MAGNETIC CHARACTERISTICS OF THE MANGANESE-/IRON-PHTHALOCYANINE INTERFACE

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ABSTRACT

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The magnetic properties of metallo-organic heterostructure interfaces are studied. These heterostructures are built with manganese phthalocyanine (MnPc) and iron phthalocyanine (FePc). Previously, the powder of each material is reported to be an Ising-like chain magnet with Arrhenius relaxation. The relaxation is slow enough to exhibit magnetic hysteresis at low temperatures. Each layer of the heterostructure is investigated separately by depositing a thin film of either iron phthalocyanine (FePc) or manganese phthalocyanine (MnPc) on a Silicon substrate heated to $150\,°C$. FePc thin films show magnetic hysteresis below $5\,K$ with a typical coercivity of $1850 \pm 50\,Oe$ and moment of about $2.2\,\mu_B$ in agreement with values from the literature. Similarly, the MnPc thin film deposited at $150\,°C$ shows magnetic hysteresis at $2.5\,K$, and no hysteresis at $5\,K$ and $10\,K$. A coercive field of $390\,Oe$ is recorded at $2.5\,K$. The saturation magnetization is near $9\,emu\,cm^{-3}$, which corresponds to an effective magnetic moment per Mn ion of about $0.6\,\mu_B$. For the MnPc/FePc thin film bilayer, the FePc is deposited at $150\,°C$ onto the Silicon substrate, the sample is cooled to room temperature followed by the MnPc deposition in situ. The magnetic moment of this heterostructure is consistent with contributions from the FePc layer only, since the room temperature deposited MnPc has antiferromagnetic characteristics. This heterostructure has magnetic hysteresis with a coercivity of $910\,Oe$. No measurable shift of the hysteresis loops - as expected for an antiferromagnetic-ferromagnetic coupled interface - is observed in this set of bilayers.

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CHAPTER 1

INTRODUCTION

Exchange bias refers to the magnetic coupling phenomenon at the interface of ferromagnetic and antiferromagnetic material. The presence of the exchange bias is apparent in the shift of the ferromagnetic hysteresis loop along the magnetic field axis. This effect is being used to pin magnetic layers, which are essential to storage media, sensors, and magnetic random access memory(MRAM) [1]. It is included in giant magnetoresistance devices for reading head in hard disks. So far, most of the research has focused on non-organic based heterostructures. In this thesis we want to investigate heterostructures based on metallo-organic molecules, the ferromagnetic/antiferromagnetic interface interaction of organic/organic iron-/manganese-phthalocyanine (FePc/MnPc). We compare this heterostructure with FePc thin film, FePc/metal-free phthalocyanine (H_2Pc) and MnPc/Co heterostructures, Figure 1. Interest in this is confirmed by recent studies on inorganic/organic based heterostructures such as manganese-phthalocyanine/europium oxide [2] and manganese-phthalocyanine/cobalt [3].

Metallo-phthalocyanines (MPcs) are small molecules that have been studied over decades due to their electronic and optical properties. Their properties can be modified chemically. Changing the metal ion results in electronic structure changes. We can also use the shape anisotropy to modify the properties of phthalocyanines.

Phthalocyanine and Metallo-Phthalocyanine

Phthalocyanine is a synthesized small molecule which is structurally related to the porphyrins. Barrett *et al.* [4] investigated the relation between the phthalocyanine and porphyrins ring. Phthalocyanine is a Greek word which consists of two parts, naphtha (rock oil) and cyanine (blue). Phthalocyanines are used commercially as blue and green pigments, where the color arises due to intense absorption in the visible region. It also has

Single Thin Film

Bilayer

FIGURE 1. Comparison of schematic of samples. In this thesis we investigate the ferromagnetic/antiferromagnetic interface interaction of metallo-organic heterostuctures, FePc/MnPc, and compare them with FePc and MnPc single thin film, FePc/H_2Pc and MnPc/Co bilayers.

a variety of applications into optical data storage (computer recordable DVDs) [5, 6], photoelectrochemical cells [7], gas sensor [8], photovoltaics, and as field-effect transistors. Phthalocyanine as an organic molecule was first synthesized accidentally by Braun and Tscherniac in 1907 during heating phthalimide [9]. Later in 1934, Linstead and Lowe [10] clarified the molecular structure of the metal free phthalocyanine. Phthalocyanines contain fourfold isoindole-centred phthalocyanato ligand in a symmetrical planar 18 π-electron aromatic macrocycle and the center cavity. The ligand can accept 70 different elemental ions in its central cavity, almost any metal from periodic table, and some metalloids, Figure 2.

A phthalocyanine molecule with a metal ion is referred to as metallo-phthalocyanine (MPc) [11]. A large variety of MPcs have been synthesized [10, 12, 13]. The first MPc was synthesized in 1927 [14]. The choice of central metal ion can strongly affect its physical properties.

Electron transfer abilities and electrochemical mechanism in an organic solvent were studied with electrochemical measurements of some phthalocyanine derivative [11]. By introducing appropriate substitutes onto the ring system low solubility in common organic solvents can be overcome. Their result showed that synthesized phthalocyanine having

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S-aryl groups at non-peripheral position have high solubility in organic solvents, has no absorption in the visible region, and exhibits high heat resistance.

Metallo-phthalocyanines as a model of small-molecule group of organic semiconductor are archetypal. They are very suitable to be grown as thin films. The packing of molecules is herringbone in the most common crystalline arrangement of MPc. When the flat molecules are face to face, molecule-molecule interaction is at its highest. This leads to columnar stacking, with the metal atoms forming one-dimensional chains. In MPc bulk and thin films, the central metal atoms form one-dimensional (1D) linear chains by columnar stacking, which are tilted by an angle with respect to the b axis. The different angles and relative positions of the chains give rise to different polymorphs. A variety of MPc crystal structures had been presented in the literature with a variety of packing motifs, and inter-molecular spacing [15]. The α and β forms are the most common phases. The magnetic properties of the MPcs depend on both the central metal-ion and the molecular ligands, and also depend on electronic ground state of the central metal atom. They are strongly dependent on stacking structural differences, which relate to the electronic ground state of the metal atom. The β-phase, which can be found in bulk crystals, is a stable phase and the angle with respect to the b axis is $\theta \sim 45°$. The β-phase can be gained by sublimation techniques or annealing the α-phase to $300\,°C$ [16]. The α-phase is a metastable phase with an angle of $\theta \sim 25°$ with respect to b axis. It can be found in bulk and in thin films at room temperature, Figure 3.

Iron Phthalocyanine Bulk and Thin Film

Iron phthalocyanine has a Fe^{2+} ion in the center of the molecule that forms quasi one-dimensional (1D) chains. The magnetic properties of α-phase powder were studied in the past by Evangelisti *et al.* [17]. They reported that in α-form FePc iron atoms are magnetically coupled into ferromagnetic Ising chains with very weak antiferromagnetic

FIGURE 2. Metal free and metallo-phthalocyanine molecule. a) Molecule of metal-free phthalocyanine with four ligands and the cavity at the center of the molecule. b) Metallo-phthalocyanine molecule with a metal in the central cavity.

FIGURE 3. The α and β phase stacking structure of metallo-phthalocyanine. The θ is the angle between the b-axis and the normal to the plane of the molecule. 1) α-phase 2) β-phase.

interchain coupling below about 10 K, while the β-phase behaves paramagnetically down to the lowest measured temperatures.

Physical properties of FePc thin films such as magnetic properties are tunable by controlling film structure [18, 19]. Film structure can be controlled by changing deposition condition such as deposition temperature and choice of substrate [20, 21]. Using different substrates we change the molecule–substrate interactions that changes the metal ion chain alignment to either perpendicular or parallel to the substrate surface, Figure 4. Increasing substrate deposition temperature causes elongated grains, with longer iron chains [22]. Iron chains with longer average grain size have larger coercivity and require a larger saturation field [22]. FePc deposited at 200 °C and less is α-phase. The magnetic moments of iron are ferromagnetically coupled along the quasi-1D metal chains. Above 200 °C FePc is β-phase that behaves like a paramagnet. These show the direct relation of the deposition

FIGURE 4. Different stacking of phthalocyanine thin film on gold and sapphire substrates. (a) On sapphire substrate the ordering of the molecules with their plane is perpendicular to the substrate plane, therefore the molecular b axis is oriented parallel to the substrate plane. (b) On gold substrate the ordering of the molecules with their plane is parallel to the substrate plane, therefore orientation of the molecular b axis is perpendicular to the substrate plane [18].

temperature, the grain size, and the phases. The stable β phase can be gained by sublimation techniques and annealing the α-phase to $300\,°\mathrm{C}$. FePc thin films in α-phase show magnetic hysteresis loop below $4.5\,\mathrm{K}$ due to interactions between the one-dimensional chains [17] and behave as non-traditional paramagnet above this temperature.

Manganese Phthalocyanine

MnPc crystals, powders and thin films have been studied using different techniques at different temperature and magnetic field strengths in order to characterize them. Barraclough *et al.* [23] reported ferromagnetic ordering in the β-MnPc crystal between adjacent molecules using magnetization and average magnetic susceptibility measurements. Their measurements confirmed that the Mn atom is an $S = \frac{3}{2}$ spin state. The state $S = \frac{3}{2}$ was explained based on crystal field calculation, and two possible exchange coupled models were investigated: the one-dimensional Ising model and the isotropic Fisher description of a linear chain of interacting atoms [24, 25].

Magnetic properties of single crystal manganese phthalocyanine were studied by Hirohazu Miyoshi *et al.* [26]. Results for AC susceptibility measurement suggest the

existence of ferromagnetic interaction between molecules by obeying the Curie-Weiss law, and suggesting a positive Curie-Weiss constant in the measured temperature range between $13.7\,\text{K}$ and $20.4\,\text{K}$. These results are in agreement with positive Weiss constant found by Lever [27]. Ferromagnetic behavior was found in low temperature region, and transition temperature from paramagnetic to ferromagnetic reported to be around $8.6\,\text{K}$ which is in agreement with Barraclough and his co-workers' [23] results. But the evaluated magnetic moment from magnetization measurements at $4.2\,\text{K}$ was smaller than expected, and for the same temperature the observable resonance absorption signal for the X-band microwave (band with frequency of $8\,\text{GHz}$ to $12\,\text{GHz}$) was absent. So, in 1974 Miyoshi [28] studied the spin structure in the ordered MnPc by magnetization and torque measurement. Results showed canted ferromagnetism with two sub-lattices at $90°$ where each sub-lattice forms a linear ferromagnetic chain. In 1982, Mitra et $al.$ [29] studied the magnetic properties of the single crystal MnPc. Based on the chain-like characteristic of the magnetic properties, they concluded ferromagnetic interaction exchange of $S = \frac{3}{2}$ ions with a weak antiferromagnetic interchange interaction. They also confirmed that in the ordered state MnPc is canted ferromagnetic.

