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Investigation of multilayer local tilt within long portion of single Co/Cu nanowires

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In this work arrays of Co/Cu multilayer nanowires were fabricated by electrodeposition to develop giant magnetoresistive sensors. Structure and morphology defects within 6 μm long portions of single nanowires have been probed by electron and ion-beam microscopies. It has been discovered that the most recurrent growth defect is a tilt of the nanowire layers, which varies along the length of the nanowires, this effect being more significant for nanowires of larger diameters; nevertheless, the nanowire arrays fabricated in this work demonstrated a magnetoresistive response which is very close to the behavior of analogous systems previously reported in the literature. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2715121]

Arrays of giant magnetoresistive (GMR) nanowires offer attractive potential to serve diverse applications, in particular, for high-density magnetic recording devices[1,2] and magnetic field sensors.[3,4] Research on this topic is enhancing knowledge concerning fundamental physics in confined matter, and it is paving the way to the formulation of an exhaustive general description of spin dependent transport phenomena in multilayer nanosystems, for which there is still a lack of data today.

In this work arrays of Co/Cu multilayer nanowires of 30, 50, and 100 nm diameters have been fabricated to gauge their potential usage as magnetic field sensors for encoder like positioning systems where very large dynamic ranges are required (e.g., for the automotive).[5] The crystal structure and morphology characteristics of single nanowires have been investigated, for the first time in this work, over a very long portion of their length (about 6 μm). In this letter, the magnetoresistive response of a type of nanowire array fabricated in this work is reported, thus allowing a comparison of behavior with analogous systems previously appeared in the literature for which structure was not investigated this deep.

To fabricate such a nanosystem, a number of different methods have been proven in the last decade. Among them, the electrodeposition used to fill nanoporous membranes is one of the most promising solutions[6,7] both in terms of cost effectiveness and production yield and due to the fact that nanolithographic postprocessing of conventional GMR stacks has not to be performed; for these reasons, in this work this technique was used. To develop GMR-nanowire arrays of identical properties by electrodeposition and from the same growth conditions, the quality of the template membrane is certainly a fundamental issue. Many groups have been working to optimize membranes in terms of improved pores' size and shape regularity, and today sensor developers can rely on regular templates such as nuclear track-etched polymeric membranes, nanochannel array glasses, mesoporous channel hosts, and self-ordered anodized aluminum oxide films. On this purpose, in this work, 12 μm thick track-etched polycarbonate templates are used; these membranes are made by nuclear track-etched technology where a freestanding film of polymer is bombarded by heavy ions accelerated in a cyclotron.[8] Specifically, our Co/Cu nanowire arrays were fabricated by pulsed electrodeposition (PED) from a single bath, a technique previously demonstrated by Piraux and co-workers[9–11] which consists in a pulse-plating method, whereby cobalt and copper ions dissolved in a single solution are reduced at a cathode by switching the anodic potential between two different values. The single bath PED is performed by driving a three-electrode electrolytic cell by a potentiostat and the deposition potentials referred to a saturated calomel electrode (SCE). Prior to deposition, a membrane is coated with gold at one side to serve as a cathode and then immersed in a bath obtained by mixing salts of the metals which have to be deposited. The electrolytic solution was prepared from high purity Co and Cu sulphates, with an element-concentration ratio highly unbalanced in favor of the metal less prone to deposition. Cu deposits at a smaller absolute potential than Co and, during the Co cycle, ions of Cu reduce as well, degrading the purity of Co layers, thus altering their magnetic properties.[12] In our experiment, the deposition bath was prepared by dissolving 520 g/l of $CoSO_4 \cdot 7H_2O$, 5.2 g/l of $CuSO_4 \cdot 5H_2O$, and 52 g/l of H_3BO_3 (as *p*H buffering agent) in purified water with resistivity higher than 16.8 MΩ cm, which results in an element-concentration ratio, $[Co^{2+}]:[Cu^{2+}]$, of about 90 to 1. The growth process was carried out by means of a Teflon cell, where a Pt grid as counterelectrode and a SCE as reference were used; in this apparatus, the membrane was arranged to have its pores' open ends oriented upwards to face the electrolyte over a 2 cm^2 wet area. Prior to deposition, the cell was placed in an ultrasonic agitation bath for 5 min to favor a uniform penetration of the electrolyte into pores and a homogeneous growth of nanowires into the whole wet membrane;[12] growth was carried out at room temperature and no stirring was used. Multilayer nanowire arrays were then fabricated by applying an alternating square voltage at the counterelec-

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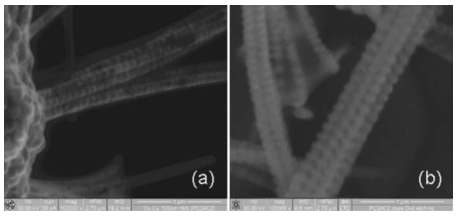

