

# **Effects of the Ar-N<sub>2</sub> Sputtering Gas Mixture on the Preferential Orientation of sputtered Ru Films**

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## **Abstract**

We have investigated the influence of N<sub>2</sub> addition to the Ar sputtering gas on the crystal orientation of sputtered Ru films. An rf magnetron sputtering apparatus with a Ru target (99.9%) and a glass substrate heated to 100°C or 300°C was used for the deposition. The crystal structure, chemical composition and electrical properties of the resultant films were investigated. X-ray diffraction (XRD) revealed the dominant orientation at 0% N<sub>2</sub> to be the *c*-axis. With increasing proportion of N<sub>2</sub> in the sputtering gas at a substrate temperature of 100°C, the intensity of the (002) peak decreased, finally disappearing at 50% N<sub>2</sub>. This *c*-axis suppressed Ru film sputtered at 50% N<sub>2</sub> was found to contain nitrogen by Auger electron spectroscopy (AES), but by annealing the film in vacuum at 400°C, the nitrogen in the film was completely removed. The film orientation remained the same as before annealing. Thus, we have demonstrated a new method for depositing Ru films with a controlled preferential orientation of either *c*-axis oriented or *c*-axis suppressed.

**Key words: sputtering, Ru film, crystal orientation, Ar-N<sub>2</sub> gas mixture, electrical resistivity**

## Introduction

Sputter deposition of metal films is generally carried out using high-purity Ar gas. It is known that the closest-packed plane of the crystal structure of the resulting films tends to be oriented parallel to the substrate surface when the substrate is made of an amorphous material, such as glass [1,2]. Fcc and bcc metal films, for example, exhibit a preferential orientation of (111) and (110), respectively. This is because there is no lattice matching between the film and substrate, and consequently, the orientation that minimizes the surface energy of the film is favored. Thus, the closest-packed plane orients usually, another preferential orientation is difficult to obtain. It will be very useful if we can deposit films with controlled orientation. The film orientation can potentially affect the orientation of the overlayer, and vary the reactivity or other properties of the film.

Several attempts to vary the preferential orientation have been made by adding a reactive gas to the sputtering atmosphere. The changes in orientation of Pt films from (111) to (100) by sputtering in Ar-O<sub>2</sub> gas mixtures have been reported [3,4]. Because the as-deposited films also contained an oxide phase, a post-anneal at 800°C was required to obtain pure (100) Pt films [4]. We hypothesized that a similar effect could also be induced in the case of N<sub>2</sub> addition to the sputtering atmosphere by selecting suitable counterpart metals. In a previous study [5,6], we prepared nearly completely (111)- or (100)-oriented Ni films by sputtering in an Ar-N<sub>2</sub> gas mixture. It is

expected that this method can be extended to the fabrication of other types of metal films.

Ru films with a hcp structure generally tend to have *c*-axis orientation. There are several reports of perfectly *c*-axis oriented Ru films obtained by sputtering in Ar-O<sub>2</sub> [7,8]. However, the influence of N<sub>2</sub> addition to the sputtering gas on the crystal orientation of the films has not been investigated. It seems interesting to attempt to change the orientation by sputtering in an Ar-N<sub>2</sub> gas mixture as well as Ni films [5] though they have different crystal structures. In the present study, we investigate the influence of N<sub>2</sub> addition to the Ar sputtering gas on the crystal orientation of sputtered Ru films. We report a method for controlling the orientation of Ru films by selecting appropriate sputtering conditions.

## Experimental

Deposition was carried out by sputtering a Ru target (99.9% purity) in an Ar-N<sub>2</sub> gas mixture using an rf sputtering system (ANELVA, L-250-FH). The system was evacuated to below  $3.7 \times 10^{-5}$  Pa, and then a sputtering gas with various N<sub>2</sub> flow ratios (0-50%) was introduced, with the total gas flow controlled at 1.0 cm<sup>3</sup>/min. The total gas pressure was fixed at 1.3 Pa during sputtering. A Corning #7059 glass substrate was used, which was maintained at 100°C or 300°C during deposition. The rf power used was 25 W, and the distance between the substrate and the target was

fixed at 40 mm. For several samples, post annealing at 400°C in vacuum was also carried out after evacuating to less than  $1.0 \times 10^{-4}$  Pa in a lamp heating furnace.

