Video Article

Chemical Vapor Deposition of an Organic Magnet, Vanadium Tetracyanoethylene

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Abstract

Recent progress in the field of organic materials has yielded devices such as organic light emitting diodes (OLEDs) which have advantages not found in traditional materials, including low cost and mechanical flexibility. In a similar vein, it would be advantageous to expand the use of organics into high frequency electronics and spin-based electronics. This work presents a synthetic process for the growth of thin films of the room temperature organic ferrimagnet, vanadium tetracyanoethylene ($V[TCNE]_x$, $x{\sim}2$) by low temperature chemical vapor deposition (CVD). The thin film is grown at <60 °C, and can accommodate a wide variety of substrates including, but not limited to, silicon, glass, Teflon and flexible substrates. The conformal deposition is conducive to pre-patterned and three-dimensional structures as well. Additionally this technique can yield films with thicknesses ranging from 30 nm to several microns. Recent progress in optimization of film growth creates a film whose qualities, such as higher Curie temperature (600 K), improved magnetic homogeneity, and narrow ferromagnetic resonance line-width (1.5 G) show promise for a variety of applications in spintronics and microwave electronics.

Video Link

The video component of this article can be found at http://www.jove.com/video/52891/

Introduction

The organic-based ferrimagnetic semiconductor vanadium tetracyanoethylene ($V[TCNE]_x$, $x{\sim}2$) exhibits room temperature magnetic ordering and promises the advantages of organic materials for magnetoelectronic applications, such as flexibility, low cost production, and chemical tunability. Previous studies have demonstrated functionality in spintronic devices, including hybrid organic/inorganic[1,2] and all-organic spin valves[3], and as a spin polarizer in an active organic/inorganic semiconductor heterostructure[4]. In addition, $V[TCNE]_{x\sim 2}$ has demonstrated promise for inclusion in high frequency electronics due to its extremely narrow ferromagnetic resonance linewidth[5].

There are four different methods which have been established for synthesizing $V[TCNE]_{x\sim 2}$[6-9]. $V[TCNE]_{x\sim 2}$ was first synthesized as powder in dichloromethane via reaction of TCNE and $V(C_6H_6)$[6]. These powders exhibited the first room temperature magnetic ordering observed in an organic-based material. However, the powder form of this material is extremely air sensitive, limiting its application in thin film devices. In 2000, a chemical vapor deposition (CVD) method was established for creating $V[TCNE]_{x\sim 2}$ thin films[7]. More recently physical vapor deposition (PVD)[8] and molecular layer deposition (MLD)[9] have also been used to fabricate thin films. The PVD method requires an ultra-high vacuum (UHV) system and both PVD and mLD methods require extremely long times to grow films thicker than 100 nm, whereas the CVD films can easily be deposited in thicknesses ranging from 30 nm to several microns. In addition to the variety of thicknesses available with the CVD method, extensive studies have yielded optimized films that consistently show high quality magnetic properties including: narrow ferromagnetic resonance (FMR) linewidth (1.5 G), high Curie temperature (600 K), and sharp magnetic switching[5].

Magnetic ordering in $V[TCNE]_{x\sim 2}$ thin films proceeds via an unconventional route. SQUID magnetometry measurements show strong local magnetic ordering, but the absence of X-ray diffraction peaks and featureless transmission electron microscopy (TEM)[10] morphology reveal a lack of long-range structural order. However, extended X-ray absorption fine-structure (EXAFS) studies[11] show that each vanadium ion is octahedrally coordinated with six different TCNE molecules, indicating a robust local structural order with a vanadium-nitrogen bond length of 2.084(5) Å. Magnetism arises from an antiferromagnetic exchange coupling between the unpaired spins of the $TCNE^-$ radical anions, which are distributed across the entire $TCNE^-$ molecule , and the spins on the V^{2+} ions, leading to a local ferrimagnetic ordering with T_C ~ 600 K for optimized films[5]. In addition to exhibiting room temperature magnetic ordering, $V[TCNE]_{x\sim 2}$ films are semiconducting with 0.5 eV bandgap[12]. Other properties of note include possible sperimagnetism below a freezing temperature of ~150 K[13,14], anomalous positive magnetoresistance[12,15,16], and photo-induced magnetism[13,17,18].

