Evidence for Ferromagnetic Order at the FeO(111) Surface

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By using spin-polarized secondary electron spectroscopy, we have found that the surface of FeO(111) prepared by oxidation of Fe(110) is ferromagnetically ordered above the bulk Néel temperature of 198 K. A possible cause of the ordering is the reconstruction of a polar FeO(111) surface to reduce electrostatic surface energy. [S0031-9007(96)01477-9]

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The surface of a magnetic material generally shows a magnetism different from that of the bulk because the translational symmetry is broken at the surface. In the last two decades, extensive experimental and theoretical studies of the surface of 3*d* transition metals have revealed interesting phenomena such as the higher surface Néel temperature of chromium [1], the ferromagnetic order at the surface of paramagnetic vanadium [2], and the enhanced surface magnetic moment of 3*d* ferromagnets [3]. For 3*d* metal oxides, in contrast, there are comparatively few studies of the surface magnetism. Namikawa, using the surface barrier resonance in low-energy electron diffraction, found that the magnetic moment at the surface of antiferromagnetic NiO decreases faster with increasing temperature than that of the bulk [4]. Similar behavior was also found, using Mössbauer spectroscopy, for ferromagnetic γ-Fe_2O_3 by Ochi *et al.* [5] and for antiferromagnetic α-Fe_2O_3 by Shinjo *et al.* [6]. This behavior is explained by the smaller exchange field due to the smaller number of neighboring magnetic ions at the surface. FeO is an antiferromagnetic material with the Néel temperature of 198 K. In this Letter we report results of our investigation of the ferromagnetic order at the surface of a paramagnetic FeO(111) film formed on an Fe(110).

The experimental apparatus used in this experiment was described elsewhere [7]. An Fe(110) sample was mounted on a horseshoe-shaped electromagnet in order to orient its magnetization in the [001] or [00$\bar{1}$] direction. The sample was cleaned by 4 keV Ar ion bombardment followed by flash heating to 860 K. The surface cleanliness and crystallinity were evaluated by Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED). After this cleaning, AES did not reveal the presence of contamination, and LEED showed crystalline order. An oxide layer was formed by keeping clean samples at 570 K, while exposing them to an oxygen atmosphere of 1.0×10^{-6} Torr for 3600 sec. All the oxidized samples except one were prepared by this method. That sample was prepared by exposing a clean Fe(110) at 470 K to an oxygen atmosphere of 7.5×10^{-7} Torr for 3500 sec. Leibbrandt *et al.* reported that the oxide layer thus prepared is 40 Å-thick FeO [8], so we used this sample as a reference to determine the oxide layer thickness of other samples. The composition of thin oxide films on iron has been reported to be either FeO, Fe_2O_3, or Fe_3O_4, depending on substrate orientation, preparation temperature, and analysis technique [9]. It is well established, however, that the oxide layer formed when an Fe(110) is exposed to oxygen at a temperature higher than 470 K is FeO(111) [10,11]. Thus the oxide films obtained in this work are expected to be FeO(111). After samples were exposed to oxygen, they were cooled to 370 K by using a liquid nitrogen reservoir. Each sample was then irradiated with a 2 keV electron beam and the secondary electrons emitted were directed through a CMA-type energy analyzer to a Mott detector for measuring polarization as a function of secondary energy. The resolution of the energy analyzer was about 0.7 eV. The depth dependencies of composition and magnetization were studied by measuring the polarization and the AES spectra during 4 keV Ar ion sputtering. To cancel the offset polarization of a few percent, we measured the polarizations P_+ and P_- for magnetizations in the [001] and [00$\bar{1}$] directions and obtained the final polarization P as $P = (P_+ - P_-)/2$. The AES spectra in this experiment were all obtained with a primary electron energy of 3 keV. The vacuum pressure in the sample chamber was initially 5×10^{-10} Torr, but it increased after several oxidation processes and reached 2×10^{-9} Torr when the experiment was concluded.

