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Effect of Bias Sputtering Condition on Structure of $LaNi_5$ Films

Kenta Nakakado*1, Makoto Ohtsuka, Yusuke Ayame*2 and Kimio Itagaki

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan

Purification of hydrogen using a hydrogen storage alloy film has various advantages such as low operation energy and low costs of the equipment. However, because of the surface roughness of a substrate, the surface of the sputtered film was not smooth and had some pinholes. It was considered that use of a bias sputtering method might solve these problems. Hence, in this study, the influence of the bias power on the composition, microstructure and crystal structure of the $LaNi_5$ sputtered film were investigated. When the film was deposited with a direct current sputter power $W_S = 50$ W and a radio frequency bias power $W_B = 20$ W, the diffraction peak of $LaNi_5$ was not observed on the film. With $W_S = 200$ W and $W_B = 20$ W, the film had crystal structures. However, when the W_B was increased more than 40 W with $W_S = 200$ W, the film became the amorphous structure. It is considered that, to make the amorphous structure and the dense film with higher W_S, the W_B has to be increased. [doi:10.2320/matertrans.48.832]

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Keywords: *bias sputtering method, lanthanum-nickel alloy, hydrogen storage alloy, hydrogen permeable film, amorphous structure*

1. Introduction

Recently, hydrogen is considered to be promising clean energy and establishment of a hydrogen energy system is highly expected due to the rapidly increasingly demand of hydrogen gas. One of the major methods to purify hydrogen gas is a gas permeation method using a metal membrane in which only hydrogen atoms permeate, and a hydrogen storage alloy film for the membrane has various advantages such as low operation energy and low cost of the equipment.

Some studies on the preparation of $LaNi_5$ film have been done hitherto. Adachi *et al.*[1,2] and Sakaguchi *et al.*[3] prepared amorphous and crystalline $LaNi_5$ films by means of flash evaporation of the alloy powders and measured the pressure composition isotherm for the prepared film. It was found that the amorphous film absorbed hydrogen without being disintegrated into the powders and the hydrogen absorption capacity of the films increased with increasing degree of crystallinity.

In the laboratory of present authors, the $LaNi_5$ film has been made by sputtering on the glass[4] and Teflon substrate. Due to the low mechanical strength and heat-resistance of the Teflon substrate, it was considered that the use of porous metals and ceramics for the substrates should be superior. However, it was clarified that the surface of the sputtered film on the porous alumina substrate was not smooth and had some pinholes.

It is generally known that the film on the edge and bottom of the porous substrate is resputtered when bias is applied on the substrate during sputtering.[5] Applying a bias on the substrate, it is able to deposit the side wall and inside the asperity on the surface of the substrate. It was reported that the step coverage of tungsten film was improved by switching bias sputtering.[6] The bias sputtering method will be a useful mean to diminish the pinhole. Hence, in this study, influence of the bias power on the composition, microstructure and crystal structure of the $LaNi_5$ sputtered film were investigated.

2. Experimental Method

$LaNi_5$ films were deposited on a porous alumina square substrate of 35 mm each side and 3 mm in thickness with a fine pore size of 0.1 μm by a magnetron sputter method. The film thickness was kept at about 2 μm by controlling the sputtering time and the substrate was cooled by cold water. A La_2Ni_7 alloy target was used in sputtering. The sputtering apparatus (Shibaura, CFS-4ES) has radio frequency (RF) and direct current (DC) power sources. In this experiment, firstly, the DC sputter power W_S was kept at 50 W, and the RF bias power W_B was changed up to 20 W. Secondly, W_S was increased to 100 ~ 200 W to get the higher deposition rate, while W_B was changed up to 50 W. The sputtering time was fixed at 31.2, 15.6, 10.4 and 7.8 ks for each sputter power of 50, 100, 150 and 200 W, respectively. The composition of the films was determined by inductively coupled plasma (ICP) spectrometry (PerkinElmer, Optima 3300). The microstructure was observed by scanning electron microscopy (SEM, Hitachi, S-4100L). The crystal structure was investigated by X-ray diffractmeter (XRD) equipment (Rigaku, RINT2200).

