Redox-Induced Modification of Magnetism in Ni Thin Film*

Norimasa Hiraoka,† Yojiro Oba, and Takeshi Watanabe
School of Integrated Design Engineering, Graduate School of Science and Technology, Keio Univ., 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan

Hideyuki Maki
Department of Applied Physics and Physico-Informatics, Faculty of Science and Technology, Keio Univ., 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan

Yasuaki Einaga
Department of Chemistry, Faculty of Science and Technology, Keio Univ., 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan

Tetsuya Sato
Department of Applied Physics and Physico-Informatics, Faculty of Science and Technology, Keio Univ., 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan

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Magnetic properties of Ni thin films which were modified through the redox reaction in alkaline solution were investigated by means of magneto-optical Faraday effect. The magnetization process of Ni film on which Ni(II) compounds electrochemically forms was different from that of fresh Ni films. This indicates that the magnetic anisotropy is modified through the redox reaction Ni(0)/Ni(II) which may induce the change in the volume of metallic nickel region and/or the magnetic coupling between the metallic Ni and some compound including Ni(II) formed on the film surface. [DOI: 10.1380/ejssnt.2009.787]

Keywords: Nickel; Magnetic films; Metal-electrolyte interface; Electrochemical methods

I. INTRODUCTION

Electrically control of magnetism has attracted much attention in the fundamental research and also in the fields of applied research which are expected to be exploited low-power-consumption memory devices. In the diluted magnetic semiconductor (In, Mn) As, the electric field-control of magnetism has been demonstrated [1, 2]. However, the possible application of this phenomenon has been limited due to the low Curie temperature $T_C$ below a room temperature, because nonmetallic materials have been exclusively researched up to now.

Some of 3d transition metals and their alloys have $T_C$ above room temperature, and thus the electric control of the intrinsic magnetic properties in such a metallic system, e.g. magnetization or magnetic anisotropy, is attractive. However, it is difficult to control the charge density in metals owing to the high density of electrons. The use of an electric double layer (EDL) which forms at the interface between a metal and an electrolyte was suggested as an elegant approach to overcome this problem [3]. Typically, the superficial surface charge density induced in the EDL can reach the values up to a few tenth of an electron per surface atom. Subsequently, the tunable magnetization in Pd [4], Pd-Co [5] and Ni-Pd alloys nanoporous [6] and the tunable magnetic coercivity of FePd and FePt thin films [7] were demonstrated. In addition, the strain and electrical resistance of nanoporous Pt [8, 9] and the electrical conductivity of nanocrystalline Au-Fe alloy [10] were also tunable by the external applied voltages in an electrochemical cell. Although such an electrically controlled magnetic phenomenon can be induced by the surface charge, the chemical effects, such as the redox reaction and the adsorption of ions from the solution, may also cause it. However, these have insufficiently taken into account, because the chemical effects were minimized under the condition of use of nonaqueous electrolytes [5–7] and moderate potential range [4–6]. Nevertheless, the chemical effects may be an interesting method to induce the modification and control of magnetic properties in metal, although there have been scarce reports on it.

In the present work, the magnetic properties of Ni thin films are controlled using application of electric field, and then the origin of change in magnetic properties is discussed in terms of the chemical effects. As the transition metal we selected Ni, since its $T_C$ is above room temperature, and the mechanism of its electrode reaction process has been attentively studied in electrochemistry and industry.

II. EXPERIMENTAL

Ni thin films of 10, 20 and 30 nm thicknesses were prepared on the quartz substrate by a vacuum deposition method under the initial pressure of $4 \times 10^{-6}$ Torr. The film thickness was measured by a crystal oscillator. For electrochemical measurements, coated Cu wires were soldered on the Ni thin films, and the plumb joints were covered with epoxy to prevent from the dissolution of solder in an electrolyte solution.

