Preparation of nanometer-scale iron dots on insulating layer

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Abstract

We studied the preparation of nanometer-sized magnetic dots on MgO tunnel barriers. The samples were formed by depositing Fe thin layers, which exhibited a 3D Volmer–Weber growth on MgO (001) substrates. The current–voltage characteristics were then measured using a scanning tunneling microscope. By comparing different preparation techniques such as the oxidation of a metallic Mg layer and direct deposition of MgO by electron beam evaporation, we found that direct deposition was the best way to achieve flat MgO surfaces and assemblies of dots with uniform heights. The growth of the Fe dots seems to be mainly governed by the density of surface defects of the buffer, which act as nucleation sites. The density of these defects appears to be modified by the insertion of an iron electrode prior to the deposition of the MgO layer.

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Tunnel junctions based on nanometric metallic clusters have been under intensive study given their potential applications in single electron transistor and magnetic random access memory [1]. In such systems, the small size of the metallic clusters leads to small capacitances (C ≈ 10−19 F) so that the charging energy EC = e2/2C becomes larger than the thermal activation. The system may therefore exhibit Coulomb blockade and Coulomb staircase, i.e. a quantization of the charge: an electron cannot tunnel into the metallic cluster unless the applied voltage overcomes a threshold given by eV ≥ EC. The period of this staircase is determined by the capacitances of the tunnel junctions involved in the transport processes. In the case of ferromagnetic particles, spin-dependent tunnel magnetoresistance (TMR) phenomena may also be observed. The interplay of Coulomb blockade and TMR gives rise to new phenomena such as a strong enhancement or oscillations of the TMR ratio [2–7]. In the theory of sequential tunneling (or orthodox theory), the current vanishes below the Coulomb threshold so that no TMR can be defined. The TMR ratio then exhibits oscillations with a period corresponding to the period of the Coulomb staircase [8]. However, previous experiments [10] showed a non-zero current and a strong enhancement of the TMR ratio below the Coulomb threshold, thus indicating that the orthodox theory cannot explain all the features of single electron tunneling. New models have then been developed including various phenomena such as spin accumulation [9], cotunneling [10] or quantization of the energy levels of the magnetic particles [11].

However, the comparison between these theories and the experimental results is made difficult by the complexity of the structure of the studied samples. The great number of particles involved in the samples may lead to current path changes during measurement which give rise to noisy I(V) characteristics. Furthermore, a broad size-distribution leads to different periods of the Coulomb staircase. As the applied voltage is increased, the smaller particles get involved in the tunneling process and the period of the staircase is averaged out by the presence of numerous different capacitances.

Hence, simple model systems have to be prepared. The number of tunneling paths may be greatly reduced by decreasing the lateral size of the samples.
using micro-fabrication, or scanning tunneling spectroscopy (STS) through the use of a scanning tunneling microscope (STM).

In order to reduce the width of the size distribution, self-organized assemblies of dots may be studied. Well-defined two-dimensional lattices of magnetic dots have been successfully prepared by using chemical techniques (colloids) [12,13]. The structure of these lattices could be changed from square to hexagonal by changing the nature of the ligand. Transport measurements performed on these samples [14] indicated the occurrence of Coulomb blockade for temperatures below 70 K. However, due to the great number of tunneling paths, no Coulomb staircase was observed.

Physical techniques were also used to obtain self-organization. Such techniques are extensively used in the field of semi-conductors in order to obtain arrays of quantum dots to study their optical properties. These arrays of semi-conductive dots were prepared by taking advantage of local strain fields and were made of pyramidal [15] or square islands [16]. Other groups proposed to use the bonding of Si (001) substrates with a twist angle in order to prepare a lateral array of nucleation sites for the growth of dots [17]. Metallic magnetic nanostructures were also successfully prepared by using Co/Au or Fe/Mo systems [18]. However, given that they are only based on metals, these systems cannot be used to observe Coulomb blockade phenomena. Recently, Gai et al. [19,20] achieved narrow size distributions by preparing Fe dots on NaCl (100) substrates. One-dimensional chains of Fe clusters were prepared since the dots preferentially grow on the edges of NaCl terraces. These results could open a new research field in the preparation of self-assembled magnetic dots for tunnel transport experiments.

