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Study of the Long-Range Exchange Coupling in Nd-Fe-B/Ti/Fe Multilayered Structure

Saeed Yazdani *, Jared Phillips, Aaron Mosey, Thomas Bsaibes, Ricardo Decca and Ruihua Cheng *

Department of Physics, Indiana University-Purdue University Indianapolis, Indianapolis, IN 46202, USA; japphill@iu.edu (J.P.); aaronmosey@protonmail.com (A.M.); tbsaibes@iupui.edu (T.B.); rdecca@iupui.edu (R.D.) * Correspondence: syazdani@iupui.edu (S.Y.); rucheng@iupui.edu (R.C.)

Abstract: The exchange coupling between two ferromagnetic thin films, one with magnetically hard and the other with soft phases, separated by a thin non-magnetic layer, is studied. Nd-Fe-B/Ti/Fe thin film heterostructures were fabricated using DC magnetron sputtering on Si substrates, which were heated in situ at 650 °C using a house-built vacuum-compatible heater. The effect of the thickness of the Ti buffer layer and the annealing temperature on the formation of various phases of Nd-Fe-B was investigated. The effect of the thickness of the non-magnetic Ti spacer layer on the exchange coupling strength between the hard phase Nd-Fe-B ferromagnetic thin layer and the soft phase transition metal Fe layer was experimentally investigated. Hysteresis loops of multilayer thin films indicate an antiferromagnetic coupling was observed when the thickness of the spacer layer was 2 nm. This is within the range of an antiferromagnetic coupling calculation based on RKKY theory predictions.

Keywords: exchange coupling; thin films; RKKY interaction; antiferromagnetic coupling

1. Introduction

Although the interactions between two ferromagnetic (FM) thin films separated by a non-magnetic metallic spacer layer were a point of interest in the last two decades, they are still receiving notable consideration due to their potential applications [1–8]. The interplay of magnetic ordering and exchange coupling continues to play a significant role in technological advancements. The investigation of long-range exchange coupling in heterogeneous structures, such as transition metal/rare earth compounds, continues to attract the attention of scientists due to the potential to harvest antiferromagnetic (AFM) ordering via the RKKY interaction [9–17]. The orbital contribution to the total magnetic moment from rare earth metal and the oscillating nature of the long-range exchange interaction provide a great avenue to engineer a structure that exhibits no net magnetic moment while possessing a spin polarization. This would effectively separate the spin degree of freedom from net magnetization and allow us to explore the hypothetical spin–spin and spin–mass interactions. These interactions are due to as yet unobserved force mediating bosons, which result in Yukawa-like potentials and are possible dark matter candidates [18–21]. This provides an interesting platform for spintronic applications.

Among other consequences, the exchange interaction is responsible for the FM and AFM phases of the compound matter [22–25]. Multilayered structure oscillatory exchange-coupling across a non-magnetic spacer layer can be used to engineer synthetic magnetic structures. A magnetic multilayer structure consists of a sequence of different thin films growing on top of each other. Thin films of FM material are separated from each other by a non-magnetic material (spacer layer). A non-magnetic layer with a small thickness plays a crucial role in the FM and AFM coupling between two magnetic thin films [26–30]. The magnetizations of the FM layers separated by the non-magnetic spacer layers are coupled by the electrons in the spacer layers. To create a multilayer structure with nonzero spin and zero magnetization, here we explore the multilayer system composed of a transition
metal FM layer and a rare earth FM layer with AFM alignment between two layers. The Nd-Fe-B-based thin films were widely investigated in both industry and research labs due to their applications in nanomagnetic devices, nanomechanical devices, and magnetic recording media [31–36]. Crystalline phases of Nd-Fe-B show distinctive characteristics such as magnetization and coercivity. To take advantage of these notable features, it is essential to optimize the nano-crystallization of the deposited amorphous films. So far, various approaches were utilized to prepare high-quality Nd-Fe-B thin films [37–42]. In the case of magnetron sputtering fabrication, several preparation parameters, such as the pressure in the chamber, deposition temperature, post-deposition treatment, target composition, substrate material, and thickness of the buffer layer, can significantly affect the structure of the films and their final magnetic properties. Achieving a well-crystalized magnetic hard phase Nd-Fe-B thin film is crucial to the development of a structure with spin-polarized mass with zero magnetization. In this study, we reported the crystallographic characterization of Nd-Fe-B thin films prepared under different parameters, as well as the magnetic properties of both single-layer Nd-Fe-B and multilayered structure Nd-Fe-B/Ti/Fe. The optimized parameters, including the effect of the thickness of a Ti buffer layer, the annealing temperature on the formation of the Nd_{2}Fe_{14}B crystalline phase for a magnetic hard Nd-Fe-B layer, and the magnetic exchange coupling interaction followed by calculation from RKKY theory, are investigated.