The CVD method for synthesizing $V[TCNE]_{x\sim 2}$ thin films is compatible with a variety of substrates due to low temperature (<60 °C) and conformal deposition. Previous studies have shown successful deposition of $V[TCNE]_{x\sim 2}$ on both rigid and flexible substrates[7]. Further, this deposition technique lends itself to tuning through modification of precursors and growth parameters.[19-22] While the protocol shown here yields the most optimized films to date, significant progress has been made in improving some of the film properties since the discovery of this method and further gains may be possible.

Protocol

1. Synthesis and Preparation of Precursors

1. Preparation of $[Et_4N][V(CO)_6]$[23]
    1. In a nitrogen glovebox, cut 1.88 g of sodium metal into ~40 pieces and mix with 14.84 g of anthracene in 320 ml of anhydrous tetrahydrofuran (THF) in a 1 L three-neck round bottom flask.
       CAUTION: Both sodium metal and tetrahydrofuran are highly flammable.
    2. Stir the solution for 4.5 hr at RT under a nitrogen atmosphere until a deep blue solution of $NaC_{14}H_{10}$ is formed.
    3. Cool the solution to 0 °C.
    4. In a nitrogen glovebox, prepare a pink-red solution of $VCL_3(THF)_3$ by adding 400 ml of anhydrous THF into 7.48 g of $VCl_3(THF)_3$ in a 500 ml round bottom flask and stir at RT for 1 hr.
    5. Remove the pink-red solution $VCl_3(THF)_3$ from the glovebox and cool to 0 °C for 20 min. Transfer to the previous solution of $NaC_{14}H_{10}$ via cannula under nitrogen atmosphere. A homogeneous deep purple solution is formed immediately after the addition is completed.
    6. Remove from the nitrogen and stir for 15 hr. Slowly warm to RT by placing flask in ice bucket allowing the ice to melt O/N.
    7. Cool the solution again to 0 °C and fill the reaction flask with carbon monoxide. The solution will change from deep purple to yellow-brown in a matter of minutes.
       CAUTION: Carbon monoxide is highly toxic. This step should not be performed alone and a carbon monoxide alarm should be installed in the lab.
    8. Stir the solution under a carbon monoxide atmosphere at 0 °C for 15 hr and then slowly warm to RT.
    9. Remove all but 200 ml of THF under vacuum. Add 500 ml of O_2 free water while stirring the solution. $V(CO)_6$ is easily oxidized and the presence of O_2 will result in a low yield.
    10. Filter the resulting yellow slurry into a solution composed of 20.8 g of tetraethylammonium bromide (Et_4NBr) in 200 ml of H_2O.
    11. Wash the filter cake with O_2 free water until it is colorless.
    12. Filter the resulting slurry of $[Et_4N][V(CO)_6]$ by vacuum filtration and dry under vacuum.
    13. Store $[Et_4N][V(CO)_6]$ in a glovebox freezer for future use.

2. Preparation of $V(CO)_6$[23]
    1. Grease the connection points for a vacuum adaptor with stopcock, glass two-way connecting tube, and cold-finger. Place a cold finger in the center neck and a vacuum adaptor with stopcock in the third opening.
    2. In an argon glovebox, mix 100 mg of $[Et_4N][V(CO)_6]$ with 1 g of phosphoric acid in a round bottom flask containing a magnetic stirring bar.
    3. Connect the round bottom flask to a three-neck round bottom flask via glass two-way connecting tube in the argon glovebox.
    4. Remove the sealed flask system from the glovebox and set up in chemical hood.
    5. Add methanol to the cold finger and stir with a spatula-while adding liquid nitrogen until methanol is frozen. Pump down the system by opening the stopcock to a vacuum line until the pressure reaches 5×10^{-2} Torr.
    6. Submerge the round bottom flask in an oil bath set to 45 °C and turn on the magnetic stirring. Once the reaction starts, the phosphoric acid will melt and a black-blue powder condenses on the cold finger.
    7. Open the vacuum line when a black powder condenses on the round bottom flask instead of the cold finger because the pressure is too high. Pump the system back to 5×10^{-2} Torr before closing again.
    8. Rotate the reaction flask as necessary to mix all of the reactants.
    9. Allow the reaction to continue until the remaining residue in round bottom flask is white-grey and no longer bubbling.
    10. Pour copper pellets into a cold safe container and cool with liquid nitrogen.
    11. Remove the methanol from the cold finger with a micropipette. Pour chilled copper pellets into the cold finger to keep it cold during transfer to glovebox.
    12. Wipe oil and condensed water off the flask system before transferring into an argon glovebox.
    13. Inside the glovebox, remove the cold finger from the flask system and use a spatula to scrape the black $V(CO)_6$ powder onto a piece of weighing paper.
    14. Store $V(CO)_6$ in a bottle under an argon atmosphere and keep below RT.

