Interface Characterization of Epitaxial Fe/MgO/Fe Magnetic Tunnel Junctions

S. G. Wang¹,²,*, R. C. C. Ward², T. Hesjedal², X.-G. Zhang³, C. Wang⁴, A. Kohn⁵, Q. L. Ma¹, Jia Zhang¹, H. F. Liu¹, and X. F. Han¹

¹State Key Laboratory of Magnetism, Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
²Clarendon Laboratory, Department of Physics, University of Oxford, Oxford OX1 3PU, UK
³Center for Nanophase Materials Sciences and Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6493, USA
⁴Department of Materials, University of Oxford, Oxford OX1 3PH, UK
⁵Department of Materials Engineering, Ilse Katz Institute for Nanoscale Science and Technology, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel

Following predictions by first-principles theory of a huge tunnel magnetoresistance (TMR) effect in epitaxial Fe/MgO/Fe magnetic tunnel junctions (MTJs), measured magnetoresistance (MR) ratios of about 200% at room temperature (RT) have been reported in MgO-based epitaxial MTJs. Recently, a MR ratio of about 600% has been reported at RT in MgO-based MTJs prepared by magnetron sputtering, using amorphous CoFeB as the ferromagnetic electrode. These MTJs show great potential for application in spintronic devices. Fully epitaxial MTJs are excellent model systems that enhance our understanding of the spin-dependent tunneling process as the interface is well defined and can be fully characterized. Both theoretical calculations and experimental results clearly indicate that the interfacial structure plays a crucial role in the coherent tunneling across a single crystal MgO barrier, especially in epitaxial MgO-based MTJs grown by molecular beam epitaxy (MBE). Surface X-ray diffraction, Auger electron spectroscopy, X-ray absorption spectra, and X-ray magnetic circular dichroism techniques have been reported previously for interface characterization. However, no consistent viewpoint has been reached on the interfacial structures (such as FeO layer formation at the bottom Fe/MgO interface), and it is still an open issue. In this article, our recent studies on the interface characterization of MgO-based epitaxial MTJs by X-ray photoelectron spectroscopy, high resolution transmission electron microscopy, and spin-dependent tunneling spectroscopy, will be presented.

Keywords: Magnetic Tunnel Junctions, Magnesium Oxide, Interface Characterization, First-Principles Theory, Spin Dependent Tunneling.

CONTENTS

1. Introduction ........................................ 1006
   1.1. MgO-Based Magnetic Tunnel Junctions ........... 1006
   1.2. Coherent Tunneling Across MgO Barrier .......... 1009
   1.3. Interfacial Structures in MgO-Based MTJs ....... 1012
2. Interface Characterization ............................. 1012
   2.1. Theoretical Models and Experimental Results ...... 1012
   2.2. High Resolution Transmission Electron Microscopy .... 1014
   2.3. X-ray Photoelectron Spectroscopy .................. 1016
   2.4. Spin Dependent Tunneling Spectroscopy ............ 1018
3. Conclusions ........................................ 1022
   Acknowledgments ................................... 1022
   References and Notes ................................ 1022

1. INTRODUCTION

1.1. MgO-Based Magnetic Tunnel Junctions

The magnetic tunnel junction (MTJ) is a key element of next generation spintronic devices¹,² such as read heads in hard disk drives, magnetic random access memory (MRAM), and magnetic sensors. A MTJ consisting of two ferromagnetic (FM) electrodes separated by a thin insulating barrier exhibits a tunnel magnetoresistance (TMR) effect, originating from different electrical resistances in the antiparallel (AP) and parallel (P) configurations of the two FM layers according to the direction of an external magnetic field. The TMR effect was first studied by Julliere³ in Fe/Ge/Co system which showed...
S. G. Wang got his bachelor degree in physics from Anhui University, and received his Ph.D. degree from the Institute of Solid State Physics, Chinese Academy of Sciences in 2001. He worked as a research fellow in the National University of Singapore from August 2001 to July 2003. Then he moved to the Max-Planck-Institute of Microstructure Physics, Halle (Saale), as a post-doctor. From February 2005 to December 2007, he worked in the Clarendon Laboratory, Department of Physics at the University of Oxford. He joined the State Key Laboratory of Magnetism, Institute of Physics, Chinese Academy of Sciences, at the end of 2007, and now is an associate professor of condensed matter physics. His research interests include the physics, materials, and device of spintronics.

R. C. C. Ward is a Senior Research Fellow in the Clarendon Laboratory, Department of Physics of the University of Oxford. He received his D.Phil. from Oxford in 1981. His research interests include the growth and characterisation of epitaxial metal films and superlattices for magnetic research, fundamental processes of growth with atomic layer control by molecular beam epitaxy (MBE) and UHV sputtering, and the growth of bulk single crystals from melts and solutions for optical and magnetic research. Most recently his work has focused on the fields of epitaxial spintronic devices, superlattices containing rare earth elements, and epitaxial films of uranium metal and compounds.

T. Hesjedal is a Lecturer in Materials Design for Condensed Matter Physics in the Clarendon Laboratory at the University of Oxford, and the Rutherford-Appleton Laboratory. He received his Ph.D. from the Humboldt University in Berlin (Germany) in 1997. Dr. Hesjedal came to Oxford from the University of Waterloo and Stanford University in late 2010, where he was Associate Professor since 2005. He focuses on the synthesis and exploration of novel quantum materials and materials for spintronics applications.

X.-G. Zhang received his bachelor degree in physics from Peking University in 1983, and Ph.D. in physics from Northwestern University, USA in 1989. He worked as a postdoctoral fellow at Lawrence Berkeley Laboratory from 1990 to 1991, a postdoctoral scholar at the University of Kentucky from 1991 to 1995. Since 1995, he is a staff scientist at Oak Ridge National Laboratory. Currently he holds the position of Senior Staff Scientist at the Center for Nanophase Materials Sciences, Oak Ridge National Laboratory. His research interests include physics and materials science on the nanoscale, in particular electron transport in spintronics and molecular electronics.

C. Wang graduated from the Department of Mechanical Engineering, Tsinghua University in 2000 and 2003 as bachelor and master. After one year as process engineer in Semiconductor Manufacturing International Corporation, Shanghai, China, he pursued his Ph.D. degree in Department of Materials, University of Oxford, U.K. In 2008, he started to work as a hardware engineer in Applied Materials Inc., California, USA. Recently, his role switches to be responsible for technology collaborations with China universities and research institutes in equipment applications for renewable energy.
A. Kohn is a senior lecturer at the Department of Materials Engineering, Ben-Gurion University of the Negev and a member of the Ilse Katz Institute for Nanoscale Science and Technology. He obtained his Ph.D. in Materials Engineering from the Technion - Israel Institute of Technology. Between 2004 and 2010, Dr. Kohn was a post-doctoral research assistant and then a Royal Academy of Engineering Research Fellow at the Department of Materials, University of Oxford, where he was a member of the Electron Microscopy and Microanalysis Group. His research focuses on understanding how the structure of magnetic and electronic materials determines the magneto-transport properties of information storage devices. To achieve the aims of his research, Dr. Kohn and his group apply analytical methodologies in transmission electron microscopy, as well as Lorentz TEM for magnetic imaging. In recent years, his interests are MgO-based magnetic tunnel junctions, Exchange-bias, amorphous ferromagnetic thin films, and the development of phase-reconstruction methodologies in Lorentz TEM.