The film thickness was estimated by multibeam interferometry. The crystal structure of the films obtained was investigated by X-ray diffraction (XRD) analysis with Cu-K $\alpha$  radiation. Auger electron spectroscopy (AES) analysis was used for qualitative analysis of the prepared films, after removing surface contamination by Ar<sup>+</sup> etching at 1 KeV. Electrical resistivity was measured by the four-point probe method, and the temperature coefficient of resistivity (TCR) was calculated using the resistance values measured at 30°C and 60°C.

## Results and Discussion

The change in the XRD patterns of Ru films with a thickness of 150 nm deposited at 100°C is shown in Fig. 1 as a function of N<sub>2</sub> ratio. As the preferential crystallographic orientation of Ru films, the (002) diffraction peak dominated at 0% N<sub>2</sub> ratio, which is indicative of the *c*-axis orientation (*c*-plane is parallel to the substrate surface). Also, (100) and (101) peaks were observed. Upon the introduction of a small amount of N<sub>2</sub> (2%), the preferential orientation of the film changed, namely, the intensity of the (002) peak decreased significantly. The intensity of the (101) and (100) peaks did not change appreciably. All peak positions, especially that of (002), shifted toward lower diffraction angles, indicating an increase in interplanar spacings. In

addition, the peak width became more or less broad and the grain sizes estimated from Scherrer's equation were reduced. For example, the size estimated from the (002) peak was reduced from 27 nm at 0% to 13 nm at 10%. Finally at 50%, the (002) peak disappeared. No peak attributable to any other phase was observed. We note that the pattern obtained for the film deposited at 50% N<sub>2</sub> was peculiar because generally the *c*-axis orientation is obtained, as mentioned above.

The films deposited at 300°C were studied using the same procedure as those deposited at 100°C. Figure 2 shows the degree of *c*-axis orientation defined by the following equation according to Lotgering's relation [9],

$$P = \frac{\sum I(00l)}{\sum I(hkl)},$$

Where *P* is the (00*l*) peak intensity ratio and *I*(00*l*) is the intensity of the (002) and (004) peaks, and *I*(*hkl*) is the intensity of all diffraction peaks. At 100°C, *P* decreased from 0.63 at 0% to zero at 50%, as predicted from the result shown in Fig. 1. *P* was maintained at approximately 0.93 for the films deposited at 300°C; the (002) peak remained dominant, and the addition of N<sub>2</sub> into the sputtering gas had no influence. It is thought that at a higher substrate temperature (*T<sub>s</sub>*), interactions such as the adsorption of reactive gas molecules on Ru atoms are negligible because the sojourn time of the gas is reduced. Concordant results were obtained by AES analysis for both films deposited at 100°C and 300°C under a N<sub>2</sub> ratio of 50%. Figure 3 shows the spectra for both films. No nitrogen was detected in the film deposited at 300°C, and

only a background fluctuation was seen. By contrast, in the case of the film deposited at 100°C, a peak attributed to the N KLL transition appeared at approximately 380 eV [10], was observed. Thus, we confirmed that the nitrogen in the sputtering chamber was incorporated into the Ru films at low  $T_s$ . Though we could detect the presence of nitrogen in the film, we could not determine its concentration due to the AES intensity change with  $Ar^+$  etching conditions. This is presumably attributable to the absence of bonding between Ru and N, i.e., the fact that they do not form a compound.

Figure 4 shows the change in electrical resistivity and TCR for films deposited at 100°C (a) and 300°C (b) under various  $N_2$  ratios. Both films deposited in pure Ar showed a low resistivity, close to that of bulk Ru ( $\rho = 7.6 \mu\Omega\text{cm}$ ). No change was observed with increasing  $N_2$  ratio for films deposited at 300°C, whereas the resistivity increased and TCR decreased in the case of films deposited at 100°C. These results are in accordance with the observation that the nitrogen in the sputtering gas is incorporated into the Ru films at a  $T_s$  of 100°C, but not at 300°C. Therefore, the increase in film resistivity can be attributed to the impurity-induced scattering effect and also the grain size reduction caused by the incorporated nitrogen.