Figure 1 shows secondary polarizations as a function of secondary energy for the clean Fe(110) surface and for an oxidized sample. Also shown are the LEED patterns. The clean Fe(110) shows a typical bcc(110) surface pattern. Its polarization spectrum is similar to that observed by Kirschner and Koike [12]: The spectrum is characterized by a peak at 2 eV and a shoulder near 17 eV. The oxidized surface shows a hexagonal $p(2 \times 2)$ pattern indicating that the surface is a reconstructed FeO(111). This kind of LEED pattern was also observed by Cappus *et al.* [11]. The polarizations, surprisingly, were negative for all energies between 0 and 19 eV. This means that the surface layer of FeO(111) is ferromagnetically ordered with magnetization probably antiparallel to that of the underlying Fe substrate.

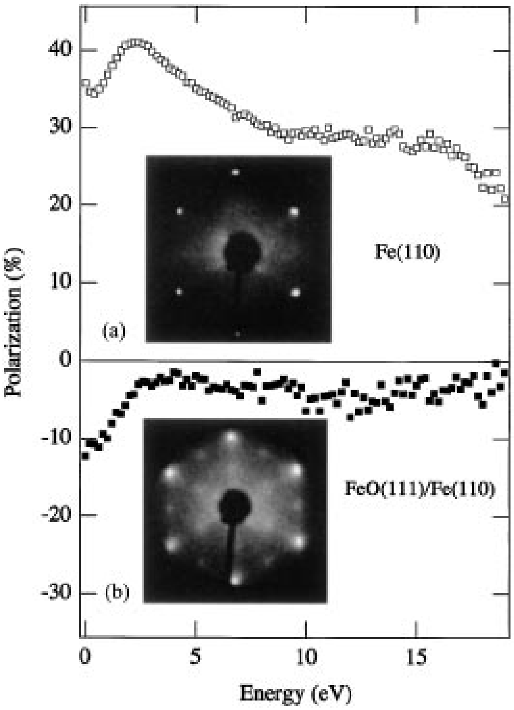

FIG. 1. Secondary polarizations as a function of secondary energy for (a) clean Fe(110) and (b) Fe(110) oxidized at 570 K in 1×10^{-6} Torr oxygen for 3600 sec. The LEED patterns shown in (a) and (b) were obtained at primary electron beam energy of 93 and 60 eV, respectively.

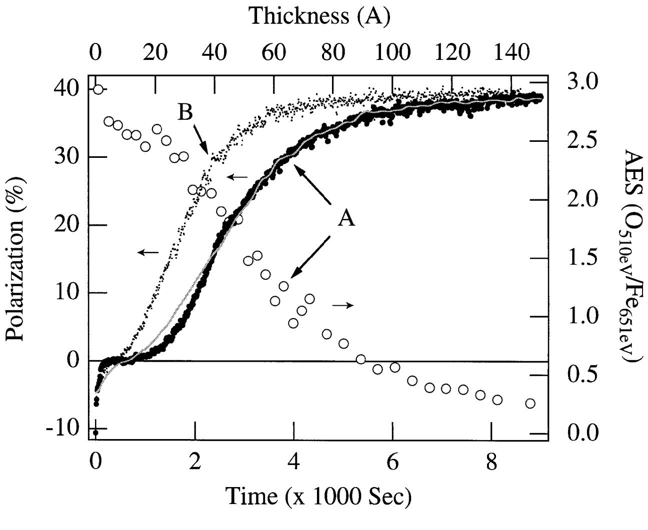

FIG. 2. The sputtering time dependency of a polarization of secondary electrons with 0 eV energy for an Fe(110) sample oxidized at 570 K in 1×10^{-6} Torr oxygen for 3600 sec (*A*) and for the reference sample (*B*). The sputtering was done with a 4 keV Ar ion beam. Also shown (open circles) is the Auger peak ratio of $O(KLL)/Fe(L_{23}M_{23}M_{45})$ for the former sample obtained with a primary electron energy of 3 keV. The scale of the top axis has an uncertainty of ±20%.

