Epitaxial strain and interfacial electronic topological transition in O-rich MgO/FeO/Fe(001) interfaces

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The effects of epitaxial strain on the electronic properties of MgO/FeO/Fe(001) interfaces were studied using *ab initio* density-functional-theory calculations. It was shown that epitaxial strain induces significant changes in the interfacial band structures of FeO: In the case of tensile strain, band narrowing of the interfacial spin-majority (MJ) states was observed, while in the case of compressive strain, band broadening was observed. Under a 5.8% tensile strain corresponding to the lattice constant of bulk MgO, the top of the interfacial spin-MJ band moved down in energy to the extent that the interfacial spin-MJ density of states at the Fermi energy disappeared. This indicates that the interfacial electronic transition occurred from ferromagnetic to half metallic states. Herein we refer to this transition as the interfacial electronic topological transition.

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I. INTRODUCTION

Anomalies in many of solid-state properties, such as anomalies in transport, thermodynamic, and vibrational properties, can occur as a result of changes in the topology of Fermi surfaces.[1–5] For example, under ambient conditions, Zn and Cd have unusually large c/a axial ratios for the hcp structure ($c/a = 1.856$ for Zn and 1.886 for Cd). Because of these large c/a axial ratios, their Fermi surfaces exhibit elements that are different from those exhibited by typical divalent hcp metals, like Mg, whose c/a axial ratio is similar to the ideal ratio ($\sqrt{8/3} \approx 1.633$). The c/a axial ratios of Zn and Cd have been reported to decrease with pressure.[3,4] As the c/a ratio decreases, the Fermi surfaces also drastically change.[5] Such topological changes have been called electronic topological transition (ETT). Despite extensive works to elucidate ETT, the underlying physical mechanism causing the unusually large c/a anomaly and the exact cause of ETT are still debated.

In this work, we present the results for the theoretical calculations of the ETT driven by epitaxial strain for interfaces like MgO/Fe magnetic junctions that have attracted considerable attention because of their large tunneling magnetoresistance (TMR) ratios.[6–11] Experimental results have shown that the MgO films grow epitaxially on Fe(001) surfaces due to favorable physical properties such as a small lattice mismatch and suitable surface-free energies of MgO and Fe.[12,13] Further, the results of experimental and theoretical studies have revealed that two MgO/Fe(001) and MgO/FeO/Fe(001) interfaces coexist.[14–18] In addition, it has also been observed that, in the case of heteroepitaxy, the material to be deposited on different materials with a lattice mismatch is inevitably under the influence of epitaxial strain accumulated during the film growth.[15] Indeed, epitaxial growth of MgO on Fe(001) is accompanied by a strain in the epitaxial MgO layer that results from a difference in lattice constants between MgO and Fe. If the thickness of the MgO film exceeds its critical value, the accumulated strain is relieved by the formation of misfit dislocations. Experimental measurements[13] showed that the MgO films grew pseudomorphically in a layer-by-layer mode up to 6 monolayers (MLs). For the MgO films thicker than 6 MLs, a partial lattice relaxation set in and misfit dislocations were formed, resulting in an increase in the lateral lattice spacing of MgO with increased surface roughness. The FeO interface layer formed on this substrate would then have the strained lateral lattice constant. For the possibility of the formation of FeO layers on top of MgO, it can be achieved by controlling a growth condition, such as O partial pressure in the growth chamber.[17] Tusche and co-workers[19,20] observed coherent growth of the top Fe electrode for Fe deposition in ambient O atmosphere leading to a coherent symmetric magnetic tunnel junction structure with FeO layers at both Fe/MgO interfaces of Fe/MgO/Fe. These experiments provide evidence that a strained FeO layer exists in the top Fe electrode interface of Fe/MgO/Fe.

