Co/Ni multilayers ordered according to a periodic, Fibonacci and Thue Morse sequence obtained by Atomic Layer Deposition

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Abstract

Co/Ni multilayers ordered according to a periodic, Fibonacci and Thue Morse sequence have been obtained by Atomic Layer Deposition and a subsequent process of thermal reduction. The morphology of the multilayers was investigated by scanning electron microscopy, while longitudinal hysteresis curves were obtained by magneto-optical magnetometry of Kerr effect. The morphology of the films varies as a function of their sequence and thickness. Multilayers exhibit coercivities much higher than expected from samples synthesized with other methods. The control of the magnetic properties of multilayers, as a function of their sequence, may allow their use in spintronic devices.

1. Introduction

The concept of quasi-periodicity, defined as the property exhibited by a system that shows an irregular periodicity, was inaugurated by Bohr in 1926, when he investigated quasi-periodic functions [1]. From this concept quasicrystals arise, discovered by Shechtman et al [2], which are expected to exhibit an intermediate behavior between disordered systems and pure crystals. The appearance of these crystals gave rise to a whole current focused on the study of the physical properties of aperiodic materials [3], with some outstanding applications, such as photonic crystals [4]. Some examples of structures that follow a quasi-periodic order are quasi-crystalline 1D structures that follow pure or generalized Fibonacci sequences [5, 6], nanowire arrays modeled with quasi-periodic structures [7], wire networks distorted according to a Fibonacci sequence [8] and aperiodic superlattices made up by rare-earths materials [9], among others. Further, Albuquerque and Cottam [10] presented a comprehensive review of the main physical properties of excitations that can propagate into multilayer structures with components arranged in a quasiperiodic form.

On the other hand, periodic magnetic multilayers have been intensively investigated [11], allowing to obtain specific magnetic properties such as perpendicular magnetic anisotropy [12–15]. To date, multilayers have been synthesized by many different techniques, such as, UHV evaporation [16], sputtering [17] and electrodeposition [18, 19]. However, it is well known that Atomic Layer Deposition (ALD) allows precise control of the thickness and excellent coverage of the films [20], even allowing 3D high-aspect ratio nanostructures to be obtained. In contrast to the periodic counterpart, there are few experimental studies that present the synthesis of magnetic quasi-periodic multilayers [16, 21], in spite of numerical results have predicted anomalous magnetic resistance [22, 23], ferromagnetic resonance (FMR) [24] and spin waves [25, 26].

In the present work, we synthesize and characterize magnetic multilayers composed of cobalt and nickel thin films arranged according to a periodic, Fibonacci and Thue Morse sequence. In particular we are interested in investigating how the magnetic properties of these multilayers change as a function of their ordering. To do this we will perform a morphological and magnetic characterization of the samples.
2. Model

We distribute two different layers according to a periodic, Fibonacci and Thue Morse sequence. The periodic sequence is given by $P_N = 2P_{N-1}, N > 1$, with $P_0 = 1$. Using two different layers A and B, the periodic sequence can be obtained considering the following inflation rule: $A \rightarrow BA, B \rightarrow BA$. In this case, the layers A and B consists respectively of nickel and cobalt, both layers having a thickness of 2 nm. When we apply this inflation rule, we obtain $P_1 = BA, P_2 = BABA, P_3 = BABAABABA and P_4 = ABABABABABABAB$, which translated into magnetic materials corresponds to the following multilayer films $P_1 = Co/Ni, P_2 = Co/Ni/Co/Ni, P_3 = Co/Ni/Co/Co/Ni/Co/Co/Ni$ and $P_4 = Co/Ni/Co/Ni/Co/Co/Ni/Co/Co/Ni/Co/Ni/Co/Ni/Co/Ni$ (see top image of figure 1).

