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Preparation of Ti and Fe Composition Gradient Thin Films by Sputtering with Mixed Powder Targets

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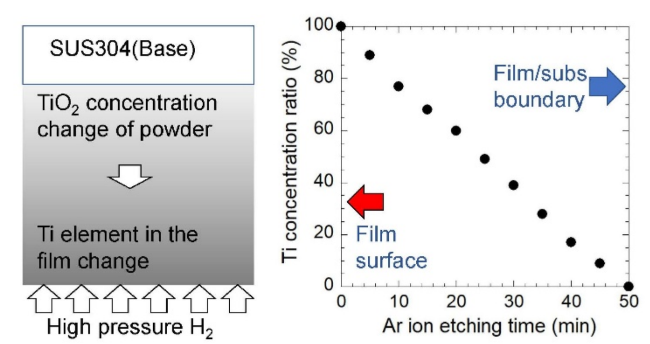

A composition-controlled functional film preparation method by plasma process using powder mixture targets. Thin films of a mixture of titanium (Ti) and stainless steel (SUS), which is known as a metal that affords a high rate of hydrogen penetration, were prepared using mixture powder targets of titanium oxide (TiO_2) and SUS in this study. Experimental results indicated that titanium and SUS mixture thin films were successfully prepared, and their mixtures could be controlled both on the SUS and Si substrate surface. In addition, the mixture of the TiO_2 and SUS powders in the target strongly affects surface morphology and/or crystallinity in the produced functional thin film. Gradient-functional thin films were prepared using 11 powder targets with variable Ti and Fe compositions. X-ray photoelectron spectroscopy depth profile results suggest that the Ti and Fe composition gradient thin films can be prepared by sputtering with mixed powder targets.

Keywords *Powder target; Sputtering deposition; Composition gradient thin film*

I. INTRODUCTION

Hydrogen embrittlement, wherein structures become brittle and fracture as a result of hydrogen penetration, is an important cause of failure of metallic materials [1, 2]. The economic loss from hydrogen embrittlement is 1% of the gross domestic product (GDP) of Japan, that is, several trillion yen [3, 4]. Therefore, the equipment necessary for working with hydrogen energy is made of the expensive metals that are resistant to hydrogen embrittlement [5]. This is one of the factors that hinder the adoption of hydrogen energy more broadly. This problem could be resolved if an inexpensive material could be coated with the material that is highly effective in preventing hydrogen embrittlement. For example, Hino *et al.* investigated the prevention of hydrogen embrittlement by several kinds of films and suggested that the films were much effectively for preventing hydrogen embrittlement [6, 7]. We also studied the formation of hydrogen embrittlement-resistant thin films on metal surfaces using aluminum alloy A6061-T6, nickel (Ni), and titanium (Ti) [8]. The thin films were prepared on the metal surface by sputtering for hydrogen embrittlement resistant in our previous works [9, 10]. As the results, several kinds of those films have the effect of inhibiting hydrogen permeation at high temperatures and pressures. However, when the crystal structures of the thin film and the substrate material differ significantly, the hydrogen ingress-prevention effect is small, and the thin film peels off from the substrate in some cases. To improve this situation, an intermediate layer between the thin film and the substrate was added. This intermediate layer is called a gradient-functional thin film because the composition differs between the substrate side and the top surface of the thin film [11]. In the fabrication of cutting materials, a high hardness and a sharp shape are required, using a 100% hard materials such as diamond. It is possible to make a high functional cutting tool at a low cost, if a thin film of high hardness can be formed on the surface of an easy-to-machine material. A functional thin film, which is close to the base material on the bonding surface and hard on the top surface of the thin film, can solve this problem. Generally, such thin films with different composition ratios at different locations are called a gradient functional thin film. They are used such as cutting tools and highly resilient materials [12, 13].