SQUID magnetometer measurements of the MnPc thin film deposited at room temperature by Yamada et $al.$ [30] displayed a large magnetic anisotropy. They used molecular beam epitaxy (MBE) to grow the thin film of the MnPc. The usual canted ferromagnetism in β-type crystal of MnPc was not observed. Negative Curie–Weiss constant found by magnetic susceptibility measurements indicated the existence of the antiferromagnetic interaction. These differences between the thin films and bulk MnPc were explained by the difference in superexchange interaction caused by microscopic modification of the stacking arrangement. The angle between the molecule and the b axis found to be $65°$. The magnetization curve for the annealed MnPc film at $100\,°\text{C}$ found to

TABLE 1. Magnetic Properties for α and β Phases of FePc and MnPc Powder and Thin Films

	Powder			Thin film		
	FePc	MnPc			FePc	MnPc
α	FM	-	$T_{dep}<100\,°C$		FM	AFM
β	PM	FM Canted	$T_{dep}>100\,°C$		FM	FM

PM=Paramagnetic, FM=Ferromagnetic, AFM=antiferromagnetic. The thin films are deposited at the temperature T_{dep}.

be similar to the bulk β-MnPc. Therefore, it was concluded by Yamada *et al.* that the thin film becomes ferromagnetic by annealing.

In 2016, magnetic properties of MnPc thin films deposited at room temperature by organic molecular beam deposition (OMBD) technique was studied by Heutz *et al.* [31] and compared to the single crystal. The thin film is crystallized as α-phase. Based on the results, negative Curie-Weiss constant implies antiferromagnetic behavior, which disappears at high temperatures or fields. This was confirmed by using simulation of a paramagnetic $S = \frac{3}{2}$ using Brillouin function. Besides, a recent study of β-MnPc powder and analysis of the temperature and magnetic field dependence of the DC and AC magnetic susceptibilities by Wang and Seehra. [25], demonstrated the absence of long range 3-dimensional (3D) magnetic order. They described the system as an Ising-like chain magnet. Recent study of MnPc by Duong confirms and adds to the previous knowledge about MnPc [32]. X-ray diffraction (XRD) analysis of MnPc by Duong suggests that deposition temperature affects the columnar stacking angle. Thin films deposited at $230\,°C$ are β-phase and thin films deposited at room temperature, and $100\,°C$, are α-phase. Magnetic property measurements of the MnPc thin film also suggests that the thin film of α MnPc is paramagnetic down to $2.6\,K$ and then becomes antiferromagnetic. However, β-MnPc displays paramagnetic behavior down to $7.2\,K$, and then becomes ferromagnetic [32] .

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Exchange Bias

Exchange bias refers to the coupling at the interface of antiferromagnetic (AF) and ferromagnetic (F) material [33]. Starting from a temperature between Néel temperature (T_N) and Curie temperature (T_c) and cooling the system below the Néel temperature of the antiferromagnet at the presence of static magnetic field, ferromagnetic hysteresis loop will be shifted to the opposite direction of the applied magnetic field. The amount of shift in the hysteresis loop is called exchange bias (EB) field. Figure 5 illustrates the phenomenological interpretation of exchange bias in an FM/AFM bilayer at a basic level. The picture shows the orientation of spin magnetic states at the interface at the various stages of the hysteresis loop [33].

At the temperature less than the Curie temperature of the FM and higher than the Néel temperature of the AFM ($T_N < T < T_c$), the FM spins are aligned in the direction of the magnetic field, while the AFM material is still in a paramagnetic state and spins remain randomly oriented, (a) in Fig 5. Cooling down the bilayer below the T_N of the AFM in the presence of strong static magnetic field, enough to saturate the FM, the AFM would endure a phase transition from paramagnetic to antiferromagnetic, (1) in Fig 5. The first interfacial layer of the AFM aligns with the FM spins, and the rest will align to produce zero net magnetization of the AFM ordering. By reversing the magnetic field, (2) in Fig 5, the FM spins will rotate in the opposite direction. The AFM spins remain unchanged for large AFM anisotropy while exerting torque on the FM spins to keep them aligned ferromagnetically. A greater force and therefore stronger magnetic field is needed to rotate the FM spins due to existence of exchange coupling at the interface. Reversing magnetic field again from negative saturation, (4) in Fig 5, the FM spins require smaller field to rotate and align in the direction of the external magnetic field, since the torque is in the same direction with the field. Consequently, the hysteresis loop is shifted.

In addition to negative shift, positive shift of the hysteresis loop is also observed,

FIGURE 5. Phenomenological model of exchange bias. Illustration of the spin configuration of an antiferromagnetic and ferromagnetic bilayer at different stages of the exchange bias hysteresis loop. a) Spin configuration of the FM at a temperature $T_N < T < T_c$. The FM is ordered while AFM is paramagnetic at the temperatures higher than T_N. 1) The spin configuration after field cooling at the temperature below the T_N. FM and AFM layers are coupled at the interface. The spin configuration in the FM/AFM bilayer during the reversal process, assuming that this takes place through in-plane rotations of the FM spins.

meaning that the hysteresis loop is shifted along with the positive value of the magnetic field. Gredig *et al.* reported positive exchange bias behavior near the blocking temperature in Co/CoO bilayers [34]. In other systems like Fe/FeF$_2$ at low temperature [35] a positive shift was observed, i.e., the shift is along with the positive value of the magnetic field axis.

The exchange bias field (H_{EB}) is defined as the displacement of the hysteresis loop from the center [33, 36]

$$H_{EB} = \frac{H_{C+} + H_{C-}}{2}. \tag{1.1}$$

The exchange bias effect was discovered by Meiklejohn and Bean in 1956 while investigating the magnetic properties of Co with CoO. They also proposed the first theoretical model which gives qualitative intuition to explain the exchange bias effect. They assumed that both the AFM and the FM are in single domain state. In the field cooling process the AFM has in-plane uniaxial anisotropy, and during the rigid rotation of the FM the orientation of the AFM spins does not change [37]. To describe the coherent rotation of the FM magnetization, Stoner-Wohlfarth model was adopted in their theoretical model [38]. In the original model of Stoner and Wohlfarth the energy per unit area before the cooling process is given by

$$E_A = -\mu_o H \ M_{FM} t_{FM} \cos(\theta - \beta) + K_{FM} t_{FM} \sin^2(\beta). \tag{1.2}$$

Meiklejohn and Bean introduced an extra term J_{EB} (exchange coupling energy per unit area at the interface) for the exchange coupling at the interface of the AFM and FM [33, 39, 40].

$$E_A = -\mu_o H \ M_{FM} t_{FM} \cos(\theta - \beta) + K_{FM} t_{FM} \sin^2(\beta) - J_{EB} \cos(\beta). \tag{1.3}$$

Here H is the applied magnetic field which makes angle θ with the easy axis of the AFM.

K_{FM} and M_{FM} are magnetocrytalline FM anisotropy constant and magnetization of the FM, respectively. M_{AFM} and K_{AFM} are the sublattice magnetization of the AFM and easy axis for uniaxial anisotropy. The parameter β is the angle between magnetization vector M_{FM} and the anisotropy direction of the FM, while t_{FM} is the thickness of the FM. It is assumed that $\theta=0°$, which means the applied magnetic field is parallel to the easy axis of AFM. With the stability condition $\frac{\partial H}{\partial \beta} = 0$. and the condition for minimum energy $\frac{\partial^2 H}{\partial^2 \beta} > 0$ we obtain two solutions. One is

$$\beta = \frac{\cos^{-1}[(J_{EB} - \mu_o H M_{FM} t_{FM})}{2K_{FM}} \tag{1.4}$$

for $\mu_o H M_{FM} t_{FM} - J_{EB} \leq 2K_{FM}$. The second one is

$$\beta = 0° \text{ or } \pi \tag{1.5}$$

for $\mu_o H M_{FM} t_{FM} - J_{EB} \geq 2K_{FM}$. Extracting the coercive field from the stability equations for $\beta = 0$ or π we find

$$H_{c+} = \frac{-2K_{FM}t_{FM} - J_{EB}}{\mu_o M_{FM} t_{FM}} \tag{1.6}$$

$$H_{c-} = \frac{2K_{FM} - J_{EB}t_{FM}}{\mu_o M_{FM} t_{FM}}. \tag{1.7}$$

Using expressions $H_c = \frac{-H_{c+}+H_{c-}}{2}$ and $H_{EB} = \frac{H_{c+}+H_{c-}}{2}$ they obtained

$$H_c = \frac{2K_{FM}}{\mu_o M_{FM}} \tag{1.8}$$

$$H_{EB} = -\frac{J_{EB}}{\mu_o M_{FM} t_{FM}}. \tag{1.9}$$

Equation (1.9) gives the EB field. However, the experimentally observed shift is several orders of magnitude smaller than the model prediction. Following Meiklejohn and Bean

FIGURE 6. Schematic view of the vectors and angles in the Meiklejohn and Bean model.

model a large variety of macroscopic, mesoscopic and microscopic model have been suggested and investigated to explain the mechanism of exchange interaction. Planar AFM Domain wall model-Néel's approach, Mauri model-partial domain wall, frozen canted interface spins-Kiwi model, partial domain wall-Kim-Stamps approach, Radu approach-The spin glass model, Interacting AFM grain model, Spin flop - Koon's model are some examples of the proposed models on exchange bias [41].

Exchange bias has extensive applications in technology. One application is in spin valve devices which uses giant magnetoresistance (GMR) effect. These applications rely on spintronics, where the electron spin is employed to carry information, and used in hard disks' read heads [42, 43].

Organic semiconducting materials are in high interest because of the possibility of implementing low cost and versatile electronic devices based on organic thin films. Organic semiconducting materials are suitable materials for spintronics. Recent experiments suggested the opportunity for application of organic semiconductors in the spintronic field. Xiong *et al.* [44] used an organic semiconductor to make an organic spin-valve which shows giant magnetoresistance. Exchange coupling has been reported in different systems.

