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# Magnetization losses in submicrometer CoFeB dots etched in a high ion density Cl<sub>2</sub>-based plasma

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Faceting of the etch masks and chlorinated etch residues can reduce the magnetization of patterning magnetic materials substantially, and therefore, constitutes a considerable concern. To get more insight into the magnetization losses, CoFeB dots were etched in a high ion density Cl<sub>2</sub>-based plasma with a width ranging from 0.3 to 6.4 μm. The magnetic properties of the CoFeB dots were measured by magnetometry. Submicrometer CoFeB dots showed significant magnetization reductions despite H<sub>2</sub>O rinsing. Scanning electron microscopy (SEM) studies revealed that etching in a Cl<sub>2</sub>-based plasma caused faceting of the masks, leading to sloped sidewalls. SEM pictures were used to determine the geometric volume, which was compared to the effective magnetic volume resulting from the magnetometry measurements. The SEM data are in good agreement with the magnetometry data, and a chloride penetration depth of only a few nanometers could be derived, indicating that the postetch rinsing is sufficient to prevent considerable corrosion of the CoFeB dots. © 2006 American Vacuum Society. [DOI: 10.1116/1.2366547]

Magnetic tunnel junctions (MTJs) can be used as bits for information storage and serve as the basic elements of magnetic random access memories (MRAMs). To substitute the current random access memory technologies with MRAMs, the surface area of an element has to decrease below 0.01 μm<sup>2</sup>.<sup>1</sup> Consequently, the patterning of magnetic material has recently attracted much attention. Nowadays, transferring the pattern by means of Ar<sup>+</sup> ion milling is a widely used etching technique. Nevertheless, the redeposition of backspattered material on the sidewalls and the low etch rate of the ion milling method are major drawbacks in patterning dense arrays of MTJs with a high throughput.<sup>2</sup>

Jung *et al.* reported about much higher etch rates of ≥50 Å/s for magnetic multilayer structures using high ion density Cl<sub>2</sub>/Ar plasmas.<sup>3</sup> However, the chlorinated etch residues on the sidewalls of the etched features tend to severely corrode the magnetic material. For etched features of approximately 2 × 15 μm<sup>2</sup>, 10 min of postetch H<sub>2</sub>O rinsing in a N<sub>2</sub> dry box or *in situ* cleaning with a H<sub>2</sub> or SF<sub>6</sub> plasma has proven to be effective in preventing this corrosion.<sup>4</sup> Furthermore, the various postetch procedures showed no significant differences in the long term magnetization. However, it has not been addressed whether postetch treatments are still effective for submicrometer elements.

Besides avoiding corrosion, an additional challenge in patterning dense arrays of elements is mastering mask erosion. During etching facets form at the sidewalls of the mask due to physical sputtering of the mask material. The initially

formed facets propagate in time and after a while the mask facets will intersect the original surface of the sample. Eventually, the mask facets propagate laterally, thereby exposing the feature to the plasma, resulting in sloped sidewalls.<sup>5</sup>

In this article, we present investigations on the reduced magnetization of patterned CoFeB dots with lateral dimensions ranging from 0.3 to 6.4 μm, dry etched with a Cl<sub>2</sub>-based plasma and a subsequent postetch H<sub>2</sub>O rinsing in a N<sub>2</sub> dry box. CoFeB was chosen as the magnetic material, because of the enormous current interest for the high tunneling spin polarization of CoFeB when combined with Al<sub>2</sub>O<sub>3</sub> or MgO barriers in MTJs. Superconducting quantum interference device (SQUID) magnetometer measurements and scanning electron microscopy (SEM) studies were performed and qualitatively analyzed in order to distinguish between the reduction of the magnetization due to chlorinated etch residues and due to faceting of the mask.

