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Investigation of thin films of organic-based magnets grown by physical vapor deposition

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Thin films of organic-based magnet, V[TCNE]_x (TCNE: tetracyanoethylene), were deposited by physical vapor deposition (PVD) based reactive evaporation. The growth conditions were studied in detail. A saturated composition of V[TCNE]_{~1.9} was determined by optimizing the growth condition. Two sets of films with different V to TCNE ratios were characterized. Both films were magnetic ordered up to 400 K and held coercive field of 60 Oe at room temperature. With the presence of excess vanadium within the film, the increase of defects created by PVD results in significant change in electronic property. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4897494>]

V[TCNE]_x is the first organic-based magnet having the magnetic ordering temperature above room temperature.¹ The exchange coupling between unpaired electrons of V²⁺ (S = 3/2) cation and TCNE⁻ (1/2) anion makes this polymeric complex ferrimagnetic with net magnetic moment of 1 μ_B. The material is overall disordered, yet with a well-defined local structure, in which each V ion is surrounded by six cyano-groups from TCNE molecules with octahedral geometry.² It has been demonstrated as a spin-polarizer in organic-based spintronics research due to its multiple advantages that include: high magnetic ordering temperature, semiconducting with activation energy ~0.5 eV,³ fully spin polarized electronic structure, and low processing temperature. These features are critical for fabricating all-organic spin devices. Spin tunnel junctions and spin-LED have both been demonstrated using V[TCNE]_x as spin polarizer.⁴⁻⁸

V[TCNE]₂ was first synthesized by the solution method.¹ Thin films of V[TCNE]_x were later deposited by several different techniques that include chemical vapor deposition (CVD),^{9,10} physical vapor deposition (PVD),¹¹ and molecular layer deposition (MLD).⁷ CVD has been the first and a promising method to deposit thin films of V[TCNE]_x. The later development of MLD was for the deposition of uniform and ultrathin films. Both CVD and MLD have mostly utilized V(CO)₆ as the vanadium source although V(C₆H₆)₂ has also been used. Alternatively, the PVD method directly utilizes metallic vanadium as the vanadium source. This makes PVD an advantageous method in studying organic-based magnets. For instance, because this method does not require organometallic precursor, it is in principal free of contamination from by-products. For the same reason, the selection of metal elements is broader.

Thin films of several metal-TCNE complexes have been previously grown by the PVD method.¹¹⁻¹⁴ However, more information is still needed to further understand the nature of V[TCNE]_x made from this method. In this work, the growth condition of V[TCNE]_x films are studied in detail. By monitoring the growth, we determined the stoichiometry of V[TCNE]_x and further identify the saturated concentration

of TCNE within the film. Meanwhile, the magnetic properties were characterized for samples of different V to TCNE ratios. Finally, we found that the difference in stoichiometry can significantly change the electronic property of the PVD-made V[TCNE]_x.

The deposition was performed in a reactor with base pressure below 10⁻⁸ Torr. Vanadium was vaporized using an e-beam evaporator. During deposition, TCNE vapor was introduced to the reactor through a leak valve. A quartz crystal microbalance (QCM) was used to monitor the deposition. Once a stable pressure of TCNE was achieved, silicon substrates were moved to the deposition zone so that V[TCNE]_x can be deposited on the substrates. After deposition, the substrates were transferred to an argon-filled drybox for further analyses. The depositions were performed at room temperature.

The growth of thin films of V[TCNE]_x can be regulated by both vanadium flux and TCNE pressure. Two sets of samples with different V/TCNE ratios were made with different vanadium fluxes while the TCNE pressure (6.5 × 10⁻⁷ Torr) was kept constant. Figure 1(a) shows the mass changes

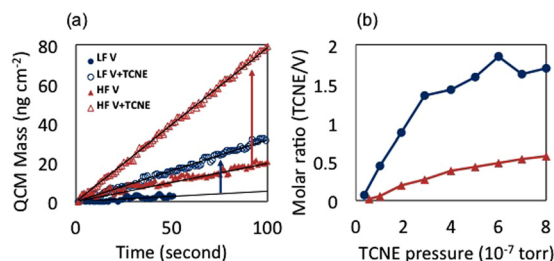


FIG. 1. (a) Changes of deposited mass during depositions monitored by QCM. The blue circles represent the data from a lower vanadium flux (LF); the red triangles represent the data from a higher vanadium flux (HF). The solid symbols represent deposition of vanadium only; the hollow symbols represent the deposition of vanadium under TCNE vapor pressure of 6.5×10^{-8} Torr. Black lines are the fitted trend lines. (b) Molar ratio determined by QCM results versus TCNE pressure with constant vanadium flux. Red triangles represent the data from a higher vanadium flux; blue dots represent the data from a lower vanadium flux.

monitored by a QCM during different growth conditions. Comparing to the deposition of only vanadium, the growth rate increases significantly in the presence of TCNE. This increase in deposition rate primitively confirmed the adsorption/reaction of TCNE with vanadium. The molar ratio of V/TCNE for each growth condition can be calculated by the deposition rates with and without the presence of TCNE vapor (see supporting information Figure S1 and Table S1).¹⁵

