

# Mn<sub>12</sub> benzoate thin films on Si substrates fabricated by matrix assisted pulsed laser evaporation

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We report on the successful implementation of Matrix Assisted Pulsed Laser Evaporation, to obtain films of the single molecule magnet Mn<sub>12</sub> benzoate on Si substrates. The films have been characterized by optical microscopy, FTIR spectroscopy and extraction magnetometry. The results indicate that this deposition technique allows the fabrication of Mn<sub>12</sub> benzoate films which are continuous and show magnetic properties similar to those of the parent molecular material.

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## 1. Introduction

The prospect of quantum computing, nano-devices and ultrahigh density information storage has provided the motivation of intense research on molecular magnets and particularly Single Molecule Magnets (SMM) [1, 2]. The SMMs are paramagnetic molecules characterized by a large spin ground state, a high zero-field splitting and negligible magnetic interaction between the molecules. Below a characteristic temperature (known as blocking temperature) they exhibit magnetic properties (such as magnetic hysteresis and irreversibility) similar to those of bulk magnets, but of molecular origin, without long-range magnetic ordering. This behavior is attributed to the extremely long relaxation time of the magnetization of each molecule which behaves as a single domain magnetic particle. The magnetization of an SMM is commencing with the application of a magnetic field and is retained even after the magnetic field is switched off.

The archetypal SMM is [Mn<sub>12</sub>O<sub>12</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>16</sub>(H<sub>2</sub>O)<sub>4</sub>], commonly referred as Mn<sub>12</sub>Ac. After the discovery that Mn<sub>12</sub>Ac behaves as nanoscale magnet, a number of Mn<sub>12</sub> derivatives were prepared in their neutral, one – electron or two – electron reduced versions with a variety of carboxylate, mixed carboxylate and mixed carboxylate / non – carboxylate ligands. All the members of the Mn<sub>12</sub> family contain the same [Mn<sub>12</sub>(μ<sub>3</sub>-O)<sub>12</sub>] core that comprises a central [Mn<sup>IV</sup><sub>4</sub>O<sub>4</sub>]<sup>8+</sup> cubane held within a non-planar ring of eight Mn<sup>III</sup> (S=2) ions (in the case of the neutral Mn<sub>12</sub> clusters) by eight μ<sub>3</sub>-O<sup>2-</sup> ions [2]. Such Mn<sub>12</sub> clusters combine a large spin ground state value (S=10) with a large easy - axis type of magnetoanisotropy

(negative axial zero – field splitting parameter, *D*) and display SMM behavior.

SMM integration in devices requires the availability of films with physical properties that compare favorably to those of single-crystal materials. Due to the low affinity with substrates and low decomposition temperature (~65°C) of Mn<sub>12</sub>, physical vapour deposition techniques (such as sputtering, e-beam, thermal evaporation and pulsed laser deposition) cannot be employed for the deposition of thin films [1]. Matrix Assisted Pulsed Laser Evaporation (MAPLE) has proven to be an appropriate technique for the film fabrication of fragile functionalized materials like fibrinogen blood protein [3], biodegradable polymers and polymeric drugs [4]. MAPLE deviates from conventional pulsed laser deposition (PLD) in regard to target preparation and deposition conditions, such as laser fluence. To this date there is only one published report on the deposition of Mn<sub>12</sub>Ac thin films by MAPLE using as a solvent tert-butyl alcohol [5].

In this study we report the deposition of the Mn<sub>12</sub> derivative known as Mn<sub>12</sub>Ph (Mn<sub>12</sub> benzoate: [Mn<sub>12</sub>O<sub>12</sub>(O<sub>2</sub>CPh)<sub>16</sub>(H<sub>2</sub>O)<sub>4</sub>]). Our aim was to implement the promising technique of MAPLE to avoid fragmentation of the Mn<sub>12</sub>Ph molecule during deposition and thus obtain functional thin films of the SMM on Si (1 0 0) single crystalline substrates.

