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Quantitative magnetometry analysis and structural characterization of multisegmented cobalt–nickel nanowires

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ABSTRACT

Understanding and measuring the magnetic properties of an individual nanowire and their relationship with crystalline structure and geometry are of scientific and technological great interest. In this work, we report the localized study of the magnetic flux distribution and the undisturbed magnetization of a single ferromagnetic nanowire that poses a bar-code like structure using off-axis electron holography (EH) under Lorentz conditions. The nanowires were grown by template-assisted electrodeposition, using AAO templates. Electron holography allows the visualization of the magnetic flux distribution within and surroundings as well as its quantification. The magnetic analysis performed at individual nanowires was correlated with the chemical composition and crystalline orientation of the nanowires.

1. Introduction

Magnetism is a collective quantum physical phenomenon that is caused by the interactions of atoms with magnetic moments arising from their electrons. In consequence, different kinds of magnetic behaviors are observed in materials with different crystallochemical features [1–3]. Recently, most of the fundamental and applied research focused on magnetic materials have been directed towards the understanding and application of the astonishing magnetic properties found in nanostructures, which are quite different from those observed in the bulk systems and exhibit unique size and shape dependences. For these reasons, the nanoscale materials with designed features, such as barcode-like structures, are excellent candidates for a large variety of technological applications [4–8]. In this matter, a need of specialized characterization techniques to measure the magnetic behavior of individual nanostructures is required [9–12]. Herein, we present the visualization of magnetic flux maps by off-axis electron holography. The *in situ* imaging magnetometry technique is able to recover the phase contours and quantification of their magnetic fields at nanoscale for ferromagnetic Co_xNi_{1-x} multisegmented nanowires.

Lately, chemical template-based methods have gained a considerable importance in the synthesis of tailored magnetic nanostructures due to their high level of accuracy in the control on the size and morphology of the resulting nanomaterials, and in the arrangement of nano-objects into the template matrix [13–16]. For instance, highly hexagonally ordered cylindrical magnetic nanowires (NWs) have been easily prepared by their electrochemical deposition into the nanopores of anodic aluminum oxide (AAO) membranes, displaying multiple technological applications including ultrahigh-density magnetic recording media [8], sensors and optoelectronic devices [17].

Interestingly, this technique not only allows the synthesis of homogeneous NWs [13], but also allows the synthesis of core–shell NWs [14] and/or multisegmented NWs with a controlled barcode-like structures [6–8], with tuned compositions and magnetic responses. However, it is important to remark that further investigations are required to establish the influence of the inner

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interphase magnetic interactions of each heterogeneous NW to comprehend the global magnetic properties observed in these NWs. Usually, the magnetic characterization techniques of nanomaterials are performed on a large assembly of magnetic nanostructures having a complex dispersion of morphology, composition, orientation and separation. Also, the interactions effects between the nano-entities play a crucial role in the total magnetic response of the sample, and the intrinsic properties of each nano-objects are frequently hidden by cooperative behaviors [18,19]. Therefore, the development of successful methods to characterize single nano-entities is a crucial requirement in order to achieve a complete picture of the physical properties of nanostructures [20–25].

Electron holography is a cutting-edge technique which utilizes the interference of two electron waves (reference and object) and can detect and quantify the electromagnetic field at nanometer scale. In this interference-based approach the magnetic vector potential A within the ferromagnetic nanowire causes a phase shift in the quantum mechanical wave functions of the electrons passing through this region (Aharonov–Bohm effect) [26]. In a general way we can describe the phase recovered by electron holography is the addition of several contributions $\varphi_{Total}=\varphi_E+\varphi_M$, where each super index stands for electrostatic and magnetostatic, respectively. Where φ_E represents the electrostatic component (may include the mean inner potential and induced polarization) and φ_M is the magnetostatic component

$$\varphi_{Total}(x, y) = C_E \int V(x, y, z)dz - \frac{e}{\hbar} \iint B_{\perp}(x, y)dx\, dz \quad (1)$$

where C_E is an energy dependent constant, for an energy of 200 kV is 0.00729 rad/V nm. By this means phase shift can be detected and evaluated quantitatively. The separation between electric and magnetic phase shifts can be carried out by some methods, for example: obtain the holograms at two different energies (*i.e.* 80 and 200 kV) [27], flipping the sample (up and down) [28] and *in situ* magnetization reversal [29]. Once the phase is recovered and separated, the contour of the pure magnetic phase image corresponds to the projected in-plane magnetic induction.

