CVD-GROWN THIN FILMS OF TETRACYANOETHYLENE-BASED ROOM-TEMPERATURE FERRIMAGNETS

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A tremendous effort has been devoted in the past two decades to the preparation and study of molecule-based magnets (1). Recent work has been directed to the study of electro-deposited (2) or vapor-deposited (3, 4) thin films of these systems.

We report on the use of new conditions of chemical vapor deposition to grow solvent-free films of $M(TCNE)_x$ molecular magnets where M is vanadium or chromium and TCNE is tetracyanoethylene. The deposition is done on nano-rough silicon (001) wafers. We also report for the first time, the use of X-ray absorption spectroscopy to extract structural data on these tetracyanoethylene-based amorphous magnetic phases.

The experimental set-up used for film preparation is a conventional hot-wall CVD apparatus using tetracyanoethylene and bis(benzene)vanadium or chromium as precursor molecules (table 1).

The films of $V(TCNE)_x$ are processed at 40°C. The deposits are further annealed at 70°C under helium to improve their stability towards air exposure. The films consist of roughly spherical sub-micrometer grains uniformly covering the silicon surface. Infrared and X-ray photoelectron data are in agreement with the presence of monoreduced tetracyanoethylene ligands (*i. e.*, $TCNE^{\bullet -}$) bound to V^{II} metallic centers. Annealed $V(TCNE)_x$ films exhibit a spontaneous magnetization at 300 K (figure 1) while annealing process destroys magnetic ordering in the corresponding solvent-containing $V(TCNE)_x$ 1/2 CH_2Cl_2 (5).

The films of $Cr(TCNE)_x$ are prepared at 80°C and further annealed at 100°C under helium to achieve the loss of the benzene rings. Scanning electron micrographs evidence a uniform film in which numerous cracks are observed. The infrared spectrum shows two ν_{CN} broad bands consistent with $TCNE^{\bullet -}$ moieties coordinated as μ_4-N-σ to chromium. X-ray photoelectron spectroscopy evidences a $Cr2p_{3/2}$ line corresponding to low-oxidation state chromium complexes. The chromium K-edge spectrum reveals an irregular octahedral environment for the Cr atoms within the deposit. At the Cr-K-edge, the Fourier transform of the EXAFS signal displays two peaks assigned to two shells around the chromium, corresponding to N and C nearest neighbors (figure 2). A mean Cr–N distance of 2.03 Å and a Cr–N–C angle of 160° are found. The $Cr(TCNE)_x$ films behave as room-temperature ferrimagnets whilst the corresponding $Cr(TCNE)_x$.y Solvent are not magnetically ordered above 2 K (6).

References

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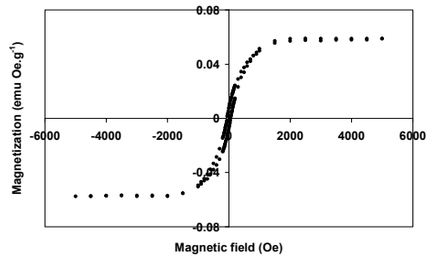

Fig. 1. Hysteresis loop at 300 K for annealed $V(TCNE)_x$ thin films

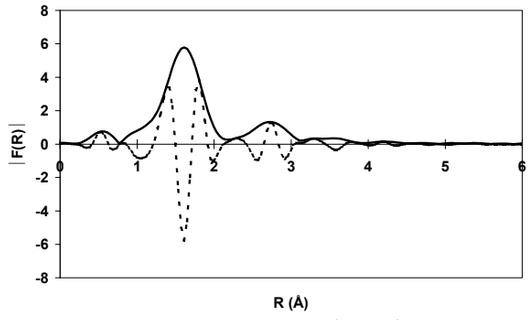

Fig. 2. Fourier transform modulus $|F(R)|$ (solid line) and imaginary part (dotted line) of the EXAFS signal at the chromium K-edge

Table 1. Experimental CVD conditions for film formation of $V(TCNE)_x$ and $Cr(TCNE)_x$

Precursor mass [mg]	Vaporization temperature [°C]	Helium flow rate [sccm]	Substrate zone temp. [°C]	Total pressure [mbar]	Deposition duration [min]
$V(C_6H_6)_2$: 150	145	28	40 [a]	0.7	180
TCNE: 180	83	10			
$Cr(C_6H_6)_2$: 145	150	17	80 [b]	0.7	90
TCNE: 190	83	10			

The deposits were further annealed at 70°C for 10 hours [a], at 100°C for 150 minutes [b]