Q. L. Ma graduated from School of Physics, Lanzhou University in 2006, and received his Ph.D. degree from the Institute of Physics, Chinese Academy of Sciences in 2011. Currently, he is working in the WPI-AIMR at Tohoku University as a post-doctor. His research fields include spintronic materials, physics and devices.

Jia Zhang graduated from Lanzhou University in 2007 and obtained his B.S. degree in theoretical physics. From 2007, he is a Ph.D. student in the Institute of Physics, Chinese Academy of Sciences. His current research focuses on the spin dependent transport phenomenon in magnetic tunneling junctions (MTJs) by using the first-principles calculations. His work tries to search the high spin-polarized magnetic electrode, tunneling barrier materials for achieving high tunneling magnetic resistance in MTJs and to design new MTJ structure, for example, MgO-MTJs with metallic insertion layers, to tailor its transport properties.

H. F. Liu graduated from School of Physics, Shandong University and obtained a bachelor’s degree in 2008. He is the Ph.D. student in the State Key Laboratory of Magnetism, Institute of Physics, Chinese Academy of Sciences. His main research fields focus on the transport properties of MgO-based magnetic tunnel junctions and spin transfer torque in MgO-based MTJs.

X. F. Han got his bachelor degree from Lanzhou University, and received his Ph.D. degree from Jilin University in 1993. From 1998 to 2002, he worked at the Center of Brazilian Physical Research (Brazil), Tohoku University (Japan), University of New Orleans (USA), and Trinity College Dublin (Ireland), respectively. He obtained financial support of the Hundred Outstanding Young Researchers Projects from Chinese Academy of Science (CAS) in 2000, the Outstanding Young Researcher Foundation from Natural Science Foundation of China (NSFC) in 2003, and the Outstanding Innovation Team Foundation together with his partners from NSFC both in 2007 and 2010. He is the head of Group M02 at the Institute of Physics, Chinese Academy of Sciences. His research interest includes the physics, materials, devices of spintronics (more details are available from group homepage: http://www.m02group.com).
a magnetoresistance (MR) ratio of 14% at low temperature. However, more intensive attention was attracted to MTJs after the discovery of junctions with amorphous aluminium oxide (AlO) as the barrier, which showed a high MR ratio of 18% at room temperature (RT).3,5 Although the MR ratio in AlO-based MTJs has since been increased to 81%, it is still lower than that needed in many spintronic devices.6

Following predictions7,8 by first-principles theory of a giant TMR effect in single-crystal Fe/MgO/Fe MTJs in 2001, two MgO-based systems with a TMR ratio of about 200% at RT were reported in 2004: CoFe/MgO/CoFe MTJs prepared by magnetron sputtering and epitaxial Fe/MgO/Fe MTJs grown by molecular beam epitaxy (MBE), respectively.9,10 The discovery of single crystal MgO-based junctions with giant MR ratio has galvanized the worldwide interest of researchers in MgO-based MTJs and MgO-based spin transfer torque devices.11 The MgO barrier has a single-crystal structure, instead of the amorphous structure of AlO barrier. A single-crystal MgO barrier exhibits a spin filtering effect due to the conservation of wave-function symmetry. The conductance in the P configuration, dominated by the majority $\Delta_1$ states, is high because $\Delta_1$ states decay relatively slowly through the barrier and can transfer into similar symmetry states in the second FM electrode. By contrast, the AP conductance is low due to the absence of receptor states in the second electrode (symmetry blocking), leading to a giant MR ratio in MgO-based MTJs.

Currently, the study of MgO-based MTJs can be generally classified into three main groups according to the materials technology involved. The first group is based on CoFeB electrodes and grown by magnetron sputtering. This is the system used for commercial production of MTJs. Post-growth thermal annealing is the critical part of the process to obtain high MR ratios. The as-grown CoFeB layers are amorphous, but remarkably the MgO barrier is crystalline with strong (001) structure.12 During the annealing process the CoFeB layers become B-depleted and crystallize by solid state epitaxy on each side of the MgO barrier. The B atoms rejected from crystallized CoFeB layers are found to be dissolved in upper amorphous Ta layers and segregated in the bottom crystalline Ta layer.13 This results in a pseudo-epitaxial CoFe/MgO/CoFe junction in which coherent tunneling leads to very high TMR ratios. Up to now, the reported record of MR ratios of 604% at RT and 1144% at 5 K were observed in sputtered CoFeB/MgO/CoFe structures.14 The second group involves using the high-polarization Heusler-alloys as electrodes grown by sputtering with MgO as the barrier, or alternatively, one Heusler electrode is used with CoFe as the other electrode.15–17 The TMR ratio reaches 330% at RT for electrodes of a Heusler-alloy film and CoFe film separated by MgO barrier.17 Again the origin of highest TMR ratio in Heusler samples is thought to be coherent tunneling when a single-crystal structure is produced.18 The third group is the fully epitaxial junctions usually grown by MBE method, such as Fe/MgO/Fe and Co/MgO/Fe, which were the first MgO-based structures to achieve huge TMR ratios.10,19–22 Although MBE-grown structures will probably not be used in devices, they remain an excellent model system to compare theoretical calculations with experimental results and to enhance our understanding of the coherent tunneling across MgO barriers. The results of such investigations can be applied generally to the other two groups where coherent tunneling is of great importance.

It is important to note the research into new and alternative barriers to MgO. For example, a MTJ with a single-crystal NaCl barrier, which has an identical crystal structure and also a markedly similar band structure to that of MgO, has been reported.23 Another example are MTJs based on single crystal MgAl2O4 barrier with the spinel structure, where Heusler alloy electrodes were used.18,24 A Mg-B-O barrier was also investigated, where a CoFeB layer was used for one of the FM electrodes.25 The current TMR ratio in MTJs with these novel barriers is still much lower than that in MgO-based MTJs, but may be developed further in the future.

In this topical article, an overview of coherent tunneling in epitaxial MgO-based is presented in the second part of the Introduction. The third part of the Introduction emphasizes the importance of the interface structure between the electrode and barrier to the efficiency of the tunneling process in MgO-based MTJs. The characterization of this interface forms most of this paper, including theoretical models and experimental results on MBE-grown samples using transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and spin dependent tunneling spectroscopy technique. Finally, a summary of the present status of interfacial characterization in epitaxial MgO-based MTJs is presented.

