Giant variation of the perpendicular magnetic anisotropy at Fe/MgO interfaces by oxygen migration: a first-principles study

F. Ibrahim,1,2,3 A. Hallal,1,2,3 B. Dieny,1,2,3 and M. Chshiev1,2,3

1 Univ. Grenoble Alpes, INAC-SPINTEC, F-38000 Grenoble, France
2 CEA, INAC-SPINTEC, F-38000 Grenoble, France
3 CNRS, SPINTEC, F-38000 Grenoble, France

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We present a systematic theoretical study of the influence of oxygen migration on the interfacial perpendicular magnetic anisotropy (PMA) at Fe/MgO interface. First, the charge-mediated effect of electric field on the PMA is calculated for both over-oxidized and oxygen-migrated Fe/MgO interfaces. The amplitude of the PMA variation induced by the electrical field is sensitive to the oxidation conditions of the interface but is rather weak in all cases (tens of fJ/(V.m)). In contrast, the PMA variation induced by oxygen ion migration at the interface under electrical field can yield much larger effect. Considering the O-migrated Fe/MgO interface thoroughly, we discuss the energetics of the O path across the interface. Depending on the applied voltage amplitude of variations, two regimes can be observed associated with reversible or irreversible oxygen ions displacement yielding different voltage controlled PMA response. The PMA values, as well as its on-site and orbital resolved contributions, are found to be highly affected by the O migration. Interestingly, according to our estimate, the "O-migration mediated" electric field influence on PMA can reach thousands of fJ/(V.m) which explains the large values reported in experiments.

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Magnetization switching using spin-polarized currents via the spin transfer torque (STT) effect has achieved remarkable progress.13 However, the energy required to write in STT-magnetic random access memories (MRAM) is still rather large (of the order of 100 fJ per write event) compared to the complementary metal-oxide semiconductors. An alternative strategy for manipulating magnetization with low power consumption relies on applying electric fields (E-field) rather than currents. Several experimental reports have demonstrated the electric-field control of magnetic properties, among which those evidencing control of the perpendicular magnetic anisotropy (PMA) are of particular importance to realize fast and low-power-consumption magnetization switching.4–13 In particular, a strong impact of the electric field on the interfacial PMA in Fe(001)/MgO-based systems was reported.5–13 Meanwhile, theoretical studies have addressed the origin of this effect which was attributed to the spin-dependent screening of the electric field in ferromagnetic metal films,19 and to the change in the relative occupancy of the 3d-orbitals of Fe atoms associated to the electrons accumulation or depletion at the Fe/MgO interface.20–21 Furthermore, the effect was shown to be correlated with the existence of a spontaneous interfacial electric dipole.22 Typical calculated values for the charge-mediated PMA variation under electric field characterized by the parameter $\beta$ are of the order of tens of fJ/(V.m)22 which agrees with the experimental observations of references 5–13.

In this letter, we present a first-principles study of the tuning of the interfacial PMA by oxygen (O) migration across the Fe/MgO interface. Firstly, the charge-mediated effect of electric field on the PMA is calculated for both over-oxidized and oxygen-migrated Fe/MgO interfaces. We find that the underlying microscopic mechanisms are sensitive to the oxidation conditions at the interface. Yet, the strength of the effect is found to be of the same order of magnitude for both types of interfaces (a few tens of fJ/(V.m)). Secondly, we studied the variation of PMA associated with oxygen migration across the Fe/MgO interface. For that, the energetics of the O migration path across the interface was investigated and the impact of the O position on the PMA calculated. It is found that the PMA value, as well as its on-site and orbital resolved contributions, are highly affected by the O migration. Besides, depending on the amplitude of the applied voltage variation, two regimes were observed associated with reversible or irreversible oxygen ions displacement yielding different voltage controlled PMA response. In the irreversible case, the PMA variation driven by electrical field induced O migration can reach thousands of fJ/(V.m) consistent with the experimental observations.23

Our first-principles calculations are based on the projector-augmented wave (PAW) method as implemented in the VASP package using the generalized gradient approximation and including spin-orbit coupling. A kinetic energy cutoff of 500 eV has been used for the plane-wave basis set and a $25 \times 25 \times 1$ K-point mesh to sample the first Brillouin zone. The electric field, applied perpendicular to the supercell, is introduced as a dipole layer placed in the vacuum region of the supercell as proposed by the dipole layer method and varied between $-2 \text{ V/\mu m}$ and $2 \text{ V/\mu m}$. The supercell comprises 5 Fe monolayers (ML) sandwiched between 5ML of MgO followed by a vacuum layer. This structure pro-
FIG. 1. (Color online) Layer-resolved variation of MAE of both interfaces as a function of electric field in MgO, calculated for the first and second Fe MLs in pure (a), over-oxidized (b), and O-migrated (c) MgO/Fe/MgO sandwich. The upper panels show the supercell structure used in each case (Red=Fe, green=O, Light blue=Mg). The slope ($\beta$) of the MAE variation with electric field is calculated and displayed for each ML. Blue(red) indicates interface 1(2).