Figure 2 shows, for another oxidized sample, the sputtering time dependency of a secondary polarization at 0 eV energy and of the AES peak ratio $O(KLL)/Fe(L_{23}M_{23}M_{45})$. Also shown is the secondary polarization for the oxidized reference sample obtained under the same sputtering condition. By comparing the polarization data for these samples, we can roughly determine the thickness of the oxide layer of the experimental sample. Since polarization data for that sample is located to the right of that of the reference sample in Fig. 2, the oxide layer thickness of the experimental sample must be greater than 40 Å. A smoothed replotting of the same data shown by the dots in Fig. 2 but with the time scale expanded by a factor of 1.54 is shown by the gray line superimposed on the filled circles. The agreement of these two kinds of data is fairly good. Considering the nonzero probing depth of polarized secondaries, the agreement indicates that the oxide layer thickness of the experimental sample is at most $40 \times 1.54 = 62$ Å. Thus the oxide layer thickness has been determined to be 51 ± 11 Å. The polarization for the experimental sample, initially 12.0%, decreases drastically to 0% within 140 sec, remains at 0% for about 600 sec, and then becomes positive. The drastic disappearance of polarization at the beginning of sputtering is due to the removal of surface layer together with destruction of surface crystallinity, and it indicates that the ferromagnetic layer is localized at the surface region. The AES peak ratio first decreases slowly and later fast, with a shoulder near 1800 sec. The average AES peak ratio during the initial slow decrease is 2.6. Since the ratio of the sensitivity of the $O(KLL)$ to that of the $Fe(L_{23}M_{23}M_{45})$ is 2.6 for the 3 keV primary electrons [13], the AES peak ratio of 2.6 confirms that the oxide in this thickness region is FeO. The polarization begins to become positive before the shoulder in the AES peak ratio. This indicates that the probing depth of the polarization is larger than that of the AES signal. VanZandt and Browning, in fact, reported that the escape depth of spin-polarized secondary electrons for an iron oxide is 20–30 Å [14], which is greater than the AES probing depth of about 10 Å [15,16]. As shown later, the crystallinity is destroyed to a depth of only a few monolayers by sputtering. The polarized secondary electrons, with a probing depth of 20–30 Å, should also reflect the magnetization of the oxide layer with good crystallinity below the destroyed oxide layer. Thus the zero polarization observed during the sputtering is more evidence that the oxide is not γ-Fe_2O_3 or Fe_3O_4 at that depth, since these oxides are ferromagnetic. The relation between the sputtering time and depth can be found as follows. According to the study of FeO/Fe by Leibbrandt *et al.* [17], the shoulder of AES peak ratio during the sputtering appears around 20 Å in advance to the real interface between FeO and Fe due to the 10 Å probing depth of the AES signal. Since the shoulder for our experimental sample appears near 1800 sec, the interface locates near 3000 sec. This reasoning was used to create the depth scale on the top of the graph in Fig. 2. It has an uncertainty of ±20%, however, because of the uncertainty of the oxide layer thickness of the experimental sample. By using this depth scale and the initial negative polarization period, we can determine the thickness of the surface ferromagnetic layer of the experimental sample to be 2.4 ± 0.5 Å. Since, in the [111] direction of FeO, O and Fe layers are alternately stacked with a period of 2.5 Å, the ferromagnetic layer thickness corresponds to about two layers of O and Fe.

