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ABSTRACT

Thin films of $Nd_2Fe_{14}B$ with a *c*-axis orientation and bulk-like magnetic properties have been grown via molecular beam epitaxy with thicknesses as low as 300 Å. The films are grown on single-crystal MgO(100) wafers overcoated with epitaxial Mo(100) buffer layers. The 2-14-1 phase is crystallized either by sequential deposition or co-deposition of Fe, Nd, and B from pure elemental evaporation sources onto 600 - 700 °C substrates. The structure of each film was characterized in-situ with RHEED and ex-situ with x-ray diffraction. For the sequentially deposited films, the in-plane saturation field is 60 - 70 kOe at 300 K, consistent with the bulk anisotropy field of 73 kOe. The spin-reorientation transition at 135 K can also be clearly seen in the in-plane and out-of-plane magnetization vs. temperature data. The out-of-plane coercivities typically range from 15 - 20 kOe at 20 K, and 3 - 8 kOe at 300 K. Co-deposition results in a multiphase structure, with $Nd_2Fe_{14}B$ now the minority phase. The multiphase structure results in reduced perpendicular anisotropy.

Fabrication of permanent magnet materials in thin film form is of interest for the optimization of microstructural effects systematically through the ability to precisely control length scales. In particular, the multilayer geometry offers the possibility of introducing intergranular phases and grain boundaries in a controlled way. In addition, energy product enhancements through the exchange coupling of hard and soft magnetic phases have been predicted, and can also be studied in the multilayer geometry.[1,2] The compound $Nd_2Fe_{14}B$, as the permanent magnet with the current highest energy product, is appealing for use as the hard magnet component in such structures. However, for this purpose it is necessary to stabilize the permanent magnet phase in film thicknesses of only 100 - 500 Å, epitaxially or at least with a strong texture, and with hard magnetic properties. Previously, single phase films of $Nd_2Fe_{14}B$ have been grown by sputter deposition in the 5 - 10 kÅ thickness range.[3-6] In this article, we report on the growth of $Nd_2Fe_{14}B$ films as thin as 300 Å with a strongly preferred *c*-axis orientation and high coercivity.

The films are grown by molecular beam epitaxy (MBE) from three separate Nd, Fe and B sources, allowing precise control of the composition. Nd and B are evaporated by e-beam heating, and Fe is evaporated from a Knudsen cell. Typically, an MgO(100) wafer with an epitaxial Mo(100) buffer layer deposited *in situ* is used as a substrate, owing to the good lattice match between the $Nd_2Fe_{14}B$ basal plane (4.4 Å along the *a* and *b* axes) and Mo(100) (4.45 Å along the face diagonals). Two approaches to the formation of the 2-14-1 phase were applied: (i) co-deposition and (ii) sequential deposition of Nd, Fe, and B. In both cases, the substrate was held at 600-700 °C to allow sufficient thermal diffusion to crystallize the film. Lower temperatures typically resulted in the absence of crystalline x-ray peaks due to the formation of an amorphous phase. Subsequent annealing of this phase also did not produce the 2-14-1 phase. The Nd:Fe ratio is also varied to compensate for re-evaporation of Nd during deposition. Typically, it is necessary to evaporate approximately twice the stoichiometric amount of Nd to obtain the desired 7:1 Fe:Nd ratio. In co-deposition, the atomic flux from each source is tuned for the desired film composition

while the sample is exposed to all three sources simultaneously. In sequential deposition, also known as block-by-block deposition, single layers consisting of stoichiometric amounts of each reactant are deposited and allowed to interdiffuse.[7] These layers, or "blocks", may be equivalent to anywhere from 1/2 to several unit cells of coverage. Typically, this process is repeated the required number of times to obtain a thickness of 300 - 500 Å. The ordering of the constituents defines a path through the Nd-Fe-B phase diagram, and so plays a crucial role in determining the final phase formation. By selecting the proper ordering, undesired phases such as the binary Fe and Nd borides can be avoided.

