Study about the Degradation Mechanism of the Magnetic Tunnel Junctions (MTJs) during the Patterning Process and Its Recovery by Using the Oxygen Showering Post-Treatment (OSP) Process

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学　位　論　文　題　目	Study about the Degradation Mechanism of the Magnetic Tunnel Junctions (MTJs) during the Patterning Process and Its Recovery by Using the Oxygen Showering Post-Treatment (OSP) Process (磁気トンネル接合素子の 微細加工プロセスダメージ現象の解析と酸化後処理によるその回復技術に関する研究)
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論文内容要約

Since the outstanding properties of the magnetic tunnel junctions (MTJs) based on the MgO tunnel barrier and those of interface perpendicular magnetic anisotropy (I-PMA) MTJs composed with CoFeB/MgO/CoFeB have been reported, spintronic devices have been recognized as a new device paradigm can replace or adopt conventional electronic industries such as semiconductor, storage, biomedical and automobile. Especially, because of its various remarkable performances as a semiconductor device, such as a low power consumption due to its non-volatility, a high speed read and write operation and the cost benefit for the mass production, a spintronic device is becoming one of candidates to be applied to the IoT, the big data and the artificial intelligent (AI) industries as well as the logic and memory devices. However, in spite of its remarkable performances, a spintronic device has not been commercialized extensively because there are some remained technology factors should be developed. Firstly, for the successful commercialization of these spintronic devices, we should improve MTJs properties such as the magnetoresistance ratio (MR), the switching efficiency and the retention. Secondly, we should set-up the optimal business target we should replace or adopt at first. And finally, we should optimize the integration process of the spintronic device including the robust MTJs patterning process to minimize patterning damages. Regarding MTJs properties, there are extensive studies and remarkable reports to improve the MR, switching efficiency and reliability. However, the MTJs patterning process to minimize patterning damages has not been studied extensively although it is indispensable to develop the optimal patterning process for the successful commercialization of the spintronic device.

In this thesis, we study about the degradation mechanism by several patterning gases and conditions and predict the electric and magnetic properties of damaged layers. With these results about the patterning damages and MTJs degradation, we propose a novel post-treatment process to recover patterning damages generated by both reactive ion etching (RIE) and ion beam etching (IBE).

In the chapter 2, we study about electric and magnetic changes by hydrogen and nitrogen plasma ions with two types of treatment conditions, which are the with-bias condition with activating applied plasma ions, and the without-bias condition with extremely suppressed activating energy on plasma ions. As a result, MTJs are degraded by the hydrogen treatment at both with- and without-bias conditions, while there is no degradation on MTJs by nitrogen plasma ions regardless of treatment conditions. Especially, at the with-bias conditions, the MR decreases from 103% to 12.5% and the resistance (R) increases from 6.4KΩ to 29.2KΩ compared to MTJs etched by the reactive ion etching (RIE) only process. It is because hydrogen ions react with MTJs materials such as CoFeB or MgO in the damage-less, and degrade crystal structures and electric/magnetic properties of patterned MTJs. However, unexpectedly, at the without-bias conditions, the MR also decreases from 103% to 85.6% and the R increases 6.4KΩ to 7.3KΩ. This is because that the generated damaged layer by hydrogen treatment at without-bias condition interfere the current flow of electron through the MTJs in damage-less area, and degrade electric and magnetic properties of the whole patterned MTJs, slightly. In addition to studies about degradation mechanism, the assumption and the prediction about electric and magnetic properties of damaged layers have been performed. Firstly, by using the assumed electric and magnetic properties of damaged layer, the MR and R trends of the patterned MTJs including the damaged layer are calculated. And then, we co-relate this calculated MR and R trends with experimental results to verify our assumptions. As a result of a calculation and a co-relation, it is recognized that the MR and R trends at the without-bias conditions are co-related with experimental results very well. This result shows that there is no mis-assumption regarding the MR and R trends of MTJs arrays treated by hydrogen plasma ions at the without-bias conditions. Consequently, by hydrogen plasma ions at the without-bias condition, MTJs are degraded by interference of damaged layers to the current flow of the whole patterned MTJs. On the other hand, by hydrogen treatments at the with-bias condition, experimental MR and R trends are not co-related with the calculated result. This result shows that there is additional degradation on the patterned MTJs by hydrogen treatment at the with-bias condition, and it is because that hydrogen ions have very high activating energy by applied bias power and react with MTJs materials in damage-less area, very easily. By all of studies, it is recognized that not only hydrogen plasma ions with high activating energy, but hydrogen with extremely suppressed activating energy and reactivity also affect MTJs degradations.

