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Air-stable organic-based semiconducting room temperature thin film magnet for spintronics applications

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Herein, we report on a preparation method of vanadium tetracyanoethylene, $V(TCNE)_x$, an organic-based semiconducting room temperature thin film magnet. Previously, this compound has been reported to be extremely air sensitive but this preparation method leads to $V(TCNE)_x$, which can retain its magnetic ordering at least several weeks in air. The electronic structure has been studied by photoelectron spectroscopy and the magnetic properties by superconducting quantum interference device. The properties mentioned above, in combination with complete spin polarization, makes this air-stable $V(TCNE)_x$ a very promising material for spintronic devices.

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Vanadium tetracyanoethylene, $V(TCNE)_x$, $x \sim 2$, is one of very few room temperature organic-based magnets¹ and belongs to the $V(TCNE)_x$ family, where $M = V, Mn, Fe, Co, Ni$, etc.²⁻⁶ The high Curie temperature in combination with semiconducting behavior and complete spin polarization⁷ makes $V(TCNE)_x$ a promising material for spintronic applications.⁸ A main problem of $V(TCNE)_x$, however, is its extreme air sensitivity^{2,9-11,13} and that residual solvent molecules and/or precursor-based by-products negatively affect magnetic properties^{11,14} as well as introduce electron trap states.¹⁵ Here, we present a *in situ* preparation method based on physical vapor deposition (PVD) resulting in films free from residual solvent molecules and precursor-based by-products. Our first result shows that PVD-prepared $V(TCNE)_x$ films can retain their magnetic properties (at least) for several weeks in air, which is a necessary step toward development of practical applications.

Organic-based magnets exhibit properties typically not associated with conventional magnets, such as tunability of properties via chemical routes, low weight, low temperature manufacturing, semiconducting to insulating conductivity, flexibility, etc.¹ When $V(TCNE)_x$ was discovered in 1991,² it was prepared by organic synthesis, forming an insoluble, solvent-containing powder, $V(TCNE)_x \cdot y(\text{solvent})$, where $x \sim 2$ and $y \sim 0.5$. In addition to residual solvent, it also contains by-products originating from the reaction between the precursors. As a solvent-containing powder, $V(TCNE)_x$ is extremely air sensitive and decomposes after a few seconds in air, sometimes in a pyrophoric manner.²

The problem of residual solvent was eliminated by the preparation of $V(TCNE)_x$ by chemical vapor deposition (CVD).^{9,10} In the CVD process, the precursors, TCNE, and bis(benzene)vanadium, $V(C_6H_6)_2$ [or vanadium hexacarbonyl, $V(CO)_6$] react, forming a solvent-free thin magnetic $V(TCNE)_x$ film onto a substrate. The lack of solvent molecules cause increased structural order, and hence, improved magnetic characteristics.¹⁴ However, the CVD-prepared

magnets still contain reacted oxygen and, generally, also residual by-products^{13,15} and degrade after only a few minutes or hours in air depending on the precursor used.^{9,10} Recently, an ultrahigh vacuum (UHV) compatible CVD-based preparation method was presented,¹² enabling both preparation and characterization of completely oxygen-free $V(TCNE)_x$ thin films. However the oxygen-free $V(TCNE)_x$ thin films also contain (traces) of by-products from the chemical reaction.^{12,13}

In order to eliminate the deleterious effect of the metal-containing precursor, we have developed a method based on PVD. Instead of precursor compounds such as $V(C_6H_6)_2$ (Ref. 2) or $V(CO)_6$,¹⁴ pure metal is used, avoiding the use of (often hazardous) metal-containing precursors, which (in addition to creating structural disorder) can be difficult to prepare and are not always commercially available. Preparation in UHV leads to completely oxygen-free thin films.

Two sets of thin films were prepared for the photoelectron spectroscopy studies. One set of $V(TCNE)_x$ thin films (tens of angstroms) was prepared by the PVD-based method. The vanadium metal (99.9% purity) was deposited by using a portable Omicron® PVD source and were allowed to react with TCNE, forming a thin film on sputter-cleaned gold substrates. The other set of $V(TCNE)_x$ thin films (a few nanometers) were deposited by an UHV-compatible CVD system of our own design.¹² The films were characterized *in situ* with x-ray spectroscopy (XPS) and ultraviolet spectroscopy (UPS), by a Scienta® ESCA 200 spectrometer. XPS and UPS were performed by using monochromatized $Al K\alpha$ x-rays at $h\nu = 1486.6$ eV and HeI at $h\nu = 21.2$ eV, respectively. The experimental condition was such that the full width at half maximum (FWHM) of the gold Au ($4f_{7/2}$) was 0.65 eV and the resolution of UPS was 0.1 eV, measured from the Fermi edge of gold.

