

Geometrical and Compositional Structure at Metal-Oxide Interfaces: MgO on Fe(001)

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The geometric structure of MgO deposited on Fe(001) in ultrahigh vacuum by electron evaporation was determined in detail by using surface x-ray diffraction. In contrast to the common belief that MgO grows in direct contact on the Fe(001) substrate, we find an FeO interface layer between the substrate and the growing MgO structure which has not been considered thus far. This result opens new perspectives for the understanding of the Fe/MgO/Fe(001) interface and the tunneling magnetoresistance effect in general.

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Since the first report of spin-dependent transport in a tunnel junction composed of two ferromagnetic layers separated by an insulating barrier [1], considerable interest has evolved in both the theoretical and experimental studies of the tunneling magnetoresistance (TMR) effect in order to understand its underlying mechanisms [2–6]. Despite its importance for the development of magnetic random access memory devices, there is until now very limited success in the thorough characterization of such junctions. On one hand, this can be attributed to incompletely defined experimental preparation conditions leading to a considerable scatter of the magnitude of the magnetoresistance, $\Delta R/R$, reported thus far. High values of up to 27% [5] are reported only for TMR junctions based on amorphous oxide barriers. In these cases, the tunnel conductance is dominated by electron scattering by local defects, which are likely to be strongly influenced by different preparation techniques. Moreover, it is difficult if not impossible to theoretically treat such complex situations as the effect of impurities in the barrier or at the barrier-metal interface on the TMR, since all theories thus far assume *ballistic* tunneling, i.e., the parallel electron momentum (k_{\parallel}) is conserved over the junction. As a consequence of this situation, single crystalline oxide barriers appear to be primary candidates for the preparation of TMR junctions, since they offer the opportunity to control their structural and physical properties in a more reproducible way. Furthermore, they are directly accessible by theory because electron tunneling is ballistic in this case [7].

In contrast to these promising properties of monocrystalline barriers, there are only a few attempts to grow and to characterize such TMR junctions. In this context, one prototype candidate is the Fe/MgO/Fe(001) system. This is because MgO can be grown epitaxially on Fe(001) by electron beam deposition [8–10] due to the low lattice mismatch (3.5%) and the large difference of the surface-free energy between Fe (2.9 J/m²) and MgO (1.1 J/m²) [11]. Although first attempts to prepare a crystalline Fe/MgO/Fe(001) junction using a MgO(001) crystal were not successful because of pinholes leading to an Ohmic contact [12], recent experiments depositing MgO by electron beam deposition on a Fe(001) whisker were able to demonstrate ballistic tunneling at room temperature, although due to equipment limitations the TMR effect could not be measured [13].

Parallel to these experimental studies, recent theoretical work provides a more detailed insight into the tunneling mechanisms. Calculations of Butler *et al.* [14] for Fe/MgO/Fe have given evidence for the importance of the symmetry relation between the propagating states in the Fe electrodes and the evanescent states in the MgO barrier. Their conclusion is that $\Delta R/R$, which is predicted to be several 1000%, is due to the strongly peaked conductance in the majority channel at $k_{\parallel} = 0$ for parallel alignment, whereas minority channel conductance is dominated by states associated with k_{\parallel} values close to interface states. From their results, it can be concluded that a reliable comparison between experiment and theory relies on the detailed knowledge of the interface structure.

Structural defects strongly influence the electron tunneling in both the majority and the minority channels. For example, the modification of interface states can result in a less peaked conductance around $k_{\parallel} = 0$, and reduce considerably the magnetoresistance $\Delta R/R$. Consequently, the detailed understanding of the metal/oxide interface structure is a prerequisite to determine the role of interface states on $\Delta R/R$.

Previous studies [8,9,15] only investigated the epitaxial relationship between MgO and Fe (MgO[100]||Fe[110]), the layer-by-layer growth mode of MgO on Fe(001) up to about 5 monolayers (ML) of thickness, and the monocrystallinity of MgO(001) by monitoring sharp low energy electron diffraction (LEED) spots. Some information on the geometric structure was provided by a LEED study only for the inverse interface [Fe/MgO(001)] suggesting that the Fe atoms adsorb on top of the O atoms at a distance of 2.0 Å [13]. In this Letter, we provide a detailed picture of the MgO/Fe(001) interface on the basis of surface x-ray diffraction (SXR) data. Direct evidence for the presence of an interfacial FeO layer is given, which is expected to have a considerable effect on the tunneling properties of the TMR junction.