On the other hand, the preparation of gradient functional thin films is expensive using conventional film deposition methods. This is because it is necessary to use several types of reactive gases to prepare the film by the plasma chemical vapor deposition method, and because many targets must be used for depositing by pulse laser deposition (PLD) methods. Sputtering and pulsed laser deposition are techniques used in various fields among the plasma processes [14–24]. We have fabricated a variety of thin films by the methods [25–29] and succeeded in fabricating high quality thin films in all of them. However, it is difficult to fabricate functional thin films with mixtures of multiple elements. To solve this problem, a new sputtering deposition method has been developed using several kinds of powder target. Because of the simple way by which the doping density can be changed the target powder mixture, the sputtering deposition method may become more attractive. This process has been applied to the preparation of different functional thin films, such as magnetic and/or optical functional thin films. As those experimental results, functional thin films whose properties are generated by elemental mixing can be prepared using a mixture powder target. In addition, the element mixture in the prepared film can be controlled by the powder target. Using this new method, we previously attempted to prepare element gradient thin films with an increased Ni content on the thin film surface being in contact with the hydrogen gas, and SUS content at the boundary to the base SUS using NiO and SUS304 powder targets [30]. Before the sputtering deposition, 11 types of different mixture powder targets were prepared. And then, gradient functional thin films were prepared by using the 11 targets in sequence. Depth profiles by X-ray photoelectron spectroscopy (XPS) suggested that the films were actually prepared by this method [8]. The results suggested that the Ni concentration ratio in the prepared Ni and SUS composition films increased almost linearly with the increase in the NiO content in the mixed powder target. This indicates that the Ni/Fe concentration ratio can be controlled during the sputter deposition process.

However, Ni has characteristic problems such as magnetic properties and, thus, it is necessary to fabricate gradient-functional thin films having similar properties using other elements to improve versatility. Ti is one of the relatively inexpensive transition metals and has an effective property of preventing hydrogen embrittlement as Ni. Previously, we successfully fabricated thin films of Ti, titanium oxide (TiO_2), and titanium nitride (TiN) by sputtering and the PLD methods [31, 32] so that we are well versed in the Ti thin film fabrication.

In this study, composition-altered gradient functional thin films were prepared by sputtering deposition using powder targets. The Ti and SUS concentration ratio of Ti and stainless steel (SUS) 304 was changed for the film thickness direction using several different TiO_2 and SUS mixture powder targets.

II. EXPERIMENTAL METHODS

Figure 1 shows an experimental apparatus of this experiment. Functional Ti and SUS304 element composed thin films were deposited on Si and SUS304 substrates by radio-frequency (RF) sputtering deposition. Deposition was performed in a chamber evacuated to about 5×10^{-3} Pa by a molecular pump and a scroll pump. After the argon gas was introduced into the experimental system to 20 Pa by a controllable gas introduction equipment.

Several kinds of powder mixture targets were prepared using a homemade particle mixer. Ti and SUS304 elements gradient functional thin films were prepared using TiO_2 and SUS304 powders. In this study, the TiO_2 powder of a mean particle diameter of 2 μm with a 99.9% concentration and the SUS304 powder of a mean diameter of 150 μm with a 99.9% concentration were used as the target materials. A SUS304 target holder was placed 30 mm apart so that it faced the substrate surface and filled with the target powder. The powder was level on the target, and the substrates were not heated. The substrate temperature after deposition was almost 350–450K. The discharge power was 100 W, and deposition time was 1–4 h.

A Langmuir probe, made of a tungsten wire of 0.3 mm in diameter and 0.5 mm in length and was placed 15 mm from the substrate surface, was used to measure the electron density and the temperature. Properties of the fabricated thin films were assessed by several measurements. An atomic force microscope (JSTM-4100, JEOL) was used for the surface morphology and roughness. An alpha-step profilometer (ET4000A, Kosaka Lab.) was used to measure the film thickness. An X-ray diffractometer (RINT2100V, Regaku) was used for the crystalline structure determination. An X-ray photoelectron spectrometer (JPS9010, JEOL) was used for the composition analysis of the films.

