

## Orientation of metal films deposited by sputtering using Ar/N<sub>2</sub> gas mixtures

Midori Kawamura, Yoshio Abe and Katsutaka Sasaki

Department of Materials Science, Kitami Institute of Technology, 165 Koen-cho,  
Kitami, 090-8507 Japan

### Abstract

The influence of adding N<sub>2</sub> to the sputtering gas on the crystal orientation of metal films was investigated. We observed a crystal orientation change of Ni films from (111) to (100) upon the addition of N<sub>2</sub> into the sputtering gas. The increase of substrate temperature resulted in higher degree of orientation of Ni films. Applying a similar deposition condition, Ag and Cu films were also deposited. However, no change was observed for Ag films. Cu films deposited at room temperature showed orientation change but the crystallinity became poor due to the incorporation of nitrogen. It is considered that the difference in the influence of N<sub>2</sub> addition is a result of the strength of interaction between nitrogen and metals. We must determine the suitable deposition conditions for the orientation change.

## Introduction

Sputter deposition of metal films is generally carried out using Ar gas of high purity. For the obtained films, it is known that the closest packed plane of the crystal structure tends to orient parallel to the substrate surface when the substrate is amorphous, such as glass[1,2]. For example, fcc metal films show preferential orientation with the (111) plane. This is because there is no lattice matching between the film and substrate, consequently, preferential orientation of the plane, which can minimize the surface energy of the film, becomes advantageous. In other words, it is difficult to prepare films with preferential orientation of another plane such as (100) plane[3].

Several attempts to change the preferential orientation have been conducted by adding reactive gas to the sputtering gas. For Pt films, orientation changes from the (111) to (100) plane by sputtering in Ar/O<sub>2</sub> gas mixtures have been reported[4,5]. However, as-deposited film itself had a poor crystallinity due to the incorporation of oxygen into the films. A postannealing process at high temperature was required to remove oxygen in the films and to obtain pure (100) Pt films[5]. We consider that a similar effect can be induced in the case of N<sub>2</sub> addition by selecting suitable counterpart metals. In a previous study, we prepared nearly singly (111)- or (100)-oriented Ni films by sputtering in Ar/N<sub>2</sub> gas mixture; the details have been described elsewhere[6]. In the case of Ni films, no

incorporation of nitrogen into the films occurred until certain N<sub>2</sub> flow ratios, which leads to highly crystalline films without any impurity.

In the present work, we report the deposition of Ni films at 200°C and 240°C. The improvement of crystallinity is aimed at here. In addition, we apply this method to other metals which are less reactive with nitrogen. Needless to say, metal reactive with nitrogen, such as Ti, must be avoided for the present purpose because it readily forms compounds with the N<sub>2</sub> added to the sputtering gas. Then, Cu and Ag are selected because Cu forms only thermally unstable nitride which decomposes at around 450°C[7] and Ag does not form a nitride, respectively.

### Experimental

Deposition was carried out by sputtering Ni, Ag and Cu targets (all 99.99% purity) in Ar/N<sub>2</sub> gas mixture using an rf sputtering system (ANELVA, SPF-210). The system was evacuated to below  $3.7 \times 10^{-5}$  Pa, and then sputtering gas with various N<sub>2</sub> flow ratios (0-14%) was introduced, with the total gas flow controlled at 3.5 cm<sup>3</sup>/min. The total gas pressure was fixed at 1.1 Pa during sputtering. Corning #7059 glass substrates with the dimensions of 30 mm x 40 mm x 1.1 mm were used. The rf power was 100 W, and the distance between the substrate and the target was fixed at 45 mm. The substrate temperature during deposition was kept at 100, 200, 240°C or room temperature (RT). The substrate

holder was set to an electrically floating potential, which generally leads to the improvement of film quality because of the substrate bias effect[8,9].

