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Parylene Protection Coatings for Thin Film V[TCNE]$_x$ Room Temperature Magnets

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The magnetic and electrical properties of chemical vapor deposited V[TCNE]$_x$ magnetic films rapidly degrade (<1 min) in the presence of oxygen and water. V[TCNE]$_x$ magnetic films coated with ~8 μm of Parylene C maintain their magnetic properties for more than 7 h after being exposed to the atmosphere. A subsequent overcoating of the 2.2-μm Parylene-coated films with a 0.1-μm layer of gold provides protection for at least 14 h. A 2-μm Parylene C coating also reduces the rate of conductivity degradation by 2 orders of magnitude at 300 K.

Introduction

The room-temperature V[TCNE]$_x$ ($x \approx 2$; TCNE = tetracyanoethylene) organic-based magnet is an attractive material for future generations of magnetic applications including spintronics;[1,2] however, the magnetic and electrical properties rapidly degrade in the presence of the atmosphere. Hence, identification of an adhering coating that can be easily deposited onto a V[TCNE]$_x$ film surface without substantial damage while protecting the magnetic film from reaction with atmospheric oxygen and moisture is essential for exploitation of V[TCNE]$_x$ magnetic films.

Bulk, powder samples of V[TCNE]$_x$·0.3CH$_2$Cl$_2$ degrade in minutes when exposed to the atmosphere, as evidenced by the rapid sharp drop in (a) the magnetic transition temperature, T_c, (b) the magnetization (Figure 1), and (c) conductivity. In contrast, freshly prepared chemical vapor deposited (CVD) V[TCNE]$_x$ films (2−5 μm thick) remain magnetic at room temperature even after 1 h exposure.[3] Nonetheless, a further significant enhancement to the ambient stability is essential for applications.

Given the requirement for a nonreacting, adhering coating to protect V[TCNE]$_x$ films from the devastating effects of exposure to the atmosphere, as well as the coating and its application process being compatible with the existing CVD fabrication of the V[TCNE]$_x$ films,[4] the paracyclophane-based Parylene coating tech-

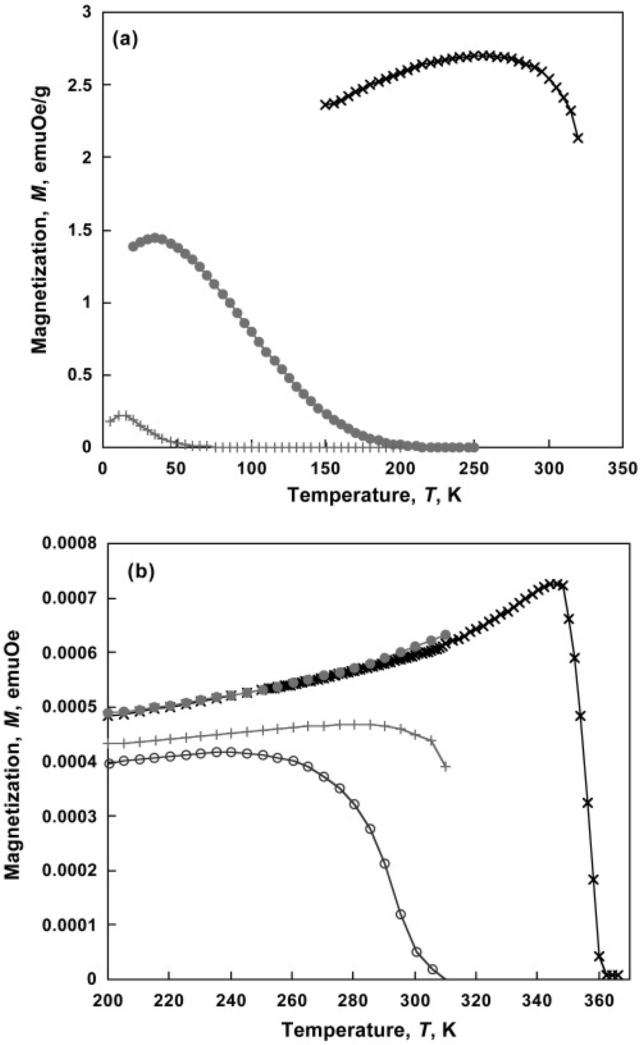

Figure 1. $M(T)$ of the powder sample of V[TCNE]$_x$·0.3CH$_2$Cl$_2$ exposed to the atmosphere for 0 min (×), 1 min (●), and 2 min (+) (a), and of the CVD-prepared V[TCNE]$_x$ unexposed film (×); film from the same batch exposed to the atmosphere for 0 (●), 15 min (+), and 62 min (○) (b).

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(1) (a) Wolf, S. A. *J. Supercond.* **2000**, *13*, 195. (b) Prinz, G. *Science* **1998**, *282*, 1660. Ohno, H.; Matsukura, F. *Solid State Commun.* **2001**, *117*, 179.

(2) Prigodin, V. N.; Raju, N. P.; Pokhodnya, K. I.; Miller, J. S.; Epstein, A. J. *Adv. Mater.* **2002**, *14*, 1230.