### 1.2. Coherent Tunneling Across MgO Barrier

A phenomenological model proposed by Julliere (called Julliere’s model) has been widely applied to explain the experimental data obtained both in Fe/Ge/Co junctions and in AlO-based junctions, where the spin polarization of the FM electrodes can be achieved by fitting TMR ratio with the model. The model is based on two assumptions: one is that the spin of electrons is conserved during tunneling process, and the other is that tunneling of up-spin and down-spin electrons is independent (two-current model). The key parameter is spin polarization, which is assumed as the total electronic density of states (DOS) of the FM layers at the Fermi energy. The value of spin polarization can also be obtained by analysis of superconducting tunneling spectroscopy where the junction consists of one FM electrode and one superconducting electrode separated by a thin barrier. However, the values obtained from fitting
TMR ratio with Julliere’s model and from superconducting tunneling spectroscopy measurement show a large variation, strongly depending on the FM electrodes. The large variation and the sample dependence of spin polarization indicates a shortcoming for Julliere’s model. The detailed discussion about Julliere’s model and its great success in AlO-based junctions could be found from other topical review papers.26–28

In order to get a better explanation for the experimental data, the Julliere’s model was further developed by Slonczewski who introduced an effective spin polarization. However, the Julliere’s model and Sloncwewski’s model can not be used to explain the experimental data in MgO-based junctions, where the barrier is single crystal structure. The validity of the Julliere’s model of spin dependent tunneling was carefully checked before.30 For example, a flat temperature dependence of the resistance in the P configuration ($R_p$) with thick MgO barrier, and even an obvious increase of $R_p$ with increasing temperature in MTJs with thinner MgO layer was observed (shown in Fig. 1).31 Another example, a flat bias (low voltage) dependence of dynamic conductance in the P configuration of epitaxial Fe/MgO/Fe junctions, shown in Figure 2, can not be explained by Julliere’s model. One of characteristic features of high quality MgO barrier is that $R_p$ is almost independent of temperature, such as 3 nm thick MgO barrier shown in Figure 1(a). This temperature dependence has also been observed in fully epitaxial Fe/MgAlOx/Fe MTJs recently,24 where the majority $\Delta_x$ states of Fe electrodes play a critical role for tunneling.

First-principles calculations done in 2001 for magnetic tunnel junctions with single crystal MgO layer as barrier predicted a huge MR ratio of over 1000%. In 2004, two typical systems with the MR ratio of about 200% at RT were reported in sputtered CoFe/MgO/CoFe MTJs and in epitaxial Fe/MgO/Fe MTJs, respectively. Before that, a lot of experimental work was carried out about growth of MgO in Fe/MgO/Fe junctions. Reprinted with permission from [21], S. G. Wang et al., Phys. Rev. B 78, 180411R (2008). © 2008, American Physical Society.

Fig. 2. Dynamic conductance (dI/dV) as a function of bias voltage in the P and AP configurations at 300 K and 10 K in epitaxial Fe/MgO/Fe junctions. Reprinted with permission from [21], S. G. Wang et al., Phys. Rev. B 78, 180411R (2008). © 2008, American Physical Society.

The large MR ratio in MgO based MTJs arises from a symmetry filtering effect in the MgO barrier layer. For epitaxial MTJs this can be explained in terms of the different decay rates of the wave functions with different lateral symmetry.27,38 Within a simple barrier represented by a constant potential $V_b$, the decay wave vector is given by

$$\kappa^2 = \frac{2m}{\hbar^2}(V_b - E) - \frac{\langle \phi | \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) | \phi \rangle}{\langle \phi | \phi \rangle}$$

where $E$ is the electron energy, $\phi$ is its wave function, and $xy$ plane is parallel to the film. The last term is positive and increases with the number of nodes of $\phi(x, y)$. Thus, for epitaxial films because the wave function symmetry parallel to the film is preserved across the interfaces, the decay rate $\kappa$ is positively correlated to the lateral symmetry of the wave function in the electrodes. In real materials the decay rate is determined by the complex band structure of the barrier material. Figure 3 shows the complex bands of bulk MgO at $k_x = k_y = 0$ near the Fermi energy ($E = 0$ eV in the figure) within the band gap of MgO. There are four complex bands shown in the figure, labeled as $\Delta_1$, $\Delta_2$, $\Delta_3$, and $\Delta_4$. These are the states with the square symmetry in
Fig. 3. Complex band structure of MgO near the Fermi energy ($E = 0$ eV).

the $xy$ plane. The $\Delta_1$ state has the smallest $\text{Im}k_z$ thus it decays the slowest within the barrier layer, leading to the largest tunneling probability.

Figure 4 shows the tunneling density of states (TDOS) for $k_z = 0$ for Fe(100)/[8MgO]/Fe(100). This is defined as the electron density due to a single incident Bloch wave from the left electrode. The TDOS for the majority spin channel is shown in the upper left panel, and for the minority channel in the upper right panel, and for the AP configuration of the two electrodes in the lower panels. In the two lower panels additional Fe layers are included to show the TDOS variation into the right electrode. Each TDOS curve is labelled by the symmetry of the incident Bloch wave in the left electrode. For the P configuration shown in the upper panels for the tunneling DOS of two spin channels, only the majority channel has the slow decaying $\Delta_1$ state, leading to a higher conductance than those of the minority channel and either of the spin channels for the AP configuration.

For the AP configuration (shown in the lower panels), electrons of $\Delta_1$ symmetry from the majority spin of left electrode readily enter the MgO barrier where they decay slowly. However, when they enter the right electrode these states cannot propagate because there are no available minority spin propagating states at the Fermi energy. Therefore they continue to decay into the right electrode, leading to a total reflection of the $\Delta_1$ Bloch state. Because the symmetry filtering effect of the MgO barrier strongly favors the transmission of electrons with the $\Delta_1$ symmetry, the conductance due to the $\Delta_1$ state is many orders of magnitude greater than the other symmetry states. On the other hand, for Fe, Co, and FeCo bcc(100) electrodes, there are no $\Delta_1$ states at the Fermi energy in the minority spin. In other words, as far as the $\Delta_1$ state is concerned, these electrodes are half-metallic. These two factors combine leading to a giant TMR ratio.

Fig. 4. Tunneling DOS for $k_z = 0$ in Fe(100)/[8MgO]/Fe(100) for majority (a) minority (b), and AP alignment of two electrodes (c, d). Additional Fe layers are included in lower panels to show the TDOS variation in Fe. Each TDOS curve is labelled by the symmetry of the incident Bloch state in the left Fe electrode. Reprinted with permission from [7], W. H. Butler et al., Phys. Rev. B 63, 054416 (2001). © 2001, American Physical Society.
The tunneling across a crystalline MgO barrier is called the coherent tunneling, in contrast to the incoherent tunneling in AlO-based MTJs. Due to the amorphous structure of the AlO tunneling barrier, there is no crystallographic symmetry inside the barrier layer. The Bloch states with various symmetries in the FM electrodes can couple with any evanescent states in the amorphous barrier, leading to approximately equal tunneling probabilities for all of the Bloch states. Additional discussion about coherent and incoherent tunneling in MgO-based MTJs could be found elsewhere.\textsuperscript{28,39}

1.3. Interfacial Structures in MgO-Based MTJs

As outlined above, a lot of experimental work has been carried out on epitaxial MgO-based junctions, following the predictions of huge MR ratios in excess of 1000% in 2001 by first-principles calculations. The value of MR ratio obtained experimentally in MBE-grown devices is still significantly lower than the theoretical one although great progress has been achieved during the last several years. For example, a MR ratio of 410% at RT was obtained in epitaxial Co/MgO/Co MTJs.\textsuperscript{22} Larger MR ratios have been achieved in sputtered CoFeB/MgO/CoFeB devices, as high as 604% at RT and 1144% at 5 K.\textsuperscript{14} The present paper addresses the origin of the considerable discrepancy between values obtained for MBE-grown junctions and theoretical predictions.