To study the reduction of the magnetization of CoFeB dots etched in a high ion density Cl<sub>2</sub>-based plasma, we used samples of the following composition: Si(001)/SiO<sub>x</sub>/150 Å Ta/155 Å CoFeB/50 Å Ta. The samples were grown in a sputter system at a rate of approximately 0.5 Å/s in an ~10<sup>-2</sup> mbar argon gas pressure. To fabricate the mask, a polymethylmethacrylate (PMMA) resist layer was spin coated on the sample and baked on a hotplate at 175 °C for 1 h. The PMMA was covered with hydrogen silsesquioxane (HSQ), a high resolution negative-tone resist, which was baked at 120 °C for 4 min after spin coating. Next, the bilayer resist was patterned by electron beam lithography at 100 kV and an exposure dose of 500 μC/cm<sup>2</sup>. To map the

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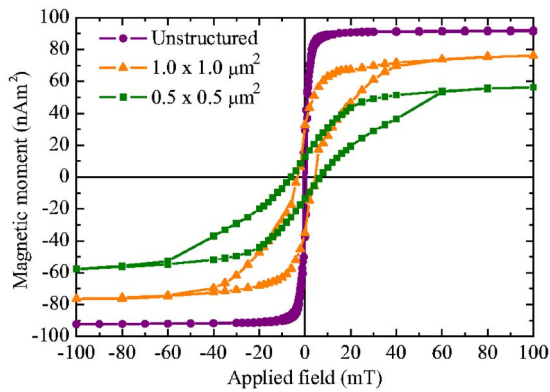


FIG. 1. Hysteresis loops of an unetched reference sample and etched samples with dots of width 1 and 0.5  $\mu\text{m}$ .

size dependency of the magnetic properties, the layout of the patterns consisted of square CoFeB dots of thickness  $t = 155 \text{ \AA}$  and width  $w$  ranging from 0.3 to 6.4  $\mu\text{m}$ . The number of dots in each layout,  $n_w$ , is chosen such that the total magnetic volume  $V = n_w t w^2$  is identical and equal to that of the unetched reference sample. Following the electron beam exposure, the HSQ was developed in Microposit MF-322 developer and the PMMA layer was etched in a low pressure  $\text{O}_2$  reactive ion plasma at a rf power of 50 W.

After fabricating the mask, a high ion density  $\text{Cl}_2/\text{BCl}_3/\text{N}_2$  plasma was used for high-speed dry etching the CoFeB dots in an Alcatel MET system,<sup>6</sup> which is equipped with an inductively coupled plasma (ICP) source. The ICP source power was set at 1000 W and the rf chuck was biased at  $-100 \text{ V}$ . The gas flows were 64 SCCM (SCCM denotes cubic centimeter per minute at STP) for  $\text{Cl}_2$  and 8 SCCM for  $\text{BCl}_3$  and  $\text{N}_2$ . Subsequently, the dots were etched for 2 min at a temperature of  $160 \text{ }^\circ\text{C}$  and a pressure of  $10 \mu\text{bar}$ . To remove the chlorinated etch residues from the sidewalls of the etched CoFeB dots, the samples were rinsed in  $\text{H}_2\text{O}$  in a  $\text{N}_2$  dry box for 10 min, before being exposed to the atmosphere.

The magnetic properties of the unetched reference sample with magnetic volume  $V$  and the etched samples were measured at room temperature with a SQUID magnetometer. The direction of the applied magnetic field was parallel to the sides of the CoFeB dots. A linear background was subtracted to correct for the diamagnetic substrate response. Figure 1 shows the hysteresis loops of the reference sample and the samples with dots of nominal width of 1.0 and 0.5  $\mu\text{m}$ . As expected for CoFeB dots with decreasing width, the magnetization is harder to switch and the coercive field increases.<sup>7</sup> Most importantly, in view of the degradation of the magnetization, Fig. 1 shows that the magnetic moment of the etched samples is significantly reduced in comparison with the reference sample. Furthermore, the sample with the  $0.5 \times 0.5 \mu\text{m}^2$  dots has an even lower saturation magnetization than that of the sample with the  $1.0 \times 1.0 \mu\text{m}^2$  dots.