(3) Even a small amount of oxygen substantially damaged the film. For ~10 ppm O$_2$ it takes ~1 month to decrease T_c below room temperature.

(4) Pokhodnya, K. I.; Epstein, A. J.; Miller, J. S. *Adv. Mater.* **2000**, *12*, 410.

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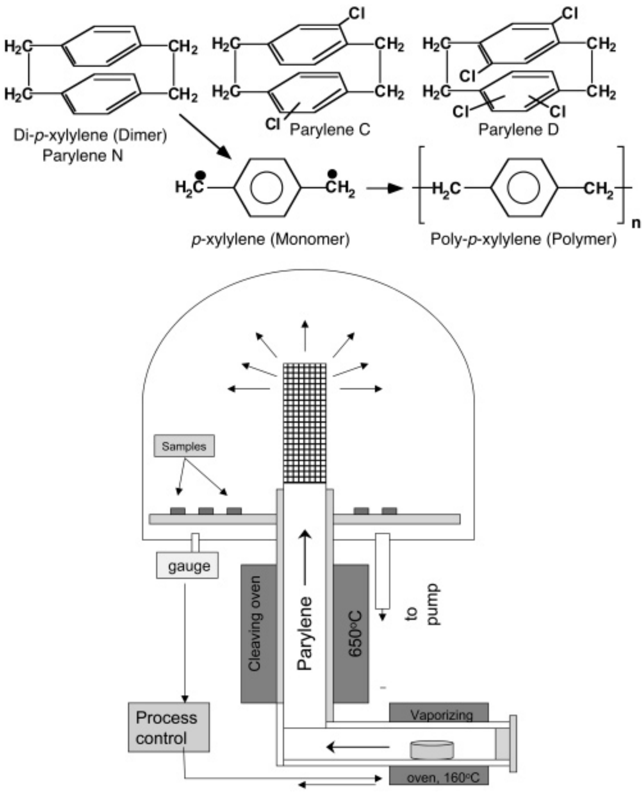

Figure 2. Chemical reaction of the Parylene polymerization (top) and the coating setup (bottom).

nology was identified for evaluation.[5] Paracyclophanes (Parylenes) are 2,2-bridged aromatic hydrocarbons [see Parylene N, C, and D, (Figure 2 top)] that upon thermolysis form chemically inert poly-*p*-xylylene coatings (Figure 2 middle).[6] Parylene is a commercially available coating precursor that exists in three forms: Parylene N, C, and D. Parylene N (di-*p*-xylylene or di-*para*-xylylene), the basic member of the series, is a crystalline material. Parylene C and D are mono- and dichloro substituted di-*p*-xylylenes, respectively. These polymer coatings provide low oxygen, nitrogen, carbon dioxide, hydrogen, and water permeability.[5] Hence, they are excellent barriers for oxygen and water. Since Parylenes are deposited from the gas phase, neither catalysts nor solvents are involved, and foreign substances that could contaminate coated V[TCNE]$_x$ films are not introduced. More importantly, the room-temperature deposition conditions are very mild, and hot vapors are not involved; therefore, the delicate chemistry of V[TCNE]$_x$ remains intact even close to the surface. The Parylene coatings are formed at ~0.05 Torr. Under these conditions the mean free path of the monomers in the deposition chamber is in the order of 1 mm. Therefore, unlike vacuum metalizing ($\sim10^{-5}$ Torr), the deposition is not line-of-sight and all sides of an object are uniformly coated. Consequently, conformal coatings of the V[TCNE]$_x$ films are expected.

Herein, we report a significant enhancement in the stability of Parylene N or C coated V[TCNE]$_x$ films with respect to degradation from exposure to the atmosphere. Furthermore, enhanced stabilization of the films by a subsequent overcoating of the Parylene coated films with a 0.1 μm layer of gold is described.

Experimental Section

A drybox housing: (i) the CVD V[TCNE]$_x$ magnetic film fabrication apparatus,[4] (ii) the coating equipment (vide infra), and (iii) the Emitech Ltd. K975x turbo evaporator for metal film deposition was built, enabling deposition of metal films as well as electrical contacts and/or additional coatings in less than a minute after V[TCNE]$_x$ film fabrication. All manipulations were performed in a nitrogen atmosphere containing less than 1 ppm of O_2. During the fabrication cycle, O_2 concentration was continuously monitored by a DF-150 oxygen analyzer (sensitivity ~0.1 ppm). This system allows monitoring and minimization of the oxygen exposure that is required to produce very high quality V[TCNE]$_x$ films suitable for device fabrication. A Dektak III bench-top surface profiler was used to measure the coating thickness ranging from 0.1 to 1000 μm. Parylene N (diX N) and C (diX C) were obtained from Uniglobe Kisco, Inc.

The electron microscopy was performed using a Hitachi S3000-N scanning electron microscope (SEM) suitable for analysis and imaging of metals, ceramics, polymers, and biomaterials. It can be operated under low vacuum as well as under a controlled environment. To analyze the coating image an energy dispersive spectroscopy (EDS) chemical analysis system was used. To avoid the charging the sample was covered with 20 nm of gold.