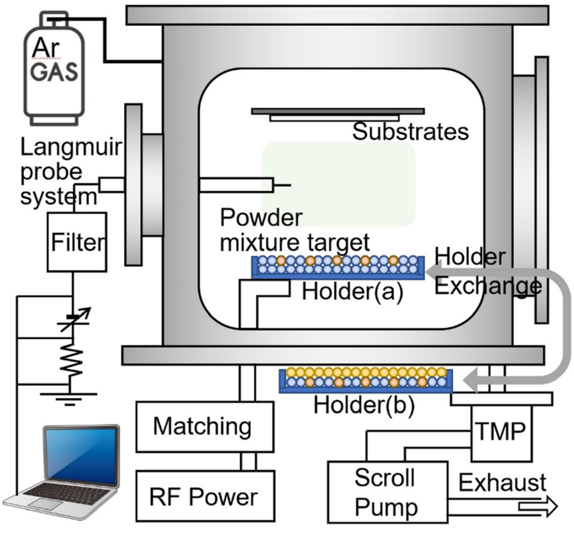

Figure 1: Experimental setup.

III. RESULTS AND DISCUSSION

A. Measurements of electron temperature and density of the plasma using powder mixture targets

In the sputtering deposition process, prepared film qualities were affected by characteristics of the processing plasma, such as the electron temperature and density. To measure the electron temperature and density, a Langmuir probe measurement was performed in the deposition process [33, 34]. The probe was placed in the processing plasma at the center position of the discharge area, as the parameters of mixed powder target of TiO_2 (20−80%)/SUS304 (80−20%). The measurements were repeated three times, and average values are shown in Figure 2. The electron temperature was 1−3 eV with an average of 2 eV. The value was almost constant regardless of the mixture ratio of Ti and SUS304 in the target powders. The electron density was approximately (2−6) × 10^9 cm^{-3} and was also almost constant. The results demonstrated that the processing plasma was almost independent of the TiO_2 powder mixture.

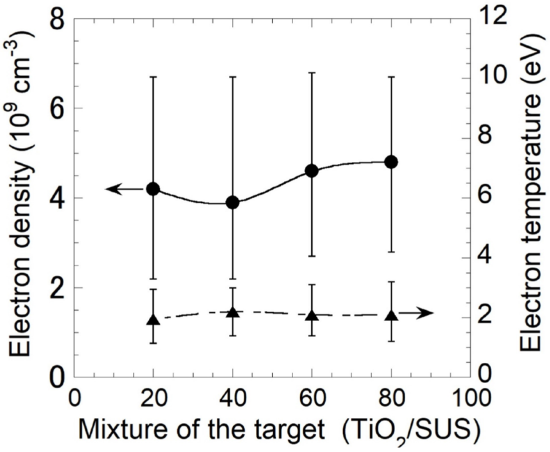

Figure 2: Dependence of electron density and temperature of the processing plasma on the TiO_2 mixture of the target.

B. Dependence of the film qualities on the powder target mixture

Dependence of prepared film qualities on the mixture of the TiO_2 and SUS powders was investigated. Surface morphology of the prepared films using the powder targets with 20, 40, 60 and 80% of TiO_2 was measured via AFM, and the results are shown in Figure 3. The surface of the film was composed of fine island-shaped particles, and their size increased as the ratio of TiO_2 increases. The relation between the TiO_2 and SUS mixture ratio and the particle diameter of the prepared film is shown in Figure 4. The mean diameter of the particle on the film with a 20% TiO_2 powder mixture was < 10 nm, and it increased with the increase in TiO_2 in the powder mixture. The dependence of the root mean square roughness (RMS) of the films on the TiO_2 and SUS ratio is also shown in Figure 4. The RMS measured by AFM was less than 5 nm at 20% TiO_2, indicating that a very uniform film was fabricated by this method. However, the RMS increased to 15 nm when the 80% TiO_2 powder mixture was used. This result is almost identical to that obtained by the thin film fabrication using NiO and SUS304 powder targets [8]. Toyoda and Sugimoto suggested that the crystallized TiO_2 thin film was possible to be prepared at the substrate temperature of 523 K using a metal organic chemical vapor deposition method and that crystallinity of the film and the deposition rate increased with increasing the substrate temperature [35]. On the other hand, Fujita *et al.* investigated