2. Materials and Methods

The process of creating the multilayered structures with a well-defined interface for our study evolved into an investigation of the optimal approach for thin film growth. To achieve precise film thickness, the growth rate of each thin film, either in the single-layer or the multilayered structure, was precisely calibrated using three different methods. Initially, an in situ single-crystalline thickness monitor was used to directly measure the growth rate of each sputtering target. Then, with the same parameters, test samples for each single sputtering target were created before the thickness was precisely measured using both an Atomic Force Microscope (AFM) and a profilometer independently. To calibrate the growth rate of different targets using a profilometer and AFM, we carefully prepared samples with various thicknesses (above 100 nm) when the growth conditions were stable. A shutter in the growth chamber was also used to precisely control the deposition time. After measuring the growth rate of relatively thick samples using AFM and a profilometer, we prepared very thin samples with proportionate growth time to achieve the desirable thickness. Eventually, we confirmed thickness measurements for the thin samples with AFM, and these measurements were in agreement with the thickness calibration obtained from the profilometer on the relatively thick samples. We calibrated all targets, including Nd-Fe-B, Fe, and T. Specifically for the Ti target, we measured two distinct slow and relatively fast growth rates for ultra-thin films (0–5 nm) and thin films (>5 nm), respectively. A slower deposition rate guarantees a more uniform film with significantly fewer pinholes for ultra-thin films. Basically, the deposition rate depends on the unique physical conditions of each HV chamber, as well as the introduced Ar gas pressure and the power supply. In our system, we found the growth rate for Nd-Fe-B to be 0.104 nm/s with an Ar gas pressure of 4 MTorr and a power supply of 30 W, and the growth rate of Fe target to be 0.088 nm/s under the same pressure and power. For the Ti target, a relatively fast growth rate of 0.225 nm/s is achieved with a 16 MTorr Ar gas pressure and 30 W power, while a slow growth rate of 0.016 nm/s is obtained with a 4 MTorr Ar gas pressure and 30 W power.

In order to prepare high-quality crystalized Nd-Fe-B thin films, a vacuum heater was designed and developed using vacuum-compatible ceramic materials. The heater enabled us to fabricate thin films at temperatures up to 700 °C during sputtering. Heating the sample during deposition leads to a better interface for multilayer structure compared to post-annealing outside of the deposition chamber. Moreover, post-annealing of all layers leads to diffusion between layers and dramatically influences the quality of the multilayered structure. In our design, various parameters were considered to achieve a
stable high temperature with minimum fluctuations during heating inside the vacuum chamber. Two parallel 2" × 2" machinable zirconia ceramic plates, attached with connection parts, form a box-like shape. To improve efficiency, two parallel tungsten filaments were used, and a Molybdenum plate was utilized as a sample holder due to its high thermal conductivity, as shown in Figure 1a. The filaments were mounted next to the 1.25" × 1.25” Molybdenum sample holder and welded to the negative and positive poles using tantalum foil. The temperature remained stable throughout the deposition and was continuously monitored with a thermocouple connected to the sample holder. The power of the heater depends on the parameters of the filament, such as length, cross-section area, and the purity of the tungsten used. With optimal parameters, such as two parallel 11 cm tungsten (99.9% purity) filament wires with a cross-section of 0.025 mm², the maximum power of the heater is around 700 W with a maximum voltage of 20 volts provided by the accessible power supply. Furthermore, to increase the efficiency of the heater, a ceramic shielding box covered by reflective tantalum foil was installed. This configuration enhances the reflection of photons from the walls of the heater to the sample holder, therefore leading to high heating efficiency. Our experiments showed that the ceramic box increased the efficiency of the heater by about 25%. Furthermore, the shielding box prevents photons and hot electrons from emitting everywhere in the chamber, resulting in better control of the stability of the temperature and the pressure of the chamber during the deposition.

