CHEMISTRY OF MATERIALS

VOLUME 12, NUMBER 3 MARCH 2000

Communications

CVD-Grown Thin Films of Molecule-Based Magnets

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Received July 9, 1999
Revised Manuscript Received January 19, 2000

Increasing interest has been given recently to the study of molecule-based materials exhibiting interesting and unusual magnetic properties.[1] Major progress has been made with the discovery of molecular systems exhibiting a memory effect, i.e., bulk magnetic order,[2,3] or spin crossover phenomenon,[4] near or above room temperature. These lighter weight materials, derived from organic, organometallic, or polymeric species, and prepared by low-temperature procedures, represent a highly interesting alternative to conventional magnets in future generations of devices. For such applications, their preparation as thin films remains a major difficulty to overcome. Some attempts to grow thin films of molecule-based magnets have been reported by using techniques such as electrochemical growth,[5] and sublimation.[6]

$[Cp^*{}_2Fe]^{\bullet +}[TCNE]^{\bullet -}$ (**1**) (Cp* = pentamethylcyclopentadienide; TCNE = tetracyanoethylene), a bulk ferromagnet with a Curie temperature T_c of 4.8 K, was obtained in solution from $Cp^*{}_2Fe$ and TCNE.[7] $V(TCNE)_2 \cdot {}^1/_2(CH_2Cl_2)$ (**2**), which exhibits field-dependent magnetization and hysteresis at room temperature, was obtained in solution from TCNE and either bis(benzene)vanadium, $V(C_6H_6)_2$,[2] or vanadium hexacarbonyl, $V(CO)_6$.[8] Cosublimation of $V(CO)_6$ and TCNE was also mentioned to produce a solvent-free $V(TCNE)_x$ phase (**3**), showing similar magnetic properties to **2**, while no reaction was reported to occur between $V(C_6H_6)_2$ and TCNE.[8]

We report in this work on the formation of thin films of **1** and **3** grown by chemical vapor deposition (CVD) using $Cp^*{}_2Fe$, TCNE and $V(C_6H_6)_2$ as precursors.

$Cp^*{}_2Fe$ and TCNE are commercially available. $V(C_6H_6)_2$ was prepared following previously described procedures[9] or purchased from Strem Chemicals. The experimental setup used for thin-film preparation is a conventional hot-wall CVD apparatus.[10] Table 1 gathers the CVD conditions for growth of thin films of **1** and **3**. Magnetic measurements (MPMS 5.5 Quantum Design SQUID magnetometer), SEM observation (JEOL model JSM 840A), IR (Perkin-Elmer 1725 FT-IR), and XRD (Seifert XRD 3000TT, Cu Kα radiation, $\lambda = 1.5418$ Å) studies were performed on films of both **1** and **3**.

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[10] Supporting Information available free of charge via the Internet at http://pubs.acs.org.

10.1021/cm9904279 CCC: $19.00 © 2000 American Chemical Society
Published on Web 02/18/2000

Table 1. Typical[a] Experimental CVD Conditions for Film Formation of $[Cp^*_2Fe]^{\bullet+}[TCNE]^{\bullet-}$ (1) and $V(TCNE)_x$ (3), on KBr Substrates

precursor: mass, mg	vaporization T, K	He flow rate, sccm	mixing zone T, K	substrate zone T, K	total P, Torr
Cp^*_2Fe: 134	383	33	433	348	0.5
TCNE: 105	348	17			
$V(C_6H_6)_2$: 94	418	17	448	348	0.5
TCNE: 119	348	10			

[a] Variation of the deposition temperature is not thoroughly studied yet. Deposition occurs up to a pressure of 10 Torr. Gas flow rate, more than temperature, appears to be the key factor to allow formation of the film. The conditions reported in this table are the best reproducible ones obtained up to now.

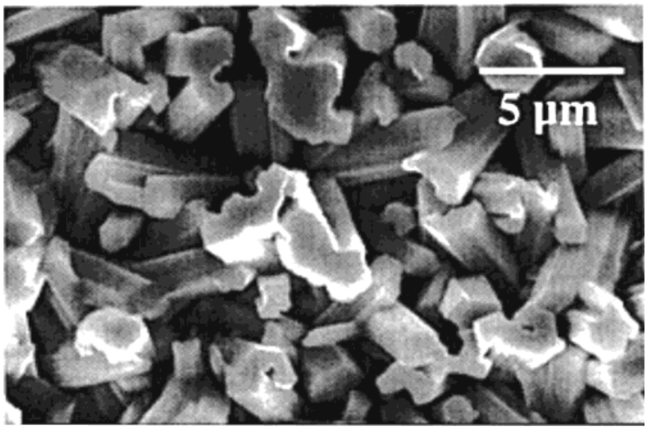

Figure 1. SEM image of $[Cp^*_2Fe]^{\bullet+}[TCNE]^{\bullet-}$ (**1**) thin film deposited on KBr pellets.