It is well known that the interfacial structure is of great importance in multilayers or superlattices, where the scattering or tunneling process at the interfaces dominates the electron transport across the spacer (GMR effect) or the barrier (TMR effect). In general, the interface structure can be complex due to defects, such as interface roughness (steps), strain, lattice mismatch, dislocations, vacancies, and contamination. One long-running important issue concerns the possible oxidation of the interfacial layer of the electrode, following the results of investigations by \textit{in-situ} surface X-ray diffraction, showing the evidence of FeO formation at the Fe/MgO and MgO/Fe interfaces of epitaxial Fe/MgO/Fe structures.\textsuperscript{40-42}

In the following sections we present the results of experimental and theoretical investigations of the crystallographic and chemical profiles at the electrode/barrier interfaces of epitaxial MTJs. Our own results on MBE-grown Fe/MgO/Fe junctions are discussed within the context of these models and experimental results reported in the literature.

2. INTERFACE CHARACTERIZATION

2.1. Theoretical Models and Experimental Results

The most studied interface effect has been the extend of oxidation of the Fe/MgO interfaces, since the first evidence of an FeO layer was provided by Meyerheim et al., using surface X-ray diffraction.\textsuperscript{40} In Figure 5, these authors’ model of the bottom oxidized Fe interface is shown, together with interlayer distances. In 2003, first-principles calculation of the electronic structure and MR ratio of Fe/FeO/MgO/Fe tunneling junctions with FeO layer at the bottom Fe/MgO interface was done by Zhang et al., with a detailed comparison to those of pure Fe/MgO/Fe junctions.\textsuperscript{43,44} It was shown that an atomic layer of FeO at the Fe/MgO interface greatly reduces the MR ratio, due to the in-plane bonding of Fe with O which reduces the conductance in the P configuration, but has little effect on conductance in the AP configuration. Furthermore, the MR ratio decreases monotonically and exponentially with the increasing O concentration in the FeO layer. Theoretical results\textsuperscript{45} of first-principles DOS calculations for the ideal interface and the oxidized interface are shown in Figure 6. With respect to an ideal interface shown on the left of Figure 6, $\Delta_1$ Bloch states in the Fe layer couple with $\Delta_1$ evanescent states in the MgO barrier in the $k_{//} = 0$ direction. This structure with an ideal interface shows a huge MR ratio.\textsuperscript{7} For an oxidized interface shown on the right of Figure 6, where there are excess oxygen atoms in the interfacial Fe monolayer, $\Delta_1$ Bloch states in the
Fe layer do not couple with $\Delta_1$ evanescent states in the MgO barrier effectively. This decoupling prevents coherent tunneling of $\Delta_1$ states and greatly reduces the MR ratio. Subsequently, more analytical techniques have been applied to the interface characterization of MgO-based epitaxial MTJs, such as Auger electron spectroscopy (AES), X-ray absorption spectra (XAS), and X-ray magnetic circular dichroism (XMCD). Auger electron spectroscopy was used to investigate the chemical nature of the different interfaces and possible segregation effects in fully epitaxial Fe/MgO/Fe(001) oriented heterostructures fabricated by combined sputtering plus laser ablation deposition techniques.\textsuperscript{45} The interfaces on each side of the MgO barrier show some differences, where the bottom Fe/MgO interface is spatially broader and with an FeO interlayer, and the top MgO/Fe interface is spatially narrower with no evidence of FeO formation. XAS and XMCD techniques were applied\textsuperscript{46} to study the interface of 6 monolayer (ML) Fe(001) in Fe/MgO bilayers, and the results showed evidence for a weak hybridization between Fe and O atoms. Unfortunately, in these latter investigations no MR data were shown for the full junctions, which could add further evidence for the possible formation of an FeO monolayer. However, the evidence for a non-oxidized interface was provided by the XAS and XMCD measurements carried out for 1 ML and 2 ML-Fe(001) facing an MgO(001) barrier in a body-centered-cubic (bcc) Co(001)/Fe(001)/MgO(001) structure.\textsuperscript{47} Attempts to avoid the FeO layer at the interface lead to the insertion of an ultrathin (1-2 atomic layers) of Mg between the Fe electrodes and the MgO barrier layer.\textsuperscript{58} This has led to either increased or reduced TMR ratio depending on the deposition techniques and the particular samples. Theoretical model\textsuperscript{19} of the ultrathin Mg interlayers shows that while adding the Mg layer generally reduces the TMR, its effect is not as severe as that of the FeO layer because the Mg layer preserves the preferential transmission of the Fe $\Delta_1$ state. Very clearly, no consistent viewpoint has been reached on the extent of interface oxidation, and this is still an open issue.

Other effects such as interface resonant states\textsuperscript{7,50} have been found to cause lower experimental MR ratios. More generally, the interfacial structure is closely related to the crystalline defects, lattice mismatch, interface roughness, dislocations, vacancies, contaminations.\textsuperscript{51-54} The crystalline defects in the Fe layers, including the surface roughness, are minimized by post-annealing,\textsuperscript{19} which can increase the MR ratio from around 100% for as-grown samples to 180% for annealed samples. The interfacial contamination, for example due to carbon impurities in the MgO substrate, was investigated as well,\textsuperscript{55,56} and the carbon contaminations could be eliminated by growing a MgO buffer on the MgO substrate before growth of the bottom Fe layer. The interface roughness, especially of the bottom Fe layer, could also be improved by using appropriate growth conditions together with thermal annealing, and/or by a thick MgO buffer.\textsuperscript{59,21} The lattice mismatch between Fe and MgO can be tuned by doping V into the bottom Fe layer (i.e., an FeV alloy film), so that the crystalline quality of the MgO barrier is improved, leading to an increase of the MR ratio despite the fact that the spin polarization in the FeV alloy is lower than that of the pure Fe layer.\textsuperscript{57}

Before the detailed discussion about interface characterization, the basic properties including the structural analysis, magnetic and transport properties in epitaxial MgO-based junctions will be described. The core part of epitaxial MTJs is a trilayered structure, such as Fe/MgO/Fe. The top Fe layer is generally adjacent to a hard layer, such as Co layer,\textsuperscript{19} or to an antiferromagnetic (AFM) layer such as Ir$_{0.22}$Mn$_{0.78}$ layer\textsuperscript{21,58} which exhibits an exchange bias effect, in order to achieve the P and AP configuration between bottom and top FM electrodes by influence of an external magnetic field.

During the deposition of multilayers by MBE, the structure of each layer is monitored by the in situ reflection high energy diffraction (RHEED) technique. Figure 7 shows typical RHEED patterns recorded from Fe/MgO/Fe/InMn multilayers on a MgO(001) substrate along the MgO[110] azimuth. It shows that the whole structure is epitaxial, including the AFM layer (InMn) on the top Fe layer.\textsuperscript{58,59} Furthermore, both the bottom and top Fe layers show good crystallinity and flatness after annealing, as shown by the clear and sharp RHEED streaks.