For the SXR experiments, a single crystalline Fe(001) substrate ($\varnothing = 9$ mm) was prepared in UHV by standard procedures until only traces of nitrogen were detectable by Auger-electron spectroscopy (AES). MgO was deposited by electron beam evaporation from a polycrystalline rod. During deposition, the pressure rose from 2×10^{-10} to 1×10^{-9} mbar. Vassent *et al.* [10] relate this to molecular oxygen generated by recombination of atomic oxygen issued from the MgO source at the walls of the UHV chamber. Integrated x-ray reflection intensities were collected *in situ* at the beam line DW12 of the storage ring at LURE (Orsay, France) using a six-circle diffractometer operated in the z -axis mode [16]. In total, seven data sets were taken for MgO coverages between 0.4 to 5 ML. AES was also used to calibrate the amount of Mg and O deposited, which was found to be in excellent agreement with SXR derived coverages [17]. For each data set, up to 125 symmetry independent reflections were measured along four different crystal truncation rods (CTRs) [18] with a maximum normal momentum transfer ($q_z = \ell \times c^*$) of $\ell = 1.8$ reciprocal lattice units (r.l.u.) (1 r.l.u. = $c^* = 2.192 \text{ \AA}^{-1}$). The CTRs arise due to the truncation of the crystal lattice planes along [001]. Neglecting absorption, the CTR structure factor amplitude, $|F|$, of the bulk truncated Fe crystal is given by $|F| = f_{\text{Fe}} / \{2 \times |\sin[\pi(h + k + \ell)/2]|\}$, where f_{Fe} represents the atomic scattering factor for Fe. The detailed analysis shows that ℓ is a continuous parameter, whereas h and k are integers [18]. The CTRs are peaked at the bulk Bragg condition, $h + k + \ell = 2n$ (n integer), but are weak in between. At the antiphase condition ($h + k + \ell = 2n + 1$), $|F| = f_{\text{Fe}}/2$; i.e., the scattered intensity equals $\frac{1}{4}$ of that corresponding to an Fe ML. Thus, an adsorbate strongly modifies the CTR intensity,

which allows one to carry out a surface sensitive structure analysis. The standard deviations (σ) of the $|F|$ values were estimated from the reproducibility of symmetry equivalent reflections and the counting statistics as outlined in Ref. [19]. In general, σ is in the 3–5% range, a value which can be considered as excellent for SXR data.

The symbols in Fig. 1 show the $|F_{hk}(q_z)|$ derived from the integrated intensities after correcting for active sample area, polarization, and Lorentz factor [19]. In the following, we concentrate on one experiment only where 2 ML MgO were deposited. Direct inspection of the intensity distribution along the rods allows some general conclusions. First, the CTRs show a rapid modulation along q_z , indicating the presence of several adlayers. Second, from the identical shape of the (10ℓ) and the (21ℓ) rod as well as of the (11ℓ) and the (20ℓ) rod only high symmetry adsorption sites such as $(x, y) = (0, 0)$ and $(\frac{1}{2}, \frac{1}{2})$ within the Fe(001) surface unit cell (plane group symmetry $p4mm$) can be inferred, since for these rods the lateral component of the scattering phases, $\exp[i2\pi(hx + ky)]$ are identical. This is compatible with the, thus, far, generally accepted model of the MgO/Fe(001) interface in which MgO directly grows on Fe(001). Consequently, we tried to refine the structure model, which is schematically outlined in Fig. 2(a). The first layer O and Mg ions are shown as red and green balls, respectively. The underlying Fe atoms of the substrate are represented as blue balls. There is a 45° -rotation angle between the [100] directions of the Fe and MgO lattice. The O and Mg ions are located at $(x, y) = (0, 0)$ and $(\frac{1}{2}, \frac{1}{2})$ within the surface Fe unit cell