SEM pictures were examined to study the cause of the reduced magnetization of the submicrometer CoFeB dots. In Fig. 2(a) a SEM picture of the cross section of the sample

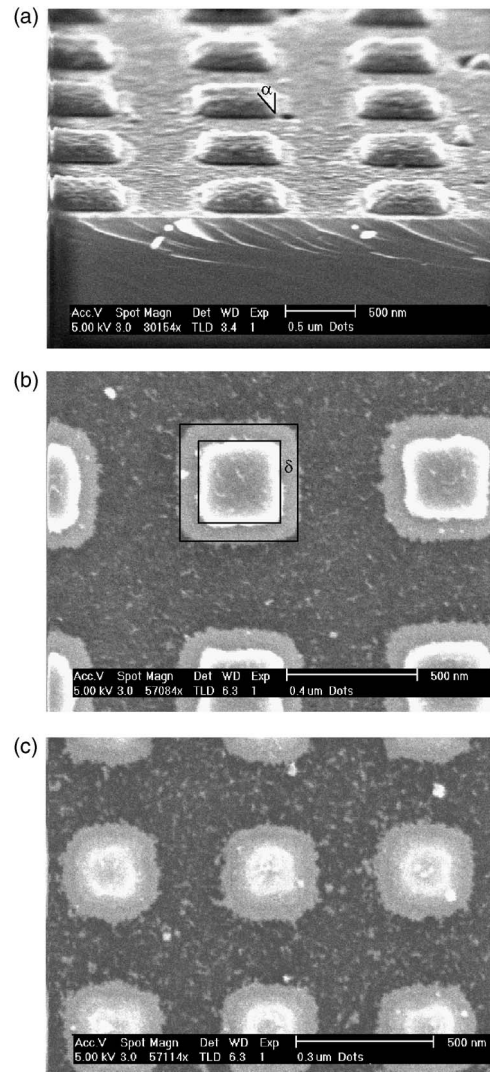


FIG. 2. Scanning electron microscopy pictures of CoFeB dots etched in a  $\text{Cl}_2/\text{BCl}_3/\text{N}_2$  plasma at  $160 \text{ }^\circ\text{C}$ . The cross section of  $0.5 \times 0.5 \mu\text{m}^2$  dots illustrates the erosion of the mask with faceting angle  $\alpha$  (a). The top views of  $0.4 \times 0.4 \mu\text{m}^2$  dots (b) and  $0.3 \times 0.3 \mu\text{m}^2$  dots (c) demonstrate the size effect.

with the  $0.5 \times 0.5 \mu\text{m}^2$  CoFeB dots is shown. The CoFeB dots are difficult to distinguish, because the total thickness of the layers is less than 30 nm. However, the mask on the dots is clearly visible. The cross section illustrates that etching in a  $\text{Cl}_2$ -based plasma causes erosion of the mask, resulting in a facet angle  $\alpha$ , as is indicated in Fig. 2(a). As stated before, faceting of the mask leads to sloped sidewalls of the CoFeB dots. This is confirmed by the top view SEM pictures of the  $0.4 \times 0.4 \mu\text{m}^2$  dots and the  $0.3 \times 0.3 \mu\text{m}^2$  dots in Figs. 2(b) and 2(c). Note that because of the proximity effect caused by the lithography process, the width of the CoFeB dots is enlarged in comparison to the nominal width  $w$ . Furthermore, the SEM pictures in Figs. 2(b) and 2(c) show that the dots are, in fact, truncated square pyramids. The sidewalls of the pyramids are light gray in color in the pictures. The top side width ( $w - 2\delta$ ) is confined by the mask, recognizable from the bright edges due to charging of the resist. The rim width

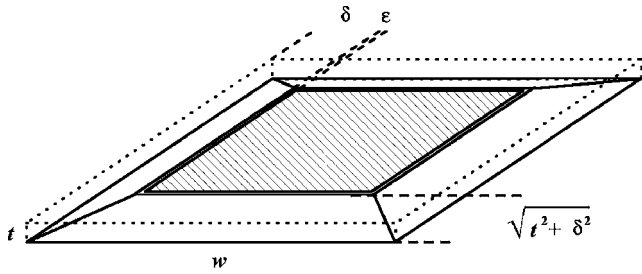


FIG. 3. Schematic drawing of a CoFeB dot. The dotted lines represent the designed dot, and the solid lines depict the truncated square pyramid with base and top side widths  $w$  and  $(w-2\delta)$ , respectively. The hatched area represents the top side of the truncated pyramid that did not corrode due to the chlorinated etch residues, with a penetration depth  $\varepsilon$ .

of the confinement  $\delta$  is determined using the base and top side circumferences, as graphically depicted in Fig. 2(b).

