Effects of hydrogenation on structure and magnetic properties of Fe/La multilayers

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Received 29 August 2003; revised 29 September 2003; accepted 16 October 2003

Abstract
We have studied the effects of hydrogenation on structure and magnetic properties of Fe (3.0 nm)/La (t nm) multilayers at the range of La layer thickness (t) from 0.3 to 4.2 nm. The effects of hydrogenation are the following. (a) All multilayers become a well-defined layered structure. (b) The bilayer thickness (L) becomes larger by a lattice expansion of only La layer. (c) The saturation magnetization ($M_s$) of the multilayers becomes larger. The increment of ($M_s$) is caused by the disproportionation of the Fe–La mixing layer to the pure Fe layer at the Fe/La interface. (d) The remanence ratio ($M_r/M_s$) and the saturation field ($H_s$) reflecting coupling state between the adjacent Fe layers change with increasing La layer thickness: the coupling state changes from a ferromagnetic (FM) state to a non-coupled (NC) state. This changing manner is the same, but the thickness range of spacer layer for FM coupling expands from 1.5 to 1.8 nm. This expansion of the thickness range is due to the change of interface structure and electronic structure caused by La-hydride formation.

Keywords: Hydrogenation; Fe/La multilayer; Interlayer exchange coupling; Ferromagnetic coupling; Fe–La mixing layer; La-hydride layer

1. Introduction
Since the rare-earth metal (REM) absorbs hydrogen easily [1], multilayers composed of the REM and magnetic transition metal (TM) have been expected to change on magnetic properties and structure before and after hydrogenation. Actually, in the previous work, we have reported the effect of hydrogenation on structure and magnetic properties of Fe (1.5 nm)/La (t nm) multilayers [2]. For example, the saturation magnetization of Fe/La multilayers is enhanced by hydrogenation. However, the interlayer exchange coupling, which is an important magnetic phenomenon [3,4], could not be observed because the 1.5-nm-thick Fe layer has an amorphous structure. The interlayer exchange coupling is expected to occur in case the Fe layers are crystalline and have the bcc structure. According to the previous work [2], Fe layer have bcc structure when the Fe thickness is thicker than 2.5 nm. Thus we choose thickness of 3.0 nm for Fe layer and we have investigated the effects of hydrogenation on structure and magnetic properties of Fe (3.0 nm)/La (t nm) multilayers as a function of La layer thickness (t) in detail, including the interlayer exchange coupling.

2. Experimental procedure
A series of Fe/La multilayers were prepared at room temperature (RT) by a UHV-dc magnetron sputtering system onto glass and surface oxidized Si (100) substrates covered with 4-nm-thick La buffer layer. The base pressure of the system was better than 4 \times 10^{-7} \text{ Pa} and the Ar pressure during sputtering was 3.4 \times 10^{-1} \text{ Pa}. The typical deposition rates for Fe and La layers were 0.06 and 0.30 nm/s, respectively. The Fe layer thickness in the multilayers was fixed at 3.0 nm and the nominal La layer thickness was varied from 0.40–4.0 nm, with 20 bilayers. All of these specimens were covered with a 10-nm-thick Pd layer in order to protect oxidation and to ensure introduction of hydrogen.
Hydrogenation was performed by keeping the deposited multilayers for 60 h at 0.1 MPa in RT hydrogen atmosphere. The electrical resistivity was measured during the hydrogenation by conventional four-point constant current technique in order to observe the degree of hydrogenation. The bilayer thickness and crystallographic structure of Fe/La multilayers before and after hydrogenation were characterized by both low- and high-angle X-ray diffraction (XRD) using Cu Kα radiation. The bilayer thickness \( (L) \) of the multilayers was evaluated by the kinematical Bragg’s law \( L = \lambda \theta / 2 \) for the \( l \)th order reflection. Here, \( \lambda \) is the X-ray wavelength and \( \theta \) is the observed diffraction angle. Since the lower order reflections are seriously influenced by the refraction effect, we accurately determined the true bilayer thickness for the higher order reflection [5]. The magnetic properties of the Fe/La multilayers before and after hydrogenation were investigated by a vibrating sample magnetometer (VSM). The magnetic field was applied along the in-plane direction of the films with a maximum field of 18 kOe at RT. Ferromagnetic resonance (FMR) measurements were carried out with an electronic paramagnetic resonance spectrometer operating at the frequency of 9.4 GHz in order to confirm and evaluate the interlayer exchange coupling in the multilayers before and after hydrogenation. The evaluation of the interlayer exchange coupling by FMR measurements followed Ref. [6–8]. The coupling state of the multilayers before and after hydrogenation can be confirmed by the sign of \( J_1 \); namely, the ferromagnetic (FM) state for \( J_1 > 0 \) and antiferromagnetic (AFM) state for \( J_1 < 0 \).

