A possible approach towards spin-polarized transport through single molecule magnets: Mn_{12} on $\text{Au}(100)/\text{Fe}(100)/\text{MgO}(100)$

S. Voss^{a,*}, M. Fonin^a, F. Zinser^{a,b}, M. Burgert^c, U. Groth^c, U. Rüdiger^a

^a Department of Physics, University of Konstanz, 78457 Konstanz, Germany

^b Max Planck Institute for Solid State Research, 70569 Stuttgart, Germany

^c Department of Chemistry, University of Konstanz, 78457 Konstanz, Germany

ABSTRACT

The possibility to use the $\text{Au}(100)/\text{Fe}(100)/\text{MgO}(100)$ system as a substrate for future spin-polarized transport measurements on Mn_{12} single molecule magnets has been investigated by means of scanning tunneling microscopy and X-ray photoelectron spectroscopy at room temperature. In particular, the stability of the iron layer during a wet chemical preparation of Mn_{12} monolayers was studied. The results demonstrate that Mn_{12} can be deposited on $\text{Au}(100)/\text{Fe}(100)/\text{MgO}(100)$ while preserving the metallic nature of the ferromagnetic iron layer which is required as a possible source of spin-polarized electrons in future studies.

Keywords:

Single molecule magnets

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1. Introduction

Stimulated by the discovery of the fascinating properties of Mn_{12} single molecule magnets (SMMs) [1,2], like quantum tunneling of magnetization or quantum phase interference effects [3a–d], different theoretical studies have predicted possibilities to address individual SMMs by means of a spin-polarized current [4a–c]. In particular, the feasibility of switching the magnetization of a SMM coupled to ferromagnetic electrodes as well as possible signatures of the switching in electronic transport spectra were investigated theoretically. Mn_{12} may be particularly suited for such studies due to its relatively high blocking temperature (~ 3.5 K) and the possibility of straightforward chemical modification of the ligand shell surrounding the magnetically active core [5a,b], which is required to deposit the molecules on a surface [6]. In principle, spin-polarized transport studies [7] on Mn_{12} can be performed in the near future as all ingredients required for the experiments are available [8]. In recent years, there has been significant progress in the field of spin-polarized scanning tunneling microscopy (STM) and spectroscopy (STS) [9a,b]. Furthermore, a large number of studies on the possibility to deposit Mn_{12} molecules on surfaces was performed [6,10a–f]. The ultimate evidence for a deposition of intact Mn_{12} molecules is still lacking. While recent studies revealed the presence of homogeneous monolayers of molecules on $\text{Au}(111)$ surfaces, no unambiguous evidence for the preservation of their magnetic properties or the usual oxidation states of the Mn ions within the Mn_{12} core ($\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$) could be

obtained so far [11a,b]. Nevertheless, there are indications that the molecules are not degraded during the deposition but due to the disruptive influence of the measurement techniques themselves [12a,b]. On the other hand, also non-destructive techniques revealed the lack of a magnetic hysteresis in Mn_{12} monolayers [10b,13] which might, however, be assigned to a reduced blocking temperature due to a molecule–surface interaction or an insufficient sensitivity of the techniques applied. Consequently, spin-polarized transport measurements at very low temperature are worth to be considered to figure out whether the magnetic properties of the Mn_{12} core are preserved after the deposition on a surface.

Here we report the preparation and investigation of Mn_{12} monolayers on $\text{Au}(100)/\text{Fe}(100)/\text{MgO}(100)$ that may be used for future spin-polarized STM and STS measurements [14a–c]. The results demonstrate that the metallic nature of the ferromagnetic iron layer can be preserved during the wet chemical preparation so that it might be used for spin injection in future experiments. Additionally, Mn_{12} was successfully grafted on $\text{Au}(100)$ what demonstrates the general suitability of techniques previously developed for the deposition on $\text{Au}(111)$.

2. Experimental

$[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CC}_6\text{H}_4\text{F})_{16}(\text{EtOH})_4]$ (Mn_{12} -pfb) and 4'-mercapto-octafluorobiphenyl-4-carboxylic acid (4-MOBFA) were synthesized as described elsewhere [10e]. The $\text{Au}(100)/\text{Fe}(100)/\text{MgO}(100)$ system was fabricated in an ultrahigh vacuum chamber (UHV; pressure below 10^{-10} mbar) in four steps: (1) MgO was annealed at 1000 K for 1 h to remove contaminants and defects. (2) Fe was

* Corresponding author. Tel.: +49 7531 883690; fax: +49 7531 883789.
E-mail address: soenke.voss@uni-konstanz.de (S. Voss).