3. Purification of TCNE by sublimation
    1. Purchase commercially available tetracyanoethylene (TCNE) and store in a chemical refrigerator.
    2. Mix ~5 g of TCNE with ~0.5 g of activated carbon and grind with a mortar and pestle.
    3. Place TCNE/carbon mixture into a glass boat or wrap in delicate task wipes and put in the bottom of a flask with a vacuum line.
    4. Place a cold finger into the top of the flask and seal the two parts together with a clamp.
    5. Add methanol to the cold finger and stir with a spatula-while adding liquid nitrogen until methanol is frozen. Place the bottom of the flask containing the TCNE in an oil bath heated to 70 °C.
    6. Open the vacuum line to reach a pressure of 10^{-4} Torr and then close the vacuum line.
    7. Occasionally open the vacuum line to maintain the pressure. TCNE condenses on the cold finger as sublimation begins. Once no more TCNE accumulates on the cold finger the sublimation is finished.
    8. Remove the methanol from the cold finger with a micropipette.
    9. Wipe oil and condensed water off the flask system before transferring into an argon glovebox.
    10. Inside the glovebox, remove the cold finger from the flask system and use a spatula to scrape the TCNE powder onto a piece of weighing paper.

    11. Store purified TCNE in a refrigerator below RT under inert atmosphere.

2. Set up Deposition System inside an Argon Glovebox

1. Assemble the reactor inside an argon glovebox as shown in **Figure 1A**.
    1. Set up a connection to a vacuum pump.
    2. Set up the gas flow connections by connecting a 3-way stopcock between a flow meter and two lines connected to micrometer valves.
    3. Slide the glass heater coil around the reactor (part A, **Figure 1B**).
    4. Wrap a glass slide with polytetrafluoroethylene (PTFE) thread seal tape.
    5. Push the glass slide approximately 10 cm from the right side of the reactor, part A.
    6. Place an O-ring on Part B and slide into the right side of the reactor. Join the two pieces together with a clamp.
    7. Attach a vacuum line to the bottom connection on part A and attach the gauge to the top connection.
    8. Place a boat filled with purified TCNE into part C near end so that the TCNE will sit in the hottest part of the reactor.
    9. Grease the connection of part C and slide it into the left side of the reactor.
    10. Grease both sides of the T-boat filled with $V(CO)_6$ and slide into the right end of part B.
    11. Connect each micrometer valve. One should be connected to the right side of the T-boat and the other to the left side of part C and clamp both in place.
    12. Run a test deposition to determine where the reaction zone is located.