3. Results and discussion

Low-angle XRD profiles for the as-deposited and hydrogenated \([\text{Fe} (3.0 \, \text{nm})/\text{La} (3.0 \, \text{nm})]_{20}\) multilayers are shown in Fig. 1. Bragg peaks resulting from an artificial periodicity are observed up to the sixth and the seventh order for as-deposited and hydrogenated Fe/La multilayers, respectively. In each profile, the broad peaks between Bragg peaks are attributed to a 10-nm-thick Pd layer. From these results, it is apparent that the specimen possesses a well-defined multilayer structure before and after hydrogenation. The position of each observed Bragg peak shifts to the lower side of diffraction angle after hydrogenation. This means that a lattice expansion occurs in the direction perpendicular to the film plane by hydrogenation. Moreover, each Bragg peak also becomes sharper after hydrogenation. These same phenomena can be observed in other Fe/La multilayers with various La layer thickness, and is coincident with those of Co/La, Fe/Y and Fe/Gd multilayers as reported in Ref. [2].

The bilayer thickness determined from the positions of Bragg peaks is shown in Fig. 2. It increases linearly with the spacer layer thickness for the as-deposited and hydrogenated Fe/La multilayers. The increment of the bilayer thickness with increase of the spacer layer thickness is larger after hydrogenation than before hydrogenation. This means that a lattice expansion occurs mainly in the La layer. From the difference of the bilayer thickness before and after hydrogenation, the average value of the expansion ratio relative to the La layer thickness can be evaluated, and is found to reach 16%. This value is equal to that of \([\text{Fe} (1.5 \, \text{nm})/\text{La} (t \, \text{nm})]_{20}\) multilayers and is lower than that of Co/La, Fe/Y and Fe/Gd multilayers [2]. The difference can be explained by considering the formation of the mixing layer at the interface, as described in Ref. [2].

High-angle XRD profiles for the as-deposited and hydrogenated \([\text{Fe} (3.0 \, \text{nm})/\text{La} (t \, \text{nm})]_{20}\) multilayers are shown in Fig. 3. In all profiles of the as-deposited Fe/La multilayers (Fig. 3a), Pd (111) and Pd (222) peaks can be observed. This means that Pd (111) planes are oriented...
preferentially in the film plane through all the multilayers. On the other hand, Fe (222), La (0004) and La (0008) peaks appear gradually with increasing La layer thickness. This means that the crystalline orientation of bcc-Fe (111) and hcp-La (0001) planes becomes preferred to the film plane with increasing La layer thickness. It is because the lattice mismatch between bcc-Fe (111) and hcp-La (0001) is small. Even after hydrogenation, Pd (111) and Pd (222) peaks can also be observed in each profile (Fig. 3b), and do not change. This means that Pd layer does not change its structure but it plays as a catalysis for hydrogenation. Each peak of the La layer observed before hydrogenation shifts to the lower sides of diffraction angle by formation of the lanthanum-hydride (LaHx) after hydrogenation. It is found that La layer absorbs hydrogen easily, and that the crystal plane of spacer layer changes from hcp-La (0001) to cubic-LaHx (111). The Fe (222) peak can be recognized even in thin spacer layer of 0.3 nm after hydrogenation although it cannot be done before hydrogenation. The peaks of LaHx are also recognized in a thinner layer after hydrogenation. This is because the lattice mismatch between Fe (111) and LaHx (111) is smaller than that between Fe (111) and La (0001). From these results, the crystal orientations of Fe layer and La spacer layer are found to become better after hydrogenation than before hydrogenation.