Wackerlin *et al.* [2] reported the presence of exchange interaction at the interface of paramagnetic organic semiconductor MnPc and ferromagnetic semiconductor Eu(II)-oxide grown on highly oriented pyrolytic graphite. The most recent exchange bias, consists of organic molecule thin film, was reported at the interface of antiferromagnetic MnPc layer and Co film at low temperature [3].

CHAPTER 2

EXPERIMENT

The aim of this chapter is to introduce the material we used for deposition of thin films. We outline the preparation of Silicon substrate, namely how to cleave and clean the substrate before the thin film deposition. The deposition process of the thin films is via the Nano-Master Thermal Evaporator 3000 (NTE 3000) and the measurements of hysteresis loops are made by the Quantum Design Physical Property measurement System (PPMS) with the vibrating sample magnetometer (VSM) module. Finally, we explain the process of sputtering cobalt thin films, and the topography measurement of the sample using atomic force microscopy.

Material

The FePc, MnPc powder, and H_2Pc powder, and the Silicon wafers were all purchased from outside sources. The iron(II)phthalocyanine (empirical formula $C_{32}H_{16}FeN_8$), the manganese(II)phthalocyanine (empirical formula $C_{32}H_{16}MnN_8$), and the metal-free or 29H,31H- phthalocyanine, β-form (empirical formula $C_{32}H_{18}N_8$) were purchased from Sigma-Aldrich. The Silicon wafers we use were purchased from University Wafer, p-doped, size 50.8 mm, with crystal orientation (111), and a thickness of 270 µm. The acetone (ACS grade) and isopropanol were purchased from Fisher Science. The 99+% extra pure methanol was purchased from Acros Organics.

Substrate Preparation

The substrates are cleaved from Silicon wafers with a diamond tipped scribe. The size of each cleaved substrate is 4×10^1 mm^2. The substrates are cleaned before deposition to remove impurities. Besides, the solvent residues are removed before thin film deposition. To do so, substrates are sonicated in an ultrasonic bath using Branson 2510 in three steps, and three different solvents are used. In the first step to remove surface contamination we sonicate the substrate for 10 minutes in acetone. Second, 10 minutes of sonication in

isopropanol removes the acetone molecules from the surface of the substrate. Finally, to remove the isopropanol molecules, we sonicate the substrate for 10 minutes in methanol. Since methanol is a small molecule, blow drying with nitrogen gas immediately after the last sonication evaporates its molecules.

Thin Film Deposition

The thin film samples are deposited using Nano Master Thermal Evaporation 3000 (NTE 3000) (Figure 7). Vacuum thermal evaporation is the common method to deposit organic small molecule thin films [45]. The substrates are placed and fixed on a substrate holder plate, Figure 8. The holder is placed in the vacuum chamber rotating stage, in the top of the vacuum chamber upside down in a way that the surface of the substrates are toward crucibles. The powder is loaded with specially cleaned tools under the chemical hood into the alumina crucible. Then, the crucible is placed in the tungsten wire basket crucible holder, which is located at the bottom of the NTE vacuum chamber. The film thickness is monitored with a quartz crystal microbalance (QCM). The thickness is reported as machine unit (u). Based on the calibration by Silverstein [46], the film thickness is converted from the calibration factor of 5 u per 2.2 Å. To start the deposition process, the vacuum chamber is closed and sealed, and using roughing pump and turbo pump the pressure brought down to at least 2.5×10^{-5} torr. The bake out process is performed to desorb water from the substrate surface. This process includes heating and cooling of the crucible and sample holder plate to 100 °C in a slow process. The heater plate temperature is easily set, while for crucible bake out performs by increasing the current through the tungsten wire baskets, which has already been set up to 7% power, with 1% increase in every two minutes until the crucible temperature reaches to 100 °C at about 12% to 14%. To cool down the crucible, the current is reduced by 3% every two minutes, until the current reaches 7%. The substrate and crucible shutters should remain closed during the bake out process to cover the substrates surfaces. The system is left overnight to reach the

FIGURE 7. NTE-3000 and the inside view of vacuum chamber. NTE-3000 thermal evaporator photo on the left, and the diagram on the right shows the inside view of vacuum chamber and its components.

stable base pressure. The plate heater is set to the desired deposition temperature and should be given enough time to stabilize at the target temperature. Once the desired deposition temperature is reached the crucible is slowly heated by 1% in every two minutes, until the rate reaches between 0.5 and 2.0 u/s. At this step, the crucible is uncovered, the substrate shutter is opened to let the sublimated material deposited onto the substrate surface and by rotating the plate, the thickness of the film on the substrate is controlled to be even. To control the rate and keep it steady, the crucible temperature is controlled. At the desired thickness, the deposition is stopped by closing the substrate shutter. By reducing the current by 3% in every two minutes until it reaches 7%, the crucible temperature is reduced and then turned off. Simultaneously, the plate heater in turned off. When the system temperature is below $50\,°C$, the turbo pump and roughing pump are turned off and the chamber is vented to room pressure. Next, the sample plate holder is removed from the chamber and the first VSM measurement is conducted afterwards.

FIGURE 8. Substrate holder plate, and substrates which are clamped and screwed on the holder using steel sheet metal clamps and screws.

Vibrating Sample Magnetometer (VSM)

The commercial Quantum Design Physical Property Measurement system is designed to perform various measurements. For all deposited thin films, the magnetic moments as a function of applied magnetic field are measured using the Vibrating Sample Magnetometer (VSM) module [47]. We measure magnetic moment vs. applied magnetic field with field cooling procedure. Using the acquired data from VSM measurement, magnetic hysteresis loops are plotted and studied. In principal, the VSM measures the magnetization of a sample by detecting the electromagnetic force induced in the coil set while magnetic flux is changing in time. Changing in magnetic flux induces voltage. The quartz paddle sample holder is placed on the mounting station. Then, the sample is placed, centered, and fixed on a quartz paddle using Kapton tape. Kapton tape physical, electrical, and mechanical properties are retained over entire range of $1.8\,\mathrm{K}$ to $400\,\mathrm{K}$. The measurements are conducted with the applied field parallel to the substrate plane. The

width of the thin films cannot exceed the width of the paddle (4.0 mm). The paddle is then attached to the sample rod and placed into the sample tube connected to the VSM linear motor. The sample is held in place in the linear motor transport by a magnetic-locking mechanism, and driven sinusoidally with mechanical vibration by the VSM linear motor. The VSM linear motor is capable of operating at 40 Hz. We had our samples being set at the offset of 3.50±0.04 cm. According to Quantum Design constant large magnetic field does not affect the VSM coil, so sensitive measurements at the highest possible field can be performed. Table 2 lists all samples deposited and measured herein, and Figure 10 displays listed samples. Deposition times and rates are included in Table 3.

TABLE 2. List of Deposited Samples

Sample	Name	M_1	M_2	t_1 (nm)	t_2 (nm)	T_{dep1} (°C)	T_{dep2} (°C)	A (mm^2)
MM160303SI4	FePc1	FePc	-	60	-	150	-	34.5
MM160322SI3	FeH2	FePc	H$_2$Pc	60	20	150	150	36.3
MM160608SI0	MnPc1	MnPc	-	60	-	150	-	37.3
MM160608SI3	FeMn1	FePC	MnPc	60	60	150	150	39.0
MM160720SI1	FeMn2	FePC	MnPc	60	76	150	RT	33.8
MM170831MnFe1	MnFe3	MnPc	FePc	40	60	RT	150	35.0
MM211116SICO	CoMn	Co	MnPC	8	60	RT	RT	33.4
MM151116SICO1	Co1	Co	-	8	-	RT	-	36.4

M_1 and M_2 are deposited materials, t stands for the thickness of the deposited material in nm, T_{dep} stands for deposition temperature in °C, and A stand for the area of the samples in mm^2. For Sample FeH2, both layers are deposited at the same time in one deposition process. For samples FeMn1, FeMn2, and CoMn layers are deposited in two different deposition processes. 76 nm is 173 u, 60 nm is 1364 u, 40 nm is 909 u, and 20 nm is 455 u.

Hysteresis Loop Measurements

Magnetic hysteresis loops of the samples are determined via field cooling process using VSM. Each sample is cooled down in the presence of in-plane magnetic field from room temperature to the desired measurement temperature and then the hysteresis loop is

TABLE 3. Sample Deposition Time and Rate for All Layers

Name	First Layer	Dep. Time First Layer (min)	Dep. Ave. Rate (u/s)	Second Layer	Dep. Time Second Layer (min)	Dep. Ave. Rate (u/s)
FePc1	FePc	28.0	0.8	-	-	-
FeH2	FePc	18.0	1.3	H_2Pc	4.0	2.0
MnPc1	MnPc	32.5	0.7	-	-	-
FeMn1	FePc	26.0	0.8	MnPc	32.5	0.7
FeMn2	FePc	13.2	1.7	MnPc	36.4	0.8
MnFe3	MnPc	16.0	0.9	FePc	15.3	1.5
CoMn	Co	-	-	MnPc	52.3	Fig. 10
Co1	Co	-	-	-	-	-

measured. After taking the hysteresis loop at the desired temperature, the sample is heated to above the Néel temperature of the AFM material to bring it back to the paramagnetic state and reset any effect from field cooling, and then again cooled back to the next desire measurement temperature. The measurements of the hysteresis loops are performed by recording the magnetic moments as a function of magnetic field in the field interval from -H to +H and the sweep speed of $10\,\mathrm{mT\,s^{-1}}$. Each cooling field and temperature is explained later.

Sputtering Cobalt Thin Film

Two cobalt samples are grown at the same time by sputtering deposition technique. The sputtering instrument we use is the Multi-Target Magnetron Sputtering System of the ATC 1800-F series from AJA International. Cobalt is deposited on the surface of the Silicon wafer. Each sample has an estimated 8 nm of cobalt deposited onto Silicon substrate. The deposition is done at room temperature. The base pressure of the chamber is 1.5×10^{-7} torr. The substrate was raised up about 2.3 cm. Argon gas is leaked to the chamber with 30 sccm flow rate so that the pressure is fixed to 5×10^{-3} torr during the sputtering deposition. The deposition rate for cobalt is 0.2 Å/s.

FIGURE 9. Sample CoMn deposition rate plotted vs. time. Deposition starts at 18 minutes time, and takes 52.3 minutes to complete.

