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The Metal/Organic Interface in Cobalt/Vinylidene Fluoride Heterostructures

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The Metal/Organic Interface in Cobalt/Vinylidene Fluoride Heterostructures

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Organic-based electronic devices are rapidly increasing in popularity, making it essential to understand and characterize the interface between organic materials and metallic electrodes. This work reports on the characterization of the interface between thin films of an emerging organic ferroelectric, vinylidene fluoride (VDF) oligomer, and Co, an important high Curie temperature ferromagnet. Using a wide battery of experimental techniques, it is shown that VDF oligomer thin films as thin as 15 nm can halt, or prevent, Co oxidation in atmospheric conditions, a necessary condition for device applications. Selectivity of magnetic properties, such as remanent magnetization, is enabled by the clarification of the time scale of Co oxidation, a topic on which there are many conflicting reports. Furthermore, this work shows evidence of chemical bonding at the interface between VDF oligomer and Co, a result with important implications for organic spintronic devices. These results establish the suitability of VDF oligomer for organic-based electronic devices.

1. Introduction

The ease of processing, increased device functionality, and price of organic-based electronics has led to a rapid increase in their development and usage. Organic materials have applications in light emission¹⁻³, solar cells⁴⁻⁸, and even flexible electronics⁹⁻¹¹. Perhaps the largest driving force behind this rapid growth is the customizable nature of organic molecules which can be designed and constructed to suit specific applications. These “designer molecules” can be used, for example, to tune band gaps and induce gap states in organic/metallic junctions¹², in striking contrast to inorganics, that do not afford anywhere near this degree of customization. Predictions indicate that the value of the organic electronics market will more than double, to nearly \$70 billion¹³, by 2026.

The present work is driven by previous experiments on the electric-field control of magnetic anisotropy in organic ferroelectric/metallic ferromagnetic heterostructures. Theoretical modeling¹⁴ and experiments¹⁵ have shown that the easy axis of a ferromagnetic Co thin film can

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3 be switched from in-plane to out-of-plane, or *vice versa*, by simply switching the polarization
4 direction of a polymer ferroelectric poly(vinylidene fluoride) (PVDF) thin film deposited on the
5 Co. Induced spin-dependent charge screening¹⁶ in the ferromagnetic Co thin film, due to the
6 electric field generated by the polarized ferroelectric film, changes the surface
7 magnetocrystalline anisotropy of the Co by up to 50% upon polarization switching. This change
8 is large enough to reorient the easy axis of thin Co films.
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14 Crucial to all organic-based electronics is the interface between the organic material and
15 the metallic electrodes. The interface plays a vital role in charge injection and transport in many
16 devices¹⁷, and in the example above, the quality of the metal/organic interface affects the
17 magnitude of the magnetoelectric coupling. In the Co/PVDF heterostructures¹⁵, the polymer
18 ferroelectric was deposited using Langmuir-Blodgett (LB) deposition, exposing the Co surface to
19 atmosphere, resulting in uncontrolled oxidation of the surface, as well as exposing the surface to
20 water in the LB trough. The oxidation of high Curie temperature ferromagnets, such as Co, also
21 causes challenges for other applications, such as spintronics, as this oxidation changes the spin
22 polarization at the surface. Our recent work on the optimal conditions for successful vacuum
23 thermal evaporation of ferroelectric vinylidene fluoride (VDF) oligomer films¹⁸ allows us to
24 investigate the interface between Co and VDF oligomer, because we control the exposure time
25 and conditions between the depositions of the two films. The VDF oligomer is an organic
26 ferroelectric with unique properties for device applications. While PVDF is already commonly
27 used on an industrial scale, the VDF oligomer features better crystallinity, a higher surface
28 charge density, and most importantly, can be deposited under vacuum conditions¹⁸.
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41 The objectives of this work are twofold: to investigate the efficacy of a VDF oligomer
42 thin film as a capping layer for Co, an important high Curie temperature ferromagnetic material,
43 and to characterize the interface between the VDF oligomer and Co thin films. Investigations
44 into the former also clarify the time dependence of oxidation for Co thin films, a topic on which
45 there are many contradictory reports. This work could help guide both future magnetoelectric
46 coupling experiments (an important research thrust in its own right) and more general
47 experiments using organic and metal thin film heterostructures.
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2. Sample Preparation and Experimental Methods