In this paper, we present results about the growth of Fe clusters on MgO substrates by physical methods. In order to obtain well-defined tunnel resistances between the dots and the bottom electrode, it is of first importance to reduce the roughness of the buffer layers. To achieve this goal, we prepared samples by using various techniques to deposit the MgO insulating layer. In a first part, we studied MgO layers prepared by oxidation of a metallic Mg layer by two different methods: natural and plasma-assisted oxidation. Finally, samples were prepared by direct deposition of a MgO layer, and all these techniques were compared to each other.

In order to perform STM measurements and to allow current-perpendicular-to-the-plane (CPP) transport measurements, the samples require a bottom Fe electrode. This Fe electrode was then covered by a thin MgO layer acting as a tunnel barrier. Finally, a thin iron layer was deposited on top of this MgO barrier. The structure of all the samples we prepared was then: Fe electrode/MgO, 0.8–1 nm/Fe, t nm where t ranges from 0.3 to 1 nm.

1. Preparation techniques of the MgO thin layer

1.1. Natural oxidation

Samples were prepared on MgO (001) substrates. After ultrasonic cleaning in aceton, the substrates were introduced in the MBE system and annealed at 500 °C for 30 min. First, a 1 nm thick Fe seed layer was deposited at 100 °C by electron beam evaporation (EBE) to promote (100) growth of the subsequent layers. A 50 nm thick Au layer was then deposited at room temperature (RT) by using a Knudsen cell. This Au buffer layer strongly improves the roughness of the samples and was covered by a 10 nm thick Fe layer deposited in the same conditions as the seed layer. In order to prepare the MgO tunnel barrier, a 1 nm thick Mg layer was deposited and oxidized under a 0.2 atm oxygen atmosphere. It should be noted that due to the respective densities of Mg and MgO, one expects a reduction of the thickness by a factor: 0.81, thus leading to a 0.8 nm thick MgO layer. Because of the large lattice mismatch between Fe and Mg, the Mg layer was polycrystalline. On the other hand, the lattice mismatch between Fe and MgO is only 3.7% in the case of a Fe (100)[110]/MgO (100)[100] epitaxial relationship. A monocrystalline MgO layer may then be achieved after oxidation of the metallic Mg layer. Despite this smaller lattice mismatch between MgO and Fe, the MgO layers obtained by natural oxidation were still polycrystalline as shown on the RHEED patterns in Fig. 1 which exhibit broad spots indicating polycrystalline structure with a preferential (001) orientation of the MgO crystallites.

A Fe layer with a nominal thickness of 1 nm was deposited on top of this polycrystalline layer, so that the final structure of the samples is: (Fe, 1 nm/Au, 50 nm/Fe, 10 nm/MgO, 0.8 nm/Fe, 1 nm). Due to the large surface energy difference between Fe (2.9 J/m²) and MgO (1.16 J/m²) [21], 3D Volmer–Weber growth occurred. The mean diameter of the iron particles determined from the STM image (Fig. 2) is about 6 nm. It should, however, be noted that due to the convolution between the STM tip and the dots, the measured absolute size may be larger than the real size of the dots but this does not prevent relative comparisons between several STM measurements.

The associated activation energy determined by a rough calculation is then: 25 meV (if we assume that $C = 4\pi\varepsilon\varepsilon_0 r$ where $r$ stands for the mean radius of the particles and $\varepsilon$ for the dielectric constant of MgO: $\varepsilon = 9.8$). This energy corresponds to a temperature of about 295 K. Therefore, these samples are not suitable for the observation of Coulomb blockade at RT.