2. Deposit $V[TCNE]_{x\sim 2}$ onto substrates
    1. Set the temperature of the reaction heating coil so that the reaction zone is set to a value near 46 °C when measured on the bottom of the reactor and the area of the TCNE boat is near 75 °C. Set the temperature of a silicone oil bath to 10 °C. Allow the temperatures to stabilize for at least 30 min.
    2. Slide the glass heater coil around the reactor (part A, **Figure 1A**).
    3. Wrap a glass slide with polytetrafluoroethylene (PTFE) thread seal tape. Arrange samples on top of covered slide within a two-inch space.
    4. Push the glass slide into the reactor so the samples are located in the reaction zone. Alternately samples can be placed directly on the bottom of the reactor, although the reaction zone may be shifted without a glass slide.
    5. Place an O-ring on Part B and slide into the right side of the reactor. Join the two pieces together with a clamp.
    6. Attach a vacuum line to the bottom connection on part A and attach the gauge to the top connection.
    7. Put 50 mg of TCNE into the TCNE boat and 5 mg of $V(CO)_6$ into the T-boat (these quantities are appropriate for an 75-90 min deposition).
    8. Slide the TCNE boat into part C near the end so that the TCNE will sit in the hottest part of the reactor which should be about 75 °C.
    9. Grease the connection of part C and slide it into the left side of the reactor.
    10. Grease both sides of the T-boat and slide into the right end of part B.
    11. Slide the flow line onto the right side of the T-boat and left sides of part C and clamp in place. The assembled set-up should resemble **Figure 1A**.
    12. Raise the oil bath to cover the entire bottom of the T-boat.
    13. Open the vacuum line to reach a pressure of 30-35 mmHg.
    14. Set the flow rate to 56 sccm for the $V(CO)_6$ and to 84 sccm for the TCNE. The reaction should begin immediately with a greenish material condensing on the wall of reaction zone.
    15. Allow reaction to proceed for the desired length of time. The thickness of the thin film is based on reaction time and location inside the reactor, as shown in **Figure 2**.
    16. To stop the reaction, close vacuum line and turn off the heater and oil bath.

3. Clean up

1. Take apart the system in any order.
2. Soak all the glassware except the heater coil in a base bath solution for at least 1-2 hr.
3. Rinse glassware with water and dry in an oven.