Figure 3 shows a schematic drawing to visualize the shape of a CoFeB dot after etching. The drawing neglects the enlargement of the dot with respect to the nominal width. The dotted lines represent the designed dot with thickness  $t$  and width  $w$ . The contours of the truncated square pyramid with base and top side widths  $w$  and  $(w-2\delta)$ , respectively, are depicted by the solid lines. As mentioned before, the thickness  $t$  and the total number of dots in each layout  $n_w$  are known. Therefore, by measuring the rim width  $\delta$  the actual geometric volume  $V_G$  can be calculated by

$$V_G = \frac{1}{3}t[w^2 + (w-2\delta)^2 + \sqrt{w^2(w-2\delta)^2}]n_w. \quad (1)$$

Due to the different magnifications of the various SEM pictures, only the rim width of the CoFeB dots with a width  $\leq 2 \mu\text{m}$  could be resolved. There was a large spread in measured values, ranging from about 30 nm to approximately 125 nm. The weighted average rim width yielded  $\bar{\delta} = 72 \pm 6$  nm.

To map the size dependency of the magnetization losses due to the faceting of the mask, we plotted the normalized saturation magnetization as a function of the nominal width of the etched CoFeB dots in Fig. 4 and compared it to that of the reference sample. In the analysis of the SQUID measurements, the data were corrected for the actual width of the CoFeB dots. As can be seen in Fig. 4, there is a considerable spread in data points due to sample to sample variation, which is confirmed by the SEM pictures. The faceting strongly depends on the exact characteristics of the mask. Variance of the resist profile due to the development process and the etching of the PMMA layer in an  $\text{O}_2$  plasma determines how a facet exactly propagates in time. Another explanation of the spread in data points is the precise conditions during etching, such as the stability, density, and lateral inhomogeneity of the plasma, which can cause differences between dots on various substrates.

However, in spite of the cloud of scattered data points, the plot of the normalized saturation magnetization showed a degradation of the magnetic properties of about 20%–40% for the CoFeB dots in the submicrometer regime. To get more insight into the effect of the sloped sidewalls on the

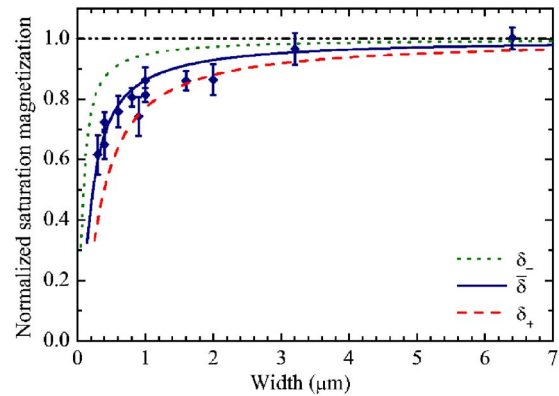


FIG. 4. Normalized saturation magnetization as a function of the width of the etched CoFeB dots. The dotted line and the dashed line are the results of calculations with  $\delta_- = 27$  nm and  $\delta_+ = 125$  nm, respectively, whereas the solid line is the result of the calculation with the weighted average rim width.

magnetization of the etched dots, we used formula (1) normalized by the volume of the reference sample to calculate the normalized saturation magnetization. The results of the calculations are plotted as function of the width  $w$  for  $w > 2\delta$  in Fig. 4. If the weighted average rim width from our SEM data is used for the calculation, the solid line resulted. The solid line is in good agreement with the SQUID data, given the fact that no fitting is used. The smallest value that could be used for the calculations is  $w = 0.15 \mu\text{m}$ . The mask is completely annihilated beyond this value, resulting in the erasure of the CoFeB dots. This implies that the feasibility of measuring the magnetic properties of etched magnetic elements with a width  $< 0.1 \mu\text{m}$  in a  $\text{Cl}_2$ -based plasma using a bilayer resist of PMMA and HSQ is questionable. In order to pattern dense arrays of magnetic memory elements with sub- $0.01\text{-}\mu\text{m}^2$  dimensions, the mask must be hard enough and the sidewalls have to be sufficiently steep. To impede mask erosion,  $\text{SiO}_2$  can be used as alternative mask material for shallow etching,<sup>8</sup> although for deep etching even harder materials are necessary. For example, a 20 nm thick Ta mask was applied for hardening mask etching MRAM multilayers using a  $\text{CO}/\text{NH}_3$  gas plasma.<sup>9</sup>