Atomic Force Microscopy

The Nanoscope MultiMode Atomic Force Microscope is a very high resolution AFM, which is used in tapping mode to acquire surface topography of the sample Co1 (8 nm cobalt deposited by sputtering). In tapping mode AFM operates by scanning the attached tip to the end of the oscillating cantilever across the sample surface. The AFM tip model is the Nanosensors PPP-NCHR-10 with resonance frequency at 237 kHz. The topography is measured in tapping mode (TM) with an oscillating probe tip.

FIGURE 10. Schematic view of the deposited samples including single thin film and bilayers. At the interface of the bilayers in which the two layers are not deposited in one deposition process oxidation occurs.

CHAPTER 3

ANALYSIS AND RESULTS

Here we present the magnetic properties of single thin films of FePc, MnPc, Co, and FePc/MnPc, Co/MnPc bilayers, Fig.10. The focus of the work is on the coercivity and the saturation magnetization. We know from previous studies that MnPc thin film deposited at room temperature is antiferromagnetic [30]. Using the AFM phase of MnPc, we combine it with the FM phase to create new interesting interfaces. We make a heterostructure with of Co/MnPc to compare with Gruber *et al.* [3]. The sample is 8 nm Co deposited onto Silicon substrate by using sputtering, and 60 nm MnPc onto cobalt thin film. Due to our instrumental limitation, we are not able to deposit both layers at the same deposition process which makes our bilayer different from their bilayer.

We measure the magnetic hysteresis loops of FePc thin films using VSM in the range of temperatures from 2.5 K to 20 K. We find that FePc thin films exhibits magnetic hysteresis below 5 K. The coercivity and the saturation magnetization decrease with increasing the measurement temperature. Our results are in agreement with previous results [18]. We also investigate the effect of oxidation over a period of one month for the same sample. For this purpose, we measure the magnetization curves of FePc thin film approximately less than two hours after deposition, after a week, and after one month to understand the change of magnetic properties with time. We find that saturation magnetization does not change over this period of time while the coercivity decreases from the first measurement to the second measurement, and stays unaffected when measured again after one month.

To add a protective layer onto the FePc thin film from oxidation, we deposit metal-free phthalocyanine onto iron phthalocyanine thin film with the same specification as before, and measure the sample in the same way, i.e. three hysteresis loops over a period of one month.

To create new heterostructure, We deposit two bilayers of MnPc/FePc at 150 °C and room temperature, respectively. Since MnPc is deposited onto FePc after some time, FePc thin film is able to oxidize. Other bilayer of MnPc/FePc is deposited. This time both layers are deposited at the same time without taking the sample out of the vacuum chamber to avoid any oxidation. We measure the magnetic properties at the interface of the bilayer with field cooling.

Magnetic Properties of Non-Organic Cobalt Included Thin Film

Sample Co1

The sample Co1, is a thin film of $8\,\mathrm{nm}$ Co, which is deposited onto a $4 \times 10^1\,\mathrm{mm^2}$ Silicon substrate. Magnetic hysteresis loops are measured with field cooling process thirteen days after the deposition. The measurements of the loops are performed in the field interval of $-3\,\mathrm{T}$ to $3\,\mathrm{T}$ at $2.5\,\mathrm{K}$, $3\,\mathrm{K}$, $14\,\mathrm{K}$, $58\,\mathrm{K}$ and $300\,\mathrm{K}$, respectively. The $3\,\mathrm{T}$ magnetic filed is applied to the sample at $300\,\mathrm{K}$. The temperature is lowered to $14\,\mathrm{K}$ and hysteresis loop is measured from $-3\,\mathrm{T}$ to $3\,\mathrm{T}$. To measure at the next temperature magnetic field is removed and sample is warmed to $300\,\mathrm{K}$. Same process of FC is applied to measure at $58\,\mathrm{K}$, $3\,\mathrm{K}$ and $2.5\,\mathrm{K}$. Data from VSM measurements are plotted in Figure 11, all the magnetic moments are divided by the area of the sample ($3.64 \times 10^{-1}\,\mathrm{cm^2}$). The hysteresis loops of the sample display a unidirectional shift along the magnetic field axis in the negative direction indicating the effect of exchange bias. Exchange bias occurs at the interface of ferromagnetic and antiferromagnetic materials. This has been observed in Co/CoO bilayers [37, 39, 48, 49]. Meiklejohn and Bean [39] argued that the displacement of the hysteresis loop is due to the existence of an oxide film on cobalt particles. To prove that, they conducted two different experiments. In one of the experiments they removed the oxide coating by hydrogen reduction and observed that hysteresis loops became symmetric and centered.

In our work the existence of the shift in the hysteresis loops, indicates the existence

of a layer of native oxidized Co. By increasing the measurement temperature, the shifted hysteresis loop goes back to be symmetric, and it vanishes at $300\,K$ (Figure 12).

The sample also displays an unusual shoulder in the upper left part of the hysteresis loops at $2.5\,K$, $3\,K$, $14\,K$ and $58\,K$, respectively. The unusual shoulder in more pronounced as the measurement temperature decreases. Figure 11 shows the measurement of the hysteresis loops at $2.5\,K$ with positive field cooling (PFC) and negative field cooling (NFC). The shoulder exists in the upper left part of the hysteresis loop for PFC and lower right part of the hysteresis loop for NFC. We can say the existence of the shoulder does not depend on the direction to which the field was first applied when field cooling and measuring the hysteresis, and pinning of the ferromagnetic layer can happen in different directions depending on the sign of the cooling field. Figure 13 shows the effect of applying higher magnetic fields . As the field gets higher the shoulder becomes less pronounced.

Leighton *et al.* [50] measured the anisotropic magnetoresistance of the MnF_2/Fe. Their results exhibits asymmetric magnetization reversal explained by two different mechanism on each side of the hysteresis (called "two-stage" rotation). They suggested that the reversal of the magnetization for certain cooling field orientations happens by coherent rotation on the high field side of the loop and by domain wall nucleation and propagation on the low field side of the loop. Their results also showed a similar shoulder in the hysteresis loop. The shoulder is associated with this effect as well. To show that the rotation can occur in two stages in Ref. [51], they used magnetometry, polarized neutron reflectometry (PNR), and anisotropic magnetoresistance (AMR). They claimed that in two stages the magnetization vector falls into a potential minimum at $90°$ to magnetic field cooling which leads to appearance of the shoulder in the hysteresis loops.

Shoulder in the hysteresis loops was also observed previously in ferromagnetic/antiferromagnetic bilayer patterned into nano-dot arrays of Co/CoO [52]. They proposed that the existence of the shoulder was due to the competition of

magnetostatic interdots and exchange bias anisotropy during the magnetic switching. Since our sample is not patterned but we are observing the shoulder in the hysteresis loops, we study the surface morphology of the sample surface using AFM.

Figure 14 shows the AFM image of the sample. The RMS roughness is $0.7\,\text{nm}$. Using WSxM [53] software, we are able to see the height of the profile as a function of the length of the profile. There exist some feature which might be created during sputtering process (bright points in Figure 14-a). The mean size of the features is $29 \pm 6\,\text{nm}$. And the mean height of them is 6.5 ± 1.1 nm. These features might be the source of the shoulder in the shifted hysteresis loops.

Sample CoMn

Sample CoMn is a bilayer thin film of $8\,\text{nm}$ ferromagnetic cobalt deposited on Silicon substrate and then $60\,\text{nm}$ of paramagnetic organic MnPc is deposited onto it at room temperature about 1 hour after sputtering Co on the Silicon substrate. Magnetization hysteresis loops are measured after deposition of MnPc with the same field cooling process as sample Co1 at $2.5\,\text{K}$, $3\,\text{K}$, $14\,\text{K}$, $58\,\text{K}$ and $300\,\text{K}$, respectively. We compare the magnetic hysteresis loops of this sample with the Co1. Based on Gruber *et al.* [3] work for Co/MnPc, we made this bilayer. Figure 15 represents the results for this measurement. Magnetic moments are divided by the area of the sample ($3.34 \times 10^{-1}\,\text{cm}^2$). The hysteresis loops are not symmetric with respect to the center of the coordinate, and display a unidirectional shift due to the exchange bias. They are shifted in the negative direction of the magnetic field axis, but the shift vanishes at $300\,\text{K}$, above the Néel temperature of CoO. At $2.5\,\text{K}$ we conduct measurement in NFC, and the measurement is in the field interval of $-3\,\text{T}$ to $3\,\text{T}$. Applying $3\,\text{T}$ magnetic field causes a shift in the negative direction of magnetic field axis, while applying $-3\,\text{T}$ magnetic field induces a shift to the positive direction. We found $1.9 \times 10^{-4}\,\text{emu}$ magnetic saturation at $2.5\,\text{K}$ and $3\,\text{K}$, $1.8 \times 10^{-4}\,\text{emu}$ at $14\,\text{K}$ and $58\,\text{K}$, and at $300\,\text{K}$ we obtain $1.7 \times 10^{-4}\,\text{emu}$. So with

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FIGURE 11. Field cooling magnetization hysteresis loop measurements of the sample CO1 (Co thin film). Measurements are performed with field cooling process at $2.5\,\mathrm{K}$, $3\,\mathrm{K}$, $14\,\mathrm{K}$, $58\,\mathrm{K}$ and $300\,\mathrm{K}$ for the sample Co1, respectively. Moments are divided by area of the sample($3.64 \times 10^{-1}\,\mathrm{cm}^2$). The hysteresis loops display a unidirectional shift in the negative direction of the magnetic field axis due to the exchange bias. The shift disappears at the $300\,\mathrm{K}$. At $2.5\,\mathrm{K}$ two measurements correspond to two FC fields. There exist an unusual shoulder in the upper left part of the hysteresis loops at $2.5\,\mathrm{K}$, $3\,\mathrm{K}$, $14\,\mathrm{K}$ and $58\,\mathrm{K}$.

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FIGURE 12. Field cooling magnetization hysteresis loop measurement of CO1 (Co thin film) at $2.5\,\mathrm{K}$, $3\,\mathrm{K}$, $14\,\mathrm{K}$ and $58\,\mathrm{K}$, respectively. The plot indicates that as the measurement temperature increases the shoulder becomes less pronounced, the coercivity, and the exchange bias field decrease.