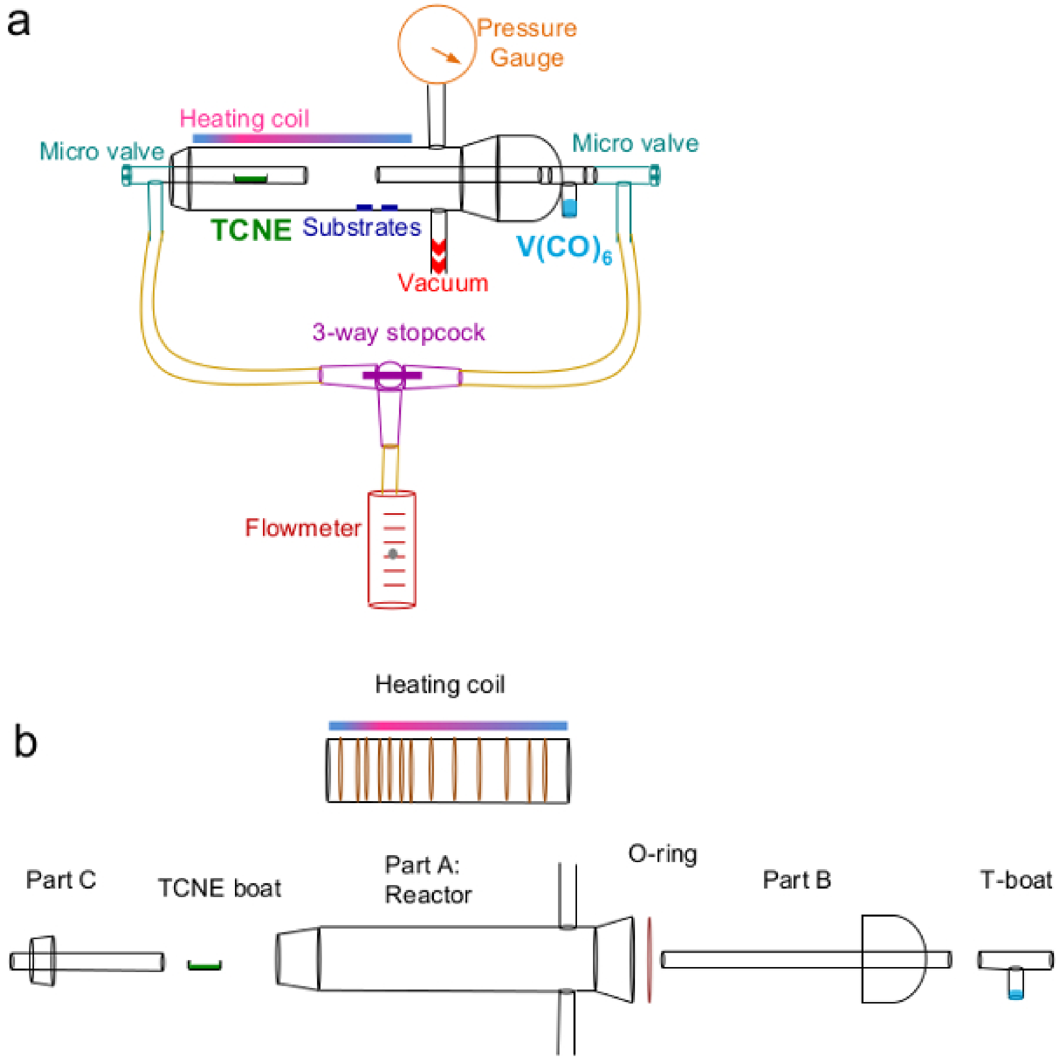

Figure 1. (**A**) Fully assembled custom chemical vapor deposition (CVD) system. (**B**) Expanded view of the components for the CVD system. Please click here to view a larger version of this figure.

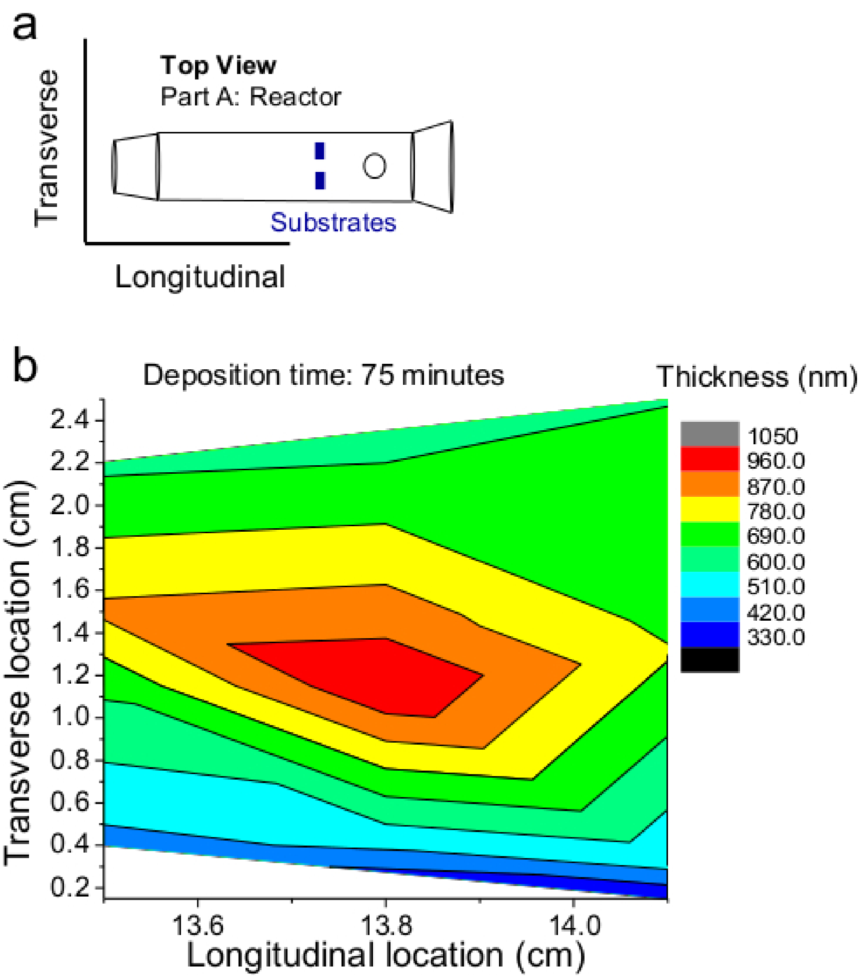

Figure 2. (**A**) A top view of the substrates in the reactor showing their location. (**B**) Approximate film thickness as function of position inside the reactor tube, Part A from **Figure 1B** for a deposition of 75 min. Please click here to view a larger version of this figure.

