Investigation of Preparation Conditions and Microstructure of Mn-N Films by Reactive Sputtering

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The crystal structure of manganese nitride material depends on the chemical composition. In this paper, we report the crystal structure of manganese nitride which depends on the deposition condition of a flow ratio of argon and nitrogen, $F_N = N_2/(Ar + N_2)$. The samples were fabricated by an RF-sputtering method. Argon and nitrogen were used as a reactive sputtering gas. The crystal structure of the obtained films was analyzed by X-ray diffraction (XRD) measurements. The stoichiometry of the film under $F_N = 5-100$ % was evaluated as M$n_3N_2$. The lattice spacing $d$ of (101) expands as the nitrogen flow ratio increases. In the case of $F_N = 1$ %, the composition was evaluated as M$n_4N$. [DOI: 10.1380/ejssnt.2008.115]

Keywords: Sputter deposition; Manganese; Nitrides; Polycrystalline thin films; Magnetic films

I. INTRODUCTION

Research on the materials of nitrogen compounds has advanced in many research organizations [1, 2]. For example, the nitrogen compound semiconductors of III-V group, such as Ga-N, InGa-N, and AlGa-N, have been studied for the application in optical devices such as the diode that emits light very strongly in the range of ultraviolet radiation. Furthermore, the research on the diluted magnetic semiconductor has become active [3]. In the field of spin-electronics, gallium manganese nitride semiconductor is expected to be a promising material for quantum computer. Consequently, the GaMn-N is capturing the spotlight in this field, and a large number of works are still being conducted. The MnN$_2$ is known as a segregation phase showing the ferromagnetic behaviors in the diluted magnetic semiconductor GaMn-N film. The previous works on the GaMn-N films usually used the molecular beam epitaxy (MBE) method or the metal organic chemical vapor deposition (MO-CVD) technique [4]. These methods have already been established as the techniques to mass-produce. However, the deposition rate of the film is slow when preparing it by using MBE apparatus. In addition, this is an unsuitable method for making the film of a large area. As for the MO-CVD, high temperature is indispensable to film growth. It is one of the production methods in which the use efficiency of raw materials is low. The worst thing is that this method needs the investment of high cost to resolve poisonous exhaust gases.

On the other hand, because of the interesting magnetic properties of nitrogen compounds of transition metal, the iron nitride has been particularly investigated. In fact, this material exhibits a giant magnetic moment with a ferrimagnetic behavior, and has as a perovskite-type crystal structure [5]. In this light, the Mn-N compound also plays a leading role and has been studied, because it exhibits interesting electric and magnetic characteristics [6, 7]. Several different phases with various composition ingredient ratio are known in the manganese-nitrogen system. The ε-Mn$_4$N of perovskite based on the face centered cubic structure is a ferrimagnetic [8], and the η-Mn$_3$N$_2$ of the tetragonal crystal is anti-ferromagnetic [9, 10]. It can be expected that the characteristics of these compounds change very much by their states.

In this paper, we have investigated the microstructure evolution of the manganese nitride with various deposition conditions. When the film was made by the sputtering method, it is possible that the plasma, in particular, the high-energy electron impact, various particles in the plasma, and incident angle to the film surface greatly affect the characteristics and the structure of the film. We have especially considered the crystal structure of manganese nitride which depends on the deposition condition of a flow ratio of argon and nitrogen, $F_N = N_2/(Ar+N_2)$.

II. EXPERIMENTAL PROCEDURE

The samples of Mn-N films were evaporated on glass substrates using a reactive RF-sputtering method. The target of manganese disk was placed on the cathode with the magnetron. The electric power density applied to the cathode was closely controlled to 26 kW/m$^2$. In this study, the main parameters through the preparation were the sputtering pressure and the flow ratio, $F_N = N_2/(Ar+N_2)$, controlled from 0 to 100 % of the reactive process gas mixture. The same deposition condition was kept for 20 minutes. The thickness of films prepared with the above condition was 400 nm. The deposition of Mn-N thin films was performed at a temperature between 20 and 570°C under a pressure between 4 and 60 Pa during the above-mentioned mixture process. A crystallographic structure and a surface morphology of Mn-N film samples were identified by X-ray diffraction (XRD) measurements. The magnetic properties of the obtained films were measured by a vibrating sample magnetometer (VSM).