To get additional evidence for the localization of the surface ferromagnetic layer, we made another experiment. The secondary polarizations, LEED pattern observed at 60 eV, and AES spectra of oxidized samples with different surface crystallinity are shown in Fig. 3. The sample for Fig. 3(a) was prepared by sputtering an oxidized sample with 5 keV Ar ions until the polarization of 0 eV secondary electrons became zero. The sample for Fig. 3(b) was the same sample after flash heating to 820 K. As is seen in Fig. 3(a), after the sputtering, the polarizations are 0% for all the observed energies between 0 and 19 eV. The LEED pattern becomes diffuse but a hexagonal pattern is still visible. Since the inelastic mean free path of 60 eV electrons is a few Å [15], the diffuse LEED pattern indicates that the crystallinity is destroyed for a distance corresponding to only a few monolayers from the surface. The LEED pattern obtained after the heating is sharper and the polarization spectrum once again resembles that shown in Fig. 1. The AES spectrum after heating, however, is almost identical to the one obtained before heating. Considering these LEED and AES results, we can see that appearance of negative polarization in Fig. 3(b) is mainly due to recrystallization of a few monolayers near the surface and that ferromagnetism is restricted to these layers. The results in Fig. 3 show that this ferromagnetism is not due to the chemisorbed excess (nonequilibrium) oxygen atoms, because the sputtering would have removed these atoms. To confirm that excess oxygen atoms are not the cause of this surface ferromagnetism, we heated another experimental sample for 15 min at 870 K and for 5 min at 920 K. Since in the process of oxidation Fe atoms are supplied to surface through an oxide layer [17], any excess surface oxygen atoms should fall into an equilibrium state by being connected to these Fe atoms. The energy distribution and sputter depth profile of polarization for this sample, however, are almost the same as those shown in Figs. 1 and 2. This confirms that the surface ferromagnetic layer is inherent in the equilibrium FeO surface.

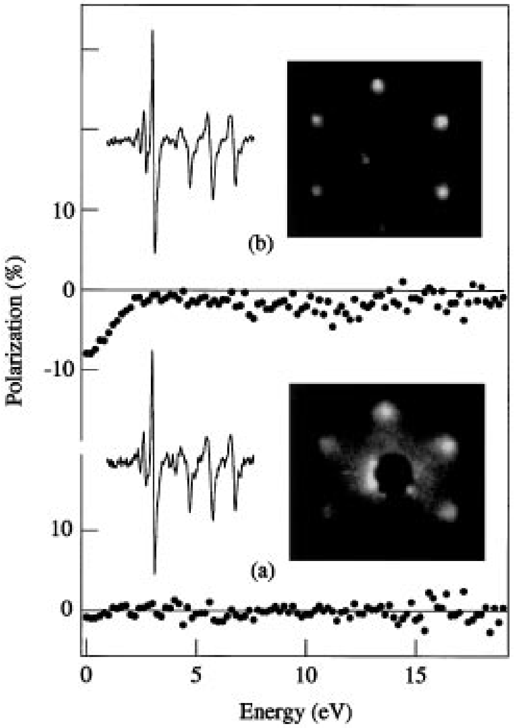

FIG. 3. Secondary polarizations, LEED pattern, and AES spectra of oxidized Fe(110) sample (a) after Ar ion sputtering and (b) after successive flash heating to 820 K.