3. Results and Discussion

The sputter deposition rate is shown in Fig. 1. The sputter deposition rate is increased with increasing W_S. By applying the bias, it is slightly increased up to $W_B = 20$ W for each W_S. However, it is decreased when W_B is increased above 20 W for each W_S. It is considered that the resputtering effect became prevailing in the range of higher W_B and the surface of film was ground down. Figure 2 shows the nickel content of the film. It is decreased with increasing W_S. By applying the bias, it becomes increasingly larger than that of $LaNi_5$ with increasing W_B. On the other hand, at a given W_B, the deviation from that of $LaNi_5$ is decreased with increasing W_S.

The microstructures of the films deposited with $W_S =$ 50 W and varying W_B are shown in Figs. 3 and 4. The under photos show a cross section fractured in liquid nitrogen. The

*1Graduate Student, Tohoku University

*2Graduate Student, Tohoku University, Present Address: Central Technical Research Laboratory, Nippon Oil Corporation, Kanagawa, 231-0815, Japan

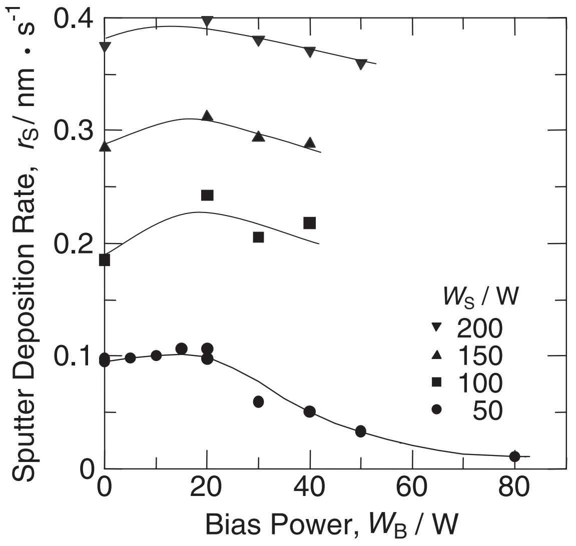

Fig. 1 Sputter deposition rate at each W_S.

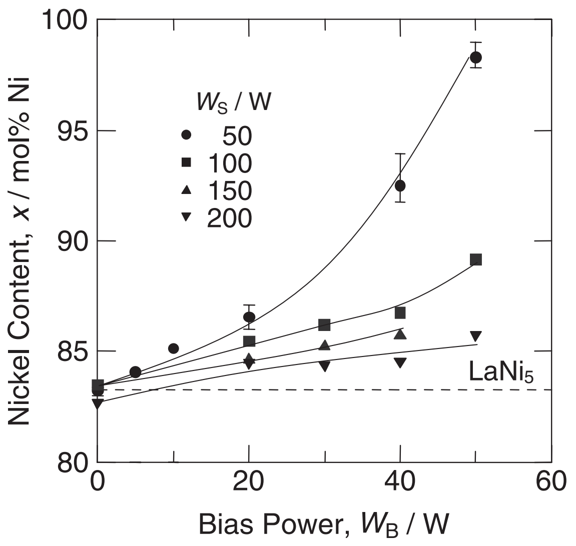

Fig. 2 Ni content of films deposited with each W_S.

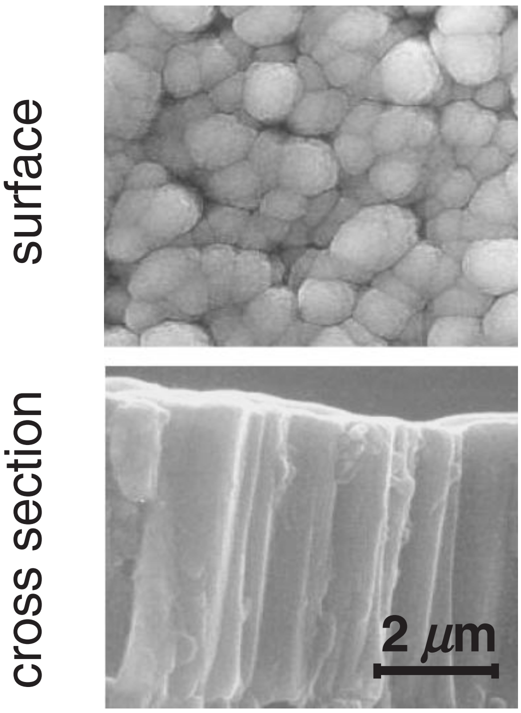

Fig. 3 Microstructures of films deposited with $W_S = 50$ W without bias.