The metallic and organic thin films comprising the heterostructures were grown in a sputtering/e-beam evaporation chamber and a custom thermal evaporation chamber¹⁹, respectively. The two chambers are connected via a gate valve so that the entire heterostructure can be made without breaking vacuum. Samples used for magnetic measurements were grown on 1 mm thick glass substrates, while those used for scanning transmission electron microscopy (STEM) and x-ray photoelectron spectroscopy (XPS) measurements were grown on Si substrates. In both cases the heterostructures consisted of Pt (50 nm)/Co (1.0-1.2 nm)/VDF (10-500 nm). The base pressures of the sputtering/e-beam and thermal evaporation chambers were 1×10^{-8} Torr and 8×10^{-8} Torr, respectively. Metallic thin films were deposited at rates of 0.2-0.5 Å/s, measured by a quartz crystal oscillator. VDF oligomer powder, $\text{CF}_3\text{-(CH}_2\text{CF}_2)_n\text{-I}$, was provided by Daikin Industries, Ltd., with $n = 14 \pm 1$ as measured by mass spectroscopy. The VDF oligomer thin films were deposited at a rate of 1 Å/s, confirmed by external optical ellipsometry measurements. Recent advances in the thermal evaporation of VDF oligomer thin films allowed for the deposition of high quality ferroelectric films¹⁸. The reader is referred to Refs. [18] and [19] for further detail on the deposition of these VDF oligomer thin films.

Optical ellipsometry measurements were performed using a J.A. Woollam M-2000 DI spectroscopic rotating compensator ellipsometer. The map of film thickness across sample area (shown below) was recorded using a beam diameter of 300 μm by measuring 121 points in a sample area measuring 2 cm by 2 cm. The data were fit using CompleteEASE® software²⁰. More details of ellipsometry measurements on VDF oligomer films can be found in Ref. [18].

Magnetic hysteresis measurements of the Co thin films were performed in ambient, atmospheric conditions using the magneto-optic Kerr effect (MOKE)²¹. Potential magnetoelectric devices require that the VDF oligomer be in the ferroelectric β-phase chain conformation²², as opposed to other non-ferroelectric chain conformations. To ensure that the interface between *ferroelectric* VDF oligomer and Co was being characterized, pyroelectric hysteresis measurements of the VDF oligomer films were performed on selected samples. These measurements were performed using the Chynoweth method²³ with a 1 mW, 658 nm wavelength diode laser modulated with an optical chopper at 2 kHz.

Two Pt/Co/VDF heterostructure cross-sectional STEM samples were prepared in an FEI Helios 660 dual-beam instrument. The bare VDF oligomer surface was first covered by a 2 μm

thick amorphous C layer to protect the film from the ion beam during the milling process. The sample was mounted on a single-tilt holder inside a 200 kV FEI Tecnai Osiris S/TEM equipped with a field emission gun. In STEM mode, elemental maps were collected for 15 minutes, and the results were quantified using the Esprit software tools²⁴. Line scan data across the Co/VDF interface was then obtained from these maps.

XPS spectra were acquired with a dual anode x-ray lamp and a hemispherical angle resolved electron analyzer (detector). The resolution of the detector, measured by the full width at half maximum (FWHM) of the F(1s) peak, was 2.5 eV. Spectra were calibrated with the Pt(4f) peak. Measurements were performed inside an ultra-high vacuum chamber, at a pressure of 1×10^{-10} Torr, to prevent impurity scattering events. The x-ray source used an Mg anode to produce Mg K α radiation at 1253.6 eV. The sample was grounded during measurements to prevent charging effects²⁵. Since photoemission is a surface sensitive technique, the depth dependence of the characteristic photoemission lines were measured by sputter etching the surface of the sample using an ionized argon (Ar⁺) beam, at a pressure of about 1×10^{-5} Torr, with cycle times ranging from five minutes to one hour. To maximize the uniformity of the reduced surface layer, the samples were rotated by $\pm 40^\circ$ with respect to the ion beam during each sputtering cycle. Spectra were collected immediately after each sputtering cycle, thereby enabling depth dependence measurements.