The (111) surface of a NaCl structure such as FeO(111) is a polar surface. Wolf proposed that such a surface reconstructs to reduce surface energy by reducing surface dipole moments [18]. The $p(2 \times 2)$ LEED pattern observed in Fig. 1 and by Cappus *et al.* [11] for FeO(111) confirms that the reconstruction occurs. A similar $p(2 \times 2)$ LEED pattern was also observed for NiO(111) by Rohr *et al.* [19] and by Ventrice *et al.* [20]. The latter authors observed the real space structure of the reconstructed surface by STM. The structure is an octopolar reconstruction, where three of four O (or Fe) atoms of the top layer and one of four O (or Fe) atoms of the second layer are removed. Although it is obvious from the LEED pattern that the FeO(111) surface reconstructs, the actual structure has not yet been identified. We therefore consider a possibility of ferromagnetic order for octopolar reconstruction with O atoms in the top layer. Here we assume that, below the Néel temperature, the Fe magnetic moments in the Fe layer parallel to the FeO(111) surface are ordered ferromagnetically and that the magnetic moments of each Fe layer are ordered antiferromagnetically along the [111] direction. The latter order is due to the superexchange interaction via O atoms. If we denote the positions of two Fe atoms as ζ and Ψ and denote the positions of one O atom as ξ, the magnitude and sign of the superexchange energy J depends on the angle $\phi = \angle \xi \Psi \zeta$, and $J = J_-$ is negative for $\phi = \pi$ and $J = J_+$ is positive for $\phi = \pi/2$ [21]. For the bulk Fe layer, the total superexchange energy J_B for orienting the magnetic moment of an Fe atom is given by $J_B = 6J_- + 12J_+ - 12J_+ = 6J_-$, where the first term of the middle expression is the antiferromagnetic interaction between neighboring Fe layers, the second term is the ferromagnetic interaction within an Fe layer, and the third term is the ferromagnetic interaction between neighboring Fe layers. The first and second terms tend to orient the magnetic moment in one direction, whereas the third term tends to orient it in the opposite direction. Similarly, for the first Fe layer from the surface of the octopolar reconstruction with a layer of O atoms on top, the total superexchange energy J_S for orienting the magnetic moment of an Fe atom is given by $J_S = 6J_+ - 6J_+ + 3J_- = 3J_-$. Since $J_S < J_B$, the surface ferromagnetic order cannot persist above the Néel temperature of the bulk. Unlike what happens in NiO, where Ni atoms ionize only to Ni^{2+}, Fe atoms in iron oxides ionize to Fe^{2+} and Fe^{3+}, forming stable iron oxides such as FeO, Fe_3O_4, γ-Fe_2O_3, and α-Fe_2O_3. Thus it is plausible that the FeO(111) surface reconstructs in a way different from the octopolar reconstruction of NiO(111). Weiss *et al.* studied the surface structure of Fe_3O_4(111) by LEED and found that the surface has a kind of reconstruction, in which three of four Fe atoms at tetrahedral positions in the top layer are removed and O atoms in the second layer largely relax probably because of surface electrostatic force [22]. In the [111] direction of Fe_3O_4, the layer stacking repeats the unit of Fe_T/O/Fe/O/, where Fe_T represents a layer composed of Fe atoms in tetrahedral positions, and the O and Fe without subscripts represent, respectively, layers composed of O and Fe atoms at octahedral positions. In the [111] direction of FeO, on the other hand, the stacking repeats the unit of Fe/O/, or Fe/O/Fe/O/ for easy comparison with Fe_3O_4. The stackings of FeO and Fe_3O_4 differ in only one of the four layers. Thus it is not unrealistic that, for example, the top two layers reconstruct like those of Fe_3O_4, since the structure of the top four layers in this case is the same for FeO(111) and Fe_3O_4(111). In this case, it is possible that the surface reconstructed layer is ordered ferromagnetically, since Fe_3O_4 is ferromagnetic. With regard to the actual structure, however, we do not have a convincing model at present.

Generally the polarization of secondary electrons reflects the polarization of the valence band [23,24]. Thus the negative secondary polarizations observed in this experiment probably indicate that the magnetization at the surface is antiparallel to that of the underlying Fe(110). We cannot, however, exclude the slight possibility that these magnetizations are parallel and that the secondary polarization is antiparallel to the valence band polarization of the ferromagnetic surface. This antiparallel polarization might be due to polarization of the empty band above the vacuum level of the surface ferromagnetic layer [25], or to spin dependent scattering of secondary electrons [24,26]. However, we do not know of any reports showing this antiparallel polarization for a secondary energy range as wide as 0–19 eV. In any case, since the secondary polarization follows the inversion of Fe substrate magnetization during the data acquisition, there should be magnetic interaction between the surface ferromagnetic layer and the Fe substrate. One candidate for this interaction is the Ruderman-Kittel-Kasuya-Yosida (RKKY)-like interaction acting through the paramagnetic FeO layer. This RKKY-like interaction is observed for a lot of nonmag/mag multilayered films that have a giant magnetoresistance [27].

In conclusion, we have found evidence that the surface of FeO(111) prepared by oxidation of Fe(110) is ferromagnetically ordered above the bulk Néel temperature of 198 K. This ordering may be due to reconstruction of a polar FeO(111) surface to reduce the high electrostatic surface energy.

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