FIGURE 13. Magnetization vs. applied field measured with field cooling process at $14\,\mathrm{K}$ in low and high magnetic field for sample Co1. As the magnetic field gets higher the shoulder becomes less pronounced.

increasing the temperature, the magnetic saturation is decreasing. At $2.5\,$K the horizontal intercepts of the hysteresis loops are $-4520\,$Oe and $570\,$Oe, and coercive field is $-2545\,$Oe. At $3\,$K are $-4480\,$Oe and $490\,$Oe, and coercive field is $2480\,$Oe. At $14\,$K are $-4127\,$Oe and $586\,$Oe, and coercive field is $2360\,$Oe. Finally at $58\,$K are $-2630\,$Oe and $1070\,$Oe, and coercive field is $1850\,$Oe. The coercivity decreases as temperature increases even above $5\,$K. We observed that for MnPc included thin films coercivity do not exist above $5\,$K. Since in CoMn bilayer coercivity exist even above $5\,$K, we conclude that CoO is the reason for the shift in the hysteresis loops. This sample also displays unusual shoulder in the upper left part of the hysteresis loops at $2.5\,$K and $3\,$T applied field. The unusual shoulder is more pronounced at lower temperatures. In NFC the shoulder exists at the lower right part of the hysteresis loop because the ferromagnetic layer is pinned in the opposite direction. Since the shoulder exists in both field cooling at $2.5\,$K, we conclude that the existence of the shoulder does not depend on the direction to which the sample in cooled filed and the field was first applied when measuring the hysteresis. But comparing this bilayer with Co1 sample, Figure 17, saturation magnetization increases in the bilayer. For Co1 and CoMn magnetization saturation are $2.9 \times 10^{-4}\,$emu/cm^2 and $5.6 \times 10^{-4}\,$emu/cm^2, respectively. Based on our calculation from obtained magnetic saturation in the area of the two samples and known value of $1300\,$emu/cm^3 for Co, we are able to calculate the remained thickness of the Co after oxidation. For CoMn, the thickness is $4.3\,$nm while for the Co sample which is measured after a while the thickness is reduced to $2.3\,$nm due to oxidation. MnPc layer has minimal or no contribution to the magnetic moment, therefore, the shift is caused by oxidation. lower saturation magnetization and higher coercivity in Co1 is consistent with exchange bias.

Magnetic Properties of Iron Phthalocyanine Thin Films

Previous works [19, 22] proposed that FePc thin film shows magnetic hysteresis below $4.5\,$K. It behaves as non-traditional paramagnet at or above $4.5\,$K and shows no

hysteresis. The hysteresis measurement temperature affects coercivity and the magnetization. The saturation magnetization decreases as the measurement temperature is increased.

We measure the magnetization curves in the temperatures range from $2.5\,K$ to $20\,K$ for the sample FePc1 which is $60\,nm$ FePc deposited on Silicon substrate at $150\,°C$. The sample is cooled down to reach the desired temperature in the presence of magnetic field. This is the process of field cooling. At the desired temperature, the sample is magnetized by applying $2\,T$ or $1\,T$ magnetic field, and the field is reversed in the opposite direction to $-2\,T$ or $-1\,T$. For instance, to measure at $2.5\,K$ the sample is cooled down from $300\,K$ to $10\,K$ with applying $2\,T$ magnetic field, then the sample is cooled down to $2.5\,K$ and hysteresis curve is measured with sweeping the magnetic field from $2\,T$ to $-2\,T$. The sample is warmed back to the $300\,K$ and the same procedure of field cooling for the next temperature is applied. Figure 18 and 19 show the magnetization vs. magnetic field measurements. Above $5\,K$ there is no magnetic hysteresis. At $2.5\,K$ magnetization saturation is $35\,emu\,cm^{-3}$ and $72 \pm 5\,\mu emu$ for the deposited thickness. At $5\,K$ the magnetization saturation is $35\,emu\,cm^{-3}$ and $73 \pm 5\,\mu emu$ for the deposited thickness. No change in saturation magnetization is observed from $2.5\,K$ to $5\,K$.

Measured values of coercivity at $2.5\,K$ and $5\,K$ are $1850 \pm 50\,Oe$ and $50 \pm 50\,Oe$, respectively. This shows that the coercivity increases as measurement temperature decreases. Measured coercivities are plotted vs. measurement temperatures in figure 20. We can see that the coercivity decreases rapidly with increasing temperature. At $2.5\,K$ coercivity is at its highest and as we measure at higher temperatures it decreases and vanishes near $5\,K$. At temperatures less than $5\,K$ FePc behaves ferromagnetic like.

Thirty days after making the sample, it was remeasured to understand the change of coercivity with time. Within the uncertainty of $50\,Oe$, the coercivity did not change; it remained at $600\,Oe$.

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Effect of Aging on FePc Thin Film Magnetic Properties

For the sample FePc1, we perform hysteresis loop measurement three times over a period of one month to investigate the effect of oxidation on the magnetic properties of the FePc thin films. Measurements are performed less than 1 hour, after one week, and after one month of the deposition. Figure 21 shows the hysteresis curves normalized by the volume of the sample. The samples are stored in vacuum to be protected against moisture in the air and from UV light. However, we are not able to prevent oxidation effect in this way. According to studies performed by Mathew Werber on the aging effect on iron phthalocyanine thin films over a year apart, the net saturation moment decreases, but the coercivity does not change [54]. As listed in Table 4, the sample is not fully saturated and we have minor loops at $2.5\,\mathrm{K}$, $3\,\mathrm{K}$ and $3.5\,\mathrm{K}$. For the first measurement, the average coercivity found to be $1850 \pm 50\,\mathrm{Oe}$ at $2.5\,\mathrm{K}$. After a week the same measurement finds that the average coercivity decreased to $1550 \pm 50\,\mathrm{Oe}$. Thirty days after making the sample, It is remeasured ,Table 4, and the average coercivity is found as $1500 \pm 50\,\mathrm{Oe}$. Within an uncertainty of $\pm 50\,\mathrm{Oe}$ we conclude that coercivity decreases from the first measurement to second measurement, and remained unchanged from the second measurement to the third measurement. Comparing the saturation magnetization for each measurement at each of the temperatures listed in Table 4, within the uncertainty of $\pm 5\,\mathrm{\mu emu}$, no change in saturation magnetization is observed over the period of one month.

Sample FeH2

We perform magnetic hysteresis loop measurements in the temperature range from $2.5\,\mathrm{K}$ to $20\,\mathrm{K}$ for the sample FeH2, three times over a period of one month. This sample was made to be $60\,\mathrm{nm}(1364\,\mathrm{u})$ FePc deposited on Silicon substrate at $150\,\mathrm{^\circ C}$ and capped with $20\,\mathrm{nm}$ $(454\,\mathrm{u})$ of (H_2Pc). Both layers are deposited at the same deposition process. We apply the FC process as for the sample FePc1, i.e. Measured and calculated details are listed in Table 5. Figure 23 shows the hysteresis loops for all the three measurements but

TABLE 4. Magnetic Properties of the Sample FePc1 Measured with VSM

1 Day

T K	H_{c+} Oe	H_{c-} Oe	H_c Oe	M_{s+} 10^{-5} emu	M_{s-} 10^{-5} emu	M_s 10^{-5} emu	M_s emu/cm^3	M_s 10^{-20} emu/$f.u$	M_s $\mu_\mathrm{B}/f.u$
2.5	1490	-2220	1850	7.7	-6.6	7.2	35	2.0	2.2
3.0	720	-940	830	7.8	-7.4	7.6	37	2.2	2.4
3.5	370	-390	380	7.5	-7.5	7.5	36	2.2	2.4
5.0	70	-30	50	7.4	-7.3	7.3	35	2.1	2.3
					1 Week				
2.5	1320	-1780	1550	7.8	-6.9	7.3	35	2.1	2.3
3.0	610	-650	630	7.9	-7.5	7.7	37	2.0	2.2
3.5	250	-300	270	8.0	-7.7	7.8	38	2.2	2.4
5.0	90	-20	60	7.6	-7.6	7.6	37	2.2	2.4
					1 Month				
2.5	1240	-1770	1500	7.2	-7.0	7.1	34	2.0	2.2
3.0	610	-610	610	7.5	-7.3	7.4	36	2.1	2.3
3.5	250	-220	230	7.5	-7.4	7.5	36	2.1	2.3
5.0	70	-30	50	7.2	-7.1	7.2	35	2.0	2.2

T stands for measurement temperature in Kelvin. H_{c+}, H_{c-}, and H_c stand for positive and negative coercivity and the average coercivity in units of Oe. M_{s+}, M_{s-}, and M_s stand for positive, negative, and average saturation magnetization in emu. M_s emu/cm^3 is the magnetic moment per volume of the sample. M_s (emu/$f.u$) is the magnetic moment per number of molecules (formula unit), and M_s ($\mu_\mathrm{B}/f.u$) is the magnetic moment per the number of molecules (formula unit) in Bohr magnetons. The uncertainty in the coercivity measurements is ± 50 Oe.

TABLE 5. Magnetic Properties for Sample FeH2 Measured with VSM

<div align="center">1 Day</div>

T K	H_{c+} Oe	H_{c-} Oe	H_c Oe	M_{s+} 10^{-5} emu	M_{s-} 10^{-5} emu	M_s 10^{-5} emu	M_s emu/cm^3	M_s 10^{-20} emu/$f.u$	M_s $\mu_{\mathrm{B}}/f.u$
2.5	1000	-1470	1230	4.2	-3.8	4.0	18	1.1	1.2
3.0	480	-470	480	4.2	-4.2	4.2	19	1.1	1.2
3.5	262	-221	240	3.9	-4.0	3.9	18	1.1	1.2
5.0	80	-50	70	3.8	-3.8	3.8	17	1.0	1.1
					1 Week				
2.5	1040	-1360	1200	4.6	-4.2	4.4	20	1.2	1.3
3.0	490	-520	510	4.8	-4.5	4.6	21	1.3	1.4
3.5	250	-230	240	4.7	-4.6	4.6	21	1.3	1.4
5.0	70	-30	50	4.4	-4.4	4.4	20	1.2	1.3
					1 Month				
2.5	970	-1380	1180	4.1	-3.6	3.9	18	1.0	1.1
3.0	560	-550	550	4.0	-3.9	4.0	18	1.1	1.2
3.5	240	-190	220	4.0	-4.0	4.0	18	1.1	1.2
5.0	80	-30	50	3.7	-3.7	3.7	17	1.0	1.1

Measurement were performed three times over a period of one month. T stands for measurement temperature in Kelvin. H_{c+}, H_{c-}, and H_c stand for positive and negative coercivity and the average coercivity in Oersted. M_{s+}, M_{s-}, and M_s stand for positive, negative, and average saturation magnetization in emu. M_s (emu/cm^3) is the magnetic moment per volume of the sample. M_s (emu/$f.u$) is the magnetic moment per number of molecules (formula unit), and M_s ($\mu_{\mathrm{B}}/f.u$) is the magnetic moment per the number of molecules (formula unit) in Bohr magnetons. The uncertainty in the coercivity measurements is ± 50 Oe.

the moments are divided by the volume of the sample. At 2.5 K for the first measurement coercivity is 1230 ± 50 Oe. Within the uncertainty of ± 50 Oe, the coercivity did not change; it remained at 1230 Oe for all three measurements, Figure 24. According to the three data point we have, it is concluded that capping FePc thin film with H_2Pc can prevent changes in coercivity.