In this study, as a suitable candidate for the interfacial electronic topological transition (IETT), we propose the strained O-rich MgO/FeO/Fe(001) interface with the interfacial FeO layer between the Fe(001) and the MgO film,[15,19,20] where the top of the interfacial spin-majority (spin-MJ) band was found to be located near the Fermi energy. The electronic structures of the strained MgO/FeO/Fe(001) interfaces were determined by performing density-functional theory (DFT) calculations.[21,22] The calculations showed significant changes, especially in interfacial spin-MJ electronic structures with in-plane strain: in the case of tensile strain, narrowing of the interfacial spin-MJ bands was observed, while in the case of compressive strain, broadening of the bands was observed. As a result, under a 5.8% tensile strain corresponding to the lattice constant of bulk MgO, the interfacial spin-MJ density of states (DOS) at the Fermi energy disappeared, which is in contrast to changes in the interfacial spin-minority (spin-MN) electronic structures with epitaxial strain found for the abrupt MgO/Fe(001) interface.[23] Further band-structure calculations and analysis were also performed to see changes in interfacial electronic band structures with in-plane strain.

II. CALCULATION METHOD

The spin-dependent DFT calculations were performed using the Vienna *Ab initio* Simulation Package (VASP) code.[24,25] The exchange-correlation functional was approximated with the Perdew-Burke-Ernzerhof (PBE) expression.[26] For electron-ion interactions, the projector augmented-wave (PAW) method[27] was used. The electronic wave functions were

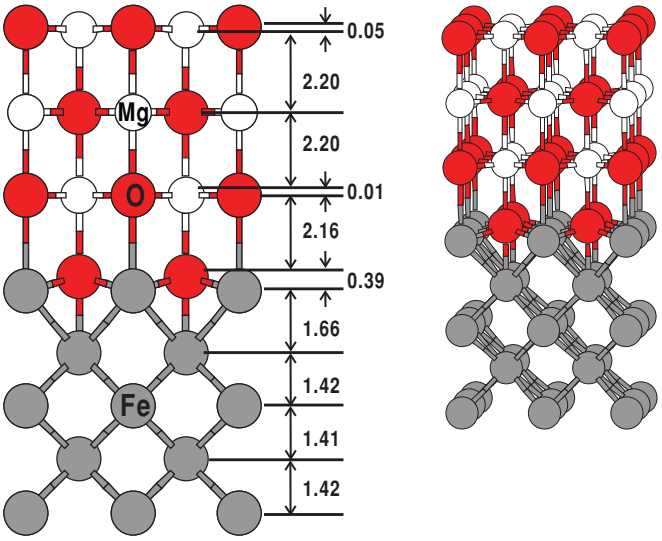

FIG. 1. (Color online) Side and perspective views of the geometry-optimized structure of the unstrained MgO(3 ML)/FeO/Fe(001). The numbers in units of Å indicate interlayer distances.

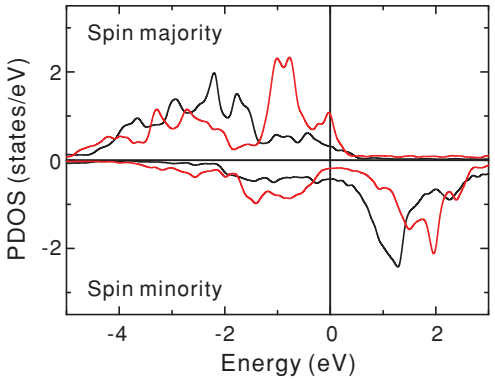

FIG. 2. (Color online) Fe-site-projected densities of states (PDOS) for the unstrained MgO/FeO/Fe(001) interface. The black and red (gray) lines represent the PDOS for the Fe atoms in the interfacial and the innermost atomic layers, respectively. The Fermi energy was taken as energy zero.

expanded in terms of the plane-wave basis set with a kinetic energy cutoff of 380 eV. This treatment yielded theoretical lattice constants of 2.832 and 4.238 Å for Fe and MgO in bulk, respectively, which are in good agreement with experimental data.[28]

