Double Pinned Perpendicular-Magnetic-Tunnel-Junction Spin-Valve Providing Multi-level Resistance States

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A new design for high density integration greater than gigabits of perpendicular-magnetic-tunnel-junction (p-MTJ) spin-valve, called the double pinned (i.e., bottom and top pinned structures) p-MTJ spin-valve achieved a multi-level memory-cell operation exhibiting four-level resistances. Three key magnetic properties, the anisotropy exchange field \((H_{ex})\) of the bottom pinned structure, the coercivity \((H_c)\) of the double free-layer, and the \(H_c\) of the top pinned structure mainly determined four-level resistances producing tunneling-magneto-resistance (TMR) ratios of 152.6%, 33.6%, and 166.5%. The three key design concepts are: i) the bottom pinned structure with a sufficiently large \(H_{ex}\) to avoid a write-error, ii) the \(H_c\) of the double free-layer (i.e., \(\sim 0.1\) kOe) much less than the \(H_c\) of the top pinned structure (i.e., \(\sim 1.0\) kOe), and iii) the top pinned structure providing different electron spin directions.

Perpendicular spin-transfer-torque magnetic-random access memory (p-STT MRAM), which consists of a perpendicular magnetic tunneling junction (p-MTJ) spin-valve and a selective device, has attracted great research interest because of its possibility in various applications. Recently, in particular, the p-STT MRAM cells have been utilized as embedded memory in system-on-chip for mobile and internet-of-things applications1–5, a stand-alone memory as a solution to the dynamic-random-access-memory (DRAM) scaling limitations below the 10-nm node6, and spin-neuron and synaptic devices for deep learning7–9. The p-STT MRAM has many advantages over current memory devices, such as non-volatility, fast read/write speed (\(\sim 10\) ns), extremely low power consumption (\(<1\) pJ/bit), high write endurance (\(>10^{12}\)), and scalability10-15.

The researches on p-STT MRAM have been based on improving three device parameters of the p-MTJ spin-valves11-13: the tunneling magnetoresistance (TMR) ratio greater than 150% for ensuring a memory margin, the thermal stability (\(\Delta = K_u V / k_B T\), where \(K_u\), \(V\), \(k_B\), and \(T\) are the magnetic anisotropy energy, the volume of the free ferromagnetic layer, the Boltzmann constant, and the temperature, respectively) above 75 for a ten-year retention-time, and the switching current density of about 1 MA/cm² for low power consumption. Moreover, these device parameters should be available at a back end of line (BEOL) temperature \(> 350\) °C16,17. The conventional double MgO based p-MTJ spin-valve consist of upper and lower synthetic anti-ferromagnetic (SyAF) [Co/Pt], multilayer separated by a Ru spacer, a Co2FeB2 magnetic pinned layer, a MgO tunneling barrier, and Co2FeB2 magnetic free layers, as shown in Fig. 1a: called a single pinned p-MTJ spin-valve18. A single pinned p-MTJ spin-valve can generate only two resistance states: the high-resistance state (HRS) from the anti-parallel spin direction, and the low-resistance state (LRS) from the parallel spin direction between the Co2FeB2 free layer and the Co2FeB2 pinned layer. Thus, these two different resistance states have been used to operate only single-bit p-STT MRAM memory cells. However, the scaling down for terabit-level integration of the p-STT MRAM cells, to compete with current DRAM19, 3-dimensional (3D) NAND flash memory, and 3-dimensional cross-point memory, would be necessary to achieve the thermal stability required for 10-year retention time20,21 and multi-level memory-cell operation like that of current 3-D NAND flash memory22,23. In our research, we designed a double pinned p-STT-MTJ spin-valve exhibiting multi-level (i.e., four) resistance states. The double pinned p-STT MTJ was composed of three main ferro-magnetic component layers: the bottom pinned structure, double free-layer, and top pinned structure (see Fig. 1b). The TMR ratio was maximized by introducing a

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bottom single SyAF [Co/Pt]₃ multilayers (Fig. 1b) because the upper [Co/Pt]₃ SyAF multilayer anti-ferro-coupled with the lower [Co/Pt]₆ SyAF multilayers (Fig. 1a) via a Ru spacer produced considerably high surface roughness. The design concept of the double pinned p-STT MTJ will be explained in more detail in the following section. In addition, we investigated static magnetic properties of the double pinned p-MTJ spin-valve, tested the achievement of four-level magnetic-resistance states, and analyzed the operation mechanism of four-level resistances.