The interfacial oxidation conditions have a strong impact on the PMA at Fe/MgO interfaces and it was pointed out that in over-oxidized Fe/MgO interfaces the PMA may be altered by the electric field. However, a detailed description of the microscopic mechanisms of the electric field control of the PMA under different oxidation conditions is still lacking. In this context, we compare in Fig. 1 the variation of the layer-resolved contributions to magnetic anisotropy energy (MAE) per interface as a function of the electric field in MgO for pure, over-oxidized and O-migrated Fe/MgO interfaces, shown respectively in Fig. 1(a), (b) and (c). Strikingly, the sum of the contributions to the E-field induced MAE variation from the first and second Fe MLs is almost the same in the pure and over-oxidized interface (pure case: $\beta = 3 + 15 = 18$ fJ/(V.m) vs over-oxidized case: $\beta = 18.6 + 0.1 = 18.7$ fJ/(V.m)). However at the microscopic level, the situations are quite different. For pure interface, the second ML is mostly responsible for the E-field induced variation of MAE whereas for the over-oxidized interface the first ML clearly plays the dominant role (cf. Fig. 1(a) and (b)). Furthermore, for O-migrated interface, the E-field induced variation of MAE is strongly reduced ($\beta = 3 + 0.6 = 3.6$ fJ/(V.m))(Fig. 1(c)).

The aforementioned sensitivity of the layer-resolved E-field induced variation of MAE to the interfacial oxidation conditions can be understood in view of the orbital hybridization-resolved contributions to MAE. The variations in these quantities induced by an electric field of $-2$ V/nm in the vacuum region are shown in Fig. 2 for both the first (upper panel) and second (lower panel) ML of Fe at interface 1. Although the variations in the individual orbital contributions of 1st ML of Fe are large in the pure interface [Fig. 2(a)], they practically cancel out due to opposite sign once integrated. As a result, the overall contribution of the 1st ML becomes negligible compared to the 2nd ML one wherein these variations sum up since they all have the same positive sign. However, the situation changes when the interfacial oxidation conditions are modified. In both cases of over-oxidized and O-migrated, the orbital hybridization resolved contributions to the anisotropy become less sensitive to the
FIG. 2. (Color online) The changes in the magnetic anisotropy of the orbital hybridization, induced by applying an electric field of $-2$ V/nm in the vacuum region, calculated for first (upper panel) and second (lower panel) ML of Fe at interface 1 in (a) pure, (b) over-oxidized, and (c) O-migrated MgO/Fe/MgO supercells.