To illustrate the uncertainty in  $\delta$ , the upper dotted and lower dashed lines in Fig. 4 are the curves using a rim width of  $\delta_- = 27$  nm and  $\delta_+ = 125$  nm, respectively. Most of the data points are within those limits, which further corroborates the consistency between the SQUID and SEM data. Nevertheless, note that the values of the SQUID data appear to be systematically lower than those of the SEM data. In order to distinguish between the reduced magnetization due to the chlorinated etch residues and the faceting of the mask, the effective magnetic volume  $V_M$  has to be determined using the SQUID data and correlated with the SEM data. We calculated the effective magnetic volume by dividing the saturation magnetization by the magnetic moment of CoFeB. Assuming that the corrosion due to the etch residues is proportional to the surface area, then the ratio of the surface area of the sidewalls to the volume of the dot becomes increasingly important for the submicrometer dots, because the

magnetic moment scales with the volume. For all dot sizes the effective magnetic volume was smaller than the geometric volume, indicating that the CoFeB dots slightly corroded due to the etch residues. If we presume that the difference  $V_{\Delta}$  between  $V_G$  and  $V_M$  is the volume that is corroded by the chlorinated etch residues, we can derive a chloride penetration depth  $\varepsilon$ . Therefore, consider again Fig. 3, the surface area of one side of the pyramid is  $\frac{1}{2}\sqrt{t^2 + \delta^2}[w + (w - 2\delta)]$ , a pyramid has four sides, and each sample has  $n_w$  pyramids. Accordingly, we can derive the chloride penetration depth  $\varepsilon$  using

$$\varepsilon = \frac{V_{\Delta}}{4\sqrt{t^2 + \delta^2}(w - \delta)n_w}. \quad (2)$$

We found a penetration depth of the chloride of less than 10 nm. However, this chloride penetration depth must be seen as a rough estimate for several reasons. First of all, the patterning by electron beam lithography causes rounding of the corners due to the proximity effect, which was not taken into account. As a consequence of this rounding, which is clearly visible in Fig. 2(c), the geometric volume  $V_G$  is overestimated. On the other hand, we disregarded the Ta layers, thereby overestimating the rim width  $\delta$  leading to underrating  $V_G$ . The samples were measured approximately 40 days after etching and subsequent rinsing. Therefore, as a first approximation, a penetration depth of less than 10 nm implies that 10 min of postetch  $H_2O$  rinsing in a  $N_2$  dry box was sufficient to prevent significant major corrosion of CoFeB dots. Furthermore, for dots with a width  $>1 \mu m$  the reduction of the magnetization due to the chlorinated etch residues would not be more than 1%. Accordingly, our results are in accordance with the results of Jung *et al.*,<sup>4</sup> which showed no significant change in magnetic properties over a period of six months.

In conclusion, a high ion density  $Cl_2/BCl_3/N_2$  plasma was used for etching CoFeB dots with a width ranging from 0.3 to 6.4  $\mu m$ . The magnetic properties were measured with a SQUID magnetometer. The hysteresis loops of the etched CoFeB dots showed a reduced magnetization. The SEM picture of the cross section of  $0.5 \times 0.5 \mu m^2$  dots showed faceting of the mask, leading to sloped sidewalls. The actual geometric volume was calculated using the measured rim widths to determine the reduction of the magnetization due to the faceting of the mask. The geometric volume derived from the SEM data was in good agreement with the effective magnetic volume resulting from the SQUID data. The difference between geometric volume and the effective magnetic volume was used to determine a chloride penetration depth of less than 10 nm. Therefore, in accordance with the results of Jung *et al.*,<sup>4</sup> 10 min of postetch  $H_2O$  rinsing in a  $N_2$  dry box was sufficient to prevent considerable corrosion of CoFeB dots.

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