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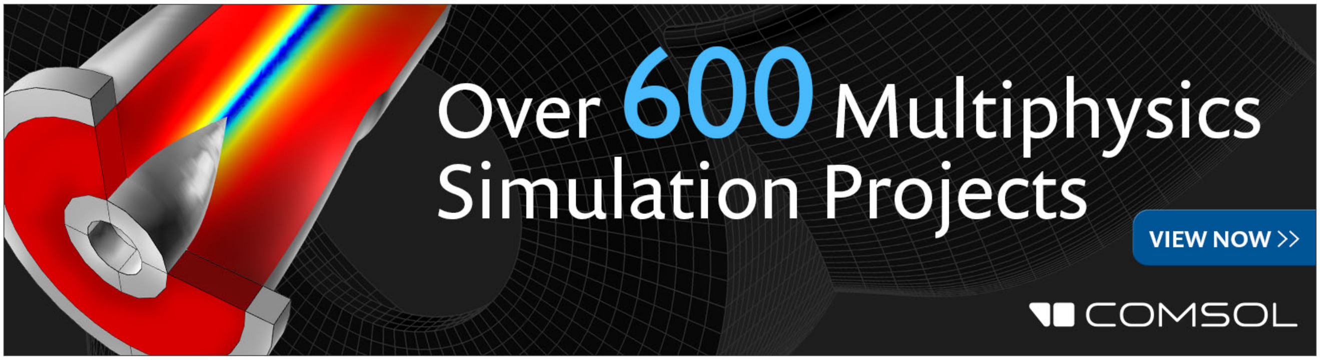

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Chemical structure of the interface between MgO films and Fe(001)

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The chemical structure of the interface formed during MgO growth on Fe(001) is studied by vibration spectroscopy employing a high resolution electron energy loss spectrometer. We find direct, spectroscopic evidence for the formation of FeO layer at the interface that is triggered by the dissociation of oxygen molecule by deposited Mg. Even though the growth conditions of MgO are widely varied, FeO cannot be eradicated at the interface. Hence, we propose that the phase where FeO and MgO coexist at the interface, is an entropically stabilized one in regards to the very small difference between the bond dissociation energy of FeO and that of MgO. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1538311]

The tunneling magnetoresistance (TMR) through magnetic tunnel junctions (MTJs)[1] has been explored extensively, especially for the application of MTJs as memory cells for nonvolatile magnetic random access memory. Currently, the growth techniques of MTJs are well developed for their practical applications. However, microscopic understanding of the TMR is still primitive. Recently, as a model MTJ, crystalline Fe/MgO/Fe(001) system has drawn attention. Because MgO film is found to grow epitaxially on Fe(001) for its thickness up to 7 monolayer (ML).[2] Its ballistic tunneling behavior[3] and atomic structure have also been studied.[4] For the ideal, crystalline MTJs with abrupt interface between MgO and Fe, the TMR values are predicted to be as high as ~2000%.[5] Zhang and Butler,[6] however, contend that the TMR value is severely reduced to be 76%, e.g., for a single crystalline MTJ with a FeO layer formed at the interface, Fe/MgO/1 ML FeO/Fe(001). It implies that if the Fe substrate is oxidized concurrently during MgO deposition as suggested by surface x-ray diffraction (SXRD) experiment,[4] such severe reduction of the TMR value is expected. A recent experiment with a single crystalline MTJ, Fe(001)/MgO/FeCo,[7] shows the TMR value only of 60% at 30 K that is very similar to the abovementioned theoretical value, 76%, and strongly suggestive of the formation of inhomogeneous interface. In regards to the strong influence of the interface to the spin-dependent tunneling behavior, we investigated the chemical structure and growth kinetics of the MgO–Fe interface by vibration spectroscopy and found direct evidence for the formation of FeO at the interface. The present work would also deepen the understanding on the spin-injection process via tunneling[8] and be helpful for the optimized growth of the tunneling barrier.

All the experiments were performed in an ultrahigh vacuum chamber with its base pressure, low 10^{-11} Torr. The substrate was cleaned by cycles of Ar^+ ion sputtering at 2.0 keV and subsequent annealing at 820 K. The cleanliness of the sample was checked by vibration spectroscopy with a commercial (LK-2000) high resolution electron energy loss spectrometer (HREELS), and no vibration peaks characteristic to the likely contaminants such as O, C, S were detected. MgO film was deposited by reactive oxidation: Mg was thermally evaporated in a chamber backfilled with oxygen molecules whose partial pressure was 2×10^{-8} Torr. The thickness of the MgO film was determined from the Auger intensity (I) ratios of I (Mg, 1174 eV) to I (Fe, 651 eV) and I (O, 503 eV) to I (Fe, 651 eV), assuming layer-by-layer growth of the MgO film as observed by Klaua *et al.*[2] Auger spectra were taken by using a cylindrical mirror analyzer-based spectrometer. The deposition rate was around 7–8 ML per minute as monitored by a quartz microbalance calibrated by an Auger electron spectrometer (AES). Since we were not sure whether the MgO films were stoichiometric, the coverage determined by AES would be a *nominal* one which served to estimate the amount of deposited MgO. The long range order of the MgO films was checked by well defined $p(1\times1)$ LEED pattern with low background intensity and sharp spots on visual inspection. The chemical structure of the films was investigated by HREELS. All the vibration spectra were taken in specular geometry with the samples at room temperature. The resolution of the HREELS determined by the full width at half maximum of the elastic peak, was around 5 meV.