## 2. Experimental

For the preparation of the targets used in the deposition process we produced powders by crushing carefully Mn<sub>12</sub>Ph single crystals. Details about the

synthesis of  $\text{Mn}_{12}\text{Ph}$  single crystals are reported in Ref. [6]. We tried several different solvents as tert-butyl alcohol, n-hexane, dichloromethane and chloroform to obtain a solution, which is required to keep homogenous the mixture to get the frozen target used in the deposition process. Initially we used tert-butyl alcohol as a solvent following the findings reported in Ref. [5]. We performed ultrasonic stirring, heating up of the  $\text{Mn}_{12}\text{Ph}$  - tert-butyl alcohol mixture for 20 min at  $30^\circ\text{C}$  and finally for 15 min at  $40^\circ\text{C}$ . After each step we observed the powder of  $\text{Mn}_{12}\text{Ph}$  was not dissolved completely and instead formed a suspension in variance with Ref [5]. Chloroform,  $\text{CHCl}_3$ , (CF) was selected as the optimum one among the four solvents we tried because it allowed the formation of solutions, and is also easily volatile and highly absorbent of 248 nm UV irradiation. As a result chloroform molecules were vaporized and removed by pumping from the chamber, whereas  $\text{Mn}_{12}$  molecules were transferred onto the Si substrate without degradation.  $\text{Mn}_{12}\text{Ph}$  solute was dissolved in a CF solvent at a concentration of 0.1 g / 20 ml. Afterwards the solution was frozen in the presence of liquid  $\text{N}_2$  creating a solid target that was kept frozen during the deposition process with the aid of a cooler.

We used a KrF\* excimer laser ( $\lambda = 248$  nm,  $\tau = 25$  ns), COMPexPro 205, and searched for the correct deposition parameters such as fluence and pulse repetition rate. The optimal values of fluence and pulse repetition rate were  $60 \text{ mJ/cm}^2$  and 3 Hz, respectively. Si substrates were ultrasonically cleaned prior to use for thin film deposition using acetone, methanol, isopropanol and deionized water and blown dried with high purity  $\text{N}_2$  gas. The substrates were heated to  $30^\circ\text{C}$  and placed parallel at 3 cm far from the rotating frozen target. The pressure in the deposition chamber was maintained between 4 and 5.3 Pa.

The fabricated samples were characterized by optical microscopy, FTIR spectroscopy (Shimadzu 8400s system), as well as extraction Magnetometry (Quantum Design - Physical Properties Measurement System). Comparison was made with the properties exhibited by the powders used for creating the solution/target.

### 3. Results and discussion

From the optical image shown in Fig. 1 we observe that the film produced using the deposition conditions described earlier is continuous and uniform to a high degree. The deposition rate of about 0.1 nanometers per pulse was observed for sample SMM-Si6, which compares well with the values obtained for other targets containing CF solvent in Ref [3]. In Fig. 2, zero field cooled (ZFC) and field cooled (FC) magnetization measurements taken for the film and the powder used to fabricate the target (insert of Fig. 2) in a magnetic field of 2 T are presented. The diamagnetic contribution of the Si substrate and the gelatine capsule holder were removed. A clear irreversibility is observable below 5K, which compares well with the blocking temperature ( $T_B$ ) of 4K previously reported [1]. The last is attributed to the characteristic slow down of the magnetization relaxation time at low temperatures of pure molecular origin. Above  $T_B$  the

sample exhibits paramagnetic behavior (see solid line in Fig. 2) with a Curie temperature of  $-38.3$  K indicating strong antiferromagnetic interaction among the Mn ions and no evidence of the secondary magnetic phase reported in Ref. [5]. We attribute this performance to the more appropriate solvent used in our depositions which allowed for a better and more homogenous transfer of the  $\text{Mn}_{12}\text{-Ph}$  compound from target to the collector. In Fig. 3 the magnetization of the film as a function of applied magnetic field measured at 2, 5, 7.5, and 20 K is illustrated. A clear hysteresis loop is visible at the lowest temperature of measurement (2K) without reaching full saturation at the highest measurement field of 4 T, indicating the presence of an additional paramagnetic phase. The inset of Fig. 3(a) shows the hysteresis loop for the powder used to fabricate the target. We conclude therefore that the grown films retain the characteristic magnetic properties found in bulk samples of the parent molecular compound.

