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Using Electron-beam Resists as Ion Milling Mask for Fabrication of Spin Transfer Devices

Hoang Yen Thi Nguyen, Hyunjung Yi, and Kyung-Ho Shin*

Nano Device Research Center, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 130-650, Korea

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Magnetic excitation and reversal by a spin polarized current via spin transfer have been a central research topic in spintronics due to its application potential. Special techniques are required to fabricate nano-scale magnetic layers in which the effect can be observed and studied. This work discusses the possibility of using electron-beam resists, the nano-scale patterning media, as ion milling mask in a subtractive fabrication method. The possibility is demonstrated by two resists, one positive tone, the ZEP 520A, and one negative tone, the ma-N2403. The advantage and the key points for success of this process will be also addressed.

Keywords : spin transfer, nano-scale junctions, spin valves, e-beam resist, subtractive process

1. Introduction

When a spin polarized current passes through a nano magnet, spin angular momentum of conduction electrons can transfers to the magnetic moment of the nano magnet, leading to magnetic excitations or/and reorientation in it [1-4]. Intensive studies have opened application possibilities of spin transfer devices such as high density non-volatile magnetic memories, nanometer-scale microwave oscillators, spin diodes, etc. [5-7]. In order to observe and study the spin transfer effects, good quality metallic multilayers patterned to desired nanometer-scale junctions with well-defined shapes must be obtained. Several fabrication methods, including both subtractive [8-10] and additive [11], have been developed by different research groups. In an additive process, nano-scale dimensions of prepatterned templates for the layer deposition usually cause a complex edge growth, resulting in a poor quality of the multilayer and interfaces. In fact, the best quality devices [5-7, 12] reported so far in the literature have been prepared by applying subtractive methods. In such a process, a metal layer can be used as an ion-milling mask [5, 6, 8, 9]. After milling, another etching sub-process such as reactive ion etching, focus ion beam etching, wet etching, or chemical-mechanical polishing after passivation of the junction is required to open the contact area of the top electrode. If electron-beam resist (ER), the patterning medium, can also serves as a milling mask, then less high-cost facilities are needed and the number of processing steps can be reduced. However, only ERs which are highly resistive to dry-etching can be considered as robust etching masks. Here we introduce such a simpler subtractive method, in which an ER, whether a positive tone, the ZEP 520A, or a negative tone, the ma-N2403 is employed. Both of these resists have high resolutions and high dry-etching resistances. The exposing conditions for them can be fulfilled by the e-beam writer JEOL FE-SEM 6500F available at the Nano Device Research Center, Korea Institute of Science and Technology. Based on the experimental results gotten from these two resists, critical points for a success in this fabrication approach are derived. These would be a useful guideline for those, who want to apply a similar process to make nano magnetic devices for spin transfer studies.

2. Experiment: Fabrication Process

Our subtractive fabrication process is a top-down approach which consists of 10 sub-processes, as shown in Fig. 1. Various types of cobalt-based spin valves (non-exchange biased, exchange biased without and with nano oxide layer(s), etc.) have been fabricated for our spin transfer study, by using this process. Each sub-process will be described as follows.

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*Corresponding author: Tel: +82-2-958-5418, Fax: +82-2-958-6851, e-mail: kshin@kist.re.kr

