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# Tunable magnetocrystalline easy axis in cobalt nanowire arrays by zinc additive

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ABSTRACT

A new approach to tuning the crystalline characteristics and magnetic properties of cobalt nanowire (NW) arrays embedded in AAO templates is reported using zinc additive. This is realized by adding low concentrations of Zn when pulse-electrodepositing cobalt NWs while also increasing the solution pH from 3 to 5. Using hysteresis loop measurements with a magnetic field applied parallel to the NW axis, coercivity and squareness of pure cobalt NWs increased from 890 Oe and 0.45 to 2150 Oe and 0.93 in $Co_{97}Zn_3$ NWs, respectively, using a Zn concentration of 0.01 M at pH = 4. XRD patterns obtained from the cobalt-rich CoZn NWs revealed that the crystalline texture of cobalt changes from [1 0 0] direction to [1 0 1] and [0 0 2] at pH = 3 and 4, respectively. For the latter, the magnetocrystalline easy axis of cobalt rotates from nearly perpendicular to parallel to the NW axis, induced by the incorporation of zinc into the *hcp* structure of cobalt.



## 1. Introduction

The continuous shrinking of magnetic materials down to nanometer dimensions has developed an interesting research field in which to investigate and discover new approaches to tailoring magnetic properties [1–3]. The fundamental methods providing this purpose range from lithography to electrochemical methods [1,4–6]. Using template assisted techniques such as the electrodeposition inside the nanopores of anodic aluminum oxide (AAO) templates, the electrochemical method has not only offered a simple methodology with different controllable physical and electrochemical parameters but have also provided patterned magnetic systems in the form of arrays of nanowires (NWs), nanotubes and nanopillars [7–10]. The emerging magnetic NW arrays hold promise for use in a variety of applications including magnetic sensors, high density magnetic recording media and thermomagnetic devices [11–14]. The physical parameters involved in the electrodeposition are mainly related to the shape, orientation and aspect ratio of NWs, following the morphology and characteristics of the corresponding templates as well as the electrodeposition time [4,8,15–17]. For example, decreasing the NW diameter from 20 to 9 nm increased the coercivity of cobalt NW arrays with aspect ratio greater than 20 up to approximately 2200 Oe [17]. Moreover, with an increase in the NW length, the coercivity of 10 nm diameter cobalt NWs reached 2300 Oe at length of 200 nm [17].

Regarding the electrochemical parameters, the electrodeposition involves the electrochemical cell parameters such as the temperature, acidity, composition and concentration of the electrolyte. In this way, a great deal of effort has been placed in the fabrication of magnetic NWs by varying both the physical and electrochemical parameters, leading to improvement in magnetic properties by increasing the magnetic coercivity and remanence ratio ($M_r/M_s$; squareness) values [18–23]. Changing electrodeposition parameters leads to varied magnetic contributions including shape anisotropy, magnetocrystalline anisotropy and magnetostatic interactions [17,24]. While increasing the aspect ratio of NWs has an effect on the magnetic behavior of single element NWs such as iron, nickel and cobalt through the shape anisotropy, it has been a challenge to explore new approaches through the magnetocrystalline anisotropy [25–27].

Particularly, due to the large magnetocrystalline anisotropy energy constant of cobalt ($K_{MC} = 4.5 \times 10^6$ erg/cm$^3$), it is desirable to rotate its magnetocrystalline easy axis (i.e. the *c*-axis along the [0 0 2] direction) toward the NW axis, thereby enhancing the total magnetic anisotropy [28,29]. In turn, this improves the magnetic properties including the coercivity and squareness of cobalt NWs

*Abbreviations:* NWs, Nanowires; AAO, anodic aluminum oxide; XRD, X-ray diffraction; *hcp*, hexagonal close-packed.

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for a magnetic field applied parallel to the NW axis (the axial direction) [20]. This has so far been realized through the electrochemical parameters using direct current (dc), alternating current (ac) and pulsed electrodeposition techniques [22,28].

By adjusting the pH (between 2 and 6.6) or the electrodeposition current density, Darques et al. [28] were able to find appropriate deposition conditions into the pores of polycarbonate membranes using a dc electrodeposition, leading to the deposition of hexagonal close-packed (*hcp*) cobalt NWs with a *c*-axis orientation either parallel (pH = 6.6) or perpendicular (pH = 3.8) to the NW axis. Their results indicated that the structure of cobalt NWs changes gradually with the pH of the solution and the *c*-axis does not rotate abruptly from perpendicular to parallel to the NW axis at a certain pH value. On the other hand, according to Zafar et al. [30], using pH ranging from 2.2 to 6.4 strongly influenced the crystallographic structure of cobalt NW arrays embedded in AAO templates, thereby affecting their magnetic properties. In this case, increasing pH from 3.5 to 6.4 increased the axial coercivity and squareness from 558 to 1254 Oe and 0.14 to 0.4, respectively. Meanwhile, the magnetocrystalline easy axis rotated from nearly perpendicular to parallel to the long axis of the cobalt NW arrays [30]. It is worth noting that, the addition of NaOH (thus increasing pH) could result in the co-deposition of unsatisfactory non-magnetic species and creating a non-steady sate electrodeposition, which in turn influences the crystallinity and magnetic properties of resulting NWs [22,28].