Although both FePc1 and FeH2 thin films contain 60 nm FePc, the magnetic moments are not consistent. Further investigation is needed to find out if this comes from deposition process or it is the effect of adding H_2Pc to the FePc layer.

FIGURE 14. AFM image of the sample Co1 (Co thin film). This sample is $8\,\mathrm{nm}$ Co deposited onto silicon using sputtering. a) Flattened image of the surface topography. b) line profile of the surface. RMS roughness of the sample is $0.7\,\mathrm{nm}$. Mean size of the features is $29 \pm 6\,\mathrm{nm}$. And the mean height of them is 6.5 ± 1.1 nm.

FIGURE 15. Field cooling magnetization hysteresis loop measurement of the sample CoMn (MnPc/Co heterostructure) at $2.5\,\mathrm{K}$, $3\,\mathrm{K}$, $14\,\mathrm{K}$, $58\,\mathrm{K}$ and $300\,\mathrm{K}$, respectively. Moments are divided by area of the sample$(3.34 \times 10^{-1}\,\mathrm{cm}^2)$. The hysteresis loops display a unidirectional shift in the negative direction of the magnetic field axis due to the exchange bias. The shift disappears at $300\,\mathrm{K}$. At $2.5\,\mathrm{K}$ two measurement at two direction of magnetic field was conducted. There also exist an unusual shoulder in the upper left part of the hysteresis loops at $2.5\,\mathrm{K}$, $3\,\mathrm{K}$, $14\,\mathrm{K}$ and $58\,\mathrm{K}$.

FIGURE 16. Field cooling magnetization hysteresis loop measurement of the sample CoMn (MnPc/Co heterostructure) at $2.5\,\mathrm{K}$, $3\,\mathrm{K}$, $14\,\mathrm{K}$ and $58\,\mathrm{K}$. The plot indicates that as measurement temperature increases, all coercivities, exchange bias fields decrease, and the unusual shoulders becomes less pronounced.

FIGURE 17. Comparison of the magnetization vs. applied field measured with field cooling process for the samples Co1 and CoMn at $2.5\,\mathrm{K}$.

FIGURE 18. Comparison between the hysteresis curves of the sample **FePc1** (60 nm **FePc** deposited at 150 °C) in the temperature range from 2 K to 20 K, using vibrating sample magnetometer. All of the curves are divided by the volume of the sample. The volume of the sample is $2.07 \times 10^{-6}\,\mathrm{cm}^3$. As measurement temperature increases coercivity decreases from 2.5 K to 5 K and magnetic saturation decreases only from 10 K to 20 K.

FIGURE 19. Hysteresis loops comparison of the sample FePc1 (FePc thin film) in the temperatures less than $5\,\mathrm{K}$ and above $5\,\mathrm{K}$. Hysteresis loops below $5\,\mathrm{K}$ indicates the presence of long-range magnetic ordering (a). At temperatures above $5\,\mathrm{K}$ hysteresis loop vanishes and the saturation decreases with increasing the temperature(b).

FIGURE 20. Temperature dependence of the average coercivity for the FePc thin film with FC process. Coercivity goes to zero around $5\,\mathrm{K}$.

FIGURE 21. Three hysteresis measurements of the sample FePc1 over a period of one month to study the effect of oxidation on the magnetic properties of the FePc thin films in the temperatures range from $2.5\,\mathrm{K}$ to $20\,\mathrm{K}$. All of the curves are divided by the volume of the sample. The volume of the sample is $2.07 \times 10^{-6}\,\mathrm{cm}^3$.

FIGURE 22. Comparison of the average coercivity vs. measurement temperature for the sample FePc1 (FePc thin film) in three times measurements. This comparison indicates that from the first time measurement the same day after deposition, which is 03/03/2016, to the after a week measurement the coercivity decreases. But, from the second measurement to the third measurement after a month no change is observed in coercivity, and it stays unchanged.

FIGURE 23. Hysteresis data for FePc thin film capped with metal free phthalocyanine sample FeH2. Three hysteresis loops measurements for the sample FeH2 ($H_2Pc/FePc$ bilayer) over a period of one month to investigate the effect of capping FePc thin film with H_2Pc on the coercivity. Magnetic moments are normalized by the volume ($2.18 \times 10^{-6}\,cm^3$) of the sample. Measurements are conducted at six different temperatures from $2.5\,K$ to $20\,K$. In all three measurements over the period of one month, no change in coercivity is observed.

FIGURE 24. Comparison of the average coercivity vs. temperature for the sample FeH2 (H$_2$Pc/FePc bilayer) in three times measurements. This sample is deposited at 150 °C. This comparison indicates that the coercivity stays the same for the three times measurement over a period on one month. Capping FePc thin film with H$_2$Pc prevents the effect of the aging on the coercivity.

Magnetic Properties Measurement of Iron/Manganese Phthalocyanine Bilayer

Sample MnPc1

Magnetic properties of $60\,\text{nm}(1364\,\text{u})$ MnPc deposited at $150\,°\text{C}$ are reported in Figure 25. Magnetization vs. applied magnetic field of the sample is measured using VSM and FC process at $2.5\,\text{K}$, $5\,\text{K}$ and $10\,\text{K}$. At $2.5\,\text{K}$ sample shows hysteretic magnetization behavior and it vanishes at $5\,\text{K}$ and $10\,\text{K}$. A coercive field of $390 \pm 50\,\text{Oe}$ is recorded at $2.5\,\text{K}$. Saturation magnetization is $21 \pm 3\,\text{µemu}$. We also calculate $0.6\ \mu_\text{B}/f.u.$ for the net effective magnetic saturation moment per the number of molecules (f.u) in Bohr magnetons. This agrees qualitatively with table 1 that MnPc thin film deposited at the temperature above $100\,°\text{C}$ is FM.

Sample FeMn1

This sample is a bilayer thin film, including $60\,\text{nm}$ ($1364\,\text{u}$) of MnPc deposited onto the $60\,\text{nm}(1364\,\text{u})$ FePc. Both layers for this sample are deposited at $150\,°\text{C}$ in two separate deposition processes. At first, FePc layer is deposited, removed from NTE, and measured in less than two hours. Then, MnPc is deposited onto FePc after 97 days, removed from NTE, and measured. Therefore, FePc layer might be oxidized due to the contact with air.

Figure 26 shows the results of VSM measurements for sample FeMn1 in the temperature range from $2.5\,\text{K}$ to $20\,\text{K}$. Magnetic moments are divided by the volume $(2.34 \times 10^{-6}\,\text{cm}^3)$ of the FePc layer. In each measurement the sample is cooled down at the presence of in-plane magnetic field (FC) and then the magnetic moment vs. applied magnetic field is measured. Magnetic field is set to $2\,\text{T}$ and sample is cooled down to $10\,\text{K}$, temperature is decreased to $2.5\,\text{K}$ with $2\,\text{T}$ applied magnetic field, and hysteresis loop is measured. To measure at the next temperature the magnetic field is removed, and temperature is raised back to $200\,\text{K}$ to remove the effect of first FC. Again FC process in applied to the sample and hysteresis loop is measured for the next desire temperature.

We observe hysteresis loops at temperatures below $5\,\text{K}$, which vanish above $5\,\text{K}$.

FIGURE 25. Magnetization vs. temperature for the sample MnPc1. After field cooling process in positive direction of the applied magnetic field, measurements are performed at $2\,\mathrm{T}$ and $2.5\,\mathrm{K}$, $5\,\mathrm{K}$ and $10\,\mathrm{K}$. Sample shows hysteretic magnetization at $2.5\,\mathrm{K}$, and it vanishes at $5\,\mathrm{K}$ and above. Magnetic moments are divided by the volume of the sample $(2.24 \times 10^{-6}\,\mathrm{cm^3})$.

This behavior is the same we observed earlier in FePc thin film. We list our data in table 6. We also calculate the net effective magnetic saturation moment per volume, per formula unit(number of the molecules), and magnetic moment per the number of molecules (formula unit) in Bohr magnetons using the magnetic saturation. We assume one molecule per formula unit for both MnPc and FePc and, the density of $1.6\,\mathrm{g\,mol^{-1}}$ These results are also presented in table 6. The first FePc layer is made at the same deposition process with

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TABLE 6. Magnetic Properties for Sample FeMn1 Measured with VSM

T	H_{c+}	H_{c-}	H_c	M_{s+}	M_{s-}	M_s	M_s	M_s	M_s
K	Oe	Oe	Oe	10^{-5} emu	10^{-5} emu	10^{-5} emu	emu/cm^3	10^{-20} emu/$f.u$	$\mu_{\mathrm{B}}/f.u$
2.5	720	-940	830	7.7	-7.3	7.5	32	1.9	2.0
3.0	390	-420	400	7.5	-7.7	7.6	32	1.9	2.0
3.5	150	-210	180	7.7	-7.9	7.8	33	2.0	2.2
5.0	90	-50	70	7.5	-7.6	7.6	32	1.9	2.0

T stands for measurement temperature in units of Kelvin. H_{c+}, H_{c-}, and H_c stand for positive and negative coercivity and the average coercivity in Oersted. M_{s+}, M_{s-}, and M_s stand for positive, negative, and average saturation magnetization in emu. M_s (emu/cm^3) is the magnetic moment per volume of the sample. M_s (emu/f u) is the magnetic moment per number of molecules (formula unit), and M_s ($\mu_{\mathrm{B}}/f.u$) is the magnetic moment per the number of molecules (formula unit) in Bohr magnetons. The uncertainty in the coercivity measurements is ± 50 Oe.

sample FePc1. At 2.5 K hysteresis loop is not fully saturated, coercivity and magnetization saturation for the sample FeMn1 are 830 ± 50 Oe and 75 ± 5 µemu, respectively. But for the sample FePc1, they are 1850 ± 50 Oe and 71 ± 5 µemu. Within the uncertainty of ± 5 µemu saturation magnetization does not change, however, coercivity is decreased. No change in saturation magnetization from FePC1 thin film to FeMn1 means magnetization moments are due to the FePc layer and MnPc layer does not have contribution to it, or MnPc contribution is negligible. The same trend is observed at 3 K, 3.5 K and 5 K. This is the reason we divided magnetic moments using the volume of FePc layer, only.