3. Results and Discussion

Co thin films readily oxidize when exposed to atmosphere²⁶⁻²⁹ and in some instances this naturally forming oxide can be useful since CoO is antiferromagnetic. For example, the naturally formed antiferromagnetic oxide was used to investigate *perpendicular* exchange bias in Co/Pt multilayer heterostructures²⁸. Another study ingeniously exploited O²⁻ ion mobility in interfacial CoO_x to demonstrate voltage controlled magnetism via voltage-induced oxidation³⁰.

In general, however, devices with Co thin films require an architecture that limits exposure and prevents oxidation, as oxidation can cause exchange bias³¹ in the device and will lead to thinner Co films causing a reduction in magnetization. A brief literature search reveals that the reported thickness and time dependence of oxide formation in Co thin films varies wildly. While the time dependence of oxidation appears to depend on both the thickness²⁷ and the previous oxidation state of the film³², earlier work often offers contradictory conclusions.

The canonical description, based on SQUID magnetometry studies of 15 Å thick Co films, assumes a self-protective layer of CoO, about 10 Å thick²⁸, formed from the topmost 6 – 7 Å of Co. However, another study used x-ray diffraction, Auger electron spectroscopy (AES), and magnetometry measurements to report that Co films with an initial thickness less than 25 Å will oxidize completely, and no metallic Co will remain, though the process may take months²⁷. Still, other studies used AES and XPS to report that 8 – 10 Å of Co(OH)₂ forms instantaneously upon exposure^{26,29}, with little additional oxide forming even after 1000 hours of exposure provided the film temperature is kept below 100 °C.

To clarify the time dependence of oxidation in ambient conditions, we first measured a series of polar MOKE (PMOKE) magnetic hysteresis loops (figure 1a) as a function of time on an exposed, uncapped Co (1.2 nm) thin film. Starting at five minutes after removal from the vacuum chamber, loops were measured at approximately 10 minute intervals, with the last loop in the series taken 124 minutes after removal from vacuum. Note that all loops are normalized to the saturation magnetization and therefore the loop heights are not to scale. The loops indicate a monotonic increase in the remanent magnetization, M_r , a signature of increasing perpendicular anisotropy (the time dependence will be discussed below). This is consistent with oxidation of the Co layer – as the film oxidizes, the Co thickness decreases proceeding through the spin reorientation transition thickness as shown in the inset. Previous reports on the spin reorientation transition thickness of Co thin films give values ranging from 1 nm²⁸ to 2 nm^{33,34}; here, it was found to be about 1 nm.

Capping the Co with a VDF oligomer thin film halts the process. Figure 1b shows PMOKE measurements from a Co (1.2 nm) thin film that was exposed to atmosphere for approximately 40 hours at room temperature, before being reinserted into the vacuum chamber for deposition of a 200 nm thick VDF oligomer thin film. Magnetic hysteresis loops taken in atmospheric conditions 14 minutes and again at 40 hours (2418 minutes) after exposure, but prior to deposition of the VDF oligomer layer, show increasing loop squareness similar to the exposed Co film corresponding to the loops shown in figure 1a. However, deposition of the VDF oligomer layer essentially locks in the magnetic properties of the Co thin film as there are no subsequent changes to the magnetic hysteresis loops, even after several days (2418-9906 minutes).

When the entire Co/VDF heterostructure is made without breaking vacuum, the magnetic properties of the Co thin film are stable with time. This is indicated in figure 1c, which shows PMOKE measurements from a Co (1.0 nm)/VDF thin film taken immediately after removal from vacuum (black) and after 24 days of atmospheric exposure (red), with no significant difference between the loops. Figures 1a-c establish that thin films of VDF oligomer act as an effective barrier for Co thin films, “locking in” the magnetic properties of the Co even over long exposure times.

Figure 1. Time dependence of PMOKE magnetic hysteresis loops for the Co/VDF heterostructures shown in the insets. (a) 1.2 nm uncapped Co thin film, showing a continual change in the magnetic properties of the thin film from 5 minutes to 2 hours after removal from vacuum. Inset: Hysteresis loop after 5 minutes (black) and 5000 minutes (red) of exposure. (b) 1.2 nm Co thin film that was exposed to atmosphere for about 40 hours before being capped with VDF oligomer. The oligomer capping layer prevents further changes in the Co thin film, locking in its magnetic properties. (c) Co/VDF heterostructure made without breaking vacuum, showing no significant differences between the first loop (black) and a loop taken 24 days later (red).