Since we grow MgO by exposing the Fe(001) to the ambient oxygen molecules, we first test whether they spontaneously form FeO on the Fe substrate at room temperature. For that purpose, we expose the Fe substrate at room temperature for more than 10 min to the backfilled oxygen of its partial pressure, 2×10^{-8} Torr, and find no oxygen related

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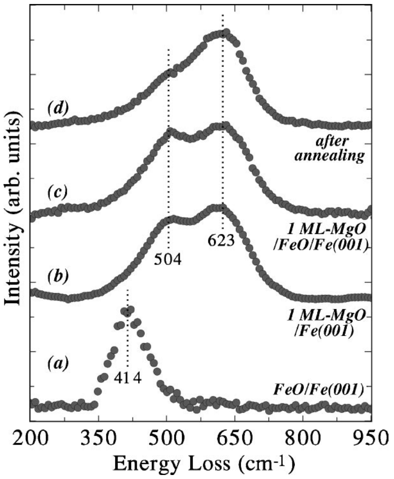

FIG. 1. (a) O–Fe stretching mode of FeO on Fe(001); (b) vibrational loss spectrum for 1 ML MgO film deposited on Fe(001); (c) vibrational loss spectrum for 1 ML MgO on 1 ML FeO-precovered Fe(001); (d) spectrum after annealing the sample in (c) at 770 K for 20 min. All the spectra were taken in specular geometry with the incident angle of the electron beam was 60° from the surface normal. The primary electron energy was 11 eV.

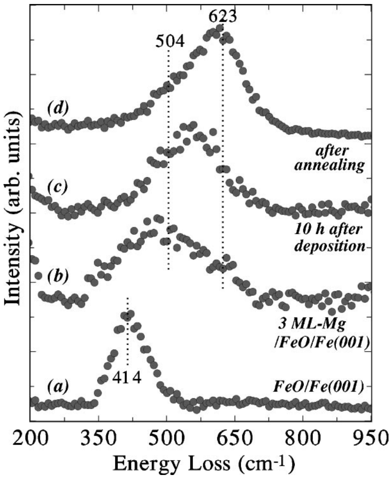

FIG. 2. (a) O–Fe stretching mode of FeO on Fe(001); (b) vibrational loss spectrum for 3 ML Mg deposited on FeO precovered Fe(001); (c) 10 h after depositing 3 ML Mg; (d) vibrational loss spectrum after annealing the sample in (c) at 770 K for 20 min. All the spectra were taken in specular geometry with the incident angle of the electron beam was 60° from the surface normal. The primary electron energy was 11 eV.

vibration loss peak. It shows that the ambient oxygen molecules are so stable that no detectable amount of oxygen adsorption to Fe(001) occurs at room temperature. When we repeat the same experiment with the substrate at 770 K, we can find the oxygen on the surface by both AES and vibration spectroscopy. Figure 1(a) shows the vibration loss peak associated with the O–Fe stretching around 414 cm^{-1} as previously found near the present loss energy by Lu *et al.*[9]

Since the backfilled oxygen molecules of 1×10^{-8} Torr, do not form FeO on Fe(001) at room temperature, we grow MgO film by the reactive oxidation method, keeping the same oxygen partial pressure with the substrate at room temperature. Figure 1(b) shows the vibration loss spectra for nominal 1 ML thick MgO film grown on Fe(001) at room temperature. Two peaks are found around 504 and 623 cm^{-1}. The peak position of the two peaks are determined by fitting the loss spectrum with two Gaussian peaks after subtracting linear background. The error limit of the loss energy is ± 7 cm^{-1} as estimated from both statistical fluctuation and uncertainties in curve fitting. Relative intensity of the latter peak to the former grows as the thickness of the MgO film increases. Hence, the latter peak is expected to originate from the MgO film. Furthermore, the loss energy of the latter peak is similar to that for the surface optical phonon or Fuchs–Kliewer mode of *bulk* MgO, 651 cm^{-1}.[10] Hence, we assign it to the Fuchs–Kliewer mode of the strained, ultrathin MgO film on Fe(001). The other loss peak at 504 cm^{-1} in Fig. 1(b) may originate from the FeO formed at the interface concomitantly with MgO film as suggested by Meyerheim *et al.*[4] To examine the idea, we grow 1 ML FeO on Fe(001) following the recipe as previously mentioned and then deposit 1 ML MgO on the top. Corresponding loss spectrum is shown in Fig. 1(c) and looks very similar to Fig. 1(b); There are two loss peaks and their peak positions are coincident with those in Fig. 1(b) within the error limit, ± 7 cm^{-1}. Then, the peak with its loss energy, ~ 504 cm^{-1} is considered to be the stretching mode of FeO under the influence of the MgO overlayer. According to above peak assignment, the present spectroscopic work offers a direct evidence for the FeO formation on Fe(001) during MgO growth through reactive oxidation.

