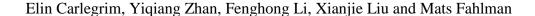
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Characterization of the $Ni/V(TCNE)_x$ interface for hybrid spintronics applications



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applications

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Abstract

Vanadium tetracyanoethylene, V(TCNE)_x, is an organic-based magnet with properties

suitable for spintronics applications, e.g. spin valves. In this paper we propose a new hybrid

organic spin valve design where V(TCNE)_x is used as a spin-transporting and spin-filtering

layer sandwiched between two ferromagnetic (FM) metal contacts, i.e. FM/V(TCNE)_x/FM.

As the spin injection and detection of such a device occurs at the interfaces the quality of

those are of crucial importance. Therefore, the Ni/V(TCNE)_x interface has been investigated

by X-ray photoelectron spectroscopy (XPS) and near edge X-ray absorption spectroscopy

(NEXAFS) as well as compared with XPS results from a model system, Ni/TCNE. Ni

chemically interact with both the vinyl and cyano groups but there is no evidence for

significant diffusion of Ni into the V(TCNE)_x film. As the chemical interaction affects the

spin injection and detection negatively by modifying the lowest unoccupied molecular orbital

(LUMO) and destroying the magnetic ordering network at the surface, these results indicate

that there is need for a buffer layer between V(TCNE)_x and Ni, and in extension most likely

between V(TCNE)_x and any FM contact.

Keywords: Organic-based molecular magnets, spintronics, interfaces, photoelectron

spectroscopy, magnetic semiconductors

1

1.1 Introduction

Spintronics is an emerging technique which exploits the spin state of the electron as well as its charge state when it is used as information carrier. The field has made major impact on today's life by improving hard drive information storage. Advantages of spintronics include cheaper production, faster data processing speeds, non-volatility and lower power consumption [1]. To date the most successful spintronic device is the spin valve. The principle of such a device is to sandwich a non-magnetic or semiconducting layer between two ferromagnetic (FM) contacts which act as spin injector and spin detector, respectively. The spin injector material has fixed magnetization while the magnetization of the spin detector material can be tuned by an external magnetic field. Hence, the magnetization of a spin valve can be altered giving high or low resistance, simulating a bit, "1" or "0" [2].

Organic-based magnets belong to the new field of organic spintronics [3] and offer advantages such as tunability of the properties via molecular design, conductivity ranging from semiconducting to insulating, low weight, low-temperature processing etc. [4], all of which make them interesting candidates for inclusion in e.g. spin valves. Vanadium tetracyanoethylene, $V(TCNE)_x$, $x\sim2$, is one of very few room temperature organic-based magnets [5]. It is however extremely air sensitive, but recently we have reported on a new preparation method leading to improved air stability [6], which should make device fabrication less complex.

The highest occupied molecular orbital (HOMO) of V(TCNE)_x is mainly localized on V(3d) and characterized by strong hybridization between V(3d) and TCNE⁻ [7,8], while the lowest unoccupied molecular orbital (LUMO) is localized on TCNE⁻ [9]. The coupling between V^{2+} and the two TCNE⁻ is antiferromagnetic, yielding a ferrimagnetic state and hence a net spin of 1/2 for V(TCNE)_x [10]. Thus, the material can be described as a fully spin-polarized semiconductor. V(TCNE)_x thus offers many of the advantages of the traditional organic semiconductors used in organic spintronics [11], but also include fully spin-polarized transport levels that should further aid both spin-injection and transport. Hence, we propose a new hybrid organic spin valve design where V(TCNE)_x is a spin-transporting *and* spin-filtering material sandwiched between two ferromagnetic (FM) metal contacts, see Fig. 1(a) and 1(b), in contrast to the previously proposed design where the V(TCNE)_x layer functions as the soft magnet (spin detector) in Fig. 1(c) [12]. The new design makes use of the fully spin-polarized transport levels of V(TCNE)_x that are expected to both enhance and preserve the injected spin polarization from the FM contacts. This spin valve could operate in a variety of modes with, e.g., a traditional soft and hard FM design or two identical FM contacts. The

former situation would enable four different resistances to be obtained, see Fig. 1(b), whereas the latter would provide only the standard on/off functionality (Fig. 1(a)) but have the advantage of using only one FM metal in the fabrication process.

As spin injection and detection in a spintronic device occurs at the FM/organic/FM interfaces, the quality of those are of crucial importance. The organic film is generally fragile and depositing a metallic material on top of it often introduces substantial damage, making the contact poorly defined. The FM atoms (or clusters) might penetrate into the organic film and chemically react with the organic molecules [15]. The magnetic properties of the FM top contact is highly dependent on the roughness of the substrate [13], which is known to be rather high of an organic surface [14], and of course of the interaction with the substrate as well. Besides, the layer between the two FMs has to be thin enough so the spins do not flip before they reach the spin detector FM [3].