**Results**

**Design of Double Pinned p-MTJ Spin-valve.** The double pinned p-MTJ spin-valve was vertically stacked with the bottom electrode, bottom Co₂Fe₆B₆ ferromagnetic pinned structure (called bottom pinned structure), double MgO based Co₂Fe₆B₆ ferromagnetic free layer (called the double free-layer), top Co₂Fe₆B₆ ferromagnetic pinned structure (called top pinned structure), and top electrode, as shown in Fig. 1b. The magnetic layers of the double pinned p-MTJ spin valve can be divided largely into five groups (M₁, M₂, M₃, M₄, and M₅ layers). The bottom electrode was made by sputtering tungsten (W) and titanium nitride (TiN) layers on a thermally oxidized 300-mm-diameter Si wafer, followed by the chemical-mechanical-planarization (CMP). For the bottom pinned structure, the Ta buffer layer was used to intersect the face-centered-cubic crystalline texturing of the TiN electrode since the Ta layer had an amorphous structure. The face-centered-cubic crystalline Pt-seed-layer was used to form the L10 crystalline structure of the bottom-lower SyAF [Co (0.47 nm)/Pt (0.23 nm)]₃ multilayer (M₁ layer) so that its spin direction was perpendicularly upward, as shown in Fig. 1c. These layers were anti-ferro-coupled with the single Co (0.51 nm)/Pt (0.23 nm)/Co (0.47 nm) buffer layer via Ru spacer, called the single SyAF [Co/Pt]₃ layer. Simultaneously, the single Co/Pt/Co buffer-layer was ferro-coupled to the bottom Co₂Fe₆B₆ ferromagnetic pinned layer (0.95 nm) via the W bridge layer, defined as M₂ layer. The spin direction of the M₂ layer was perpendicularly downward, as shown Fig. 1c. Thus, the spin directions of the M₁ and M₂ layers always face vertically inward towards each other. In particular, the anisotropy exchange field (Hₑₓₐ) of the bottom pinned structure should be sufficiently higher than the coercivity (Hₑ) of the top pinned structure to fix the spin direction of both the M₁ and
$M_4$ layers. Then, the double Co$_{50}$Fe$_{50}$B$_3$ free-layer ($M_4$ layer) was stacked on the $M_3$ layer, where the thicknesses of the bottom MgO tunneling-barrier, Fe insertion layer, lower Co$_{50}$Fe$_{50}$B$_3$ ferromagnetic free layer, W spacer, upper Co$_{50}$Fe$_{50}$B$_3$ ferromagnetic free layer, and top MgO tunneling-barrier layer were 1.15, 0.3, 1.0-0.5, 0.2, 1.05, and 1.0 nm, respectively. The spin direction of $M_4$ layer was dependent of the polarity of the applied perpendicular-magnetic-field; i.e. vertically downward for a negative field and vertically upward for a positive field, as shown in Fig 1c. In particular, the $H_{c}$ of $M_4$ layer should be considerably smaller than the $H_{c}$ of the top pinned structure to make four different spin direction states between the $M_1$ and $M_4$ layers, as shown in Fig 1c. To form four different spin direction states, we essentially need three key-design concepts: 1) for designing the bottom pinned structure, the spin direction of the $M_1$ and $M_2$ layers should face always inward toward each other, 2) for designing $M_1$ layer, its $H_{c}$ should be remarkably smaller than the $H_{c}$ of the $M_2$ layer to assure to produce four different spin direction states between the $M_1$ and $M_4$ layers, and 3) for designing the top pinned structure, the $H_{c}$ of the $M_4$ layers should be sufficiently higher than the $H_{c}$ of the $M_2$ layer to avoid a write-error. These three key-design concepts will be treated later in detail.