Our data also shed light on the time dependence of oxidation and subsequent anisotropy changes of Co thin films. Time dependent changes in the intensity of the Kerr signal ($\Delta I/I_{max}$) and the squareness (M_r/M_s) of the magnetic hysteresis loops for uncapped Co (1.2 nm) thin films and those with a VDF oligomer capping layer are plotted in figures 2a and 2b. Weighted exponential fits for the time dependence of the data corresponding to the uncapped Co thin films are shown in blue. We use the difference in Kerr signal intensity between up and down magnetic saturation for a given hysteresis loop (ΔI) normalized to the maximum intensity corresponding to a particular saturation state (I_{max}) as a measure of the quantity of ferromagnetic material³⁵. Because MOKE does not measure the absolute magnetization, we cannot compare this quantity across samples. However, for a single sample, this is an acceptable measure of relative changes in the

amount of ferromagnetic material. Both the decrease in Kerr signal and the increasing squareness of the uncapped film with time (figure 2b) are signatures of a decreasing thickness of ferromagnetic material^{28,33,34}.

Figures 2c and 2d show the weighted exponential fits from figures 2a and 2b on much longer time scales, with the fitting error represented by the red bands. A simple exponential function of the form $f(t) = a + be^{-t/\tau}$ produces the best fits, with both signatures saturating by ~10,000 minutes. From these fits, the time constants of the changes in magnetic hysteresis of uncapped Co thin films can be extracted: $\tau = 760$ minutes for the decrease in $\Delta I/I_{max}$ (figures c), and $\tau = 910$ minutes for the increase in M_r/M_s (figures d). However, PMOKE measurements performed on these same uncapped Co (1.2 nm) thin films taken a very long time after initial exposure show no ferromagnetic magnetic signature. Figure 2e shows such a measurement collected about 290,000 minutes (200 days) after initial exposure to atmosphere, at which time only the paramagnetic signature from the Pt seed layer is observed. Therefore, we are careful to restrict the applicability of the exponential fits to the time dependent changes of the magnetic hysteresis to only the first several thousand minutes after initial exposure to atmosphere.

The difference in the time constants of $\Delta I/I_{max}$ and M_r/M_s can be explained by considering the relationship between the thickness of the film, d (which is proportional to $\Delta I/I_{max}$), and M_r/M_s . Under the assumption that irreversible magnetic domain losses are comparable for the in-plane and out-of-plane directions, the difference in area in the first quadrant of the in-plane and out-of-plane magnetic hysteresis curves gives the effective anisotropy energy, $K_{eff} = K_v + K_s/d$. This approach is commonly referred to as the “area method”^{15,36}, and yields the equation for K_{eff} :

$$K_v + \frac{K_s}{d} = \frac{\mu_0}{2} M_s \left(H_c + \frac{M_r}{M_s} H_s \right) \quad (1)$$

where K_v and K_s are the volume and surface anisotropy energies, respectively, M_s and M_r are the saturation and remanent magnetizations, respectively, and H_c and H_s are the coercive and saturation fields, respectively. From equation 1, it is clear that d and M_r/M_s are not directly proportional, and so it is not expected that the time constants in figure 2 be identical. Rather, additional quantities on the right hand side of equation 1 may change with time, albeit very slowly. Figure 1a, for example, shows that H_c , though nearly constant, changes very slowly with time. The time dependence of additional quantities may reconcile the difference in time constants of $\Delta I/I_{max}$ and M_r/M_s .

From the data in figure 2, we conclude that the oxidation process for these 1.2 nm thick exposed Co thin films occurs over the course of months, eventually leading to complete oxidation through the depth of the film. Our results differ from those reported in Refs. [26] and [28], but are in line with those reported in Ref. [27]. Moreover, our measurements definitively establish that a VDF oligomer thin film deposited on a Co thin film prevents oxidation, a crucial result with important implications for any future devices based on these ferroelectric/ferromagnetic heterostructures. We also note that these slow changes in magnetic behavior could, for example, serve as a selector of magnetic properties, such as perpendicular anisotropy or remanence, by controlling the exposure time before capping with VDF oligomer as demonstrated in figure 1b.