In this paper X-ray photoelectron spectroscopy (XPS) and near edge X-ray absorption fine structure spectroscopy (NEXAFS) results on the $Ni/V(TCNE)_x$ interface are reported in comparison with XPS results the Ni/TCNE interface model system.

1.2 Materials and methods

 $V(TCNE)_x$ thin films (<100 Å) were prepared by a method based on physical vapor deposition, PVD [6]. The vanadium metal (purity 99.9%) was deposited using a portable Omicron® PVD source and were allowed to react with TCNE in room temperature, forming thin films on sputter-cleaned Au substrates. Thin films (~50 Å) of pristine TCNE were deposited on sputter-cleaned Au substrates at -160 °C. The base pressure in the chamber was in the high 10^{-10} mbar range and the pressure was in the low 10^{-8} mbar range during preparation of both types of films. Nickel was deposited by an Omicron® PVD source in small steps, ranging from a (sub)monolayer (~5 Å) to a multilayer (~20 Å).

The Ni/V(TCNE)_x interface was studied *in situ* using XPS and NEXAFS (performed in the partial electron yield method) at beamline D1011 of the MAX-II storage ring at the synchrotron radiation facility MAX-lab in Lund, Sweden. The end-station is equipped with a SES-200 electron energy analyzer and the base pressure of the system is low 10⁻⁹ mbar. The energy calibration was performed such as errors of the monochromator and the analyzer were taken into consideration.

Preparation and XPS of Ni/TCNE as well as preparation and additional XPS of Ni/V(TCNE)_x were performed in the home laboratory using a Scienta[®] ESCA 200 spectrometer. X-ray photoelectron spectroscopy (XPS) were performed using

monochromatized $Al(K_{\alpha})$ X-rays at $h\upsilon = 1486.6$ eV. The $Ni/V(TCNE)_x$ and Ni/TCNE interfaces were prepared under the same conditions in the home laboratory as in MAX-lab.

1.3 Results

$1.3.1 \, Ni/V(TCNE)_x$ interface

The features in the C(1s) spectrum (Fig. 2(a), bottom spectrum) of pristine V(TCNE)_x has previously been assigned to a main peak located at 285.9 eV and a shake-up on its higher binding energy side [7]. Depending on preparation method there might also be a shoulder on the lower binding energy side (at ~284 eV) of the main peak, originating from residual byproducts from the chemical reaction between the precursors [7]. For V(TCNE)_x prepared by the PVD technique this shoulder is not present since only pure vanadium and TCNE are used in the film preparation [6]. However, an excess of metal upon PVD preparation gives a low binding energy feature, which was explained by metal binding to the vinyl bridge of TCNE [6,16]. Upon increasing Ni, a shoulder on the low binding energy side of C(1s) emerges. When the sample is tilted with respect to the detector, making the measurement more surface sensitive, the shoulder becomes even more pronounced (not shown here).

The N(1s) core level (Fig. 2(b), bottom spectrum) of pristine V(TCNE)_x has its main feature at 398.5 eV. It origins from high to low binding energy from, a shake-up, vanadium-coordinated nitrogen and uncoordinated nitrogen, the latter responsible for the asymmetric N(1s) peak [7]. Given that the V^{2+} in V(TCNE)_x is known to coordinate to six nitrogen atoms, some must remain uncoordinated since each TCNE molecule contains four nitrogen [17]. Upon increasing Ni coverage, the N(1s) spectra are modified on the lower binding energy side of the main peak. However, the changes are not as evident as for C(1s) and are seen only as a broadening of the N(1s) core level. When the sample is tilted, as described above, the broadening of the N(1s) core level becomes even more obvious. The V(2p) core level (spectra not shown here) remains unchanged upon increasing Ni.

The C K-edge of pristine $V(TCNE)_x$ (Fig. 3(a)) has its absorption onset located at 284 eV, originating from a transition to the LUMO of $V(TCNE)_x$ [9,18]. When Ni is deposited on $V(TCNE)_x$, the absorption onset decreases in intensity. The same occurs for the N K-edge (Fig. 3(b)), which has its absorption onset at 397 eV [18]. The V L-edge (not shown here) remains unchanged upon Ni deposition.

1.3.2 Ni/TCNE interface

The C(1s) core level of pristine TCNE is located at 287.4 eV (Fig. 4(a), bottom spectrum). The asymmetry of the C(1s) peak originates from cyano and vinyl carbon which differs with 0.4 eV only [19]. Upon increasing Ni deposition two new features appear on the lower binding energy side of C(1s). The new features are slightly more pronounced when making the measurements more surface sensitive, but their relative intensity is still significantly lower at the corresponding multilayer coverage compared to Ni/V(TCNE)_x, suggesting a more extended interface region for Ni/TCNE.