Representative Results

The first and easiest method for determining if a deposition is successful is to do a visual inspection of the films. The film should appear dark purple with a mirror finish that is uniform across the substrates. If there are spots on the surface of the substrate where there is no $\mathrm{V[TCNE]}_{x\sim2}$ or it is lighter in color, then this is likely due to the presence of solvents or other impurities on the substrate surface. Additionally the film should be opaque. Unless a thin film was deposited over a short time span of only a few minutes, translucent films often means there may have been a problem with the flow rate of the precursors during the deposition.

It is important to note that in addition to sub-optimal growth conditions, atmospheric exposure can degrade the film which may result in films whose qualities appear to be less favorable; therefore it is essential to prevent oxygen exposure when transporting and measuring the samples for analysis. Transportation of the sample outside the glovebox requires encapsulation of the film with materials such as epoxy[24] or parylene[25] or enclosing the sample in custom-designed cans that fit the measurement tool[4]. Local structure and film composition can be characterized by X-ray photoemission spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR).

Magnetic properties can be measured using a SQUID magnetometer. Optimized films yield an extrapolated Curie temperature (T_C) around 500-600 K. Due to film breakdown above RT, the value of T_C is extracted from a magnetization versus temperature measurement, such as the one shown in **Figure 3A**. This measurement is performed in a Quantum Design SQUID Magnetometer with an applied field of 100 Oe. The presence of a large splitting of the zero-field cooled (ZFC) and field-cooled (FC) magnetization values at low temperature is evidence of isolation of local spin environments and is a larger presence in lower quality films. The T_C of the films can be extracted by fitting the magnetization values above the peak to the Bloch law

$M_s(T) = M_s(0)(1 - BT^{3/2})$,

where M_S is the saturation magnetization and B is a fitting parameter. For the data shown in **Figure 3A** this fit yields a T_C of 600 K.

In addition to characterizing the magnetic response to temperature, the magnetization as a function of applied field can also be measured resulting in a hysteresis loop like the one shown in **Figure 3B.** For optimized films the switching of the magnetization is sharp, achieving saturation by 100 Oe. The coercivity should be about 20 Oe at 300 K.

Ferromagnetic resonance (FMR) studies are a key technique for identifying successful film growth. The presence of a single, narrow peak in the FMR measurement is strong evidence of an ideal growth. The best films have full width at half maximum (FWHM) linewidth on the order of 1-2 G. Measurements of resonance sub-optimal growth will result in a spectrum which shows multiple resonance features at some or all angles of rotation. **Figure 4** shows the FMR spectrum of an ideal film at various angles of the applied microwave and DC fields, rotating from in-plane (90°) to out-of-plane (0°) at 300 K with an applied microwave frequency of 9.85 GHz. The samples are normalized to account for variation in the magnitude of the intensity due to cavity conditions.

Electrical properties of the films can be characterized through transport measurements. The simplest measurement geometry is a two-probe measurement to measure current as a function of voltage for various temperatures. **Figure 5A** shows a film deposited on glass with 30 nm of Al and 40 nm of Au top contacts created by thermal evaporation. Electrical contact is made through indium press to a custom air-tight puck for a Quantum Design physical properties measurement system (PPMS). Current-voltage (I-V) measurements are performed using a Keithley 2400 sourcemeter. These measurements reveal Ohmic I-V characteristics at all temperatures with resistance that increases with decreasing temperature as shown in **Figure 5B.** The temperature dependent resistance data can be fit to an Arrhenius equation

$R = R_0\, e^{-E_a/k_BT}$,

to extract an activation energy, E_a~0.50 eV. This value represents the band gap energy in the electronic structure for this semiconducting material[12].