2. Experimental

The multisegmented nanowires were growth by electrochemical deposition *via* assisted AAO template. In order to protect the NWs from corrosion, the membranes were coated with a SiO_2 thin layer, deposited by atomic layer depositions at 150 °C. The multisegmented NWs were electrochemically grown by using an electrolyte that contains 0.36 M $CoSO_4$, 0.04 M $CoCl_2$, 0.76 M $NiSO_4$, 0.13 M $NiCl_2$ and 0.73 M H_3BO_3, having a pH of 4–1.2 by adding 1 M NaOH. The electrodeposition processes were carried out at 35 °C under potentiostatic conditions. The composition of the Co–Ni alloy NWs of each individual segment was tuned by adjusting the deposition potential in the range between −0.8 and −1.4 V *vs* the Ag/AgCl reference electrode. The multisegmented NWs were released from the alumina membrane by dissolving it in a mixture of H_3PO_4 (6 wt%) and CrO_3 (1.8 wt%) at 45 °C for 48 h. Then, the coated NWs were filtered and suspended in absolute ethanol solvent and dispersed in ethanol–distilled water mixture (1:1), subsequently sonicated for 30 min at room temperature (RT) and finally they were dropped in a Lacey carbon grid, which was dried for 30 min under ambient environment for evaporating the solvent.

The crystalline structure and orientation of the multisegmented nanowires was determined by selected area diffraction (SAED) patterns and additionally measured along the nanowire axis by electron diffraction using simultaneous scanning transmission electron microscopy (STEM) in a probe corrected JEOL ARM200F microscope. The chemical composition was analyzed by energy dispersive X-ray spectroscopy (EDS) line profile along the nanowire axis in STEM mode at 200 kV. When referring to magnetic materials, electron holography requires to be performed under Lorentz mode (field free condition), this means with the objective lens turned off to keep undisturbed the remanent magnetization state of the sample and using the Lorentz lens, a lens that is not standard for all microscopes. We measured the residual magnetic field of the objective lens for this microscope, and we found that for this microscope JEOL ARM 200F, the residual field is about 50 Oe. The holograms have to be acquired using high fringe contrast (≈ 15%), which can be adjusted with a bias voltage applied to the biprism particularly in these nanowires we use a biprism voltage ranging from 70 to75 V to cover the field of view of the object. In our experiment the nanowires have been oriented longitudinally in a parallel direction of the interference fringes. For the registered holograms, single exposure using exposure times of 2–4 s were used to enhance the phase resolution.

The holograms were recorded with Gatan's software Digital Micrograph (DM), and reconstructed by a beta version of HoloWorks 5.0.7, which includes as new feature the extraction of the magnetic induction and magnetic contours from (live) phase images (up to several frames per second). Every retrieved phase was numerical reconstructed using a reference hologram and the object hologram to remove the influence of the perturbed reference wave. The phase separation between the electrostatic potential and the magnetic field, is corrected by flipping (up and down) the sample and subtracting the phase maps obtained from the two phase maps.

3. Results and discussion

The electron microscopy studies revealed that the nanowires have a mean diameter of 185 ± 20 nm, around 300 nm of interspacing distance and ~14 μm in length. A transmission electron microscope (TEM) image of a single nanowire is shown in Fig. 1a as well as its indexed SAED pattern displayed in b, which indicates the zone axis and the growth direction ⟨0110⟩. Electrodeposited

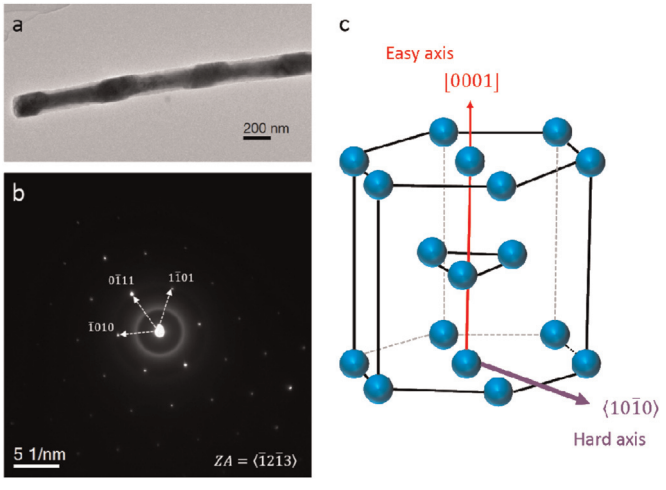

Fig. 1. (a) Transmission electron micrographs of a single cobalt–nickel alloy nanowire, displaying the multi-segmented structure. (b) The indexed selected area diffraction pattern from the segment with concentration Co_xNi_{1-x}, showing the hexagonal crystalline structure with its corresponding growth direction with the *c*-axis perpendicular to the nanowire axis. (c) Hcp cobalt structure showing the magnetocrystalline anisotropy, the magnetization easy axis and hard axis. (Crystalline directions are shown without following the formal notation, just for illustration purposes.)