For the same sample we conduct magnetization vs. magnetic field measurement applying magnetic field in both directions at 2.5 K. For the second measurement at 2.5 K, the same FC process is applied but instead the sample is magnetized in the negative direction of 2 T (NFC), then hysteresis loops are measured from -2 T to 2 T to -2 T. Within the uncertainty of ± 50 Oe both values of the measured coercivities in both FC are in agreement (830 ± 50 Oe). Figure 27 shows the hysteresis loop comparison for these measurements. All the measured magnetic moments are divided by the volume

FIGURE 26. Hysteresis data for the sample FeMn1 (MnPc/FePc heterostructure deposited at $150\,°C$, measured in six different temperatures from $2.5\,K$ to $20\,K$ with FC. The magnetic moments are divided by the volume $(2.34 \times 10^{-4}\,cm^3)$ of the sample. Two different magnetic regimes is observed less than $5\,K$ and above $5\,K$. No Hysteresis is observed at and above $5\,K$.

$(2.34 \times 10^{-6}\,\mathrm{cm}^3)$ of the FePc layer only in figure 27. No shift of the hysteresis loops is observed.

Sample FeMn2

Here, we investigate the FePc/MnPc magnetic properties in which FePc is deposited with the same specification, but MnPc is deposited at RT instead of $150\,°\mathrm{C}$. The $60\,\mathrm{nm}$ ($1364\,\mathrm{u}$) FePc is deposited at $150\,°\mathrm{C}$ on Silicon substrate. Magnetic properties of the sample are measured with VSM with field cooling process in the temperatures range from $2.5\,\mathrm{K}$ to $20\,\mathrm{K}$, less that 1 hour after deposition. We apply $3\,\mathrm{T}$ magnetic field and cool down the sample to $10\,\mathrm{K}$ from $300\,\mathrm{K}$, wait and cool down to $2.5\,\mathrm{K}$ and measure the hysteresis loop from $-3\,\mathrm{T}$ to $3\,\mathrm{T}$. We set the field to 0 and warm up the sample to $200\,\mathrm{K}$. We apply $3\,\mathrm{T}$ magnetic field again and cool the sample to $3\,\mathrm{K}$ from $200\,\mathrm{K}$ to measure the hysteresis loop. Results are presented in Figure 28. After VSM measurement of the FePc sample were completed, $76\,\mathrm{nm}$ ($1727\,\mathrm{u}$) MnPc is deposited onto the FePc sample at room temperature after 28 days. Since we removed the FePc sample out of the vacuum chamber of the NTE and performed measurements, the sample will have oxidized. Magnetic hysteresis loops of the new bilayer are measured with the same FC process as the FePc sample. This enables us to investigate the effect of depositing MnPc onto FePc. Results are shown in figure 29. At $2.5\,\mathrm{K}$ we measure hysteresis loop again, but this time sample is cooled down from $200\,\mathrm{K}$ to $10\,\mathrm{K}$ with applying $-3\,\mathrm{T}$ magnetic field in the negative direction, wait and cool down to $2.5\,\mathrm{K}$ and measurement starts from $-3\,\mathrm{T}$ (NFC), figure 31. In the positive applied magnetic filed direction (PFC) measurement we found $1310 \pm 50\,\mathrm{Oe}$ coercivity while in the NFC we got $1290 \pm 50\,\mathrm{Oe}$. Within the uncertainty of $\pm 50\,\mathrm{Oe}$, coercivities are consistent. The direction to which the field was first applied in FC process and while measuring the hysteresis does not affect the coercivity. We can conclude that coercivity does not change with field cooling in positive and negative direction of the magnetic field, and sweeping the field from positive or negative saturation.

FIGURE 27. Hysteresis loops measurements for the sample FeMn1 (MnPc/FePc heterostructure) in PFC and NFC process at $2.5\,\mathrm{K}$ and $2\,\mathrm{T}$ magnetic field. Magnetic moments are divided by the volume ($2.34 \times 10^{-6}\,\mathrm{cm}^3$) of the sample.

Yamada and Gruber *et al.* [3, 30] found AFM interaction in MnPc deposited at RT. Gruber *et al.* observed exchange bias in bilayer of co and paramagnetic organic MnPc deposited at RT, also. According to their observations, we expected AFM interaction in MnPc deposited at RT as well. But, No shift of the hysteresis loop is observed in our results.

In figure 30, the results for FC VSM measurements of the two samples are plotted together for comparison. The coercivity and the magnetic saturation for both measurements are measured and listed in the Table 7. We calculate the net effective magnetic saturation moment per volume, per formula unit, and the magnetic moment per the number of molecules (formula unit) in Bohr magnetons using magnetic saturation and results are presented in table 7. Within the uncertainty of $\pm 5\,\mu$emu, $M_{s+} = M_{s-}$ at different temperatures. This show that the sample is fully saturated and we have major loops. At 2.5 K for the FePc layer, coercivity and saturation magnetization are 1330 ± 50 Oe and $53 \pm 5\,\mu$emu, respectively. For the bilayer at 2.5 K coercivity and saturation magnetization are 1310 ± 50 Oe and $51 \pm 5\,\mu$emu, respectively. We can say that coercivity and saturation magnetization do not change between two measurements of these two samples at each temperature. The magnetization moments are from the FePc layer only.

Since exchange bias occurs at the interface of ferromagnetic and antiferromagnetic materials when the sample is cooled down to the temperature less the Néel temperature of the antiferromagnetic at the presence of magnetic field, we try to lower the measurement temperature and measure with higher magnetic field. The sample is cooled down to 100 K from 300 K while applying 1 T magnetic filed, temperature is decreased to 5 K and then to 2 K. At 2 K hysteresis loop is measured with sweeping 5 T magnetic field in both directions, PFC and NFC. In both loops magnetic saturation average is 2.1×10^{-4} emu. The sample is fully saturated, and we have major loops. Applying magnetic field in both positive and

negative direction, the coercivity average is 960 ± 50 Oe. Results of both measurements at 2 K are shown in Figure 32. We expected higher value for the coercivity than the coercivity at 2.5 K. There is a 65 days difference between these two measurements. The reason needs more investigation.

According to the results, no measurable changes are observed in hysteresis loops, and magnetic properties do not change between FePc/Si thin film and MnPc/FePc/Si thin film. Therefore, MnPc indeed is antiferromagnetic.

TABLE 7. Magnetic Properties of Samples FeMn2 Measured with VSM

					FePc				
T K	H_{c+} Oe	H_{c-} Oe	H_c Oe	M_{s+} 10^{-5} emu	M_{s-} 10^{-5} emu	M_s 10^{-5} emu	M_s emu/cm^3	M_s 10^{-20} emu/$f.u$	M_s $\mu_B/f.u$
2.5	1300	-1360	1300	5.3	-5.2	5.3	26	1.5	1.6
3	470	-520	490	5.6	-5.7	5.7	28	1.6	1.7
3.5	220	-240	230	5.5	-5.4	5.4	27	1.6	1.7
					FePc/MnPc				
2.5	1270	-1340	1310	5.2	-5.1	5.1	25	1.5	1.6
3	490	-480	490	5.6	-5.7	5.6	27	1.6	1.7
3.5	230	-180	210	5.3	-5.3	5.0	26	1.5	1.6

The measurement temperature (T) is measured in units of Kelvin. H_{c+}, H_{c-}, and H_c stand for positive and negative coercivity and the average coercivity in Oersted. M_{s+}, M_{s-}, and M_s stand for positive, negative, and average saturation magnetization in emu. M_s (emu/cm^3) is the magnetic moment per volume of the sample. M_s (emu/f u) is the magnetic moment per number of molecules (formula unit), and M_s ($\mu_B/f.u$) is the magnetic moment per the number of molecules (formula unit) in Bohr magneton.

Sample MnFe3

Sample MnFe3 is a bilayer of 38 nm (868 u) MnPc and 60 nm (1364 u) FePc deposited at RT and 150 °C, respectively. Both layers of this thin film are deposited in one deposition process to exclude the effect of oxidation present in sample FeMn1 and FeMn2. The MnPc is deposited as the first layer and FePc as the second layer. Both MnPc and FePc powders are purified. Magnetic hysteresis loops are measured in field cooling process in the presence of 6 T magnetic field at 2.5 K and 300 K, respectively. Results are shown in figure 33. At 2.5 K coercivity and saturation magnetization are 910 ± 50 Oe and

FIGURE 28. Magnetization vs. applied field graph for the sample FeMn2 (FePc thin film). Measurements are performed with FC process at six different temperatures range from $2.5\,\mathrm{K}$ to $20\,\mathrm{K}$. Magnetic moments are divided by the volume of the sample $(2.03 \times 10^{-6}\,\mathrm{cm^3})$.

$60 \pm 5\,\mu$emu. It has an effective magnetic moment of 1.8 $\mu_{\mathrm{B}}/f.u.$ Figure 34 shows the comparison of the hysteresis loops between samples FeMn2 and MnFe3, measured at 2.5 K. For both samples saturation magnetization are $25 \pm 5\,\mathrm{emu/cm}^3$ and $28 \pm 5\,\mathrm{emu/cm}^3$, respectively. The magnetic moment is coming from the FePc layer for the sample FeMn2 and MnPc layer does not contribute. These two samples' saturation magnetization are consistent with each other. Therefore, for sample MnFe3 the magnetic moment signal is from FePc Layer, and there is no contribution from MnPc. No measurable shift of the hysteresis loop is observed for MnFe3 bilayer.

Figure 35 is the comparison of the hysteresis loops for all the MnPc included samples. Saturation magnetization for sample MnPc1 is $9.3 \pm 1\,\mathrm{emu/cm}^3$. Depositing FePC onto MnPc layer (sample FeMn1), saturation magnetization of the FePc layer is added to the to the MnPc layer and increase it to $32 \pm 5\,\mathrm{emu/cm}^3$. However, MnPc deposited at RT in FeMn2 and MnFe3 samples shows less increase in saturation magnetization of the bilayers since they are $25 \pm 5\,\mathrm{emu/cm}^3$ and $28 \pm 5\,\mathrm{emu/cm}^3$.