Film thickness was estimated by multibeam interferometry. The crystal structure of the obtained films was investigated by X-ray diffraction (XRD) analysis with Cu-K $\alpha$  radiation. Crystallite size was calculated using Scherrer's equation on the basis of the full width at half maximum (FWHMs) values of (200) peaks of normal  $\theta$ - $2\theta$  scans. Rocking curve measurement was also carried out to investigate the angular spread of the plane normals about the substrate normal. To generate rocking curves,  $2\theta$  of the detector was locked at the position of diffraction peaks and the goniometer  $\theta$  drive was applied.

## Results and Discussion

### *Preparation of Ni films*

The change of the XRD patterns for Ni films deposited at 200°C and 240°C is shown in Fig. 1 as a function of N<sub>2</sub> flow ratio. As shown in Fig.1a, for the film sputtered at 200°C with an N<sub>2</sub> flow ratio of 0%, the Ni (111) peak is dominant and the Ni (200) peak is very small. Other small diffraction peaks of (311) and (222) are also observed. By introducing a small amount of N<sub>2</sub> (N<sub>2</sub> flow ratio: 0.5%), the preferential orientation of the film was changed to (200), and the (200) peak became stronger with increasing N<sub>2</sub> flow ratio up to 6%. At 7%, the peak intensity

of (200) begins to decrease and finally, a peak attributed to Ni<sub>3</sub>N (002) appears at 12% in addition to the peaks of the Ni phase. Thus almost single-orientation Ni (100) films are obtained under certain N<sub>2</sub> flow ratios (1% < N<sub>2</sub> < 7%). The reason for this interesting orientation change is not yet fully understood, but it is considered that preferential adsorption of nitrogen on Ni (111) suppresses the growth of the plane and enhances the growth of the Ni (100) plane.

At 240°C (Fig.1b), similar orientation change from (111) to (100) is seen upon the addition of N<sub>2</sub> into the sputtering gas. Here, the intensity of (200) peaks is much higher. Another difference at this substrate temperature is that the nitride phase does not appear, even in the film deposited with an N<sub>2</sub> flow ratio of 14%. For the sputtering process in the present Ni-N<sub>2</sub> reaction system, we previously reported that the reaction at the substrate surface is dominant[10], although a target reaction mode is also possible in general. Consequently, the formation phase is governed by the local nitrogen concentration around the substrate. It is considered that with increasing temperature, the desorption reaction is promoted and the sojourn time of nitrogen on the film surface is shortened. This can explain why the nitride phase does not appear at 240°C.

Figure 2 shows the crystallite size of the films deposited at temperatures of 200°C and 240°C as a function of N<sub>2</sub> flow ratio. The size is about 36 nm for (100)-oriented Ni films deposited at 200°C and increases to about 45 nm for the

films deposited at 240°C. At the same substrate temperature, the size decreases slightly with increasing N<sub>2</sub> flow ratio. It is also found that the deterioration of orientation observed at 7% N<sub>2</sub> and 200°C is related to the reduction of the crystallite size. Figure 3 shows the FWHM values obtained from rocking curves for films deposited at each temperature. The smallest FWHM value decreases from 13° at 200°C to 8.5° at 240°C. As a result, it is found that an increase of substrate temperature leads to grain growth of Ni films and improvement of orientation.

#### *Preparation of Ag and Cu films*

A similar sputtering process was also applied to the deposition of Ag and Cu films. Figure 4 shows the change of XRD patterns for Ag films deposited at RT and 100°C as a function of N<sub>2</sub> flow ratio. Film deposition at higher temperature was not carried out because Ag atoms easily agglomerate under such a condition. The obtained d-spacings of Ag films are in accord with those in literature[11] and do not change with the increase of N<sub>2</sub> flow ratio. In this figure, no difference in the crystal orientation of the films is seen. Consequently, the addition of a small amount of N<sub>2</sub> is not always useful for changing the orientation. Because Ag does not form any nitride phase, the interaction between Ag atoms and nitrogen is considered to be weaker than that in the previous case (Ni). Further experimental

runs are required to explore more detailed conditions, such as a much higher N<sub>2</sub> flow ratio, to confirm the possibility of orientation change of this system.

