A dissociation reaction of (CH$_3$)$_2$S (dimethyl sulfide; DMS) on a Pd capped Mg layer surface has been studied by using sulfur K-edge near edge X-ray absorption fine structure (NEXAFS) technique. The Pd thin film is prepared by two deposition methods, one is vacuum deposition, and the other is DC magnetron sputtering. The surface morphology is observed by Atomic Force Microscopy (AFM). The AFM observation reveals that there are many nano sized particles on the Pd/Mg surface, and an average size of the particle prepared by DC magnetron sputtering is obviously smaller than that prepared by vacuum deposition. NEXAFS analysis reveals that DMS dissociation is weakened on the Pd surface prepared by DC magnetron sputtering and promoted on the Pd surface prepared by vacuum deposition. It seems that any adosorption reactions are promoted on small sized metal particles, however, the DMS dissociation reaction is promoted on the Pd surface prepared by vacuum deposition, which has big sized Pd particles.

**Keywords:** Near edge extended X-ray absorption fine structure (NEXAFS); Atomic force microscopy; X-ray photoelectron spectroscopy; Pd-Mg alloy; Sulfur Poisoning

---

**I. INTRODUCTION**

Recently the hydrogen energy system is expected to serve as one of the alternatives to the fossil fuel system, and it is needed to store the hydrogen molecules in a tank and transport them to use the system. In this case, there is a problem that the weight of a storage tank is so heavier than the total amount of the hydrogen inside the tank. Mg metal is lightweight and inexpensive metal, and possesses high hydrogen storage ability of 7.6 wt% [1]. But a pressure of 1 bar requires a high temperature of about 570 K in order to absorb hydrogen into Mg bulk [2]. A presence of Pd which is known as a hydrogen-dissociation catalyst on Mg surface enhances hydrogen storage properties. It was revealed that Pd cap film was observed to play a key role as a catalyst in enhancing the rate-limiting dissociation of hydrogen molecules at the sample surface, and lowering the hydrogen loading and desorbing temperatures significantly [3]. In particular, Yoshimura et al. reported that the Mg layer covered with the Pd thin film could absorb and release hydrogen at room temperature and atmospheric pressure [4]. Thus we have paid attention to a Pd/Mg hydrogen storage material.

From the standpoint of the dangerousness of explosive hydrogen gas, it is important to detect a leak of the gas from the storage tank. Though, detecting the hydrogen gas is difficult since the hydrogen gas is colorless and odorless. Therefore it is suggested that the sulfur-containing molecules added into the hydrogen gas as an odorant. The sulfur-containing molecules inactivate the Pd catalyst when those molecules adsorb on the Pd catalyst surface and occupy its active site, as named Sulfur Poisoning. We use (CH$_3$)$_2$S (dimethyl sulfide; DMS) to study the Sulfur Poisoning because DMS is one of the major odorant gases for the leakage. In our previous studies, we have revealed the adsorption reaction of DMS on the Pd nanoparticle surface, and the adsorption reaction is that DMS dissociates into (CH$_3$)S (methane thiolate; MT) and atomic S [5, 6]. It is supposed that DMS on the Pd/Mg film makes the dissociation reaction.

We have prepared the Pd thin film by two methods, one is DC magnetron sputtering and the other is vacuum deposition, after preparing the Mg layer by DC magnetron sputtering on a Ni substrate. A clean metal film can be produced by these methods, and they are expected to be applied for industrial use. We speculate that the reaction of the DMS dissociation on the Pd thin film surface is different due to the two deposition methods. The purpose of this study is to reveal the adsorption reaction of DMS on the Pd/Mg thin film by using atomic force microscopy (AFM), near edge X-ray absorption fine structure (NEXAFS) and X-ray photoelectron spectroscopy (XPS) techniques.

