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Thermally stable voltage-controlled perpendicular magnetic anisotropy in Mo|CoFeB|MgO structures

Xiang Li,1,a) Guoqiang Yu,1 Hao Wu,2 P. V. Ong,3 Kin Wong,1 Qi Hu,4 Farbod Ebrahim,4 Pramey Upadhyaya,1 Mustafa Akyol,1 Nicholas Kioussis,3 Xiufeng Han,2 Pedram Khalili Amiri,1,4,b) and Kang L. Wang1,c)

1Department of Electrical Engineering, University of California, Los Angeles, California 90095, USA
2Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
3Department of Physics and Astronomy, California State University Northridge, Northridge, California 91330, USA
4Inston Inc., Los Angeles, California 90095, USA

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We study voltage-controlled magnetic anisotropy (VCMA) and other magnetic properties in annealed Mo|CoFeB|MgO layered structures. The interfacial perpendicular magnetic anisotropy (PMA) is observed to increase with annealing over the studied temperature range, and a VCMA coefficient of about 40 fJ/V-m is sustained after annealing at temperatures as high as 430 °C. Ab initio electronic structure calculation results of interfacial PMA as a function of strain further show that strain relaxation may lead to the increase of interfacial PMA at higher annealing temperatures. Measurements also show that there is no significant VCMA and interfacial PMA dependence on the CoFeB thickness over the studied range, which illustrates the interfacial origin of the anisotropy and its voltage dependence, i.e., the VCMA effect. The high thermal annealing stability of Mo|CoFeB|MgO structures makes them compatible with advanced CMOS back-end-of-line processes, and will be important for integration of magnetoelectric random access memory into on-chip embedded applications. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4932553]

Writing of information using electric fields in perpendicular magnetic tunnel junctions (MTJs) is being investigated intensively, with the goal of realizing energy-efficient and high density Magnetoelectric Random Access Memory (MeRAM) devices. Particularly, the Ta/CoFeB|MgO material system has attracted great interest as it combines high tunneling magnetoresistance (TMR) for reading,8,9 perpendicular magnetic anisotropy (PMA) for high density and scaling,10,11 and voltage-controlled magnetic anisotropy (VCMA) for energy-efficient writing.1–7,12 In face of the increasing static power dissipation of CMOS technology at smaller nodes, it is also highly desirable to further integrate embedded MeRAM into CMOS logic circuits to achieve non-volatile electronic systems with low standby power and instant-on operation capability.13,14

However, in the commonly used Ta|CoFeB|MgO system, the PMA and TMR cannot be sustained when annealing temperatures above 400 °C are used,15,16 making it incompatible with advanced CMOS back-end-of-line processes, where the low-k dielectrics used between interconnects require a thermal budget over 400 °C.17,18 Several works have recently explored MTJs with improved thermally stable TMR and PMA for spin-transfer torque magnetic random access memory (STT-MRAM) applications, primarily by blocking or eliminating Ta diffusion under high temperatures.17–20 Nevertheless, for VCMA-based embedded memory applications, it is critical to develop new material systems that can also provide thermally stable VCMA after annealing at 400 °C.

A possible route to achieve this goal is to exploit the effect of the metal seed (or cap) layer on the PMA21–23 and VCMA in MTJ structures.23–26 Only recently, there have been reports on improving the thermal stability of PMA, TMR, and VCMA in MTJs by changing the Ta-based material stacks to Mo|CoFeB|MgO27–29 and W|CoFeB|MgO.30,31 However, a detailed study on the thermal stability of VCMA in the Mo|CoFeB|MgO material system, particularly after annealing above 400 °C, is still needed.