To simulate the pre-oxidized MgO/FeO/Fe(001) interface, we used a repeating slab structure consisting of nine Fe layers with a 11.0-Å vacuum region. The MgO films were deposited symmetrically on both sides of the slab and MgO[110] was set to parallel to Fe[100], as shown in Fig. 1. Using the calculated theoretical lattice constants of bcc Fe and MgO in bulk, a theoretical lattice mismatch of 5.8% of MgO with respect to Fe was obtained, which slightly differs from the experimental lattice mismatch of 3.9%.[28] The small difference is attributed to the smaller theoretical lattice constant of Fe by 1.2% than the experimental value. In contrast to the abrupt MgO/Fe(001) interface, some excess oxygen atoms were incorporated into the interface between MgO and Fe in this case; thus the FeO interface layer was formed. For the calculations, we used the 1×1 surface unit cells. The **k**-space integration was performed with finite sampling of special **k** points on an 11×11 mesh in the surface Brillouin zone (SBZ) of the 1×1 unit cell, which were generated according to the Monkhorst-Pack scheme.[29] All the atoms in the slab were relaxed, except for the central three Fe-layer atoms. The geometry optimization was performed until the remaining forces became smaller than 0.02 eV/Å. Additional results on the adequacy of this computational approach can be found elsewhere.[30,31]

III. RESULTS AND DISCUSSION

A. Unstrained MgO/FeO/Fe(001) interface

To understand the electronic structure of the unstrained MgO/FeO/Fe(001) interface, we first investigated the atomic structure of the MgO(3 ML)/FeO/Fe(001) interface. We used the lattice constant of Fe in bulk ($a_o = 2.832$ Å) as the in-plane lattice constant a_s of the unstrained MgO/FeO/Fe(001). The calculated structural parameters of the geometry-optimized unstrained MgO(3 ML)/FeO/Fe(001) interface are shown in Fig. 1. In the optimized geometry, the interfacial FeO layer experienced a pronounced rumpling of 0.39 Å. This rumpling of the FeO layer is very similar to that of the previous calculation for MgO(1 ML)/FeO/Fe(001).[17] The interlayer distance between the Fe atom of the FeO layer and the underlying Fe substrate atom was found to be 1.66 Å, which is an expansion by 17%, compared to the bulk interlayer distance of Fe(001). The calculated structural parameters were also in good agreement with the corresponding values obtained by a surface x-ray-diffraction experiment.[15]

Figure 2 presents the calculated spin-majority (MJ) and spin-minority (MN) densities of states for the unstrained MgO/FeO/Fe(001) interface. The local properties of the densities of states were obtained by projecting the wave functions onto spherical harmonics centered on the atomic sites. In the projected density of states (PDOS) calculations, a denser 23×23 **k**-point mesh in the SBZ and the Fermi-smearing method with a smearing width of 0.02 eV were used. The spin-MJ PDOS at the Fermi energy for the Fe atom of the interfacial FeO layer was smaller than that for the inner Fe atoms situated in bulk positions, whereas for the MN spin, the reverse pattern was obtained. Here it was also noted that the top of the interfacial spin-MJ band was located slightly above the Fermi energy.

B. Strained MgO/FeO/Fe(001) interfaces

For the investigation of the effects of epitaxial strain on the interfacial electronic properties of MgO/FeO/Fe(001), we next made atomic models of the tensile (compressive) strained MgO/FeO/Fe(001) interfaces using an increased (reduced) theoretical in-plane lattice constant a_s of a calculation unit cell with respect to the theoretical equilibrium in-plane lattice constant of Fe(001). For each in-plane lattice constant, the bulklike interlayer distance in the central three Fe layers of the slab was determined from calculations of laterally strained bulk Fe. Using these atomic models, we