The films were characterized structurally both by reflection high energy electron diffraction (RHEED) and *ex-situ* x-ray diffraction, and magnetically in an extraction magnetometer with a maximum applied field of 9 T. The Fe:Nd ratio was determined by scanning electron microscopy with energy dispersive x-ray analysis, and the composition of select samples was verified by atomic emission spectroscopy. Typical x-ray diffraction data from a co-deposited film and a block-by-block deposited film are shown in Fig. 1. The co-deposited film (Fig. 1a) shows evidence for *c*-axis oriented $Nd_2Fe_{14}B$, as seen from the (00*l*) peaks indicated, with at least one other phase present (indicated by arrows in Fig 1a) which has not been definitively identified. High Nd:Fe ratios result in more intense x-ray peaks from this phase, while less Nd results in α-Fe, suggesting that the second phase is Nd-rich, possibly a binary Fe-Nd compound. In the sequentially deposited samples, several different paths through the Nd-Fe-B phase diagram were taken to determine the best path for 2-14-1 phase formation. The best results were obtained with each block representing 1/2 unit cell, and with the path chosen to avoid the very stable binary borides. These block-by-block depositions resulted in improved phase purity and *c*-axis orientation over the co-deposited films (e.g., see Fig. 1b). In this case we see only (00*l*) and (105) lines, with a minority second phase and no α-Fe. Rocking curve widths from the (004) line are typically ~5°. RHEED patterns were monitored during growth, and

indicate that the initial growth in block-by-block deposition is crystalline, but with a rough surface. After 8-12 unit cells have been deposited, polycrystalline growth is observed. This suggests that the second phase may be associated with the initial growth. A 5-unit-cell-thick film was grown to test this idea, and showed no evidence for 2-14-1 diffraction peaks, while still showing a peak close to the second phase. This leads to the conclusion that the initial growth is epitaxial, but is not the 2-14-1 phase. After about 10 unit cells have been deposited, 2-14-1 nucleates and then dominates the growth. In co-deposition, the loss of single crystalline order occurs sooner (after 1-4 unit cells), but the poor phase purity indicates that the polycrystalline overgrowth is probably not only the 2-14-1 phase.

Magnetic hysteresis loops were measured for both in-plane and out-of-plane magnetization in fields up to 9 T. Figure 2 shows these loops taken at room temperature for a 500 Å thick block-by-block deposited sample. In all the block-by-block samples, the easy axis is perpendicular to the film plane, as expected for *c*-axis oriented $Nd_2Fe_{14}B$. The coercivities in the perpendicular loops are typically 0.3 - 0.8 T at 300 K and 1 - 2 T at 20 K. The field required to saturate the magnetization in-plane is ~7 - 8 T at 300 K and > 9 T at 20 K. These coercivity and anisotropy values are observed in films as thin as 300 Å. The corresponding values for the bulk anisotropy field are 7.3 T at 300 K[8] and 17 T at 4.2 K[9], which shows that the block-by-block deposition process yields bulk-like properties even in 300 Å-thick films.

As noted in Fig. 1, co-deposition resulted in degraded phase purity and less *c*-axis texturing. Not surprisingly, the perpendicular anisotropy is also reduced, with the in-plane loops being nearly identical to the out-of-plane loops in some cases. However, the coercivity of the co-deposited films can be higher than that of the block-by-block films. To illustrate this, Fig. 3 shows 20 K loops taken from two ~500-Å films grown by sequential and co-deposition. The co-deposited film (solid line) has a 3.1 T coercivity, which is the highest of any of the MBE grown films in this series, while the 2 T coercivity of the block-by-block film (dashed line) represents the highest value obtained by this deposition

process. This suggests that because the co-deposited films are poorer structurally, additional grain boundaries and intergranular phases provide more pinning sites for domain wall motion. It is perhaps not surprising that the better quality films have low coercivities since $Nd_2Fe_{14}B$ single crystals, which have no grain boundaries to provide pinning sites, typically have room temperature coercivity values two orders of magnitude lower than those of bulk powders.