Here, we present a detailed study on the effect of annealing on PMA, saturation magnetization ($M_s$), and VCMA in Mo|CoFeB|MgO film stacks. A VCMA coefficient ($\xi$) of 40 fJ/V-m is demonstrated after annealing at 430 °C for 30 min.32 We also observe a higher $\xi$ of 50 fJ/V-m at lower annealing temperature ($T_A$) of 360 °C. These reported VCMA coefficients are comparable to the best high-temperature VCMA (>400 °C) values (40–50 fJ/V-m) reported to date for W-based samples in Ref. 31, as well as typical $\xi$ values (30–60 fJ/V-m) measured in the Ta|CoFeB|MgO system.12,25,33–35 The results also show that higher annealing temperature improves the $M_s$, as well as the interfacial PMA $K_i$ of the film stack within the studied temperature range. Ab initio electronic structure calculation results further show that the calculated $K_i$ values increase as the epitaxial tensile strain on the FeCo layers relaxes. In addition, the CoFeB thickness dependence of the VCMA and $K_i$ is studied in this work upon annealing at different temperatures, showing no significant dependence over the measured thickness range.

The magnetic film stacks were deposited in a magnetron sputtering system on a thermally oxidized Si|SiO$_2$ substrate. We deposited samples with uniform CoFeB thickness with the following structures: Mo(5)Co$_{30}$Fe$_{60}$B$_{20}$(t = 0.94, 1.06, 1.10, 1.15, and 1.20). The CoFeB|MgO MLs were 40 nm thick, and the MgO layer between the MLs was 4 nm thick. The CoFeB layer thicknesses for MLs were 5, 7, 9, 11, and 13 nm.

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1.18|MgO(2.5)|Al2O3(5), with the numbers in parentheses designating nominal thickness in nm. We also deposited samples with gradually changing (wedged) CoFeB thickness consisted of similar structures: Mo(5)|Co30Fe70B30(t)|MgO(2.5)|Al2O3(5), where the CoFeB thickness t was continuously varied in the range of 0.65–1.45 nm across the wafer. All metallic layers were grown using DC sputtering, while the MgO and Al2O3 layers were RF sputtered from insulating MgO and Al2O3 targets. Stacks were annealed at 360 ºC, 400 ºC, and 430 ºC, respectively, for 30 min under vacuum (<10−7 Torr). The rise time of the annealing system was less than 2 min, while the cool-down time from 430 ºC to 200 ºC was approximately 30 min. The samples were subsequently patterned into Hall bar devices by standard photolithography and dry etching techniques, and further covered by a 33 nm Al2O3 gate oxide using atomic layer deposition (ALD). Last, a patterned ITO electrode was fabricated for top gating. The dielectric constants of MgO and Al2O3 are assumed to be 10 and 7, respectively, according to literature. The dimensions of the Hall bars were 20 μm × 130 μm. For the wedged samples, the Hall bar length was perpendicular to the wedge direction.

Ab initio electronic structure calculations were carried out within the framework of the projector augmented-wave formalism, as implemented in the Vienna ab initio simulation package (VASP) at the generalized gradient approximation level. The slab supercell model of the magnetic layered structure consists of three monolayers (MLs) of bcc Mo, on top of three MLs of B2-type FeCo, on top of seven MLs of MgO, and a 15-Å-thick vacuum region. The O atoms at the interface are placed atop Fe atoms.

The unpatterned films were first characterized by vibrating sample magnetometer (VSM) to obtain the M-H loops, in order to study the change of PMA and Ms with different annealing temperatures. Exemplary results from a sample with uniform CoFeB thickness of 1.06 nm are shown in Fig. 1(a), where the magnetic field is swept in the out-of-plane direction. As the annealing temperature increases, the squareness of the M-H loop improves, and the out-of-plane saturation field decreases, which indicates that the PMA of the film increases at higher annealing temperature. Similar results were also observed for samples with CoFeB thicknesses of 0.94 and 1.18 nm. By carrying out a linear fit of the magnetic moment per unit area as a function of the CoFeB thickness, we further obtained the saturation magnetization (Ms) and dead layer thickness (td) values at different annealing temperatures. As shown in Fig. 1(b), both the Ms and td values increase at higher annealing temperatures. Note that all CoFeB thicknesses mentioned in the paper refer to the nominal thickness without dead layer subtraction.

This increase of PMA, Ms, and td in the Mo|CoFeB|MgO system with annealing temperature is consistent with observations of Ref. 27, and can be associated with the competition between boron diffusion from the CoFeB layer into the molybdenum film, and molybdenum diffusion into the CoFeB layer upon annealing. It is known that the diffusion of boron promotes better crystallization of CoFe from the amorphous state to a bcc(001) crystal structure, resulting in a higher saturation magnetization. According to ab initio calculations, the PMA in the CoFeB|MgO system stems primarily from the hybridized Fe/Co 3d orbitals and O 2p orbitals at the interface, hence, the decrease of boron atoms at the interface might be expected to induce stronger orbital hybridization and higher PMA.