The schematic view of the measurement system is shown in Fig. 1. To obtain in situ magnetic data, we used the magneto-optical Faraday ellipticity which reflects the magnetization of the Ni thin film. Faraday ellipticity was

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†Corresponding author: hiraoka@az.appi.keio.ac.jp
detected by the optical retardation modulation (ORM) method using a photo-elastic modulator [11]. The ellipticity signals due to the quartz substrate and electrolyte were negligibly small. The electrochemical measurements were performed in a self-made electrochemical cell at ambient temperature using a potentiostat (HSV-100, Hokuto), where the magnetic field was applied perpendicular to the film surface using an electron magnet. The Ni thin films for magnetic measurements as working electrodes, a Pt sheet as a counter electrode, and a commercial Ag/AgCl electrode as a reference electrode and borate buffered solution (pH 9) as an electrolyte were used. An oxide with a few atomic layers was formed after the exposure of Ni thin films to the air for several days, and an additional hydroxide is formed on top of the air-formed oxide upon the immersion of film into alkaline solution [12].

III. RESULTS AND DISCUSSIONS

Figure 2 shows the cyclic voltammogram of Ni thin film in borate buffered solution, in which the cathodic peak at −0.8 V with concomitant evolution of H2 is assigned to the reduction of Ni(II) compounds, i.e. the transformation of NiO and α-Ni(OH)2 back to metallic nickel, and the anodic peak at −0.6 V corresponds to the oxidation of nickel to NiO and α-Ni(OH)2, and the small current between −0.4 and 0.2V indicates that the dominant process is capacitive double layer charging [12]. Figure 3 shows the potential dependence of the Faraday ellipticity in the Ni thin film at a magnetic field of 1 and 6 kOe between −0.9 and 0.2 V. Both the data of the Faraday ellipticity at 1 and 6 kOe varied synchronously with the potential change. In Fig. 3, one can see the two regions; the Faraday ellipticity remarkably changed in the potential between −0.9 and −0.4 V where the redox reaction occurs and the slowly changed between −0.4 and 0.2 V in the EDL region denoted by the double-headed arrow in Fig. 2. The amplitude of oscillatory Faraday ellipticity induced by the redox reaction between −0.9 and −0.4 V is larger than that induced by the surface charge between −0.4 and 0.2 V. Thus the magnetic properties of the Ni thin film can be modified by the redox reaction Ni(0)/Ni(II). The small irreversible increase or decrease in Faraday ellipticity observed in Fig. 3 is attributed to the film degradation such as the irreversible transformation among various kinds of Ni(II) compounds, e.g., transformation of α-Ni(OH)2 to β-Ni(OH)2 that cannot be reduced back to the metallic nickel [13].

The other redox reaction is shown in Fig. 4 which displays the cyclic voltammogram of the same system (Ni/borate buffered solution) in the different potential range between 0.2 and 0.8 V, where the anodic process at 0.75 V should be related to the oxidation of the β-NiOOH phase to hydrous Ni(III) oxide, i.e., β-NiOOH phase [13]. Therefore, we can control the variety of oxidation state with applying appropriate potentials: Ni(0) at −0.9 V where the reduction of NiO and Ni(OH)2 to metallic nickel takes place (Fig. 5(a)), Ni(II) at 0.2 V where NiO and Ni(OH)2 forms on the surface of Ni films (Fig. 5(b)), and Ni(III) at 0.8 V where the additional oxidation of Ni(OH)2 to NiOOH forms on the NiO layer (Fig. 5(c)). In detailed, β-NiOOH in which the nickel oxidation state is 3, transforms at 0.8 V into γ-NiOOH in which the Ni oxidation state is 3.5–3.7. The potential dependent change in the Faraday ellipticity was also ob-
is only attributed to the Ni film and NiO, Ni(OH)
that the magnetic field dependence of Faraday ellipticity
ity at 6 kOe as shown in Fig. 6.