A further indication of bulk-like properties is seen in the spin-reorientation transition observed at 140 K in the in-plane and out-of-plane remanent magnetization vs. temperature behavior for the block-by-block samples. Figure 4 shows the canting angle (Θ) vs. T obtained from these measurements. The temperature scans were taken by saturating the sample at room temperature in a 9 T field, then cooling to 20 K, reducing the field to 10 Oe, then warming while measuring the magnetic moment. The abrupt increase in Θ at 135 K indicates the spin reorientation transition, in which the easy axis switches from the <001> direction to canted toward the <011> directions. The transition temperature is identical to the bulk value, however the maximum canting angle measured from the thin films (~40°) can exceed the bulk value of ~30°, which is attributed to the additional effect of the demagnetizing field in the thin film geometry. As with the other bulk-like properties, the spin-reorientation transition is observed down to a thickness of 300 Å.

To summarize, thin films of $Nd_2Fe_{14}B$ with a strong *c*-axis texture have been grown by MBE. The films are deposited either by co-deposition or by block-by-block deposition from elemental Nd, Fe, and B sources. Better phase purity and a higher degree of *c*-axis orientation are obtained via the block-by-block deposition method. With this approach, the 2-14-1 phase can be stabilized in films as thin as 300 Å. Such films also display magnetic properties that are nearly identical to bulk $Nd_2Fe_{14}B$, as evidenced by the strong uniaxial anisotropy and the spin reorientation transition observed at 135 K. In addition, the films also have high coercivity. Since the thicknesses of these hard magnet

films are similar to the length scales involved in optimal hard magnet microstructures, the block-by-block growth technique offers promise for the fabrication and systematic study of tailored microstructures.

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Figure Captions:

Figure 1. X-ray diffraction data taken from $Nd_2Fe_{14}B$ films prepared by (a) co-deposition and (b) block-by-block deposition. Lines associated with the 2-14-1 phase are indexed, and arrows indicate minority phases.

Figure 2. Room temperature magnetic hysteresis loops of a $Nd_2Fe_{14}B$ film grown by block-by-block deposition. The in-plane and out-of-plane loops show the bulk-like (~7 T) anisotropy field.

Figure 3. Comparison of magnetic properties for ~500 Å films prepared by co-deposition and block-by-block deposition. Although the block-by-block films are generally of higher quality, the coercivity is often lower, as shown in this data taken at 20 K. This is consistent with results from single crystals which show low coercivities.

Figure 4. Magnetization canting angle (Θ) with respect to the film normal vs. temperature, showing the bulk spin-reorientation transition at 135 K. The film thickness in this case is ~500 Å.

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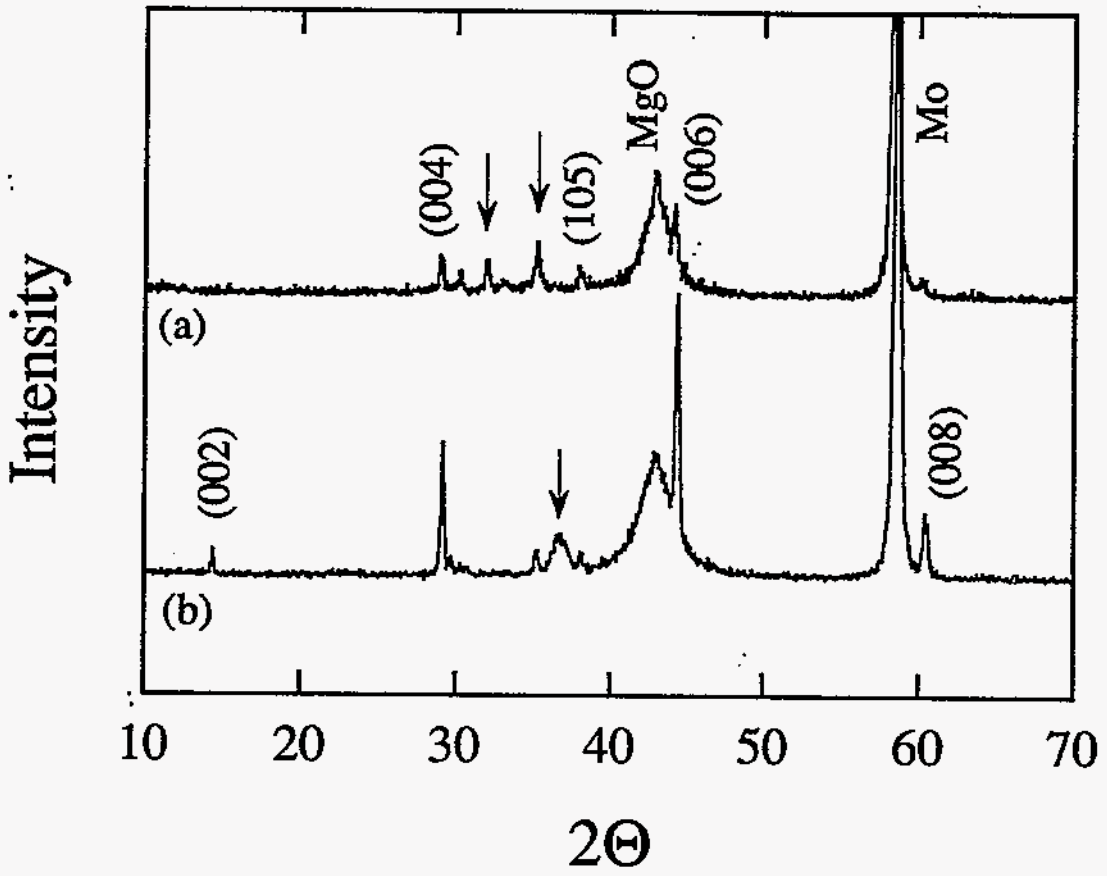