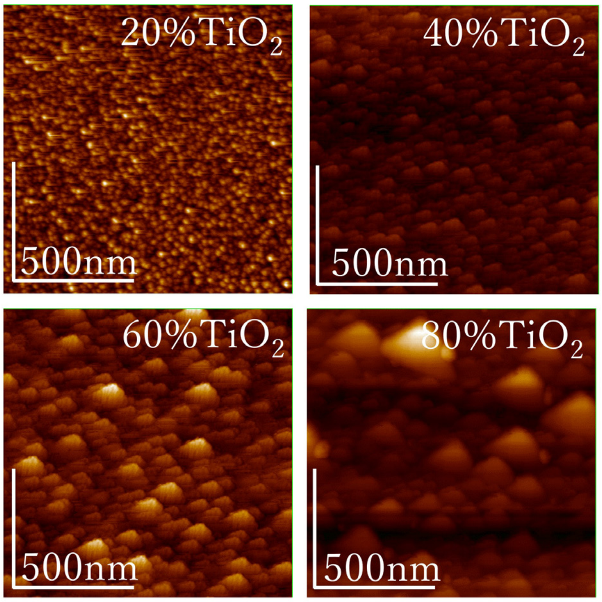

Figure 3: Surface morphology of the prepared film using the TiO_2 and SUS powder target mixtures.

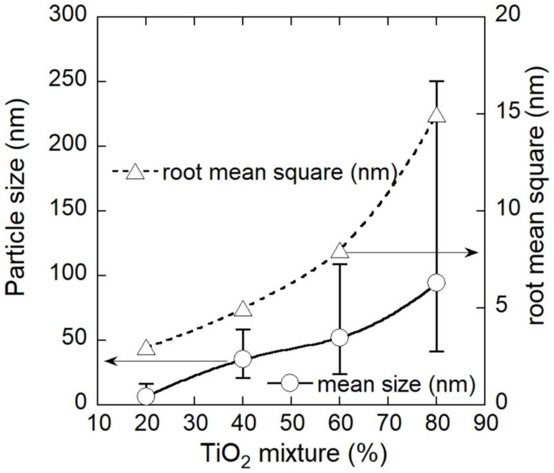

Figure 4: Dependence of the particle diameter and RMS roughness of the films on the mixtures powder target, measured by AFM shown in Figure 3.

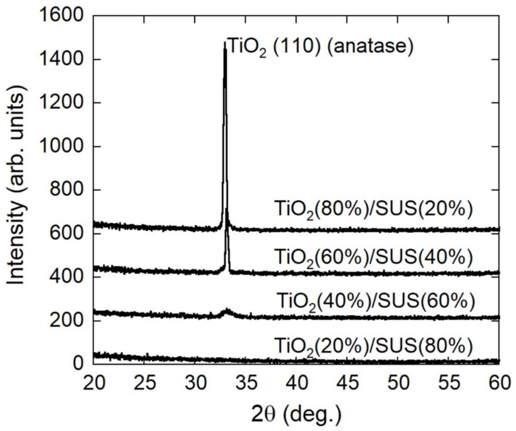

Figure 5: XRD spectra of the prepared film using the TiO_2 and SUS powder target mixtures.

the crystallization of amorphous alloys and a subsequent grain growth by after annealing in vacuum [36]. The results show that the material remained amorphous after annealing up to 693 K, with no image contrast due to Bragg reflection; at 703 K, bcc Fe primary crystals of about 6 nm diameter were formed, followed by progressive crystallization with increasing temperature [36]. Since these experimental conditions are different from those in the present study, a simple comparison cannot be made. Therefore, it is not yet clear why the grain size of the deposited thin film increases as the ratio of the TiO_2 powder increases. However, it may be related to the fact that the crystallization temperature of TiO_2 is lower than that of iron oxide [37].