FIG. 1. Microscopy of Co/Cu multilayer nanowires. (a) FIB imaging: nanowires cleaned by FIB; (b) SEM imaging: "backbone" shaped nanowires, evidence of layering.

trode; the deposition potential was rapidly and continuously switched from the Co deposition potential to the Cu one at defined constant time pairs, one defining the Co cycle duration, and the Cu one. Pure Cu was deposited at −0.4 V and Co at −0.9 V with respect to the SCE. A full control of deposition potentials and durations determines the mass deposited in each layer, which, if related to the pore diameter and density, gives the thickness of each layer and the period of the nanowires, parameters fundamental to determine the array magnetoelectric response. The complete filling of the membrane's pores can be assessed during the growth process when the deposition current density increases; this is due to a deposition area enhancement at the bottom electrode because of a nanowire spillage effect.

Structural and morphological analyses of the nanowires were performed by electron microscopy [scanning electron microscopy (SEM)/transmission electron microscopy (TEM)] and focused ion beam (FIB). Such techniques were both used to study the growth homogeneity by observing the nanowires embedded in the membranes (top views and cross sections) and, after having dissolved the polycarbonate template in dichloroethane, to probe the crystal structure and the layer morphology of single nanowires. To free the nanowires from the template membrane, sample parts were placed on proper sample holders (Al stab for SEM or Cu grid for TEM) and there flushed several times with the solvent; this method demonstrated to be appropriate and better than centrifugal separation, both in terms of time saving and nanowire aggregation. TEM imaging of the nanowires following the membrane dissolution did not yield precise information regarding the layer thickness; in fact, after being released from the membrane, the nanowires are still enveloped into a thin polymer film which contributes to imaging additional overlapping fringes.[12] This drawback was overcome by FIB cleaning, and the results can be appreciated by observing Fig. 1(a). Another typical problem faced during measurements is a lower contrast between layers, due to the very close mass densities of their constituting metals (8900 kg m^{-3} for Co and 8920 kg m^{-3} for Cu), than the one resulting from structure grains oriented differently. To cut out the most external nanowire skin where gallium ions are implanted (beam energy: 10 keV; implantation depth=4.5 nm in Co and 4.7 nm in Cu) during FIB cleaning[13,14] and to make contrast between layers dominate over the contrast between grains, a selective oxidation process and a selective chemical etching of Co were used; in fact, layers of smaller diameter present higher transmittance to the probing electrons with respect to the layers of larger diameter. The nanowires treated this way assume the shape of a "backbone," see Fig. 1(b), and determining how this shape affects spin dependent transport phenomena is a goal of future research. Figure 2(a) is a high contrast TEM image of a 30 nm etched nanowire; a single-crystal nanowire formation across stratification is apparent in long nanowire parts (superlattice).[12] This growth technique is acknowledged as being straightforward and it is often assumed that layers are all parallel to each other along the entire length of the nanowires; for this reason, the thicknesses of the layers are usually calculated from the deposition electric load or directly measured only over small portions of single nanowires. It is reported here the bilayer periodicity local variation measured by TEM throughout a large portion of backbone Co/Cu nanowires. Figures 2(b)–2(d) show, respectively, the period variation of