Fig 1

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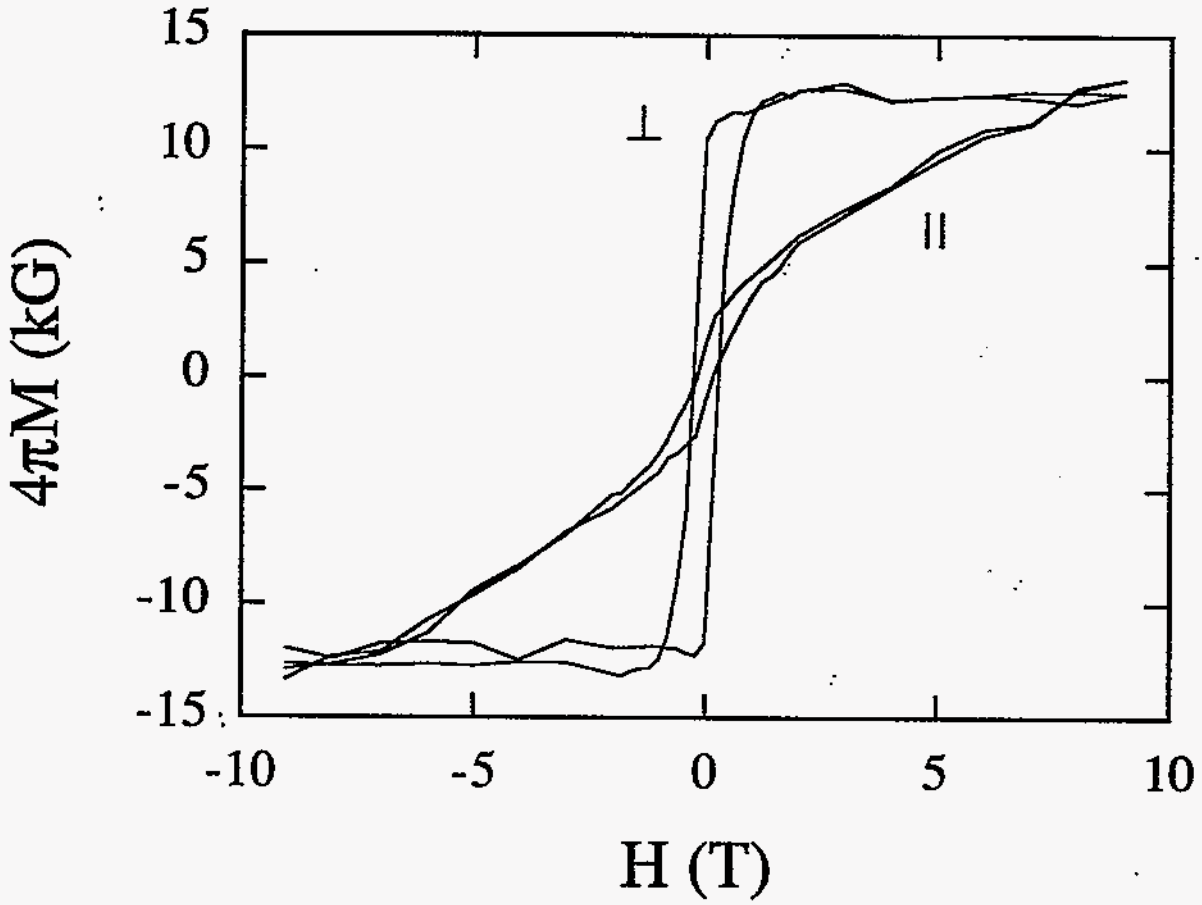