The studies reported herein were done in Salt Lake City, which is at an altitude of ~4400 ft (1340 m) above sea level and has an average atmospheric pressure of 644 Torr (0.85 atm). Consequently, the oxygen partial pressure in the atmosphere is reduced from 160 to 135 Torr, which slows the degradation of the V[TCNE]$_x$ films. The data reported herein were not corrected for STP conditions.

Magnetic Measurements. V[TCNE]$_x$ films (3−5 μm) were deposited on 5 × 5 mm glass slides according to the known procedure,[4] and loaded in airtight Delrin holders for magnetic measurements. To elucidate the efficacy of the protective coatings the DC magnetization as a function of temperature, $M(T)$, was measured by cooling in zero field and then data collecting upon warming in 5 Oe external magnetic field using a Quantum Design MPMS-5XL 5 T SQUID magnetometer equipped with a reciprocating sample measurement system, low field option, and continuous low-temperature control with enhanced thermometry features. It should be noted that annealing of V[TCNE]$_x$ films at above 330 K causes irreversible transformations/damage, which substantially degrade the magnetic properties. Therefore, if a series of $M(T)$ measurements were run for different atmosphere exposure times, the maximum temperature was limited to 320 K.

Electrical Measurements. For the conductivity, σ, measurements two 5 × 5 mm gold contact pads were deposited on a thin glass slide. The gap between contacts was ~20 μm wide and ~100 nm deep. Up to 5-μm-thick V[TCNE]$_x$ films were deposited over the gap between contact pads via CVD.[4] Two 0.1-mm-diameter silver wires were soldered with indium onto the contact pads. Since the contact resistance is much smaller than the sample resistance, the two contact method was used. I−V characteristics of all the samples were linear up to 10 V applied voltage indicating their ohmic behavior. The V[TCNE]$_x$ film sample was attached to the sample holder puck with thermo-conducting grease and then loaded into the Quantum Design PPMS using an airtight homemade antechamber after three He gas purging cycles and subsequent evacuation to 5 Torr.

Measurements of $\sigma(T)$ of the V[TCNE]$_x$ film were performed using a Quantum Design 9 T PPMS with its resistivity option, between 60 and 400 K. When the conductivity of the sample dropped below 10^{-6} S, a Keithley 6497 Picoammeter/voltage source for $10^{-6} > \sigma > 10^{-11}$ S was used.

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(5) (a) M. Szwarc and Union Carbide Corporation. US Patents 3288728, 2341754, 637651, 650947, 740886, 883939, 973901, 11120422, 1112894, 1428168. (b) Szwarc, M. S. *Polym. Eng. Sci.* **1976**, *16*, 473.

(6) The average molecular weight of the Parylene polymer is 31 288 assuming that the degree of polymerization is 2000−4000.[5]

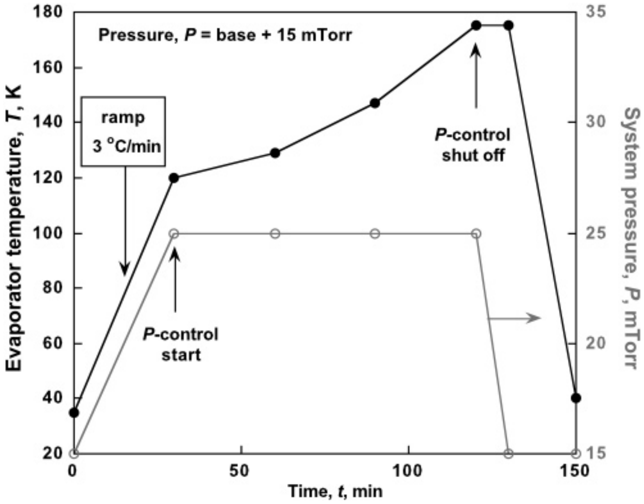

Figure 3. Temperature and pressure dependencies as a function of time for a typical Parylene C deposition cycle.

Table 1. Typical Parameters of the Parylene Deposition Process

Parylene	sublimation temp. range (°C)	chamber pressure (mTorr)	pyrolysis temp. (°C)	deposition rate (μm/h)
N	110−160	base + 55 ± 2	650 ± 1	0.7 ± 0.1
C	120−175	base + 15 ± 2	690 ± 1	3 ± 0.5

Parylene Deposition. The Parylene coating process consists of three distinct steps (Figure 2 middle): (i) sublimation of the Parylene (N or C) solid dimer at ~150 °C and 15−20 mTorr; (ii) pyrolysis (cleaving) of the dimer molecule (in gas phase) into monomers, which is achieved at 650−690 °C in a high-temperature tube furnace; and finally (iii) polymerization of the gaseous monomer at room temperature and onto the substrate in the vacuum chamber (Figure 2 bottom). During the deposition cycle the pressure in the deposition chamber was used to control the deposition rate.