The structure of multilayers is further investigated by X-ray diffraction (XRD) although it is hard to differentiate the MgO barrier from MgO substrate due to its thickness (such as 2 or 3 nm). Figure 8 presents the XRD pattern for Fe/MgO/Fe trilayers, which indicates a good epitaxial growth of the entire structure as well. The epitaxial relationship between Fe and MgO layers of Fe(001)[100]/MgO(001)[110]/FeO(001)[100] was confirmed, where MgO axes rotate 45° with respect to the equivalent Fe axes.\textsuperscript{57}
Finally, the structure of the multilayers was examined using transmission electron microscopy (TEM). Figure 9(a) presents a high-angle annular dark-field TEM image (Z-contrast) of a multilayer with structure of Fe/MgO/Fe/IrMn/Cr (Cr as capping layer), indicating different layers clearly. The cross sectional high resolution TEM image across MgO barrier is shown in Figure 9(b). The zone axis is along Fe[100] (MgO[110] as well). The well-known epitaxial relationship of Fe(001)[100]//MgO(001)[110]//Fe(001)[100] is confirmed again, together with the observation of sharp interfaces across the MgO barrier. We also found that the interface is semicoherent due to dislocations at the interface, which originates from the approximately 3.5% lattice mismatch between the MgO(100) and Fe(110) planes. Therefore, the epitaxial structures observed by RHEED, XRD, and HRTEM are in good agreement, indicating a high quality sample grown by MBE.

The multilayers were fabricated into micro-meter size junctions by UV-lithography together with Ar ion milling. In Figure 10, a typical R–H loop (obtained from a patterned junction) at RT is shown by open circles, and a M–H loop (obtained from the unpatterned sample) by open squares, respectively. It shows that the R–H loop for patterned junctions is in good agreement with the M–H loop obtained for the as-grown continuous sample, with sharp magnetization switches for the P and AP configurations. The MR ratio is 174% at RT and increases to 318% at 10 K. The results shown from Figures 6 to 9 indicate that the fully epitaxial Fe/MgO/Fe/IrMn junction has a high quality structure with a large MR ratio. The related work described in the following sections by the authors is based on these high quality epitaxial samples, except when specified otherwise.

2.2. High Resolution Transmission Electron Microscopy

Transmission electron microscopy (TEM) is a powerful tool to investigate the crystal structure of materials at the...
atomic level, and especially useful for studying locally the interface structure in multilayers. Recently, by using high-resolution imaging with a small negative value of the spherical aberration of the objective lens in an aberration-corrected TEM, atomic columns of oxygen in BaTiO$_3$ thin films were imaged and quantified. However, in a conventional TEM (with spherical aberration), we could make use of the high spatial resolution of HRTEM in order to examine the formation of an Fe–O monolayer at the Fe/MgO interface. HRTEM images of samples in a cross sectional view were obtained using a JEOL 4000EX. This microscope has a spherical aberration (Cs), point-resolution and information limit of 1 mm, 0.16 nm, and less than 0.12 nm, respectively. The sample, with a core structure of Fe/MgO/Fe, was prepared by a traditional method comprised of cutting, polishing, dimpling, and ion milling. In order to find the evidence of an FeO layer, it is necessary to compare these experimental images to simulated ones because direct interpretation is not straightforward. The TEM images are simulated using the weak phase approximation, namely a single scattering event. Java electron microscopy software (JEMS) was used to simulate the images for various defoci and thickness values of the specimens obtained in the JEOL 4000 EX microscope. Super-cell models of the interface for both sharp and oxidized interfaces were constructed, shown in Figure 11. By an oxidized Fe/MgO interface, we mean that an FeO layer is inserted between the Fe and MgO layers.

The zone axis of the cross section view was selected along MgO[110] orientation (Fe[100] as well). This direction was chosen because the atomic columns imaged in the MgO layer are either O or Mg. The best match between experimental and simulated images was obtained for an approximately 5 nm thick sample, shown in Figure 12(b, center), along with two simulated images of the Fe/FeO/MgO shown in Figure 12(a, left) and Fe/MgO structures shown in Figure 12(c, right). Away from the interface, the simulated Fe/FeO/MgO and Fe/MgO images appear similar because both are based on bulk Fe and MgO interplanar distances. Close to the interface, the simulated images of the two structures show subtle differences. For the abrupt Fe–MgO interface, the image appears sharper (see arrow denoting the bright spot), while for the oxidized Fe–FeO–MgO interface, this region is dimmer, probably due to the existence of oxygen.

We note that due to the spherical aberration, the differentiation between the two proposed models is indeed subtle. This result emphasizes the importance of using an aberration-corrected TEM for determining the structure of the interface. Recent work conducted in our group, clearly found a sharp interface using this approach. An additional route to check whether the interface is oxidized is to examine the Fe–O interplanar distances. For the sharp interface, the Fe–O distance is 0.2169 nm (according to first-principles calculations). For an oxidized interface, the Fe–O distance of 0.235 nm was reported following an experimental measurement. In order to fit the interplanar distance between the Fe and O layers at the interface to the experimental HRTEM results, distances varying from 0.19 to 0.26 nm were introduced into the sharp Fe/MgO model for the multi-slice calculations. Figure 13 shows simulation results for interplanar distances of 0.235 nm (a, left), and 0.220 nm (c, right) for the Fe–O distance, indicating a better fit to an Fe–O interface distance of 0.22 nm. The arrow in (a) highlights the discrepancy of the interplanar spacing between the simulated interplanar distances of 0.235 nm and the experimental distances of 0.220 nm.
Interface Characterization of Epitaxial Fe/MgO/Fe Magnetic Tunnel Junctions

Wang et al.

Fig. 13. Experimental (b) and simulated HRTEM images for Fe–O distance of (a) 0.235 nm, (c) 0.220 nm, both simulated at defocus of 36 nm and 5 nm thickness. The arrow in (a) highlights the discrepancy of the interplanar spacing between the simulated (a) and experimental image (b), whereas the arrow in (c) highlights a good agreement. Reprinted with permission from [62]. C. Wang et al., IEEE Trans. Magn. 43, 2779 (2007). © 2007, IEEE.

image (b, center), whereas the arrow in the simulated interplanar distances of 0.220 nm highlights a good agreement. More detailed analysis of interfacial structures by HRTEM and electron energy loss spectroscopy (EELS) is reported in our recent publications, as well as by Serin et al.60, 64, 65

The bottom interface appears smooth while the top interface has considerably more atomic column steps, typically one or two atomic planes in width, marked by arrows in Figure 13.

Based on the above detailed experimental HRTEM and simulations of Fe/MgO/Fe multilayers, along with our recent TEM studies,60 we conclude the bottom Fe/MgO interface is sharp. More exactly, at least some sections of the interface are non-oxidized with sharp interfaces. The interface roughness was characterized and compared using high-angle annular dark-field scanning TEM.60 The bottom Fe/MgO interface appears smooth while the top interface has considerably more atomic column steps, typically one or two atomic planes in width. In order to further elucidate the issue of interfacial structures, it is also helpful to characterize the interface using additional experimental techniques, such as XPS and spin dependent tunneling spectroscopy with a focus on the evidence of FeO formation, which will be discussed in the following parts.