Figure 5 shows the change of XRD patterns for Cu films deposited at RT and 200°C as a function of N<sub>2</sub> flow ratio. At RT, almost single-orientation film with (111) is obtained at 0%, but the Cu (200) peak intensity and intensity ratio of (200) to (111) increase at an N<sub>2</sub> flow ratio of 1%. At the same time, peak intensities of the films become weaker with the increase of N<sub>2</sub> flow ratio. At 10%, only a small peak of (111) is seen. At 200°C (Fig.5b), the (111) peak is the main peak, and almost no difference in the preferential orientation is observed between the films from 0% to 10% N<sub>2</sub>. The d-spacings of both (111) and (200) peaks of the films are shown in Fig. 6. At RT, the d-spacings of both peaks increase with the increase of N<sub>2</sub> flow ratio, as shown in Fig. 6a. This indicates that nitrogen in the sputtering gas is incorporated into the crystal lattice of Cu films. It is believed that this impurity incorporation causes the deterioration of the crystallinity of Cu film. The reason for the increase of the (200) peak intensity is considered to be same as that in the case of Pt films[5] where oxygen incorporation played an important role in the change of the peak intensity ratio. Namely, since oxygen-incorporated Pt (111) planes have a larger distortion than oxygen-incorporated Pt (200) planes, this results in the (200) preferential orientation[5]. At 200°C, on the other hand, no change of the d-spacing is seen, that indicating no nitrogen is incorporated into

the films. Thus, nitrogen incorporation occurs at RT but not when the substrate is heated. A similar tendency was also observed in the case of Ni films[10], though highly oriented (100) Ni films are obtained under certain conditions, as described above. Compared with the case of Ag films, it is found that the interaction between Cu atoms and nitrogen is stronger because Cu nitride can be formed, though it is reported to be thermally unstable. Considering the similarity with the result for Pt films, it might be possible to obtain highly oriented (100) Cu films after postannealing treatment.

We have found different results of the influence of N<sub>2</sub> added to sputtering gas. For Ni film preparation, the addition of a small amount of N<sub>2</sub> leads to preferential orientation change from (111) to (100). However, highly oriented (100) films were not obtained for Ag and Cu films in spite of up to 10% N<sub>2</sub> addition, probably because of the different strength of interaction between metal atoms and nitrogen. The possibility of changing the crystal orientation still remains, but conditions far different from those applied for the Ni films must be examined.

## Conclusion

We have investigated the influence of adding N<sub>2</sub> to the sputtering gas on the crystal orientation of several metal films (Ni, Ag and Cu) which are known to be unreactive with nitrogen. Films were deposited in Ar/N<sub>2</sub> gas mixtures and were

characterized by XRD measurement. It is found that sputtering in Ar/N<sub>2</sub> gas mixtures can change the crystal orientation of Ni films. We can control the preferential orientation of the films by selecting the appropriate sputtering gas composition and substrate temperature. A similar sputtering process was also applied for the deposition of Cu and Ag films. However, highly oriented (100) films were not obtained in either case. This was probably due to the difference in the interaction between metal atoms and reactive gas (nitrogen).

#### Acknowledgement

We would like to thank K. Iibuchi and N. Minamiya for their assistance on sample preparation and characterization.

## References

- [1] K. L. Chopra, Thin Film Phenomena, McGraw-Hill, New York NY, 1969.
- [2] M. Mashita, Hyoumen Kagaku, 1 (1981) 46 (in Japanese).
- [3] C-A. Chang, J. Vac. Sci. Technol. A 8 (1990) 3779
- [4] M. Hecq and A. Hecq, J. Vac. Sci. Technol. 18 (1981) 219.
- [5] M. H. Kim, T. S. Park, E. Yoon, D. Su. Lee, D. Y. Park, H. J. Woo, D. I. Chun and J. Ha, J. Mater. Res. 14 (1999)1255.
- [6] M. Kawamura, K. Iibuchi, Y. Abe and K. Sasaki, Jpn. J. Appl. Phys. (to be published)
- [7] L. Maya, J. Vac. Sci. Technol. A 11 (1993) 604.
- [8] A. P. Huang, S. L. Xu, M. K. Zhu, B. Wang, H. Yan and T. Liu, Appl. Phys. Lett. 83 (2003) 3278
- [9] T. Q. Li, S. Noda, F. Okada and H. Komiyama, J. Vac. Sci. Technol. B 21 (2003) 2512
- [10] M. Kawamura, Y. Abe and K. Sasaki, Vacuum 59 (2000) 721.
- [11] JCPDS –International Center of Diffraction Data, PDF-2 Database CD-ROM version, No.4-783 (2000).