The temperature and pressure dependencies as a function of time for a typical Parylene C deposition cycle is shown in Figure 3. After loading of 1 g of the Parylene and the substrate into the deposition apparatus, it was evacuated to a base pressure of ~15 mTorr. The temperature of a vaporizing zone was ramped at a rate of 3 °C/min up to 120 °C, and the process control system was initialized to stabilize the pressure in the apparatus at the base +15 mTorr level regulating the vaporizing zone temperature. Upon Parylene vaporization the vaporizing zone temperature slowly increased to 175 °C during ~90 min. When all the Parylene was vaporized, the pressure abruptly dropped, the control system automatically shut down, and the apparatus cooled to room temperature.

Note that all parts of the Parylene deposition apparatus get coated during the sample coating process. After several coatings, the inner surfaces need to be cleaned by burning the polymer at 600 °C in an oven.

The Parylene (N or C) coating thickness is a function of the amount of vaporized dimer and chamber dwell time and can be controlled to ±5% of targeted thickness for typical applications.

It is important to note that the growth rate of the Parylene film in the deposition chamber is proportional to the partial pressure of monomer gas. In the gas phase cleaved Parylene N (or C) molecules are extremely elastic and will collide with the substrate many times before depositing and polymerizing. This has the net effect of greater penetration into small openings than the other types of Parylene.[5b] The expected pressure increase in the deposition chamber during a coating run is controlled at a higher pressure for Parylene N than the other Parylenes and, therefore, it deposits at a rate much slower than Parylene C (Table 1).

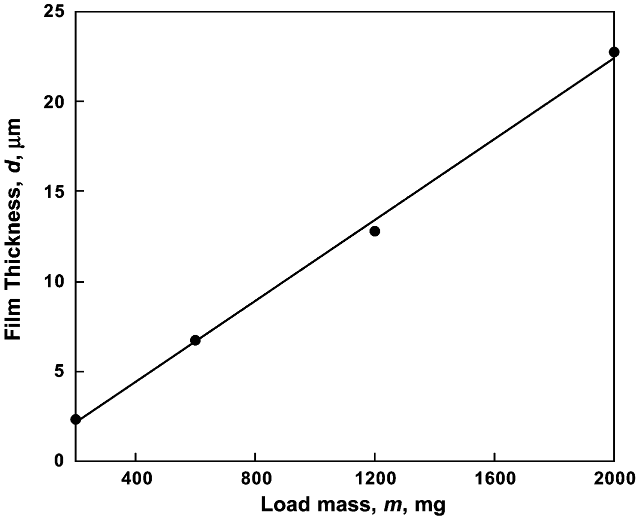

Figure 4. Parylene N film thickness as a function of mass of the dimer load for V[TCNE]$_x$ film coating (11.29 μm/g).

For the less-elastic Parylene C the equilibrium in the deposition chamber is shifted toward polymerization and, therefore, the corresponding pressure increase is about one-third to that for Parylene N, and the deposition rate is 7 times higher. Note that the deposition rates in Table 1 correspond to the most successful runs in which the best coating properties with respect to V[TCNE]$_x$ film protection were achieved. Generally, the slower the deposition, the more uniform and clear the Parylene coating. Coating with higher rates causes cloudiness or whiteness of the Parylene and uneven coating thickness. Clear coatings have fewer light scattering sites or grain boundaries and consequently fewer pinholes (vide infra), and provide a better protective coating.

Parylene Barrier Properties. The volume of oxygen gas that can diffuse through the Parylene coating due to an atmosphere exposure can be evaluated using eq 1

$$V[\mathrm{cm}^3] = G \times \frac{S[\mathrm{in.}^2] \times t[\mathrm{h}] \times p[\mathrm{atm}]}{100 \times d[\mathrm{mil}] \times 24} \quad (1)$$

where G is the Parylene gas permeability in cm^3·mil/(100 in^2·day·atm) at 23 °C),[5b] d is the coating thickness in mils; S is the sample area in sq in.; t is the exposure time in hours; and p is the partial pressure of oxygen in atm. Taking G_{O_2} of 39.2 in.^{2}·day·atm for Parylene N,[5b] and assuming that all oxygen diffused from the atmosphere immediately reacts with V[TCNE]$_x$ films, about 4% of the 5 × 5 mm × 5 μm V[TCNE]$_x$ film coated with 7 μm of Parylene N will be damaged (oxidized) in 1 h upon atmosphere exposure. The G_{O_2} of Parylene D is 32 in^2·day·atm,[5b] which is substantially higher than that for Parylene C; therefore, the optimization of Parylene C deposition was sought.

Based upon the permeability for moisture, G_{H_2O}, of 1.6 in^2·day·atm,[5b] water will react at least 20 times slower than oxygen. The V[TCNE]$_x$ film sensitivity to moisture is also considerably smaller [i.e., powder samples do not change T_c upon 1 h exposure to an oxygen free (<1 ppm) wet box atmosphere]. Hence, protecting V[TCNE]$_x$ films from oxygen with Parylene automatically shields them against moisture.