**II. EXPERIMENTAL**

A Pd/Mg thin film was deposited on a Ni substrate (10×10 mm$^2$, 0.50 mm thickness). The substrate was mechanically polished using Al$_2$O$_3$ with 0.05 μm diameter to a mirror finish, and a Mg thin film was prepared by DC magnetron sputtering. Before depositing a Pd layer, the Mg thin film surface was sputtered by Ar$^+$ (3 keV)
to remove impurities of sulfur, carbon and oxygen under an ultra-high vacuum condition. Then a Pd thin film was prepared on the Mg layer. The Pd cap layer is necessary for not only enhancement of the hydrogen dissociation but also protection of the Mg layer against the atmosphere. We used two different deposition methods in order to deposit the Pd thin film and two samples were prepared. The one was (a) Pd (sputtered) sample; the Pd top layer was deposited by DC magnetron sputtering with \(10\) nm thickness. The other was (b) Pd (evaporated) sample; the Pd top layer was deposited by vacuum deposition with \(5\) nm thickness. We used electron bombardment heating in order to evaporate a Pd bulk rod source. These two samples were exposed to DMS atmosphere for more than half a day at room temperature and under atmospheric environment. A vapor pressure of DMS is about 500 Torr at 293 K.

In order to study a chemical interaction between Pd and Mg, we prepared a sample (Pd/Mg) and measured it by using XPS in the in-situ condition. The sample (Pd/Mg) was Pd [evaporated 4 nm]/Mg [sputtered]/Ni. We deposited the Pd thin film by vacuum deposition on the Mg film which was deposited by DC magnetron sputtering on the Ni substrate. During the deposition of the Pd thin film, the pressure was below \(4 \times 10^{-6}\) mbar. Before depositing the Pd thin film, we etched the Mg film in order to remove a surface MgO layer. It took 5 min to deposit the Pd thin film, and a thickness of the film was estimated about 4 nm.

The surface structure and the particle sizes were obtained by AFM measurement for the height value of the particles. The AFM images were measured by NanoScope III-a (Veeco Instruments) with tapping mode. The XPS measurement was carried out by the Mg Kα X-ray (1253.6 eV) and the hemispherical electron analyzer (PHOIBOS150-CCD, SPECS). The base pressure of XPS analysis chamber was \(2.9 \times 10^{-10}\) mbar. We used S K-edge NEXAFS measurement for studying the DMS dissociation reaction, because the method allows analysis of a local structure around an absorption edge of a selected element. The measurement was carried out with He-path system at the soft X-ray double crystal monochromator beamline of BL-3 on Hiroshima Synchrotron Radiation Center (HiSOR) [7, 8].

III. RESULTS AND DISCUSSIONS

A. AFM images

Figure 1 shows the AFM images for the surface of the Pd (sputtered) and the Pd (evaporated), respectively. Many nano sized features can be observed in both samples. The average size of the Pd (sputtered) is clearly smaller than that of the Pd (evaporated). In case of the DC magnetron sputtering, the Pd atoms are sputtered by accelerated Ar\(^+\) ions. On the other hand, in case of the vacuum deposition, the Pd atoms are evaporated by heating a Pd bulk rod source. We speculate that the different particle size depends upon the kinetic energy of the Pd atoms generated from the bulk source. When we prepare the Pd thin film by the vacuum deposition method, a kinetic energy of the evaporated Pd atoms is smaller than that of the sputtered Pd atoms. The larger nanoparticles are formed by the vacuum deposition because the Pd atoms that have low kinetic energy easily cause aggregation.

B. S K-edge NEXAFS

Figure 2 shows the S K-edge NEXAFS spectra for the DMS adsorbed on the Pd (sputtered) and the Pd (evaporated)/Ni substrates. We have also shown the spectra in Fig. 2 for atomic S, DMS, and SO\(_4^{2-}\) as standard. For the atomic S, DMS and SO\(_4^{2-}\), we have prepared c(2\(\times 2\)) S/Pd(100) surface, the multilayer DMS on the Ni substrate at 90 K and powder sample of K\(_2\)SO\(_4\), respectively. We use our previously study as a reference in order to decide the peak position of MT [5]. The Pd (sputtered) and the Pd (evaporated) samples were taken out to atmosphere before these measurements. The difference between the post-edge at 2488 eV and the pre-edge at 2465 eV is the edge-jump value. The value means a total amount of S atoms. The edge-jump values of the Pd (sputtered) is larger than that of the Pd (sputtered). Therefore an amount of S atoms on the Pd (sputtered) is larger than that on the Pd (evaporated). The spectra are normalized with the edge-jump to compare the difference of the chemical states per S atom for both of samples. The
FIG. 2: The S K-edge NEXAFS spectra for Pd (sputtered), Pd (evaporated), atomic S, DMS, and SO$_4^{2-}$.