It is worth noting that the observed monotonic increase of both Ms and PMA from 360 ºC to 430 ºC in the Mo-based system is in sharp contrast to the Ta-based system, where Ms and PMA both drop when annealed at temperatures higher than 300 ºC. Similarly, the dead layer thickness of the Ta|CoFeB|MgO system increases above 0.5 nm at around 330 ºC (Ref. 27) while the dead layer thickness increases above 0.5 nm at a higher temperature of around 430 ºC for the Mo|CoFeB|MgO system. This better thermal annealing stability of PMA and Ms in Mo|CoFeB|MgO structures can be explained by a number of causes. Namely, the smaller negative formation enthalpy of Mo oxides compared to Ta oxides, the crystalline structure of the sputtered Mo film, and the smaller negative formation energy of Fe-Mo alloys compared to Fe-Ta, all contribute to the prevention of molybdenum atoms from significantly diffusing into the free layer, leading to a more stable PMA and Ms after high-temperature annealing. On the other hand, the decrease of Ms in the Ta-based system at higher annealing temperatures has been attributed to intermixing of CoFeB and Ta, while the decrease of PMA results mainly from the diffusion of Ta into the CoFeB|MgO interface. Hence, in our Mo|CoFeB|MgO system, boron diffusion (out of the free layer) has a dominating effect over molybdenum diffusion (into the free layer) over the studied temperature range, thus continuing to improve the magnetic properties at higher annealing temperature.

The VCMA was subsequently characterized as follows. The Hall resistance RH was measured under a sweeping out-of-plane magnetic field, while different gate voltages were applied. A positive gate voltage is defined as the top gate electrode being at a positive electric potential, as shown.

![FIG. 1. (a) M-H curves for different annealing temperatures (T A). M/A refers to magnetic moment per unit area. H¿ refers to out-of-plane magnetic field. The CoFeB thickness (t) is 1.06 nm. (b) Saturation magnetization (Ms) and dead layer thickness (td) dependence on T A.](image-url)
in Fig. 2, top right inset. Fig. 2 shows the measurement results for a CoFeB thickness of 1.45 nm on the wedged sample, annealed at 430 °C for 30 min, where three different gate voltages are applied. As the CoFeB in this case has an in-plane easy-axis, an out-of-plane (i.e., hard-axis) magnetic field is applied in order to obtain the perpendicular anisotropy energy \( E_{\text{perp}} \). As can be seen from the bottom left inset of Fig. 2, a noticeable difference of the R-H loop is observed for different applied electric fields.

To measure the VCMA coefficient \( \zeta \), we follow an approach similar to Ref. 12. The value of \( E_{\text{perp}} \) is obtained from the equation 
\[ E_{\text{perp}} = -M_S \frac{1}{2} H Z \left[ \frac{2(R^{\text{AHE}} - R^{\text{AHE}}_{\min})/(R^{\text{AHE}}_{\max} - R^{\text{AHE}}_{\min})}{1} \right], \]
where \( 2(R^{\text{AHE}} - R^{\text{AHE}}_{\min})/(R^{\text{AHE}}_{\max} - R^{\text{AHE}}_{\min}) \) equals the normalized \( M_Z/M_S \) value. Here, \( M_S \) is the saturation magnetization, \( M_Z \) is the perpendicular component of the magnetization, \( H_Z \) is the out-of-plane external magnetic field, \( R^{\text{AHE}} \) is the anomalous Hall resistance, and \( R^{\text{AHE}}_{\max} \) (\( R^{\text{AHE}}_{\min} \)) is the maximum (minimum) of \( R^{\text{AHE}} \) values measured. The value of \( R^{\text{AHE}} \) can be extracted from \( R_{\text{Hall}} \) by subtraction of ordinary Hall contributions according to 
\[ R_{\text{Hall}} = R_0 H Z / t + R_S M_Z / t, \]
where the first term is the ordinary Hall resistance, and the second term represents \( R^{\text{AHE}} \). Here, \( R_0 \) and \( R_S \) are the ordinary and anomalous Hall coefficients, respectively, and \( \mu_0 \) is the permeability of free space. The ordinary Hall coefficients can be obtained from a fit to the \( R_{\text{Hall}} - H_Z \) loop at the high field regions. From this, we can obtain the electric field dependence of the perpendicular anisotropy energy \( E_{\text{perp}}(E) \), and hence, the electric field dependent interfacial PMA \( (K_i) \) can be calculated using 
\[ E_{\text{perp}}(E) = K_i(E) / (t - t_0) - 2 \pi M_Z^2. \]
Hence, one can obtain the electric field dependence of \( K_i \) and measure the VCMA coefficient \( \zeta \).