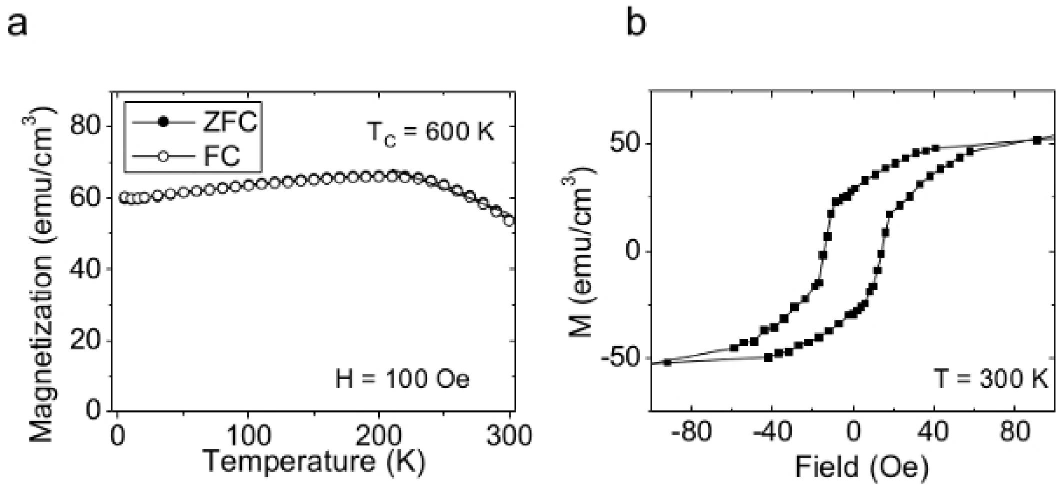

Figure 3. (**A**) Field cooled (open circles) and zero field cooled (filled circles) magnetization versus temperature with an applied magnetic field of 100 Oe. Solid black line is a fit used to extract T_C of 600 K. (**B**) Magnetization versus field measured at 300 K. Please click here to view a larger version of this figure.

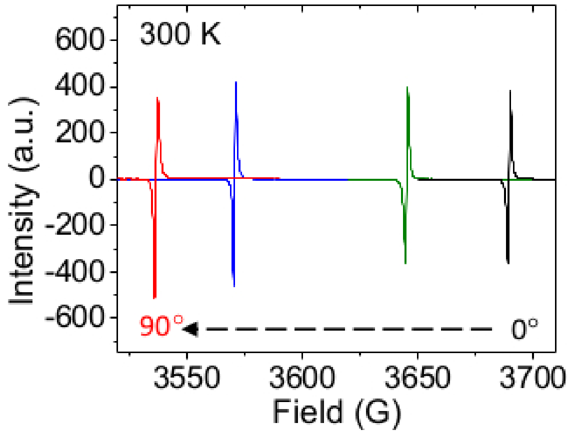

Figure 4. Room temperature FMR spectra as a function of angle from in-plane (90°) to out-of-plane (0°). Please click here to view a larger version of this figure.