The number of elements of the Fibonacci sequence is given by the recursive relation $F_N = F_{N-1} + F_{N-2}$, $N > 2$, with $F_1 = F_2 = 1$. Here, the Fibonacci sequence is obtained considering the inflation rule which defines the golden mean sequence: $A \rightarrow AB, B \rightarrow A$ [27]. Applying this inflation rule, we obtain $F_1 = B, F_2 = A, F_3 = AB, F_4 = ABA, F_5 = ABAAB and F_6 = ABAABABA$, which translated into magnetic materials corresponds to the following multilayer films $F_1 = Co, F_2 = Ni, F_3 = Ni/Co, F_4 = Ni/Co/Ni, F_5 = Ni/Co/Ni/Co and F_6 = Ni/Co/Ni/Ni/Co/Co/Ni/Co/Ni$ (see central image of figure 1).

The Thue Morse sequence is given by $T_N = 2T_{N-1}, N > 1$, with $T_0 = 1$. Here, the Thue Morse sequence is given by the inflation rule: $A \rightarrow AB, B \rightarrow BA$, so that we obtain $T_1 = BA, T_2 = BAAB, T_3 = BAABABA$ and $T_4 = BAABABBAABABAAB$, which translated into magnetic materials corresponds to the following multilayer films $T_1 = Co/Ni, T_2 = Co/Ni/Co/Ni, T_3 = Co/Ni/Co/Ni/Co/Co/Ni$ and $T_4 = Co/Ni/Co/Ni/Co/Co/Ni/Co/Co/Ni/Co/Co/Ni/Co/Ni/Co/Ni/Co/Ni$ (see bottom image of figure 1).

3. Experimental section

The growth of multilayers was carried out in a Savannah S100 ALD equipment from Ultratech. Si(100) wafers with 210 nm of thermally grown SiO$_2$ on top were used as substrates. Nickelocene (NiCp$_2$) and ozone (O$_3$) were used to deposit NiO films at 200 °C, and cobaltocene (CoCp$_2$) and ozone (O$_3$) to deposit CoO films at 250 °C. The nickelocene and cobaltocene were heated to 80 °C and 90 °C, respectively. During the whole deposition process, a flow of 20 sccm of nitrogen was maintained. Each ALD cycle (stop/exposure mode) considers a pulse, exposure and purge time for each of the precursors. Thus, the pulse times of NiCp$_2$, CoCp$_2$ and O$_3$ were 4 s, 4 s and 0.2 s, respectively. Besides, the exposure and purge times were 10 s and 30 s, respectively.
The Co/Ni multilayers are formed by numerous single layers, each of which has a thickness of 2 nm (70 ALD cycles for CoO or 180 ALD cycles for NiO), so that the multilayers considered exhibit a thickness that varies between 6 and 32 nm. In order to obtain multilayer metallic films, the multilayers were subjected to a thermal reduction process at 400 °C for 4 h using an oven GSL-1100X from MTI Corporation under a controlled atmosphere of hydrogen (4%) and argon (96%) [28, 29]. Considering that this process has been used to reduce much more complex structures such as ferromagnetic nanotubes [30], that both x-rays and the measurement of magnetic properties allow us to clearly identify the variation that occurred after the thermal reduction process, we estimate that almost 100% of the cobalt oxide and nickel oxide are reduced to cobalt and nickel, respectively.

Multilayer films were characterized by atomic force microscopy (Bruker Dimension Icon microscope operating in non-contact mode and commercial AFM probes (Nanosensors, type PPM-FM)), scanning electron microscopy (Zeiss EVO MA10 SEM, Oberkochen, Germany) at 20 kV, transmission electron microscopy (Hitachi HT7700 high resolution TEM, Chiyoda, Tokyo, Japan) at 100 kV, and x-ray diffraction (Bruker D8 system with Cu-Kα radiation, λ = 0.154 06 nm), in a range between 10° and 90° in 2θ, at a sweep rate of 0.02° s⁻¹. On the other hand, the thickness of the films was obtained by an ellipsometer (alpha-SE from J. A. Wollam), while the magnetic properties were measured by magneto-optic Kerr effect (NanoMOKE3 from Quantum Design) with the magnetic field applied parallel and perpendicular to the substrate plane.