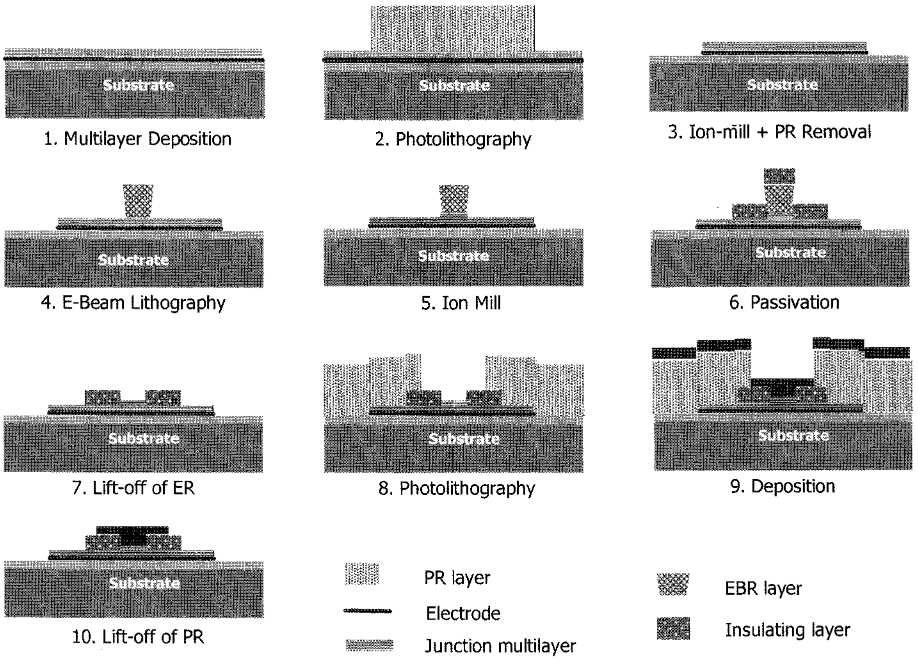

Fig. 1. Subtractive process to fabricate nano-scale devices for spin transfer studies. Step 1 to 3 are to prepare the bottom electrode (consisting of the whole multilayer except the top electrode); step 4 to 7 are to form nano-scale junctions; and step 8 to 10 are to make the top electrodes.

Step 1 – multilayer deposition: the metallic multilayer of the desired layer structure is deposited onto a cleaned Si/SiO$_2$-substrate by using DC magnetron sputtering at room temperature (RT), in an external magnetic field of ~200 Oe. For a high quality of multilayers and interfaces, the main chamber base pressure prior deposition must be low enough, e.g. not higher than 2×10^{-7} Torr, and the deposition conditions must be optimized for smooth surfaces.

Step 2 and 3 – photolithography and ion milling to pattern bottom electrodes: the multilayer is patterned to the form of extended bottom electrodes by photolithography, in which double LOL/PR layers (or a single PR only) are coated on the sample surface. The expose is done on the Karl Suss MA6 Aligner. The multilayer area, where it is not covered by the resist, is the milled out by argon ion milling. Milling time is defined by mill-out time of a reference sample with the same layer structure and thickness. After that, the lift-off (LOL) and photolithography resist (PR) layers are removed from the sample surfaces by LOL remover and acetone, respectively, at room temperature with less than ten minutes of ultrasonic.

Step 4 – electron-beam lithography to pattern nano-scale junctions: the nano-scale junction shape and size are transferred to the ER covering the multilayer by applying electron-beam lithography (EBL). The pattern transfer is done on the electron-beam writer JEOL FE-SEM 6500F equipped with lithography software Elphy Plus, Raith GmbH. Good junction shapes, i.e., well defined shapes with regular boundaries, enough small junction sizes, and an acceptable possibility of opening electric contact to junctions by lift-off technique are the most important criteria to optimize the EBL conditions. The optimal sets of EBL parameters were found as follows.

For the positive tone resist ZEP520A:

- Spin coating: 6000 rpm for 60 sec; baked at 180°C on hotplate for 2 min;
- Exposing: acceleration voltage 25 KV; step size 5pxl; area dose 45 μC/cm^2; position dose factor 0.95; elemental dose factor 1;
- Development in ZED-N50 for 1 min; rinsed in ZMD-B for 10 sec.

The final thickness of the resist is about 3500 Å.

For the negative tone resist ma-N2403:

- Spin coating: 4000-4500 rpm for 30 sec; baked at 90°C on hotplate for 1 min;
- Exposing: acceleration voltage 20 KV; step size 2pxl; area dose 200 μC/cm^2; position dose factor 1.9; elemental dose factor 1;
- Development in ma-D 532K for 3 min; rinsed in running DI water for 5 min.

The final thickness of the resist is about 3000 Å.

Note that both of these resists are white-light sensitive. It is therefore critical to protect the samples coated with the resists from white light as long as samples are not developed yet.

Step 5 – ion milling to form nano-scale junctions: in this step the patterned ER gotten after development serves as a milling mask. The milling is timed by the removal time of reference layers on a glass substrate mounted closest to the main samples in the milling chamber.

Step 6 – junction passivation: nano-scale junctions are protected by an oxide layer, e.g. tantalum or silicon oxide, deposited by reactive DC sputtering. This oxide layer also electrically isolates the bottom from the top electrodes.

Step 7 – ER lift-off: to open electrical contacts to the junction areas, the ER layer covering the junctions is removed by immersing samples in ER remover at elevated temperature and applying ultrasonic for few minutes. This step is the most crucial in order to obtain good quality devices.