Since the oxygen permeability is of primary concern, Parylene C provides the best protection (G_{O_2} = 7.2 in^2·day·atm),[5b] as only 0.75% of the film will be damaged using an equal thickness of this coating. Nevertheless, Parylene N is more conformal; therefore, thickness control is much easier (Figure 4), and consequently, it was used for the coating optimization. Although the equipment settings differ slightly, all learned “know-how” from the Parylene N deposition is applicable to Parylene C.

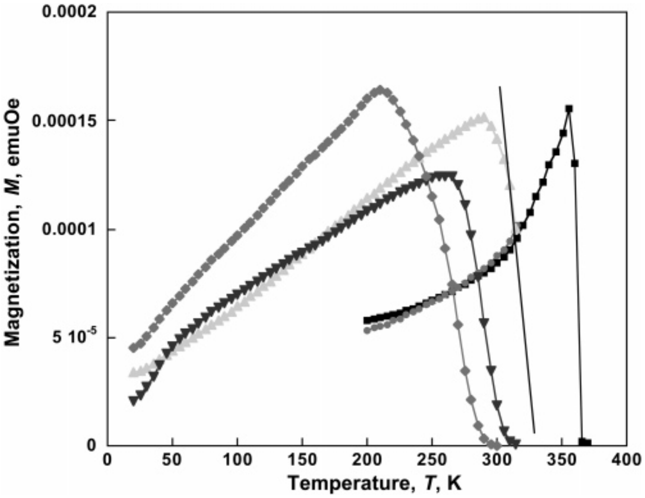

Figure 5. $M(T)$ of the uncoated V[TCNE]$_x$ film (■), and the film from the same batch coated with 6.73 μm of Parylene N. The film was exposed to the atmosphere for 0 h (●), 1 h (▲), 2 h (▼); and 3 h (◆). Due to thermo-degradation effects in V[TCNE]$_x$ when heated above 330 K (see text), the $M(T)$ behavior for 1 h exposure above 320 K was extrapolated by a straight line.

Gold Sputtering Deposition. Protective gold films were deposited onto the top of Parylene coatings using the magnetron sputtering option available in the K975x turbo evaporator.

Results and Discussion

To ascertain the protection from the oxygen as a function of the coating thickness, d, the V[TCNE]$_x$ films were coated with 2.73, 6.73, 12.78, and 22.8 μm of Parylene N and then each film was exposed to the ambient atmosphere for 1, 2, and 3 h. The family of $M(T)$ curves was obtained for each thickness, and the representative results for $d = 6.73$ μm are shown in Figure 5.

The Parylene N coating does not qualitatively change the magnetic properties of the film (in Figure 5 the uncoated, (■), and coated, (●), curves almost coincide). However, exposure to the ambient atmosphere altered them substantially, shifting both the onset of the magnetic transition, T_{on}, and the temperature at which the maximum in $M(T)$ occurs, $T_{\max}$, toward lower temperatures. It is known that oxygen reacts first with V^{2+} centers of V[TCNE]$_x$ forming a strong V^{IV}=O bond which reveals itself as a new feature in the IR spectra as a strong band near 980−1000 cm^{-1} as well as a degradation of the magnetic ordering.[7] It is thought that in the early stage of oxidation (when the infinite magnetic cluster is still intact) this process effectively blocks the superexchange pathways decreasing T_c and its corresponding T_{on}. Simultaneously, a substitution of V^{2+} ions ($S = 3/2$) with V^{4+} ones ($S = 1/2$) introduces a substantial disorder in the system, which makes the magnetic transition more diffuse and shifts $T_{\max}$ to lower temperature. Therefore, shifts in T_{on} and $T_{\max}$ reflect the effects of early stage oxidation.

Although, as calculated, ~4% of a V[TCNE]$_x$ film coated with 7 μm of Parylene N will be damaged in 1 h upon atmospheric exposure, T_{on} does not change after 1 h exposure for $d \geq 7$ μm indicating that the diffusion through the coating and its damage is minimal (Figure 6). However, $T_{\max}$ shifts to lower temperature by ~5%, implying that there are some small random damages, apparently due to penetration through pinholes. Electron microscopy studies reveal the presence of irregular shaped pinholes ~1−5 μm in cross section (Figure 7). During prolonged 2 h exposure to air for the same thickness of Parylene N, damage due to the diffusion through the Parylene coating and penetration through the pinholes becomes comparable, as both $T_{\max}$ and T_{on} drop at the same rate (Figure 6).

Formation and the consequences of pinhole defects have been studied for many decades.[8] The most important factor that determines pinhole formation is the condition of the substrate surface. Despite the very low level of O_2/water vapor in our DryBox the amount of dust particles per cubic feet exceeds that of the lowest class (ISO Class 10) clean room. In addition, the level of static electricity in the DryBox is very high. Both of these factors increase the probability of having several charged micro particles adhere to the substrate that may prevent it from being coated; thus, creating pinholes.

