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D.J. Keavney, Eric E. Fullerton, J.E. Pearson, and S.D. Bader

*Materials Science Division
Argonne National Laboratory, Argonne, IL 60439*

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Magnetic Properties of *c*-axis Textured Nd₂Fe₁₄B Thin Films

D. J. Keavney, Eric E. Fullerton, J. E. Pearson, and S. D. Bader
Materials Science Division, Argonne National Laboratory
9700 S. Cass Avenue, Argonne, IL 60439

Abstract—Thin films of Nd₂Fe₁₄B (~30-60 nm) were grown with *c*-axis texture by means of molecular beam epitaxy. A two-phase structure is observed in both the x-ray diffraction and the hysteresis loops, due to an interfacial reaction during the initial growth. Coercivities are 1-2 T at 20 K, and the anisotropy fields are bulk-like. Microstructural analysis by atomic and magnetic force microscopies reveal lateral grain sizes of ~200 nm, which could explain the hard magnetic properties.

I. Introduction

Nd₂Fe₁₄B [1] is the permanent magnet with the highest energy product, and has been used in widespread applications. Since its magnetic properties depend on microstructure, it is of interest to systematically vary the length scales and intergranular phases to optimize its magnetic properties. Thin film studies offer an opportunity to do this, as the film thickness can be controlled to high accuracy, and multilayer configurations containing Nd₂Fe₁₄B can be used to simulate the presence of an intergranular phase. In addition, thin film studies offer the possibility of testing ideas relating to exchange hardening via coupling to a soft, high-magnetization phase[2,3].

Several sputtered R₂Fe₁₄B film systems have been studied, where R is a rare earth[4-7]. Most of these were on thick ($\geq 1\mu\text{m}$) films, and so involved bulk-like properties. A preferred *c*-axis orientation was observed in some studies[4,5]. We report herein on oriented Nd₂Fe₁₄B films of 30-60 nm thickness for eventual use in artificially microstructured configurations.

II. Sample Fabrication and Characterization

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Two approaches to the formation of the 2-14-1 phase in thin films are possible: (i) co-deposition and (ii) superlattice deposition, followed by solid-state reaction, also known as block-by-block deposition[8]. In the latter approach, adapted herein, each building block was taken to represent half a unit cell because of the layered Nd₂Fe₁₄B structure with a mirror plane at *c*/2. The order in which the elemental component layers are deposited defines a path through the ternary Nd-Fe-B phase diagram, and consequently, appropriate paths may be chosen to avoid undesired phase formation. Figure 1 shows three of the paths tried in this study superimposed onto the low-temperature Nd-Fe-B phase diagram. Path 1 (solid line) represents simple block-by-block deposition, in which the quantities of each superlattice component are defined by the stoichiometry. Paths 2 (dotted line) and 3 (dashed line) refine this approach; they represent the initial formation of the basal plane containing Nd, Fe, and B, followed by more Fe deposition for the Fe planes. In general, the binary borides are avoided, as they have high heat of formation and would remove

Figure 1. Low-temperature Nd-Fe-B phase diagram showing the three paths (heavy solid, dotted, and dashed lines) taken during the deposition of the thin films. φ represents the 2-14-1 phase and η is the 1-4-4 phase. Paths 2 and 3 represent the formation of the Nd₂Fe₁₄B basal plane, followed by the Fe planes.

reactants from the system. Phase diagram information in Fig. 1 is from Buschow[9].

The superlattices were deposited under ultrahigh-vacuum conditions from pure elemental sources onto MgO(100) or (110) single-crystal wafers coated with 20-nm epitaxial Mo buffer layers of (100) and (211) orientation, respectively. Electron beam evaporators were used for Nd, B and Mo, while Fe was deposited from a Knudsen cell. The deposition rate from each source was monitored by a quartz crystal microbalance. Reflection high energy electron diffraction (RHEED) was used to monitor the deposition of the buffer layer and each Nd-Fe-B superlattice repeat. To provide sufficient thermal energy to allow the solid-state reaction to take place, the deposition was either at high temperature (675°C) or at low temperature, followed by a short high-temperature anneal. The ordering of the superlattice components was varied such that several different paths through the phase diagram were sampled.

Structural characterization and phase identification utilized standard $\Theta-2\Theta$ x-ray diffraction. Additional structural techniques employed on selected samples were scanning electron microscopy with energy dispersive x-ray analysis for verification of composition, and atomic and magnetic force microscopy (AFM/MFM) for morphology and magnetic domain information.