As shown in Figure 1, CVD grown films of **1** are made of thick polygonal crystallites, uniformly covering the substrate surface.[10] The average size of the crystallites is 1−5 μm in diameter and several tens of micrometers in length. The IR spectrum of these films was recorded directly on the compressed KBr pellets used as substrate.[10] The vibration frequencies observed at 2144 and 2183 cm^{-1} in the ν_{CN} region are characteristic of the $TCNE^{\bullet-}$ anion.[7] The frequency shift of the ν_{CN} bands observed when going from neutral TCNE (2228 and 2262 cm^{-1}) to the deposited material indicates that a charge transfer type reaction actually took place between Cp^*_2Fe and TCNE. During the experiment, film formation occurs on the substrate and also on the reactor wall. The magnetic susceptibility was measured between 2 and 300 K on the substrate/film composite and on pure compound collected from the reactor wall. Both samples obey the Curie−Weiss law above 125 K with a θ value of +45 K and the χT vs T plots show a maximum at 12 K.[10] Moreover, magnetization versus applied magnetic field was studied at 2 and 4 K on the substrate/film composite. An hysteresis loop is observed at 2 K (Figure 2) and shows a coercive field of ~500 G to be compared with 1000 G for the orthorhombic solution-grown phase.[7] The absence of hysteresis at 4 K is consistent with ZFC/FC measurements that give a T_c value of 3.7 K (spin blocking temperature) for thin films,[10] while a T_c of 4.8 K was reported for the solution-grown phase.[7] The XRD pattern of the compound collected from the reactor wall shows four lines in the range d = 7.5−3 Å.[10] The values $d(I)$: 7.31(85), 7.07(100), 3.46(44), 3.37(47), are consistent with those of the orthorhombic phase.[7] Indeed, using a = 10.613, b = 16.102, c = 14.580 Å, the calculated d spacings and (hkl) indices are 7.290 (002), 7.048 (021), 3.455 (310), 3.371 (114). The XRD pattern of the substrate/film composite only shows the two strongest lines $d(I)$: 7.24(100), 6.99(20).[10] The inversion in the relative intensity for these two lines indicates a preferred orientation of the crystallites with the [001] direction perpendicular to the surface of the substrate. Such a feature is often encountered in CVD growth of thin films.[6,11] We note that the interreticular distances measured for the layer are somewhat smaller than those measured for the powder collected on the reactor wall. A possible explanation for such a decrease could be the epitaxial effect of the substrate which may induce internal stress within the layer. Additional deposition on different kinds of substrates are underway for clarifying this point.

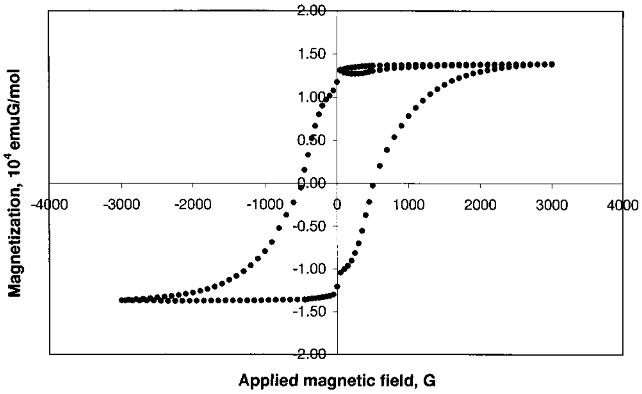

Figure 2. Hysteresis $M(H)$ of vapor-deposited $[Cp^*_2Fe]^{\bullet+}[TCNE]^{\bullet-}$ (**1**) at 2 K.

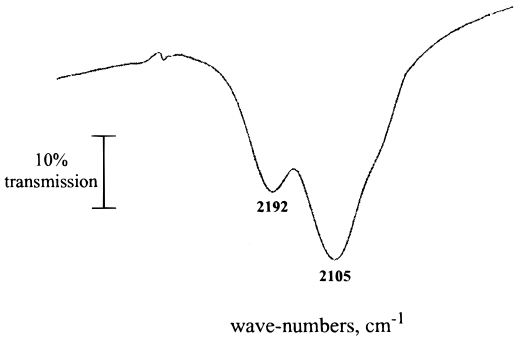

Figure 3. IR spectrum of thin films of $V(TCNE)_x$ (**3**).