Figure 7 shows the hysteresis loops of Faraday ellipticity at −0.9, 0.2 and 0.8 V. The magnetization process at 0.8 V was essentially same as that at 0.2 V. This indicates that the magnetic field dependence of Faraday ellipticity is only attributed to the Ni film and NiO, Ni(OH)$_2$ and NiOOH, formed on the surface of Ni films, do not bring any magnetic contribution. On the other hand, the magnetization process at −0.9 V was different from that at 0.2 V, i.e., the Faraday ellipticity at −0.9 V is saturated at a higher applied magnetic field and has a larger saturated value compared with data at 0.2 V. Such a characteristic is also observed in Fig. 3, i.e., the Faraday ellipticity at −0.9 V was smaller than that at 0.2 V in a field of 1 kOe and the relation was reversed at 6 kOe. This indicates that the saturated value of Faraday ellipticity and the magnetic anisotropy are modified through the redox reaction on the Ni film.

Figure 8 shows the hysteresis loops of the Ni thin films with 10, 20 and 30 nm in thickness measured at −0.9 and 0.2 V. The difference of saturated Faraday ellipticity between −0.9 and 0.2 V decreases with increasing film thickness. In addition, the magnetic field, at which the magnetization is saturated, decreases as the film thickness decreases.

Based on Figs. 7 and 8, the characteristics of hysteresis loops at −0.9 and 0.2 V can be explained as follow. The modified saturated value of Faraday ellipticity should be explained by the change in the magnetic moment of Ni film and/or the modification of coupling coefficient between the Faraday ellipticity and the magnetization. Al-

though it is difficult to directly verify the change in the magnetic moment in Ni thin film, the magnetic moment of Ni films should be changed through the change in Ni film thickness based on the formation of Ni(II) compounds because the magnetic contribution from NiO, Ni(OH)$_2$ and NiOOH phases formed on Ni film is significantly small. This interpretation is supported by the film thickness dependence of difference between the data at −0.9 and 0.2 V in Fig. 8, i.e., the volume ratio of nonmagnetic layer to metallic Ni decreases with increasing the film thickness. In addition, the modification of anisotropy should be induced by the change in the direction of magnetic anisotropy from parallel to perpendicular to the film plane and/or the decrease in the magnetic anisotropy may occur through the reduction of NiO and NiOOH$_2$ formed on the surface of Ni film to metallic nickel. Figure 8 clearly shows that the modification of the magnetic anisotropy is attributed to the change in the thickness of metallic nickel region. This may be attributed to the change in the direction of magnetic anisotropy that is peculiar to the Ni film [14]. On the other hand, the exchange coupling between Ni and NiO layers can be another reason for the variation of the magnetic anisotropy. The exchange cou-

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The redox-induced modifications of the magnetism in Ni thin film synchronously with the potential change were observed. The magnetization process at $-0.9\, \text{V}$, where the reduction of Ni(OH)$_2$ and/or NiO on the surface of Ni film to metallic nickel takes place, was different from that at 0.2 V where Ni(OH)$_2$ and/or NiO forms, whereas the magnetization process at 0.8 V, where the oxidation of Ni(OH)$_2$ to NiOOH occurs on the top of the NiO layer on Ni film takes place, was almost same as that at 0.2 V. This indicates that the magnetic anisotropy is modified through the redox reaction Ni(0)/Ni(II) which induce the change in the volume of metallic nickel region and/or the exchange coupling of Ni/NiO.

IV. CONCLUSIONS

be formed, shows the soft magnetic behavior compared to that at 0.2 and 0.8 V where the formation of Ni/NiO interface occurs. Thus, the detailed study is necessary to clarify the origin of the modified anisotropy dependent on the applied voltage.

![Graph showing magnetic field dependence of Faraday ellipticity of Ni thin film (20 nm) at $-0.9$ and 0.2 V.](image)

FIG. 8: Magnetic field dependence of Faraday ellipticity of Ni thin film (20 nm) at $-0.9$ and 0.2 V.

neglecting between ferromagnetic and antiferromagnetic layers through Ni/NiO interface can be related to the enhancement of coercivity [15]. In fact, the hysteresis loop at $-0.9\, \text{V}$ in Fig. 7, where the Ni/NiO interface should not

\[\text{Coercivity enhancement} = \frac{\text{Coercivity at } -0.9 \, \text{V}}{\text{Coercivity at } 0.2 \, \text{V}}\]

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