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Control of Elemental Composition in the Prepared Thin Films by Sputtering Method Using Powder Targets

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***Abstract*— Fabrication method of the functional thin films with laterally graded elemental compositions have been developed by sputtering using multiple powder targets with different elemental mixing ratios. The mixed powder was sealed in a target holder with several holes. The composition cost was arranged to change sequentially. Using this target, thin films were prepared by sputtering method. The lateral distribution of the obtained thin films was examined, and it was found that thin films with a gradient in the planar direction could be produced using the same deposition equipment. The slope of this distribution was found to become more gradual as the distance between the substrate and target increased. The electron temperature and density of the sputtering plasma are found to be largely unaffected by the target type. On the other hand, the processing plasma changes with discharge voltage and gas pressure. This result suggests that deposition mechanism was controlled by gas pressure and discharge voltage.**

***Keywords*—Sputtering deposition, Powder target, Thin film, Multi-elements**

I. INTRODUCTION

Research and development to create new, highly functional materials has been proposed as a Japanese national strategy to solve social issues and to achieve the United Nations Sustainable Development Goals and 'Society 5.0'[1,2]. Moreover, the exploration of conventional materials is approaching its limits in most fields, making it necessary to expand the scope of exploration to new functional materials. However, the search for multisystem materials becomes more complex as the number of elements in the material increases.

Gradient-functional thin films, in which composition and function vary continuously or gradient within a single material, are in high demand in a variety of fields[3-13]. They are already used in familiar applications such as antireflective films for eyeglasses and transparent conductive films for touch panels, as well as in integrated devices such as solar cells, gas sensors, high-hardness materials for golf club heads, and multilayer filters for high-speed optical fiber communications. In recent years, it has been used in biological applications (artificial bones and teeth) and in the outer walls of spacecraft. It is expected that gradient functional thin films will be needed in many fields in the future. Chemical vapor deposition (CVD) methods have usually been used to fabricate gradient functional thin films. However, these methods have disadvantages such as difficulty in precise composition control and the need for multiple depositions. On the other hand, the sputtering deposition method has been used for thin film fabrication in various fields because it requires simple equipment and is inexpensive[14-23]. The sputtering deposition method also offers a wide choice of materials, easy processing, high deposition speed, and high uniformity. In addition, in many cases, harmless noble gases are used to generate process plasma at low energy. Therefore, it is safer than other plasma processing methods such as CVD and laser-based methods. However, the problem of this sputtering deposition method is that it increases cost when multi-element mixed thin films, and low melting point material thin films depotition, because high-density bulk targets are generally used for the sputtering deposition. Therefore, it is necessary to initially fabricate targets, utilize shutters, or use multiple targets. it is necessary to make new targets by other methods, such as spark-plasma sintering, and/or conduct sputter deposition using multiple targets. These target preparations are usually time-consuming and costly. As an alternative, plasma processes using multielement powder targets have been used to prepare functional multielement thin films in single-step processes[24-30]. In this process, several kinds of powder can be mixed and placed in a target holder in a vacuum chamber. Thin films are then deposited on a substrate mounted on the opposite side of the vacuum chamber to the target holder. It is possible to obtain a few samples with different doping densities during one cycle. For example, Sn-doped SiO_2 thin films were prepared using SnO_2 and SiO_2 mixed-powder targets. The elemental concentrations in the thin films can be controlled by the composition of the powder mixture.

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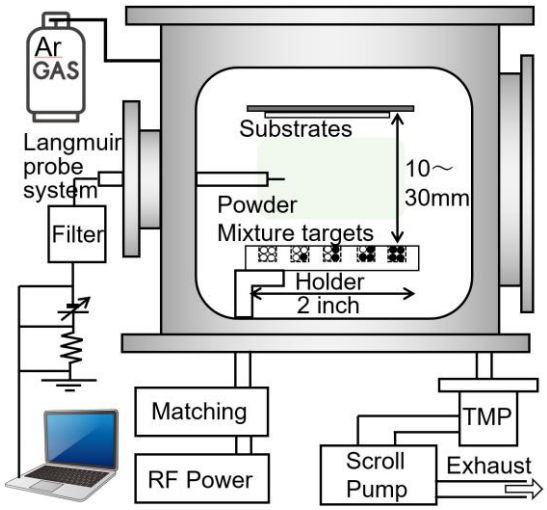
In recent years, gradient functional thin films have attracted much attention. Gradient functional thin films are the thin film with an intermediate layer in which the composition and properties (hardness, etc.) of the thin film are varied depending on the location. For example, in the fabrication of cutting tools, highly hard materials such as diamond are required to be made into sharp shapes, which requires advanced technology. For highly functional cutting tools can be made at a low cost, it is necessary to use a relatively low-hardness material such as stainless steel, etc., and process it into a sharp shape, and then form a high-hardness thin film on its surface. In this case, the adhesion of the thin film can be improved by making the bonding surface closer to the base metal and gradually increasing the hardness toward the topmost surface of the thin film. We have also used the sputtering method for hydrogen embrittlement prevention thin films. As a result, several types of thin films were found to be effective in inhibiting hydrogen ingress under high temperature and high pressure. However, when the crystal structures of the thin films and the base material were very different, the adhesion of the thin films was small and the thin films sometimes peeled off from the base material. To improve this situation, a gradient-functional thin film was provided between the thin film and the substrate. As a result, the degree of adhesion was improved and hydrogen embrittlement prevention thin film was successfully fabricated. We have succeeded in fabricating thin films with a gradient in the film thickness direction. However, we have not succeeded in fabricating a thin film with a gradient in the same plane at different locations. Such thin films can be used in the fabrication of golf club heads and gas sensors that detect multiple gases with the same detector.