III. RESULTS AND DISCUSSIONS

The suitable substrate temperature that was one of the deposition conditions was investigated in the beginning.
Figure 1 shows the result of the relation between the substrate temperature during the film preparation and the crystallite size calculated using the Scherrer equation. The crystallite size for each sample was calculated using the Scherrer formula considering the most intense peak (101). The crystallite size increases from 127 to 194 angstrom with the temperature increase from 20 to 200°C. However, the crystallite size has decreased rapidly when the temperature is raised further. The above observation tells us that an appropriate temperature exists for the crystal growth. The substrate temperature affects the molecular concentration at the surface of the crystal, and hence, the crystal growth. The experimental condition that the substrate temperature is kept constant at 200°C will be used in the following experiments. This experimental condition of the substrate temperature may not be the most suitable value. However, it is a reliable value, judging from the high reproducibility in our experiments. Figure 2 shows the X-ray diffraction patterns of the manganese nitride films for each preparation condition. In Fig. 2, the sputtering pressure is the parameter for preparing samples at the deposition with each condition marked (a) to (d) in brackets. During the first phase, the data from the standard JCPDS file #01-1158 and the observed diffraction lines are compared. The measured film samples are determined as Mn$_3$N$_2$ compounds. The Miller indexes corresponding to respective peaks are shown in the figure, and correspond to (101), (110), (200), and (103) diffraction lines. This figure shows that the main diffraction line of these profiles is (101). As for the main peak, there is a tendency for intensity to decrease with the increase in the sputtering pressure at the deposition as shown. In other words, there is a correlation between low pressure and well oriented crystal growth of this film compound.

Suitable conditions for the sputtering pressure of 4 Pa were examined, and the results of the experiments are shown below. Figure 3 shows the X-ray diffraction patterns of the manganese and manganese nitride films for each preparation condition. In this figure, the nitrogen flow ratio $F_N$ is the parameter for preparing samples at the deposition with each condition marked (a) to (i) in brackets. In addition, the Miller indexes corresponding to respective diffraction peaks were indicated. The observed diffraction profiles from respective samples are compared with the data from JCPDS file #01-1158, 01-1202, and 32-0637. Then measured film samples are identified to Mn$_3$N$_2$ and Mn$_4$N compounds and metallic $\alpha$-Mn. As shown in profile (a) in Fig. 3, the film compound closest to metallic $\alpha$-Mn was obtained without introducing nitrogen in the chamber.

Moreover, a nitrogen gas flow ratio $F_N$ of 1% was introduced and resulted in film changes to the chemical structure of Mn$_4$N. These are clearly seen in Fig. 3 (b). It is important to note that the chemical structure starts to change with the addition of only 1% of nitrogen. Thus, it is necessary to control the conditions here very strictly. Generally, the manganese nitride compounds Mn$_4$N of the polycrystalline films have a structure of $A_4B$ type based on the face-centered cubic structure. The details of the Mn$_4$N crystal structure of this system are as follows: the nitrogen atom is arranged at the center of the cube as a body-centered position, and the Mn atom at the face-centered position forms an octahedral structure with the Mn atoms arranged at the corners of the cube [11]. In the present work, we consider the electronic relationship between the manganese and nitrogen ions in the Mn$_4$N film. It is thought that in this system there is no electronic overlap between N ion and Mn ions arranged at the corners of the cube. In other words, it is possible that the magnetic structure is correlated with the relationship of the electronic orbits between N-2p and Mn-3d at the face-centered positions forming an octahedral structure [12]. Thus, since the chemical composition of the obtained film is Mn$_4$N, it is supposed that a ferromagnetic character-
FIG. 3: The X-ray diffraction patterns of thin films prepared under the different nitrogen flow rates, N$_2$/(Ar+N$_2$); (a) 0, (b) 1, (c) 5, (d) 8, (e) 10, (f) 20, (g) 30, (h) 40, and (i) 100 %.

The characteristic exists. In Fig. 4, it was drawn the M-H loop of the magnetization by an applied magnetic field to this sample using the VSM, when an applied magnetic field is in a range of 5 kOe.

When the nitrogen flow ratio $F_N$ ranges from 5 to 100 %, the structure changes and becomes the stoichiometric Mn$_3$N$_2$ compound. The crystal structure of the film produced in the region of $F_N = 5$-100 % was a tetragonal structure. The main peak is (101). In addition, clear diffraction peaks (200) and (102) were observed. That is, although these films are polycrystalline, oriented to (101), they are almost all single-phase compounds. However, as for the diffraction peaks, it is interesting to note that their direction shifts to a low angle gradually as the quantity of nitrogen increases. Observing the main diffraction line (101), the calculations were made in order to investigate the influence of the flow ratio of nitrogen on the lattice spacing $d$. Figure 5 shows the result of the relation between the amount of nitrogen in preparation and the lattice spacing of the crystal. The nitrogen flow ratio is shown along the horizontal axis, while the lattice spacing is shown along the vertical axis. When the nitrogen flow is less than 10 %, the lattice spacing increases quickly. Beyond 10 %, the lattice spacing increases more slowly. This increase can be understood as follows: as the nitrogen flow ratio increases, the nitrogen ions in the plasma increase which cause the lattice distortion due to superfluous nitrogen ions mixed and crowded in the film.

IV. CONCLUSIONS

We have investigated the manganese nitride crystal structure which depends on the deposition condition of a flow ratio of argon and nitrogen, $F_N = N_2/(Ar+N_2)$.

The stoichiometry of the film under $F_N = 5$-100 % was evaluated as Mn$_3$N$_2$. The lattice spacing $d$ of (101) expands as the nitrogen flow ratio increases. This is because the increase of the nitrogen ions in the plasma causes the lattice distortion due to superfluous nitrogen ions mixed and crowded in the film. In the case of $F_N = 1$ %, the composition was evaluated as the Mn$_4$N compound with ferromagnetic characteristics.

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