

# Sputter-deposition of Ag films in a nitrogen discharge

Midori Kawamura, Yoshio Abe and Katsutaka Sasaki

Department of Materials Science, Kitami Institute of Technology,

165 koen-cho, Kitami, Hokkaido, 090-8507 Japan

phone: +81-157-269451, fax: +81-157-264973

e-mail: [kawamumd@mail.kitami-it.ac.jp](mailto:kawamumd@mail.kitami-it.ac.jp)

## Abstract

In general, the presence of a reactive gas in the sputtering atmosphere must be avoided to prevent the formation of any other phases during the preparation of metal films. However, we hypothesized that films of metals, which do not form a nitride phase, could be prepared even in 100% nitrogen. Ag films were sputter-deposited in nitrogen and characterized. We found that it is feasible to obtain pure Ag films by rf sputtering in a nitrogen discharge. No other phase but Ag was detected by X-ray diffraction (XRD) analysis and nitrogen was not detected in the film by Auger electron spectroscopy. Electrical resistivity was also as low as  $2.8 \mu\Omega\text{cm}$ . Moreover, we found that Ag films thus deposited at a substrate temperature of  $100^\circ\text{C}$  exhibited preferential orientation of (100), though that of (111) is generally observed in films sputtered in Ar. At other substrate temperatures, the degree of (100) orientation decreased. Consequently, we have found that sputter-deposition by the present method is useful for preparing pure Ag films with texture controlled by selecting the appropriate conditions.

Keywords: crystal orientation, Ag film, rf sputtering, interaction between nitrogen and metal, XRD, electrical resistivity

PACS codes: 61.10.Nz, 68.55.Jk, 81.15.Cd

## Introduction

The sputtering method is widely used for the deposition of metal and compound thin films for various purposes. The deposited metal film tends to orient its closest packed plane parallel to the amorphous substrate surface to achieve minimum surface energy of the film. For example, fcc metal films, such as Pt, Ni and Al, tend to show preferential crystallographic orientation with (111), its closest packed plane, on glass or SiO<sub>2</sub>/Si substrates [1-3]. When films with another texture are favored, we cannot simply deposit them in the conventional way. Typically, sputter-deposition of metal films is carried out in pure Ar gas to prevent any compound formation. However, it has been reported that the addition of a small amount of reactive gas (such as O<sub>2</sub> or N<sub>2</sub>) gives rise to a change in the crystal orientation [4-8]. For instance, we have reported that the addition of N<sub>2</sub> to the sputtering gas changes the preferential orientation of Ni films from (111) to (100)[6]. Here, Ni has the feature of a low adsorption energy with N<sub>2</sub>. Apparently, the present method can be useful only with a combination of reactive gas and a less reactive counterpart metal. In that sense, we can expect to apply the method to Pt group metals, Au and Ag, because they do not form nitride phase. It may even be possible to obtain metal films by sputtering in pure N<sub>2</sub>. In the present work we undertake to deposit Ag films. Although its azide (AgN<sub>3</sub>), which is also a nitrogen-containing compound, is well known to exist, it is usually prepared in the liquid phase [9]. We

report that it is feasible to fabricate Ag metal films by sputtering in N<sub>2</sub>. The crystal orientation change compared with the conventional films deposited in Ar is also shown.

## **Experimental**

Ag films with a thickness of approximately 200 nm were prepared by sputtering an Ag target (99.99% purity) in N<sub>2</sub> gas using an rf sputtering system (ANELVA, SPF-210). For comparison, film deposition in Ar gas was also carried out. The system was evacuated to below  $3.7 \times 10^{-5}$  Pa, and then high-purity nitrogen gas was introduced with the gas flow controlled at 3.50 cm<sup>3</sup>/min. The sputtering gas pressure was fixed at 1.6 Pa during the sputtering. Corning #7059 glass was used as substrates. The rf power was 100 W, and the distance between the substrate and the target was fixed at 45 mm. The substrate temperature (T<sub>s</sub>) during deposition was set to either 100, 150, 200°C or room temperature (RT).