It is interesting to notice that the STM image shows a partial alignment of the dots. This feature may be due to the high roughness (see line profile of Fig. 2) of the MgO underlayer since the Fe dots may grow preferentially on step edges [19].
1.2. Plasma-assisted oxidation

The MgO (001) substrates have been cleaned by using the same procedure as previously described and were then annealed at 600 °C after insertion in the deposition chamber. First, a 20 nm thick Fe layer was deposited by EBE at RT at a rate of 0.2 Å/s and annealed at 200 °C during 2 min to improve its flatness. The expected Fe (100)[110]/MgO (100)[100] epitaxial relationship was observed. A thin Mg layer was subsequently deposited at RT on top of this Fe electrode. The Mg layer was then plasma-oxidized under a (4 Pa + 20% O₂) atmosphere. By using a RF power of 10 W, the oxidation time was about 2–3 min.

In the case of a plasma-assisted oxidation of the Mg layer, a monocrystalline MgO layer was achieved. The RHEED patterns, shown on Fig. 3, indicate the expected Fe (100)[110]/MgO (100)[100] [21] epitaxial relationship. However, as indicated in Fig. 3, they are made of broad streaks which originate from the poor crystallinity of the MgO layer. The nature of the structural defects cannot be determined from the RHEED patterns and transmission electron microscopy (TEM) measurements are needed to get a better understanding of the exact MgO structure. Furthermore, the RHEED patterns show additional streaks that may be due to surface contamination or to the formation of a Mg–Fe–O ternary alloy. However, such MgO layers have been included in two-dimensional tunnel junctions in which spin-dependent tunneling was successfully evidenced [22] indicating good insulating properties.

As in the case of natural oxidation, the deposition of a thin iron layer, the nominal thickness of which is 1 nm, leads to 3D growth of a non-uniform assembly of dots, as shown in the STM image of Fig. 4. The mean diameter of the dots is now strongly reduced: \( d = 3 \text{ nm} \). The associated activation energy is therefore increased and Coulomb blockade may be observed at RT since the activation energy \( E_c = 51 \text{ meV} \) corresponds to a temperature of about 590 K. It appears from the line profile shown in Fig. 4 that the flatness of the samples has been improved, but the peak-to-peak roughness is still larger than 1 nm. Furthermore, the samples showed no lateral ordering and no well-defined first-neighbour interparticle distance could be measured. This configuration is therefore difficult to use in devices since the distribution of both the diameters and the interparticles distance leads to various resistances and capacitances of the tunnel junctions so that the Coulomb staircase will rapidly be averaged out.

1.3. Direct deposition of a MgO layer

In these experiments, samples were prepared from a MgO source by using EBE. This technique has already been

Fig. 1. RHEED patterns of the MgO tunnel barrier obtained by natural oxidation of a Mg layer, and of the Fe dots layer obtained.

Fig. 2. STM image and typical line profile of Fe dots deposited on top of a MgO layer obtained by natural oxidation of Mg.
studied in the case of Fe/MgO systems and good quality of the layers was demonstrated [21]. All our samples were prepared on MgO (001) substrates. The cleaning procedure was the same as previously described, and the substrates were annealed at 600 °C under ultra-high vacuum for 30 min. Firstly, a 20 nm thick MgO layer was deposited at RT and annealed at 600 °C during 30 min to improve its crystallinity. A 20 nm thick bottom Fe electrode was deposited on top of this MgO buffer. In order to improve its flatness, this layer was annealed at 400 °C during 15 min. The resulting RHEED pattern consists of narrow streaks, thus confirming the smooth surface of the Fe electrode. Furthermore, it indicates that the epitaxial relationship between the MgO buffer and the Fe layer is Fe (001)[110]/MgO (001)[100] as observed in the preparation of oxidized Mg. A 1 nm thick MgO layer was then deposited at RT by EBE at a deposition rate of 0.3 Å/s. Finally, a thin iron layer, the thickness of which is comprised between 0.3 and 1 nm was prepared at RT at a rate of 0.2 Å/s.