4. Results and discussion

In a previous article, we verified that when working with an ALD supercycle that considers one cycle of one material and another cycle of another, the result is an alloy and not a multilayer system [31]. However, in this case we are considering 180 cycles of NiO and 70 cycles of CoO, so we expect to effectively face a multilayer system since as Gupta et al [32] showed, it is indeed possible to maintain the layered structure even after annealing at temperatures as high as 400 °C, although obviously with some diffusion between the layers due to the high temperature. The diffusion between the layers produces cracks or holes in the surfaces of the films, which produces a reduction in their thicknesses.

Figure 2 shows a TEM image of a F₅ = Ni/Co/Ni/Ni/Co multilayer obtained after the thermal reduction process, which shows that the sample still maintains the layered structure.

Figure 3 shows SEM images of cobalt and nickel multilayers distributed following a periodic (figures 3(a)–(c)), Fibonacci (figures 3(d)–(f)) and Thue-Morse (figures 3(g)–(i)) sequence obtained after the thermal reduction process. It is important to note that the periodic multilayers exhibit a greater inhomogeneity than those exhibited by Fibonacci or Thue-Morse multilayers. This is mainly due to a greater number of interfaces between Co and Ni films that exist in this system.

On the other hand, if we focus on Fibonacci or Thue-Morse multilayers, we can see that when the multilayer system has few layers (see figures 3(d) and (g)), the upper film is quite homogeneous, however, as we increase the number of layers, and due to the release of oxygen from the samples during the thermal reduction process, a phenomenon known as dewetting process, some quite irregular agglomerates appear on the samples (see figures 3(e) and (h)), which increase in size as the number of layers increases (see figures 3(f) and (i)). This phenomenon can be understood if we consider that the temperature at which the dewetting process occurs

![Figure 2: TEM image of a F₅ = Ni/Co/Ni/Ni/Co multilayer obtained after the thermal reduction process. The colored bars are a guide for the eye.](image-url)
decreases with the thickness of the multilayer [33]. This means that, since the thermal reduction process of the different samples was carried out at the same temperature, the thicker multilayers begin with the dewetting process before thinner multilayers. Besides, it is well known that the dewetting process generally progresses through at least three distinct stages: hole formation, hole growth and impingement, and ligament breakup [34]. In fact, the process of dewetting either occurs at preexisting holes or at film edges or requires the formation of new holes. These holes then grow to form dewetted regions that eventually overlap, so that the entire system is dewetted.

In AFM measurements performed on multilayer films of the same thickness (see figure 4), some differences in roughness can be observed considering the different multilayers, where sample F4 exhibits the lowest roughness with an RMS of 0.21 nm, while sample P3 is the one with the highest roughness, with an RMS of 1.68 nm. This is because the periodic samples exhibit a greater number of interfaces corresponding to different materials. While the growth of NiO films directly on CoO films leads to a well-defined interface, the thermal reduction process to which the multilayers are subjected leads to a rough interface and significant intermixing between Ni and Co.

To analyse the composition of the multilayers, we have synthesized CoO and NiO films that are then reduced. The idea is to analyse the XRD pattern of the individual films before and after being reduced. The diffraction patterns of the CoO and NiO films, as well as those that were subjected to a thermal reduction process, Co and Ni films, are shown in figure 5. According to card No. 96-900-5888, the cobalt oxide pattern corresponds to a spinel structure with three well-defined peaks that correspond to planes (022), (113) and (004). In addition, JCPDS card No. 15-0806 indicates that the cobalt pattern corresponds to a face-centred cubic (FCC) structure with two peaks corresponding to planes (111) and (002). On the other hand, according to the JCPDS card No. 71-1179 the nickel oxide film corresponds to a single-phase face-centred cubic (FCC) structure with two peaks corresponding to planes (200) and (111). Additionally, JCPDS card No. 04-0850 indicates that the nickel pattern exhibits a displacement of the planes (200) and (111).

