NIOBIUM AND MOLYBDENUM-BASED MOLECULAR MAGNETS GROWN AS THIN FILMS BY CHEMICAL VAPOR DEPOSITION

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Tetracyanoethylene-based molecular magnets, $M(TCNE)_x$, are only known with first-row transition metals. They behave as ferri-magnets with critical temperatures that exceed 44 K (1). Two of them (with M = V and Cr) have been processed as thin films by chemical vapor deposition on various substrates (2-4). The deposits behave as room temperature ferri-magnets with coercive fields ranging from 5 to 80 Oe depending on the nature of the metal precursor and the preparation conditions.

We report here on the use of chemical vapor deposition to grow films of the two first examples of $M(TCNE)_x$ molecular magnets where M is a second-row transition metal, namely, niobium (group 5) and molybdenum (group 6). The deposition was studied on both alkali halide and (001)-oriented silicon substrates.

The experimental set-up used for film preparation was a conventional hot-wall CVD apparatus using tetracyanoethylene, tris(1,4-diisopropyl-1,4-diaza buta-1,3-diene)niobium and bis(toluene) molybdenum as starting materials (table 1).

Amorphous films of $Nb(TCNE)_x$ consist of thick polygonal grains on KBr (figure 1). On Si(001) wafers, a uniform film (~3 μm in thickness) is obtained (figure 1). Infrared and X-ray photoelectron spectra evidence the presence of reduced tetracyanoethylene moieties bound to Nb^{II} centers. The critical temperature of the films is ~210 K, according to the zero field cooling (ZFC) / field cooling (FC) processes. At 2.5 K, the coercive field is ~200 Oe and the saturation induction is ~20 kOe, a value comparable to that obtained for $V(TCNE)_x$ deposits at 2 K (5).

Amorphous deposits of $Mo(TCNE)_x$ consist of small micro-grains (size: 1-7 μm on KBr; 0.5-2 μm on silicon) uniformly covering the substrate surface (figure 2). The infrared spectrum shows two ν_{CN} broad bands whose positions are similar to those observed for solvent-free V and Cr-TCNE phases (2, 4). X-ray photoelectron data evidence a $Mo3d_{5/2}$ binding energy corresponding to Mo^{II}-complexes. The hysteresis loop (magnetization *vs*. applied magnetic field) at 2 K evidence that the sample nearly saturates for an applied magnetic field of 50 kOe. However, saturation magnetization (~0.5 emuOe g^{-1}) and coercive field (~20 Oe) are smaller than those for $Cr(TCNE)_x$ deposits (~11 emuOe g^{-1} and ~150 Oe, respectively at 2.5 K) (5).

References

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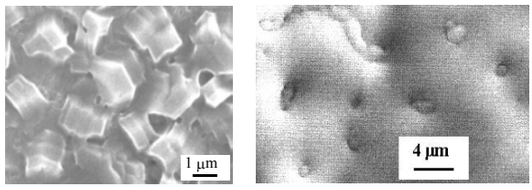

Fig. 1. SEM images of a $Nb(TCNE)_x$ thin film: (left) on KBr pellet, (right) on Si(001)

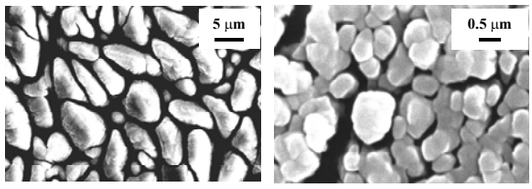

Fig. 2. SEM images of a $Mo(TCNE)_x$ thin film: (left) on KBr pellet, (right) on Si(001)

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

Precursor mass [mg]	Vaporization temperature [K]	Helium flow rate [sccm]	Substrate zone temp. [K]	Total pressure [Pa]	Deposition duration [min]
$Nb(iPr_2\text{-dad})_3$: 110	418	17	353	72	180
TCNE: 110	356	10			
$Mo(C_6H_5CH_3)_2$: 220	388	10	373	72	40
TCNE: 240	356	10			