Effects of the magnetoelastic anisotropy in Ni nanowire arrays


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Nanoporous anodic alumina films on Al substrates have been used as templates for the growth of electrodeposited Ni nanowires. The nanowire diameter ranges between 35 and 65 nm, and the hexagonal symmetry lattice constant is 105 nm. The magnetization curves for these nanowire arrays with and without the Al substrate have been measured in a temperature range from 5 to 300 K, from which the effective magnetic anisotropy, coercivity, and remanence have been determined. The effective easy magnetization axis changes from parallel to perpendicular to the Ni nanowire axis as temperature decreases, as a result of the magnetocrysalline and the magnetoelastic anisotropy terms, arising from the different thermal expansion coefficients of the ferromagnetic nanowires, the alumina and Al. © 2008 American Institute of Physics. [DOI: 10.1063/1.2834719]

I. INTRODUCTION

During the last decade, advances both in the use of different fabrication processes including lithography, self-assembly, or chemical synthesis methods and in characterization techniques have enabled the development of magnetic structures in which the dimensions have been continuously decreased. Metallic nanowires are among the most interesting nanometer-sized materials due to their potential applications in areas such as magnetic recording, spintronics, and chemical, optical or biological sensors.1-3

Many physical properties of nanowires, and particularly the magnetic behavior, strongly depend on the mechanical stresses to which the nanowires are subjected. The magnetic behavior of ferromagnetic nanowire arrays (Ni, Fe, Co, and different alloys) grown inside the pores of anodic alumina films by electrodeposition has been extensively studied at room temperature.4-8 The behavior of the arrays is determined by the structure of the individual nanowires, including their composition, crystallinity, grain orientation, and shape and size, and by the magnetic interactions among the nanowires. Typically, due to the shape anisotropy term, nanowire arrays exhibit uniaxial anisotropy with the easy axis aligned along the wire axis and perpendicular to the plane.4,7,9 However, their temperature-dependent properties have not received the same attention.7,10-14 In this work, we describe changes in the uniaxial anisotropy of nanowire arrays and relate these changes to the stresses caused by the different thermal expansion coefficients of the alumina matrix, the ferromagnetic wires, and the aluminium substrate.

II. EXPERIMENTAL METHODS

Highly ordered Ni nanowire arrays were produced by electroplating into nanopores of alumina films. Nanoporous alumina films with long-range hexagonal ordering were obtained by a two-step anodization process.15,16 The pore diameters were increased by immersing the nanoporous alumina membranes in 5% phosphoric acid solution at 35 °C, in which the pore diameter widening rate is 1.5 nm/min. The ferromagnetic nanowires were grown by pulse electrodeposition.5 Ni Watts-Bath were used as electrolyte. During the electrodeposition, the solution was stirred and the temperature held constant at 35 °C. The pH of the solution was kept constant at 4.5. In some cases, the Al substrates were removed by a selective chemical etching (3.6 g CuCl₂·2H₂O and 50 ml HCl dissolved in 100 ml H₂O) at low temperature (less than 10 °C) to avoid damaging the alumina template. Before removing the Al substrate, the ferromagnetic nanowires were protected by a polymer film which was eventually dissolved in acetone.

Morphological characterization was performed by scanning electron microscopy (SEM) in a JEOL JM-6400 at 5 kV. X-ray diffraction (XRD) of the Ni nanowire arrays was performed on a Siemens D-501 diffractometer with Cu Ka radiation (λ=1.5406 Å) in the range of 30° ≤ 2θ ≤ 100°. Hysteresis loops with a maximum applied field of 1 T, in a range of temperature from 5 to 300 K of the arrays as a whole were performed in a superconducting quantum interference device Quantum Design magnetometer, model 5S.

III. RESULTS AND DISCUSSION

Figure 1 shows SEM images of the nanoporous anodic alumina films. The nanopores are ordered in a hexagonal structure with the same interpore distance (105 nm) but different pore diameters in the range from 35 to 65 nm. SEM cross section images (not shown in this work) indicate that the alumina film thickness and the nanowires length are ~2 μm, the wires are parallel to each other and perpendicular to the film plane, and the Al substrate is ~300 μm thick.
The XRD pattern suggests that the Ni nanowires crystallize as a face-centered-cubic phase. The intensity for (111) is greatest which indicates that the Ni nanowires have a preferred orientation with [111] parallel to the wire axis.

At room temperature, we observed the same magnetic behavior as reported elsewhere. Large out-of-plane remanence and coercivity were found for the smallest wire diameter. The results suggest that the magnetic behavior of the Ni nanowire arrays is mainly controlled by shape anisotropy since magnetocrystalline anisotropy is negligible at room temperature. The nanowire arrays possess uniaxial shape anisotropy with the easy magnetization axis aligned along the wire and perpendicular to the plane of the porous alumina film. The reduction in out-of-plane remanence and coercivity for increasing diameter is attributed to magnetostatic interactions between the nanowires.

Our interest has focused on the study of the magnetic behavior as a function of temperature. Hysteresis loops were measured for Ni samples with and without Al substrates for various diameters (from 35 to 65 nm) in the temperature range of 5–350 K from which the saturation magnetization, normalized saturation magnetization, and out-of-plane remanence followed the trend in $M_S(T)$ for the Ni nanowire arrays without Al substrate. In contrast, the Ni nanowire arrays with Al substrates showed opposite behavior [Fig. 2].

