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Hydrogen Absorption Characteristics of Amorphous $LaNi_{5.0}$ Films Prepared by Reactive Sputtering

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Amorphous $LaNi_5$ thin films are expected to be one of the promising materials for use in hydrogen separation[1–5] and battery electrodes,[6,7] because the durability of the films is great in regard to the hydrogen absorption–desorption cycling process[8] and the films have excellent resistance to harmful impurities in the hydrogen gas in comparison with the crystalline bulk material.[5]

The hydrogen density is, however, much smaller for the amorphous films than for the crystalline bulk.[7,9–11] Structural analyses using extended X-ray absorption fine structure (EXAFS)[12] have revealed that this is because the distortion of sites in which hydrogen atoms are considered to occupy is generated in the amorphous film.

If hydrogen becomes incorporated into $LaNi_5$ during the preparation of film, the resulting film may have large hydrogen density. Consequently, the amorphous $LaNi_5$ film obtained will be extremely useful hydrogen storage materials.

In the present study, a reactive sputtering method using an H_2–Ar gas mixture[7] was adopted to the film preparation in order to increase hydrogen density of the amorphous $LaNi_{5.0}$ film, and the characteristics of hydrogen absorption for the film obtained were investigated.

Films of amorphous $LaNi_{5.0}$ were deposited by a radio frequency magnetron sputtering apparatus (Daia Vacuum Engineering Co., Ltd.) in which the target and substrate holder were in a plane parallel configuration with 40-mm separation. The sputtering target was the La–Ni alloy disk (80-mm diameter) consisted of $LaNi_{3.0}$ and $LaNi_{4.4}$ plates. The alloy plates were supplied by Santoku Metal Industry, Kobe, Japan. Quartz crystal disks and glass plates were used as substrate and were attached to a water-cooled stainless steel holder.

An Ar (50 mol %)–H_2 (50 mol %) gas mixture was used as a sputtering gas and a pressure of the gas was maintained at 0.66 Pa. The rf input power was 400 W. Utilizing these specific parameters resulted in a deposition rate of 2.8 nm s^{-1}.

As for a conventional sputtering, a sputtering gas was 99.9999% pure argon, and the resulting deposition rate was 6.0 nm s^{-1}.[10] The temperature of substrate during sputtering was kept at less than 313 K. To desorb hydrogen from the films obtained by reactive sputtering, the films were heated in situ at 373 K for 3.6 × 10^{3} s.

The thickness of the films obtained was determined by direct observation of the cross section of the sample on the glass substrate using a Hitachi S-800 scanning electron microscope. X-ray diffraction work was made to verify the amorphous state. The determination of film composition and oxygen concentration in the films was done with a Rigaku System 3270A X-ray fluorescence spectrometer.

The hydrogen content in the films was determined by a quartz-crystal mass-monitoring (QCMM) method which takes advantage of a linear relationship between the frequency shift of quartz crystal and the mass change of hydrogen absorbed in the films.[13,14] Details of the measuring technique have previously been described.[9,10] The films prepared were transformed into a high-vacuum high-pressure apparatus under an atmosphere of 99.9999% pure argon gas to protect the surface of the films against oxidation and was exposed to hydrogen in pressure increments varying from 1.3 × 10^{-3} to 5.0 × 10^{6} Pa at 333, 363, and 393 K. The frequency shift was measured by a Nichiden Anelva EVM 32B quartz-crystal mass monitor equipped with a Advantest TR5822 universal counter. The frequency shift is induced by both the mass change of hydrogen in the films and the elastic stresses developed within the films following the dissolution of hydrogen:

$$f = f_{\mathrm{m}} + f_{\mathrm{s}} \qquad (1)$$

where f is the total frequency shift, f_{m} the frequency shift caused by the mass change and f_{s} the frequency shift induced by the elastic stress, respectively. To remove the contribution of the elastic stress from the frequency shift, the duplicate runs were carried out using a deuterium gas. It is known that both protium (H) and deuterium (D) atoms accommodated the same sites in $LaNi_5$,[15] the amount of deuterium taken up by the alloy almost consists with that of protium due to the small isotope effect,[16] and both isotopes have a same atomic size. Therefore, the hydrogen content in the films was calculated by the following relation which can be expected to hold for the frequency shift:

$$f_{\mathrm{m}}(\mathrm{H}) = f(\mathrm{D}) - f(\mathrm{H}) \qquad (2)$$

where

$$f(\mathrm{H}) = f_{\mathrm{m}}(\mathrm{H}) + f_{\mathrm{s}}(\mathrm{H})$$

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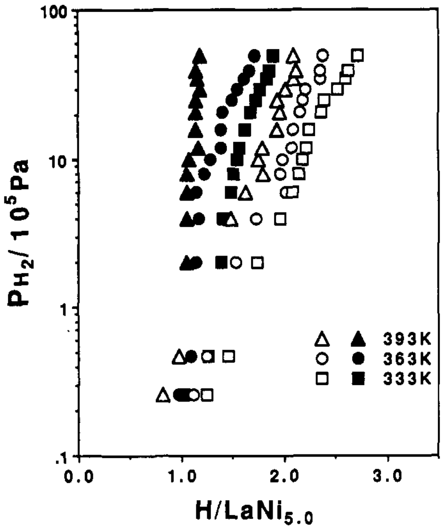