**Design and Static Perpendicular-Magnetic Behaviour of Bottom Pinned Structure and Double Free-Layer.** In the bottom pinned structure ($M_1$ and $M_2$ layers) in Fig. 1b, the spin direction of the $M_2$ layer should always face perpendicularly inward toward with that of the $M_1$ layer, as shown in Fig. 1c. Thus, this bottom pinned-structure needs as large $H_{c}$ of the $M_1$ layer as possible. In our previous studies, the spin directions of the $M_1$ and $M_4$ layers are always facing perpendicularly inward against each other when the number of the bottom-upper SyAF [Co(0.4 nm)/Pt(0.2 nm)] layers (i.e., 3) is less than that of the bottom-lower SyAF [Co(0.4 nm)/Pt(0.2 nm)] layers (i.e., 6). Also, we implemented the p-MTJ spin-valves with a single SyAF [Co/Pt]$_{n}$ layer which showed large $H_{c}$ of the the SyAF multilayer was ferro-coupled with the top Co$_2$Fe$_6$B$_2$ ferro-magnetic pinned-layer (0.75 nm) via a W bridge layer and Co/Pt seed layer, which is defined as $M_4$ layer. The spin direction of the $M_4$ layer was dependent of the polarity of the applied magnetic-field. Simultaneously, $M_4$ layer was always anti-ferro-coupled with the top-upper [Co(0.47 nm)/Pt(0.23 nm)]$_n$ SyAF multilayers ($M_3$ layer), via the Ru spacer. Thus, the spin direction of the $M_3$ layer was always in the opposite of the $M_4$ layers, as shown in Fig. (1c). In particular, the number (m) of the top-lower [Co(0.47 nm)/Pt(0.23 nm)]$_n$ SyAF multilayers should be higher than that (n) of the top-upper [Co(0.47 nm)/Pt(0.23 nm)]$_m$ multilayers to produce four different spin direction states between the $M_1$ and $M_3$ layers. If m is lower than n, only two different spin direction states would be generated between the $M_3$ and $M_4$ layers. Finally, a top Ta/Ru electrode was stacked on the $M_3$ layer.

In summary, the design of the double pinned p-MTJ spin-valve could produce four different spin direction states between the $M_1$ and $M_4$ layers: AP state 1 (perpendicularly upward spin direction for both $M_3$ and $M_4$ layers), AP state 2 (spin direction facing outward between $M_3$ and $M_4$ layers), P state (downward spin direction for both $M_3$ and $M_4$ layers), and AP state 3 (spin direction facing inward between the $M_3$ and $M_4$ layers, as shown in Fig. 1c). To form four different spin direction states, we essentially need three key-design concepts: 1) for designing the bottom pinned structure, the spin direction of the $M_1$ and $M_2$ layers should face always inward toward each other, 2) for designing $M_1$ layer, its $H_{c}$ should be remarkably smaller than the $H_{c}$ of the $M_2$ layer to assure to produce four different spin direction states between the $M_1$ and $M_4$ layers, and 3) for designing the top pinned structure, the $H_{c}$ of the $M_4$ layers should be sufficiently higher than the $H_{c}$ of the $M_2$ layer to avoid a write-error. These three key-design concepts will be treated later in detail.