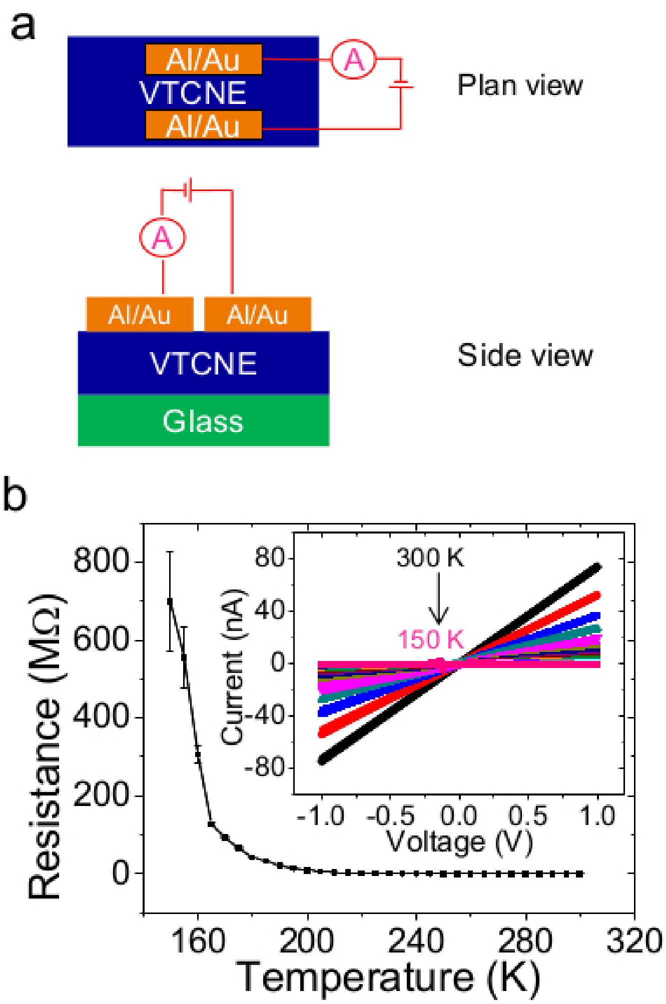

Figure 5. (**A**) Schematic of sample structure for transport sample. (**B**) Resistance values extracted from the current-voltage measurements shown in the inset for temperatures from 150 K to 300 K. Please click here to view a larger version of this figure.

Discussion

The key parameters for V[TCNE]$_{x\sim2}$ deposition include temperature, carrier gas flow, pressure, and ratio of precursors. Because the chemical vapor deposition set-up is not commercially available these parameters will need to be optimized for each system. A previous study by Shima *et al.* revealed that the temperature has the largest impact on the sublimation rate of the TCNE precursor[26]. The temperature can be modified both by the value set on the temperature controller and also by making adjustments to the wire spacing on the heating coil and as such will need to be calibrated for each system. Temperature calibration is performed by measuring inside the reactor before fully assembling the system for deposition. It is important to place the TCNE boat in the hottest zone of the reactor at a temperature near 75 °C.

The next most important parameter is carrier gas flow. The carrier gas flow rate for the TCNE should be higher than for V(CO)$_6$. The recommended flow rates are 56 sccm for the V(CO)$_6$ and to 84 sccm for the TCNE, and it is important to monitor these flow rates during deposition to ensure stability (a sampling frequency of roughly 10 min is typically sufficient).

If the pressure is above 35 mmHg the reaction will likely not occur. If the pressure is high and the reaction has not started (there is no V[TCNE]$_{x\sim2}$ appearing) there is likely a leak in the system. A large leak means the system will not pump down at all, but if there is a small leak the system may reach 40-50 mmHg. The first place to check for leaks is at all of the glassware connections. Most commonly, the vacuum grease on the flow lines can get dirty and needs to be wiped clean and replaced. In addition to leaks, pressure problems can be caused by unclean glassware or the presence of contaminants that outgas inside the chamber. For this reason it is important to carefully consider any material placed within the reaction chamber.

In addition to optimizing the reaction parameters, the surface treatment of substrates is critical for good film growth. V[TCNE]$_{x\sim2}$ can be deposited onto a wide variety of substrates, but the surface must be clean and free of residual solvents. Even touching substrate surfaces with tweezers can contaminate them. Also, samples that have been processed may require additional cleaning steps. For example, to deposit V[TCNE]$_{x\sim2}$ onto photoresist, the photoresist must have been baked for long enough to remove any trace of solvents. Additionally, for deposition of V[TCNE]$_{x\sim2}$ onto a chemically processed surface, such as a self-assembled monolayer may require semiconductor grade chemicals for the processing.

CVD-grown films of V[TCNE]$_{x\sim2}$ are ideal for incorporation in device structures; however there is limited processing that can be done to the V[TCNE]$_{x\sim2}$ films because they are sensitive to solvents, water, air, and high temperatures. V[TCNE]$_{x\sim2}$ films can be shadow masked for thermal, e-beam, or sputter deposition of other organics or metals. Various encapsulation techniques can be used to transport samples with V[TCNE]$_{x\sim2}$ to measurement tools, but is a challenge for working with this material. However, this difficulty is also common for other organic devices, such as organic light emitting diodes (OLEDs), so there is a significant body of work on techniques for encapsulation[27-29].

Beyond the ability to grow films of V[TCNE]$_{x\sim2}$ for many different applications, this method of chemical vapor deposition is suitable to chemical tunability and exploration of other types of organic thin films, such as V[MeTCEC][30]. This technique provides the ability to create a thin film organic magnet in a thickness ranging from a few tens of nanometers to several micrometers for applications from spintronics devices to microwave applications and beyond.

Disclosures

The authors have nothing to disclose.

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