Our studies reveal that the chamber pressure during the coating procedure is the most important factor affecting substrate-coating quality. Excessive coating pressure results in defect formation that leads to

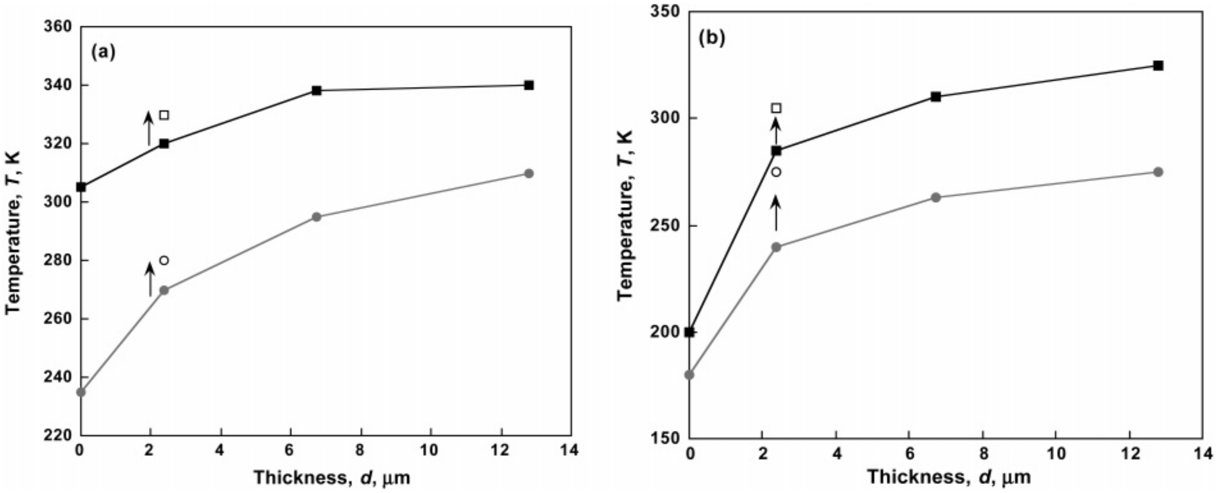

Figure 6. $T_{\mathrm{on}}(d)$ (■) and $T_{\max}(d)$ (●) of a Parylene N coated V(TCNE)$_x$ film after 1 h (a) and 2 h (b) atmosphere exposures. Open squares and circles represent data for 2.37 μm optimized transparent coating (see text).

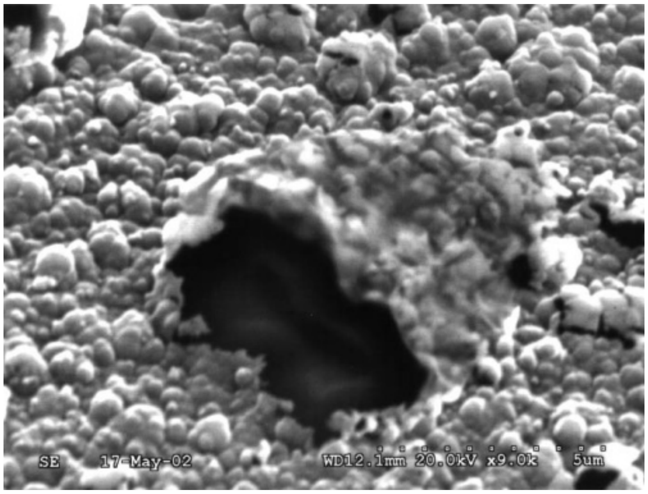

Figure 7. Image of the surface of a V[TCNE]$_x$ thin film overcoated with gold showing a 2 × 5 μm oblong pinhole.

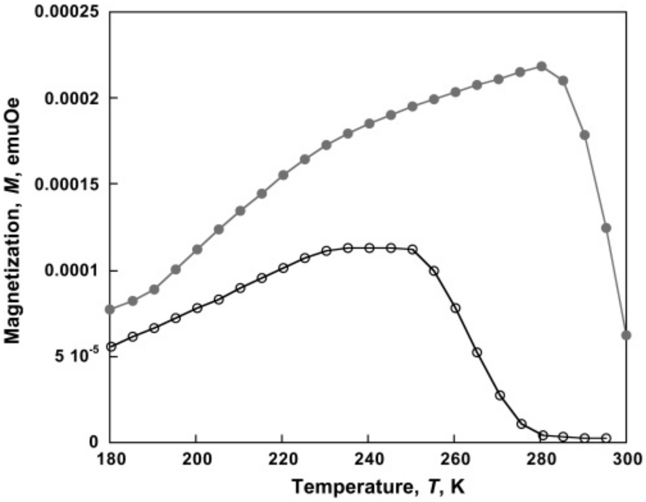

Figure 8. $M(T)$ of V[TCNE]$_x$ film coated with ~2.7 μm of Parylene N in optimized conditions (clear coating) (●); $M(T)$ of similar V[TCNE]$_x$ film coated with the same thickness Parylene N in nonoptimized conditions (visible cloudiness) (○). Both samples were exposed to the atmosphere for 2 h.

cloudiness, frosting, or formation of coating nodules. These defects provide interfacial boundaries enabling oxygen penetration. Optimization of the coating process for Parylene N by the parameters listed in Table 1 leads to clear coatings with considerably reduced oxygen penetration and minimizes the degradation of the magnetic ordering of the V[TCNE]$_x$ film ((□) and (○) in Figure 6), and electrical conductivity (vide infra). Hence, for the same coating thickness the shifts of $T_{\max}$ and T_{on} in $M(T)$ are substantially reduced especially for the 2 h exposure (Figure 8).