There are few reports on changing the crystal orientation of Ru films. This is presumably because, generally, only the *c*-axis orientation occurs and other orientations have never been observed. Compared with other crystal structures, *c*-axis growth is considered to be predominantly stable in the case of hcp, and the

next most stable texture is under discussion [11]. The present study is the first to report the formation of a *c*-axis-suppressed orientation in hcp metal films. However, the mechanism of this transformation remains unclear. For the orientation change of Pt films deposited in Ar-O<sub>2</sub>, it was reported that the strain in (111), the closest-packed plane, exceeded that of (200) in oxygen-incorporated Pt films, which resulted in the preferential growth of (200) [4]. Analogously, the *c*-axis orientation may have become unfavorable and suppressed in the Ru films, which were slightly strained due to nitrogen incorporation. Another possible mechanism, namely the preferential adsorption of nitrogen on (002), could explain the suppressed growth of the (002). This was thought to be most probable in the case of Ni films because nitrogen was not incorporated into the films [5].

We also compared the orientation change of our Ru films with that reported for AlN films, which have a wurtzite structure exhibiting hcp packing. It was found that sputtering gas composition could be a key parameter for AlN films. Namely, it was reported that the *c*-axis grows by sputtering in Ar- N<sub>2</sub>, the standard processing gas, whereas the *a*-axis grows in Ar-N<sub>2</sub>-H<sub>2</sub> [12,13]. These results agree with the present result that the *c*-axis of Ru films grows by sputtering in Ar and is suppressed in the Ar-N<sub>2</sub> gas mixture. Thus, the presence of some kind of chemical interaction may influence the properties of the deposited film. Among the several possibilities discussed above, the most probable mechanism is the first one since the Ru films

contained nitrogen as shown in Fig. 3-4.

Thus, we obtained Ru films with two types of orientation, namely, the *c*-axis orientation and the *c*-axis-suppressed orientation. The latter contained nitrogen, as mentioned above. To remove the nitrogen we annealed the films in vacuum at the relatively low temperature of 400°C. In the case of oxygen-incorporated Pt films, a post-anneal at 800°C was required to obtain a pure metal film [4]. Ru is not expected to require such a high annealing temperature because Ru and N do not form a bond. Figure 5 shows the XRD pattern of the Ru film deposited at 100°C under 50% N<sub>2</sub> ratio, before and after the post-anneal at 400°C. As can be seen, the original orientation was preserved and no (002) peak appeared. The peak positions shifted slightly due to the elimination of nitrogen. This indicates that even fine-grained (002) crystallites were absent in the as-deposited films. Using AES analysis, we confirmed that there was no detectable nitrogen in the annealed Ru film (results not shown). Thus, as we expected, nitrogen was removed easily.

The annealed film described above, however, contained cracks and pinholes, which are undesirable. Electrical properties of such films cannot be accurately measured. This is presumably due to the intrinsic weak adhesive force between Ru and the glass substrate because the film is thought to be slightly strained by nitrogen incorporation. When we reduced the Ru film thickness to 50 nm, which showed the same crystal orientation in the as-deposited state, no cracks or pinholes were

observed after annealing. Thus, the use a substrate with a stronger adhesion to Ru films or the insertion of a thin adhesive layer between the substrate and Ru film would enable the fabrication of thicker Ru films.

The present study is the first to describe how to prepare Ru films with *c*-axis-suppressed orientation. By selecting appropriate sputtering conditions, Ru films can be deposited with controlled preferential orientation. Films with different crystal orientations can be used in further studies, e.g., to investigate the relation between chemical reactivity or physical properties and film orientation.

The current findings also suggest that the method can be applied to a wide variety of films provided the metal is not reactive toward nitrogen.

## Conclusion

We have deposited Ru films by sputtering in the presence of N<sub>2</sub>. It is found that sputtering in an Ar-N<sub>2</sub> gas mixture can change the Ru film orientation from the *c*-axis orientation in the absence of N<sub>2</sub> to a *c*-axis-suppressed orientation under a N<sub>2</sub> ratio of 50% at 100°C. The latter type of films contained nitrogen, which could be removed by a post-anneal at 400°C without changing the crystal orientation. Thus, we have demonstrated a new method for depositing Ru films with a controlled preferential orientation of either *c*-axis oriented or *c*-axis suppressed. The present results, along with our previous results on Ni films, show the applicability of the present method to a

wide variety of material systems.