In order to learn the state of the Fe/La interface in as-deposited and hydrogenated Fe/La multilayers, we investigated the saturation magnetization \( M_s \) per Fe unit volume at room temperature of the as-deposited and hydrogenated [Fe (3.0 nm)/La (t nm)]\( _{20} \) multilayers. As seen in Fig. 4, \( (M_s)_{Fe} \) decreases monotonically with increasing La layer thickness up to 1.2 nm, and each value is much lower than that of bulk Fe (1707 G) [9]. This reveals that some parts of the adjacent Fe layers are directly connected each other since each La layer become discontinuous state like an island structure. This also indicates that the spacer layer is not consisted of a pure-La layer but is the composed layer of a Fe phase and a Fe–La mixing phase. In the region of La layer thickness more than 1.5 nm, \( (M_s)_{Fe} \) is almost constant and is about 1550 G. This result means that each spacer layer changes from the discontinuous state like an island structure to the continuous state like a layered structure. This result is supported by that of the high-angle XRD, as shown in Fig. 3(a). The slight reduction of \( M_s \) should be attributed to the Fe-La mixing layer formed at the Fe/La interface.

On the other hand, \( (M_s)_{Fe} \) after hydrogenation is independent of spacer layer thickness, and is almost 1600 G. At the range of spacer layer thickness less than 1.5 nm, \( (M_s)_{Fe} \) is much higher after hydrogenation than before hydrogenation. This means that the disproportionation reaction occurs mainly in the La layer. It can be also considered that the Fe–La mixing layer in the La layer almost separates into a pure-Fe layer and a lanthanum-hydride (LaHx) layer after hydrogenation. Furthermore, at the range of spacer layer thickness more than 1.5 nm, \( (M_s)_{Fe} \) slightly becomes higher after hydrogenation than that before hydrogenation. It is because the Fe–La mixing layer at the Fe/La interface separates into a pure-Fe layer and a lanthanum-hydride (LaHx) layer by disproportionation reaction.

In Fig. 5, the remanence ratio \( M_r/M_s \) and the saturation field \( H_s \) are summarized as a function of spacer layer thickness for the as-deposited and hydrogenated Fe/La multilayers. For the as-deposited Fe/La multilayers, \( M_r/M_s \) slightly decreases with increasing La layer thickness up to 1.2 nm, and then rapidly decreases at the range of La layer thickness between 1.2 – 1.5 nm. \( H_s \) is almost 0 with increasing La layer thickness up to 0.9 nm, and then...
drastically increases at the range of La layer thickness between 0.9 – 1.5 nm. In the region of La layer thickness more than 1.5 nm, \( M_r = M_s \) slightly decreases again, and is almost constant at the thickness range of La layer more than 2.7 nm. \( H_s \) is almost constant at the thickness range of La layer more than 1.5 nm. From the behavior of these parameters, it can be considered that the coupling state between the adjacent Fe layers changes from a ferromagnetic (FM) state to a non-coupled (NC) state with increasing La layer thickness.

On the other hand, for the hydrogenated Fe/La multilayers, at the range of spacer layer thickness less than 0.9 nm, \( M_r = M_s \) and \( H_s \) are almost constant, and are about 0.98 and 0 kOe, respectively. At the thickness range of spacer layer between 0.9–1.8 nm, \( M_r = M_s \) and \( H_s \) remarkably change with increasing the spacer layer thickness. Furthermore, for the spacer layer thickness more than 1.8 nm, \( M_r = M_s \) and \( H_s \) are independent of La layer thickness, and are about 0.80 and 0.90 kOe, respectively. The behavior of these parameters suggests that the coupling state does not change from that before hydrogenation. \( H_s \) also becomes lower after hydrogenation than before hydrogenation at the thickness range of spacer layer more than 0.9 nm. These should be attributed to change of both the state of the Fe/La interface and the electronic structure of La layer by hydrogenation.