**Design and Static Perpendicular-Magnetic Behaviour of Top Co$_{50}$Fe$_{50}$B$_3$ Ferro-Magnetic Pinned Structure.** In the top pinned structure, the top Co$_{50}$Fe$_{50}$B$_3$ magnetic pinned-layer was ferro-coupled with the top-lower SyAF [Co/Pt]$_{n}$ layer via W bridge layer ($M_3$ layer), which was then anti-ferro-coupled with the top-upper SyAF [Co/Pt]$_{n}$ layer ($M_3$ layer) via Ru spacer, as shown in Fig. 3a. In addition, the number of the top-lower [Co(0.47 nm)/Pt(0.23 nm)]$_n$ layers (m) of the $M_3$ layer should be less than the number of the top-upper [Co(0.47 nm)/Pt(0.23 nm)]$_m$ layers (n) of the $M_3$ layer, and the $H_{c}$ of the top pinned structure should be as large as possible to avoid a write-error. Unlike the bottom pinned structure in Fig. 2d, the top pinned structure should be able to generate four different electron-spin states between the $M_3$ and $M_4$ layer, resulting in four different
resistance states. Thus, within the scanning magnetic-field range less than the $H_{ex}$ of the top pinned structure, the spin direction of the $M_4$ layer could be rotated from upward to downward or downward to upward when the polarity of the magnetic-field changes from positive to negative or from negative to positive. To test whether or not the spin directions of the top pinned structure were variable, we investigated the $M$-$H$ loop of a basic top pinned-structure with the $m:n$ ratio of 6:3 of the number of [Co(0.47 nm)/Pt(0.23 nm)] multilayers in the $M_4$ and $M_5$ layers, as shown in Fig. 3b. At the applied magnetic-field of $+15$ kOe, the spin direction of both the $M_4$ and $M_5$ layers faced perpendicularly upward. As the magnetic-field decreased from $+15$ to $+4$ kOe, the magnetic moment decreased from $+0.6$ to $+0.3$ memu, corresponding to the magnetic moment of the $M_5$ layer (i.e., 0.3 memu) rotating the spin direction of the $M_5$ layer from upward to downward. This occurred at the $H_{ex}$ of $~4.9$ kOe arising from the anti-ferro coupling across the Ru spacer layer. As the magnetic-field decreased from $+4$ to $-4$ kOe, the magnetic moment changed from $+0.3$ to $-0.3$ memu, responding to the magnetic moment of the $M_4$ and $M_5$ layers (i.e., 0.6 memu), rotating the spin direction of the $M_4$ layer from upward to downward. Simultaneously, the spin direction of the $M_5$ layers rotated from downward to upward to hold the anti-ferro coupling via the Ru spacer stably. As a result, the spin directions of the $M_4$ and $M_5$ layers facing perpendicularly inward changed to facing perpendicularly outward. As the magnetic-field increased over $-4$ kOe, the spin direction of the $M_5$ layer rotated from upward to downward so that the spin directions of both the $M_4$ and $M_5$ layers were perpendicularly downward. In contrast, as the magnetic-field changed from negative to positive direction, the change of the spin directions of the $M_4$ and $M_5$ layers followed the same order as the magnetic-field changed from positive to negative direction. In particular, the spin directions of the $M_4$ and $M_5$ layers facing perpendicularly outward changed to facing perpendicularly inward. Thus, this top pinned structure could produce two spin directions between the $M_4$ and $M_5$ layers when the magnetic-field is greater than the $H_c$ of the top pinned structure; facing perpendicularly outward for the negative magnetic-field and facing perpendicularly inward for the positive magnetic-field. Although the top-lower SyAF [Co(0.47 nm)/Pt(0.23 nm)]$_6$ layer and top-upper SyAF [Co(0.47 nm)/Pt(0.23 nm)]$_3$ layer and could provide variable spin directions between the $M_4$ and $M_5$ layers, the top-lower SyAF [Co(0.47 nm)/Pt(0.23 nm)]$_6$ layer is too thick to maximize the TMR ratio of the p-MTJ spin-valve. The TMR ratio is strongly dependent on the coherent tunneling of the $\Delta_s$ Bloch state induced from the hybridization of the Fe-d$_z^2$ and O-p$_z$ orbitals at the MgO/CoFeB interface. Even a small defect at the interface reduces the coherent tunneling of the...
spin-polarized electrons\(^{31,39}\). The roughness increases with the number of top-lower SyAF [Co/Pt]\(_n\) layers from about 150 pm to 240 pm as seen in Supplementary 4. The roughness needs to be reduced to maximize the TMR ratio to assure four levels of the double pinned p-MTJ spin-valve.