## References

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## Figure Captions

Figure 1: XRD patterns of sputtered Ru films with various N<sub>2</sub> flow ratios at a T<sub>s</sub> of 100°C.

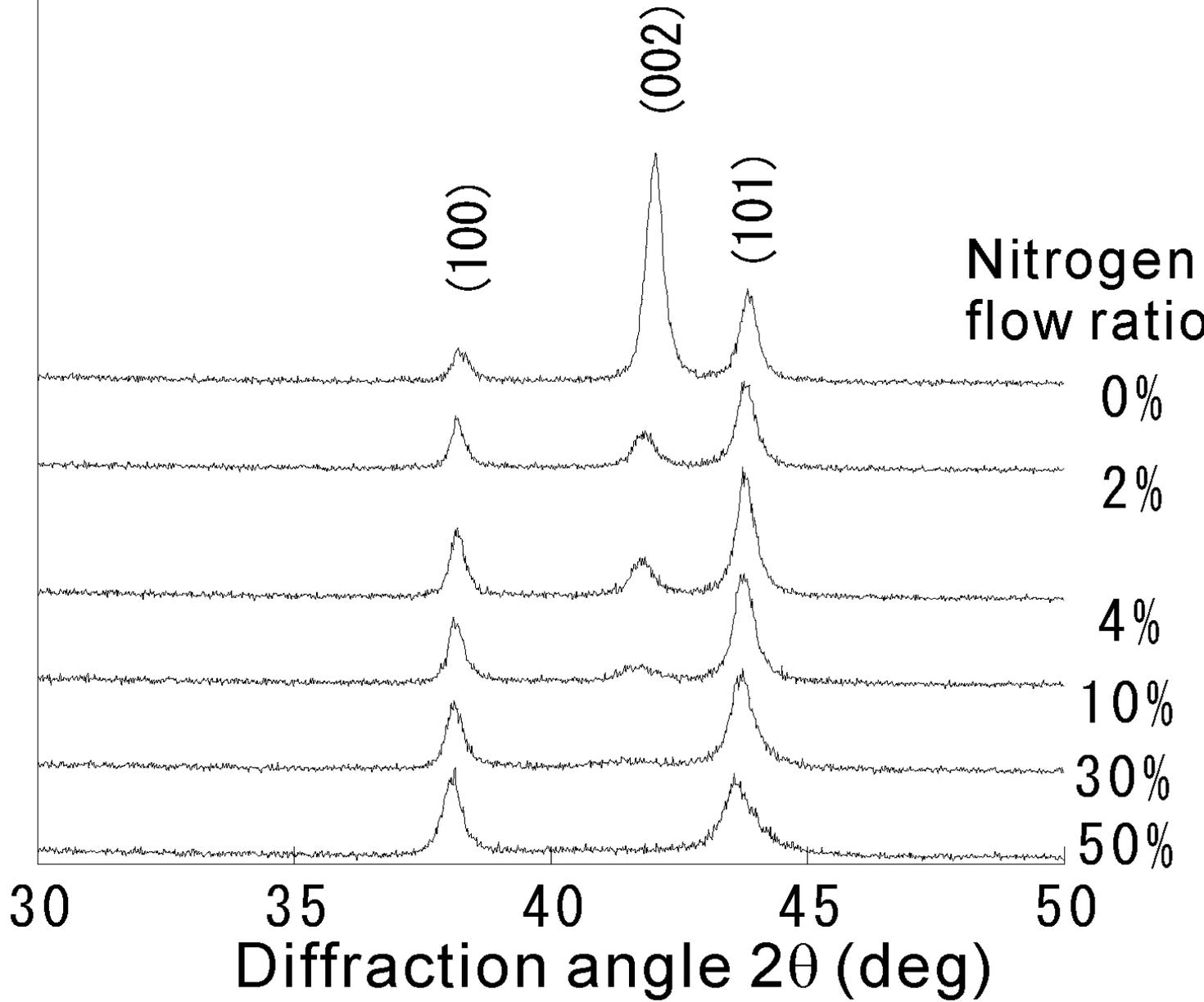
Figure 2: Change in orientation degree(P) of (00l) as a function of N<sub>2</sub> flow ratio at T<sub>s</sub> of 100°C and 300°C, respectively.