The N(1s) core level (Fig. 4(b)) of pristine TCNE is found at 400.1 eV. Since there is only one type of nitrogen present in TCNE, the peak is symmetric and well defined. Upon increasing the thickness of the Ni layer, a new feature on the low binding energy side appears. It mimics C(1s) in that the feature is more distinct when the measurements are performed more surface sensitive. The new features appear at the same deposition step for both C(1s) and N(1s) core levels.

1.4 Discussion

Both the XPS and NEXAFS results clearly show chemical interaction between Ni and TCNE. As the V(3d) core levels and V L-edge remain unaffected by Ni there is no vanadiumnickel interaction. Hence, the possible binding situations that can occur are cyano groups bonded to Ni, vinyl groups bonded to Ni, or a combination of both bonded to Ni. Studies of similar systems (π -conjugated organic materials with vinyl- and cyano groups forming interfaces with transition metal atoms) [20] showed that the transition metal preferentially bond to the cyano group but also that the vinyl group is an option. The Ni/TCNE system indicate an interaction where both the carbon and nitrogen atoms simultaneously are affected by the Ni deposition and furthermore that two different new peaks appear in the C(1s) core level as the interface forms. This suggests that Ni attacks both the vinyl and the cyano groups of the TCNE molecule. The evolution of the C(1s) and N(1s) core levels upon Ni-deposition for the V(TCNE)_x is quite different, however. The C(1s) core level shows only one strong new peak appearing with a weak low-binding energy shoulder upon Ni-deposition. The N(1s) core level undergoes a broadening but does not display the new extended low-bonding energy feature of Ni/TCNE. This suggests that the Ni interaction with V(TCNE)_x occurs mainly at the vinyl linkage of TCNE. The likely explanation for the difference is that most of the cyano groups of V(TCNE)_x are coordinated to vanadium ions and hence not available as reaction sites. The distinct peak closest to the original C(1s) core level feature in Figs. 2(a) and 4(a) are thus assigned to vinyl carbon – nickel bonds and the weak shoulder in Fig. 2(a) (second new peak in Fig. 4(a)) are assigned to cyano group – nickel bonds, the latter producing the new low binding energy feature in the N(1s) core level spectra of Fig. 4(a). The evidence for lesser Ni diffusion into the $V(TCNE)_x$ as compared to TCNE is likely an affect of the compactness of the $V(TCNE)_x$ films obtained from PVD fabrication [6].

The Ni induced disruption of the vinyl linkage (and non-coordinated cyano groups) greatly modifies the LUMO of V(TCNE)_x (as evident from the sharp decrease in intensity of the C and N K-edge absorption edges). This will increase the electron injection barrier as well as degrade the magnetic property of the interface region. Hence, a Ni/V(TCNE)_x contact, and in extension probably any FM transition metal contact, is not optimal for use in a spin valve based on V(TCNE)_x. In conventional organic electronics, inserting a buffer layer between the top contact and the organic layer has been widely adopted in order to eliminate the risk of chemical interaction between the layers and hence improve the device performance [21, 22]. This approach has recently successfully been adopted in spintronics devices, as well [23]. The results above indicate that a buffer layer between V(TCNE)_x and Ni should be employed in design and fabrication of devices based on V(TCNE)_x.

1.5 Conclusions

In this paper a new hybrid organic spin valve design, i.e. $FM/V(TCNE)_x/FM$, is proposed, where the semiconducting $V(TCNE)_x$ layer delivers both spin-transporting and spin-filtering functionality. The electronic structure of the $Ni/V(TCNE)_x$ interface was investigated by means of XPS and NEXAFS and the results were interpreted together with XPS studies of the Ni/TCNE model system. $V(TCNE)_x$ and Ni interact chemically at the interface and both the cyano (that are not coordinated to V) and the vinyl groups participating in the reaction while vanadium remains unaffected. The interface region is fairly abrupt with no significant Ni diffusion into the $V(TCNE)_x$. The disruption of the vinyl linkage (and non-coordinated cyano groups) greatly modify the former LUMO of $V(TCNE)_x$ which will increase the electron injection barrier as well as degrade the magnetic network at the surface. These results indicate the need for a buffer layer between $V(TCNE)_x$ and Ni, and in extension most likely for any FM contact in the $FM/V(TCNE)_x$ structure.

Acknowledgements

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Figure captions

Figure 1. Different spin valve designs and their possible resistances. (a) $V(TCNE)_x$ sandwiched between two identical FM contacts. (b) $V(TCNE)_x$ sandwiched between two different FM contacts. (c) $V(TCNE)_x$ and a FM contact sandwiching an organic semiconductor. Since $V(TCNE)_x$ is a semiconductor, a metallic contact on top of $V(TCNE)_x$ is needed. (d) The chemical structure of TCNE.