To reduce the thickness of the top pinned structure, first of all, we investigated the \(M-H\) loop of the top pinned structure with the ratio of the [Co(0.47 nm)/Pt(0.23 nm)]\(_3\) layers of the \(M_4\) and \(M_5\) layers (\(m:n\) ratio) of 3:1, as shown in Fig. 3c. Its static magnetic behaviour was similar to the top pinned structure with the ratio of \(m:n\) ratio of 6:3, showing the magnetic moment of the \(M_4\) and \(M_5\) layers, \(H_c\), and \(H_{ex}\) were 0.1 and 0.5 memu, ~0.3 kOe, and ~12 kOe. Although this top pinned structure could produce two variable spin directions between the \(M_4\) and \(M_5\) layers, the \(H_c\) of ~0.3 kOe was too small to generate four different spin direction states between the \(M_3\) and \(M_4\) layers in the double pinned p-MTJ spin-valve (Fig. 1c) since the \(H_c\) of the top pinned structure (i.e., ~0.3 kOe) was not sufficiently higher than the \(H_c\) of the double free-layer (Fig. 2d: i.e., ~0.2 kOe) to avoid the write error. Thus, we observed the dependency of the \(H_c\) of the top pinned structure on the \(m:n\) ratio, as shown in Fig. 3d. The \(m:n\) ratios of 1:3, 2:3, and 3:3 showed \(H_c\) values of ~0.4, ~0.6, and ~1 kOe, as shown in the inset of Fig. 3d, and all \(m:n\) ratios demonstrated two variable spin directions between the \(M_4\) and \(M_5\) layers. This result indicates that the \(H_c\) of the top pinned structure increases with the number of [Co(0.47 nm)/Pt(0.23 nm)]\(_3\) layers in the \(M_5\) layer, while \(H_{ex}\) decreases with the number of [Co(0.47 nm)/Pt(0.23 nm)]\(_3\) layers in the \(M_5\) layer. In particular, the \(m:n\) ratio of 3:3 showed a sufficient \(H_c\) (i.e., ~1 kOe), which could produce four different spin direction states between the \(M_4\) and \(M_5\) layers (Fig. 1c) since it is considerably larger than the \(H_c\) of the double free-layer (~0.1 kOe) (Fig. 2d).

Recall that at the \(m:n\) ratio of 3:3 the static magnetic moment of the \(M_4\) layer was slightly larger than that of the \(M_5\) layer so that the spin direction of the top pinned structure (\(M_4\) and \(M_5\) layers) faced vertically outward for the negative applied magnetic-field and vertically inward for the positive applied magnetic-field. If \(n\) is larger than \(m\), the spin directions of the \(M_4\) and \(M_5\) layers could not be variable. Therefore, the design of choosing a proper \(H_c\) and \(H_{ex}\) of the top pinned structure would be a key research to stably produce four different spin direction states between \(M_3\) and \(M_4\) layers.

**Static Perpendicular-Magnetic Behaviour and Multi-level TMR ratio for Double Pinned p-MTJ Spin-Valve.** By combining the top (3:3 of \(m:n\) in Fig. 3d) and bottom p-MTJ structures with the double free-layer (Fig. 2d), we fabricated the double pinned p-MTJ spin-valve shown in Fig. 1b. The \(M-H\) loop of the double pinned p-MTJ spin-valve showed the \(H_{ex}\) of 4.9 kOe when the applied magnetic-field was scanned from...
−6.5 kOe to +6.5 kOe, as shown in Supplementary 5a. In addition, the resistance-vs.-magnetic-field (\(R-H\)) loop presented only three resistance states, when the applied magnetic-field was scanned from \(-H_{\text{ex}}\) to \(+H_{\text{ex}}\) kOe, as shown in Supplementary 5b,c. In order to produce four different resistance states, thus, the maximum scanning range of the applied magnetic-field should be sufficiently less than \(\pm H_{\text{ex}}\) (i.e., ~4.2 kOe) of the bottom pinned p-MTJ spin-valve, but greater than \(\pm H_{\text{ex}}\) (i.e., ~1 kOe) of the top pinned structure (\(M_4\) and \(M_5\) layers); i.e., \(\pm 2\) kOe. Thus, four different spin directions between the \(M_3\) and \(M_4\) layers could be stably produced when the applied magnetic-field was scanned from \(-2\) kOe to \(+2\) kOe, as shown in the \(M-H\) loop of Fig. 4a. First, the AP state 1 was produced when the applied magnetic-field was scanned from \(+2\) kOe to \(+0.5\) kOe, where the spin directions of both the \(M_3\) and \(M_4\) layers were vertically upward and parallel while the spin directions of the \(M_4\) and \(M_5\) layers faced vertically inward toward each other via an anti-ferro-coupling, as shown in Fig. 4a,b. Recall that this result corresponds to the combination of the top pinned structure (\(M_4\) and \(M_5\) layers) in Fig. 3d and the bottom pinned structure (\(M_1\) and \(M_2\) layers) with the double free-layer (\(M_3\) layer) in Fig. 2d at the positive applied magnetic-field. Then, when the applied magnetic-field was scanned from \(+0.5\) kOe to \(+0.5\) kOe, the spin direction of only the \(M_3\) layer was rotated from upward to downward while the spin directions of both the \(M_4\) and \(M_5\) layer remained facing vertically outward from each other, generating the AP state 2, where the spin direction of the \(M_3\) layer faced vertically outward against that of the \(M_4\) layer, as shown in Fig. 4a,b. Furthermore, when the applied magnetic-field was scanned from \(-0.5\) kOe to \(-2.0\) kOe, the spin directions between the \(M_4\) and \(M_5\) layers facing vertically inward were rotated to face vertically outward while the spin direction of the double free-layer was sustained downward, forming the P state, where the spin directions of both the \(M_4\) and \(M_5\) layers were vertically downward and in parallel, as shown in Fig. 4a,b. Subsequently, when the applied magnetic-field was scanned from \(-2.0\) kOe to \(+0.5\) kOe, the spin direction of only the \(M_3\) layer rotated from downward to upward while the spin directions of both the \(M_1\) and \(M_2\) layers remained facing vertically outward from each other, generating the AP state 3, where the spin direction of the \(M_1\) layer remained facing upward, returning to the AP 1 state, where the spin directions of both the \(M_3\) and \(M_4\) layers facing vertically inward transited to facing vertically and parallel upward, as shown in Figure 4.