Fig 2

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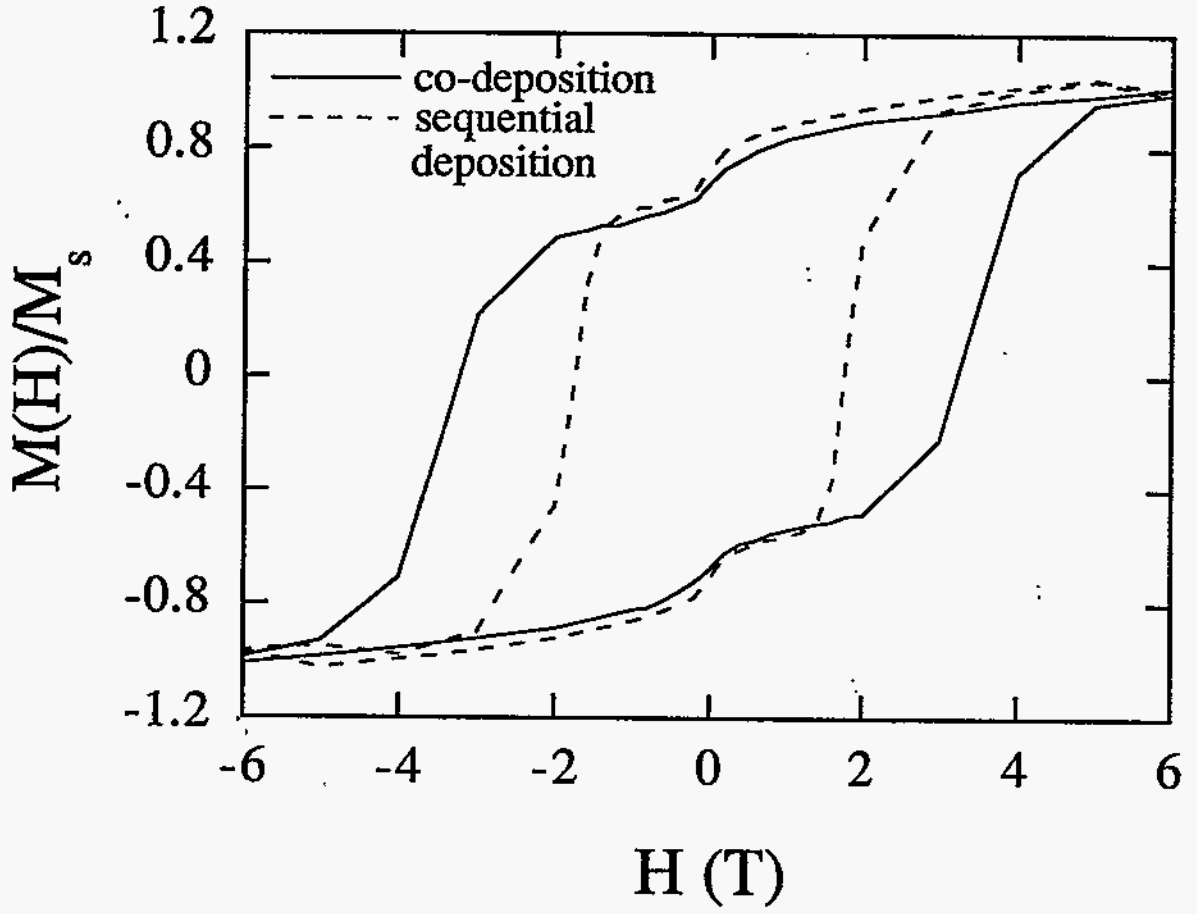
1.2
0.8
0.4
0
-0.4
-0.8
-1.2
-6
-4
-2
0
2
4
6
co-deposition
sequential
deposition
M(H)/M_s
H (T)