Figure 1(a) depicts the XPS core level spectra of C (1s) of PVD- and CVD-prepared $V(TCNE)_x$, respectively. The features in the C (1s) spectrum of the CVD-prepared $V(TCNE)_x$ originates from high to low binding energy to shake up events and the main peak. The C (1s) core level features of PVD-prepared $V(TCNE)_x$ with a main peak lo-

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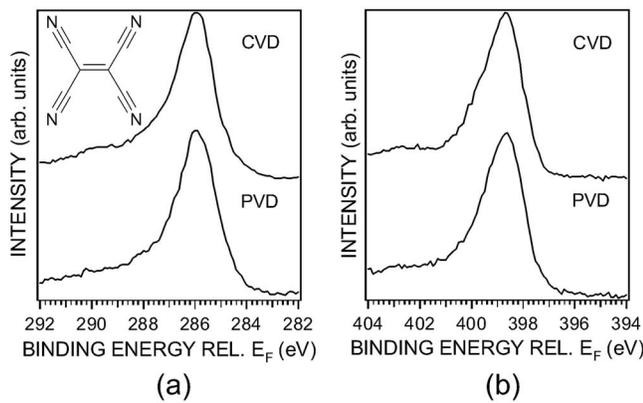


FIG. 1. XPS core levels of $V(TCNE)_x$ prepared by PVD and CVD, respectively. (a) C (1s). (b) N (1s). The chemical structure of TCNE is inserted in (a).

cated at 285.9 eV mimics the corresponding “best practice” CVD $V(TCNE)_x$. The N (1s) XPS core level spectra of the PVD- and CVD-prepared $V(TCNE)_x$ films are shown in Fig. 1(b). The features in the N (1s) core level spectra of the CVD-prepared thin film is assigned to, from high to low binding energy; shake up, uncoordinated nitrogen and vanadium-coordinated nitrogen of $TCNE^-$.¹² Similar to the C (1s), the N (1s) peak of PVD-prepared film is identical to N (1s) of the CVD-prepared thin film, indicating an identical chemical environment for the carbon and nitrogen species in the two systems. The V (2p) core levels (not shown here) are also identical for the CVD- and PVD-prepared $V(TCNE)_x$ films, with the V (2p) doublet located at around 514 eV [$V(2p)_{3/2}$] and 521 eV [$V(2p)_{1/2}$], and hence, assigned to be in the V^{2+} state.^{9,10,16} The ratio between vanadium and nitrogen was determined by comparing the relative heights of the XPS peaks of the PVD- and CVD-prepared $V(TCNE)_x$ thin films, respectively, and the vanadium to nitrogen ratio is the same, both (within the error bars for the measurement) giving a stoichiometry of roughly two TCNE molecules per vanadium ion as expected.

Previous studies of the valence band of CVD-prepared $V(TCNE)_x$ thin films show three features in the 5–0 eV binding energy region.^{12,13} These peaks can be assigned to the destabilized highest occupied molecular orbital of TCNE at 3.5 eV, the $(TCNE)^-$ singly occupied molecular orbital at 2.5 eV, and the triply occupied 3d level of the V^{2+} ion at 1.0 eV, respectively.¹² (Note that the frontier occupied electronic structure in fact is slightly more complex due to the hybridization effects between V (3d) and π -orbital(s) of TCNE).^{12,13} The same features are present (see Fig. 2) for both the PVD- and CVD-prepared thin films but the features are slightly more pronounced in the spectrum of PVD-prepared $V(TCNE)_x$. This is a sign of increased structural (and chemical) order in the thin films obtained by the PVD-based method, as compared to the CVD films.