Since the FeO does not form on Fe(001) at room temperature just by the ambient oxygen molecules of 2×10^{-8} Torr, the present observation of FeO layer formed at the interface during reactive oxidation shows that Mg should play a catalytic role to promote the oxidation of Fe substrate. Since Mg(O) is very electropositive (negative), thermally evaporated Mg atoms bond to oxygen molecules by donating their electrons to the antibonding molecular orbital, $5\sigma^*$ of the oxygen molecules, and induce the dissociation of the oxygen molecules releasing MgO molecules and oxygen atoms. Then, the oxygen atoms react readily not only with other Mg atoms, but also with the Fe substrate to form FeO at the interface.

Since the inhomogeneous interface is not desirable as a model system and also degrades the TMR value of MTJ severely,[5] measures to form sharp interface should be conceived. There appears to be a probable solution to remove the FeO layer at the interface, when we look into the thermodynamic behavior of the film. Comparing Fig. 1(c) with Fig. 1(d), we find that after annealing 1 ML MgO/1 ML FeO/Fe(001) at 770 K for 20 min, the loss peak associated with the MgO is strongly enhanced in sacrifice of the FeO peak. It can be viewed as the transfer of oxygen from FeO to unoxidized Mg atoms in the MgO film to form MgO molecules. (It implies that the oxygen partial pressure, 2×10^{-8} Torr, is not enough to fully oxidize the deposited Mg, and there is unoxidized Mg in the MgO film.) It hints that if we supply enough unoxidized Mg atoms to take the oxygen from FeO, then FeO-free interface would form.

To examine the abovementioned idea, we initially form 1 ML thick FeO layer on Fe(001) [Fig. 2(a)], then, 3 ML thick Mg film is deposited on the FeO covered surface at room temperature *without backfilling the chamber with oxygen*. Figure 2(b) shows a very broad peak with its centroid slightly below 500 cm^{-1}. Since it is so broad, it seems to be composed of many different peaks, possibly originating from pristine FeO layer, Mg covered FeO layer, and MgO overlayer. As we leave the system for 10 h at room temperature, the centroid of the loss peak shifts to the higher energy with narrowed width, implying that the contribution from MgO gradually increases and that of pristine FeO decreases [Fig. 2(c)]. It shows that the oxygen transfer from FeO to Mg seems to be a very efficient process even at room temperature. After annealing the sample at 770 K for 20 min, the MgO derived peak becomes dominant at the expense of the FeO peak [Fig. 2(d)]. (All the measurements are made after the sample is cooled down to room temperature.) However, the FeO peak still remains as a shoulder near 500 cm^{-1} loss energy. Even when the annealing temperature is raised up to 870 K, the loss spectrum changes little from Fig. 2(d). We do not think that the remnant FeO originates from the insufficient annealing temperature or time because the oxygen transfer from FeO to Mg is such an efficient process. Rather, the coexistence of the FeO and MgO at the interface seems to be thermodynamically driven on the following grounds; The bond dissociation energies of MgO and FeO are very close, 394 and 409 kJ per mole, respectively.[11] In the strained ultrathin MgO film, the formation energy of MgO becomes larger than that for FeO, as evidenced by the dominant MgO loss peak after annealing the sample [Fig. 2(d)]. If the difference of their formation energies is still so small that the entropic contribution to the interface free energy is not negligible, then, the coexistence of FeO and MgO at the interface is thermodynamically favored to the FeO-free interface. This argument is consistent with our observation of similar relative intensity of the FeO peak irrespective of the sample annealing temperatures from 470 to 870 K. (All the loss spectra are taken at room temperature.)

In summary, vibration spectroscopy of MgO films on Fe(001) reveals that the interface between MgO and Fe(001) is inhomogeneous due to the concomitant growth of FeO at the interface. Although the population of the FeO can be minimized through reduction of FeO by unoxidized Mg, it cannot be removed from the interface. We propose that the inhomogeneous interface is stabilized by the entropic contribution to the interface free energy.

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