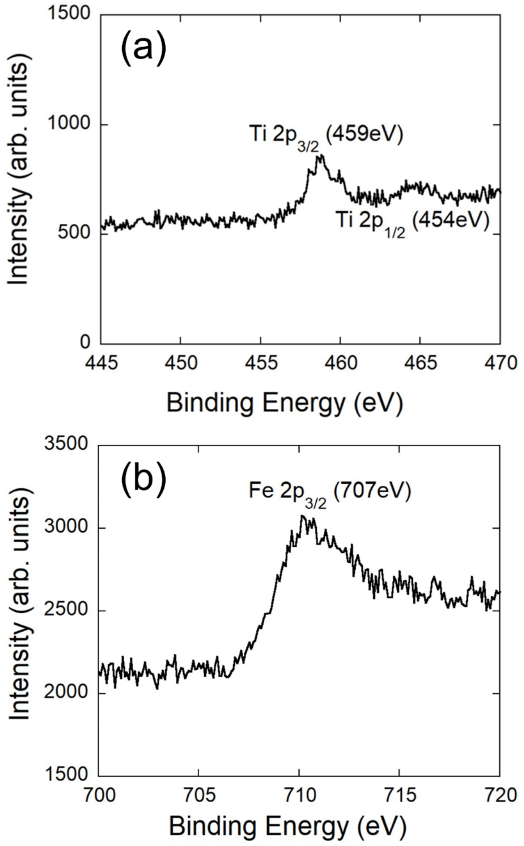

Figure 6: XPS spectra in (a) the Ti 2p and (b) Fe 2p core-level regions of the film prepared by sputtering using the powder target.

Figure 5 shows X-ray diffraction (XRD) patterns of the film, from which crystallinity of the film was assessed. For the 20% TiO_2 powder mixture, a crystal peak could not be observed in the prepared films. For the 40−80% TiO_2 powder mixtures, a TiO_2 anatase peak was observed and the peak intensity increased with the increase in the TiO_2 ratio.

Figure 6 shows XPS spectra of the films prepared using the TiO_2 and SUS mixed powder targets. 459- and 464-eV peaks are related to the Ti $2p_{3/2}$ and $2p_{1/2}$ core levels, and a 707-eV peak is associated with the Fe $2p_{3/2}$ core level. The results suggest that the films were composed by Ti and Fe. In the spectra, some peaks were shifted chemically. In addition, some Ti peaks were split. These results indicate that the films prepared by this method were oxidized.

The Ti and Fe concentration ratio of the film as a function of the TiO_2/SUS mass ratio in the powder mixture is shown in Figure 7. The mass ratio means the ratio of masses of the TiO_2 and SUS powders in the same target holder. The concentration ratio of Ti and Fe in the film was found to be almost linearly changed with the TiO_2/SUS mass ratio.

C. Gradient functional thin films with TiO_2 and SUS304 mixed powder targets

The gradient functional thin films were prepared by sputtering using the mixed powder targets. Deposition was almost the same method as that employed in our previous study [28] for the Ni/SUS gradient functional thin film using a 100% SUS304 powder, a TiO_2 (10%)/SUS304 (90%) mixture powder, TiO_2 (20%)/SUS304 (80%), and so on. In the present study, a 100% TiO_2 powder target was used. The RF power of the deposition was 100 W, and the deposition time was 1 h. The substrate surface was kept at room temperature.

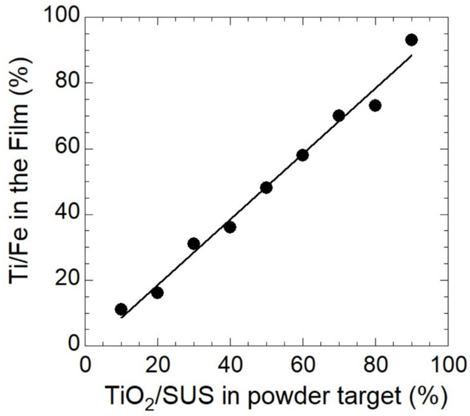

Figure 7: Dependence of the Ti and Fe element mixture on the TiO_2 and SUS powder target mixtures in the prepared films.