In this study, we have fabricated such thin films with a tilted surface direction using a powder target via one-step sputtering deposition using several kinds of mixed-powder targets.

II. EXPERIMENTAL SETUP

A schematic of the experimental setup is shown in Fig. 1(a). The stainless-steel deposition chamber had a diameter of 400 mm and height of 450 mm. A powder target was placed in a 50.8 mm diameter handmade target holder composed of stainless steel with multiple holes was used. First, powder targets were placed in the multiple holes at the target holder. The hole sizes were 3 mmϕ and powder size of the target materials was 2~8 μmϕ for TiO_2 and 2~10 μmϕ for NiO. The process chamber was evacuated to a base pressure of about 1×10^{-3} Pa using a turbomolecular pump and a scroll pump. The total deposition pressure was 10 Pa with Ar gas (99.99%) introduced at a 10sccm flow rate. Sputtering deposition was performed with radio frequency (13.56 MHz) plasmas. The plasma was generated by applying a 100W discharge power to the powered electrode. Prior to loading in the deposition chamber, substrates were cleaned in an ultrasonic agitator several times, followed by washing with high-purity deionized water. The surface of the substrate was not heated and was almost at room temperature.

Si substrate was placed on the front side of the target. The substrate was located at a distance of 10~20 mm from the target. Prior to loading into the deposition chamber, the Si substrate was cleaned multiple times in ethanol using an ultrasonicator, followed by rinsing with high-purity deionized water each time.



(a) System setup

(b) Target holder

Fig. 1 Apparatus of the sputtering deposition with powder target. (a) System setup, (b) Target holder

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The plasma properties were studied by its optical emission spectra measured using emission spectrometer (Ocean Optics MAYA2000) and Langmuir probe method. The surface morphology and film thickness were measured by an atomic force microscope (AFM**:** JEOL JSPM4210) and a surface profilometer (Kosaka Laboratory Surfcorder ET4000A). The crystalline structure and crystallographic orientation of the prepared thin films were measured by X-ray diffraction (XRD: Rigaku RINT2100V) using CuKα radiation. The elemental composition ratio was measured by X-ray photoelectron spectroscopy (XPS; JEOL JPS9010).

III. Measurements of Electron Temperature and Density of the Plasma Using Powder Mixture Targets

In the sputtering deposition process, prepared film qualities were affected by the characteristics of the processing plasma, for example, the electron temperature and density and/or emission spectroscopy of the processing plasma. To measure the electron temperature and density, a Langmuir probe measurement was performed in the deposition process. [31,32] Langmuir probe was fid into the processing plasma at the center position of the discharge area as shown in Fig. 1. Figure 2 shows measurement results of the electron temperature and density as the parameters of mixed powder target of TiO_2(20–80%)/NiO(80–20%). In this experiment, three measurements were taken, and the average is shown. The electron temperature were 1~3 eV and average value was 2eV. The value was almost constant independent for TiO_2/NiO mixture in the target powders.

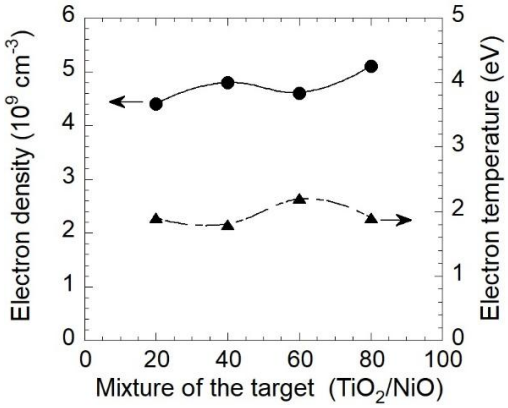

Fig. 2 Dependence of the electron temperature and density on the mixture of the TiO_2(20–80%)/NiO(80–20%) targets.