substrate plane is held on the lower side. These microstructure are shown for the typically observed surface and cross section for the film deposited at each condition. Although, without the bias, there seem some holes at the grain boundaries on the surface and the columnar crystal at the cross section of the films, they disappeared by applying the RF bias. It is considered to be ascribed to the resputtering effect. The XRD patterns of the films deposited with $W_S =$ 50 W and varying W_B are shown in Fig. 5. The effect of RF bias on the nuclear growth of $LaNi_5$ seems complicated. No diffraction peak of $LaNi_5$ is observed for the film deposited without the bias in Fig. 5. It shows an amorphous structure. For the films deposited with $W_B = 5$ W, the diffraction peaks of $LaNi_5$, such as (200) and (111) are observed, and with $W_B = 10$ W, (101), (110), (200) and (111) are observed. They

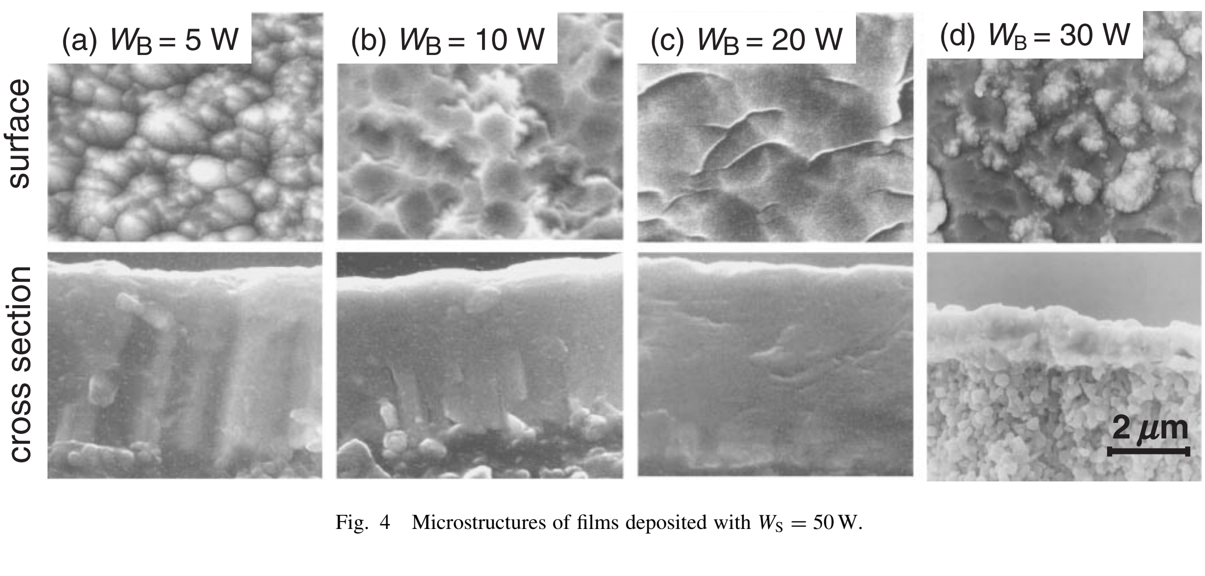

Fig. 4 Microstructures of films deposited with $W_S = 50$ W.