The crystal structure of the obtained films was investigated by X-ray diffraction (XRD) analysis with Cu-K $\alpha$  radiation. The grain size was calculated using Scherrer's equation. Electrical resistivity was measured by the four-point-probe method, and the temperature coefficient of resistivity (TCR) was calculated using the values of resistance measured at 30°C and 60°C. Film thickness was estimated by multi beam interferometry. Auger electron spectroscopy (AES) was used to examine the existence of nitrogen in the film because it is known to be as sensitive to light elements. The spectrum was acquired under an accelerating voltage of 3 kV for qualitative analysis of the films.

## Results and Discussion

The XRD patterns of Ag films deposited in N<sub>2</sub> and in Ar at 100°C are shown in Fig. 1. For the film sputtered in Ar gas, the Ag (111) peak is dominant, as is usually observed. The Ag (200) peak and other small diffraction peaks of (220) and (311) are also seen. With sputtering in N<sub>2</sub>, the preferential orientation of the film is changed to (200) and the peaks of (311) and (222) disappear. A similar change was observed in the case of Ni films sputtered in Ar-N<sub>2</sub> mixed gas [6]. No shift of the Ag peak position and no peaks attributed to other phases are seen. Thus, it is feasible to prepare Ag film by sputtering in pure nitrogen discharge, as we predicted. Moreover, the orientation with (100), although it is not yet a single orientation, is obtained, which is not possible conventionally. In general, to prepare (100)Ag films, it is necessary to use (100) MgO as the substrate. The present method has the merit of yielding the (100)-preferred orientation without the need of use such a single-crystal substrate.

Figure 2 shows the AES spectrum of the film deposited in pure nitrogen discharge at 100°C after the surface contamination was removed by Ar ion etching. Peaks appearing at around 260, 304, 351, and 356 eV are all attributed to the Ag MNN transition [10]. Peaks for nitrogen (379 eV), carbon (271 eV), oxygen (503 eV) and sulfur (152 eV) are not observed in the spectrum. Although AES is a known to be sensitive to light elements, it is clear that nitrogen and other impurity elements do not exist in the Ag film or their concentrations are below the detection limit. Thus, we found that no nitrogen was incorporated into the Ag films with (100)-preferred orientation even though they were deposited in nitrogen discharge. This is beneficial because we will not require post-annealing of the films at high temperature to remove the processing gas, which was required in the case of Pt films deposited in Ar-O<sub>2</sub>[5].

The deposition of Ag film was also carried out at several substrate temperatures ( $T_s$ ). Figure 3 shows the intensities of XRD diffraction peaks for (111) and (200) and their intensity ratios to the total intensity for all peaks as a function of  $T_s$ . Here, the intensity ratios were calculated based on  $I(111)/\Sigma I(hkl)$  and  $I(200)/\Sigma I(hkl)$ , respectively. It is clear that both the intensity and its ratio strongly depend on the  $T_s$ . Namely, at 100°C, both the intensity and intensity ratio of the (200) peak become maximum. The intensities of (111) and (200) are comparable at other  $T_s$ . It is reasonable that the degree of (100) orientation strongly depends on  $T_s$  because this new orientation occurs due to the interaction between nitrogen and sputtered Ag atoms. The interaction becomes weaker with increasing substrate temperature because the sojourn time of gas molecules decreases. In the sputtering atmosphere, processing gas is mostly ionized or excited. Hence the reactivity of such species would be higher than that of molecules in the neutral state. However, in the present case where no Ag-N bonds form, it is considered that high temperature is disadvantageous for promoting the interaction.

Unlike the peak intensity, the grain size of the film based on the (200) peak increased with increasing  $T_s$ : 19 nm, 24 nm and 42 nm for RT, 100°C and 200°C, respectively. As a result, it was found that the film deposited at 100°C shows a strong (100) orientation but consists of small crystals. The peak position of the film deposited at RT deviated slightly from that of the reference [11], indicating a lattice expansion. Consequently, it is considered that nitrogen is incorporated into the film at this temperature due to the increased sojourn time.