2.3. X-ray Photoelectron Spectroscopy

With respect to the evidence of FeO formation at the Fe/MgO interfaces, the measurement of X-ray photoelectron spectroscopy (XPS) has been proven to be a very useful tool.55,66,67 Generally, the measurements include two different ways. One is directly to use the real structure as same as junctions, where the XPS facility is equipped with ion milling gun, enabling to peel sample layer by layer till the interfaces.66 The other way is an in situ measurement, where a very thin MgO layer (for example, 2 monolayers) is deposited onto a thick Fe layer.55,67 For in situ measurements, typical results are shown in Figure 14, where the evidence for weak hybridization between Fe and MgO was provided. However, it is the best way to carry out the XPS measurements on the samples that have the same structure (cut from the same sample or samples grown at the same conditions) showing good electrical and magnetic properties together with a high MR ratio.

The resistance as a function of magnetic fields for junction with structure of Fe(50)/MgO(3)/Fe(10)/IrMn(10) thickness in nm) at RT is shown in Figure 15, where the junction size is 6 × 8 μm². For this sample, the analysis from RHEED patterns, XRD curve, and HRTEM images confirmed the high quality of junctions. However, the value of MR ratio is only 61% at RT, indicating the imperfection of the junctions which can not be identified by above mentioned techniques. Then the XPS measurement was carried out on the sample grown with same structure and same growth conditions. The multilayers were etched by ion milling layer by layer, and the Fe 2p high-resolution XPS spectra at the Fe/MgO interface was collected and presented in Figure 16. The thin solid line shows experimental data, and the thick solid line is the fitting curve. As well as the main peak at 706.6 eV, there are two small peaks along the higher energy shoulder. From the XPS handbook, peak 0 at 706.6 eV is characteristic of a metallic Fe 2p3/2 peak; peak 1 at 708.2 eV and peak 2 at 710.4 eV correspond to Fe²⁺ 2p3/2 and Fe³⁺ 2p3/2 peaks, respectively. After MgO layer was completely removed, only a
single peak (peak 0 here) was observed for pure Fe layer. Above results could be taken as an evidence of FeO formation at the bottom Fe/MgO interface. The formation of the FeO layer is attributed to Mg, which acts as a catalyst to promote the oxidation of Fe at the Fe/MgO interface. During deposition, MgO single-crystal source decomposes as elemental Mg and oxygen molecules, which provides Mg as catalyst for the FeO formation.

Following these studies, further optimization of the growth parameters resulted in significant increase of the MR ratio. For example, MR ratio reaches about 174% at RT and 318% at 10 K in the junctions of Fe(25)/MgO(3)/Fe(10)/IrMn(10) (thickness in nm), with typical R–H loops at temperatures of 300 K, 100 K and 10 K shown in Figure 17. As before, XPS measurements (Thermo Scientific ESCALAB 250 machine) were carried out.

The sample for XPS measurements has the structure of Fe(25)/MgO(5)/Fe(3)/Cr(5) (thickness in nm), where 5 nm thick MgO barrier is used instead of 3 nm in real junctions in order to distinguish the XPS signal of bottom Fe layer from that of top Fe layer. In order to locate the interfaces more exactly, the etching rate is reduced to 0.5 nm/etching (etching time is fixed for 120 seconds). After each etching, the XPS measurement is carried out, including the whole range energy survey (such as from 0 eV to 1350 eV to check all elements in our systems), Fe 2p spectra, Mg 1s spectra, O 1s spectra, Mg 2p spectra, C 1s spectra, and Cr 2p spectra. With etching, the peak from Mg 1s appears, indicating the location of the top Fe/MgO interface (TI), meanwhile the intensity of Fe 2p from top Fe layer shows a little decrease. With etching step by step, the intensity of Fe 2p from top Fe layer decreases. Then, the intensity of Fe 2p shows a great enhancement, indicating location of the bottom MgO/Fe interface. The typical XPS spectra of Fe 2p, Mg 1s, and O 1s are shown in Figures 18, 19 and 20, respectively. The spectra at top interface, bottom interface, and in the MgO barrier are shown by blue, red, and black lines, respectively. The spectra in the bottom thick Fe layer and in the top Fe layer are also shown for reference.
The focus is given on Fe 2p high resolution spectra first shown in Figure 18. The Fe 2p spectra in the bottom Fe layer (its top layers is removed completely by ion milling) shown by the pink line as a reference in Figure 18, is a typical curve with two peaks located at about 707.0 eV and 720.0 eV for Fe 2p_{1/2} and Fe 2p_{3/2}, respectively. The spectrum with sharp peaks and high intensity is a characteristic of metallic Fe. No additional peaks were observed at higher energy of main Fe 2p_{3/2} peak, which were clearly shown in Figure 16 for samples with relatively low MR ratio (60%) at RT. The Fe 2p spectra at the top interface and even in the MgO barrier is similar to pure Fe curve without any additional peaks or any peak shifts. However, the Fe 2p spectra at the bottom Fe/MgO interface shown by the red line presents an energy shift of about 1.0 eV, although the whole curve looks similar with ones from the top interface and from the MgO barrier, suggesting a strong Fe–O bonding at the bottom interface. Based on the comparison of Fe 2p spectra from samples with low and high MR ratio shown in Figure 16 and 18, respectively, it is reasonable to conclude that much less FeO formation exists at the bottom interface in samples with higher MR ratio. Unfortunately, little information about top MgO/Fe interface could be obtained from current XPS results.

The Mg 1s spectra are presented in Figure 19. With the etching, the peak located at around 1303.5 eV appears, indicating the exact location of top MgO/Fe interface. Then the intensity of main peak of Mg 1s shows a dramatic increase in the MgO barrier, without any shift of peak position. However, the peak position shifts to higher energy at the bottom Fe/MgO interface, where the intensity of main peak of Fe 2p increases sharply shown in Figure 18. The binding energy shift of Mg 1s at bottom interface should be due to the strong bonding between Fe and O, as discussed above for Fe 2p spectra. It is worthy to point out that the intensity scale for Mg 1s at T1 and BI is different as shown on the right and left, respectively. The O 1s spectra are shown in Figure 20. With respect to O 1s spectra, the main peak locates at the typical binding energy at top MgO/Fe interface, but shows a shift at bottom Fe/MgO interfaces. The same mechanism discussed above for Fe 2p and Mg 1s spectra can be applied here.

In this part, a detailed discussion for the interface characterization by using XPS technique is given. The XPS measurement was carried out in the same samples or samples with same growth conditions which could be compared directly. For the samples with low MR ratio (such as 60% at RT), two small peaks were observed in the Fe 2p spectra, showing an evidence of FeO formation at the bottom Fe/MgO interface. For the samples with high MR ratio (such as 170% at RT), the binding energy shift in the Fe 2p, Mg 1s, and O 1s spectra, showing a strong bonding between Fe and O. Based on the comparison of Fe 2p spectra from samples with low and high MR ratio shown in Figure 16 and 18, respectively, we conclude that the bottom interface is less oxidized in samples with higher MR ratios. Unfortunately, no conclusive information regarding the top MgO/Fe interface was achieved from these XPS results. Therefore, at this stage, XPS measurements and HRTEM images, have not characterized conclusively the structure of the top MgO/Fe interface.