The hysteresis curves measured with the field applied parallel to the plane of the substrate and at room temperature are shown in figure 6. We obtained coercivities between 25 and 65 mT, and normalized remanence values between 0.4 and 1.0. We highlight the fact that the measured coercivity is much higher than that exhibited...
Figure 4. Atomic force measurements of selected samples. Sampling size was 1-micron square for all the samples. Sample P3 exhibits an RMS value for the roughness of 1.68 nm. Samples F4 and F5 shows an RMS value for the roughness of 0.21 nm and 0.37 nm, respectively. Sample T4 shows an RMS value for roughness of 0.5 nm.

Figure 5. XRD patterns of CoO, NiO, Co and Ni films.
by other films with similar thicknesses [35–37]. For example, Potocnik et al [35] fabricated a 25 nm thick Ni film by electron beam evaporation of Ni using Glancing Angle Deposition technique onto the glass substrate that exhibits a coercivity of approximately 1 mT when the field is applied parallel to the substrate. Additionally, Parlak et al [36] fabricated a 2.4 nm thick Ni film at room temperature using a magnetron sputtering system that exhibits a coercivity of approximately 3 mT when the field is applied parallel to the substrate. As the depositions in our article were developed at temperatures higher than 200 °C, we do not expect that the increase in coercivity is due to the appearance of impurities.

Figure 6. Hysteresis curves for multilayers that follow (a) periodic, (b) Fibonacci and (c) Thue Morse sequence, measured at room temperature with the magnetic field applied parallel to the plane of the substrate.
Multilayers that follow a periodic sequence (see figure 6(a)) exhibit a non-monotonic behaviour for both coercivity and remanence as a function of the number of layers, that is, they present maximum coercivity and remanence for P2, both values decrease for P3, but increase again for P4. Multilayers that follow a Fibonacci sequence (see figure 6(b)) do not vary much their coercivity or remanence as a function of the number of layers, that is, when we move between F4 and F6. Multilayers that follow a Thue-Morse sequence (see figure 6(c)) also follow a non-monotonic behaviour for both coercivity and remanence as a function of the number of layers, but in this case it is the opposite behaviour to that exhibited by the periodic multilayers, that is, they exhibit the minimum coercivity and remanence for T2, both values increase for T3, but decrease again for T4.

Figure 7 presents a summary of the measurements of coercivity and normalized remanence for the different multilayers. From this figure we can see that both coercivity and remanence follow a complex behaviour as a function of the thickness and sequence of the multilayer. The maximum coercivity is obtained for P2 while the minimum coercivity occurs for T3. Both samples exhibit the same thickness, and the same percentage of cobalt films, so the only difference is the number of cobalt and nickel interfaces, where P2 offers three interfaces, and T2 only two. In this way, it is concluded that the number of interfaces plays a fundamental role in this type of multilayer systems.

In the case of multilayers that follow a Fibonacci sequence, we see that the coercivity exhibits a non-monotonic behaviour as a function of the thickness of the films. This can be understood if we remember that cobalt films exhibit a higher coercivity than nickel films [28, 29], so a multilayer with a higher percentage of cobalt films will exhibit greater coercivity when the magnetic field is applied parallel to the plane of the substrate. In this way, if we look closely at figure 1 we will realize that the sample F4 has $1/3 = 33\%$ of cobalt films, sample
F5 has $\frac{2}{5} = 40\%$, and sample F6, $\frac{3}{8} = 37.5\%$. This may explain the non-monotonic behaviour observed for the coercivity.