To understand the results for Ni nanowire arrays with Al substrate, the effective anisotropy energies ($K_{\text{eff}}$) were estimated from the hysteresis loops using the following approximation:

$$K_{\text{eff}} = \int_0^{M_S} \left[ -H_C - H \right] dM - \int_0^{M_S} \left[ -H_C - H \right] dM_0,$$

where $M_i$ is the saturation magnetization moment and $H_C$ is the coercivity. The easy magnetization axis is along the wire axis when $K_{\text{eff}} > 0$ and transverse to the wire axis for $K_{\text{eff}} < 0$. The theoretical shape anisotropy energy ($K_{\text{shape}}$) has also been calculated and it is expected to follow the temperature dependence of $M_S$. Figure 3 shows the temperature dependence of both $K_{\text{shape}}$ (Ni nanowire arrays with 35 nm wire diameter) and $K_{\text{eff}}$ for Ni nanowire arrays with different wire diameters on an Al substrate. For Ni nanowire arrays with the smallest wire diameter (35 nm), the easy magnetization axis is along the wire axis for all temperatures, but the anisotropy decreased when the temperature was reduced. In contrast, the easy magnetization axis is transverse to the wire axis for all temperatures for the array with 65 nm wire diameter. An intermediate case was observed for the array with 50 nm wire diameter in which $K_{\text{eff}}$ changed sign at a temperature of around 270 K implying that above this temperature the easy axis is along the wire axis, whereas below 270 K the easy axis is transverse. The negative $K_{\text{eff}}$ at room temperature is attributed to the existence of magnetostatic interactions between nanowires. The estimated magnetostatic interaction values increase when the wire diameter increases for the same interwire distance (105 nm), reducing $K_{\text{eff}}$ for the wider wires and even changing its sign. This magnetostatic contribution to $K_{\text{eff}}$ will increase slowly as temperature decreases, tracking $M_S$.

These trends in $K_{\text{eff}}$ cannot be explained by temperature-dependent shape anisotropy or magnetostatic interactions. Additional anisotropy terms, such as magnetocrystalline and...
magnetoelastic anisotropies, have to be introduced. At room temperature, the magnetocrystalline anisotropy term can be neglected because its value is much smaller than the shape term for Ni nanowires. However, the cubic magnetocrystalline anisotropy constants change considerably with temperature. \cite{19,20} $K_1$ changes from $-0.45 \times 10^4$ to $-1.2 \times 10^4$ J/m$^3$ and $K_2$ from $-0.23 \times 10^4$ to $0.3 \times 10^4$ J/m$^3$ for Ni when the temperature changes from 300 to 4.2 K.

The existence of magnetoelastic anisotropy terms ($K_{me}$) have been also suggested, arising from the different thermal expansion coefficients between the Ni/alumina layer and the Al substrate. \cite{11,14} We estimate $K_{me}=\lambda_S(\sigma_{\text{axial}}-\sigma_{\text{in.plane}})$, where $\lambda_S$ ($\lambda_{111}=-24 \times 10^{-6}$) is the magnetostriiction constant and $\sigma$ are the axial and in-plane external stresses. \cite{19} If we assume that $\sigma_{\text{axial}}=0$, $K_{me}$ comes from $\sigma_{\text{in.plane}}$. As the thermal expansion of the Al is higher than that of the Ni and alumina, and the thickness of the Al substrate (~300 \mu m) is also very large in comparison to the Ni and alumina system (~2 \mu m), the thermal mismatch stress imposed on the ferromagnetic nanowires by the Al substrate is the dominant factor. We consider that the Ni nanowire arrays are in a state of in-plane equibiaxial strain \cite{21}. $\varepsilon_{\text{in.plane}}=\varepsilon_{\text{in.plane}}^{\text{Ni/Al}}$. Then, the in-plane strain of the Ni is determined by the following equation: \cite{22}

$$\varepsilon_{\text{Ni/Al}}^{\text{in.plane}} = \frac{\Delta l}{l} = \int_{T_0}^{T_1} \left[ \alpha_{\text{Ni}}(T) - \alpha_{\text{Al}}(T) \right] dT,$$

(2)

where $\Delta l/l$ is the fractional change in length, $\alpha_{\text{Ni}}(T)$ and $\alpha_{\text{Al}}(T)$ are the thermal expansion coefficients of the Ni and Al substrates respectively, and $T_0$ and $T_1$ are the fabrication and measured temperatures. Thermal strains originated by cooling or heating have a “+” sign for tension or elongation and a “−” for compression or contraction. This strain state corresponds to an in-plane stress given by

$$\sigma_{\text{Ni/Al}}^{\text{in.plane}} = E_{\text{Ni}}\varepsilon_{\text{Ni/Al}}^{\text{in.plane}},$$

(3)

where $E_{\text{Ni}}$ is the Young modulus for Ni (214 GPa).

Figure 4 shows the experimental and the calculated effective anisotropies for the Ni nanowire arrays with 35 nm wire diameter on the Al substrate. The [111] direction, which is an easy magnetization axis at room temperature, becomes hard at low temperatures. The stresses caused by the different thermal expansion coefficients also contribute toward the temperature dependent magnetic anisotropy energy of the Ni nanowire arrays on Al substrates. Considering the temperature dependence of the magnetocrystalline and the magnetoelastic terms, the difference between the calculated shape anisotropy and the measured effective magnetic anisotropy as a function of temperature has been described. Furthermore, the difference between the experimental and calculated anisotropy energy (Fig. 4) has been associated with the contribution of the interwire magnetostatic interactions.

FIG. 4. Temperature dependence of the measured effective anisotropy energy ($K_{\text{eff}}$ (■)), calculated shape anisotropy ($K_{\text{shape}}$ (●)), and calculated “shape+magnetoelastic+magetocrystalline” anisotropy (○) for Ni nanowire arrays on Al substrate and with 35 nm diameter.

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