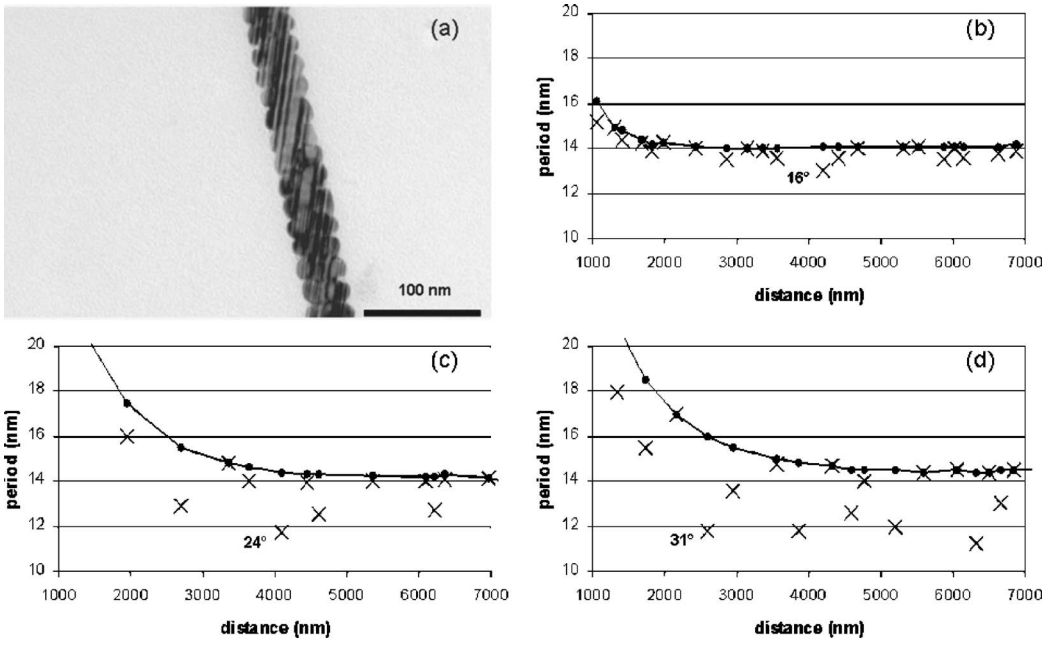

FIG. 2. (a) High contrast TEM image of a 30 nm diameter backbone shaped nanowire. (b), (c), and (d) show, respectively, the period variation of single nanowires of 30, 50, and 100 nm diameters over a length of about 6 μm from their bottom ends (left side). For each nanowire type the maximum tilt angle measured is reported.

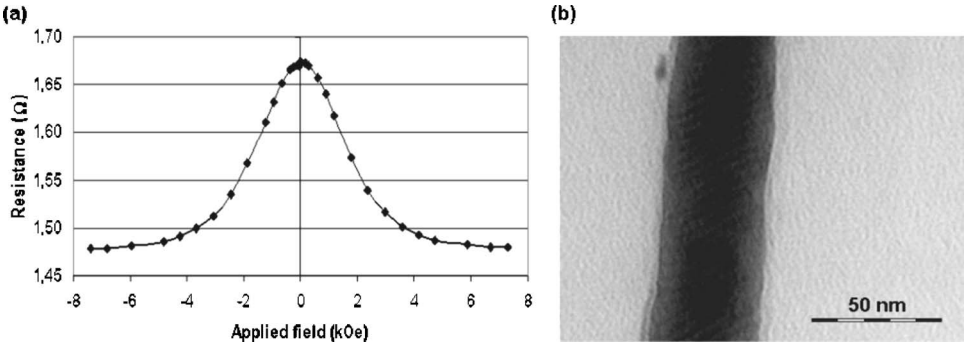

FIG. 3. (a) Magnetoresistive response of arrays of Co/Cu nanowire of 50 nm diameter. (b) A high contrast TEM image of one Co/Cu nanowire belonging to the array whose behavior is depicted in (a).

single nanowires of 30, 50, and 100 nm diameters over a length of about 6 μm from their bottom ends (left side); these measurements were corroborated by high resolution TEM imaging of nanowires' parts not treated in this way. The investigation of the first micron length at the lower end of the nanowires fabricated is not shown in these figures since the period change within these parts is mainly due to a variation of the pore diameter; in fact, for each nanowire type, a 20% average variation of the diameter between the nanowires' ends and their central parts was measured.[7] In these figures, the cross-shaped markers represent the nanowire local period measured along the direction normal to the layer planes; instead, the continuous curves represent the calculated period variation of the same nanowires as their layers were all grown perfectly orthogonal to the nanowire axis (no layers tilt). These values have been calculated directly from geometrical considerations, i.e., from the measured thickness of tilted bilayers, the tilt angle, and the pore local diameter. When the cross-shaped markers do not fall on said curves, the corresponding bilayers are tilted with respect to the planes orthogonal to the nanowire axis; as is apparent from these figures, the multilayer local tilt increases with the nanowire diameter.

In the present work, the magnetoresistive response of our "imperfect" systems was probed at room temperature using a four point measurement setup.[15] Figure 3(a) shows a TEM image of a Co/Cu nanowire of 50 nm diameter whose period, averaged over a length of 6 μm, is about 5 nm; the magnetoresistive response, leading to a MR ratio of about 13% of the corresponding array, is reported in Fig. 3(b). It is apparent from Fig. 3(a) that the behavior of this array is very similar to those reported in the literature for analogous systems[16] and with the performances of commercial GMR systems fabricated by conventional techniques which allow a full control, at the angstrom level, of the single layer thickness and orientation.[17]

In conclusion, if the goal is to design a magnetic field sensor or to study spin dependent transport phenomena in structures made in this way, it is necessary to consider that the magnetoelectric response of the whole array is a contribution of a multitude of nanowires connected in parallel, where each nanowire has to be treated as a very long series of Co/Cu/Co elementary cells of different thicknesses and orientations which differently contribute to the overall system magnetoresistive response. Despite the dispersion in the intrinsic properties of the nanowires, GMR sensors can still be designed and developed thanks to the sheer multitude of them. Their huge number enables the designer to average their effects and consider arrays grown in the same manner as to be equivalent. This statement is corroborated by the identical magnetoelectrical response exhibited by arrays fabricated from the same growth parameters. From this result, we consider the electrodeposition to be a promising technique to have GMR systems fabricated, especially when compared to the conventional high vacuum deposition techniques which are time consuming and require vast investments. Instead, if the aim is to model the spin dependent transport phenomena which occur in these systems, transport measurements of single elementary cells are mandatory. This remains one of the main goals for the future.

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