In a high vacuum environment with the base pressure of 7 × 10⁻⁷ Torr, several Nd-Fe-B monolayer structures with a thickness of 300 nm were created using a sputtering target with the composition of Nd₂₀Fe₆₄B₁₆ (Figure 1b). All the samples were deposited on single-crystal silicon substrates while they were annealed in situ at different temperatures (600 °C and 650 °C). Annealing continued for 20 more minutes after finishing deposition to create a homogeneous crystalline of Nd₂Fe₁₄B phases. Finally, after cooling down, a 20 nm Ti layer was added to prevent oxidation for subsequent characterization. The effect of Ti buffer layer thickness on the crystalline formation of Nd₂Fe₁₄B was also investigated.

Magnetic coupling between two ferromagnets, a soft phase Fe and a hard phase Nd-Fe-B primarily in the Nd₂Fe₁₄B phase, was systematically studied using a house-developed vibrating sample magnetometer (VSM) [43], and the crystalline structure was investigated using 1-D X-ray diffraction (XRD, Bruker AXS D8 Discover A25, Karlsruhe, Germany). The details of the in-house developed VSM can be found elsewhere [43]. All samples were grown via DC magnetron sputtering in a high vacuum environment. All three targets, Nd₂₀Fe₆₄B₁₆, iron (Fe), and titanium (Ti) targets were installed in the same sputtering chamber, which facilitated the in situ growth of the entire structure, intended to minimize oxidation. For the exchange interaction study, multilayered structures which are shown in Figure 1c, with different thicknesses of the Ti spacer layer were fabricated. A total of

Figure 1. Schematic image of (a) lab-built vacuum-compatible heater, (b) single-layer Nd-Fe-B (300 nm) thin films with various Ti buffer layer thicknesses, and (c) multilayer Nd-Fe-B/Ti/Fe thin films with various Ti spacer layer thicknesses.
300 nm of Nd$_2$Fe$_{14}$B was sputtered onto a silicon substrate with a 15 nm Ti buffer layer and annealed at 650 °C from the results of single-layer Nd-Fe-B thin film studies, followed by a Ti spacer layer of X (0–5) nm thickness, and a 270 nm Fe layer, which will be presented in the results section. A thin Ti capping layer (20 nm) was added to avoid oxidation. The growth ratios for all three targets of Ti, Fe, and Nd-Fe-B were calibrated while the introduced pressure of Ar gas was fixed on 4 mTorr. However, for the Ti layer used as a spacer layer, the deposition growth rate was a relatively smaller number (1 nm/min) to achieve a more uniform film without a pinhole. In situ annealing processing was performed based on the results from single-layer test samples. Samples were then cool cooled down at the rate of 3 °C/min until room temperature. The next day, Ti spacer layer, Fe layer, and Ti capping layer sputtered at room temperature. Fabrication of the thickness of each FM layer of multilayered structure to achieve a zero magnetization while possessing net spin and while FM layers interact with each other completely antiferromagnetically from RKKY theory is calculated in the Supplementary Materials.

3. Results and Discussion

Various phases of single-layer Nd-Fe-B thin film fabricated with different thicknesses of the Ti buffer layer and annealed in situ at different temperatures are studied using XRD. As shown in Figure 2, the marked points indicate the XRD peaks corresponding to the tetragonal Nd$_2$Fe$_{14}$B phase. The XRD data indicate that the structure of the thin films depends upon the in situ annealing temperature and the buffer layer thickness. Nano-crystalline Nd$_2$Fe$_{14}$B formation does not occur at temperatures below 600 °C. It is known that an amorphous SiO$_2$ layer with a thickness below 30 nm can form on the Si surface. If the Nd-Fe-B film is directly deposited on the bare Si substrate, the Nd atoms will react with the SiO$_2$ layer at high temperatures, which can lead to defects in the Nd$_2$Fe$_{14}$B phase formation.