The charge-mediated impact of electric field on PMA at Fe/MgO interfaces cannot explain the large variation of MAE versus electric field reaching thousands of fJ/(V.m) as reported recently [13, 23]. In the following, we consider a different mechanism associated with E-field induced O-displacement around the Fe/MgO interface and its impact on the interfacial MAE. For that, a oxygen migration path is created by moving the O atom starting from the initial pure interface [Fig. 1(a)] towards the first Fe monolayer [Fig. 1(c)]. At each point along this path, the total energy per atom relative to the initial state is calculated. The result is plotted by line-squares in Fig. 3(a) as a function of the O atom displacement from the MgO plane. Interestingly, the total energy shows a local minimum at an oxygen displacement of about 1.84 Å separated from the initial position by an energy maximum for a displacement $z_c$. The corresponding energy barrier that should be overcome to pass from pure interface to the O-migrated one is about 0.35 eV/atom. This value is likely underestimated since we consider here the motion of an O atom in a quite narrow supercell. For larger supercell, a significant reduction of the energy barrier may be expected as reported recently [34]. Besides, we assumed that the O migration path follows a straight line between its initial and final position whereas the lowest energy path may be more complex yielding a lower energy barrier. Nevertheless, despite the likely overestimation of our calculated energy barrier height for O migration, the following discussion remains semi-quantitatively valid. Using our calculated value of the energy barrier for O migration accross the Fe/MgO, we can estimate the force acting on the oxygen ion (charge 2e) and the corresponding critical electric field $E_c$ needed to overcome the energy barrier. This value is $E_c = \frac{\Delta V}{\Delta z} = 1.9$ V/nm. in Fig. 3(a), the variation of $K_s$ versus O-displacement is also plotted. Two parts can be seen in this variation: a slight almost linear negative slope between the origin and O-displacement of 0.8 Å, and a steep decrease afterwards till the O-migrated interface state is reached. Actually, two regimes of oxygen displacement can be distinguished. 1) If the electrical field is lower than $E_c$, the oxygen ion is reversibly moving around its equilibrium
A second regime is then expected when the applied electrical field is large enough to pull the oxygen atom above the migration barrier so that it relaxes towards its new position within the interfacial Fe plane (position corresponding to the O-migrated interface). In this case, using the aforementioned \( E_c \) value and the variation in \( K_s \) between the cases of pure and O-migrated interfaces, we estimate \( \beta = -1630 \) \( \text{fJ/(V.m)} \) which is in good agreement with the experimental value in \cite{13} \( (\beta = -1150 \text{ fJ/(V.m)}) \) and of the same order of magnitude as in Ref. \cite{23}. In this case, because the oxygen displacement is irreversible and can be thermally activated, the associated time-scale of the anisotropy variation can be much longer as observed in the experiments Ref. \cite{23}

In Fig. 3(b) we plot the layer-resolved MAE contributions into \( K_s \) as a function of the O-displacement shown for the 1st and 2nd Fe ML. It can be seen that the slight negative slope region of the \( K_s \) variation (displacement=0.8A) originates from a partial balance between the decrease and the counter increase of the MAE respectively in 1st and 2nd Fe ML. On the contrary, the simultaneous decrease of the MAE of both layers observed for larger oxygen displacement results in the steep decreases of \( K_s \).

In order to elucidate the microscopic mechanisms of such behavior, we employed again the orbital hybridization-resolved analysis for pure and O-migrated interface shown in Fig. 3(c) and (d). It reveals the substantial change of the layer-resolved MAE upon O-migration at the Fe/MgO interface. For instance, the in-plane orbitals \( (d_{x^2-y^2}, d_{xy}) \) within the 1st Fe ML, shown by blue bars in Fig 3(c) and (d), are most influenced by the O-migration leading to a change of their sign as the migrated O atom approaches the Fe plane. Hence, the \( (d_{x^2-y^2}, d_{xy}) \) orbitals of the 1st ML of Fe carry the largest contribution to the anisotropy change. On the other hand, the MAE changes of the 2nd ML of Fe upon O-migration seem to originate from the out-of-plane orbitals. In particular, the major changes in the MAE con-
tributions occur in \((d_{x^2}, d_{y^2})\) and \((d_{xz}, d_{yz})\) orbitals represented respectively by red and yellow bars in Fig. 3(c) and (d). Those orbitals favor in-plane (out-of-plane) magnetic anisotropy in the O-migrated (pure) interface.

In summary, we have presented a detailed study of the mechanisms underlying the electric-field impact on the PMA of Fe/MgO interfaces depending on interfacial oxidation conditions. The charge-mediated effect is found to be substantially weak in all considered cases. We have demonstrated that the O-migration across the Fe/MgO interface can provide a much more effective way to tune the PMA. Inspired by recent experiments, we propose the interface can provide a much more effective way to tune the PMA of Fe/MgO interfaces depending on interfacial oxidation.

In summary, we have presented a detailed study of the electric-field impact on the MAE of Fe/MgO interfaces. Our findings support this argument from the energetics point of view. Two regimes are expected: a reversible one under moderate electrical field and an irreversible one under larger electric field. Interestingly, the estimated rate of the MAE variation associated with interfacial O migration exceeds thousand of fJ/(V.m) in the regime of irreversible O-migration in agreement with experimental results. Following those results, one can distinguish from the order of magnitude of \(\beta\) which mechanism is driving the electric field effect on MAE: An effect of several tens of fJ/(V.m) is likely associated to charge-mediated effect combined with slightly reversible oxygen displacement whereas an effect of the order of thousands of fJ/(V.m) is more likely associated with irreversible oxygen ionic migration effect.

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