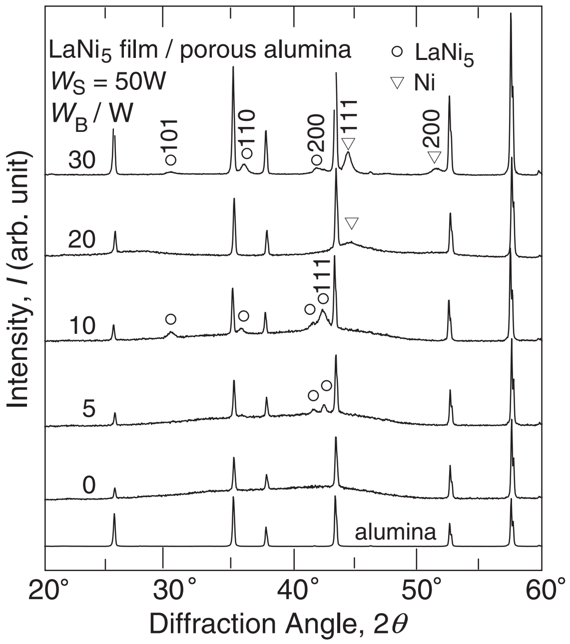

Fig. 5 X-ray diffraction patterns of films deposited with $W_S = 50\,W$.

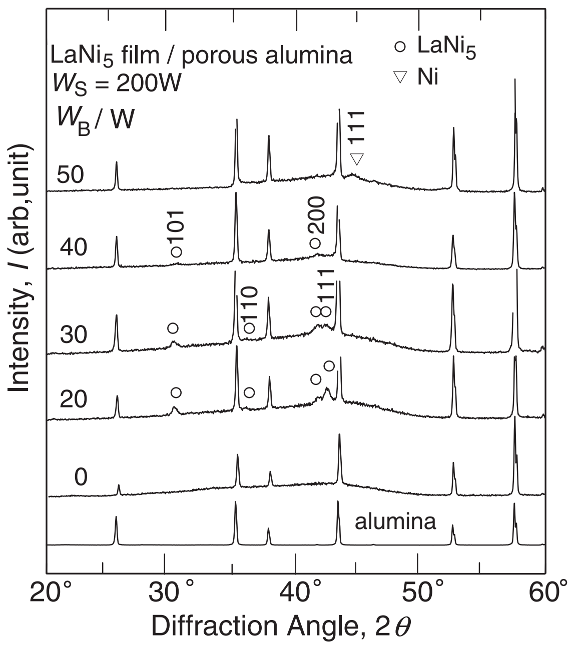

Fig. 7 X-ray diffraction patterns of films deposited with $W_S = 200\,W$.

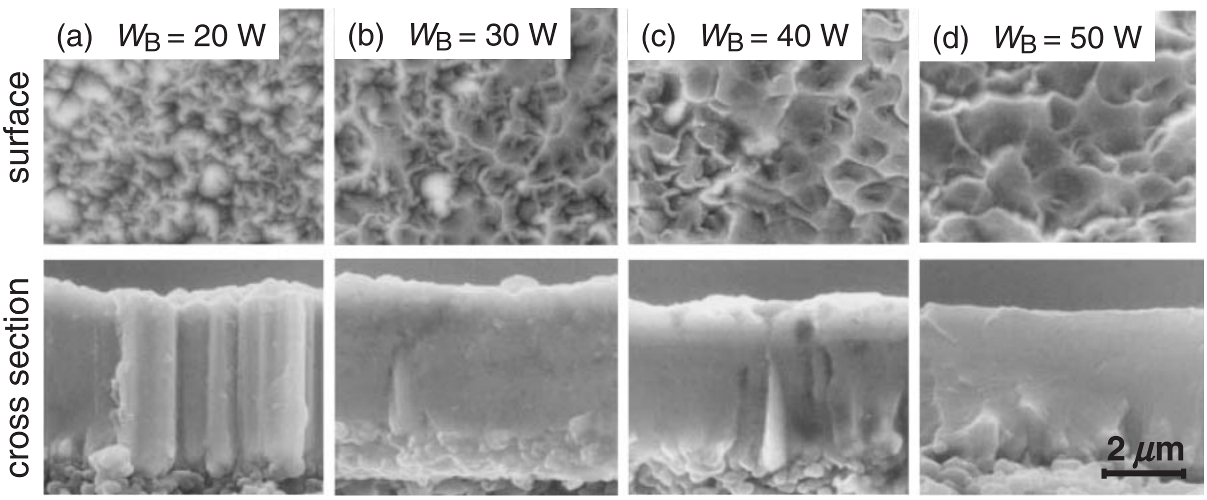

Fig. 6 Microstructures of films deposited with $W_S = 200\,W$.