The RHEED patterns of the 1 nm thick MgO layer consist of sharp streaks (see Fig. 5) indicating that its crystallinity has been improved. These patterns offer a striking contrast with the previous results obtained for oxidized Mg layers. Therefore, direct deposition of a MgO layer seems to be more suitable for obtaining atomically flat surfaces.

The RHEED patterns of a 1 nm thick Fe layer grown on top of the MgO insulating barrier (see Fig. 5) consist of discrete spots, thus indicating 3D growth of bcc iron. Similar RHEED patterns were obtained for 0.3 and 0.5 nm thick iron layers. However, when the thickness of the Fe layer is decreased, streaks originating from the underlying MgO layer progressively superimpose to the spotty pattern of the iron clusters, thus indicating a decrease of the area covered by the iron dots.

Fig. 6 shows the images obtained by STM for various Fe thicknesses. These images confirm the 3D growth and the improvement of the flatness of the MgO surface. The percolation threshold has been reached in the case of the 1 nm thick layer, thus leading to elongated Fe stripes. On the other hand, the 0.3 and 0.5 nm thick samples have a similar structure made of rounded particles. As revealed by the cross-section corresponding to a 0.5 nm thick Fe layer (see Fig. 7), the uniformity of the assembly of particles has been improved compared to the results obtained for the oxidation of a metallic Mg layer. The connection between dots occurring for a 1 nm thick Fe layers is then probably due to the improved flatness of the MgO underlayer. In the previous situations in which the MgO layer was prepared by oxidation of a Mg layer, the high roughness prevented the dots to coalesce together when the deposited thickness was increased.
It is interesting to notice that the calculated density is independent of the deposited thickness, varying from $6.5 \times 10^{12} \text{ cm}^{-2}$ for a deposited thickness of 0.5 nm to $6.8 \times 10^{12} \text{ cm}^{-2}$ for 0.3 nm. This result indicates that the growth of the iron particles occurs on well-defined nucleation sites, the density of which is determined by the growth conditions of the underlying MgO tunnel barrier. The pinning energy of these sites is large enough to prevent the lateral diffusion of the clusters after nucleation [23]. Therefore, the deposition of additional material only leads to the increase of the mean diameter, keeping the density of the particles constant. This is confirmed by a statistical analysis of the assembly of dots. The STM images have been filtered in order to enhance contrast, and the dots have then been outlined using a commercial software (Digital Micrograph 3.3.3). We therefore obtained histograms of the area of the particles. These histograms have been fitted by using a log-normal law:

$$F(S) = A \times \frac{\exp\left(-\frac{(\ln(S/S_m))^2}{2\sigma^2}\right)}{S\sigma\sqrt{2\pi}}$$

where $S$ stands for the area of the dots, $S_m$ for the mean area, $\sigma$ for the standard deviation, and $A$ is a scaling coefficient.

The mean diameter of the dots was determined by assuming a circular shape of the dots and therefore using the formula: $d_m = \sqrt{S_m/\pi}$ where $d_m$ is the mean diameter [24].

The results of the fits are gathered in Table 1. As expected, the mean diameter of the dots increases with increasing the deposited thickness. It also appears that the size distribution is broader in the case of the 0.3 nm thick sample. This is due to the great amount of very small dots that have not yet coalesced with their neighbours. Such a broad size distribution prevents observation of Coulomb staircase.

A study of the influence of the deposition temperature also confirmed the strong role played by the surface defects as nucleation sites. The following sample, in which the Fe dots were deposited at $300^\circ C$, was prepared: (MgO, 20 nm/Fe, 20 nm/MgO, 1 nm/Fe, 1 nm). The results of the statistical analysis are indicated in Table 1. These results indicated that the density is nearly constant when the deposition temperature rises from RT to $300^\circ C$ whereas, if the nucleation were perfectly homogeneous, the density should vary by at least one order of magnitude as demonstrated by Monte-Carlo simulations [23].