One emerging alternative to improving the magnetic properties of NWs is the use of an appropriate non-magnetic element when electrodepositing the magnetic element. In other words, the co-deposition of a non-magnetic element in the form of alloy NWs such as CoCr [31], CoPt [32], CoCu [33] and CoZn [34,35] has shown useful coercivity and reasonably square hysteresis loop. However, this needs a further processing, that is, the thermal annealing, making the mass production of these NWs doubtful as for magnetic storage media. Furthermore, the presence of the non-magnetic element such as zinc could provide useful properties for NWs including wear and corrosion resistance [36]. From the previous studies, using a pulsed electrodeposition technique with designated off-time between pulses, annealing of CoZn NW arrays led to an increase in coercivity up to 1785 Oe, starting from 240 Oe before annealing [34]. As has been proposed for cobalt NWs, using additives is expected to improve the magnetic properties [31].

This article aims to report the effect of zinc additive on the composition, magnetic properties and crystalline characteristics of cobalt NW arrays, embedded in AAO templates. To this end, both pure cobalt and cobalt-rich CoZn NW arrays were fabricated using a pulsed ac electrodeposition with constant off-time duration between pulses. The concentration of Zn electrolyte was adjusted between 0.0005 M and 0.015 M. The pH value was set to be between 3 and 5 in order to compare between the effect of solution pH and zinc additive on the rotation of magnetocrystalline easy axis. The effect of thermal annealing on the magnetic properties of the resulting CoZn NW arrays was also investigated. This article will show that the incorporation of a small zinc content into the cobalt structure could act as the increased pH value in terms of rotating the magnetocrystalline easy axis toward the long axis of NWs, which reinforces the shape anisotropy.

## 2. Experimental details

### 2.1. Fabrication of AAO template

To prepare AAO templates with highly ordered nanopore arrays, high purity Al disks (99.999% from Alfa Aesar; 0.25 mm in thickness and 8 mm in diameter) were ultrasonically cleaned in acetone. They were then electropolished in a mixture of ethanol and perchloric acid solution (4:1 in volume) at 4 °C under a constant potential of 20 V for 3 min. Afterwards, the conventional two-step anodization was used, as described in details in Ref. [37]. Briefly, using a constant potential of 40 V for 5 h, the Al disks were anodized in an electrolyte of 0.3 M oxalic acid at 17 °C as for the first step. Subsequently, the anodized layer was etched using a mixture of 0.3 M chromic and 0.5 M phosphoric acid solution at 60 °C. The second step was performed using the same parameters as those of the first step except that the duration of anodization was reduced to 2 h.

### 2.2. Pulsed electrodeposition of pure cobalt and cobalt-rich CoZn NW arrays

In this study, a pulsed ac electrodeposition technique was used to fabricate both pure cobalt and cobalt-rich CoZn NW arrays. Due to the presence of the insulating alumina barrier layer at the pores' bottom, the final anodization voltage (i.e. 40 V) was stepwise reduced to 10 V during 28 min prior to performing the pulsed electrodeposition. This promotes the thinning of the barrier layer and facilities the electrodeposition of ions inside the nanopores. For the electrodeposition of pure cobalt NWs into the AAO templates, a chemical cell containing of 0.3 M $CoSO_4{\cdot}7H_2O$ with 45 g $l^{-1}$ boric acid was used. As mentioned earlier, the effect of acidity of the deposition solution on the resulting properties have been investigated. In this regard, the pH of the cell was adjusted between 3 and 5 using a solution of $NaHCO_3$. While the chemical cell was constantly stirred, its temperature was kept constant to 30 °C using circulating heating water. To investigate the effect of zinc additive, a Zn electrolyte ($ZnSO_4.7H_2O$) with concentrations of 0.0005, 0.005, 0.01 and 0.015 M was added to the previous cell. The remaining Al of the AAO template and a roll of graphite were served as the working and counter electrodes, respectively.

Using a pulsed ac power supply (GW-Instek SFG-830) controlled by a programmable logger, an asymmetric sine waveform with reduction/oxidation potentials and reduction/oxidation times of 12/11 V and 2.4/2.4 ms was created at the onset of the pulsed electrodeposition process. Based on our previous work [34], the duration of off-time between pulses can affect the composition, magnetic properties and crystalline characteristics of cobalt and cobalt-based NWs. Therefore, to nullify this, the off-time duration was constant to 48 ms for all samples. Additionally, O-ring seals were employed to fix surface area so that the current density (i.e. the peak of the cathodic current density pulse) and the charged passed during the electrodeposition process were set to be approximately 30 mA $cm^{-2}$ and 1 C, respectively, for all samples studied.

### 2.3. Thermal annealing of cobalt-rich CoZn NW arrays

To investigate the effect of thermal annealing on the magnetic properties of cobalt-rich CoZn NW arrays, the NW samples were put in a furnace with an atmosphere containing 80% Ar and 20% $N_2$. They were then heated progressively up to 570 °C and were kept at this temperature for 30 min. Finally, the process was followed by progressively cooling NW samples to room temperature.

### 2.4. Characterization

The morphology of the AAO template and NW samples was investigated using atomic force microscopy (AFM, NT-MDT) and scanning electron microscopy (SEM; MIRA3 TESCAN operating at 15 kV). To carefully investigate the composition of cobalt-rich CoZn NWs, the remaining Al at the back of the samples was removed using a saturated solution of $CuCl_2$. Subsequently, the composition of the NW samples was characterized by energy dispersive spectroscopy (EDS) attached to the SEM and X-ray fluorescence (XRF, equipped with a Cu target). The crystalline