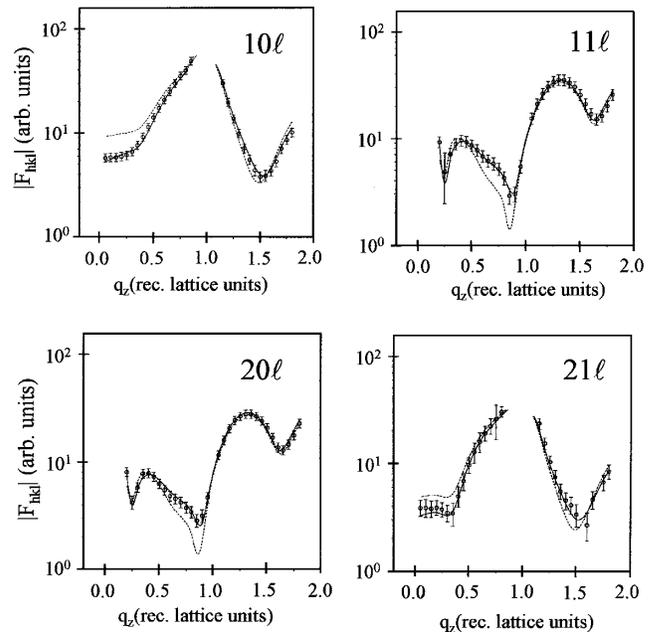


FIG. 1. Measured (symbols) and calculated structure factor amplitudes along the (10ℓ) , (11ℓ) , (20ℓ) , and (21ℓ) crystal truncation rod for 2 ML MgO/Fe(001). Solid lines and dashed lines correspond to calculated structure factor amplitudes based on the model outlined in Fig. 2 with and without the FeO layer.

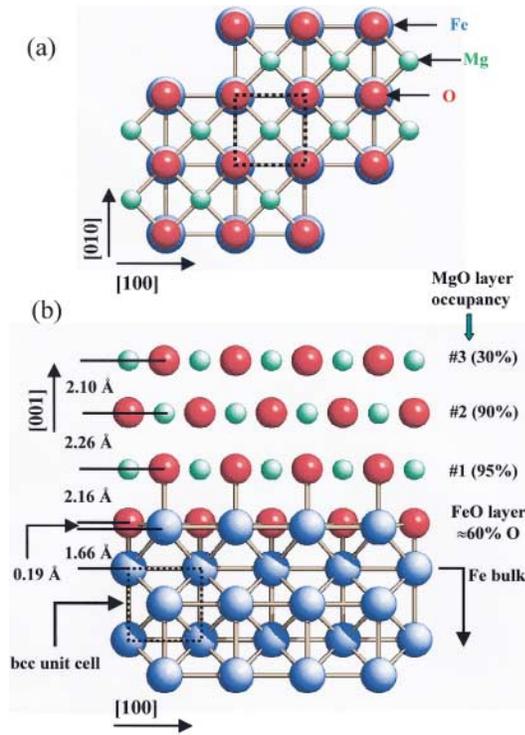


FIG. 2 (color). (a) Top view of the MgO/Fe(001) interface. The dashed square indicates the Fe(001) surface unit cell. Only the first MgO layer is shown. (b) Perspective view of the best fit structure model. The error bar for the MgO interlayer distances is about 0.15 Å.

(indicated by the dashed square). The second MgO layer is stacked on the first one by placing the second layer O and Mg ions on top of the first layer Mg and O ions, respectively (not shown). For refining this model, several fit parameters were used. Apart from allowing for variations of the normal distances between the MgO layers, between the first MgO layer and the Fe substrate, and between the first and the second Fe layer, the occupancy factors for the MgO layers were varied. Different layer occupancies accommodate the results of our scanning tunneling microscopy studies; the layer-by-layer growth mode is not perfect, the second (third) layer is formed before completion of the first (second) atomic layer. One overall scale factor was used for all rods, and the thermal Debye parameters were kept constant at $B = 0.6 \text{ \AA}^2$. Using this model, no satisfactory agreement with the data could be achieved; the unweighted residuum R_u [20] was in the range of 10%. This means that the disagreement between the fit and data is more than 2 standard deviations on average indicating that the model is not correct in detail. Moreover, some results are not entirely plausible in the framework of this model. For example, the first substrate interlayer distance, d_{12} , was found expanded by 16% relative to the bulk value (1.43 Å). This can hardly be induced by MgO growth on the bare metal surface, since theoretical analyses [14,21] have indicated a weak chemical interaction between Fe and MgO.

In order to improve the fit, we went one step further by introducing O ions near the first Fe layer, thus introducing an FeO-like interface layer between the bulk Fe metal and the MgO crystal. Several arguments have led us to this trial structure. First, the 16% first Fe-interlayer expansion is characteristic for the O/Fe(001)-(1 × 1) interface. Our value is in between results reported by LEED (8%) [22] and theory (23%) [23]. Second, with O ions in Fe surface hollow sites, the first layer Mg ions are in a bulklike octahedral environment. Otherwise, they would experience fivefold coordination only. A fivefold coordination of the Mg ions next to the Fe surface appears energetically unfavorable, possibly due to ionic repulsion, although detailed calculations are not available thus far.