## Figure Captions

Figure 1: XRD patterns of sputtered Ni films with various N<sub>2</sub> flow ratios.

The substrate temperature was (a) 200°C and (b) 240°C.

Figure 2 : Change of crystallite size for the Ni films deposited at 200°C and 240°C as a function of nitrogen flow ratio.

Figure 3: The FWHM values obtained from the rocking curve of Ni films.

Figure 4: XRD patterns of sputtered Ag films with various N<sub>2</sub> flow ratios.

The substrate temperature was (a) RT and b) 100°C.

Figure 5: XRD patterns of sputtered Cu films with various N<sub>2</sub> flow ratios.

The substrate temperature was (a) RT and b) 200°C.

Figure 6: Change of d-spacings of (111) and (200) planes for Cu films deposited at RT and 200°C with various N<sub>2</sub> flow ratios.

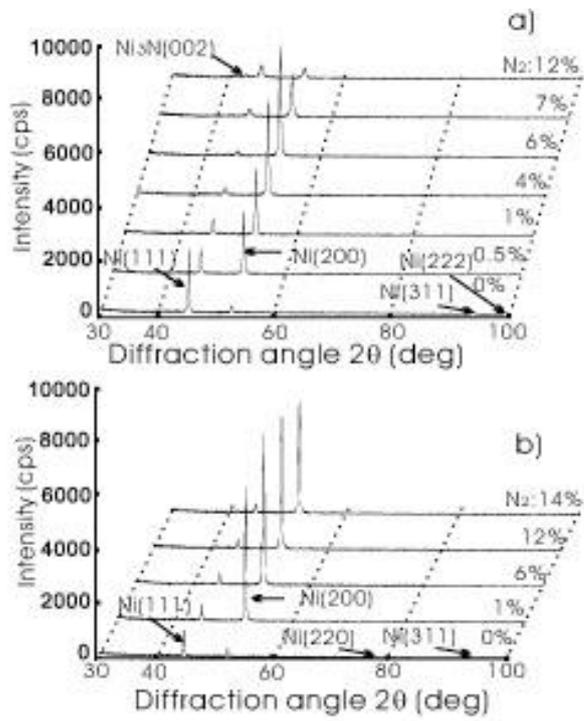


Fig.1

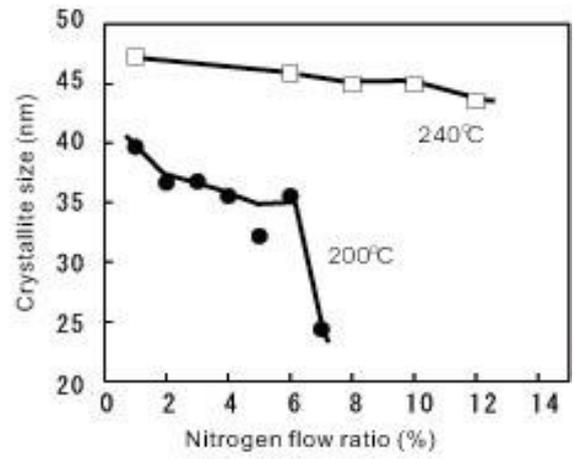


Fig.2

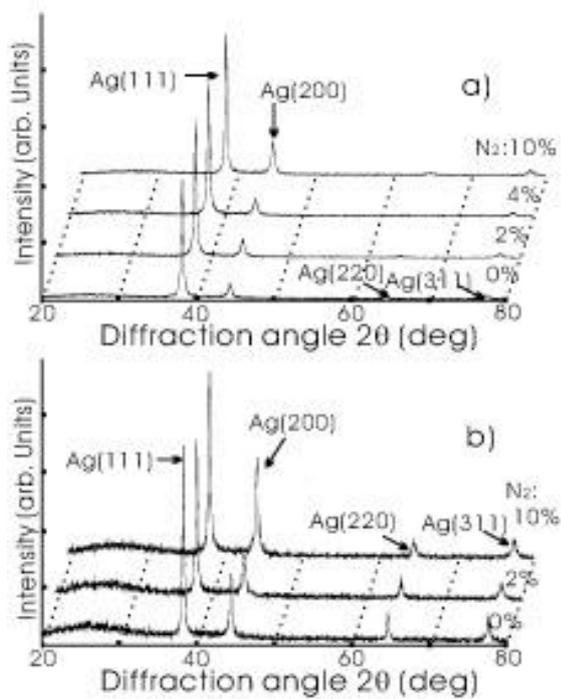
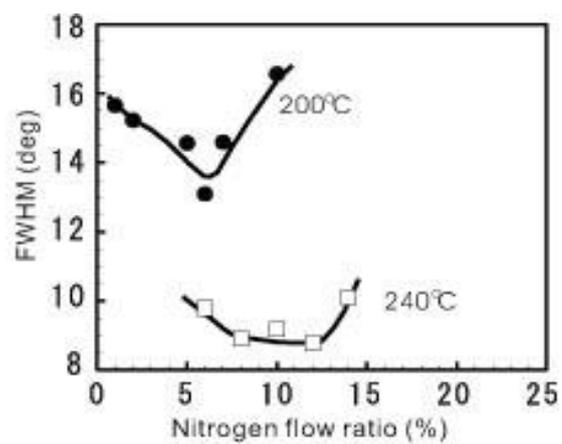


Fig.3

Fig.4

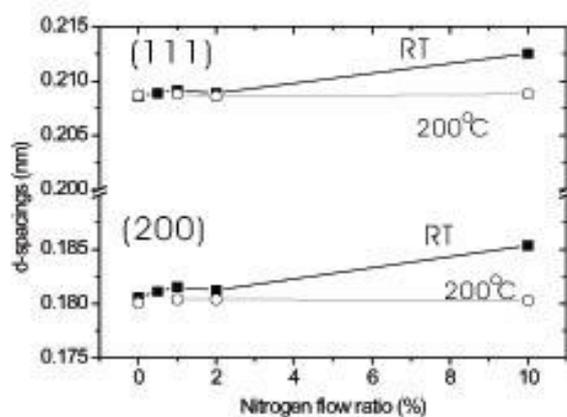
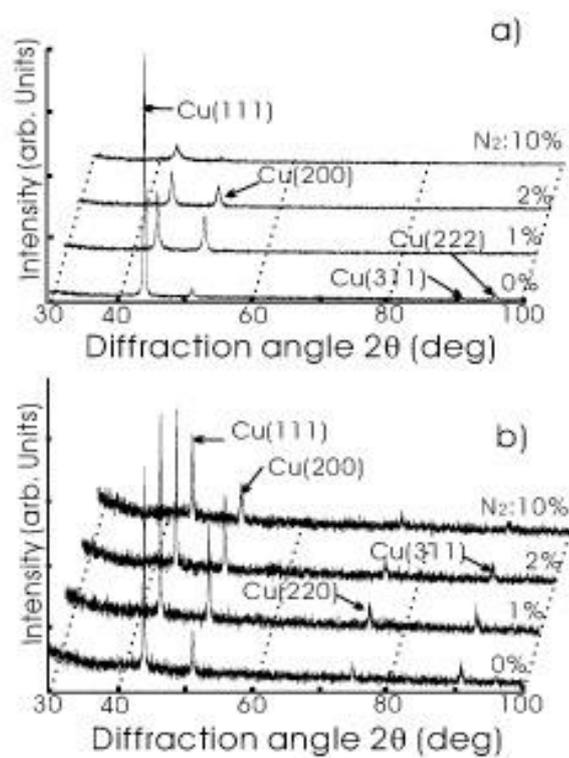


Fig.6

Fig.5