Figure 3: AES spectra of nitrogen for films deposited under 50% N<sub>2</sub> flow ratio at 100°C and 300°C, respectively.

Figure 4: Changes in electrical resistivity and TCR of Ru films as a function of N<sub>2</sub> flow ratio. T<sub>s</sub> was (a) 100°C and b) 300°C.

Figure 5: XRD patterns of Ru film deposited under 50% N<sub>2</sub> flow ratio at a T<sub>s</sub> of 100°C, before and after post-annealing at 400°C.

Intensity (arb. Units)



Nitrogen  
flow ratio

0%

2%

4%

10%

30%

50%

30

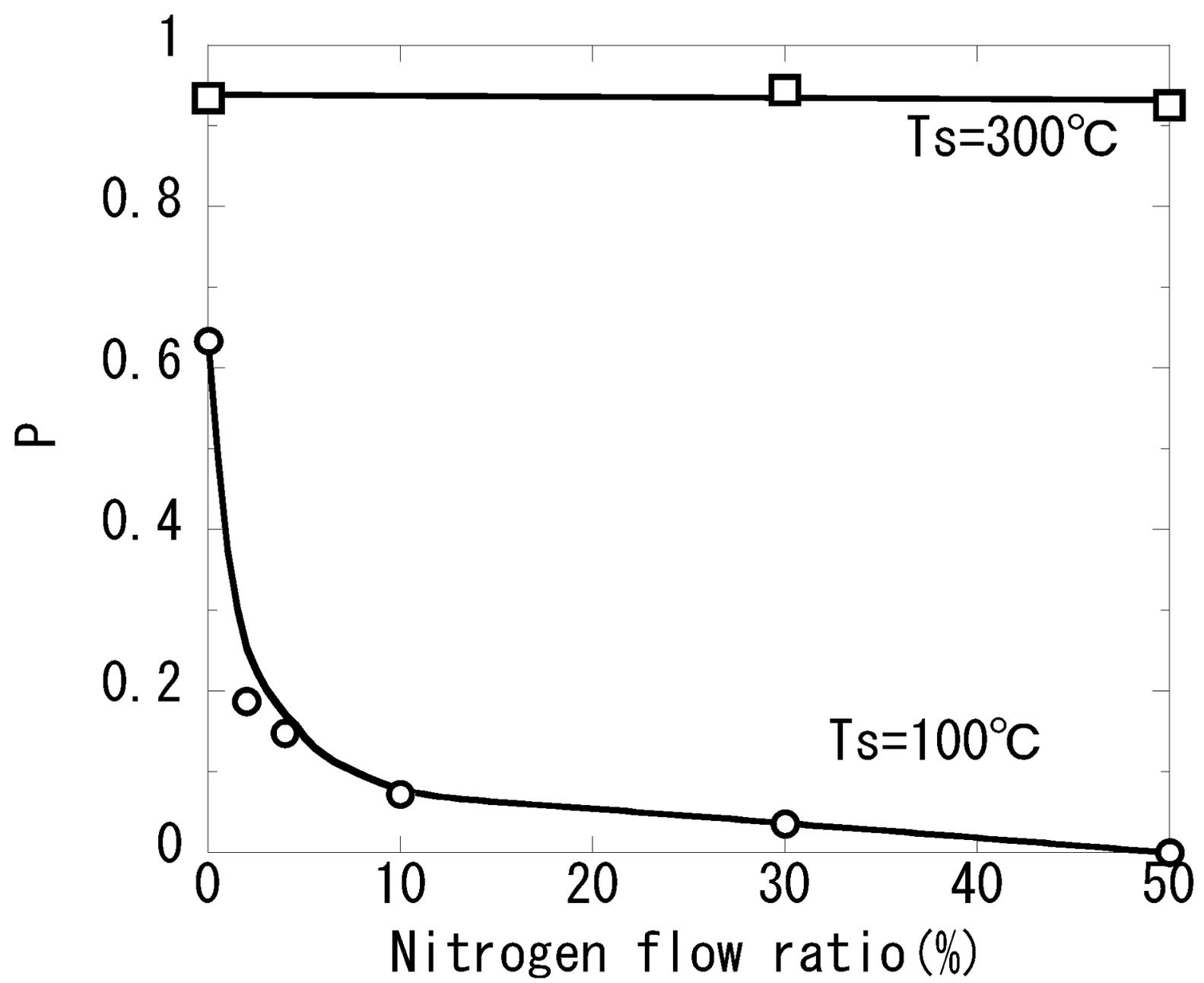
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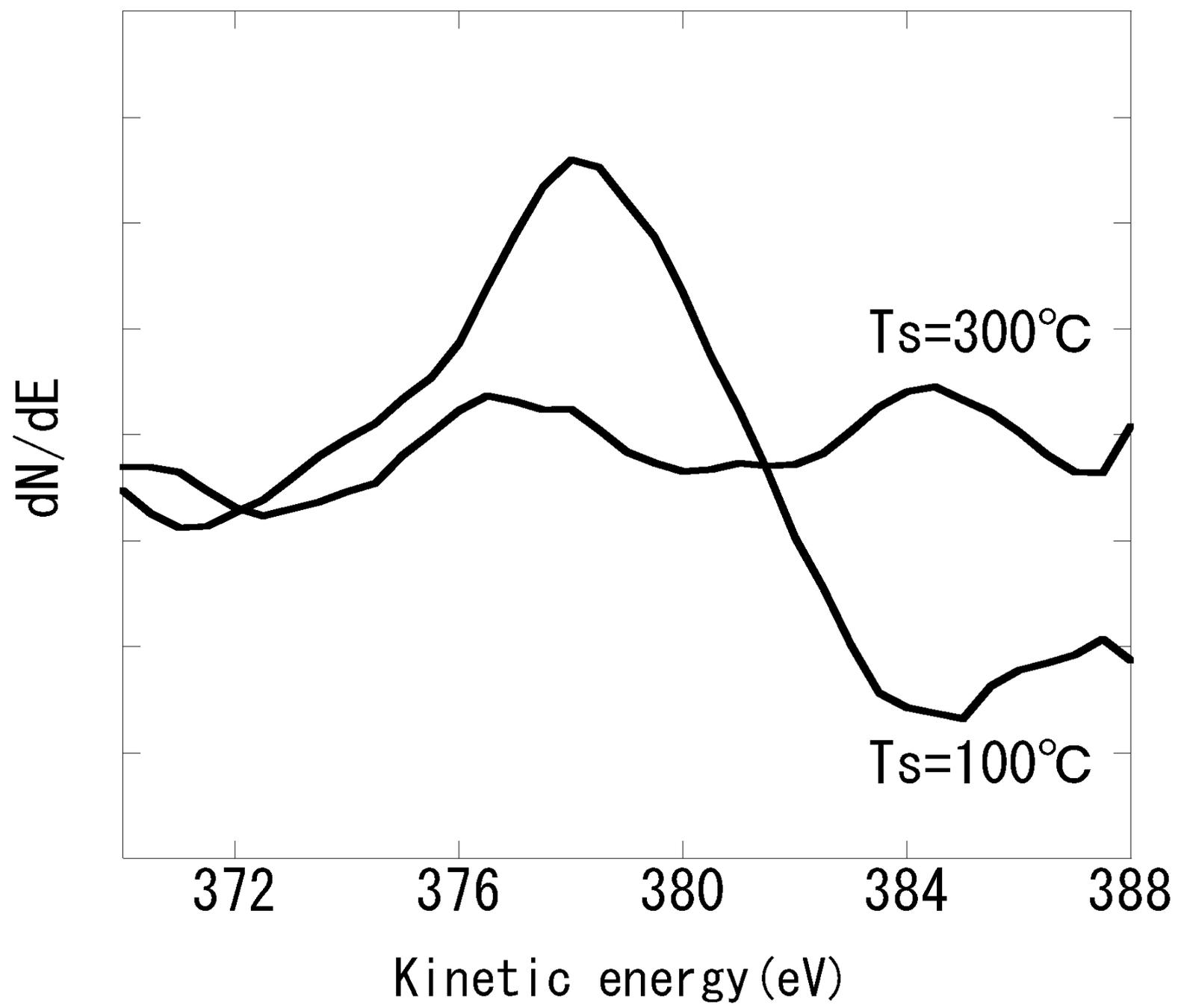