Figure 4 shows the change of the resistivity and TCR of the films deposited in nitrogen discharge at various  $T_s$ . The film deposited at RT shows high resistivity compared with the value for bulk Ag (1.6

$\mu\Omega\text{cm}$ ). However, films deposited at or above  $100^\circ\text{C}$  show low resistivity (below  $2.8 \mu\Omega\text{cm}$ ) and high TCR (above  $1500 \text{ ppm}/^\circ\text{C}$ ), as shown in the figure. They have different preferential orientations but no significant difference is seen in their electrical properties. Another film with (111) orientation, which was deposited in Ar discharge at  $100^\circ\text{C}$ , was also examined. The resistivity of this film was  $2.1 \mu\Omega\text{cm}$ , being in the same range as those of the films deposited in nitrogen discharge.

Although several reports have been published on the effect of the reactive gas on the crystal orientation of deposited films, the exact mechanism remains elusive. However, the crystal orientation change upon the use of  $\text{N}_2$  at least means that some interactions exist between the reactive gas and sputtered Ag atoms. In the case of Pt films deposited in Ar- $\text{O}_2$  mixed gas, oxygen was incorporated into the Pt films and the mechanism of crystal orientation change was explained as follows: the lower total strain energy of the (200) plane after the incorporation of  $\text{O}_2$  causes the preferential growth of (200)[5]. On the other hand, another mechanism was also proposed that in the reaction system, the growth of the (111) plane is suppressed by the preferential adsorption of oxygen on the plane [4].

In the case of Ni films [6], nitrogen considerably influenced the orientation but was not incorporated into the films. As a consequence, the latter mechanism in which the surface energy of the films is modified by the interaction seemed to be reasonable. In the present case of Ag films, results are very similar to those for Ni films; sputtering in the presence of nitrogen produced film with (100)-preferred orientation without incorporation of the gas. Because Ag does not form nitride, we predicted that the interaction should be extremely weak. The result of the influence of nitrogen on the orientation, however, shows that the interaction still occurs to some degree in this system (Ag- $\text{N}_2$ ). It is

possible to consider that the reactive gas desorbed spontaneously after a short sojourn at the Ag film surface by which it influenced the arrangement of the arriving atoms.

We have described the feasibility of metal film deposition in the presence of nitrogen, giving two possible mechanisms by which the reactive gas in the sputtering atmosphere changes the crystal orientation of the deposited films. On the basis of the present results and previously reported results, we believe that this sputtering method is useful for preparing pure metal films with controlling the texture by selecting appropriate conditions and is applicable to relatively less-reactive combinations of metals and gases. As a rough indication of feasibility, it will be one idea to draw upon thermodynamic data, such as adsorption energy, as was discussed previously [6], though this may not always provide a correct approximation for the sputtering atmosphere.

## **Conclusions**

It is feasible to prepare single-phase Ag films by sputtering in nitrogen discharge. The obtained films have strong (100) preferential orientation when they are deposited at 100°C. In addition, no impurities including the processing gas were detected in the film by AES. At higher  $T_s$ , Ag films show (111) orientation though the electrical properties remain comparable. As the role of nitrogen in the sputtering, it is considered that nitrogen influences the arrangement of the arriving atoms by way of a short sojourn at the Ag film surface, after which it spontaneously desorbs.

## References

- [1] K. L. Chopra: Thin Film Phenomena (McGraw-Hill, New York, 1969).
- [2] M. Mashita: Hyoumen Kagaku. **1** (1981) 46 [in Japanese].
- [3] I. Petrov, P. B. Barna, L. Hultman, J. E. Greene, J. Vac. Sci. Technol. A **21** (2003) S117
- [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, Y. Abe and K. Sasaki: Jpn. J. Appl. Phys. **43** (2004) 4361.
- [7] M. Kawamura, Y. Abe and K. Sasaki: Thin Solid Films **469-470** (2004) 491
- [8] M. Kawamura, K. Yagi, Y. Abe and K. Sasaki: Thin Solid Films (submitted)
- [9] L. Grocholl, J. Wang and E. G. Gillan, Mater. Res. Bull. **38** (2003) 213
- [10] L. E. Davis et al : Handbook of Auger electron spectroscopy (Perkin-Elmer Corporation, 1978).
- [11] JCPDS –International Center of Diffraction Data, PDF-2 Database CD-ROM version, No.4-783 (2000).