![Figure 2](image-url)

Figure 2. XRD analysis of single-layer SiO$_2$/X nm Ti/300 nm Nd-Fe-B/20 nm Ti annealed in situ at various temperatures.

Based on the XRD data of samples fabricated with different buffer layers at 600 °C and 650 °C, more crystalline phases of Nd$_2$Fe$_{14}$B formed when the thickness of the buffer layer is 15 nm. The sample with a 30 nm Ti buffer layer and annealed in situ at 600 °C exhibits only (410) peak of Nd$_2$Fe$_{14}$B at around a 2-theta value of 43°. A sample with the same Ti buffer layer thickness annealed at 650 °C does not show an obvious Nd$_2$Fe$_{14}$B peak. However, an Fe peak with high intensity suggests that Fe atoms were not coupled with rare earth Nd and B atoms to form Nd$_2$Fe$_{14}$B crystalline phase. Samples created with a 15 nm Ti and annealed in situ at 650 °C showed the most crystalline phase of Nd$_2$Fe$_{14}$B. A proper thickness of the buffer layer can reduce the roughness of the film and protect the thin film from oxidization. An excessively thick buffer layer leads to high surface roughness. The optimal buffer layer thickness is determined to be 15 nm.
Magnetic data of Nd-Fe-B thin films was measured using a VSM for samples annealed at different temperatures and fabricated with different thicknesses of the Ti buffer layer (Figure 3). The VSM data for samples annealed in situ at 600 °C and 650 °C indicate that those with a 15 nm Ti buffer layer exhibit noticeable magnetic remanence and a relatively large coercivity field. All the samples were measured with the magnetic field applied in the plane, with the data indicating an in-plane magnetic easy axis. In the single-layer Nd-Fe-B thin film, the coercivity for the sample annealed at 650 °C and with a 15 nm Ti buffer layer is the highest among samples, which is very consistent with XRD data. Figure 3c,f shows that if a thick Ti buffer layer is annealed in situ at a high temperature of 600 °C and 650 °C respectively, it can cause diffusion between layers. This diffusion may cause FM grains to be separated by Ti grains, and the magnetic coupling could occur between those FM grains, resulting in a low coercivity/remanence. Magnetic measurements confirm a larger coercivity, and consequently, a magnetic hard phase FM was achieved when the tetragonal crystalline structure of Nd$_2$Fe$_{14}$B formed, as verified in the XRD spectra.

![Figure 3. Hysteresis loop of single-layer Nd-Fe-B thin film annealed in situ at 600 °C with Ti buffer layer (a) 0 nm, (b) 15 nm, and (c) 30 nm and thin films annealed in situ at 650 °C with Ti buffer layer (d) 0 nm, (e) 15 nm, and (f) 30 nm.](image-url)