Due to the reduced permeability toward O_2, Parylene C provides a significant increase in V[TCNE]$_x$ film stability. The T_{on} of a 3.72 μm coating of Parylene C on a 5.0 ± 0.5 μm V[TCNE]$_x$ film remains well above 310 K even upon 7.5 h of atmosphere exposure, and $T_{\max}$ shifts below 310 K only after 5 h (Figure 9). Increasing the coating thickness to 7.79 μm keeps $T_{\max}$ above 310 K for 7 h of exposure. As observed for the $M(T)$ for 3.5, 5, and 7 h exposure times the magnetization increases with exposure time. The genesis of this is attributed to random diffusion oxygen (through coating defects) that persists, creating a small number of magnetization pinning centers.

Still greater V[TCNE]$_x$ film stability has been achieved via overcoating of a Parylene-coated film with a thin layer of gold film[9] (0.1 μm) using vacuum sputtering (Figure 10). Although not yet optimized, this double coating stabilized T_c for at least 7 h for Parylene N and 14 h for Parylene C with respect to reaction with O_2/H_2O. Furthermore, the T_c is enhanced to 112 °C (385 K) from 92 °C (365 K) suggesting that higher T_c magnetic films can be fabricated when the coating immediately follows the film deposition. Interestingly, both degradation-sensitive parameters $T_{\max}$ and T_{on} remain above 320 K even after 14 h of atmosphere exposure. We assume that the 2−3 μm Parylene C + 0.1 μm Au coating totally blocks the oxygen diffusion through the surface. Slow decreases of the V[TCNE]$_x$ film magnetization most probably occur due to oxygen diffusion through the sides faces where the coating is obviously thinner.

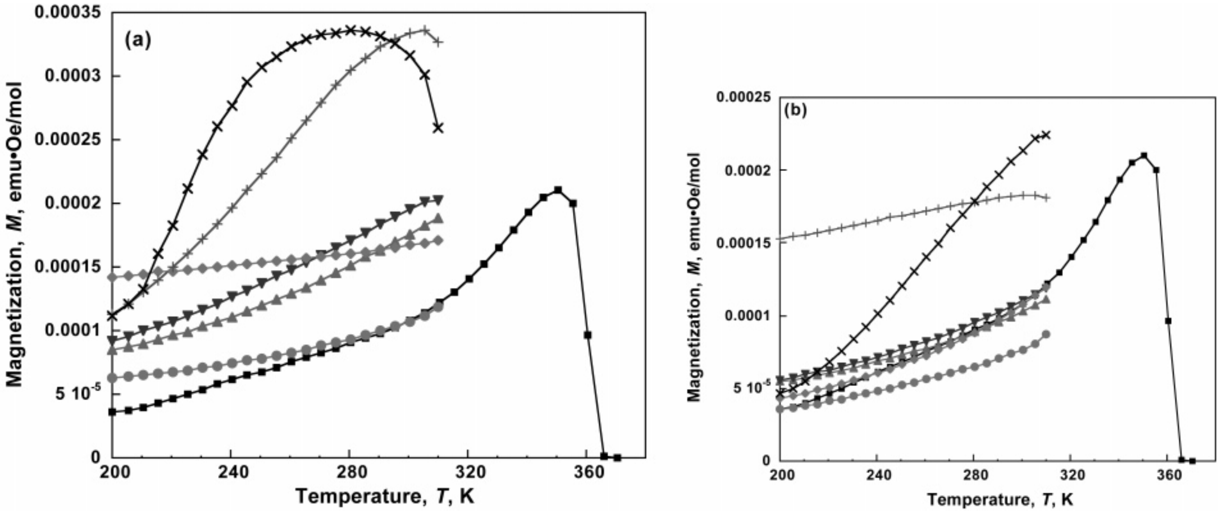

Figure 9. $M(T)$ of V[TCNE]$_x$ uncoated film (■) and film from the same batch coated with 3.72 μm of Parylene C and exposed to the atmosphere for 0 h (●), 1 h (▲), 2 h (▼), 3 h (◆), 5 h (+), and 7 h (×) (a), and film from the same batch coated with 7.79 μm of Parylene C and exposed to the atmosphere for 0 h (●), 1 h (▲), 2 h (▼), 3.5 h (◆), 5.5 h (+), and 7.5 h (×) (b).

