

Fabrication of Structurally Tailored Cobalt Nanowires

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ABSTRACT

. Controlling the microstructure of nanowires offers a very practical means of producing nanostructures that are amenable to the needs of technological applications. Here we report an interesting observation of structural transition of electrochemically deposited cobalt nanowires with change in aspect ratio of the nanowires. These nanowires were deposited in PCT polycarbonate template single side coated with silver from an optimized $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ bath (50mM) and subsequently their crystal structure were studied using X-Ray Diffraction. At room temperature (303K) change in the aspect ratio (length to diameter) of the nanowires brought in a change in their crystal structure from hexagonal close packing (HCP) to face centered cubic (FCC) as we kept on increasing their aspect ratio by varying the deposition time from 200 to 1000 seconds. Rate of deposition for a fixed bath concentration was studied and using that a critical aspect ratio for the conversion was calculated which came out to be approximately 40. This interesting finding has useful bearing in designing the magnetic behavior and switching characteristics of the wires for device applications.

Keywords: nanowires, structural transition, electrodeposition

1 INTRODUCTION

Most of the magnetic storage media used today is a thin magnetic film supported by a non magnetic disc. Such a film consists of many tiny polycrystalline grains or particles having a broad distribution of size, shape and crystalline orientations. Magnetization orientation of such grains is also random unless a magnetic writing head orients them using an external magnetic field. However in such media storage capacity gets limited due to some factors such as, the superparamagnetic limit, transition width between two neighbouring sections having opposite magnetization orientations, side tracks due to fringing field of the write head etc [1]. Nanowires are aligned magnetic elements which can be magnetically oriented along a preferred direction. They have recently attracted considerable attention motivated by applications in the area of ultra high density perpendicular magnetic recording and magnetic sensors [2]. Magnetic nanowire arrays filled in templates

offer great potential for recording media because of the fact that they can achieve a recording density of more than 100 Gbit/in² which is much higher than that of current commercial hard discs (3.7 Gbit/in²) [3]. Moreover low dimensionality plays an important role in deciding the magnetic properties of materials and hence magnetic nanowires are an ideal playground for exploring the fundamentals of magnetism and spin related phenomena [4].

Methods of fabrication of nanoparticles range from lithographic to chemical processes. Nanowires and nanotubes can be synthesized by various methods including atomic layer growth, hydrothermal synthesis, thermal decomposition of precursors etc. Among all these electrodeposition is a simple as well as cost-effective technique to fabricate nanowires in cylindrical pores. Size and composition of the wires can also be controlled easily while fabricating by this method. Many groups across the globe have electrochemically synthesized nanowires of different ferromagnetic materials [5-7]. They have also studied effect of different parameters such as current density, pH value, temperature of the bath, pore density of template, pore size, presence of external magnetic field at the time of deposition etc on structural and magnetic properties of the fabricated nanowires.

2 EXPERIMENTAL DETAILS

. Deposition of Co nanowires was done in track-etched polycarbonate membranes of pore diameter 50 nm and pore length of 6 μm , in a three-electrode cell at room temperature (303K). All solutions were prepared by dissolving reagent-grade chemicals in doubly deionized (DI) water. An optimized 50mM $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ bath was used for this purpose. Boric acid was also added as a buffer reagent and the bath pH was maintained at 3. For deposition purpose one side of the templates was coated with Ag layer (100nm) which served as the working electrode. Computer controlled CHI-1100A potentiostat in the three electrode cell geometry was employed for the deposition purpose. The electrochemical cell consisted of a standard calomel (Hg/ HgCl_2 / KCl) reference electrode and a 2 cm \times 1.5 cm platinum sheet as the counter electrode. Deposition potential as estimated using cyclic voltammetry came out to be around -0.8 V. Deposition took place with a constant current density of 1mA/cm² and the deposition time varied

from 200 sec to 1000 sec from S1 to S4 as shown in the Table 1.

Crystal structure of the synthesized nanowires was subsequently studied by Philips X'PertPRO X-Ray diffractometer (40 mA, 45 kV) using Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). Scan rate was kept fixed at $1.5^\circ/\text{min}$. Transmission Electron Microscope (TEM) images of nanowires was obtained from a .CM 20 Philips TEM.