The electron density was approximately $4\times10^9 \sim 6\times10^9$ cm^{-3}, and the value was almost constant independent of the TiO_2/NiO powder mixture used. The results demonstrated that the processing plasma was almost independent of the TiO_2/NiO powder mixture.

Figure 3 shows the optical emission spectrum of the processing plasma at 10 Pa and 100 W on the mixture of the TiO_2(50%)/NiO(50%) targets. Ar atoms (Ar I) can be detected, however, Ti and Ni emission cannot be detected. This result suggests that emission Ti and Ni atoms not existed in the processing plasma.

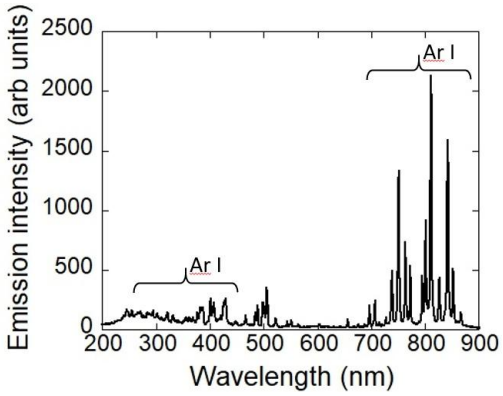

Fig. 3 The optical emission spectrum of the processing plasma at 10 Pa and 100 W on the mixture of the TiO_2(50%)/NiO(50%) targets.

IV. Measurements of Film Qualities Prepared Using Powder Target

A. Distribution of the prepared film thickness.

Figure 4 shows the distribution of the film thickness prepared using TiO_2(50%)/NiO(50%) targets measured by surfcorder (ET4000A). In this experiment, powder target was set on the center position under the substrate as shown in Fig. 4. RF powder was 100 W and Ar gas pressure was 10 Pa, and 40 Pa. As the results, thickness of the prepared film shows convex shape, and the shape of the film thickness distribution becomes gentler with increasing the gas pressure. In both case, the thickest film thickness was found to be just below the target.

B. XPS spectrum of the prepared films.

Figure 5 shows the XPS spectra of the film prepared at the center position of the substrate using TiO_2(50%)/NiO(50%)

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target. As the results, Ti $2p_{3/2}$ and Ni$2p_{3/2}$ peaks were observed at the same positions of the substrate.

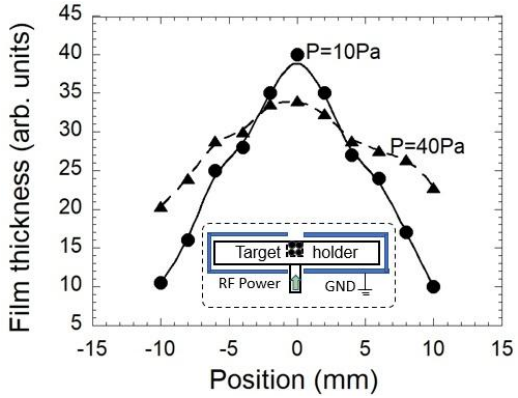

Fig. 4 Distribution of the film thickness prepared using TiO_2(50%)/NiO(50%) targets measured by surfcorder (ET4000A).

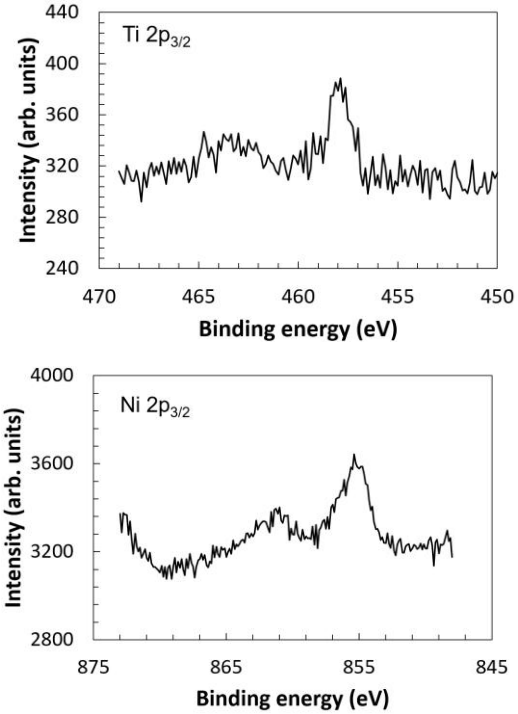

Fig. 5 XPS spectra of the film prepared at the center position of the substrate using TiO_2(50%)/NiO(50%) target.