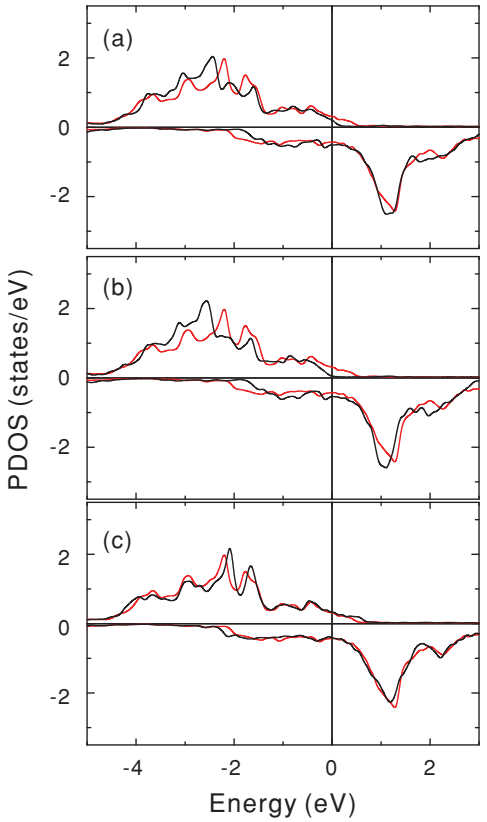

FIG. 3. (Color online) Interfacial Fe PDOS for the MgO/FeO/Fe(001) interfaces with (a) 4.0%, (b) 5.8%, and (c) −2.0% in-plane lattice strain. The red (gray) lines represent the PDOS for the interfacial Fe atom of unstrained MgO/FeO/Fe(001). The Fermi energy was taken as energy zero.

performed the electronic structure calculations for the strained MgO/FeO/Fe(001) interfaces.

Figure 3 shows the results for the local electronic properties of the interfacial Fe atom of the FeO layer in the strained MgO/FeO/Fe(001) interfaces with in-plane lattice constants corresponding to 4.0% and 5.8% expansion, and 2.0% compression, respectively. The PDOS calculations showed significant changes in both interfacial spin-MJ and spin-MN Fe states with lattice strain: in the case of tensile strain with lattice expansion, band narrowing occurred, while in the case of compressive strain with lattice compression, band broadening occurred. Interestingly, in the case of 4.0% strained MgO/FeO/Fe(001), the spin-MJ PDOS was more narrow and the top of the interfacial spin-MJ band was seen to move down in energy in comparison to that of unstrained MgO/FeO/Fe(001). When the lateral tensile strain was increased to 5.8% corresponding to the theoretical lattice constant of bulk MgO, the move became larger. More interestingly, the interfacial spin-MJ PDOS at the Fermi energy was found to disappear, which indicated the electronic transition from ferromagnetic to half metallic states [see Fig. 3(b)]. In addition, in the case of compressive strain, the opposite effect was observed, i.e., the top of the interfacial spin-MJ band moved up in energy [see Fig. 3(c)]. These changes in the interfacial spin-MJ PDOS of MgO/FeO/Fe(001) with epitaxial strain are in sharp contrast to the previous results

TABLE I. The root-mean-square (rms) bandwidth $W_{\rm rms}$ and the position of the band center ε_c relative to the Fermi energy for the interfacial spin-MJ band with in-plane lattice strain $[(a_s - a_o)/a_o]$.

Lattice strain (%)	$W_{\rm rms}$ (eV)	ε_c (eV)
−2.0	1.23	−2.20
0.0	1.19	−2.25
4.0	1.11	−2.37
5.8	1.08	−2.44

for strained MgO/Fe(001), which showed changes in the interfacial spin-MN PDOS peak states.[23]

Such strain-dependent changes could also be quantified by calculating the root-mean-square (rms) bandwidth $W_{\rm rms}$ and band center ε_c of the interfacial spin-MJ bands. The results are summarized in Table I. The narrowing of the interfacial spin-MJ band with lattice expansion was seen to be characterized by a decrease in both the rms bandwidth and the band center, whereas the broadening of the interfacial band with lattice compression was associated with an increase in both the the rms bandwidth and the band center. This feature can be attributed to the fact that band narrowing and broadening occurred with the bottom of the band fixed, as shown in Fig. 3.

To obtain further information on the interfacial electronic transition from ferromagnetic to half metallic states with lattice strain, we also performed electronic structure calculations for the geometry-optimized unstrained and 5.8% strained MgO/FeO/Fe(001) interface structures. The MgO/FeO/Fe(001) films that were used in this study were