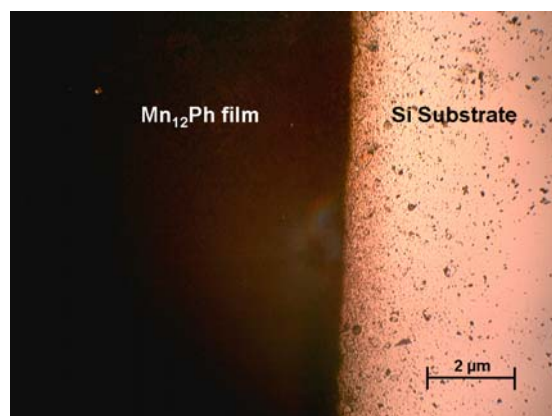


Fig. 1. Optical microscopy of the  $\text{Mn}_{12}\text{Ph}$  film deposited on Si substrate (top view) by MAPLE at  $30^\circ\text{C}$ .

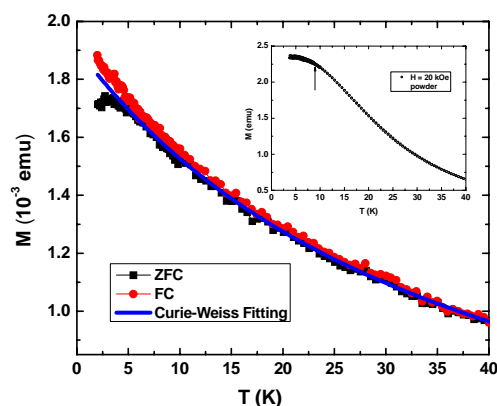


Fig. 2. Zero field cooled (ZFC) and field cooled (FC) magnetization measurements in a magnetic field of 2 T of a  $\text{Mn}_{12}\text{Ph}$  film deposited on Si substrate by MAPLE. The solid line is the fit of the ZFC magnetization to Curie-Weiss Law. The inset shows the ZFC and the FC magnetization for the powder used to fabricate the film. The arrows indicate the irreversibility temperature.

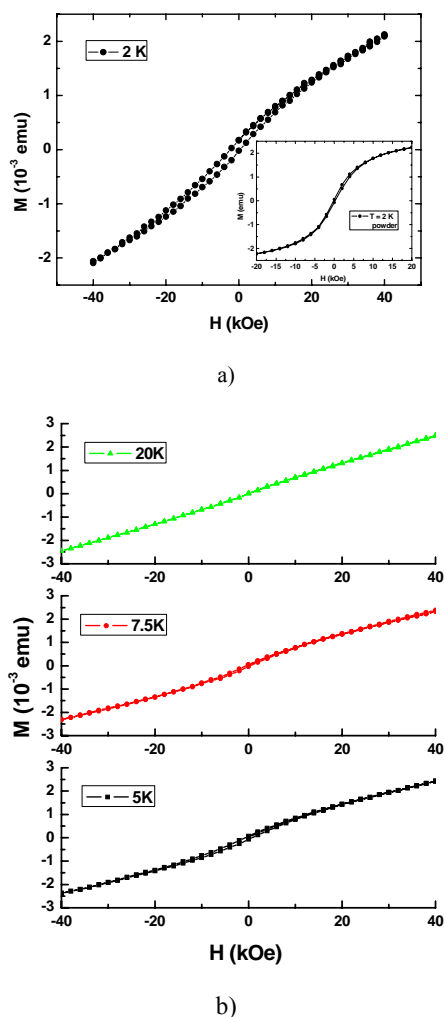
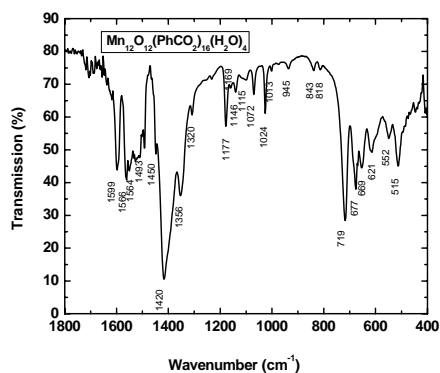