$V(C_6H_6)_2$ and TCNE were vaporized in the conditions reported in Table 1. Black thin films of **3** were deposited on KBr pellets. As observed for solution grown material, the films are highly air sensitive. The IR spectrum (Figure 3) was performed on four independently prepared films of **3** protected with adhesive tape. For all samples, the two absorptions observed in the ν_{CN} region at 2105 ± 4 (s,br) cm^{-1} and 2192 ± 4 (m,br) cm^{-1} are consistent with those obtained for **2** and correspond to the presence of $TCNE^{\bullet-}$ species with some N atoms bound to vanadium.[2] No ν_{CH} bands corresponding to the presence of benzene rings are observed. Thus, during

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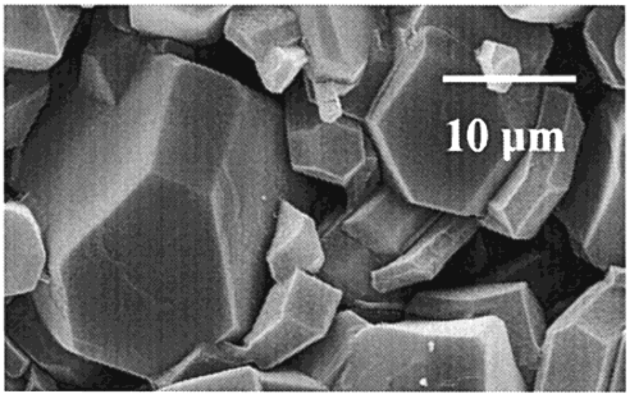

Figure 4. SEM image of V(TCNE)$_x$ (**3**) thin film deposited on KBr pellets.

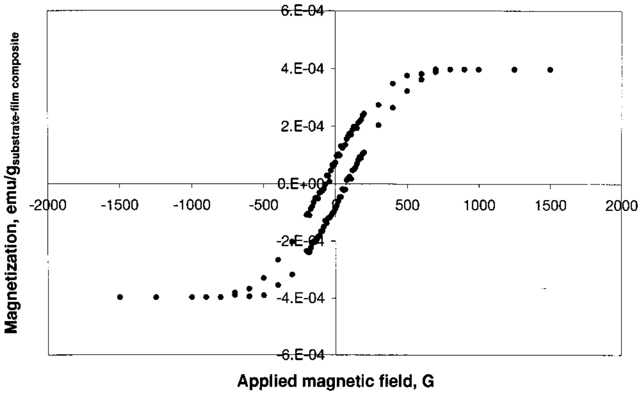

Figure 5. Hysteresis *M*(*H*) of vapor deposited V(TCNE)$_x$ (**3**) at 300 K.

the CVD experiment, the reaction between V(C$_6$H$_6$)$_2$ and TCNE seems to occur following the same mechanism as in solution, i.e., a charge transfer accompanied by a ligand exchange on the vanadium atom. Films, protected with a 15-nm sputtered silver layer, were observed by SEM (Figure 4). They consist of faceted 10-μm-thick grains uniformly covering the surface.[10] EDX analysis confirms the presence of V within the grains. XRD study of these films shows no lines within the range $d = 7.5-3.5$ Å. Given the faceted morphology of the grains, the amorphous character of **3** is somewhat surprising. On the other hand, it should be recalled that the structural correlation length was reported to be ~25 Å for the parent solution-grown material **2**.[12] Magnetic measurements, performed on four independently prepared samples collected and stored under inert conditions, gave reproducible results. The hysteresis loop shown in Figure 5, recorded at 300 K on the substrate/film composite, shows a coercive field H_c of 80 G (60 G for **2**). The saturation magnetization of **3** is not reached as rapidly as for **2**: the thin-film saturation induction (B_S) is ~800 G to be compared with 140 G for **2**.[13] Differences in B_S values, previously observed when the nature of the solvent was varied, were attributed to a larger disorder in the structure.[12] Unlike the solution procedure, the present CVD process necessarily leads to solvent-free V(TCNE)$_x$ films. The B_S value obtained in the case of the films may also be attributed to a larger disorder in the structure, as the reaction from a gas phase, and the nature of the substrate, may induce a different molecular connectivity in this supposedly polymer-like material.[2]

We have shown the feasibility of processing thin films of molecule-based magnets in the case of [Cp*$_2$Fe]$^{\bullet+}$[TCNE]$^{\bullet-}$ and V(TCNE)$_x$. Thin films of both systems exhibit similar magnetic properties as for the solution grown samples. The differences observed in the ordering temperature T_c of [Cp*$_2$Fe]$^{\bullet+}$[TCNE]$^{\bullet-}$ and B_S value of V(TCNE)$_x$ reflect a specific structural organization of the compound on the substrate surface directly connected to the film formation process.

Acknowledgment. The authors gratefully acknowledge, A. Mari for magnetic measurements, M. Reversat for SEM and XRD results, and M. Respaud for helpful discussion.

Supporting Information Available: CVD setup and procedure; low magnification SEM image for **1**; CN stretching vibrations of TCNE$^{\bullet-}$ in **1**; 1/χ vs *T* and χT vs *T* curves for **1**; XRD patterns of the sample collected from the reactor wall and of thin film for **1**; ZFC/FC curves for **1**; low magnification SEM image for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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