Lift-off procedure for ZEP520A:

1. Immersing samples in ZDMAC, the ZEP remover, put on hotplate at 45°C for 1-1.5 hrs;
2. Applying ultrasonic for 3 min;
3. Checking junctions by microscope: if they look dark, apply ultrasonic again; if they look bright, do the next step;
4. Rinsing lifted-off samples in methanol, then in running DI water.

Lift-off procedure for ma-N2403:

1. Immersing samples in mr-660, the ma-N2403 remover, put on hotplate at 60°C-65°C for 1.5-2 hrs;
2. Applying ultrasonic for 3 min, at temperature set at 45°C;
3. Checking junctions by microscope, if they look dark, apply ultrasonic again; if they look bright, do the next step;
4. Rinsing lifted-off samples in running DI water;

Step 8, 9, and 10 – forming the top electrodes: Cu top electrodes are formed by using lift-off technique, consisting of photolithography (step 8), deposition by DC sputtering (step 9), and finally the lift-off (step 10) by acetone and then by LOL Microposit™ Remover 1165.

3. Results and Discussion

Clearly, to get the same final junction, the scanning patterns of the electron beam to expose the positive and the negative ERs must be different. The positive resist area(s) exposed to or the negative resist area(s) not exposed to the electron beam will be dissolved in the corre-

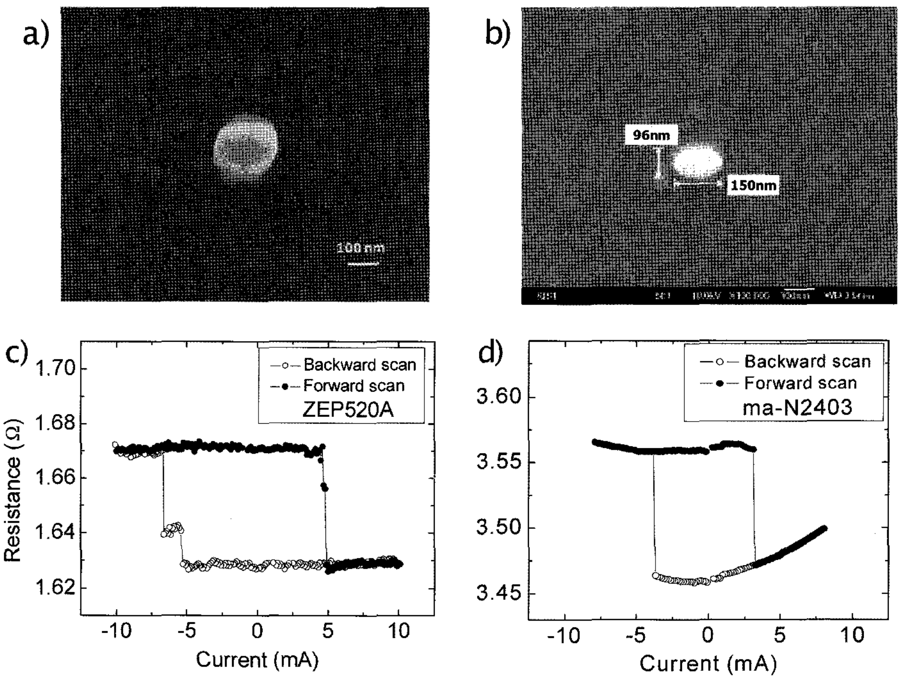

Fig. 2. a) and b): SEM images of nano-scale junctions made by applying the positive resist ZEP520A and by using the negative resist ma-N2403, respectively; c) and d): Spin transfer magnetization switchings of nano-scale trilayer spin valves made by using ZEP520A (c) and by using ma-N2403 (d) as a milling mask. Both have the same layer structure of Ru 10/Cu 50/ Co 11/Cu 6/Co 2/ Cu 2/Au 5/Cu100 (nm).