The magnetic properties of the multilayer films are extremely sensitive to the thickness of the spacer layer Ti. The VSM data are shown in Figure 4 for (Si/15 nm Ti/Nd-Fe-B (300 nm)/Ti (x nm)/Fe (270 nm)/Ti (20 nm)) thin films with various Ti spacer layer thickness. Figure 4 demonstrates that the hysteresis loops have a strong dependence upon the thickness of the Ti layer. At 0 to 1 nm thicknesses, both Fe and Nd-Fe-B layers switch at the same field, and the two layers are strongly FM coupled. As the thickness of the Ti layer goes to 1.5 nm, Fe, the magnetically soft layer, and Nd-Fe-B, the magnetically hard layer, switch at a relatively smaller field, indicating a weak AFM coupling. Here, a kink as a sign of weak AFM coupling was noticed. For a 2 nm Ti thickness, the magnetic hysteresis loop exhibits a stepwise switching field, and it corresponds to antiparallel alignment, a harsh kink in the hysteresis loop indicating a strong AFM coupling between soft and hard thin film. The 2 nm spacer layer is in the range of values predicted by the RKKY exchange coupling theoretical calculation. When the thickness of the spacer layer was more than 2 nm, FM layers coupled ferromagnetically again due to the periodic oscillation of RKKY interaction. The kink was mild when the Ti spacer layer thickness was 3 nm and smoother when the Ti thickness increased to 5 nm.
In this study, an engineered multilayered thin film structure was fabricated using a vacuum-compatible heater. The magnetic properties of the multilayer films are extremely sensitive to the thickness of the spacer layer. Figure 5a,b show the remanence and coercivity of multilayer thin films as a function of Ti spacer layer thickness. The overall range of the coercivity of the multilayer films is between 51.5 Oe (corresponding to the sample with a 2 nm spacer layer) and 218 Oe (corresponding to the sample with a 5 nm spacer layer). This coercivity field range is significantly smaller than 700 Oe, the coercive field of a single-layer Nd-Fe-B thin film fabricated on a 15 nm buffer layer and annealed in situ at 650 °C. This observation emphasizes that a strong magnetic coupling between multilayer samples has occurred. In other words, the electrons in the Nd-Fe-B film of the multilayer structure cannot preserve the single-layer properties, and they exhibit interactions with the magnetic soft Fe layer. For the film made with a 5 nm spacer layer, since the Fe moment very weakly interacted with the Nd-Fe-B layer and rotated more easily in the presence of the external magnetic field, the Fe layer did not completely interact with the Nd-Fe-B layer and did not lead to a rotation of the moments in the Nd-Fe-B layer, so the coercivity of the film was larger relatively due to its higher dependence on the Nd-Fe-B layer. The RKKY model considers that when localized magnetic moments interact, they are mediated by a conducting electron. Dynamic calculations between localized magnetic moments of the Ti spacer layer are shown in Figure 5c, indicating that the maximum AFM interaction strength occurs when the thickness of the spacer layer is around 2 nm, which is verified experimentally [44].

Figure 4. Hysteresis loop of multilayer (Si/15 nm, Ti/300 nm, Nd-Fe-B/X nm, Ti/270 nm, Fe/20 nm) thin films with (a) 0 nm, (b) 1 nm, (c) 1.5 nm, (d) 2 nm, (e) 3 nm, and (f) 5 nm Ti spacer layer thickness.

Figure 5. (a) The remanence and (b) the coercivity of multilayered structure vs. Ti spacer Layer thickness. (c) Interaction strength of exchange coupling for Ti non-magnet metals used as a spacer layer between FM thin films.
Moreover, although these results were obtained for a simplified model where local spins were considered, it perfectly agrees with the RKKY interaction strength for 2D and 3D systems and thin films, which predicts a ferroelectric interaction would result when the thickness of the spacer layer is between 1 nm to 2 nm [45]. Our calculation results, shown in Figure 5c, indicate that for the multilayered structure we used experimentally, the maximum AFM interaction occurs when the thickness of the Ti spacer layer is between 1.3 and 2.2 nm. While the experimental results for the thickness of the Ti spacer layer below 3 nm are fairly in agreement with the results predicted by simulations, both the collected experimental data and simulations predict that an AFM coupling between soft and hard FM exits for spacer layers is around 1.5–2 nm.

4. Conclusions

In this study, an engineered multilayered thin film structure with AFM ordering between two magnetic layers could potentially lead to a net spin moment with negligible magnetization. The magnetization of the FM layers, separated by spacer layers, is indirectly coupled by electrons in the spacer layer based on RKKY theory. The crystalline properties of the structure are characterized using XRD, and the magnetic properties are studied using a VSM. The data indicate that when the thickness of the spacer layer is around 2 nm, the magnetic coupling switches from FM coupling to AFM coupling, which agrees with simulations and other experimental works [44]. Magnetic measurements along the easy axis direction indicate that when the thickness of the Ti spacer layer was around 2 nm, a kink was evidenced in the hysteresis loop, implying an AFM coupling between a soft Fe film and a magnetically hard Nd-Fe-B thin film. Periodic switching from an FM coupling to an AFM coupled layer as a function of the thickness of a non-magnet spacer layer opens up new windows for eliminating magnetization while the multilayer structure possesses mass and pure spin for use in spin–mass Yukawa-like potential studies.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/cryst14020119/s1, The calculations of thicknesses of soft and hard FM layers in the multilayered structure to achieve zero net magnetization and uncompensated pure spin are included in the supplementary file. The actual image of the vacuum-compatible heater are also provided in the supplementary file. Figure S1. Actual image of lab-built vacuum-compatible heater.

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