Fig. 1. Schematic representation of the STM investigation of Mn_{12} -pfb deposited on $\text{Au}(100)/\text{Fe}(100)/\text{MgO}(100)$ via ligand exchange reaction with 4-MOB-CA.

evaporated onto MgO from an electron beam evaporator at room temperature at a rate of $1.5 \text{ \AA}/\text{min}$. (3) After the Fe deposition the sample was annealed at 870 K for 30 min . (4) Finally, Au was evaporated from a thermal evaporator (effusion cell) at a rate of $6.5 \text{ \AA}/\text{min}$ at a sample temperature of 600 K . After the preparation and investigation of $\text{Au}(100)/\text{Fe}(100)/\text{MgO}(100)$, Mn_{12} -pfb was deposited on the surface via ligand exchange reaction with 4-MOB-CA as described elsewhere [10e]. A sketch of the sample configuration is shown in Fig. 1. STM, STS and X-ray photoelectron spectroscopy (XPS) measurements were performed in an Omicron Multiprobe UHV system at room temperature. For the STM/STS measurements, electrochemically etched tungsten tips, flash-annealed by electron bombardment were used. XPS spectra were obtained with $\text{Al K}\alpha$ radiation ($h\nu = 1486.6 \text{ eV}$) with the resolution of the EA 125 energy analyzer set to 0.65 eV .

3. Results and discussion

Fig. 2 shows two STM images obtained from $\text{Fe}(100)/\text{MgO}(100)$ (a; 16 nm thick iron layer) and from $\text{Au}(100)/\text{Fe}(100)/\text{MgO}(100)$ (b; 20 nm thick gold layer). In Fig. 2a, Fe terraces along with monoatomic steps with perpendicular edges are visible which is in agreement with previous studies [15a,b]. Fig. 2b shows terraces and monoatomic steps of the $\text{Au}(100)$ surface. The inset of Fig. 2b shows the surface reconstruction of $\text{Au}(100)$ which appears as a straight line pattern in contrast to the herringbone reconstruction of $\text{Au}(111)$. The surface morphology is in agreement with previous studies [16]. In the present study, the preparation parameters were optimized to fabricate surfaces with low roughness and sufficiently large Au terraces facilitating the addressing of Mn_{12} monolayers deposited on the surface by means of STM.

Fig. 3 shows an STM image obtained after deposition of Mn_{12} -pfb on $\text{Au}(100)/\text{Fe}(100)/\text{MgO}(100)$ via ligand exchange reaction with 4-MOB-CA. A monolayer of clusters is visible which is in agreement with previous STM studies on Mn_{12} monolayers deposited on $\text{Au}(111)$ single crystals [10e,12a]. The shape of the subjacent terraces and steps can be estimated due to slight differences of the apparent height that are visible in the image. The individual molecules have been further investigated by means of scanning tunneling spectroscopy (STS; see inset of Fig. 3) which revealed the presence of a large conductance gap in agreement with previous studies [17]. In addition, XPS confirmed the presence of the Mn $2p$ peaks also observed in previous works (see Fig. 4) [10e,12a]. The agreement with previous studies demonstrates that Mn_{12} -

Fig. 2. STM images ($100 \times 50 \text{ nm}^2$) of (a) $\text{Fe}(100)/\text{MgO}(100)$ and (b) $\text{Au}(100)/\text{Fe}(100)/\text{MgO}(100)$. The inset of (b) shows a $20 \times 20 \text{ nm}^2$ STM image of the surface reconstruction of $\text{Au}(100)$.