Figure 2. Core levels upon increasing Ni deposition on $V(TCNE)_x$. The spectra are shifted with respect to pristine $V(TCNE)_x$. (a) C(1s), taken at photon energy 400 eV. (b) N(1s), taken at photon energy 720 eV.

Figure 3. NEXAFS spectra upon increasing deposition of Ni on $V(TCNE)_x$. (a) C K-edge. (b) N K-edge.

Figure 4. Core levels upon increasing Ni deposition on pristine TCNE. The spectra are measured with respect to the Fermi level energy. (a) C(1s). (b) N(1s). The two topmost spectra of C(1s) and N(1s), respectively, are taken at the same Ni thickness, but the sample position with respect to the detector is different in order to make the measurements of the topmost of all spectra more surface sensitive.

Figures

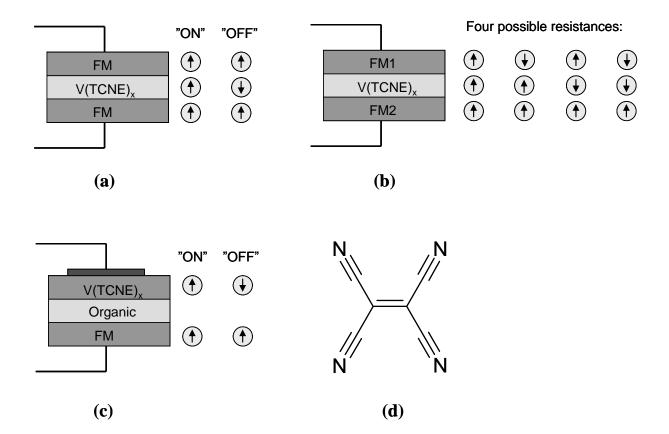


Figure 1.

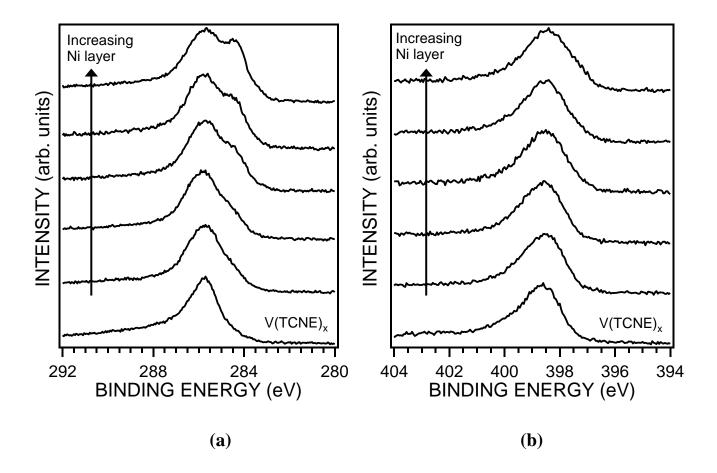


Figure 2.

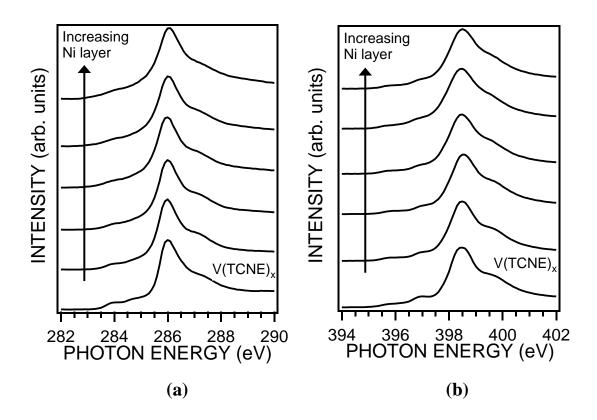


Figure 3.

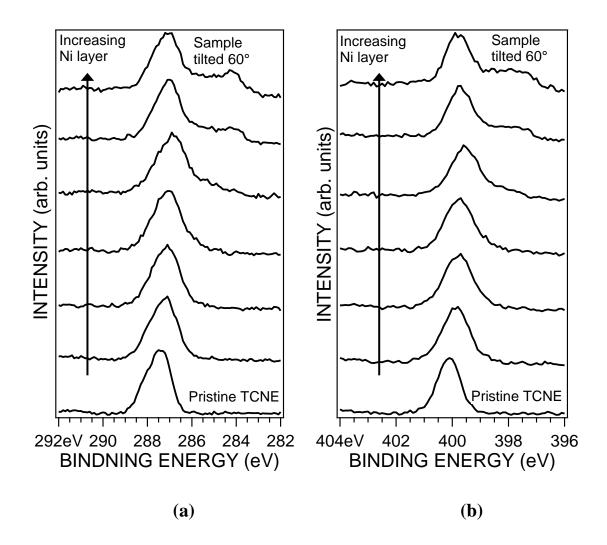


Figure 4.