Figure 6 shows the pictures of the substrate prepared on the film using 5 holes targets holder. In this preparation, mixture of the TiO_2(0–100%)/NiO(100–0%) targets were set on the as shown in Fig. 1(b). As the results, surface color changes in areas corresponding to the mixing ratio of the target as shown Fig. 6.

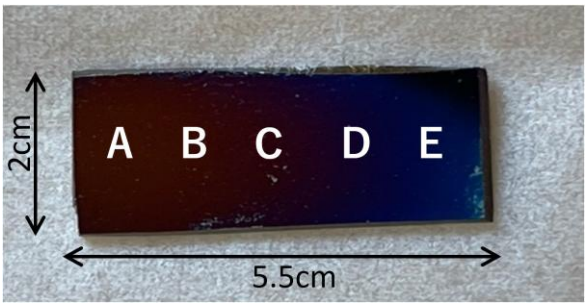

Fig. 6 Pictures of the substrate prepared on the film using 5 holes targets holder. The location of the deposition (A~E) corresponds to Fig. 1(b).

C. *Element distribution of the prepared film*

Figure 7 shows the Ti and Ni elements concentration distribution of the prepared film measured by XPS. As the result, element of Ti 2p3/2 was >90% at the position A, where TiO_2(100%). On the other hand, element of Ni 2p3/2 was >90% at the position E, where NiO (100%). This result suggests that a gradient in the plane direction could be fabricated in one process using powder target sputtering method.

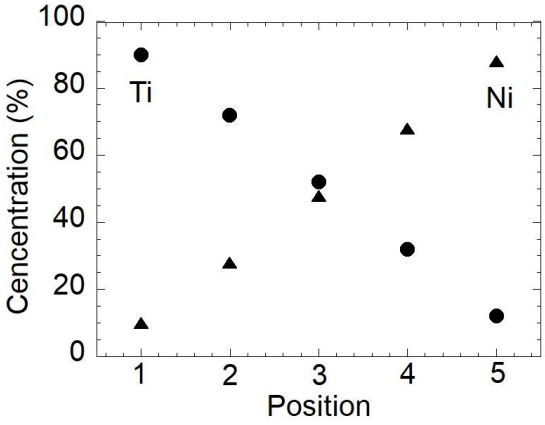

Fig. 7 Ti and Ni elements concentration distribution of the prepared film measured by XPS.

V. RELATIONSHIP BETWEEN THE PRPCESSING PLASMA CONDITION AND THE FILM QUALITY

Functional thin films with the gradient in the plane direction could be fabricated using powder targets in one sputtering process. The process of the sputtering deposition using powder target was considered with the experimental results. The electron temperature and density, measured by Langmuir probe, were almost constant independent for TiO_2/NiO mixture in the target powders as shown in Fig.2. The results demonstrated that the processing plasma was almost independent of the TiO_2/NiO powder mixture. The optical emission spectrum of the processing plasma, as shown Fig.3, suggests that emission Ti and Ni atoms does not exist in the processing plasma. On the other hand, XPS spectra of the film prepared at the center position of the substrate using TiO_2(50%)/NiO(50%) target shows Ti $2p_{3/2}$ and Ni $2p_{3/2}$ peaks on the substrate. Those results suggest that Ti and Ni mixture thin film can be prepared using mixture powder target at one sputtering process. The functional thin film was fabricated by surface reaction on a substrate involving non-luminescent titanium and nickel species sputtered in atomic or molecular form. Those sputtered particles reach the substrate while spreading. In addition, the sputtered particles are neutral, so they reach the substrate unaffected by the magnetic field and become a film by surface reaction. The behavior of the sputtered particles varies as a function of the incident ion energy, and gas pressure.

VI. CONCLUSIONS

Thin films with laterally graded elemental compositions have been developed by sputtering using multiple powder targets with different elemental mixing ratios. The mixed powder was sealed in a target holder with several holes. The composition cost was arranged to change sequentially. Using this target, thin films were prepared by sputtering method. The lateral distribution of the obtained thin films was examined, and it was found that thin films with a gradient in the planar direction could be produced using the same deposition equipment. The slope of this distribution was found to become more gradual as the distance between the substrate and target increased. The deposition mechanism was also found to be generalized by gas pressure and discharge voltage.

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