniform in composition and size. A toluene-based solution of AgCo nanoparticles was prepared by thermal decomposition of cobalt octacarbonyl (Co\textsubscript{2}(CO)\textsubscript{8}) in the presence of water-free silver perchlorate (AgClO\textsubscript{4}) in an Ar atmosphere. Octanoic acid and tridodecylamin were used as stabilizing ligands, which

\textsuperscript{1}E. E. Carpenter et al., J. Appl. Phys. 85, 5184 (1999)
\textsuperscript{2}S. Sun et al., Science 287, 1989 (2000)

Fig. 1: (a) A high resolution TEM image of an AgCo nanoparticle. (b) SAED pattern of AgCo nanoparticles. Diffraction rings corresponding to bulk-like fcc planes of Ag and Co phases are marked.
cover the particles, control their size and prevent their agglomeration. The mixture of Ag and Co reagents was chosen as to obtain a Co concentration of 45 molar that is about 20 wt.\% in the final particles. After washing with ethanol the particles were redispersed in toluene with a small amount of oleic acid. Details of the synthesis will be published elsewhere.\(^3\) For TEM investigations, the particles were deposited from a 3 \(\mu l\) drop of the solution onto a carbon-coated copper grid. Low magnification TEM (for example, see Fig. 2a) shows that the particles are spherical with an average diameter of 11.5 nm. X-ray energy dispersive spectroscopy (XEDS) confirmed that the average Co contents of the particles is 45 molar as was expected from the preparation conditions. The crystal structure of the nanoparticles was studied with a high-voltage transmission electron microscope operated at 800 kV. Fig. 1a shows an atomically resolved image of one AgCo nanoparticle supported on an amorphous carbon film. The image shows that the particle is polycrystalline with a grain size of 2-3 nm. The Fourier transform (not shown) of this image reveals that some grains within the particle are bulk-like fcc Ag. We could not resolve the crystal structure of the other grains, since they are too small for a reliable Fourier analysis. In addition, the fcc (200) Ag (0.2043 nm) and the (111) Co (0.2046 nm) interplanar spacings are very close, and it is impossible to draw a clear conclusion about the grain composition. To gain further insight in the composition, we performed selected area electron diffraction (SAED). The diffraction rings obtained from an array of the particles (Fig. 1b) show reflections of the pure bulk-like fcc Ag and fcc Co phases only, as indicated in Fig. 1b. There is no evidence for alloy formation. That is understandable since Ag and Co are immiscible. Spatially-resolved chemical analysis of the nanoparticles was performed by spectral imaging of the sample. Electron Energy-Loss Spectroscopy (EELS) experiments were carried out with the Philips CM200/FEG instrument designed

\(^3\)N. Sobal at el., to be published

Fig. 2: (a) TEM image of AgCo nanoparticles. Energy filtered images at the Ag M-edge at \(\approx 719\) eV (b) and at the Co L-edge at \(\approx 778\) eV (c). The scale bar is for all three images.
for chemical analysis with 1 nm spatial resolution and 0.9 eV energy resolution. Fig. 2 shows a low magnification TEM image of an array of the nanoparticles (Fig. 2a) and two energy filtered images recorded (b) at the Ag M-edge (≈ 719 eV) and (c) at the Co L-edge (≈ 778 eV). In the TEM image (Fig. 2a), different shades of gray (contrast changes) within the particles indicate their polycrystalline structure. The contrast of the energy-filtered images shows the spatial distribution of Ag and Co across the individual particles. Ag seems to be concentrated in the center of the particles (higher brightness in Fig. 2b) while cobalt is found predominantly at the surface of the particles (Fig. 2c). Spatially resolved (2 nm) XEDS confirms this finding. The presence of Co at the particle surface sheds light on the growth process of the particles. It seems that firstly Ag nuclei are created in the solution during thermal decomposition followed by Co adsorption on the Ag nuclei. This interpretation is supported by the fact that no pure Co particles but some pure Ag particles are found in the solution.

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