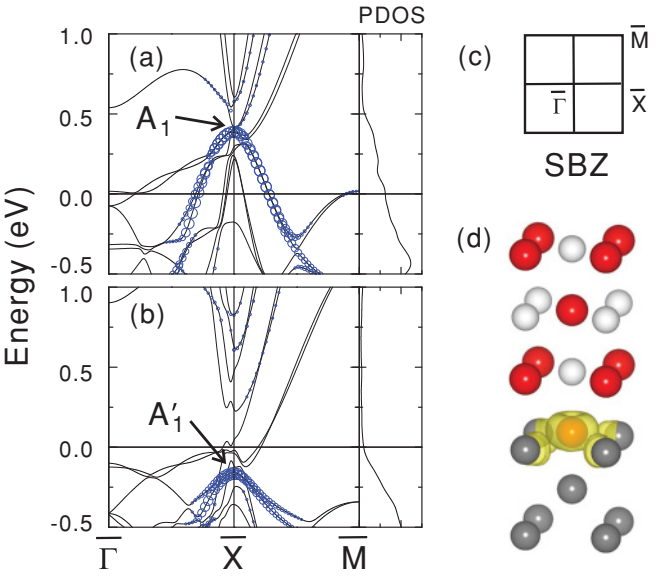

FIG. 4. (Color online) Calculated spin-MJ band structures and PDOS of the (a) unstrained and the (b) 5.8% strained MgO/FeO/Fe(001) interfaces along the $\overline{\Gamma} - \overline{X} - \overline{M}$ line of the (c) 1×1 SBZ. The open-circle lines represent bands of interfacial states. The size of the circles indicates the degree of localization in the Fe atom of the interfacial FeO layer. (d) Isosurface plot of the empty state A_1 at the $\overline{X}$ point. The isosurface level was 0.002 e/bohr^3. The Fermi energy was taken as energy zero.

symmetric under reflection in their central layer. Therefore the electronic states of the MgO/FeO/Fe(001) films had even or odd parity under this reflection. In Fig. 4, we showed both even and odd parity states for the explanation of the strain-dependent variation in the interfacial spin-MJ PDOS. Figure 4(a) shows the calculated spin-MJ band structure for the unstrained MgO/FeO/Fe(001)-1 × 1 interface. We found that the interface-related electronic states were near the Fermi energy around the $\overline{X}$ point in the 1 × 1 SBZ.[32] For instance, the state A_1 was located 0.39 eV above the Fermi energy. State A_1 was apparently represented by the charge distribution localized mostly around the interfacial FeO layer [see Fig. 4(d)]. It was also found to exhibit nodal planes between the Fe and O atoms of the FeO layer. This indicates that state A_1 consists of antibonding Fe-O hybridization. Such laterally localized antibonding states can be expected to be easily influenced by the lateral strain. Indeed, our calculated band structure of the 5.8% strained MgO/FeO/Fe(001) interface showed a significant change [see Fig. 4(b)]. State A_1' corresponding to state A_1 in the unstrained MgO/FeO/Fe(001) was found to be located lower in energy than the Fermi energy. This provides a good explanation of the variation of the interfacial spin-MJ PDOS observed for the strained MgO/FeO/Fe(001) interfaces. Our results for the strained MgO/FeO/Fe(001) interfaces clearly suggest that epitaxial strain encountered during heteroepitaxial growth of films can result in interfacial electronic topological transition from ferromagnetic to half metallic states.

IV. SUMMARY

In summary, changes in the interfacial electronic properties of MgO/FeO/Fe(001) interfaces with epitaxial strain were investigated using *ab initio* electronic structure calculations based on DFT. The calculations showed that the epitaxial strain significantly affected the interfacial spin-MJ bands of MgO/FeO/Fe(001) resulting in narrowing of the bands in the case of tensile strain and broadening of the bands in the case of compressive strain. As a result, at a 5.8% tensile strain corresponding to the lattice constant of bulk MgO, the interfacial PDOS near the Fermi energy shifted downward in energy with respect to that of the unstrained MgO/FeO/Fe(001). It was observed that the interfacial PDOS at the Fermi energy disappeared; this disappearance resulted in the half metallic interfacial states. These results show that epitaxial strain accumulated during the heteroepitaxial growth can give rise to electronic topological transitions at the interface, similar to the transition from ferromagnetic to half metallic states. We hope that the results presented here will motivate further experimental investigation of the electronic topological transition at the MgO/FeO/Fe(001) interface.

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[32] Due to the finite size of the slab, the interaction between the two equivalent interfaces across the central Fe layer may affect the interfacial electronic structures. We have very carefully checked the size effect by increasing the thickness of the Fe slab from 9 to 11 layers. The test results showed that the size effect on the interfacial electronic structures is negligibly small when the aforementioned calculation slab was used.