On the basis of this trial structure, an almost perfect fit of the data could be achieved. We obtained $R_u = 4.7\%$, which is an improvement by more than a factor of 2 as compared to the best fit obtained without the interface O layer. In Fig. 1, the solid lines and dashed lines represent the structure factor amplitudes calculated for the structure model with and without the interface layer, respectively. Figure 2(b) shows the best fit model in side view; the atomic coordinates are listed in Table I. In detail, we find a fraction of 0.60(10) ML of O ions located 0.19(15) Å above the first Fe layer, which is shifted outward by 0.23(5) Å from its bulk truncated position. The nearest Fe-O distances are 2.03(15) Å (lateral) and 1.85(15) Å (vertical). These are slightly lower than the Fe-O distances in bulk FeO (2.154 Å) but still in the range normally seen in bulk Fe-O structures (1.85–2.31 Å) [24]. The vertical MgO interlayer distances [see Fig. 2(b)] are slightly enhanced as compared with bulk MgO (2.106 Å). The vertical enhancement can be related to the 3.5% lateral compression of the MgO overlayer.

TABLE I. Structure parameters for the best fit. The relative coordinates are given with respect the bcc Fe unit cell ($a = 2.8664 \text{ \AA}$). The bulk truncated Fe(001) surface is at $z = 0.00$. Parameters labeled by (*) were kept fixed.

	Occupancy	x^*	y^*	z
Substrate:				
Fe ₍₂₎	1.00	$\frac{1}{2}$	$\frac{1}{2}$	-0.50*
Fe ₍₁₎	1.00	0.0	0.0	0.08(1)
Interfacial oxygen:				
O	0.60(10)	$\frac{1}{2}$	$\frac{1}{2}$	0.15(5)
1st MgO layer:				
O	0.95(10)	0.0	0.0	0.90(5)
Mg	0.95(10)	$\frac{1}{2}$	$\frac{1}{2}$	0.89(2)
2nd MgO layer:				
O	0.90(10)	$\frac{1}{2}$	$\frac{1}{2}$	1.69(2)
Mg	0.90(10)	0.0	0.0	1.68(5)
3rd MgO layer:				
O	0.30(10)	0.0	0.0	2.42(5)
Mg	0.30(10)	$\frac{1}{2}$	$\frac{1}{2}$	2.42(5)

Our study provides important results concerning the formation of metallic/dielectric interfaces, and has direct impact on spin dependent tunneling for Fe/MgO/Fe(001) TMR junctions. We have evidence for the formation of an interfacial FeO-like layer between the Fe substrate and the MgO barrier. Thus far, it has been a very common approach in all calculations on TMR junctions to assume an “ideal” interface, i.e., a direct transition of the metal to the insulating barrier. Our analysis shows that this is clearly not the case. Although our results directly deal only with the MgO/Fe(001) interface, it seems plausible that different metal/barrier interfaces are not as ideal as generally assumed. Our results are important for the first principles calculations of Fe/MgO/Fe TMR junctions. These were carried out assuming a simple abrupt MgO/Fe(001) interface [14]. They showed that the symmetry of the majority and the minority states and the interface states of the minority electrons dominate the TMR. The minority interface states are expected to be strongly altered by any modification of the interface; consequently, the spin dependent tunneling might be significantly changed as compared to that in an ideal interface. Preliminary calculations of Zhang *et al.* [25] using our structure model (but with a complete O-interface layer) are in favor of this assumption. A (more realistic) TMR of only 76% is found for $T = 0$ K instead of several 1000% without the FeO layer.

Moreover, our results support recent mass-spectroscopic and thermodynamic analyses by Vassent *et al.* [10]. In the beam incident on the Fe(001) surface, only Mg and atomic O was found, whereas MgO and O₂ molecules are almost absent. The authors conclude that there is an excess of atomic O over Mg, which favors oxidation of the Fe(001) surface during the first stages of growth. This is in agreement with our deposition time dependent SXRD analyses indicating that the oxidation of the Fe(001) surface takes place at the very beginning (total MgO coverage $\Theta \ll 1$ ML) of the MgO deposition process [17].

Finally, our structure analysis points to a new direction for improving the Fe/MgO/Fe junction. Thus, far, it has been difficult to prepare smooth Fe layers on top of the MgO barrier which is due to the different surface-free energies [11,13]. Based on the results of this work, it appears tempting to introduce an FeO layer at the top electrode interface, MgO/Fe, creating a “mirror image” of the bottom electrode interface. We may speculate that, in this way, a smoother Fe-top electrode layer may be achieved.

In summary, we have carried out a detailed x-ray structure investigation of the MgO/Fe(001) interface. Our analysis gives direct evidence for the presence of an FeO interface layer between the Fe electrode and the MgO barrier. Our results provide new information for the deeper understanding of the TMR effect and are important, in general, for the electron transport involving metal/oxide barriers.

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