Figure 2. Magnetic signatures obtained from the hysteresis loops shown in figure 1. (a) Change in Kerr signal intensity ($\Delta I/I_{\max}$) of magnetic hysteresis loops as a function of time for a 1.2 nm uncapped Co thin film (black) and an all-vacuum deposited Co/VDF heterostructure (red). (b) Squareness (M_r/M_s) of magnetic hysteresis loops as a function of time for a 1.2 nm uncapped Co thin film (black) and an all-vacuum deposited Co/VDF heterostructure (red). Weighted exponential fits are shown in blue. (c) and (d) show these fitted functions on much longer time scales, with the fit error represented by the red bands. (e) PMOKE measurements on the same 1.2 nm thick Co corresponding to the data in figure 1a after about 200 days exposure. These data clarify the time dependence of Co oxidation and clearly demonstrate the protective nature of the VDF oligomer on Co thin films, which is extremely important for potential technological applications of these materials.

Because the thicknesses of these evaporated VDF oligomer thin films show the expected $1/r^2$ dependence¹⁸ (where r is the distance from the source to the substrate), we are able to investigate the thickness dependence of the VDF oligomer as a capping layer on a single large area sample. The contour map in figure 3 shows the thickness of a VDF oligomer thin film, measured with spectroscopic ellipsometry, across the full 4 cm² area of a Pt (50 nm)/Co (1.2 nm)/VDF heterostructure deposited without breaking vacuum. PMOKE measurements were taken in succession by cycling through the points labeled 1-5 on the contour map. One hysteresis loop was measured at each point during each cycle for a total of six cycles. Thus, a total of six hysteresis loops were collected periodically at each point during the first 500 minutes after the heterostructure was removed from vacuum. At all five locations, there is no change in the magnetic properties of the heterostructure during this time. Similar MOKE and ellipsometry measurements (not shown) across several separate Co/VDF heterostructures with progressively thinner VDF oligomer films indicate an oligomer film as thin as 15 nm is capable of preserving the magnetic properties of the Co thin film, an important result for device applications.

Figure 3. Thickness dependence of the VDF oligomer's ability to preserve the magnetic properties of a Co thin film. The magnetic hysteresis loops were collected in succession at the corresponding spots labeled on the thickness map. Each collection of hysteresis loops were taken over the first 500 minutes of exposure to atmosphere.

It is also important to consider the temperature dependence of the protective nature of VDF oligomer thin films. A previous study¹⁸ on the temperature dependence of VDF oligomer thin film properties found that the films begin to melt at 75 °C and are completely destroyed by 98 °C. X-ray diffraction measurements find only trace amounts of VDF oligomer remaining on the sample surface after heating to 98 °C, meaning that any Co underneath the VDF oligomer

would no longer be protected from the atmosphere. It is important to note, however, that for device applications, heating to any temperature above the ferroelectric ordering temperature, which was found to be 61 °C, renders the VDF oligomer essentially useless, as it will be in the paraelectric phase. Thin VDF oligomer films remain structurally sound up to that temperature¹⁸.

The magnetic hysteresis data shown in figures 1 and 2 clearly indicate changes in the Co thickness, but provide no information about the chemical or elemental nature of these changes. Scanning transmission electron microscopy (STEM) can be used to acquire high resolution images of the cross section of these heterostructures. However, STEM images alone show little detail of the Co/VDF oligomer interface (these images are shown in the insets of figure 4). Hence, we turned to STEM with energy dispersive spectroscopy (EDS), which allows for the acquisition of elemental composition maps across the metal/organic interface. The line scan through a STEM map of a Pt (50 nm)/Co (1 nm)/VDF heterostructure prepared without breaking vacuum between the Co and VDF oligomer depositions (as in figure 1c) is shown in figure 4a. Only the elements of interest, Co and O, are shown in figure 4a. This line scan, across the Co/VDF interface, shows an abrupt and well-defined Co layer. Due to electron interactions with the sample, STEM mapping is known to exaggerate the thickness of thin film layers due to the interaction volume which increases with transmission depth³⁷. Moreover, sample tilt within the electron microscope can affect apparent film thickness. Therefore, although there appears to be a small region of overlap between Co and O at the top interface (gray band), this is likely due to their exaggerated thicknesses.