Figure 4. Magnetic and resistance properties of double pinned p-MTJ spin-valve in narrow scanning magnetic-field range (\(-2\) kOe to \(+2\) kOe). (a) \(M-H\) loop, (b) four-different spin-electron-directions depending on the polarity and magnitude of the scanning magnetic-field, (c) \(R\)-\(H\) loop of double pinned p-MTJ spin-valve with cell size of 2 \(\mu\)m\(^2\), and (d) TMR ratios of double pinned p-MTJ spin-valve.
iv in Fig. 4a,b. As a result, four different spin directions between the $M_4$ and $M_1$ layers could be stably produced in a magnetic-field scanning range of $\pm 2.0 \text{kOe}$. The $R$-$H$ loop corresponding to the $M$-$H$ loop in Fig. 4a was shown in Fig. 4c. The resistance changed from the AP state 1, AP state 2, AP state 3, P state, and AP state 1 when the applied magnetic-field was scanned from $+2.0 \text{kOe}$, $-2.0 \text{kOe}$, and $+2.0 \text{kOe}$. The sequence of a higher resistance of the double pinned p-MTJ spin-valve was followed by AP state 3, AP state 1, AP state 2, and P state. The highest resistance was achieved when the $M_4$ layers became the anti-parallel states against both the $M_1$ and $M_2$ layers; i.e., the AP state 3, corresponding to the sum of serial connection $(R_{\text{AP}3})$ of the anti-parallel resistance between the $M_3$ and $M_4$ layers $(R_{\text{AP}3})$ with the anti-parallel resistance between the $M_1$ and $M_2$ layers $(R_{\text{AP}1})$, as shown in Fig. 4d. The second highest resistance was obtained, when the $M_4$ layers became the parallel state against the $M_1$ layers while it was in the anti-parallel state against the $M_2$ layers; i.e., the AP state 1, responding to the sum of serial connection $(R_{\text{AP}1})$ of the parallel resistance between the $M_1$ and $M_2$ layers $(R_{\text{AP}1})$ with the anti-parallel resistance between the $M_3$ and $M_4$ layers $(R_{\text{AP}3})$. The third highest resistance was achieved, when the $M_4$ layers became the anti-parallel state against the $M_1$ layers while it did the parallel state against the $M_2$ layers; i.e., the AP state 2, indicating to the sum of serial connection $(R_{\text{AP}2})$ of the anti-parallel resistance between the $M_1$ and $M_2$ layers $(R_{\text{AP}2})$ with the parallel resistance between the $M_3$ and $M_4$ layers $(R_{\text{AP}1})$. Note that the anti-parallel resistance between the $M_1$ and $M_2$ layers $(R_{\text{AP}1})$ is much larger than the anti-parallel resistance between the $M_1$ and $M_2$ layers $(R_{\text{AP}1})$ since the thickness of the bottom MgO tunneling barrier (1.15 nm) was greater than that of the top MgO tunneling barrier (1.0 nm). This is confirmed by the high-resolution transmission-electro-microscopy (HR-TEM) observation shown in Supplementary 3. Thus, the resistance of the AP state 1 was larger than that of the AP state 2.