Thicker films of $V(TCNE)_x$ (tens of nm) for superconducting quantum interference device (SQUID) measurements were prepared by the PVD method on 0.0007 mm thin Mylar (polyethylene terephthalate) foil. The film of $V(TCNE)_x$ deposited on Mylar foil was characterized by a Quantum Design magnetic property measurement system (MPMS) XL SQUID magnetometer. The measurements were made by using the reciprocating sample option mode which gives the

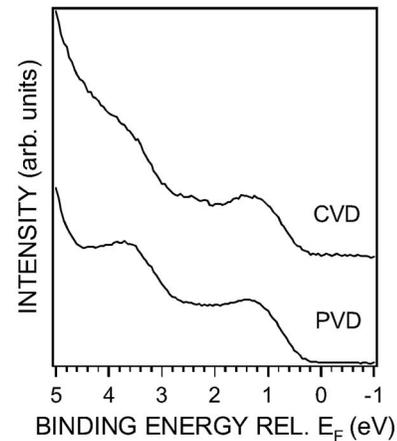


FIG. 2. HeI UPS valence region electronic structure of $V(TCNE)_x$ prepared by PVD and CVD, respectively.

highest possible sensitivity (5×10^{-9} emu) for the MPMS. Note that the film had been stored in ambient atmosphere (air) for several weeks before the SQUID measurements were performed.

A magnetization versus applied field $M(H)$ curve taken at 200 K is depicted in Fig. 3(a), where a ferromagnetic hysteresis behavior superposed on a paramagnetic background signal is observed, the latter originating from the Mylar film. The coercive field obtained is ~ 65 Oe, which is higher than expected for defect-rich CVD-prepared $V(TCNE)_x$ but similar to what is obtained for relatively defect-free CVD-prepared $V(TCNE)_x$.¹¹ The temperature dependence (zero field cooled) of the magnetization at an applied field of 20 Oe is depicted in Fig. 3(b). The Curie temperature is extrapolated from the sharp drop/edge of the $M(T)$ curve as $T_C \sim 365$ K, also is in line with the reported values for CVD-prepared $V(TCNE)_x$ (320–400 K).^{11,14} More importantly, the magnetic measurements showed a largely improved air stability and $V(TCNE)_x$ thin films fabricated by this PVD-based technique can retain their magnetic ordering even after *several weeks* in air.

The reason for the largely improved air stability is not clear. The photoelectron spectroscopy results show that the two materials are very similar in question of composition and electronic structure, although the results clearly point to better ordered films with fewer defects for the PVD method. Most likely, the $V(TCNE)_x$ network becomes stronger as impurities (such as residual solvent and/or by-products) prevent

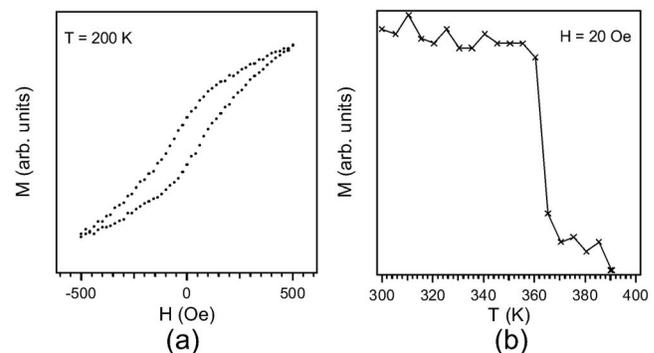


FIG. 3. SQUID measurements of $V(TCNE)_x$ prepared by PVD. (a) Hysteresis curve at 200 K. (b) Temperature dependence at 20 Oe applied field (zero field cooled).

long-range magnetic ordering and uncoordinated or incorrectly coordinated V and TCNE may act as reaction sites for oxidation. The PVD-prepared magnets may also be denser packed due to the lack of solvent and residual byproducts in the film, making it more difficult for oxygen and water to penetrate/diffuse into the film. These mechanisms have been previously used to explain improved air stability in $M(\text{TCNE})_x$ magnets¹¹ and are consistent with the experimental results presented.

Another advantage is that the PVD method enables preparation of an unlimited number of other organic-based magnets in this family, by varying the metal, the organic molecule or both, as well as preparation of multimolecule or multimetal systems such as $M'_z M''_{1-z}(\text{TCNE})_x$, $0 < z < 1$,^{17,18} without having to synthesize suitable precursors.

In summary, we have developed a preparation method based on PVD of the semiconducting room temperature molecular magnet $V(\text{TCNE})_x$. This method produces $V(\text{TCNE})_x$ that lacks the problem with residual solvent and precursor materials, which has shown to negatively affect the magnetic properties of the material. Preparation by this method results in $V(\text{TCNE})_x$, which retain room temperature ordering (at least several weeks) in air. It also enables preparation of an unlimited number of other organic-based magnets in this family. Hence, the technique should facilitate a much more rapid development of new organic-based magnets as well as enable “real” devices to be fabricated and used in ambient environments.

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