Fig. 3

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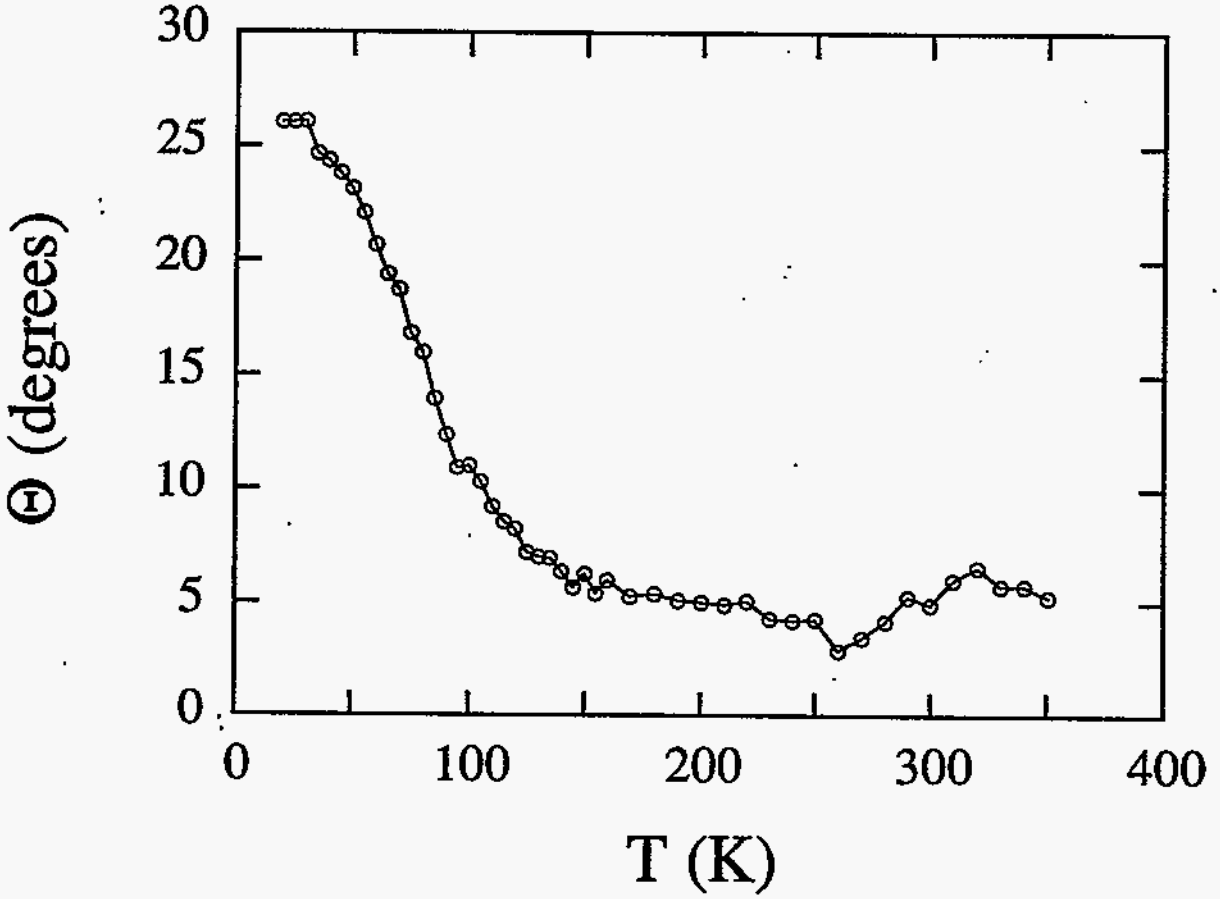

Fig 4

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