FIGURE 29. Magnetization vs. applied field graph for the sample FeMn2 (MnPc/FePc heterostructure). MnPc is deposited onto FePc at room temperature. The measurements are performed with field cooling process in six different temperatures range from $2.5\,\mathrm{K}$ to $20\,\mathrm{K}$. Magnetic moments are divided by the volume of the FePc layer $(2.03 \times 10^{-6}\,\mathrm{cm^3})$.

FIGURE 30. Normalized hysteresis loops comparison measured at $2.5\,\mathrm{K}$ for the sample **FeMn2** between the first layer FePc and then after depositing MnPc onto that (FePc thin film and MnPc/FePc heterostructure). The graph shows the comparison of the hysteresis loops at $2.5\,\mathrm{K}$ and $3\,\mathrm{T}$. $60\,\mathrm{nm}$ **FePc** is deposited at $150\,^{\circ}\mathrm{C}$ while $60\,\mathrm{nm}$ **MnPc** is deposited onto FePc at room temperature. We first deposit FePc on Silicon and measure it. Then we deposit MnPc onto FePc. There is a chance of oxidation for FePc layer. For the FePC layer we measure a coercive field of $1330 \pm 50\,\mathrm{Oe}$ while for **MnPc/FePc** it is $1310 \pm 50\,\mathrm{Oe}$. These two values are consistent. No measurable change is observed between these to hysteresis loops and magnetic properties.

FIGURE 31. Magnetization vs. temperature for the sample FeMn2 (MnPc/FePc heterostructure) in PFC and NFC at $2.5\,\mathrm{K}$. After field cooling process at $2.5\,\mathrm{K}$ and $3\,\mathrm{T}$. Measured coercivities are within 1% agreement for both direction. The direction to which the field was first applied in FC process and when measuring the hysteresis does not affect the coercivity. Magnetic moments are divided with the volume of the FePC layer($2.03 \times 10^{-6}\,\mathrm{cm}^3$).

FIGURE 32. Magnetization vs. temperature for the sample FeMn2 (MnPc/FePc heterostructure) in both $5\,\mathrm{T}$ magnetic field direction measured at $2\,\mathrm{K}$. Loops are measured at a higher magnetic field at $5\,\mathrm{T}$ and measurement temperature is lower at $2\,\mathrm{K}$. Magnetic moments are divided by the volume of the FePc layer$(2.03 \times 10^{-6}\,\mathrm{cm}^3)$. No measurable shift of the hysteresis loop is observed with higher magnetic field and lower measurement temperature.

FIGURE 33. Field cooling magnetization hysteresis loop measurement of the sample MnFe3 (MnPc/FePc heterostructure) at $2.5\,\mathrm{K}$ and $300\,\mathrm{K}$. At $2.5\,\mathrm{K}$ coercivity and saturation magnetization are $910 \pm 50\,\mathrm{Oe}$ and $60 \pm 5\,\mathrm{\mu emu}$. Magnetic moments are divided by the volume of the FePc layer$(2.10 \times 10^{-6}\,\mathrm{cm^3})$.

FIGURE 34. Comparison of hysteresis loops measured with field cooling process at $2.5\,\mathrm{K}$ for samples FeMn2 and MnFe3. For both samples saturation magnetization are $25 \pm 5\,\mathrm{emu/cm^3}$ and $28 \pm 5\,\mathrm{emu/cm^3}$, respectively.

FIGURE 35. Comparison of hysteresis loops for all the samples include MnPc layer. Hysteresis loops are measured with field cooling process at $2.5\,\mathrm{K}$.

CHAPTER 4

CONCLUSION

Exchange bias is a significant phenomenon occurring at the interface of ferromagnets (FM) and antiferromagnets (AFM). The AFM layer alters the response of the ferromagnet evidenced in the hysteresis loop [33,39]. Extensive use of exchange bias in technology has motivated research in this area. Despite applications of exchange bias in technology and numerous experimental and theoretical studies, the fundamental physical mechanism of exchange bias is still an ongoing debate.

Field cooling (FC) can freeze in the state of the AFM layer, so that the hysteresis loop of the bilayer shifts in response to the interfacial exchange coupling, which can be modeled effectively as the result of a unidirectional anisotropy. This behavior is useful in spin valves [55], which have two ferromagnets. One of which is pinned by the exchange bias effect making it hard, while the other ferromagnetic layer is free to rotate at low fields. This effect is currently used in read heads of hard disk drives and memory elements in magnetic random access memory [1,56]. More recently in 2015, manganese-phthalocyanine/europium oxide heterostructure [2] and manganese-phthalocyanine/cobalt heterostructures [3] have been investigated to explore exchange bias. Exploiting interfaces to modify, control, enhance, or even create and annihilate magnetic order and properties is an exciting new direction. Emerging materials, such as phthalocyanine and its derivatives can be processed and tuned easily. They have advantages to be inexpensive, optically active, and mechanically flexible. Magnetic properties of the metallo-phthalocyanines depend on the central metal ion, which can be Manganese or Iron. Their physical properties are tunable by controlling deposition conditions, such as temperature, and by changing the substrate.

Herein, we explore fabrication of novel bilayer structures that contain organic-AFM/organic-FM interfaces. For this purpose, we investigate cobalt/manganese phthalocyanine, and manganese phthalocyanine/iron phthalocyanine bilayers. Additionally,

single layers of iron phthalocyanine and manganese phthalocyanine are made for reference. The samples are deposited via thermal sublimation. We study the magnetic properties via measuring hysteresis loops after field cooling the samples. Throughout our work, we use Silicon substrates. We have made eight different structures of samples and compared their magnetic properties.

The first structure is Si/Co/CoO(native)/MnPc. The hysteresis loops are measured at $2.5\,\mathrm{K}$, $3\,\mathrm{K}$, $14\,\mathrm{K}$ and $58\,\mathrm{K}$ in FC process. This sample shows a unidirectional shift of the hysteresis loop indicating the presence of exchange bias. In order to distinguish the effect of the MnPc layer from the exchange bias effect of the native CoO, which is also an antiferromagnet, a single layer of Cobalt is measured. Both samples exhibit similarly shaped hysteresis loops and the effect of the additional MnPc (room temperature) layer could not be separated out. The dominant shift is attributed to the CoO/Co interface coupling. Additionally, the shift in both samples is measurable at $58\,\mathrm{K}$ in agreement with the high Néel temperature of CoO. An unusual shoulder on the upper left side of the hysteresis loop becomes more pronounced at lower measurement temperature. The shoulder is attributed to a two-stage rotation of the ferromagnet.

Single layers of FePc and MnPc are studied to provide insight into bilayers. Results for the FePc thin films deposited at $150\,^\circ\mathrm{C}$ show the existence of two magnetic regimes. The thin film has magnetic hysteresis that vanishes above $5\,\mathrm{K}$. Both magnetization saturation and coercivity increase as the measurement temperature is lowered. A large coercivity, approximately $1850\,\mathrm{Oe}$, is measured at $2.5\,\mathrm{K}$ in agreement with earlier measurement that FePc is an Ising-like magnet with Arrhenius relaxation [57]. There is also an effect of time, so that seven and thirty days after deposition, the hysteresis curves of FePc thin film exhibit changes in their magnetic properties. The coercivity decreases from the first measurement to the second measurement and does not change to the third measurement. At the same time, the saturation magnetization does not change for all three

measurements. The addition of a capping layer of H_2Pc to the FePc thin film prevents a change in coercivity as evidenced in sample FePC1.

According to the experiments from Refs. [2, 3, 30], MnPc thin films deposited at room temperature have AFM characteristics. Our measurements show FM characteristics for MnPc thin films at $150\,°C$ in a thin film of $60\,nm$, sample MnPc1. Magnetization vs. applied magnetic field of the sample is measured with FC process at $2.5\,°C$, $5\,°C$ and $10\,°C$. At $2.5\,K$ sample shows hysteretic magnetization behavior and no hysteresis at $5\,K$ and $10\,K$. A coercive field of $350 \pm 50\,Oe$ is recorded at $2.5\,K$. The saturation magnetization is $21 \pm 3\,\mu emu$ for this sample. Taking into effect the thickness, it corresponds to $0.6\ \mu_B/f.u.$.

A bilayer of $60\,nm$ FePc capped with $60\,nm$ of MnPc is named sample FeMn1. Both layers for this sample are deposited at $150\,°C$ in two separate deposition processes. At first, FePc layer is deposited, removed from NTE, and measured with the results discussed above for sample FePc1. Then, MnPc is deposited onto FePc after 97 days and the magnetic properties are measured. From the previous measurements of a single layer of FePc it is expected that the coercivity may have changed due to the surface interactions with ambient air. In the bilayer magnetic sweeps at temperatures below $5\,K$ have coercivity. This behavior is the same as observed in the single layer of FePc($60\,nm$). At $2.5\,K$ coercivity and magnetization saturation for the sample FeMn1 are $830 \pm 50\,Oe$ and $75 \pm 5\,\mu emu$, respectively. But for the sample FePc1, they are $1850 \pm 50\,Oe$ and $72 \pm 5\,\mu emu$. Comparing these data, we notice that saturation magnetization does not change, however, the coercivity decreases. The same trend is observed at $3\,K$, $3.5\,K$ and $5\,K$. From the previous single layer measurements, an increase by 25% in magnetic moment would be expected due to the additional MnPc($150\,°C$). The absence could be due to the surface interactions with water and oxygen, since the sample was measured several months after deposition of FePc.

A third sample was deposited with the MnPc on Silicon followed by FePc without

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opening the system to avoid any oxidation of the interface. This sample is labeled MnFe3. The deposition temperatures are the same as for FeMn2, but the thicknesses are MnPc(38 nm)/FePc(60 nm)). At 2.5 K coercivity and saturation magnetization are 910 ± 50 Oe and 60 ± 5 μemu, respectively.

In all three novel bilayers with FePc/MnPc thin films, no shift of the hysteresis loop is observed. Preliminary data shows that MnPc deposited at room temperature does not contribute significantly to the saturation magnetization, however, if deposited at 150 °C it contributes with a moment of 0.6 μ_B per MnPc molecule. It is possible that the interfacial coupling is enhanced, if the FePc grows lying flat, as it would on a metallic surface, such as Gold. In this case, the metal centers would be closer, as opposed to the coupling on Silicon surface, where the b-axis runs parallel to the substrate.

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