Multi-level TMR ratios of the double pinned p-MTJ spin-valve were measure by CIPT (current-in-plane tunneling) measurement scanning the magnetic-field of $\pm 2.0 \text{kOe}$. The TMR ratios were 152.6% for AP state 1, 33.6% for AP state 2, and 166.5% for AP state 3. These values correlated well with the four different resistance levels in the $R$-$H$ loop in Fig. 4c. A higher TMR ratio was accounted for when the spin direction of the $M_1$ layer becomes anti-parallel to that of the $M_2$ layer (i.e., $R_{\text{AP}1}$). This result evidently indicates that the double pinned p-MTJ spin-valve can perform multi-level (i.e., four-level) non-volatile memory-cell operation.

**Discussion**

Our proposed double pinned p-MTJ spin-valve well demonstrated four-level resistance as a multi-level p-STT MRAM-cell, resulting in the TMR ratios of 152.6, 33.6, and 166.5% for AP state 2, and 166.5% for AP state 3. These values correlated well with the four different resistance levels in the $R$-$H$ loop. In particular, the conventional p-MTJ spin-valve structure was comprised of a 12-inch SiO$_2$ wafer, W/TiN bottom electrode, Ta buffer layer, Pt seed layer, bottom-lower SyAF [Co(0.47 nm)/Pt(0.23 nm)]$_1$ layers/Co(0.51 nm) (M$_1$ layer), Ru spacer layer (0.85 nm), Co(0.51 nm)/Pt(0.23 nm) bottom-upper SyAF [Co(0.47 nm)/Pt(0.23 nm)]$_1$ layers, and a Co buffer layer (0.47 nm). The W bridge layer of 0.22 nm was used to ferro-couple the bottom-upper SyAF layer to the pinned layer. The p-MTJ consisted of a Co$_5$Fe$_{6}$B$_2$ bottom pinned layer (1.05 nm), MgO tunneling barrier (1.15 nm), Fe insertion layer (0.3 nm), Co$_5$Fe$_{6}$B$_2$ free layers (1.05 nm), W spacer layer (0.4 nm), Co$_5$Fe$_{6}$B$_2$ (1.05 nm), and MgO (1.0 nm)/W capping layer. The ferro-coupled bottom-upper SyAF [Co(0.47 nm)/Pt(0.23 nm)]$_1$ layers and the Co$_5$Fe$_{6}$B$_2$ bottom pinned layer is defined as the $M_2$ layer. The bottom pinned structure of the double pinned p-MTJ spin-valve using a single SyAF [Co/Pt]$_n$ layer and double free-layer were fabricated wherein the ratio of the number of [Co/Pt]$_n$ layers between the upper and lower SyAF [Co/Pt]$_n$ layer was varied from 3:6 (i.e., a double SyAF [Co/Pt]$_n$ layer) to 0:3, as shown in Fig. 1b. In addition, a Co/Pt/Co buffer layer was used to bridge instead of the top-upper SyAF [Co(0.47 nm)/Pt(0.23 nm)]$_1$ layer (compare Fig. 1a,b). The MgO capping layer of the conventional double MgO-based p-MTJ spin-valve structure was used as the top MgO tunneling barrier followed by an Fe insertion layer (0.3 nm), Co$_5$Fe$_{6}$B$_2$ (0.75 nm) top pinned layer, W bridge layer (0.42 nm), Co(0.47 nm)/Pt(0.23 nm) buffer layer, and top-lower SyAF [Co(0.47 nm)/Pt(0.23 nm)]$_1$ layer/Co(0.51 nm). The ferro-coupled Co$_5$Fe$_{6}$B$_2$ top pinned layer and the top-lower SyAF [Co(0.47 nm)/Pt(0.23 nm)]$_1$ layer is defined as the top-pinned layer $(M_1)$ layer. Following the $M_1$ layer is the Ru spacer layer (0.85 nm), Co(0.51 nm)/Pt(0.23 nm) top-upper SyAF [Co(0.47 nm)/Pt(0.23 nm)]$_1$ layer $(M_2)$ layer, and Ta/Ru top electrode. The spin-valves were ex-situ annealed at 350 °C for 30 min under a vacuum below 10$^{-6}$ torr and a perpendicular magnetic-field of 3 tesla. The TMR ratios of the double pinned p-MTJ spin-valves fabricated on 12-inch Si wafers were estimated by using CIPT at room temperature. The wafers were cut into 1 cm$^2$ pieces. The magnetic properties of the double pinned spin-valves were characterized by using vibrating-sample magnetometer (VSM) at room temperature. The $R$-$H$ curve was measured with a p-MTJ spin-valve with the cell size of 2 $\mu$m $\times$ 2 $\mu$m. The 2 $\mu$m-scale p-MTJ spin-valves were wire-bonded to the sample holder and were installed into a home-made electrical probing system with a $\sim$1 Tesla electromagnet using a Keithley 236 source measure unit and Agilent B2902A semiconductor parameter analyzer.
References