### 2.4. Spin Dependent Tunneling Spectroscopy

For MTJs, the measurement of dynamic conductance \((dI/dV)\) and inelastic electron tunnel spectrum (IETS-\(d^2I/dV^2\)) has been proven to be a powerful tool to study the spin dependent tunneling.\(^{70-78}\) Using this method, the influence of the density of states (DOS) and inelastic scattering process on conductance can be clarified by measuring first and second derivative conductance \((dI/dV, d^2I/dV^2)\). In tunneling spectroscopy, measured \(dI/dV\) curves of common tunnel junctions are rather featureless. Peaks in \(d^2I/dV^2\) are used to identify inelastic processes in tunneling, usually called inelastic electron tunneling spectroscopy (IETS). Very recently, analytic expression for contributions to the IETS from surface magnon scattering and magnetic impurity scattering has been published.\(^ {79}\) It is shown that surface magnon scattering alone does not

![Fig. 19. Mg 1s high resolution XPS spectra for sample with structure of Fe(25)/MgO(5)/Fe(3)/Cr(5) (thickness in nm).](image)

![Fig. 20. O 1s high resolution XPS spectra for sample with structure of Fe(25)/MgO(5)/Fe(3)/Cr(5) (thickness in nm).](image)
lead to peaks in the IETS. The peaks at small bias often observed in the IETS of magnetic junctions are due to magnetic impurity scattering, in agreement with the traditional model for zero-bias anomaly.

Exception for very few works,\(^ {20,78} \) most \( dI/dV \) measurements for both P and AP configurations are featureless. However, the IET spectra \( (d^2I/dV^2) \) for P and AP configurations show a different behavior. There are usually multiple peaks in the \( d^2I/dV^2 \) of the P configuration, which are generally identified with the electron–magnon and electron–phonon scattering processes. For the AP configuration, the dominant features are the peaks in \( d^2I/dV^2 \) due to the logarithmic singularity of the zero bias anomaly, which is attributed to the electron–magnon scattering.\(^ {40} \)

Due to the lack of features in the measured dynamic conductance, spin-dependent tunneling spectroscopy has not been able to provide much information on interfacial structures of MTJs despite the realization that such measurements should be sensitive to the changes at the interfaces.\(^ {81} \)

Recently, the dynamic conductance of the P configuration at 10 K in high quality epitaxial Fe/MgO/Fe MTJs was presented with some features, where the junction showed a MR ratio of about 330% at 10 K.\(^ {20} \) The peaks could be seen in the top panel of Figure 21, but no explanation was offered in that work. However, this observation of features in \( dI/dV \) curve shows a good chance to compare the experimental data with first-principles calculation.

Another detailed investigation of dynamic conductance and inelastic electron tunnel spectrum has been carried out very recently on the epitaxial Fe/MgO/Fe MTJs, together with theoretical calculations.\(^ {78} \) Firstly, the evidence for high quality epitaxial MTJs was provided from the MR ratio and the MgO thickness dependence of product of resistance and junction area \((RA)\). Figure 22(a) shows the normalized MR ratio \(((R/R_P)_\text{norm}} \times 100\%\) as a function of magnetic field at 4.2 K for junctions with structure of \( \text{Fe(25)/MgO(}t_{\text{MgO}}\text{)/Fe(10)/IrMn(10)} \) (in nm) with \( t_{\text{MgO}} = 3.0, 2.1, \text{and } 1.5 \text{ nm}, \) where \( R \) is the resistance at different magnetic fields. The MR ratio of these junctions at low temperatures is 318%, 218%, and 164% for MgO thicknesses of 3.0, 2.1, and 1.5 nm, respectively. Figure 22(b) shows the product of resistance and area \((RA)\) as a function of MgO thickness at 4.2 K. The exponential increase in \( RA \) as a function of \( t_{\text{MgO}} \) is typical of high quality tunnel junctions, and the barrier height of 0.60 eV is obtained from the slope of log \((RA)\) versus MgO thickness. The results shown in Figure 22, together with results from RHEED, XRD, HRTEM and XPS measurements presented above, indicate that the sample is of high epitaxial quality, and therefore used for the measurement of dynamic conductance and inelastic electron tunneling spectroscopy.

In Figure 23, the dynamic conductance \((dI/dV)\) is shown in panels (a) and (b) and IET spectrum \((d^2I/\) \(dV^2 = V)\) is shown in panels (c) and (d) for the P and AP configurations, respectively. Here, the positive bias means the dc current flowing from bottom to top electrode, or electrons injected from the top electrode. A strong asymmetry in the \( dI/dV \) curve between positive and negative biases is observed shown in Figures 23(a) and (b), even though the epitaxial Fe/MgO/Fe structure is stoichiometrically symmetric. This asymmetry is further evident by a broad shoulder around 0.2 V in Figure 23(b), which is only observed in the positive bias. Such asymmetry has been reported previously by some groups.\(^ {20,82} \) Possible explanations include the interface dislocations,\(^ {82} \) different electronic structures...
Another important characteristic of dynamic conductance is that the $dI/dV$ curve for the P configuration in Figure 23(a) shows some unambiguous features. The IET spectrum presented in Figure 23(c) shows several peaks as well, but all of which can be obtained from the derivative of the peaks in Figure 23(a). Here it is necessary to point out that the IET spectrum shown in Figure 23(c) is measured by lock-in method, not numerically obtained from $dI/dV$ data shown in Figure 23(a), different from the work reported before.73

To understand the origin of these peaks, dynamic conductance and IET spectra were measured for three samples with different barrier thicknesses (3.0, 2.1, and 1.5 nm shown in Fig. 22), and as functions of the temperature and applied magnetic fields. No difference in the peak positions between three samples were observed. The sample independence and the barrier thickness independence exclude both the defect scattering inside the barrier and the interference effect of tunneling states in the MgO barrier7, 10, 82 as possible origins of these peaks. In-plane magnetic fields up to 10 T (not shown here) were applied during the measurement for the P configuration (AP configuration is possible only at low magnetic fields). The peaks do not show any changes under the magnetic fields. With respect to temperature variation, all peak positions remain unchanged below 77 K. Above 77 K the peaks become unobservable due to thermal smearing. The absence of any magnetic field dependence and temperature dependence of the peak positions also make magnon and phonon scattering unlikely origins.

In the previous works,7, 83 an ideally symmetric Fe/MgO/Fe structure and an asymmetric Fe/FeO/MgO/Fe structure where a single atomic FeO layer is assumed at the bottom interface were calculated by the first-principles theory. Recently, a third asymmetric structure in Fe/MgO/Fe junction, called Fe/MgO/vacancy/Fe structure with vacancies on the oxygen sublattice of the top MgO layer, is also calculated, in order to compare the calculation with the experimental measurements. The details about the theoretical calculations can be found in another paper.78 The oxygen vacancies might form due to the decomposing process of MgO into O atoms that form O$_2$ molecules in ultra high vacuum chamber and the continuous pumping out of the chamber during MgO growth by evaporation.10 The vacancy concentration should not
not exceed the measurement resolution of 1%. A previous first-principles study found that oxygen vacancies can greatly reduce the MR ratio, and produce a resonant tunneling at a high bias of 1 V. Three different contents vacancy (0%, 0.5%, and 1%) was calculated using the coherent potential approximation. Calculations with less vacancies were not carried out because the extra peaks in the spectrum would diminish so much that it looks very similar to that of pure Fe/MgO/Fe structure.