High-temperature deposition resulted in initial epitaxial growth, followed by polycrystalline overgrowth after 8-12 unit cells. RHEED also

indicated the initial crystalline growth was of three-dimensional islands. Fig. 2 shows the x-ray diffraction from 25-unit-cell-thick films grown on Mo(100) and (211). On Mo(100), the films have a two-phase structure, with the 2-14-1 phase showing strong (00 ℓ) lines and a weaker (105) line. Rocking curves measured on the (004) reflection typically have $\sim 5^\circ$ widths. On Mo(211), only the (00 ℓ) and (105) lines of the 2-14-1 phase appear, but with $\sim 10^\circ$ rocking curves. These x-ray results confirm the lack of epitaxial orientation observed by RHEED, but indicate a strong *c*-axis texture. Identification of the secondary phase in the (100) films is not conclusive given the low number of x-ray reflections, but the *d*-spacings are consistent with reflections from the 1-4-4 phase and tetragonal boron. A 5-unit-cell-thick film grown at 675 °C on Mo(100) showed no evidence for the 2-14-1 reflections, but had a peak close to the secondary phase. This shows that initially the secondary phase grows epitaxially, and after about 10 unit cell equivalents, 2-14-1 crystallites nucleate at the surface and grow until they dominate. It also suggests that the secondary phase is related to interdiffusion of the Mo buffer layer with the Nd, Fe and B reactants. Interestingly, Nd₂Fe₁₇ is not observed even if the system passes through the composition of this phase on the way to the 2-14-1 phase. In fact, as long as the Nd and Fe borides are avoided, the final phase composition appears to be relatively insensitive to the path taken through the phase diagram. This suggests that the

Figure 2. X-ray diffraction from 30 nm Nd₂Fe₁₄B films deposited on (211) [top] and (100) [bottom] Mo templates. In both cases a strong *c*-axis texture is apparent, but on Mo(100) a secondary phase is also present.

Figure 3. Perpendicular magnetization loops from a 30 nm Nd₂Fe₁₄B film. The kink at low field in the 20 K loop is associated with the secondary phase observed by x-ray diffraction.

formation of 2-14-1 is more exothermic than other phases of close composition.

Magnetization loops were measured for both perpendicular and in-plane applied fields, and are shown for a typical sample in Fig. 3. All the samples have strong perpendicular anisotropy and high coercivities (1-2 T at 20 K) in the perpendicular direction. The anisotropy field is ~ 6 T at 300 K and increases to >9 T at 20 K. A soft magnetic phase is also present, as seen from the magnetization kink at low field in both the perpendicular and in-plane loops. This soft phase is likely related to the additional phase identified in the x-ray diffraction data, however it exists in both the (211) and (100) films, while the additional phase is only apparent in the diffraction from the (100) films. The soft phase reduces the remanent magnetization to 60-70% of saturation.

The bulk spin-reorientation transition at a T_R value of 135 K, in which the easy axis switches from the c -axis to one canted toward the (110) direction, can be seen in Fig. 4. The data were taken on previously magnetized samples in a 10-Oe field. The zero in-plane moment above T_R shows the perpendicular anisotropy, while below T_R the in-plane moment is increasing at the expense of the perpendicular moment. By 20 K the canting angle is $\sim 40^\circ$, which is higher than has been observed in bulk single crystals[10]. Note that the sharp reduction in perpendicular moment near 300 K is the result of a

Figure 4. Spin-reorientation transition in a textured $\text{Nd}_2\text{Fe}_{14}\text{B}$ film. The dashed line shows the bulk reorientation temperature. The loss of $M_{||}$ above T_R indicates perpendicular anisotropy, while below T_R the magnetization is canted toward the film plane. At 40 K, the canting angle is $\sim 40^\circ$.

reduction in the remanence, and does not indicate a reduced Curie temperature.

AFM shows that the lateral grain size is ~ 200 nm, and that the rms roughness is ~ 14 nm in the high-temperature grown films. This shows that at the temperature required for 2-14-1 formation, there is also significant lateral diffusion, resulting in three-dimensional island growth. MFM indicates that the length scale for the domains in an unmagnetized sample is less than the island size, which is attributed to the formation of closure domains within the islands.

In conclusion, thin films of $\text{Nd}_2\text{Fe}_{14}\text{B}$ have been grown with a c -axis texture by MBE on $\text{MgO}(100)$ and (110) seeded with $\text{Mo}(100)$ and (211) , respectively, using high-temperature block-by-block deposition. The films are magnetically hard, with the easy axis perpendicular to the film plane, consistent with the observed c -axis texture. A secondary phase also exists in the films, which appears to be associated with the initial growth. The secondary phase is magnetically soft, and probably accounts for the low-field features in the magnetization loops.

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