spectra for the DMS on the Pd (sputtered) and the Pd (evaporated) surface have four characteristic peaks corresponding to the chemical states of atomic S, MT, DMS, and SO$_4^{2-}$. The DMS molecule on the Pd surface dissociates to MT, and the MT dissociates to atomic S [5]. Then the atomic S is oxidized to SO$_4^{2-}$ by air. The spectra for atomic S, MT, DMS, and SO$_4^{2-}$ are inserted in the figure as standard samples. Comparing these two spectra, the peak intensity of SO$_4^{2-}$ for the Pd (evaporated) is larger than that of the Pd (sputtered), and the peak intensity of MT for the Pd (evaporated) is smaller than that of the Pd (sputtered). These results indicate that the amount of atomic S dissociated from MT on the Pd (evaporated) surface is large in comparison with that on the Pd (sputtered) surface. It is indicated that the dissociation reaction of DMS is promoted on the Pd (evaporated) and weakened on the Pd (sputtered).

AFM results show that the average size for the Pd (sputtered) particle is smaller than that for the Pd (evaporated). An activity of catalyst for a nanoparticle can be dramatically influenced by the particle size. The difference of particle size alters the electron properties and the adsorption properties. It is reported that any adsorption reactions are promoted on small sized metal particles [9, 10]. Actually, the amount of DMS adsorption on Pd (sputtered) is larger than that on Pd (evaporated). By contrast, the dissociation reaction of DMS is more promoted on Pd (evaporated) than on Pd (sputtered). Thus there is a different factor from nanoparticle size which influences to the DMS dissociation reaction.

In our previous studies, it was indicated that there was the Pd-Mg alloy layer when we prepared the Pd thin film on the Mg thin layer by means of both vacuum deposition and DC magnetron sputtering methods [11]. Therefore, we propose the different factor originated from a presence of a Pd-Mg alloy layer. In the next section we discuss about the details of the factor.

C. Pd 3d and the Mg 2p XPS

If the Pd and the Mg make alloy layer, these elements have a chemical interaction between them. And, the DMS dissociation reaction is not affected by the Pd-Mg alloy layer when the Pd layer is thickly deposited. On the other hand, the dissociation reaction may depend on both Pd and Mg when the Pd-Mg alloy layer is thickly deposited and Mg atoms are presenting near the sample surface. Thus we consider that the factor affecting to the DMS dissociation reaction is the Pd-Mg alloy layer. In order to make clear the envisioned factor, it is needed to understand two factors. The first one of these factors is the chemical interaction between the Pd and the Mg. It was investigated that the Pd was oxidized and the Mg was reduced at Pd/Mg interface by former researches [4, 11]. Judging from those results, when the Pd binds chemically to the Mg, the Pd loses some electrons and the Mg picks up the electrons between the Pd and the Mg. The second one is that whether the Pd-Mg alloy is presented at the surface Pd layer. If the Mg atoms are presenting near the sample surface, the DMS dissociation reaction is dominantly affected by the Mg atoms. In contrast, the Mg atoms are not presenting near the sample surface, the reaction is not affected by the Mg atoms. These factors may cause the difference of the behavior for the DMS dissociation reaction. Thus, in order to make clear the difference, we have investigated the chemical interaction of Pd-Mg by using XPS.