1. Song, Y. J. et al. Highly Functional and Reliable 8Mb STT-MRAM Embedded in 28nm Logic. IEDM, 27.2.1–27.2.4, https://doi.org/10.1109/IEDM.2016.7838891 (2017).

2. Antonyan, A., Pyo, S., Jung, H. & Song, T. Embedded MRAM Macro for eFlash Replacement. IEEE International Symposium on Circuits and Systems (ISCAS), 2–5, https://doi.org/10.1109/ISCAS.2018.8351201 (2018).

3. Jan, G. et al. Demonstration of fully functional 8Mb perpendicular STT-MRAM chips with sub-5ns writing for non-volatile embedded memories. Dig. Tech. Pap. - Symp. VLSI Technol. 09, 3008, 8–9, https://doi.org/10.1109/VLSIT.2014.6984357 (2014).

4. Lu, Y. et al. Fully functional perpendicular STT-MRAM macro embedded in 40 nm logic for energy-efficient IOT applications. IEEE Int. Electron Devices Meeting, IEDM, 26.1.1–26.1.4, https://doi.org/10.1109/IEDM.2015.7409770 (2016).

5. Aitken, R. et al. Device and technology implications of the Internet of Things. Symp. VLSI Technol. Dig. Tech. Papers, 1–4, https://doi.org/10.1109/VLSIT.2016.7484359 (2016).

6. Durlam, M. et al. MRAM Memory for Embedded and Stand Alone Systems, IEEE Int. Conf. Integ. Circuit Des. Technol. (ICICDT), 75–78, https://doi.org/10.1109/ICICDT.2007.4299546 (2007).

7. Grollier, J., Querlioz, D. & Stiles, M. D. Spintronic Nanodevices for Bioinspired Computing. Proc IEEE Instr Elecstr Electron Eng. 10(4), 2024–2039, https://doi.org/10.1109/JPROC.2016.2597152 (2016).

8. Chae, K. S., Shim, T. H. & Park, J. G. Dependency of anti-ferro-magnetic coupling strength on Ru spacer thickness of [Co/Pd] n layers. J. Appl. Phys. 110, 033904, https://doi.org/10.1063/1.3507994 (2011).

9. Chae, K. S., Lee, D. Y., Shim, T. H., Hong, J. P. & Park, J. G. Correlation of the structural properties of a Pt seed layer with the synthetic-anti-ferromagnetic layer in perpendicular magnetic-tunnel-junctions fabricated on 12-inch TiN electrode wafer. J. Appl. Phys. 113, 264309, https://doi.org/10.1063/1.4832459 (2013).

10. Lee, D. Y., Shim, T. H. & Park, J. G. Effect of coupling ability between a synthetic antiferromagnetic layer and pinned layer on a bridging layer of Ta, Ti, and Pt in perpendicular-magnetic tunnel junctions. Nanotechnology 27(29), 295705 (2016).
Acknowledgements
This work was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (No. 2017R1A2A1A05001285) and Brain Korea 21 PLUS Program in 2014.

Author Contributions
J.Y. Choi and J.G. Park conceived and designed the study. J.Y. Choi, H. Jun, K. Ashiba fabricated all patterns and carried out experiments, with the help of J.G. Park. Contributions to the measurements were made by J.Y. Choi, H. Jun, K. Ashiba, and J.U. Baek. All authors contributed to discussions regarding the research. J.Y. Choi, T.H. Shim and J.G. Park wrote the manuscript.

Additional Information
Supplementary information accompanies this paper at https://doi.org/10.1038/s41598-019-48311-0.

Competing Interests: The authors declare no competing interests.

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