The calculated results for three types of junctions, symmetric Fe/MgO/Fe, asymmetric Fe/MgO/vacancy/Fe (0.5% and 1% vacancy) and Fe/FeO/MgO/Fe are shown in Figure 24. For each calculation, the transmission probability is integrated over 8256 k-points in the irreducible two-dimensional Brillouin zone. The total conductance including both majority and minority spin is plotted. For ideal Fe/MgO/Fe structure, there is one main peak at zero bias, and two symmetric shoulders at about ±0.27 V, shown in Figure 24(a). For Fe/MgO/vacancy/Fe, in addition to the features similar to ideal Fe/MgO/Fe structure, there is also a strong peak at about ±0.04 V, and a shoulder at about ±0.17 V. The peak positions do not shift for different vacancy content, but the intensity increases with increasing vacancy content. For Fe/FeO/MgO/Fe, one strong peak appears in the negative bias at about −0.11 V shown in Figure 24(b). The antiparallel conductance was also calculated (not shown here), without major peaks, in good agreement with experimental measurement shown in Figure 24(b). For the symmetric Fe/vacancy/MgO/vacancy/Fe with 0.5% vacancy (not shown here), both the positive and the negative bias sides of the spectrum are essentially the same as the positive bias part of the asymmetric Fe/MgO/vacancy/Fe spectrum.

In Figure 25 the calculated $G(E, V)$ is compared with the measured $dI/dV$ for the P configuration for two junctions with $t_{MgO} = 2.1$ and 3.0 nm shown by open circles and open squares, respectively. To facilitate the comparison, we plot the positive and negative biases separately in panels (a) and (b). A fourth-order polynomial background is removed from the experimental data to accentuate the peaks. Each calculated spectrum is also shifted by a constant in order to be plotted in the same range as the experimental data. The asymmetric structure of Fe/MgO/vacancy/Fe with 1% vacancy was used in Figure 25. The solid lines in Figure 25 from top to bottom are calculations for Fe/MgO/Fe, Fe/MgO/vacancy/Fe, and Fe/FeO/MgO/Fe structure, respectively. For the positive bias in Figure 25(a), where the electrons are injected from the top electrode, an experimental peak at 0.026 V and a shoulder at 0.13 V are matched well with the calculated spectrum for the Fe/MgO/vacancy/Fe structure. For the negative bias in Figure 25(b), where the electrons are injected from the bottom electrode, there are a peak at $−0.11$ V and a shoulder at around $−0.24$ V in the experimental spectrum. The former matches with the calculated peak for the Fe/FeO/MgO/Fe structure, while the latter matches with the shoulder for the ideal Fe/MgO/Fe structure.

It is reasonable to conclude that for the positive bias voltage, the main features in $dI/dV$ are due to the Fe/MgO/vacancy/Fe structure, and that for the negative bias voltage, the main features in $dI/dV$ are due to the Fe/FeO/MgO/Fe and Fe/FeO/MgO/Fe structures. There have been theoretical suggestions together with experimental support that an FeO layer is formed at the interface between the bottom electrode and the MgO layer, and that the interface between the MgO layer and the top electrode has dislocations and vacancies. The results from spin-dependent tunneling spectroscopy here present direct evidence of the existence of a mixture of Fe/MgO and Fe/FeO/MgO at the bottom interface, and the presence of oxygen vacancies at the top interface. Dynamic conductance measurement also suggests that only the interface on the side of the electrons injecting electrode determines the spin dependent tunneling spectrum. This is consistent with the presence of diffusive scattering inside the MgO barrier layer. The previous estimate of the scattering length inside MgO barrier is about 2 nm. It is necessary to emphasize that the top interfacial structure could be studied by the dynamic conductance together with theoretical calculations.

Further refinement of both experiment and theory may allow spin-dependent tunneling spectroscopy to determine interface structures quantitatively. For example, the difference in the relative heights of the two measured peaks for two samples in Figure 25(b) might indicate different amount of FeO at the bottom interface in two samples, which was further proved by the MTJ samples with MgO barrier grown at 200 °C (not shown here) compared to the sample grown at RT used for this study.

Fig. 25. Parallel $dI/dV$ for two junctions with $t_{MgO} = 2.1$ nm (open circles) and 3.0 nm (open squares) compared to calculations (solid curves) (a) positive bias and (b) negative bias. Reprinted with permission from [78], G. X. Du et al., Phys. Rev. B 81, 064438 (2010). © 2010, American Physical Society.
3. CONCLUSIONS

In this topical review article, the interface characterization in epitaxial Fe/MgO/Fe magnetic tunnel junctions is the main focus, together with a brief introduction on recent development of MgO-based MTJs. In epitaxial MTJs, the interfacial structures play a critical role in the spin dependent tunneling, such as the MR ratio, which has been a debating issue during past several years. The techniques applied to investigate the interfaces include the surface X-ray diffraction, Auger electron spectroscopy, X-ray absorption spectra, and X-ray magnetic circular dichroism, high resolution and analytical transmission electron microscopy, and spin dependent tunneling spectroscopy. Different techniques and measurements are sensitive to various properties. For example, the measurement of XMCD shows the different Fe chemical states, and XPS technique is sensitive to the environmental bonding of specified elements. Fortunately, the different methods could be used together, probably from various groups, to elucidate the mechanism behind. Based on the review of results from many groups and/or from different experimental methods (sometime with support from theoretical calculations), it is reasonable to conclude that there is bonding between Fe and O at the bottom Fe/MgO interface, and this bonding could be decreased under the optimization of growth conditions. The bonding has a close relationship to the MR ratio in the junctions. With respect to the bottom Fe/MgO interface, most parts are sharp and non-oxidized. These parts contribute to the tunneling process, leading to a high MR ratio. More exactly, the bottom Fe/MgO interface should be a mixture of sharp and clean structures and some oxidized/bonded parts. The top MgO/Fe interface includes the dislocations and oxygen vacancies.

It is worthy to point out that only the interface on the side of electrons injecting electrodes plays a dominant role on the coherent tunneling process, based on the analysis of dynamic conductance together with first-principles calculation. In short, the interfacial structure is of great importance to the spin dependent tunneling in epitaxial MgO-based junctions, probably in CoFeB/MgO/CoFeB junctions, but is a complicated issue as well. We hope this topical review article could shed some light on this issue.

Acknowledgments: This work was supported by the National Basic Research Program of China (MOST, No. 2009CB929203 and 2010CB934400), Chinese National Natural Science Foundation (NSFC, No. 50972163, 50721001, and 10934009), the U. K. Engineering and Physical Research Council (EPSRC) and the Royal Academy of Engineering. Portion of the research was conducted at the CNMS of ORNL, operated by UT-Battelle for Office of User Facilities, Basic Energy Sciences, US Department of Energy. The authors thank Keith Belcher from Oxford University for his technical expertise in MBE growth and Bin Cheng from Beijing University of Chemical Technology for the XPS measurement.

References and Notes