sponding developer and removed from the sample surface during development process. For the positive ZEP520A, a nano-scale area which determines the active junction must be protected from the beam while a big area of 20×20 μm^2 encompassing the junction must be completely exposed by the beam. We had successfully developed a proximity correction [13] which fulfills this specific exposing requirement. With this correction, very clean sample surfaces were gotten as shown by a scanning electron microscope (SEM) image of a nano junction in Fig. 2a. In contrast, for the negative ma-N2403, only a nano-scale area defining the active junction is exposed to the electron beam. The beam scanning path is therefore simpler for negative resists. Fig. 2b presents a SEM image of a nano junction formed by using ma-N2403 as an ion milling mask. The opposite electron beam scanning paths to form a nano junction lead to opposite junction size deviations from the designed sizes. The final junction of (150×200) nm^2 made by ZEP520A shown in Fig. 2a is smaller than its designed unexposed area of (250×400) nm^2, while the final junction of (96×150) nm^2 made by ma-N2403 shown in Fig. 2b is larger than its designed exposed area of (70×140) nm^2. Those deviations are also caused by the proximity effect, including the back and ford electron scatterings [14]. The most important criterion of the device quality lies in the magneto-electric signals obtained from the device. In both junction types made by using ZEP520A (Fig. 2c) and by using ma-N2403 (Fig. 2d), we have observed the spin transfer magnetization switching (STMS) with very clear and abrupt changes in device resistances at certain injected dc currents. Both these devices have the same spin valve layer structure of Ru 10/Cu 50/Co 11/ Cu 6/Co 2/Cu 2/Au 5/Cu100 (nm), where the fixed (thicker) Co layer was not patterned to nano size, but left extended and served as a part of the bottom electrode. These prove that both these resists can be used as a milling mask to fabricate nano junctions for spin transfer studies.

However, the ZEP520 is highly sensitive to electron beam, i.e., only low energy is needed to break its bonding. Thus, the processing reproducibility for such a small size is not sufficient. The junction shape is generally not good enough due to some irregular deformations from drawn shapes. In addition, ZDMAC, the ZEP remover, is more aggressive to metals than mr-660, the ma-N2403 remover. As a result, the STMS is somehow rarely obtained in junctions made with ZEP520A. Using ma-N2403 as a milling mask yields a much higher reproducibility of good quality devices. Our excellent spin transfer spin valves [10, 12] were fabricated with this resist.

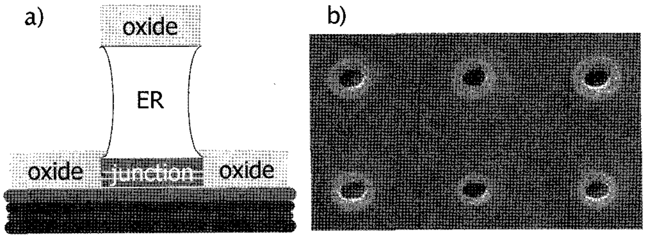

Fig. 3. a) "tree's foot" profile of patterned e-beam resist after the passivation step; b) SEM image (top view) of nano junctions successfully lifted-off.

Metallic, including magnetic, layers are always present in device layer structures for spin transfer studies. They are easily attacked by chemicals and even by solvents used in device processing, leading to low or bad device qualities. Therefore, in every step, where samples are treated by chemicals and/or solvents (developers, removers, rinses, acetone, etc.), the treatment time durations must be as short as possible, and temperature of treatment solutions must be as low as possible. In the following, some tips will be given for produce of good quality devices based on our experiences.

1. For photolithography: The recipe with shortest development time should be chosen to minimize damages of metallic layers by developer;
2. For EBL:
- Coating the resist as close as possible to the expose; developing samples as soon as possible after the expose; performing further steps (including lift-off, at least) within a time duration as short as possible for a successful lift-off;
- Using a resist, if available, which allows forming a "tree's foot" profile of patterned resist as illustrated by the cartoon in Fig. 3a. The oxide part covering this "foot" can protect nano junctions from being corroded at their edges inward where metallic multilayer is exposed to resist remover and solvent during lift-off process.
3. Avoiding any mistake which leads to a longer evacuation time inside the milling and/or the sputtering chambers in order to prevent the patterned resist from being dried, and thus becoming more difficult to be lifted-off;
4. For ER lift-off: trade-off between ultrasonic power, ultrasonic time and solvent temperature, immersing time must be carefully done in order to avoid corrosion of junctions by the resist remover during lift-off process.

4. Conclusion

We have introduced a subtractive fabrication method, in which an electron beam resist serves not only as a patterning medium but also as a mask for ion milling. There are fewer sub-processes and a smaller number of high-cost facilities required in our approach than in the other ones, where hard masks are used for dry etching. The negative resist ma-N2403 can yield a high reproducibility of good device quality, provided that a "tree's foot" profile of the patterned resist is formed by the lithography. Other critical points for a good device quality derived from our experiences have been also addressed.

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