As described above, thin films of two different compositions were deposited by tuning vanadium flux. Thin films that have QCM-estimated composition of $V[TCNE]_{1.2}$ were deposited with a higher vanadium flux (deposition rate, $\sim 0.20 \text{ ng cm}^{-2} \text{ s}^{-1}$). To increase the TCNE concentration of the film, lower vanadium flux (deposition rate, $\sim 0.05 \text{ ng cm}^{-2} \text{ s}^{-1}$) was used and a sample with composition of $V[TCNE]_{1.8}$ was made. The compositions of these films were determined by x-ray photoelectron spectra of V 2p and N 1s orbitals, where the molar ratios of TCNE/V were 1.2 for sample with higher vanadium flux and 1.9 for sample with lower vanadium flux. The results are consistent with the molar ratios estimated from QCM data. However, it should be noted that the TCNE concentration would easily be over-estimated by calculation based on the QCM results. This is likely due to the adsorption/reaction of other reactive species such as oxygen. Therefore, the QCM-determined molar ratio is only valid when the precursor cell is well-evacuated prior to the deposition. Densities of both films were found to be about 1.3 g/cm^3 by combining the QCM results and film thicknesses determined by atomic force microscopy (AFM). The density is between those of $V[TCNE]_x$ made by solution method and MLD.^{7,16}

Alternatively, the molar ratio between V and TCNE can be tuned by varying the TCNE pressure while keeping the vanadium flux constant. We utilized this approach to determine the saturated stoichiometry of $V[TCNE]_x$. The relationship between TCNE vapor pressure and molar ratio of the resulting films is shown in Figure 1(b). With a constant vanadium flux, the TCNE concentration continuously increased when the TCNE pressure increasing from $5 \times 10^{-8} \text{ Torr}$ to $8 \times 10^{-7} \text{ Torr}$. To pursue the saturation ratio, while keeping the TCNE pressure within the same range, we used a lower vanadium flux. At the lower vanadium flux, the TCNE concentration increased linearly at pressure up to $8 \times 10^{-7} \text{ Torr}$ and then started leveling off at TCNE pressure of $3 \times 10^{-7} \text{ Torr}$. The maximum TCNE/V ratio is close to 1.9. This saturation value is close to the previously reported results of $V[TCNE]_x$ made from solution and CVD methods that both hold the value of ~ 2 .^{1,9} Moreover, it is in good agreement with previously reported $V[TCNE]_x$ and analogues made from the PVD method.^{11–13}

Figure 2 shows the XP spectra of thin films of the two different stoichiometries, $V[TCNE]_{1.9}$ and $V[TCNE]_{1.2}$, described in Figure 1(a). Figure 2(b) shows the C1s spectra, where the carbon peaks close to 286 eV with shoulder on the high energy side are consistent with previously reported result for $V[TCNE]_x$.¹¹ The peaks around 284.6 eV are attributed to adventitious carbon. Without considering the contribution from adventitious carbon, the carbon to nitrogen ratios are 1.61 and 1.48 for the $V[TCNE]_{1.9}$ and $V[TCNE]_{1.2}$

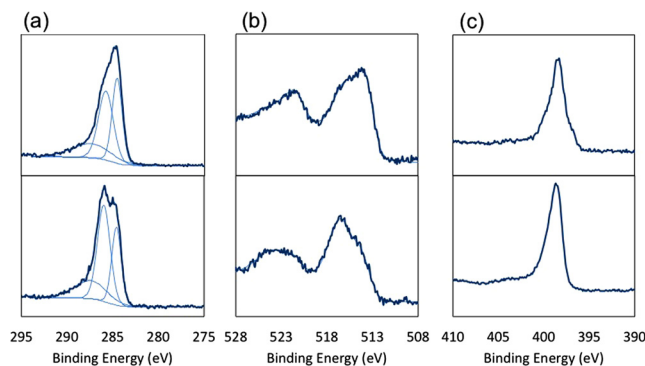


FIG. 2. XPS spectra of (a) C 1s, (b) V 2p, and (c) N 1s, where the top spectra were taken from the $V[TCNE]_{1.1}$ sample and bottom spectra were from the $V[TCNE]_{1.9}$ sample.

samples, respectively, that are close to the theoretical ratio of 1.5 for TCNE molecule. Figure 2(b) shows the V 2p spectra. The two bands in spectra are due to spin-orbit coupling. In each band, the lower-energy part is attributed to V^{2+} for $V[TCNE]_x$ and the higher-energy part is due to oxidized species.⁹ Comparing to $V[TCNE]_{1.9}$, the $V[TCNE]_{1.2}$ film has a higher percentage of V^{2+} than vanadium species with higher oxidation states. This observation reflects that vanadium is the electron donor in this charge-transfer polymeric complex; therefore, higher concentration of vanadium would result in a more reduced material. Figure 2(c) shows the N 1s XPS spectra. The spectrum for $V[TCNE]_{1.9}$ film shows a main peak around 398.5 eV with a broad shake-up band that is similar to the previously reported results.^{9,11} However, in the N 1s spectrum of $V[TCNE]_{1.2}$ film, a shoulder at the low energy side of the main peak was observed. This shoulder may result from the alternative bonding between vanadium and TCNE due to the direct reaction of vanadium atoms to TCNE, which has been proposed for other metal/TCNE complexes made by the PVD-based methods.^{12–14,17}