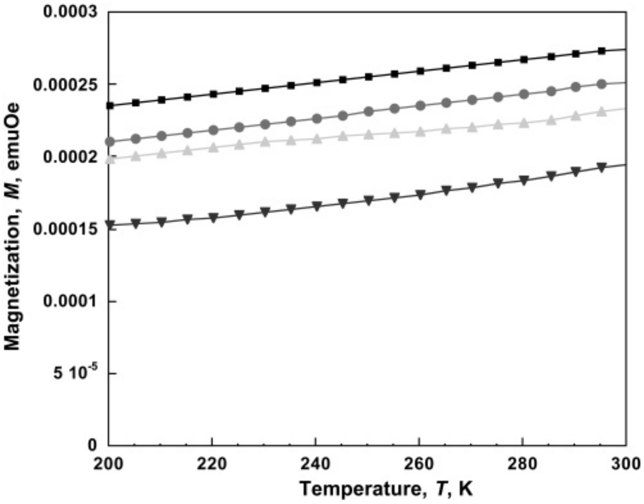

Figure 10. $M(T)$ of V[TCNE]$_x$ protected with 2.2 μm of Parylene C and overcoated with 0.1 μm of Au. The film was exposed to the atmosphere for 0 h (■), 1 h (●), 3 h (▲), and 14 h (▼).

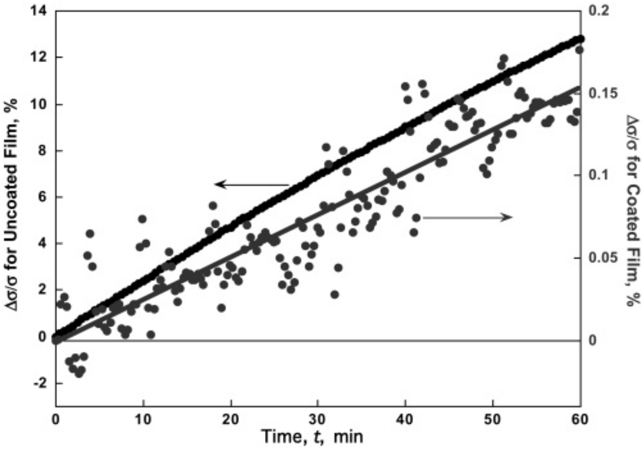

Figure 11. Time dependence of the V[TCNE]$_x$ film normalized conductivity change (%) due to oxidation: (■) uncoated film; (●) film coated with 2 μm of Parylene C.

Electron transport properties of the V[TCNE]$_x$ film are much more sensitive than magnetic properties, presumably due to a percolation character of conductivity in this material. The conductivity, σ, of V[TCNE]$_x$ films gradually decreases with a rate of $v_R \approx 12.8\%$/h (Figure 11) while the magnetization and T_{on} degradation become significant only after ~12 h. When a ~2 μm Parylene C coating was deposited on top of the film immediately after the CVD fabrication, the v_R dramatically decreased to ~0.2%/h at room temperature (Figure 11). Since the degradation rate decreases exponentially[10] with temperature ($v_R < 0.002\%$ at 200 K), the process is assumed to be limited by the rate of oxygen diffusion.

Conclusion

Protective Parylene N and C coatings of the V[TCNE]$_x$ thin film room-temperature magnet provide protection from reaction with the atmosphere. Immediate coating after V[TCNE]$_x$ film deposition stabilizes the T_c at 112 °C (385 K) in contrast to the earlier reported 92 °C (365 K).[4] An ~8 μm coating of Parylene C stabilizes the magnetic properties of the room-temperature V[TCNE]$_x$ magnetic film for more than 7 h, which is appropriate for the final device packaging. Overcoating 2−3 μm Parylene C with 0.1 μm Au stabilizes T_c for at least 14 h with respect to reaction with O_2/H_2O. To enhance the stability of the films for longer times several approaches can be pursued. These include (a) thicker Parylene coatings, (b) thicker gold overcoating films, and (c) reduction of deleterious pinholes.

Preliminary studies, however, reveal that Parylene N coatings exceeding 10 μm plus and overcoated with 0.1 μm Au have a tendency to peal off or/and crack. Since the same protection may be achieved with less than 2 μm Parylene C coating the optimization of metallized Parylene C composite coatings is preferable.

The polymerization of Parylene being an exothermic process may cause local heating and degradation to the magnetic and electrical properties. Nonetheless, no visible damage was observed for up to 8 μm Parylene C coating (~1 to 1.5 h deposition cycle); however, doubling or tripling of the deposition time may heat the sample and alter the magnetic and, especially, the conductivity properties of the film. Likewise, gold overcoating of the Parylene coating would introduce further heating. Additionally, due to a difference between thermal expansion coefficients of V[TCNE]$_x$ film and conformal Parylene coating, a thicker Parylene coating (>10 μm) has a tendency to peel off and/or crack after a thermal cycling.

Thus, there are several coating options depending upon the required level of protection. If the V[TCNE]$_2$ film has to be transferred from one research facility into another within ~1 h time interval, 7 μm of Parylene N or 2 μm of Parylene C coating will work well. For 7 h of protection 8−10 μm of Parylene C coating is needed. For longer storage (10−14 h) in open air the composite coating (7 μm Parylene C + 100 nm gold film) is required.

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(8) Decker, W.; Henry, B. Basic Principles of Thin-Film Barrier Coatings. In Proceedings of the 45th Annual Technical Conference of the Society of Vacuum Coaters, Orlando, Florida, 2002; p 492.

(9) Ag, Al, or other low melting point metals should also be effective.

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