Fig. 3. STM image ($150 \times 150 \text{ nm}^2$) of Mn_{12} -pfb molecules ($U_T = 2.5 \text{ V}$; $I_T = 8.6 \text{ pA}$). The inset shows an STS spectrum of a single Mn_{12} -pfb molecule obtained at a set voltage of 2.7 V (set current 6.9 pA).

pfb was successfully deposited on $\text{Au}(100)/\text{Fe}(100)/\text{MgO}(100)$. Furthermore, the results demonstrate that details of the gold surface morphology, like different surface reconstructions or terrace shapes in the case of $\text{Au}(100)$ and $\text{Au}(111)$ do not significantly influence the arrangement of the Mn_{12} molecules. This observation is in agreement with a previous study which suggested a statistical arrangement of Mn_{12} on 4-MOB-CA/Au [10e].

To investigate a possible influence of the wet chemical deposition of Mn_{12} on the properties of the Au-covered iron layer, XPS measurements were performed in order to detect a possible oxidation of the iron. Fig. 5a shows a Fe $2p$ spectrum obtained from $\text{Fe}(100)/\text{MgO}(100)$. The peak positions (Fe $2p_{1/2}$: 719.9 eV , Fe

Fig. 4. XPS Mn 2p/Au 4p_{1/2} spectrum obtained after deposition of Mn₁₂-pfb on Au(100)/Fe(100)/MgO(100).

Fig. 5. XPS Fe 2p spectra of (a) Fe(100)/MgO(100) (after in situ Fe evaporation), (b) Mn₁₂-pfb on Au(100)/20 nm/Fe(100)/MgO(100) after removal of Mn₁₂, 4-MOBICA, and Au via sputtering, (c) Mn₁₂-pfb on Au(100)/2 nm/Fe(100)/MgO(100) after removal of Mn₁₂, 4-MOBICA, and Au via sputtering.

2p_{3/2}: 706.8 eV) as well as the shape of the spectrum are consistent with metallic iron [18]. This measurement was performed immediately after the deposition of Fe on MgO. It is well known that removing the unprotected iron layer from the UHV would result in an oxidation. Hence, sensitive samples are usually covered with protection layers like gold thin films prior to sample transfers or further processing. Nevertheless, it is important to carefully investigate the Mn₁₂/Au(100)/Fe(100)/MgO(100) system since the adopted preparation steps (immersion in solvents [19], possibly corrosive 4-MOBICA etc.) are significantly different from an ordinary sample transfer. To study a possible oxidation of the iron layer during the preparation ex situ, the Mn₁₂/4-MOBICA/Au(100) layers had to be removed from the sample because the information depth of XPS is limited to a few nm [20]. To this end, the sample was continually sputtered with Ar⁺ ions at 800 eV for 10 min in each step. After each sputtering cycle, an XPS spectrum was recorded. Due to the XPS information depth of a few nm the transition from a pure Au to a mixed Au/Fe signal could be easily identified and the sputtering was terminated at this time to avoid an accidental removal of a possibly oxidized iron layer. Subsequently, a XPS Fe 2p

spectrum was recorded. Fig. 5b shows the spectrum obtained from the sample previously covered with Mn₁₂. The spectrum coincides with those of metallic iron and thus provides evidence that the iron layer was not oxidized. In the next step, a control experiment was performed with an only 2 nm thick Au layer while all different parameters and preparation steps were identical to those of the previous sample. Fig. 5c shows an Fe 2p spectrum that reveals the occurrence of additional Fe 2p peaks after the exposure to ambient conditions. The comparison of the position of the additional Fe 2p_{3/2} peak (710.5 eV) with previous studies indicates a partial oxidation of the iron layer [18].

The comparison of the XPS spectra demonstrates that the iron layer underneath the 20 nm Au layer is not oxidized during the wet chemical deposition of Mn₁₂ while in the case of a thin layer an oxidation cannot be ruled out. This observation suggests a trade-off between oxidation protection and spin polarization. Although the spin diffusion length in Au can be significantly larger than 20 nm [21], a thin buffer layer may be preferable to achieve a sufficient spin injection.

In conclusion, a possibility to fabricate samples for future spin-polarized transport studies on Mn₁₂ single molecule magnets was investigated. The results demonstrate that Mn₁₂ molecules can be deposited on Au(100)/Fe(100)/MgO(100) layer systems by means of wet chemical deposition methods without altering the metallic nature of the ferromagnetic iron which is required as a source for spin-polarized electrons. The insights will contribute to future transport studies on Mn₁₂ and possibly different single molecule magnets.

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