Periodic and Thue-Morse multilayers exhibit a quite unexpected behaviour. In these cases, there is a non-monotonic behaviour as a function of the thickness of the samples. Since the percentage of cobalt layers is the same, regardless of the thickness of the sample, then we might think that the number of interfaces between cobalt and nickel is responsible, but since these sequences exhibit completely a different behaviour despite the fact that the number of interfaces increases with thickness, we can assure that the agglomerations and holes that occur in the sample noticeably affect the magnetization reversal mechanism, introducing pinning areas for the domain walls. In this way, the observed behaviour is the result of a competition between the materials involved, the associated interfaces, and the thickness of the samples. It is important to keep in mind that the coercivity also

Figure 8. Hysteresis curves obtained by means of micromagnetic simulations for a (a) P3, (b) F6 and (c) T3 multilayer system (all with the same thickness) of $1 \times 1 \mu\text{m}^2$. Points A, B, C and D correspond to $M/M_s$ equal to 0.9, 0.7, 0.5 and 0.3, respectively.
depends on the structure, microstructure and defects of the multilayers, the latter very important after the process of thermal reduction to which the multilayers are subjected.

Figure 7(b) shows the normalized remanence as a function of the thickness of the multilayers for the different sequences considered. From this figure we can see that the remanence follows a behaviour quite similar to the one that exhibits coercivity for the different sequences.

To understand in detail the magnetization reversal mechanism of these multilayers, we have simulated the hysteresis curves of a periodic, quasi-periodic (Fibonacci) and aperiodic (Thue-Morse) sample considering the same thickness, that is, P3, F6 and T3, respectively (see figure 8). Micromagnetic simulations allow solving the Landau–Lifshitz–Gilbert (LLG) equation within the framework of the finite difference method [38]:

\[
\frac{dM}{dt} = -\gamma M \times H_{\text{eff}} + \frac{\alpha}{M_s} M \times \frac{dM}{dt}
\]

where \(M_s\) is the saturation magnetization, \(\gamma\) is the gyromagnetic ratio and \(\alpha\) is the damping constant. We used exchange constants \(A^{\text{Ni}} = 0.86 \times 10^{-11}\) J m\(^{-1}\) and \(A^{\text{Co}} = 2.81 \times 10^{-11}\) J m\(^{-1}\). The saturated magnetizations for Ni and Co were \(M_{s}\text{Ni} = 484 \times 10^{3}\) A m\(^{-1}\) and \(M_{s}\text{Co} = 1422 \times 10^{3}\) A m\(^{-1}\), respectively. In all the simulations we considered a damping constant equal to 0.5.

From these figures we can see that, regardless of the sequence considered, the hysteresis curves are very similar, with similar coercivity and remanence values. In this way, we can conclude that in the absence of irregularities, such as agglomerations or holes produced by the dewetting process to which the samples are subjected, there should be no greater variation in the magnetic properties, at least for the materials and the range of values considered in this study. The magnetization reversal mechanism is similar in all three cases, first rotating the spins located on the surfaces perpendicular to the direction in which the external magnetic field was applied (x-axis, see snapshot A). This rotation produces triangular domains both to the left and to the right of the sample (see snapshot B), which completely revert their magnetization (see snapshot C) before even colliding with each other (see snapshot D). Eventually the domains collide and collapse, causing the magnetization reversal of the entire sample.

5. Conclusions

In conclusion, we have synthesized Co/Ni multilayers that follow a periodic, Fibonacci and Thue–Morse sequence using the atomic layer deposition technique and a subsequent process of thermal reduction. Periodic multilayers exhibited greater roughness than Fibonacci or Thue–Morse multilayers due mainly to the number of cobalt/nickel interfaces that appeared in the system. The coercivity measured for all samples is much higher than that expected for thin films of similar thicknesses and the observed behaviour is the result of a competition between the materials involved, the associated interfaces, and the thickness of the samples. It is important to keep in mind that the coercivity also depends on the structure, microstructure and defects of the multilayers, the latter very important after the process of thermal reduction to which the multilayers are subjected. Finally, these multilayers can be used in applications associated with the field known as magnon spintronics.

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