Fig. 3. Magnetization versus applied magnetic field measurements taken at (a) 2K and (b) 5, 7.5 and 20 K for a Mn<sub>12</sub>Ph film deposited on Si substrate by MAPLE. The inset in (a) shows the hysteresis loop for the powder used to fabricate the target measured at 2 K. The coercive field for the powder is 0.21 kOe and for the thin film is 1.331



kOe.

Fig. 4. Room-temperature FTIR spectrum for powder Mn<sub>12</sub>Ph.

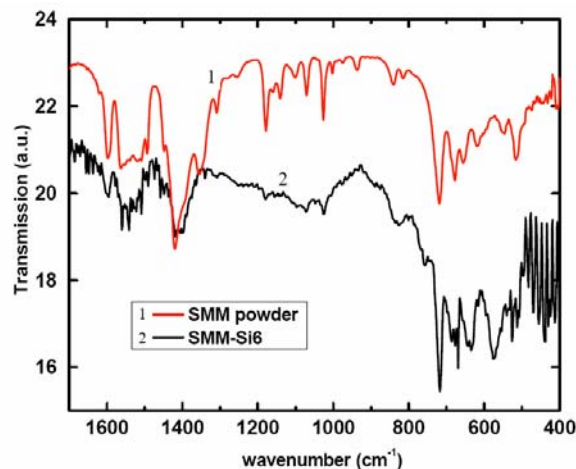


Fig.5. Room-temperature FTIR spectra for the Mn<sub>12</sub>Ph powder and the as-deposited Mn<sub>12</sub>Ph film. The Si substrate contribution has been removed from the raw data of the film. However, the main peak of Si at around 610 cm<sup>-1</sup> is still present in the spectrum of the film.

FTIR spectra (4000 – 400 cm<sup>-1</sup>) of the Mn<sub>12</sub>Ph molecule, the as-deposited film and the Si substrate were recorded. The FTIR spectrum of the Mn<sub>12</sub>Ph molecule that is shown in Fig. 4 is consistent with that reported in the literature [6]. Several bands appear in the 1600-1400 cm<sup>-1</sup> range which are due to contributions from the benzoate  $\nu_{as}(\text{CO}_2)$  and  $\nu_s(\text{CO}_2)$  modes that are expected in this region, and also the stretching vibrations of the aromatic rings of the benzoate ligands. The strong bands at 1566 and 1420 cm<sup>-1</sup> have  $\nu_{as}(\text{CO}_2)$  and  $\nu_s(\text{CO}_2)$  characters [7], respectively. Finally, the medium intensity bands at 621 and 669 cm<sup>-1</sup> are tentatively assigned to vibrations involving Mn<sup>n+</sup>-O<sup>2-</sup> stretching [8]. In Fig. 5, the FTIR spectra of the Mn<sub>12</sub>Ph molecule, the Si substrate and the as-deposited film are shown. This comparison reveals that the IR spectra of the as-deposited film: i) contains the main bands present in that of the Mn<sub>12</sub>Ph molecule ii) does not display any significant additional bands that could be attributed to a decomposition product. Thus the FTIR spectra provide evidence that there is no significant fragmentation of the Mn<sub>12</sub>Ph molecules taking place during the deposition process.

#### 4. Conclusions

The MAPLE technique was proven to be an adequate method for thin film deposition of the SMM Mn<sub>12</sub>Ph. The best film was obtained using CF solvent, fluence of 60 mJ/cm<sup>2</sup> and pulse laser repetition rate of 3 Hz. FTIR analysis of powders and the best as-deposited film provides evidence that no significant degradation of the Mn<sub>12</sub>-based molecules takes place during the deposition process. These results were corroborated with the magnetic measurements which provide evidence that the magnetic features of the SMMs (hysteresis and irreversibility) were preserved for deposited thin films without the presence of a secondary magnetic phase.

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