Figure 3 shows the coercive fields of samples of different vanadium to TCNE stoichiometry at 100 K and 300 K. Other than the slightly lower coercivity for the sample with high vanadium concentration, there was no significant V/TCNE-ratio dependence in their coercive fields. All films showed coercivities close to 60 Oe at 300 K and 80 Oe at 100 K, which are in line with previously reported values.¹¹ Figure 4 shows the temperature dependence of magnetization in two sets of samples, $V[TCNE]_{1.9}$ and $V[TCNE]_{1.2}$, as

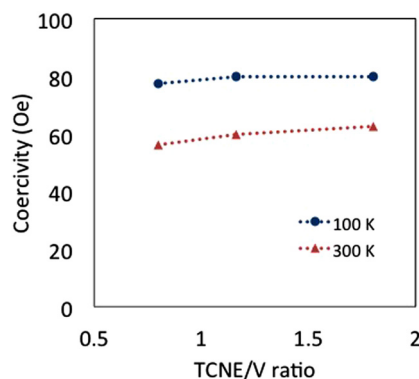


FIG. 3. Coercivities of sample of different V:TCNE ratios at 100 K and 300 K.

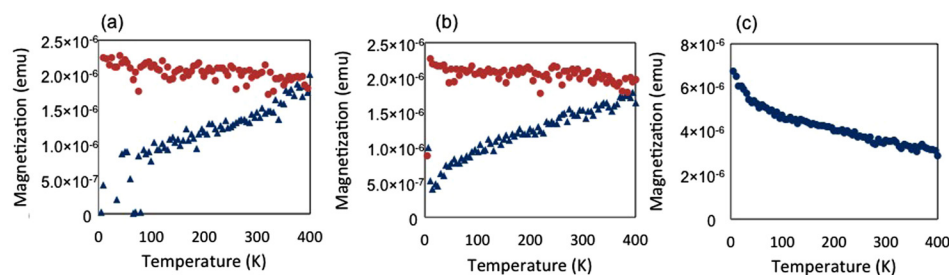


FIG. 4. (a) FC (red dots) and ZFC (blue triangles); (b) FC (red dots) and ZFC (blue triangles); (c) magnetic remanence after cooling with 1000 Oe magnetic field.

those in Figure 1(a). Figures 4(a) and 4(b) show the zero-field- and field-cooled curves of both films at 100 Oe, and Figure 4(c) shows the remanence of the V[TCNE]_{1,2} film after applying a 1000 Oe magnetic field. Both types of samples were showing magnetic-ordering up to 400 K. Some of the samples were observed with a more clear partial drop in magnetization at temperature as high as ~ 360 K (see supporting information Figure S2).¹⁵ This is qualitatively consistent with the result from previously reported V[TCNE]_x made by PVD-based method and other methods.^{9,11} The reason for the magnetization close to 400 K is not understood. This, either the delay of the structural rearrangement or any alternative structure that contributes to the magnetism, suggests the samples made from our method are more complicated in structure than previously reported V[TCNE]_x. More details on the structure are needed to clarify the origin of the material properties.

The activation energies of V[TCNE]_{1,9} and V[TCNE]_{1,2} were examined by the temperature dependence of electrical resistivity.³ The activation energy of V[TCNE]_{1,9} was found to be 0.57 eV, which is higher than the previously reported value for V[TCNE]_x (0.45–0.5 eV).^{3,7} Based on a proposed model, however, the measured activation energy would decrease due to the increase in structural disorder.¹⁸ Therefore, the difference in activation energy here, comparing to previously reported V[TCNE]_x, may be affected by not only structural disorder but also bonding defects due to the PVD process as well as possible degradation of the sample. V[TCNE]_{1,2} was not measured with a meaningful result by analyzing with the simple Arrhenius equation. This may be caused by the higher degree of defects in the sample generated with higher vanadium concentration.

In conclusion, thin films of V[TCNE]_x of different V/TCNE ratios were grown by PVD. The saturated concentration of TCNE was determined to be ~ 1.9 that is close to the previously reported composition of V[TCNE]_{~2}. The magnetic ordering temperature is relatively high and shows no stoichiometry-dependence. There is a significant variation in activation energies of films of different V to TCNE ratio. The transport property is different from V[TCNE]_x made by

other methods; meanwhile, it can be significantly affected by the presence of excess vanadium. As the magnetic and electronic structures of the PVD-made V[TCNE]_x are complex, with better understanding, it can be an intriguing target in organic-based magnets and organic spintronics.

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¹⁵See supplementary material at <http://dx.doi.org/10.1063/1.4897494> for detailed QCM analyses and temperature dependence of magnetization.

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