3 RESULTS AND DISCUSSIONS

Crystal structure of fabricated nanowires was studied using X-ray diffraction in θ - 2θ mode. The X-ray diffractograms are shown in Fig. 1. From the standard JCPDS data file no. (05-0727), 2θ values of 41.68° , 44.76° and 47.59° correspond to (10 $\bar{1}$ 0), (0002) and (10 $\bar{1}$ 1) planes of HCP phase respectively. On the other hand, from the standard JCPDS data file no. (01-1259), 2θ values of 44.37° , 51.28° and 75.37° correspond to (111), (200) and (220) planes of FCC phase respectively. Comparison with standard JCPDS data shows presence of only HCP phase in case of nanowires grown for 200 sec. While wires grown for 500 sec had a mixed phase of both HCP and FCC. The FCC phase becomes dominant for nanowires grown for longer deposition time. Nanowires grown for 1000 sec only show the FCC phase with sharp intense peaks.

Intensity of (111) and (0002) combined peak at 44.76° decreases initially when deposition time increases from 200 sec to 750 sec. On further increasing the deposition time to 1000 sec the intensity of this peak increases significantly. On the other hand the intensity of the Co (10 $\bar{1}$ 0) HCP peak decreases and that of the Co (200) peak increases continuously with increase in deposition time. One possible explanation for such a behaviour can be put in the following way. In the initial stage, growth is single phasic

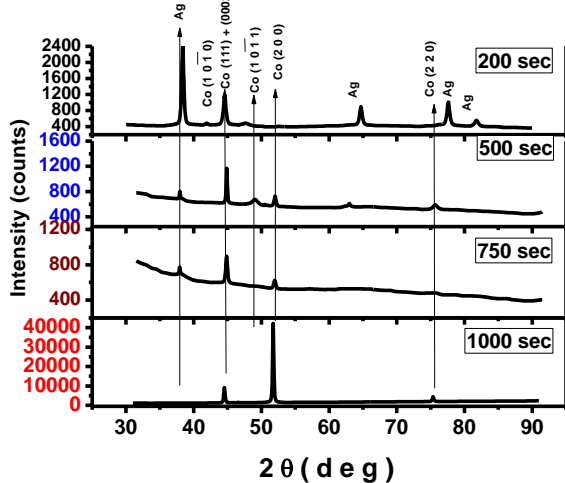


Figure 1: X-Ray Diffraction of Cobalt nanowires deposited for different times at room temperature (303 K) in 50 nm. diameter PCT.

with HCP phase forming predominantly, and hence intensity of the mixed peak is due to (0002) plane of HCP only. As growth continues, the FCC phase starts evolving and there is competition between the two phases and as a result the intensity of this particular peak changes in magnitude due to contribution from (111) peak of FCC cobalt and (0002) peak of HCP cobalt, as in case of 500 sec and 750 sec grown wires. In addition the peak-width increases with significantly larger level of background intensity. This indicates smaller grains with randomized orientations. For deposition time of 1000 sec wires show the presence of FCC phase only with a clear evidence of (200) preferred oriented growth. The change over from HCP to FCC growth with increasing time of growth is also evidenced by closely looking at the (10 $\bar{1}$ 0) and (10 $\bar{1}$ 1) peaks of HCP and the (220) peak of FCC, as shown in Fig. 2. These peaks are due to single phase only and their evolution with time clearly points towards phase change over. From the analysis of the peak intensities and peak position, the calculated value of the FCC fraction in 500 sec and 750 sec samples is found to be 68% and 80%.

Morphology of the synthesized nanowires was studied using Transmission Electron Microscopy (TEM). Fig. 3 shows an image of a Co nanowire grown for 500 sec, whose length and diameter come out to be approximately 2 μm . and 50 nm respectively. The TEM image of the nanowire shows that it is still covered with the polymer around it. From the TEM images, deposition rate was calculated by taking the ratio of length and deposition time which came out to be 4 nm per second. This was assumed to remain uniform during the entire period of growth of nanowires. The diameter of the nanowires came out to be approximately 50 nm, which was the diameter of the PCT pore used for deposition purpose. The aspect-ratios calculated for the nanowires are listed in Table 1. The change in the crystal structure of the nanowires was thus linked to aspect-ratio. Nanowires with aspect-ratio smaller than 40 possess HCP structure, whereas those with aspect-

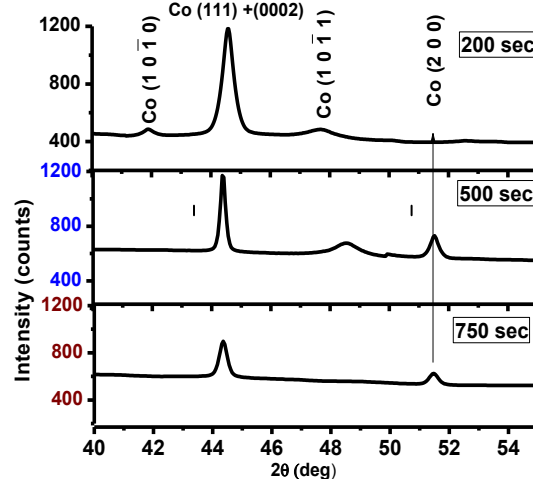


Figure 2: Details in 2θ range of 40° - 50° showing HCP growth.