In contrast, figure 4b shows a line scan through a STEM map of a sample that was exposed to atmosphere for one week prior to the deposition of the VDF oligomer thin film. Here, even taking into account the exaggeration of the layer thicknesses, there is a region atop the Co layer with significant counts of both Co and O (yellow band). The increased total thickness of the Co film upon exposure to oxygen is consistent with previous reports²⁷. These data, in conjunction with the magnetic hysteresis measurements, are consistent with oxide layer formation.

Figure 4. Line scans across the metal/organic interface from elemental composition maps of Co/VDF heterostructures acquired with STEM. (a) Co and O content at the Co layer in an all-vacuum deposited Co/VDF heterostructure. There is a region with overlapping Co and O counts due to volumetric interactions (gray band). (b) Co and O content at the Co layer in a heterostructure that was exposed to atmosphere for one week prior to the deposition of a VDF oligomer capping layer. There is a region with significant counts of *both* Co and O (yellow band) atop the pure Co layer in (b) that is not present in (a), supporting the assumption that the changes in the magnetic properties of the Co thin films observed in figure 1 are due to the formation of native oxide. **STEM maps are shown in the insets.**

We note that the Co counts found above and below the Co thin film layer could be due to interlayer diffusion. Furthermore, STEM measurements reveal the elemental composition at the metal/organic interface, but not the oxidation state. X-ray photoelectron spectroscopy (XPS) allows for a determination of the oxidation state by looking for changes in the binding energies of core electrons that occur due to chemical bonding. Therefore, these measurements also shed light on whether the Co counts detected atop the Co thin film via STEM are due to the presence of CoO or simply due to interlayer diffusion. XPS spectra are acquired by irradiating a given sample with x-rays and measuring the kinetic energy of the resulting core level photoelectrons. Conservation of energy then gives the binding energy of the core level electrons while shifts in these binding energies indicate the formation of chemical bonds. Cross-referencing the XPS spectra collected from the metal/organic heterostructures with the online NIST database³⁸ identifies the element or compound corresponding to each observed photoelectron peak. For a

more detailed discussion on the principles and experimental details of XPS, the reader is referred to Ref. [25].

XPS measurements, together with periodic Ar^+ sputter etching of the sample surface, provide a depth profile of the chemical composition of Co/VDF heterostructures prepared with and without breaking vacuum during deposition. Figure 5a shows the XPS spectra in the region of the Co(2p) peak from a bare, uncapped Co thin film exposed to atmosphere for two weeks. At the surface of the film (black line), the peak positions correspond to oxide states of Co: the peak at 780 eV is attributed to CoO while the peak at 796 eV could be attributed to CoO and/or Co_3O_4 , as the binding energy of those compounds differ by only a few tenths of eV in this region. Deeper within the film (red line), the clear broadening of the peaks spanning 778 – 780 eV and 793 – 796 eV indicate the presence of both oxides and metallic Co. Pure metallic Co is only found near the Pt seed layer (blue line), as indicated by the narrower peaks at 778 eV and 793 eV. This is consistent with the PMOKE data shown in figure 2a, indicating a rapid decrease in magnetization of the uncapped Co thin film. The peaks at 786 eV and 802 eV in figure 5a are satellites caused by perturbations to the photo-emitted electrons due to the holes left in their place²⁵.

Figure 5. Co(2p) XPS spectra of Co/VDF heterostructures. (a) XPS spectra of a 1.2 nm uncapped Co thin film. At the surface (black line), the film is dominated by oxidized Co, while deeper in the film (red line), the broadening of the Co(2p) peaks indicate both oxidized Co and metallic Co. Only near the Pt seed layer (blue line), do the peaks correspond to metallic Co. (b) Depth profile of the XPS peak position for both exposed Co/VDF and all-vacuum Co/VDF heterostructures, indicating that all-vacuum deposition prevents the Co from oxidizing. The colored bands indicate the positions of the peaks for CoO (pink), Co_3O_4 (yellow) and metallic Co (grey). Together, parts (a) and (b) show XPS spectra for all three samples types discussed: uncapped Co, exposed Co/VDF, and all-vacuum Co/VDF.