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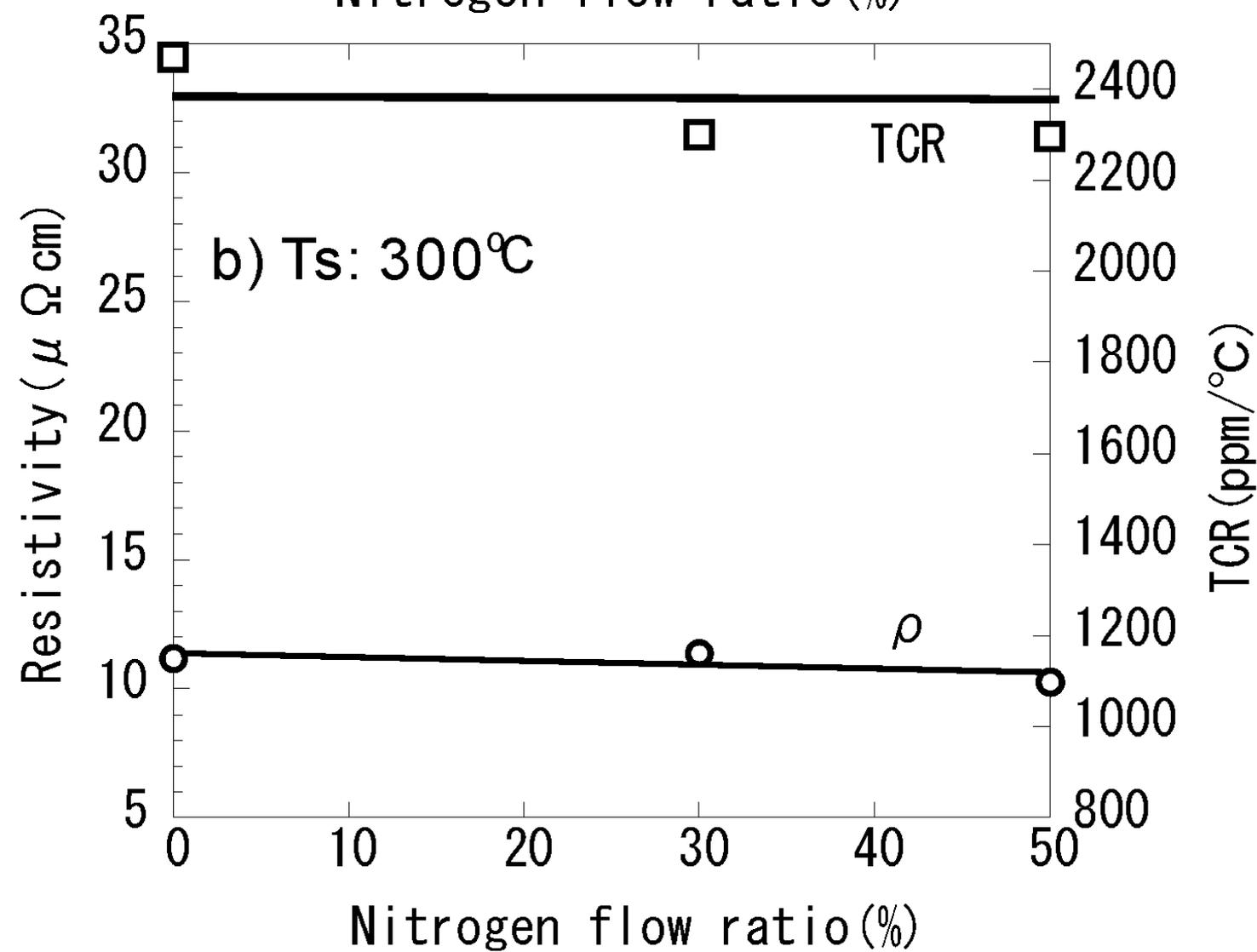
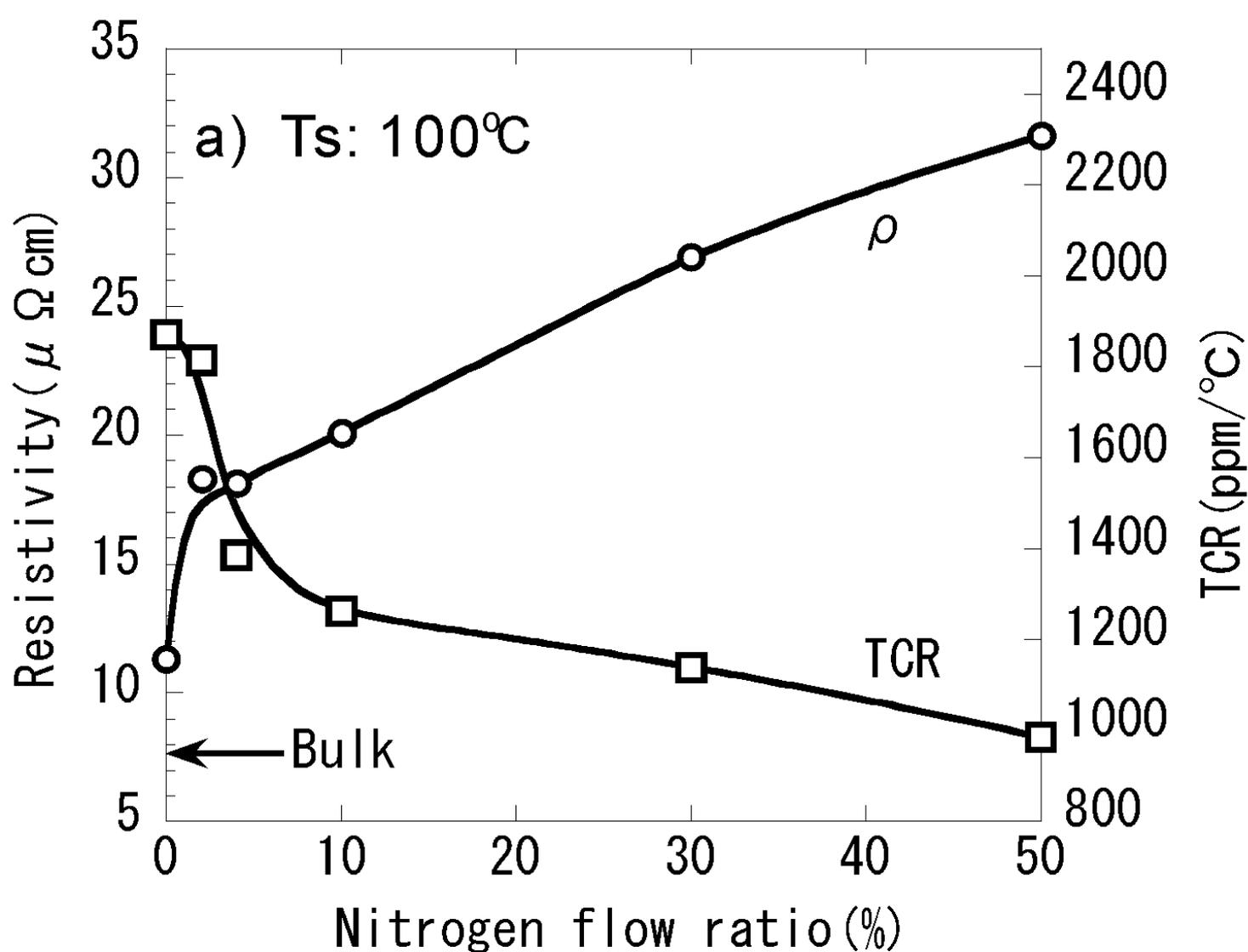
45

50

Diffraction angle  $2\theta$  (deg)







Intensity (arb. units)