2. Influence of the Fe bottom electrode

If the clusters are deposited on the 20 nm thick MgO buffer, without metallic bottom electrode, the situation is different. Because of the very good crystallinity of the MgO buffer, the density of nucleation sites is low. Therefore, the mean inter-particle distance is increased as indicated by the corresponding RHEED pattern shown in Fig. 8. The streaks

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![Fig. 5. Patterns of both MgO, 1 nm and Fe, 1 nm for a (MgO, 20 nm/Fe, 20 nm/MgO, 1 nm/Fe, 1 nm) sample. The Fe RHEED patterns exhibit spots characteristic of a 3D growth.](image)

![Fig. 6. STM images of Fe dots deposited on top of a MgO layer deposited by electron beam evaporation. From left to right, the nominal thickness of Fe is: 1, 0.5, 0.3 nm.](image)
related to the underlying MgO buffer are now clearly seen even at the position of the spots due to the 3D growth of the iron dots, which was not the case if a thick Fe electrode is inserted prior to the deposition of the dots. The bottom Fe electrode therefore seems to play a significant role in the crystallinity of our samples.

This result is confirmed by the study of the growth of Co dots on MgO. The same deposition procedure was used to prepare (MgO, 20 nm/Fe, 20 nm/MgO, 1 nm/Co, 1 nm) and (MgO, 20 nm/Co, 1 nm) samples. Fig. 9 shows the RHEED patterns of the Co layers obtained in these two samples. The deposition of a thin Co layer on top of the 20 nm thick MgO layer leads to a spotty RHEED pattern indicating 3D growth of hcp cobalt. The epitaxial relationship between the Co and MgO layers is found to be: MgO (001)[100]/Co (110)[001] and MgO (001)[010]/Co (110)[001]. On the other hand, if a 20 nm thick Fe bottom electrode is grown prior to the deposition of the Co layer, then the RHEED pattern indicates 3D growth of Co dots with random orientations (see Fig. 9). Be that as it may, the RHEED patterns of the 20 nm thick MgO buffer and the 1 nm thick MgO tunnel barrier show no visible difference. Meyerheim et al. [25] reported that a FeO oxide layer due to interdiffusion is found when MgO is grown on Fe. Such a layer located at the (Fe, 20 nm/MgO, 1 nm) interface could modify the structure of a thin MgO layer and perturb the subsequent growth of Fe dots. Furthermore, in their electrical characterization of Fe/MgO/Fe tunnel junctions Klaua et al. [26] reported the presence of high-conduction defects whose position is related neither to Fe steps nor to MgO dislocations. These high-conduction zones are attributed by the authors to defects inside the MgO layer acting as additional energy-levels in the MgO band-gap. However, the lateral size of these zones was found to be about a few nanometers which is too large to explain the density of our clusters.

Hence, high-resolution TEM measurements have to be performed in order to get accurate information on the structures of both these MgO layers.

3. Measurement of $I(V)$ characteristics

As described in the previous sections, the broad size distribution of the assembly of dots may prevent the observation of Coulomb staircase. Therefore, in order to measure a single dot, we performed STS measurements. In these experiments, the STM tip is placed above a metallic...
The direct deposition of MgO by using EBE allowed us to prepare flat MgO surfaces. However, the assembly of dots deposited on this thin layer also exhibited a broad size distribution due to a great number of surface defects acting as nucleation sites. The pinning energy of these sites being larger than the thermal activation, the mobility of the dots is reduced. This reduced mobility prevents the dots from coalescing together, therefore leading to the presence of both small and large dots which cause the broadening of the size distribution.

The great number of these structural defects originates from the insertion of a bottom Fe electrode which affects the growth of the MgO tunnel barrier. This feature is of first importance for developing devices that are to be measured in CPP configuration.

4. Conclusion

Fe dots have been deposited on top of MgO layer prepared by various techniques. Preparation of MgO layers by oxidation of a pre-deposited metallic layer, which is a technique commonly used in the elaboration of tunnel junctions, appeared to give an important roughness, then leading to a broad size distribution of the Fe dots.

Fig. 10. Typical $I(V)$ characteristics obtained by scanning tunneling spectroscopy.

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