Figure 1. Pressure–composition isotherms of amorphous $LaNi_{5.0}$ films sputtered using $Ar–H_2$ and Ar gases. (□, ○, △) Reactive sputtered film using $Ar–H_2$ gas mixture ($LaNi_{5.02\pm0.01}$, 0.58 ± 0.03 μm thick). (■, ●, ▲) Conventional sputtered film using Ar gas ($LaNi_{5.04\pm0.02}$, 0.57 ± 0.03 μm thick).

$$f(\mathrm{D}) = f_{\mathrm{m}}(\mathrm{D}) + f_{\mathrm{s}}(\mathrm{D})$$

$$f_{\mathrm{m}}(\mathrm{D}) = 2f_{\mathrm{m}}(\mathrm{H})$$

$$f_{\mathrm{s}}(\mathrm{D}) = f_{\mathrm{s}}(\mathrm{H})$$

Besides the contribution of the elastic stress developed in the films to the frequency shift was estimated using the following equation:

$$f_{\mathrm{s}}(\mathrm{H}) = 2f(\mathrm{H}) - f(\mathrm{D}) \tag{3}$$

The density ρ_s of the sputtered films was also determined using the QCMM and was estimated by the following known equation:

$$\rho_{\mathrm{s}} = -\frac{\mathrm{d}f\,\rho_{\mathrm{q}}N}{f^2\,\mathrm{d}t} \tag{4}$$

where df is the measured frequency shift for the film deposition, ρ_q the density of quartz crystal used (2.65 g cm^{-3}), N the frequency constant of 1.67 MHz mm^{-1}, f the vibrational frequency of 6.00 MHz and dt the thickness of the sputtered films determined by the scanning electron microscope.

The reactive sputtered film (RS film) obtained was a composition of $LaNi_{5.02\pm0.01}$ having a thickness of 0.58 ± 0.03 μm. The composition and thickness of the RS film almost coincided with those of the conventional sputtered film (CS film), being $LaNi_{5.04\pm0.02}$ and 0.57 ± 0.03 μm. Both the films exhibited a broad band characteristics of an amorphous material.

Figure 1 illustrates the pressure–composition–temperature curves of the $LaNi_{5.0}$ films at 333, 363, and 393 K. As for the pressure dependence on hydrogen concentration (H/$LaNi_{5.0}$) in the RS film, the concentration increases monotonically with hydrogen pressure despite the variation in temperature. Absence of a pressure plateau appears to indicate that existence of a single crystalline phase upon the dissolution of hydrogen atoms is predominant for the amorphous films.[10,17,18] The results for the CS film are analogous to those for the RS film.[10]

Table I. Frequency Shifts Due to the Hydrogen-Induced Stress

hydrogen densities (H/$LaNi_5$)	reactive sputtered film f_s(H) (Hz)	conventional sputtered film f_s(H) (Hz)
1.12	99.3	143.6
1.73	130.2	175.8

On a hydrogen pressure of 1 × 10^6 Pa at 363 K, the amount of hydrogen taken up by the RS film was 2.0 for a formula weight of $LaNi_{5.0}$, which was found to be one and a half times larger than that by the CS film. The increase in hydrogen concentration on the RS film was also observed for two other temperatures. This appears to be because the concentration of sites that can be occupied by hydrogen atoms is larger for the RS film than the CS film. If the oxygen concentration in the $LaNi_{5.0}$ film decreases by hydrogen reduction during the reactive sputtering, the amount of hydrogen taken up by the film should increase. There, however, was no difference of oxygen concentration between the RS film (0.0300 wt %) and the CS film (0.0302 wt %), so that the increase in the hydrogen density for the RS films is considered to be independent of the oxygen concentration.

The elastic stress is known to generate in $LaNi_5$ due to the expansion of lattice when it absorbs hydrogen. The contribution of the elastic stress developed in the films due to the dissolution of hydrogen to the frequency shift is shown in Table I. Hydrogen-induced stress in the RS film was found to be two-thirds as large as that in the CS film at the same hydrogen concentration in both films. This may indicate that the hydrogen sites in the RS film partially differ from those in the CS film, denoting the appearance of a new site having less structural restriction. Another explanation could be the expansion of hydrogen sites, since hydrogen atoms become incorporated into the lattice of $LaNi_5$ at the formation of a film. This hypothesis was, however, rejected because the density of the RS film (6.5 ± 0.3 g cm^{-3}) coincided with that of the CS film (6.2 ± 0.3 g cm^{-3}) within the error.

The reason for differences of hydrogen absorption characteristics between the RS film and the CS film appears to be revealed by structural analyses using EXAFS and neutron diffraction. These experiments are currently being prepared.

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