## Figure captions

Fig.1 XRD patterns of Ag films deposited at 100°C in Ar and N<sub>2</sub>.

Fig.2 AES spectrum for the Ag film deposited in N<sub>2</sub> at 100°C.

Fig.3 Changes of XRD diffraction peak intensity and intensity ratios of (111) and (200) to  $\Sigma I(hkl)$  for the Ag films deposited in N<sub>2</sub> as a function of substrate temperature.

Fig.4 Changes of electrical resistivity and TCR of the films deposited in N<sub>2</sub> as a function of substrate temperature.

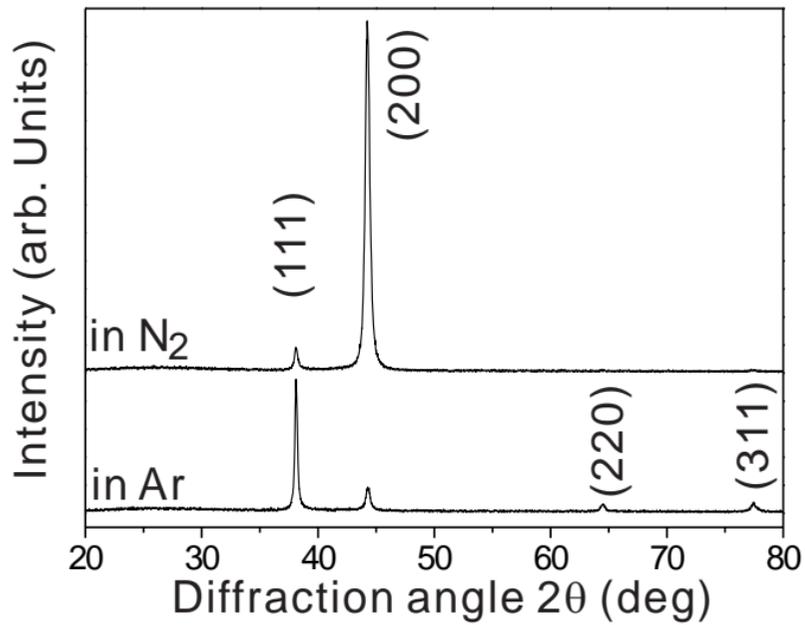


Fig. 1

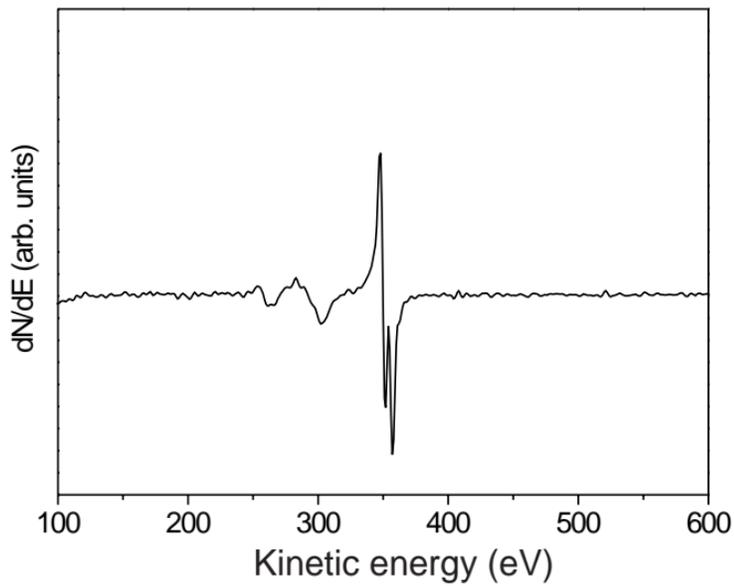


Fig .2

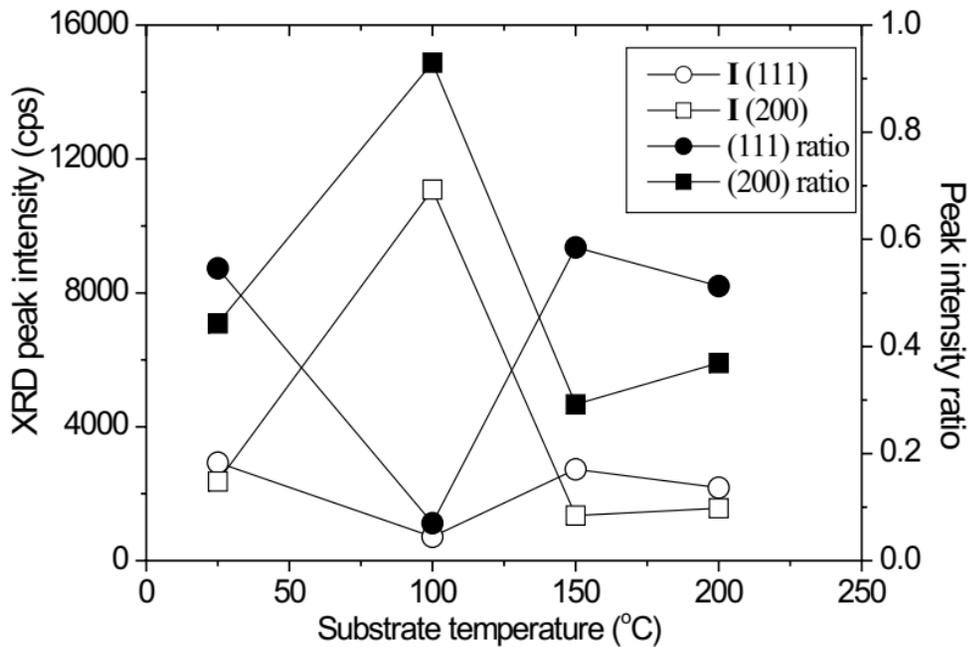


Fig.3

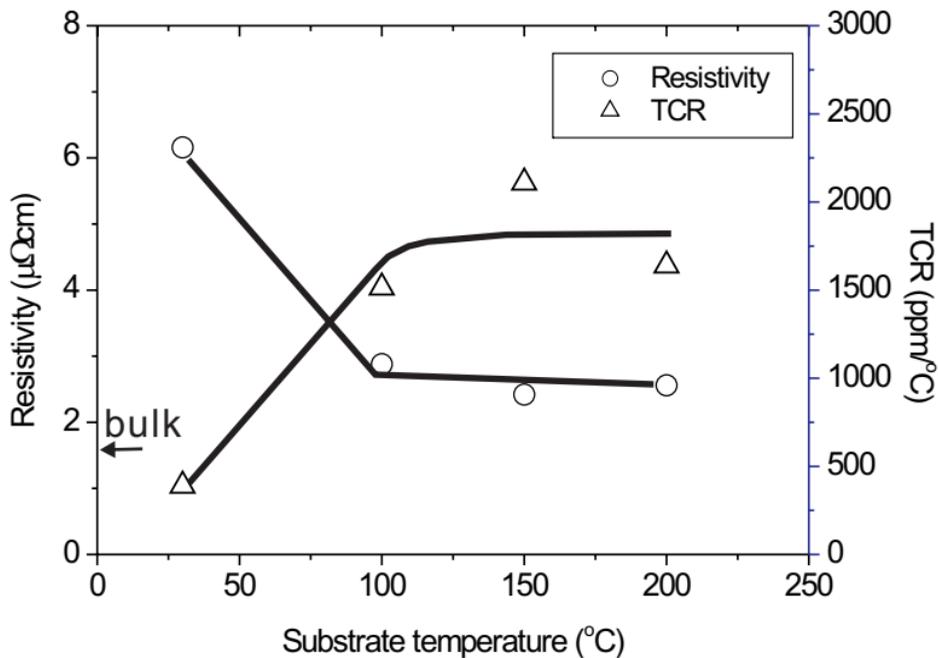


Fig.4