Figures 3 and 4 show the Pd 3d and the Mg 2p XPS spectra for the sample (Pd/Mg), as described in experimental section. The spectra for the Pd 3d$_{5/2}$, Pd 3d$_{3/2}$, and Mg 2p are deconvoluted into three peaks as shown in both figures. Figure 3 shows that two components are presented at higher binding energy side of the Pd metal peak (335.6 eV). One of those components, which located at the higher energy side, corresponds to the chemical states of PdO (340.9 eV) [11]. Nevertheless the sample (Pd/Mg)
FIG. 4: Mg 2p XPS spectrum with deconvoluted component peaks for sample (Pd/Mg).

was kept in the in-situ condition during the sample preparation, the PdO component was formed. We supposed that the PdO component was derived from the Pd evaporation source because the source was covered with PdO. We tried to remove the surface PdO layer of the source by the pre-heating, but it was impossible to remove all PdO. We indicate that the other remaining peak shown at 337.1 eV corresponds to the chemical state of the Pd-Mg interaction. The peak position of Pd-Mg is higher binding energy side than that of Pd metal. In Fig. 4, the peak of MgO (50.8 eV) is presented at higher binding energy side of the Mg metal peak (49.8 eV). We show that the other remaining peak at 49.3 eV corresponds to chemical state of the Pd-Mg interaction. The peak position of Pd-Mg is lower binding energy side than that of Mg metal. For these reasons, Pd is oxidized and Mg is reduced at the Pd/Mg interface. In other words, Pd loses some electrons and Mg picks up the electrons from the Pd. In the future, we have a plan to make clear a depth profile of the Pd-Mg alloy layer and a roll of the alloy layer in the DMS dissociation reaction, because the chemical interaction between the Pd and the Mg has studied.

IV. CONCLUSIONS

We have formed the Pd thin film on the Mg layer by using DC magnetron sputtering and vacuum deposition and there were differences between these two deposition methods. The average size of the Pd particle prepared by DC magnetron sputtering was previously smaller than that prepared by vacuum deposition by AFM observation. In NEXAFS study, DMS dissociation is weakened at surface of Pd prepared by DC magnetron sputtering and promoted on Pd prepared by vacuum deposition. The dissociation reaction is promoted on the Pd surface prepared by vacuum deposition, which has big sized Pd particles.

Acknowledgments

The authors are grateful for the financial of a Grant-in-Aid for Scientific Research from Ministry of Education, Science and Culture, Japan (No. 19008872), Knowledge Cluster II in Aichi/Nagoya area, and Innovation Hiroshima/Tokai of JST (Japan Science and Technology Agency). This work was performed under the approvals of HSRC Program Advisory Committee (No. 10-A-16).

[1] A Züttel, Materials Today 6, 24 (2003).
[2] L. Schlaphbach and A. Züttel. Nature 414, 353 (2001).
[3] S. Singh, S. W. H. Ejtt, M. W. Zandbergen, W. J. Leg-erstee, and V. L. Svetchnikov, J. Alloys Compd, 441, 344 (2007).
[4] K. Yoshimura, Y. Yamada, and M. Okada, Surf. Sci. 566-568, 751 (2004).
[5] M. Morihara, K. Miura, T. Nomoto, and S. Yagi, J. Surface Anal. 14, 462 (2008).
[6] M. Morihara, K. Miura, T. Nomoto, and S. Yagi, e-J. Surf. Sci. Nanotech. 7, 298 (2009).
[7] S. Yagi, G. Kutluk, T. Matsui, A. Matano, A. Hiraya, E. Hashimoto, and M. Taniguchi, Nucl. Instrum. Meth. A 723, 467 (2001).
[8] S. Yagi, G. Kutluk, H. Namatame, A. Hirata, and M. Taniguchi, HSRC Activity Report, 1996-1997.
[9] I. Star and V. Matolin, Surf. Sci. 313, 99 (1994).
[10] J. Jiang, G. Oberdörster, A. Elder, R. Gelein, P. Mercer, and P. Biswas, Nanotoxicology 2, 33 (2008).
[11] S. Murakami, S. Ogawa, K. Shirai, C. Tsukada, S. Yagi, K. Nakanishi, and T. Ohta, e-J. Surf. Sci. Nanotech. 9, 438 (2011).