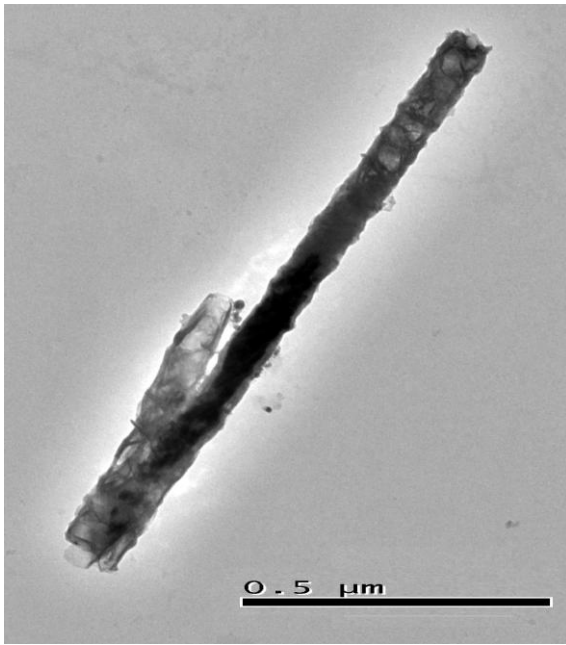


Figure 3: High Resolution Transmission Electron Microscope image of a nanowire grown for 500 sec.

ratio more than 40 have FCC structure. Comparison of positions of (111) and (0002) combined peak in all the four cases shows a small shift in its position as deposition time changes from 200 seconds to 500 sec. Probably, the introduction of FCC phase in a HCP growing nanowire incorporates a strain which results in this shifting. With increase in deposition time, contribution of FCC phase increases and position of this peak becomes fixed. At higher deposition time of 1000 sec, intensities of FCC (111) and (220) peaks reduce significantly. The strain is now reduced due to single phasic growth and crystallinity improves significantly, resulting in preferred orientation of growth along (200) plane.

It is known that poly-crystallinity favours formation of magnetic multi domain structure whereas single-crystallinity supports aligned magnetic mono domains. Magneto-crystalline anisotropy energy density for FCC-Co phase is almost one order of magnitude smaller than the shape anisotropy energy density. Whereas for HCP-Co both the anisotropy energy densities are of same order of magnitude [9]. Hence effectively magnetic anisotropy of FCC-Co nanowires are determined by the shape anisotropy. Direction of magnetization easy axis depends on interplay among various anisotropy energy densities. They also play decisive role in determining the preferred growth orientation of nanowires. Chances of having defects are also more in poly-crystalline materials. As length keeps on increasing, the growth of the nanowire becomes effectively confined in two dimensions and hence defects become less possible. Thus probably conversion of HCP phase into FCC in case of Cobalt nanowires can be explained by the joint effect of magnetic anisotropy and crystallinity.

Table 1: Dependence of crystal structure on aspect-ratio of the nanowires.

Sample Name	Deposition time (sec.)	Length (nm.)	Aspect-ratio	Crystal structure
S1	200	800	16	HCP
S2	500	2000	40	32% HCP+ 68% FCC
S3	750	3000	60	20% HCP+ 80% FCC
S4	1000	4000	80	FCC (Preferred orientation)

4 CONCLUSION

Thus we conclude that by controlling the deposition time alone under low dimensionality conditions, one can successfully control the microstructure of the cobalt nanowires. The HCP/FCC structurally tailored deposition of cobalt nanowires is achieved by varying the deposition time. The control of structure and hence magnetic anisotropy can be effected with change in aspect ratio of nanowires. We have successfully shown the hcp-fcc structural transition of cobalt nanowires at an aspect ratio of approximately 40. The change in growth in confined dimensions could be related to lowering of strain and surface energies etc. leading to highly oriented FCC growth. Magnetic studies on these samples with different phases can be very helpful to study the basics of magnetism in these nanostructures.

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