show a crystal structure. However, it is noted that the diffraction peaks of $LaNi_5$ are not observed for the film deposited with $W_B = 20\,W$, while observed with $W_B = 30$ W. It is considered that the film deposited with $W_B = 0\,W$ becomes amorphous due to rapid cooling of the sputtered substance on the cold substrate without being heated by the bias. The substrate temperature is increased with W_B, making the crystal structure with $W_B = 5 \sim 10\,W$. It is considered that due to the applied RF bias, the argon ion was accelerated and broke the $LaNi_5$ structure. This effect with $W_B = 20\,W$ is considered to prevail over the effect of elevating the substrate temperature. With $W_B = 30\,W$, as shown in Fig. 5, the effect of elevating the substrate temperature prevail over the resputtering effect. The diffraction peak of nickel is also observed in the XRD patterns with $W_B = 20$ and 30 W. It is considered that the nickel content of the film becomes increasingly larger than that of $LaNi_5$ with increasing W_B, as shown in Fig. 2.

Then, in order to make a dense film and make an improvement of the deposition rate, W_S was increased to $100 \sim 200\,W$, while W_B was changed between 20 and 50 W. The microstructures and XRD patterns of the films made with $W_S = 200\,W$ and varying W_B are shown in Figs. 6 and 7, respectively. The film deposited without the bias also has an amorphous structure. It is found that the columnar grain structure is observed only for $W_B = 20\,W$ (Fig. 6(a)) and the diffraction peaks of $LaNi_5$, such as (101), (110), (200) and (111) are observed only for $W_B = 20$ and 30 W (Fig. 7). For the film deposited with $W_B = 40\,W$, the diffraction peaks of $LaNi_5$, (101) and (200) are slightly observed, and with $W_B = 50\,W$, none of them are observed however a diffraction peak of nickel, (111) is observed (Fig. 7). It was clarified in

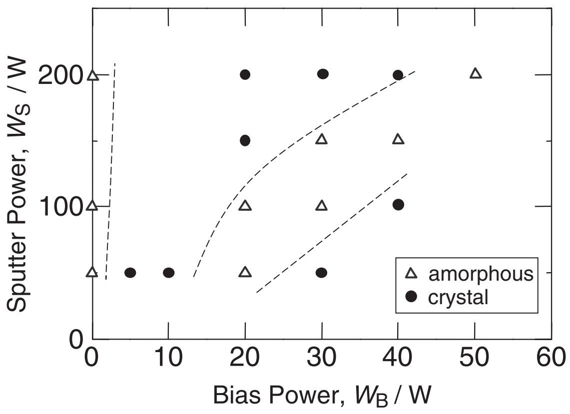

Fig. 8 Crystal structures of films deposited with each W_S and W_B.

the sputtering experiments with $W_S = 150$ W that the film has the columnar grain structure and the diffraction peaks of $LaNi_5$ are observed only for $W_B = 20$ W. The diffraction peak of nickel is observed with $W_B = 40$ W. With $W_S = 100$ W, the film has columnar grain structure for $W_B = 30$ and 40 W. The diffraction peaks of nickel observed for $W_B =$ 40 W.

It is clarified in this study that resputtering caused by the bias power applied on the substrate is effective to diminish pinholes of the film. On the other hand, it is found that, when W_S is increased, the amount of sputtered substance deposited on the substrate is also increased and overtook the resputtering effect. Figure 8 shows the structure of the film made with each W_S and W_B. It is noted that the area where the film has an amorphous structure is shifted to higher W_B when W_S is increased. By taking it into account that the amorphous structure is superior for the hydrogen permeable film, it is suggested from Fig. 7 that higher W_B is required to make a dense film with higher W_S.

4. Conclusions

The results obtained in the present study are summarized as follows:

(1) By applying the bias, the sputter deposition rate was slightly increased up to $W_B = 20$ W, however, it was decreased when W_B was increased above 20 W for each W_S.
(2) The nickel content of the film increasingly deviated from that of $LaNi_5$ with increasing W_B, but the deviation at a given W_B was decreased with increasing W_S.
(3) The film deposited with $W_S = 50$ W and $W_B = 20$ W, has the dense and amorphous structure. In order to make such a film, with higher W_S for the improvement of the deposition rate, higher W_B was required.

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