In order to confirm the coupling state between the adjacent Fe layers in as-deposited and hydrogenated Fe/La multilayers directly, FMR measurements were performed. FMR spectra for the various thickness of the spacer layer in the as-deposited and hydrogenated Fe/La multilayers are shown in Figs. 6 and 7, where spectra for Fe films of 3 and 30 nm thick are shown as a reference. The resonance peak position \( (H_R) \) and the full width of the half maximum (FWHM) of the peak \( (\Delta H_R) \) are estimated by the fitting of the Lorentz function to the integral spectrum of the FMR spectrum. As to the as-deposited Fe/La multilayers (Fig. 6a-c), in the region of the La layer thickness less than 0.6 nm, each FMR spectrum shows a single absorption peak, and each \( H_R \) is almost the same as that of a 30-nm-thick Fe film as a thick film. Furthermore, each \( \Delta H_R \) is much broader than that of a 30-nm-thick Fe film. It is because the adjacent Fe layers are directly connected to each other since the La layer becomes a discontinuous state like an island structure. Therefore, it is found that the interlayer exchange coupling does not exist for the La layer thickness of less than 0.6 nm. At the thickness range of La layer between 0.9 – 1.2 nm, each FMR spectrum shows a single absorption peak, each \( H_R \) is different from that of a 30-nm-thick Fe film, and becomes close to that of a 3-nm-thick Fe film. The observed single absorption peak is derived from an acoustic resonance peak, which can be observed in the magnetic multilayer where the interlayer exchange coupling

![Fig. 5. Change of (a) remanence ratio \((M_r/M_s)\) and (b) saturation field \((H_s)\) with the spacer layer thickness for the as-deposited and hydrogenated \([\text{Fe} (3.0 \text{ nm})/\text{La} (t \text{ nm})]_{20}\) multilayers. Open circles (○) and solid circles (●) show as-deposited and hydrogenated Fe/La multilayers, respectively.](image)

![Fig. 6. (a) FMR spectra for the various La layer thickness \((t)\) in the as-deposited \([\text{Fe} (3.0 \text{ nm})/\text{La} (t \text{ nm})]_{20}\) multilayers. (b) Resonance peak position \((H_R)\) for the various La layer thickness. (c) Full width of the half maximum of the peak \((\Delta H_R)\) for the various La layer thickness. As the comparison, the FMR spectra of 3 and 30 nm thick Fe films are shown.](image)
comparison, the FMR spectra of 3 and 30 nm thick Fe films are shown. However, an optic resonance peak cannot be observed around the acoustic resonance peak. Furthermore, for the spacer layer thickness more than 1.8 nm, each \( H_R \) is nearly equal to that of a 3-nm-thick Fe film, but each FMR spectrum shows an asymmetric single absorption peak. It is because magnetic properties of each Fe layer are non-equivalent. \( M_r/M_s \) and \( H_s \) are also very different from those in a FM coupling state. These results indicate that the coupling state is in a NC state at this thickness range of spacer layer. As mentioned above, for the hydrogenated Fe/La multilayers, the interlayer exchange coupling is found to transfer from a FM state to a NC state as the spacer layer thickness increases. It is also found that the range of spacer layer thickness being in a FM state is extended from 1.5 to 1.8 nm after hydrogenation. This expansion is considered to be due to the change of both the state of the interface and the electronic structure by hydrogenation.

4. Conclusion

The effects of the hydrogenation on structure and magnetic properties of \([\text{Fe (3.0 nm)/La (t nm)}]_{30}\) multilayers have been investigated in detail. The structure and magnetic properties have changed by hydrogenation. As to structure, the improvement of layered structure and the expansion of the lattice occurred. These changes are caused by the disproportionation of the Fe–La mixing layer to the pure Fe layer at the Fe/La interface. As to the magnetic properties, the increment of the saturation magnetization and the change of both the remanence ratio and the saturation field with La layer thickness, namely the change of the interlayer exchange coupling, occurred. This change is caused by the change of the interface structure and electronic structure by the transformation from La to La-hydride.

Acknowledgements

This work was partly supported by a Grant-in-Aid for Scientific Research (S) and Encouragement of Young Scientists (B) from the Japanese Ministry of Education, Culture, Sports, Science, and Technology. This work was also partially supported by ‘Priority Assistance od the Formation of Worldwide Renowned Centers of Research—The 21st Century COE program (Project: Center of
Excellence for Advanced Structural and Functional Materials Design’ from the Japanese Ministry of Education, Culture, Sports, Science, and Technology.

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