Figure 5b shows the location of the most prominent Co(2p_{3/2}) peak, between 778 – 780 eV and determined via Gaussian peak fitting, for two samples, one a Co/VDF sample prepared entirely in vacuum and one that was exposed for several weeks prior to being capped with VDF oligomer. The left-most data points in figure 5b correspond to depths near the interface of the Co and VDF oligomer. Subsequent spectra collected after successive rounds of Ar⁺ ion sputtering correspond to increased depths in the heterostructures and continued until the magnitude of the Pt peak stopped increasing, implying that the etch had reached the Co/Pt interface (see supplemental information). Therefore, the data points on the right correspond to the bottom of the Co thin film. For the all-vacuum deposited sample, the location of the Co(2p) peaks stays constant throughout the depth of the sample, at about 778.3 eV, corresponding to pure metallic Co. However, for the sample that was exposed to atmosphere prior to capping with VDF oligomer, the location of the Co(2p) peak corresponds to that of oxidized Co, with the monoxide, CoO, dominating the bulk of the film, consistent with previous reports^{26-29,32}. **This data also suggests that the Co counts atop the Co thin film in figure 4b are at least in part due to CoO, and not exclusively interlayer diffusion.** Further details on the extraction of Co(2p) peak locations from the XPS spectra can be found in the supplemental material accompanying this work. From figure 5b, it is clear that VDF oligomer preserves the Co thin film in its vacuum deposited state.

The bonding mechanism between the metal and organic thin films plays an important role in metal/organic heterostructures. For example, hybridization of the molecular orbitals at the interface is known to play a role in the energy level landscape, broadening and shifting the molecular energy levels at the interface^{39,40}. Furthermore, if the metal is ferromagnetic, this hybridization can be spin dependent⁴¹, which has important implications for spintronic device applications utilizing metal/organic interfaces, as the interface plays an important role in spin lifetime and charge injection.

Because the metal/organic interface plays such an important role in any potential device, there have been many studies on the topic of metal/organic bonding^{17,42}, with most falling into one of two categories: polymer on metal⁴³⁻⁴⁵ or small molecule on metal⁴⁶⁻⁴⁸ interfaces. Most studies on metal/organic interfaces employ either ultraviolet photoelectron spectroscopy (UPS) or XPS to probe binding energies at the interface. Small molecule films are soft organic materials bound by weak intermolecular van der Waals bonds, and can be vacuum deposited on clean metal surfaces. Therefore, the resulting interface should be abrupt, with chemical bonding, if

present, limited to the first molecular layer. Polymer/metal interfaces present certain challenges when using the UPS/XPS technique, however, as local structure and defects along the polymer chain, which can affect photoemission, are difficult to control: past studies have linked polymer morphology and photophysics by showing the chain length of certain conjugated polymers can affect exciton binding energy^{17,49,50}, whereas chain defects can perturb forward scattered photoelectrons⁵¹⁻⁵³.

Studies on oligomer/metal interfaces are less common than polymer/metal or small molecule/metal interfaces, and there are few, if any, UPS/XPS studies on Co/fluorinated oligomer interfaces to compare. Photoemission spectroscopy has, however, been used to probe the bonding mechanism at other metal/oligomer interfaces⁵⁴ and chemical bond formation at the interface of metallic Co and other organics, namely polybutadiene and polyimide, has been observed⁴⁴. Hence, chemical bonds may form at the Co/VDF interface, and will be manifested as XPS peak shifts of either the Co(2p) and F(1s) peaks (or both), with the shift being characteristic of such metal/organic bonding⁴⁶. For both types of heterostructures, those made entirely in vacuum and those that were exposed to atmosphere, there are no Co(2p) peaks at 782 – 783 eV, the binding energy corresponding to CoF compounds³⁸, at any depth in the heterostructures. Measurements of the F(1s) XPS peak location are shown in figure 6 as a function of VDF oligomer film depth for both all-vacuum and exposed Co/VDF heterostructures. The left-most data points correspond to spectra collected from the surface of the VDF oligomer thin film – the large shift in binding energy is attributed to surface contaminants – while the right-most data points correspond to the Co/VDF interface as inferred by the disappearance of the F(1s) peak (see supplemental information). Deeper in the film, the surface contaminants are no longer present, and the location of the F(1s) peak appears at 688.2 eV, the binding energy associated with the CH₂CF₂ monomer³⁸. As the VDF is etched away, accessing deeper regions of the film, the peak shifts to slightly lower energies (by about 0.2 eV) at the interface between VDF and Co. Typical metal fluoride peaks correspond to a much larger shift, occurring in the region of 684-685.5 eV, (i.e. shifts of 2.7-4.2 eV). This small shift may be due to bonding between the Co surface and other elements of the chain, resulting in a small shift in the F(1s) peak. For example, XPS measurements on Alq₃ on Mg show a 0.2-0.4eV shift in the Al line⁴⁶, which is attributed to Mg-C bonding⁵⁵.

