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Enhanced magnetic anisotropy of Mn_{12}-acetate

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Abstract

Thin films of the single molecule magnet $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$ (Mn_{12}-acetate) have been fabricated on a Si-substrate by the dip-and-dry method, a simple and robust technique. Atomic force microscopy and X-ray photoelectron spectroscopy characterizations reveal that homogeneous, thin films of a few molecular layers with smoothness at the molecular level are deposited. Significant changes in magnetic properties of Mn_{12}-acetate exposed to the same solvent were observed in zero field-cooled and field-cooled magnetization, as well as AC-susceptibility measurements. The blocking temperature was found to increase to $T_B > 10\,K$ at low magnetic fields, indicating an enhanced magnetic anisotropy.

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Keywords: Mn_{12}-acetate; Thin film; Blocking temperature; Magnetic anisotropy

1. Introduction

Single molecule magnets (SMMs), the most studied of which is $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$ (Mn_{12}-acetate) [1–4], provide a model system for the study of quantum tunneling of the magnetization [3]. Stepwise magnetization hysteresis loops and out-of-phase AC susceptibility signals are due to a high spin ground state and a strong uniaxial magnetic anisotropy of Mn_{12}-acetate [2], in which eight Mn^{3+} ($S = 2$) ions and four Mn^{4+} ($S = 3/2$) ions are magnetically coupled by oxygen bridges to form the $S = 10$ ground state [5]. Moreover, these compounds have also been considered for future applications such as quantum computing and information storage devices [6,7]. The interesting magnetic properties in these materials arise from individual molecules rather than intermolecular interactions. For this reason, single molecules can, in principle, be used to store magnetic information. In order to use these molecules in devices, however, an

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increase of the blocking temperature (T_B) of these materials is essential.

There are few reports on the film production of Mn_{12} derivatives to date [8–14], and even less reports on the significant enhancement of magnetic properties from that of the parent compound [11,12]. Here we report the production of thin, homogeneous Mn_{12}-acetate films of continuous coverage by the dip-and-dry (DAD) method, and the enhancement of the magnetic anisotropy of Mn_{12}-acetate, which has undergone similar solvent exposure. Two studies regarding the magnetic properties of Mn_{12} derivatives formed by thermal transformation and gas inclusion as well as incorporation into mesoporous silica have been reported [15,16]. In the present study, an increase of T_B to >10 K in DC-susceptibility measurements was observed, a significant change from the parent compound behavior that shows a zero-field blocking temperature of ~3.5 K, as observed in Ref. [3] and in our as-produced Mn_{12}-acetate powder. These observations are of fundamental importance and a promising first step for potential applications of these materials. Atomic force microscopy (AFM) was used to investigate the surface morphology and the thickness of the films, which revealed roughness on the molecular scale and a thickness of ~1 molecular layer per dip. X-ray photoelectron spectroscopy (XPS) measurements were also carried out to analyze the electronic structure of the thin films.

2. Experimental

A fresh sample of Mn_{12}-acetate was prepared following the customary procedure [1]. For a typical preparation of films described below by the DAD technique, 2.2 ± 0.1 mg of Mn_{12}-acetate was dissolved in 10 mL of acetonitrile (CH_3CN) to produce a 1.1×10^{-4} mol L^{-1} solution. Prior to the DAD step, the Si/SiO_2 substrate was rinsed with acetone and isopropanol. The clean wafer was dipped in the prepared Mn_{12}-acetate solution and immediately removed. A thin film of the solution was subsequently observed on the substrate, which dried within several seconds to produce a thin film of Mn_{12}-acetate. All procedures were carried out inside a fume hood under ambient conditions.

After preparation of thin films by the DAD technique, the surface morphology of the films was studied by AFM, with a Digital Instruments Nanoscope IIIa. The AFM images were acquired in the tapping mode with a silicon cantilever and tip under ambient conditions. Room temperature core level XPS measurements were performed using a Kratos AXIS ULTRA spectrometer equipped with a concentric hemispherical analyzer using the Al Kα radiation ($h\nu = 1486.6$ eV) and a base pressure of $\sim 2 \times 10^{-8}$ Torr. The binding energies were calibrated with respect to the C 1s peak (284.8 eV).

3. Results and discussion

3.1. AFM and XPS characterizations

Fig. 1 shows AFM images of the Mn_{12}-acetate thin film. A topographical top-view, the corresponding 3D image, and height profile are shown for $1 \times 1\ \mu m^2$ scan size, respectively from (a) to (c). This figure shows a Mn_{12}-acetate thin film, which, considering the simplicity of the DAD method, is surprisingly homogeneous and smooth. In a control experiment, the DAD method was used with pure acetonitrile instead of the Mn_{12}-acetate solution. As expected, the resulting images (not shown) did not show any substantial surface corrugations. Detailed examination of the AFM images (Fig. 1) reveals that the typical horizontal size of pictured Mn_{12}-acetate clusters is about 25 nm and the average vertical height is about 2 nm, close to a molecular diameter. As a result of the radius of curvature of an AFM tip (~10 nm) [17], the typical horizontal size of a cluster appears larger than a single molecule. The height information, however, indicates that nearly all of the particles on the film form a monolayer instead of clusters. The root mean square (RMS) roughness of the surface is 0.73 nm, considerably smaller than the size of a single molecule (1.7 nm) [1].

The thickness of the films after a single DAD step was measured and found to be ~2 nm in