In the chapter 3, the novel post-treatment process called the oxygen showering post-treatment (OSP) process to recover patterning damages is proposed. At the OSP process, oxygen plasma ions with suppressed activating energy and reactivity are used to recover patterning damages by the selective oxidation of the damaged layer. Generally, oxygen is un-suitable gas to use the MTJs patterning process because it makes over-oxidation of MTJs by reacted with magnesium oxide (MgO) and causes MTJs degradations. However, in this study, we suppressed the activating energy and the reactivity of applied oxygen plasma ions by the control of the applied bias voltage. With suppressed oxygen plasma ions, damaged layer can be oxidized selectively without additional oxidation of damage-less patterned MTJs because damaged layers are composed of un-stoichiometric materials which have very low binding energy and the enthalpy of formation, which is very easy to react with applied plasma ions. By this OSP process, we study about the damage recovery of the patterned MTJs etched at both RIE and IBE schemes.

In the chapter 4, damage recovery and electric/magnetic improvements of the patterned MTJs by the OSP process at the RIE scheme have been studied. After the RIE process, damaged layers are generated at the edge side of MTJs by the chemical reaction and the plasma damage. We oxidize this damaged layer by using the OSP process. As a result, by the OSP process, the MR is improved from 98% to 110% at the same R level, ~15 KΩ, compared to MTJs arrays etched by the RIE only process. Moreover, sigma distribution is also improved from 5.3σ to 13σ by the damage recovery of the damaged layer. This damage recovery also can be verified by the co-relation of calculated and experimental MR and R trends. By the calculation and co-relation, it is recognized that the damaged layer width of the recovered MTJs is around 0.1nm, compared that of MTJs by the RIE only process is around 3nm.

In the chapter 5, damaged recovery and electric/magnetic improvements of the patterned MTJs by the OSP process at the IBE scheme have been studied. By its physical etching mechanism, the IBE process generates metallic by-products, and at MTJ arrays, generated metallic by-products by the IBE process are re-deposited at the edge side of patterned MTJs, and cause electric short fails of MTJs arrays. In order to avoid these electric short fails by the re-deposition of metallic by-products, we control the IBE angle and remove metallic by-products deposited at the edge side of the patterned MTJs. However, at the small cell-to-cell space widths, it is difficult to control the IBE angle to remove by-products at the edge side of MTJs, effectively. In this chapter, we study about the electric short fail trends as changes of the cell-to-cell space width and the ion beam angle. As a result, it is recognized that the probability of electric short fails at MTJs arrays increase more than 25% when the IBE angle is higher than 35° from the bottom electrode, and the cell-to-cell space width is more than 1.43 times compared to the MTJs height including hard mask (HM). By the OSP process, we recover electric short fails generated by the IBE process. As a result, by the OSP process, electric short fails generated by the IBE process used lower than 35° of the IBE angle are reduced from 25% to 0.3%, and this is because metallic by-products at the edge side of MTJs are oxidized by the OSP process, effectively. Moreover, the MR and the sigma distribution are also increased from 99%, 2.9σ to 120%, 13.7σ, respectively. However, at MTJs arrays etched by the IBE process used higher than 35° of the IBE angle, electric short fails are not recovered by the OSP process, and it is because there are too much remained re-deposition at the edge side of MTJs arrays to oxidize by using the OSP process. By this result, it is verified that the IBE process can be used as the main etching scheme of the spintronic devices even at the high density arrays by using the OSP process.

In the chapter 6, the engineering margin and the best condition of the OSP process are studied. By using the design of experiment (DOE) method, we evaluate the effectiveness of several treatment factors at the OSP process, which are the pressure flow time and temperature. By this study, it is recognized that the MR increases and the R decreases at the high pressure and the low flow time and temperature. In addition, by the effects plot of the DOE method, it is also recognized that the oxygen flow time is the most effective factor to affect the MR and R changes. With these results, the oxygen flowing time is subdivided from 0sec to 200sec to study about the engineering margin of the OSP process and also obtain the most optimal MTJs properties. As a result, the MR by the OSP process from 15sec to 45sec of the oxygen flow time increases gradually at the same resistance level. Moreover, the best MR is obtained at the specific OSP condition, which is 5Pa of treatment pressure, 27℃ of flowing temperature and 45sec of flowing time. With all of studies, it is verified that the OSP process have enough engineering margin which is from 15sec to 45sec regarding the oxygen flow time. Moreover, it is recognized that the OSP can be used at any etched conditions of MTJs by optimizing the treatment conditions.