Next, we compare three exemplary dependencies of \( K_i \) as a function of electric field, for devices with the same CoFeB thickness annealed at different temperatures. As shown in Fig. 3(a), a linear dependence with a negative slope is obtained, which means that depletion of electrons at the CoFeB/MgO interface increases the interfacial perpendicular magnetic anisotropy. From the fitted curves, a \( \zeta \) of \( \sim 40 \text{ fJ/V-m} \) is demonstrated after annealing at 430 °C, along with a higher \( \zeta \) of \( \sim 50 \text{ fJ/V-m} \) at 360 °C annealing temperature.

addition, we carried out gate voltage-dependent hard-axis \( R_{\text{Hall}} - H_Z \) measurements for devices along the length of the wedge-shaped sample, to study the CoFeB thickness dependence of the VCMA coefficient \( (\zeta) \) and interfacial PMA \( (K_i) \) at different annealing temperatures, as shown in Figs. 3(b) and 3(c). No significant CoFeB thickness dependence of either \( \zeta \) or \( K_i \) is observed over the measured thickness range, which is consistent with previous reports, indicating that the interfacial anisotropy and its electric field control originate primarily from the CoFeB interfaces.

The dependences of \( \zeta \) and \( K_i \) (averaging over the measured thickness values) on the annealing temperature are summarized in Figs. 4(a) and 4(b). Apart from the slight decrease of the VCMA coefficient, \( K_i \) increases by 20% from 0.74 mJ/m² to 0.89 mJ/m² after annealing. This slight drop of \( \zeta \) along with a continued increase of \( K_i \) at higher annealing temperature is consistent with previous reports in Ir[CoFeB|MgO] and W[CoFeB|MgO systems. A possible reason for the increase of \( K_i \) and slight VCMA degradation at higher annealing temperature is that the annealing relaxes the compressive strain of the MgO layer, such that the lattice constant of the MgO approaches its bulk value.

To further investigate the effect of strain on \( K_i \), we performed ab initio...
It is also worth noting that a number of reports have shown large \( \xi \) values of 100–1200 fJ/V-m\(^{-1}\) which can be attributed to mobile ionic charges in the oxides besides the MgO layer. These charges may, however, be too slow to achieve high frequency memory writing using voltage pulses. To eliminate the possibility of such an ionic effect in our films, we carried out a hysteretic sweep of the gate voltage\(^{-9} \) from \(-10\) V to 10 V and back to \(-10\) V. The \( K_i \) vs electric field plots for different sweeping directions coincide with each other and are within the error bars of the measurement, hence confirming that there is no contribution from mobile charges in our films.

In conclusion, it was demonstrated that the interfacial PMA in Mo[CoFeB|MgO] structures increases and the VCMA is sustained with annealing temperatures up to 430°C. A VCMA coefficient of 40 fJ/V-m was demonstrated after annealing at 430°C, indicating a VCMA effect comparable to Ta-seeded systems, along with a marked improvement in its temperature stability. \textit{Ab initio} electronic structure calculations further corroborated the enhancement of experimental \( K_i \) values at high temperatures. No significant CoFeB dependence of the VCMA effect and the interfacial PMA was observed over the thickness range studied. The demonstration of thermally stable VCMA and PMA provides a pathway for the integration of Mo[CoFeB|MgO] into Magnetoelectric RAM devices compatible with advanced embedded CMOS technologies.

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