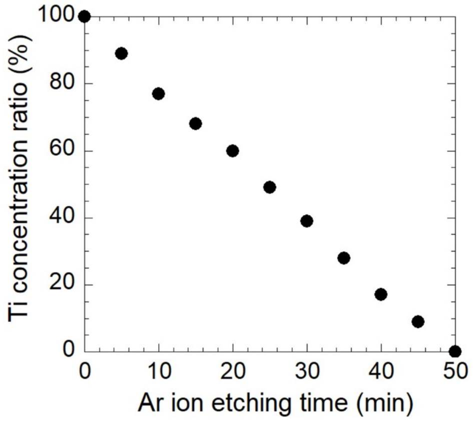

Figure 8: Change in the Ti concentration ratio of the prepared film as a function of the Ar ion etching time.

An XPS depth profile of the prepared film is shown in Figure 8 with Ar ion etching performed for 5 min between each measurement, corresponding to etching of several tens of nanometers. The result shows that the Ti concentration ratio of the prepared film decreased with the etching time and suggests that the gradient functional thin films with variable Ti and Fe compositions were prepared by our sputtering deposition method with TiO_2 and SUS304 mixed powder targets. Our experimental result indicates that the Ti/Fe concentration ratio of the prepared films varied almost linearly with the TiO_2/SUS304 ratio of the mixed powder target (Figure 7). The Ti/Fe concentration ratio can be controlled during the sputtering process by altering the powder target composition. Hence, the XPS depth profile suggests that the Ti and SUS304 composition varied almost linearly changed with the etching times (Figure. 8). This results strongly suggest that Ti and Fe composition gradient thin film can be prepared using by sputtering with mixed powder targets.

D. Element mixture thin film preparation process using TiO_2 and SUS mixture powder targets

The Ti and SUS composition-changed thin films were fabricated using the TiO_2 and SUS304 powder mixture targets by the sputtering method. It is revealed that the concentration ratio of Ti and Fe in the fabricated films increased almost linearly with the increase the TiO_2 content in the mixed powder target. The prepared films qualities were also changed by the TiO_2 and SUS304 powder mixture targets, along with the changes in surface morphology and crystallinity. Crystallinity of the prepared film increased with the increase of TiO_2 in the mixture. As the amount of the TiO_2 powder in the target mixture increased, the number of the Ti atoms and clusters in the process plasma increased. In this experiment, because the relatively high base pressures were used, oxygen and water remained in the ambient gas. The oxygen atoms and molecules may also be generated by sputtering from the TiO_2 and SUS surfaces used as the targets because Ti atoms are easily oxidized, which is one reason that they are used in photocatalysis. As a result, the crystalline nature of TiO_2 may have increased in the fabricated thin films. We have fabricated anti-hydrogen embrittlement coatings. We have found that metal and/or metal-oxide doped thin films, such as Ti and/or TiO_2, are effective in preventing hydrogen embrittlement. The conditions for thin films with high hydrogen embrittlement resistance are considered to be highly crystalline and dense for single composition films. Therefore, it is desirable to search for deposition conditions to fabricate such thin films. On the other hand, when thin films of multiple materials are used, we believe that the optimum value of the composition depends on the pressure of hydrogen and the duration of hydrogen exposure to the film surface. Furthermore, it has been reported that hydrogen is trapped in the intermediate region in the membrane where the body-centered cubic and face-centered cubic structures are combined [3, 9]. This suggests that a gradient-mechanism deposition like the present one improves the anti-hydrogen embrittlement effect. Although we were unable to present optimal thin film fabrication conditions in the present study, we would like to conduct further research to fabricate thin films with a higher hydrogen embrittlement prevention effect.

IV. CONCLUSIONS

Functional thin films, whose composition ratio of Ti and SUS were changed, were fabricated using sputtering deposition with TiO_2 and SUS304 powder mixture targets. The Ti and SUS mixture thin films were successfully prepared, and their mixture ratio could be controlled on the surfaces of both the SUS and Si substrates. In addition, the TiO_2/SUS ratio in the target strongly affects surface morphology and/or crystallinity in the fabricated functional thin film. We used this method to deposit gradient functional thin films with variable Ti and Fe compositions from 11 powder targets. The XPS depth profile results suggest that the Ti and Fe composition gradient thin film can be prepared using by sputtering with mixed powder targets.

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Note

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