Figure 6. F(1s) peak location as a function of VDF oligomer film depth for both exposed and all-vacuum deposited Co/VDF heterostructures. The large shift at the surface is attributed to surface contaminants. In both cases the location of the peak corresponds to the VDF monomer. Near the metallic Co substrate, the F(1s) peak shifts by 0.2 eV, which may suggest chemical bonding. The error bars represent the peak fitting error.

There is some evidence of chemical bonding at a metal interface (Al) in similar ferroelectric copolymers of VDF (70%) and trifluoroethylene (30%), P(VDF-TrFE)⁵⁶. Like PVDF and its copolymers, the reversible ferroelectric polarization of the VDF oligomer film is associated with axial chain rotation, indicating that weak van der Waals forces dominate the bulk of the organic layer. In Ref. [56], Bune *et al* analyzed the static and dynamic conductance switching under DC bias of P(VDF-TrFE) films. The large contrast in conductance associated with the ferroelectric saturation states and a significant difference in the time needed to saturate to each conductance state, was modeled by assuming that the monolayer of P(VDF-TrFE) in direct contact with the metal electrode is pinned, unable to rotate and contribute to a saturated ferroelectric polarization state. The F(1s) XPS peak positions (figure 6) suggest that the VDF oligomer closest to the metal/organic interface is chemically bonded, providing experimental evidence corroborating the model proposed in Ref. [56].

The oligomer/metal interface is distinct from other organic/metal interface counterparts, namely small molecule/metal and polymer/metal interfaces. As mentioned above, polymer chain defects and local morphology can affect photoemission spectra. However, since the oligomer used in this study is made of short, well-defined chains, chain folding is unlikely and VDF oligomer thin films have improved crystallinity as compared to films made of the polymer (PVDF)¹⁸. Therefore, from the oligomeric nature of the chains, together with the size of the shift and the observation that the shift in binding energy only occurs near the metal interface, not throughout the bulk of the organic layer, we conclude that this shift is not due to chain

morphology, but may indeed be due to chemical bonding. Alternatively, it is possible that this small shift should be discounted, and that the Co/VDF interface bonding occurs purely via van der Waal forces.

4. Conclusions

In conclusion, we have characterized the interface between the organic ferroelectric VDF oligomer and metallic ferromagnetic Co. Using a combination of MOKE, electron microscopy and XPS, we have definitively established the time dependence of magnetization changes in exposed Co thin films and attribute these to the formation of CoO. These changes occur over long periods of time, with time scales on the order of days and the naturally occurring CoO layer is not self-passivating. Thermally evaporated VDF oligomer films deposited on Co act as excellent protective barriers, even at thicknesses down to 15 nm, resulting in no changes in magnetic properties, little to no oxidation, and stability over a time period of at least a few weeks. XPS measurements of the F(1s) peak indicate the possibility of chemical bonding at the interface, but rule out CoF compounds. The ability of VDF thin films to “lock-in” magnetic properties could potentially serve as a mechanism for selecting desired magnetic properties, such as loop squareness, by simply timing Co exposure before depositing a capping layer.

Heterostructured Co/VDF devices are a promising candidate in the field of voltage controlled magnetism, making the characterization of the Co/VDF interface particularly important and the ability to maintain a pristine, controlled interface is imperative in understanding the magnetoelectric coupling in such a heterostructure. Our work demonstrates that the VDF oligomer is a viable candidate for use in organic-based electronics.

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