In the chapter 7, we study about the improvement of the switching efficiency of the patterned MTJs by the OSP process. By the OSP process, electric damages at the damaged layer are recovered almost perfectly. However, magnetically, damages are not recovered effectively, and the electron spin direction in the damaged layer is not perpendicular, but it is pseudo in-plane. However, this pseudo in-plane spin may pay a role as the catalyst to reduce the switching current of the patterned MTJs by accelerating the magnetization of damage-less area with its rotating field. In order to confirm this assumption, we measured the switching current and thermal stabilities of MTJs arrays by the OSP process and compared with those by the RIE or the IBE process. As a result, by the OSP process, the switching current of the 25nm patterned MTJs is reduced from 40uA to 27uA compared to the MTJs etched by the RIE or the IBE only process, without any degradation of the thermal stability. Consequently, the switching efficiency of the patterned MTJs by the OSP process is increased from 1.4 to 1.7 compared to the MTJs by the RIE or the IBE only process.

From all, it is recognized that MTJs are degraded not only by the RIE process by reaction of hydrogen with MTJs materials, but also degraded by the IBE process by re-depositions of metallic by-products at the edge side of patterned MTJs. In order to recover patterning damages generated by both RIE and IBE processes, we proposed the novel post-treatment process which is called the OSP process to oxidize damaged layers selectively by using oxygen plasma ions with extremely suppressed activating energy and the reactivity. By the OSP, electric and magnetic properties of patterned MTJs are recovered and even improved at both RIE and the IBE scheme. We also confirmed that the OSP process has an enough engineering margin to be used at any etching conditions. Finally, it is also recognized that the MTJs size can be reduced by using the OSP with same electric and magnetic properties. Table 1 is the electric and magnetic comparison results between the 35nm sized MTJs by the RIE only process and the 25nm sized MTJs by the OSP process, if we match the MR between two MTJs, as shown in figure 1. As shown in table, electric and magnetic properties of the 25nm sized MTJs by the OSP process are much better than those of the 35nm sized MTJs by the RIE only process, except the thermal stability. But thermal stability of the 25nm sized MTJs by the OSP is not too small compared to the 35nm sized MTJs by the RIE only process. It is because the MTJs have enough anisotropic value to keep the thermal stability to 25nm sized MTJs. By all of these results, it is verified that the OSP can be the universal post-treatment process to recover patterning damages effectively, even beyond 20nm design rule to use both reactive ion etching and IBE schemes.

Table 1. Electric and magnetic comparison between the 35nm MTJs by the RIE and the 35nm / 25nm MTJs by the RIE+OSP

Factors	35nm by RIE only	35nm by RIE + OSP	25nm by RIE + OSP
Junction size (nm)	35	35	25
MR (%)	95	120	95
RA (Ω*cm^2)	11.5	11.7	11.9
Isw (uA)	79	67	31
$\triangle$	55	54	51
Switching efficiency	0.696	1.012	1.645

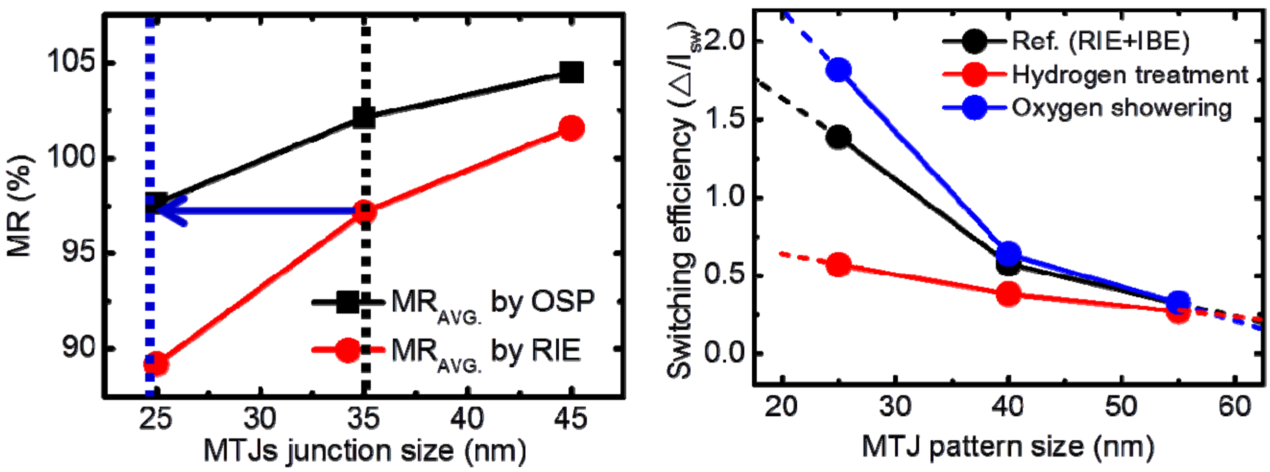

Figure 1. The feasibility to reduce MTJs sizes by using the OSP process. At the same MR, by the OSP process, the MTJs size can be reduced from 35nm to 25nm compared to the MTJs by the RIE only process.